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50 years
in the service of science
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**INSTITUTE
OF NUCLEAR CHEMISTRY
AND TECHNOLOGY**

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GENERAL INFORMATION

The Institute of Nuclear Chemistry and Technology (INCT) is one of the successors of the Institute of Nuclear Research (INR) which was established in 1955. The latter Institute, once the biggest Institute in Poland, has exerted a great influence on the scientific and intelectual life in this country. The INCT came into being as one of the independent units established after the dissolution of the INR in 1983.

At present, the Institute research activity is focused on:
- radiation chemistry and technology,
- radiochemistry and coordination chemistry,
- radiobiology,
- application of nuclear methods in material and process engineering,
- design of instruments based on nuclear techniques,
- trace analysis and radioanalytical techniques,
- environmental research.

In the above fields we offer research programmes for Ph.D. students.

At this moment, with its nine electron accelerators in operation and with the staff experienced in the field of electron beam (EB) applications, the Institute is one of the most advanced centres of radiation research and EB processing. The accelerators are installed in the following Institute units:
- pilot plant for radiation sterilization of medical devices and transplants,
- pilot plant for radiation modification of polymers,
- experimental pilot plant for food irradiation,
- pilot plant for removal of SO_2 and NO_x from flue gases,
- pulse radiolysis laboratory, in which the nanosecond set-up was put into operation in 2001. A new 10 MeV accelerator was constructed in the INCT for this purpose.

Based on the technology elaborated in our Institute, an industrial installation for electron beam flue gas treatment has been implemented at the EPS “Pomorzany” (Dolna Odra PS Group). This is the second full scale industrial EB installation for SO_2 and NO_x removal all over the world.

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In 2005, the INCT scientists published 76 papers in scientific journals registered in the Philadelphia list, among them 46 papers in journals with an impact factor (IF) higher than 1.0. The INCT research workers are also the authors of 23 chapters in scientific books published in 2005.

In 2005, the Ministry of Education and Science (MES) granted 5 research projects. Altogether the INCT is carrying out 23 MES research projects including 3 ordered projects and 1 implementation project, and 6 research projects supported financially by the European Commission.

Annual rewards of the INCT Director-General for the best publications in 2005 were granted to the following research teams:
- First degree group award to **Krzysztof Bobrowski, Dariusz Pogocki, Grażyna Strzelczak, Paweł Wiśniowski, Anna Korzeniowska-Sobczuk** for a series of papers concerning radiation and photochemically induced radical processes in thioether compounds.

- Second degree group award to **Aleksander Bilewicz** and **Krzysztof Łyczko** for the contribution to a series of papers concerning fundamental studies and relativistic effects and their influence on cations of the heavy elements of the sixth period.
- Third degree individual award to **Andrzej Pawlukojć** for the contribution to a series of papers concerning the application of inelastic scattering of thermal neutrons as well as Raman spectroscopy and infrared methods for studying the structure of organic charge transfer (CT) compounds.

In 2005, the INCT scientific community was especially active in organizing scientific conferences. In total, in 2005, ten international meetings have been organized:

- Mini-symposium "Free Radicals and Neurodegeneration" (24 January 2005, Warszawa);
- First Planning and Coordinating Meeting in the frame of the Technical Cooperation Project RER/8/010 "Quality Control Methods and Procedures for Radiation Technology" (21-25 February 2005, Warszawa);
- Future INCT Research Programmes – Preparation of IAEA Country Programme Framework (CPF) for Poland 2006-2012 (28 April 2005, Warszawa);
- Fourth National Conference on Radiochemistry and Nuclear Chemistry (9-11 May 2005, Kraków-Przegorzały);
- European Young Investigator Conference 2005 (EYIC 2005) (7-12 June 2005, Gniezno)
- National Symposium on Nuclear Technique in Industry, Medicine, Agriculture and Environmental Protection (7-9 September 2005, Kraków)
- VI International Comet Assay Workshop (22-24 September 2005, Warszawa)
- 2nd Poland-Japan Workshop on Materials Science "Materials for Sustainable Development in 21st Century" (12-15 October 2005, Warszawa);
- VIII Training Course on Radiation Steerilization and Hygienization (20-21 October 2005, Warszawa);
- III Conference on Problems of Waste Disposal (21 November 2005, Warszawa).

The international journal for nuclear research – NUKLEONIKA, published by the INCT, was mentioned in the SCI Journal Citation List.

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RADIATION CHEMISTRY
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RADIATION TECHNOLOGIES

STABILIZATION OF SULFIDE RADICAL CATIONS IN CYCLIC L-Met-L-Met PEPTIDE. SPECTROPHOTOMETRIC AND CONDUCTOMETRIC PULSE RADIOLYSIS STUDIES

Krzysztof Bobrowski, Gordon L. Hug[1/]**, Dariusz Pogocki, Bronisław Marciniak**[2/]**, Christian Schöneich**[3/]

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Sulfide radical cations ($>S^{+\bullet}$) are implicated in assorted biological electron transfers where they are likely intermediates in biological redox processes [1]. There is an unambiguous theoretical and experimental evidence that sulfide radical cations can be stabilized through intramolecular complexation with neighboring nucleophilic groups [2]. Reactions of this type are of special interest to biology and medicine when stabilization of methionine sulfide radical cations Met($S^{+\bullet}$) occurs in peptides an proteins [1,3]. Interaction with particular peptide or protein domain could be vital in stabilizing of Met($S^{+\bullet}$). The effective neighboring-group interactions would likely involve nucleophilic functionalities in the side chains of amino acids residues. However, very often heteroatoms in peptide bonds are the only nucleophiles present in the vicinity of the sulfide radical cations site. In this regard, it was recently shown that such interactions play an important role in oligopepides of the form N-Ac-GMG and N-Ac-GGGMGGG [4]. Intramolecularly bonded sulfide radical cations Met($S^{+\bullet}$), were directly observed in these systems with the bonding partner being either the carbonyl oxygen or the amide nitrogen of a peptide bond.

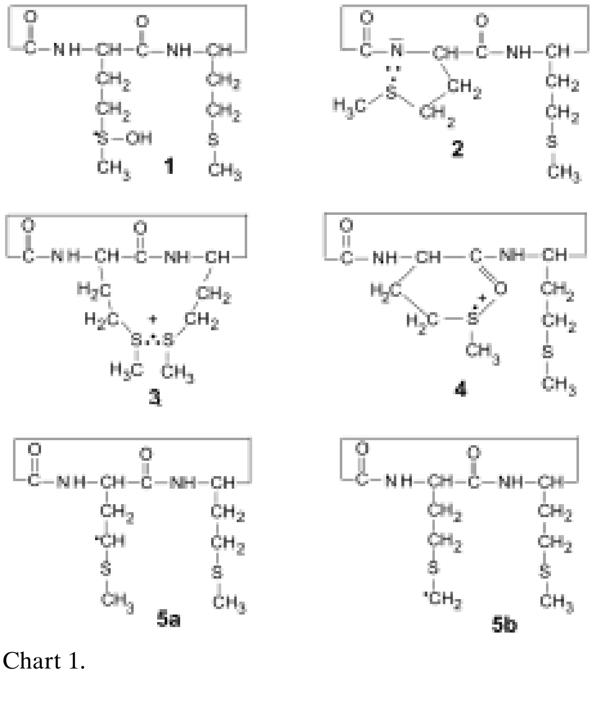

Chart 1.

Cyclic dipeptides are suitable model compounds for the study of peptide free radical chemistry. While appearing very small to be models for proteins, they have the unique feature of having no terminal groups. This makes them invaluable for studying interactions between side chains and peptide bonds. In order to define potential reactions of Met($S^{+\bullet}$) in long oligopeptides and proteins containing multiple and adjacent Met residues, an attempt has been made to isolate some of the mechanistic steps during $^{\bullet}OH$-induced oxidation of a cyclic dipeptide (L-Met-L-Met).

In the present study, we have identified, characterized, and quantified three complexed sulfide radical cations from cyclic L-Met-L-Met: the intramolecular (S∴S)-bonded radical cations, cyclo-Met-Met(S∴S)$^+$, the intramolecular sulfur-nitrogen three-electron-bonded radical Met(S∴N), and the intramolecular sulfur-oxygen three-electron-bonded radical cation Met(S∴O)$^+$. We have also

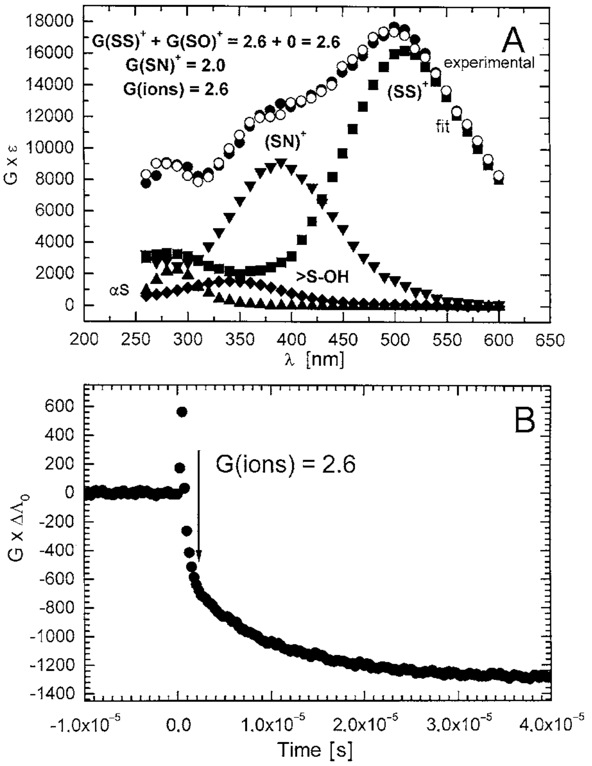

Fig.1. (A) Resolution of the spectral components in the transient absorption spectra following the $^{\bullet}OH$-induced oxidation of c-(L-Met-L-Met) (0.2 mM) in N_2O-saturated aqueous solutions at pH 4.3 taken 2 μs after the pulse. (B) Equivalent conductivity changes represented as ($G\times\Delta\Lambda_0$) *vs.* time profile following the $^{\bullet}OH$-induced oxidation of c-(L-Met-L-Met) (0.2 mM) in N_2O-saturated aqueous solutions at pH 4.3.

performed DFT (density functional theory) computations for optimizations and energy calculations of the parent molecules c-(L-Met-L-Met) and its simplified model c-(L-Met-Gly). In c-(L-Met-Gly), one of the Met side chains is replaced by a hydrogen atom, and the other Met side chain contains either a Met(S∴O)$^+$ radical cation or a Met(S∴N) radical derived from the Met side chain.

The $^{\bullet}$OH-induced reaction pathways in c-(L-Met-L-Met) have been characterized by the pulse radiolysis measurements coupled to time-resolved UV-VIS spectroscopy. The optical spectrum recorded 2 μs after pulse irradiation can be resolved into contributions from the following components (Chart 1): the hydroxysulfuranyl radical (**1**), the intramolecular sulfur-nitrogen three-electron-bonded radical (**2**), the intramolecular sulfur-sulfur three-electron-bonded radical cation (**3**), and two α-(alkylthio)alkyl radicals (**5a**/**5b**) (Fig.1A). The sum over all component spectra with their respective yields resulted in an excellent fit to the experimental spectrum. The G-value of radical cations (**3**), $G_3=2.6$, matched perfectly the G-value of radical ions, G(ions)=2.6, measured by time-resolved conductivity experiments (Fig.1B). It is important to note that an excellent spectral resolution was achieved using the intermediates **1** and **3**, the intramolecular sulfur-oxygen three-electron-bonded radical cation (**4**) and **5a**/**5b** with the respective yields for **3** and **4**: 2.4 and 2.4. However, in contrast to the previous spectral resolution the yield of the sulfur radical cations $G_{3+4}=4.8$, does not match G(ions)=2.6 determined by conductivity measurements.

In this report, we have provided an experimental proof that one-electron oxidation by $^{\bullet}$OH radicals of simple cyclic dipeptide containing two-methionine residues leads to efficient formation of the Met(S∴N) radicals. This is a strongly competitive process to the formation of the Met(S∴S)$^+$ and Met(S∴O)$^+$ radical cations in spite of the close proximity of sulfur atoms located in the side chains of Met residues and the close proximity of sulfur atoms and oxygen atoms located in the peptide bonds.

References

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[3]. Davies M.: Biochim. Biophys. Acta, 1703, 93-109 (2005).

[4]. Schöneich C., Pogocki D., Hug G.L., Bobrowski K.: J. Am. Chem. Soc., 125, 13700-13713 (2003).

RADIATION-INDUCED OXIDATION OF DIPEPTIDES CONTAINING TYROSINE AND METHIONINE – INFLUENCE OF AMINO ACID SEQUENCE AND pH

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One-electron induced oxidation by hydroxyl radicals ($^{\bullet}$OH) of two dipeptides, tyrosyl-methionine (Tyr-Met) and methionyl-tyrosine (Met-Tyr), were carried out by means of pulse radiolysis. The formation of tyrosyl radicals (TyrO$^{\bullet}$) in these compounds occurs *via* dehydration of dihydroxycyclohexadienyl radicals (Tyr$^{\bullet}$(OH)OH) – reaction (2). This latter radical is the product of an addition of $^{\bullet}$OH radicals to the aromatic ring of a tyrosine residue – reaction (1):

$$\text{Tyr} + {}^{\bullet}\text{OH} \rightarrow \text{Tyr}^{\bullet}\text{(OH)OH} \qquad (1)$$

$$\text{Tyr}^{\bullet}\text{(OH)OH} + \text{H}^+ \rightarrow \text{TyrO}^{\bullet} + \text{H}_2\text{O} \qquad (2)$$

The reaction of $^{-}$OH elimination is catalyzed by protons (reaction 2) and is particularly efficient at pH~1. The other possible reaction pathway that leads to TyrO$^{\bullet}$ radicals is an electron transfer between an intact tyrosine residue and sulfur-centered radicals located in the methionine residue. This reaction pathway was previously identified during $Br_2^{\bullet-}$ oxidation of oligopeptides containing both methionine and tyrosine residues [1,2]. In our experiments, the $^{\bullet}$OH radical was used since this radical is responsible for oxidative stress in living cells. Therefore, our results can be extrapolated to biological systems. Since the rate constants of the reactions between the $^{\bullet}$OH radical and both amino acids are very similar – $k=1.2\times10^{10}$ dm^3 mol^{-1} s^{-1}, the primary $^{\bullet}$OH radical attack should be divided almost equally between the two amino acid residues of each dipeptide. Our studies were aimed at the identification of the sulfur-centered radicals that are involved in electron transfer, leading to the formation of TyrO$^{\bullet}$ radicals.

Oxidation of Tyr-Met by $^{\bullet}$OH radicals

Transient spectra recorded during the oxidation of Tyr-Met at pH 6.6 (Fig.1) were assigned to dihydroxycyclohexadienyl (Tyr$^{\bullet}$(OH)OH-Met) and tyrosyl (TyrO$^{\bullet}$-Met) radicals. Concentration profiles for both radicals were created after resolution of absorption spectra at any desired time delay following the electron pulse. Similar yields of both detected radicals Tyr$^{\bullet}$(OH)OH-Met and TyrO$^{\bullet}$-Met were observed in the first 5 μs. The radiation chemical yield of each radical amounted to half of the total yield of $^{\bullet}$OH radicals. After several hundred microseconds, the concentration of TyrO$^{\bullet}$-Met radicals was stable, but the Tyr$^{\bullet}$(OH)OH-Met radicals had decayed by half (Fig.1, inset). A complementary experiment, performed on solutions containing tyrosine-glycine (Tyr-Gly) under similar conditions (pH, concentration), revealed that the decay kinetics of dihydroxycyclohexadienyl radicals in both compounds (Tyr-Met and Tyr-Gly) were identical. However, in solutions containing Tyr-Gly the formation of TyrO$^{\bullet}$-Gly radicals occurred only at the expense of the decay of Tyr$^{\bullet}$(OH)OH-Gly. All these observations taken together show that Tyr$^{\bullet}$(OH)OH-Met radicals cannot be precursors of TyrO$^{\bullet}$-Met radicals on a microsecond time scale at pH~6 in Tyr-Met. Furthermore, no absorption due to radicals centered on the sulfur of the methionine residue in Tyr-Met was observed.

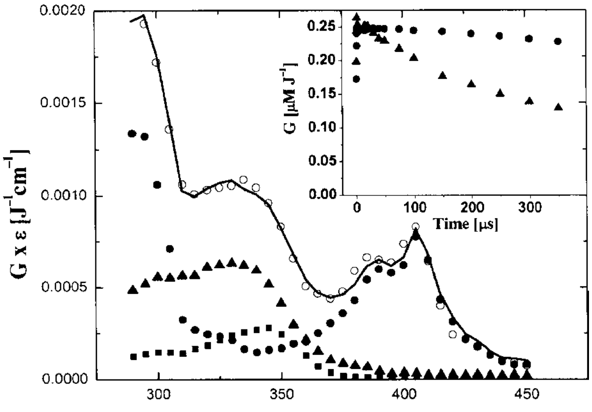

Fig.1. Resolution of the spectra components in transient absorption spectra following $^{\bullet}$OH-induced oxidation of aqueous solution 0.2 mM Tyr-Met sat. N_2O at pH 6.6. Inset: the radiation chemical yield of transients (G [μM J^{-1}]) *vs.* time: ● TyrO$^{\bullet}$-Met, ▲ Tyr$^{\bullet}$(OH)OH-Met, ■ Tyr$^{\bullet}$(H)OH-Met, ○ experiment, – fit.

Transient spectrum, recorded 5 μs after the electron pulse in a solution containing Tyr-Met at pH 1.0 (Fig.2), shows the presence of only two kinds of radicals: hydroxycyclohexadienyl radicals Tyr$^{\bullet}$(H)OH-Met (hydrogen adduct to the aromatic ring of tyrosine) and tyrosyl radicals TyrO$^{\bullet}$-Met. The yield of tyrosyl radicals was equal to the total radiation chemical yield of $^{\bullet}$OH radicals generated in this system.

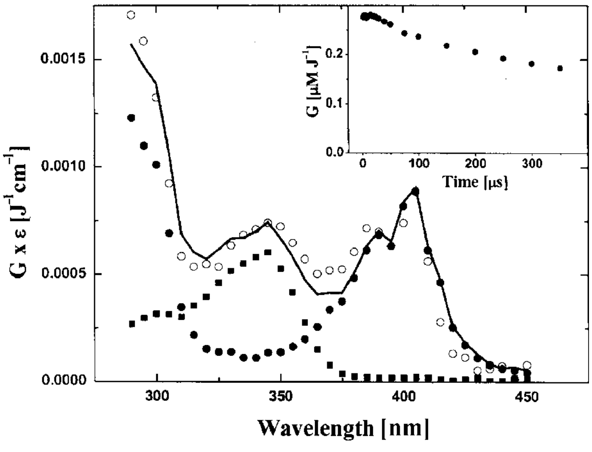

Fig.2. Resolution of the spectra components in transient absorption spectra following $^{\bullet}$OH-induced oxidation of aqueous solution 0.2 mM Tyr-Met sat. N_2O at pH 1.0. Inset: the radiation chemical yield of transients (G [μM J^{-1}]) *vs.* time: ● TyrO$^{\bullet}$-Met, ■ Tyr$^{\bullet}$(H)OH-Met, ○ experiment, – fit.

Oxidation of Met-Tyr by $^{\bullet}$OH radicals

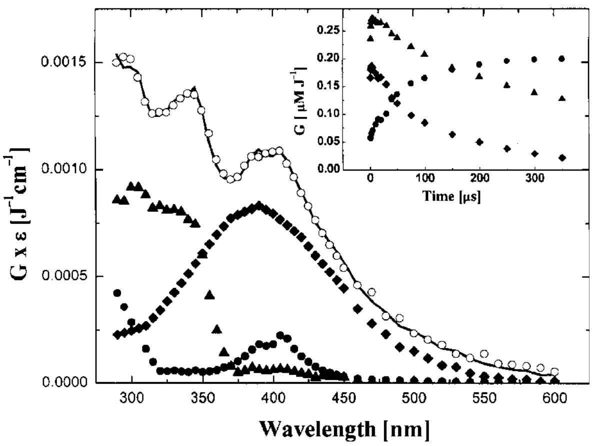

Fig.3. Resolution of the spectra components in transient absorption spectra following $^{\bullet}$OH – induced oxidation of aqueous solution 0.2 mM Met-Tyr sat. N_2O at pH 6.1. Inset: the radiation chemical yield of transients (G [μM J^{-1}]) *vs.* time: ● Met-TyrO$^{\bullet}$, ▲ Met-Tyr$^{\bullet}$(OH)OH, ◆ (S∴N)$^{+}$Met-Tyr, ○ experiment, – fit.

Different spectral features were observed following the reaction of $^{\bullet}$OH radicals with Met-Tyr. Three distinct, broad absorption bands were observed at pH 6 after 5 μs with maxima located at λ=295, 350, and 400 nm (Fig.3). This spectrum was best resolved into contributions from the sulfur-nitrogen bonded radical cation (S∴N)$^{+}$Met-Tyr, the tyrosyl radical Met-TyrO$^{\bullet}$, and the dihydroxycyclohexadienyl radical Met-Tyr$^{\bullet}$(OH)OH. From resolutions of absorption spectra, the formation of Tyr$^{\bullet}$(OH)OH-Met radical was observed in the first 5 μs. The yield of Tyr$^{\bullet}$(OH)OH-Met radical accounted for a half of the total radiation chemical yield of $^{\bullet}$OH radicals. Furthermore, the second half of the total yield of $^{\bullet}$OH radicals was equal to the total radiation chemical yield of the (S∴N)$^{+}$Met radical and the Met-TyrO$^{\bullet}$ radical. Moreover, the rate of decay of the Tyr$^{\bullet}$(OH)OH-Met radical was similar to the analogous radical in Tyr-Met. The (S∴N)$^{+}$Met-Tyr radical was also formed within the 5 μs. However, the decay of the corresponding (S∴N)$^{+}$Met radical in Met-Gly proceeded more slowly. All these observations provided evidence that the (S∴N)$^{+}$Met radicals in Met-Tyr decayed

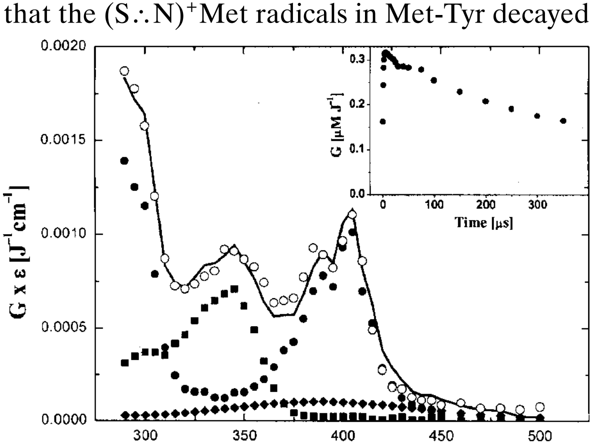

Fig.4. Resolution of the spectra components in transient absorption spectra following $^{\bullet}$OH-induced oxidation of aqueous solution 0.2 mM Met-Tyr sat. N_2O at pH 1.0. Inset: the radiation chemical yield of transients (G [μM J^{-1}]) *vs.* time: ● Met-TyrO$^{\bullet}$, ▲ Met-Tyr$^{\bullet}$(OH)OH, ◆ (S∴N)$^{+}$Met-Tyr, ■ Met-Tyr$^{\bullet}$(H)OH, ○ experiment, – fit.

via different mechanism than the analogous radicals in Met-Gly. The decay kinetics of the $(S\therefore N)^{+}$Met-Tyr radical matches the formation kinetics of the Met-TyrO$^{\bullet}$ radical (Fig.3, inset). These kinetic results confirm the hypothesis that an intramolecular electron transfer proceeds between the intact tyrosine residue and the $(S\therefore N)^{+}$Met-Tyr radical.

In a solution containing Met-Tyr at pH 1.0 (Fig.4), the absorption spectrum recorded 5 μs after the electron pulse was similar to the absorption spectrum recorded in a solution of Tyr-Met at pH 1.0, excluding a small absorption of $(S\therefore N)^{+}$Met radical in the spectrum recorded in the Met-Tyr solution.

Conclusions

A variety of transient products was formed during $^{\bullet}$OH oxidation of Met-Tyr and Tyr-Met. The main difference in the transient-products pattern concerns the $(S\therefore N)^{+}$Met radical.

The observed slow decay of dihydroxycyclohexadienyl radicals excluded them as a source of tyrosyl radicals in both peptides, on the short time scale at pH$\sim$6. The remaining fraction of hydroxyl radicals reacted with methionine residues forming hydroxysulfuranyl radicals Met(>S$^{\bullet}$-OH). These radicals were transformed into sulfur-centered radical cations Met(>S$^{+\bullet}$) *via* proton-catalyzed dehydration.

Due to a large difference in redox potentials of the Met(>S$^{+\bullet}$) radical E^{0}(Met(>S$^{+\bullet}$)/Met)$\sim$1.6 V [3] and the TyrO$^{\bullet}$ radical E^{0}(TyrO$^{\bullet}$)/Tyr)$\sim$0.94 V [4], fast electron transfer likely occurred, making the observation of Met(>S$^{+\bullet}$) radicals unfeasible. Hence, we assume a mechanism of the electron transfer for both dipeptides at pH$\sim$1 – reactions (3a) and (3b):

$$\text{Met(>S}^{+\bullet}\text{)-Tyr} \rightarrow \text{Met-TyrO}^{\bullet} \quad (3a)$$

$$\text{Tyr-Met(>S}^{+\bullet}\text{)} \rightarrow \text{TyrO}^{\bullet}\text{-Met} \quad (3b)$$

The hydroxysulfuranyl radical Tyr-Met(>S$^{\bullet}$-OH) was excluded as a precursor of the TyrO$^{\bullet}$ radical at pH$\sim$6, because its redox potential E^{0} (Met(>S$^{\bullet}$-OH) /Met)$\sim$1.43 V [3] is lower than the potential of Met(>S$^{+\bullet}$). Other reaction pathways involving the Met(>S$^{+\bullet}$) radicals (*e.g.* decarboxylation) were experimentally excluded.

Another reaction pathway was observed during the oxidation of Met-Tyr at pH$\sim$6. The H$_{3}$N^{+}-Met (>S$^{\bullet}$-OH)Tyr radical underwent deprotonation using a proton from the protonated amino group. As a result, the sulfur-nitrogen bonded radical cation $(S\therefore N)^{+}$Met-Tyr was formed – reaction (4).

$$\text{H}_3\text{N}^{+}\text{-Met(>S}^{\bullet}\text{-OH)Tyr} \rightarrow (S\therefore N)^{+}\text{Met-Tyr} \quad (4)$$

Subsequently, an intramolecular electron transfer occurred between the intact tyrosine and the $(S\therefore N)^{+}$Met-Tyr radical – reaction (5):

$$(S\therefore N)^{+}\text{Met-Tyr} \rightarrow \text{Met-TyrO}^{\bullet} + \text{H}^{+} \quad (5)$$

Reaction (5) proceeded with slower rate compared to reaction (3) which is in line with lower redox potential of the $(S\therefore N)^{+}$Met radical at pH$\sim$6 (E^{0} ($(S\therefore N)$ $^{+}$Met/Met)$\sim$1.44 V [5]).

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EPR STUDY OF DIPEPTIDES CONTAINING TYROSINE

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Tyrosine radicals play an essential role in a number of biological processes. They are postulated in mediation of long-distance electron-transfer reactions in a number of enzymes including galactose oxidase [1], ribonucleotide reductase [2], prostaglandin H synthase [3] and photosystem II [4]. Previous work on tyrosyl radicals in polycrystalline tyrosine-containing peptides by means of FT-IR (Fourier-transform infrared) spectroscopy provided evidence for a migration of unpaired spin density from the phenoxyl ring to the terminal amino group suggesting an interaction between the π system of the tyrosyl radical and the amino group [5].

The aim of our study was to test that such an interaction occurs and whether it has an effect on the character of forming radicals. Therefore, tyrosyl radicals were generated in dipeptides with various neighbouring amino acid residues located at the C-terminus of tyrosine.

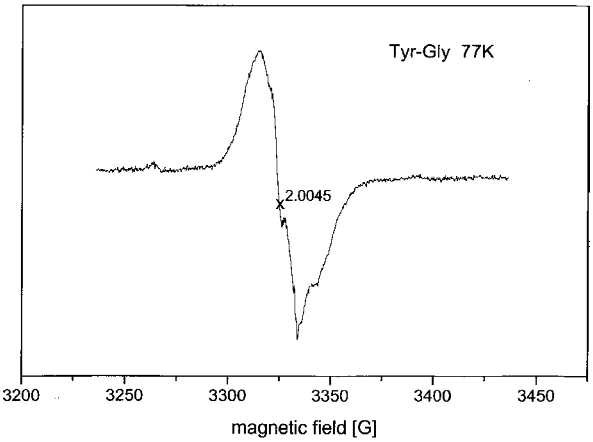

Fig.1. EPR spectrum of tyrosyl radical detected at 77 K in Tyr-Gly.

Polycrystalline dipeptides Tyr-Gly, Tyr-Leu, Tyr-Met were irradiated in a ^{60}Co-gamma source with doses of 3 kGy in liquid nitrogen. Radicals were identified by the electron paramagnetic resonance (EPR) spectroscopy method. EPR experiments were performed using a Bruker ESP-300 spectrometer equipped with a cryostat with a variable temperature unit over the temperature range 77-293 K.

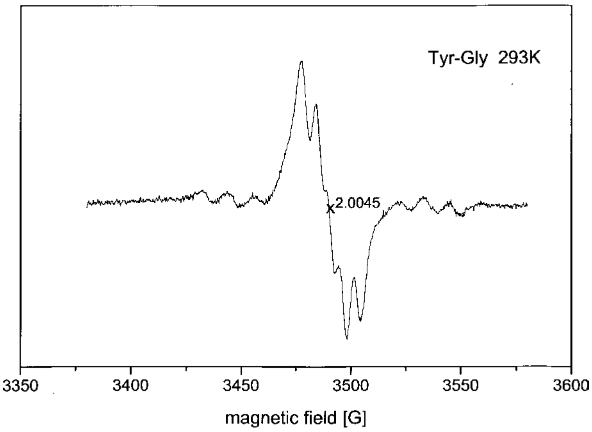

Fig.2. EPR spectrum of tyrosyl radical and N-centered radical detected at room temperature in Tyr-Gly.

The main EPR signals observed at low temperature 77-180 K in dipeptides containing N-terminal tyrosine were anisotropic singlets with very similar $g_{av}=2.0045$ assigned to the tyrosyl radicals (Fig.1).

Warming the samples up to the room temperature resulted in the appearance of an additional signal. Triplet of triplets with hyperfine splittings $a_N=1.1$ mT and $a_{2H}=4.4$ mT was detected (Fig.2).

This spectrum was assigned to the N-centered radical localized on the amino group of tyrosyl residue. Both these radicals were stable at room temperature.

The presence of N-centered radicals suggests that spin delocalization from the phenoxyl radical to the amino group might occur by a through-space mechanism. This observation is in line with earlier experimental vibrational studies and DFT (density functional theory) calculation [5].

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ELECTRON PARAMAGNETIC RESONANCE STUDIES ON SILVER ATOMS AND CLUSTERS IN REGULARLY INTERSTRATIFIED CLAY MINERALS

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Phyllosilicates, regularly interstratified clay minerals, are composed of two or more kinds of layers stacked in fixed vertical sequence [1,2]. A schematic representations of regularly interstratified clay minerals – smectite-chlorite (Sm/Ch) and smectite-mica (Sm/M) are shown in Fig.1. Sm/Ch smectite units alternate regularly with chlorite unit, while Sm/M with mica units. Both smectite and mica units consist of two oxygen-coordinated tetrahedral sheets occupied by Al(III) and Si(IV) and one octahedral sheet containing Mg(II) and Al(III). They are denoted hereafter as the 2:1 layers (tetrahedral-octahedral-tetrahedral). The amount of interlayer cations is different in smectite and mica sheets corresponding to the amount of negative lattice charge originating from the isomorphous lattice substitution in the 2:1 layers: 0.25-0.60 monovalent cations for a half unit cell formula of smectite and one cation for mica. Octahedral sheets are occupied predominantly by Mg(II) in trioctahedral clay and by Al(III) in dioctahedral clay (where only two-thirds of the octahedral sites are filled). Chlorite unit consists of negatively charged 2:1 layers and positively charged octahedral sheets. The occupancy of cations in octahedral and tetrahedral sheet of chlorite is similar to those in smectite. Half unit cell formulas of different sheets are the following: smectites – beidellite $Na_{0.33}Al_2(Si_{3.67}Al_{0.33})O_{10}(OH)_2$ and saponite $Na_{0.33}Mg_3(Si_{3.67}Al_{0.33})O_{10}(OH)_2$, trioctahedral chlorite $Mg_3(Si_3Al)O_{10}(OH)_8(Mg_2Al)$ and dioctahedral mica $NaAl_2(Si_3Al)O_{10}(OH)_2$. Many types of interstratified clay minerals, mica-smectite, chlorite-smectite, *etc.*, have been found in nature.

The regularly interstratified clay minerals were loaded with silver cations by stirring overnight with an aqueous solution of silver nitrate at room temperature. Next, the samples were filtered and wash-

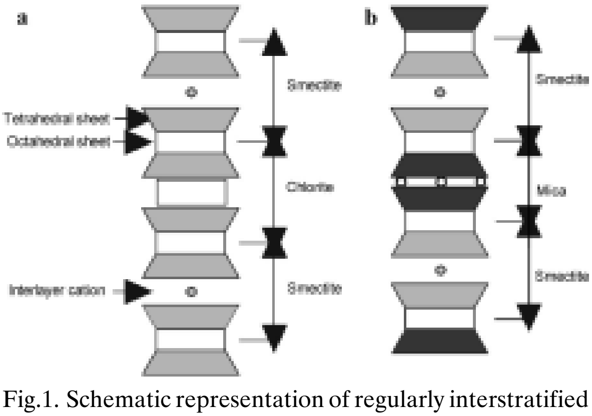

Fig.1. Schematic representation of regularly interstratified clay minerals: (a) Sm/Ch and (b) Sm/M. In Sm/Ch, smectite units alternate regularly with chlorite units and in Sm/M with mica units. Interlayer cations are denoted by circles.

ed with distilled water several times. After drying at room temperature, the samples were placed into 2 mm i.d. by 3 mm o.d. Suprasil quartz tubes and dehydrated under vacuum with gradually increasing temperature till 200°C. Some clay samples were exposed in the vacuum line to water or methanol under their vapor pressure at room temperature. All samples were irradiated at 77 K in a ^{60}Co source with a dose of 4 kGy. The electron paramagnetic resonance (EPR) spectra were recorded with a Bruker ESP-300e spectrometer in the temperature range 110-310 K using a Bruker variable temperature unit.

The EPR spectra of dehydrated trioctahedral Ag-smectite/chlorite (Ag-tri-Sm/Ch) and dioctahedral Ag-smetite/mica (Ag-di-Sm/M) recorded after irradiation at 77 K and subsequently thermally annealed are shown in Fig.2. Strong singlets L_1, L_2 and L_3 represent radiation-induced paramagnetic centers in clay lattice; a doublet of hydrogen atoms is due to hydrogen atoms generated radiolytically in the EPR suprasil glass tubes. The silver species, namely silver atoms are represented by EPR doublets with hyperfine splittings larger than 60 mT. In di-Sm/M samples the doublet lines of ^{107}Ag^0(A): A_{iso}=60.0 mT, g_{iso}=2.002 and ^{109}Ag^0(A): A_{iso}=68.6 mT, g_{iso}=2.002 are isotropic with relatively large linewidth, ΔH_{pp}=2.5 mT (Fig.2a). They decay completely above 270 K without any evidence of silver cluster formation. In tri-Sm/Ch samples, the wide lines of Ag^0(A) doublets are partly overlapped with much narrower Ag^0(B) lines of asymmetric line shape which results from the anisotropy of hyperfine splittings: ^{107}Ag^0(A): $A_\perp$ =63.0 mT, g=2.002 and ^{109}Ag^0(A): $A_\perp$ =2.6 mT, g=2.002 (Fig.2b). The parallel components of silver lines are not very well defined making impossible to measure the values of $A_{\parallel}$ and $g_{\parallel}$ tensors. At 270 K, the Ag^0(A) doublets are not observed, whereas Ag^0(B) lines with their characteristic anisotropy are still recorded but with reduced intensity. They decay completely above 310 K. The EPR measurements clearly indicate that in tri-Sm/Ch the Ag^0 atoms are located at two different sites and only at one site in di-Sm/M clays. Silver atoms are formed during low temperature radiolysis as a result of electron capture by silver cations. The first EPR spectra were also measured at low temperature (110 K) at which Ag^0 atoms remain still immobile. Thus, they can be considered as the magnetic probes indicating the preferential locations of silver cations in clay matrices. It is proposed, basing on the EPR results that Ag^0 atoms appear at different sites in both matrices: in tri-Sm/Ch both in the middle of smectite interlayer and in hexagonal cavities in the silicate sheets of tetrahedron layer and in di-Sm/M in hexagonal cavities only.

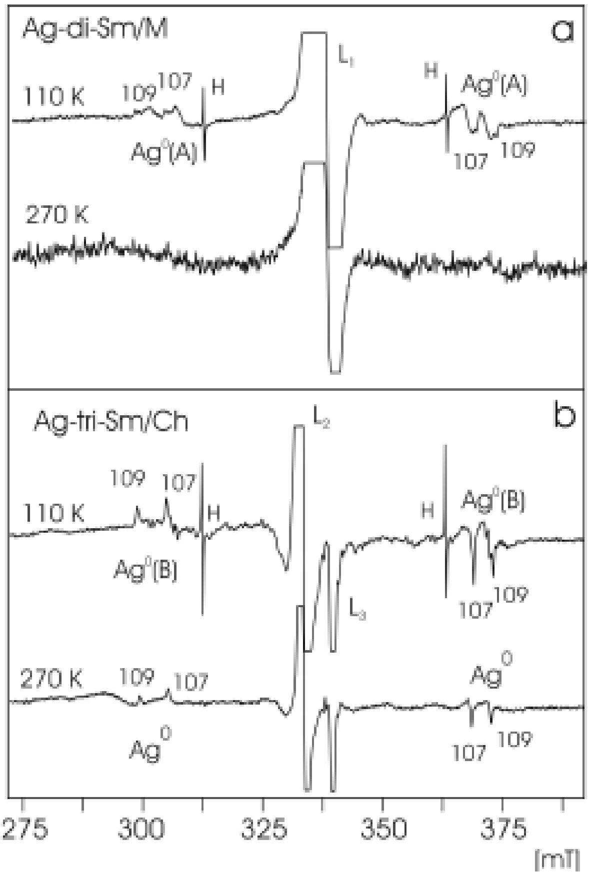

Fig.2. EPR spectra of dehydrated interstratified clay minerals irradiated at 77 K and annealed at different temperatures: (a) Ag-di-Sm/M and (b) Ag-tri-Sm/Ch.

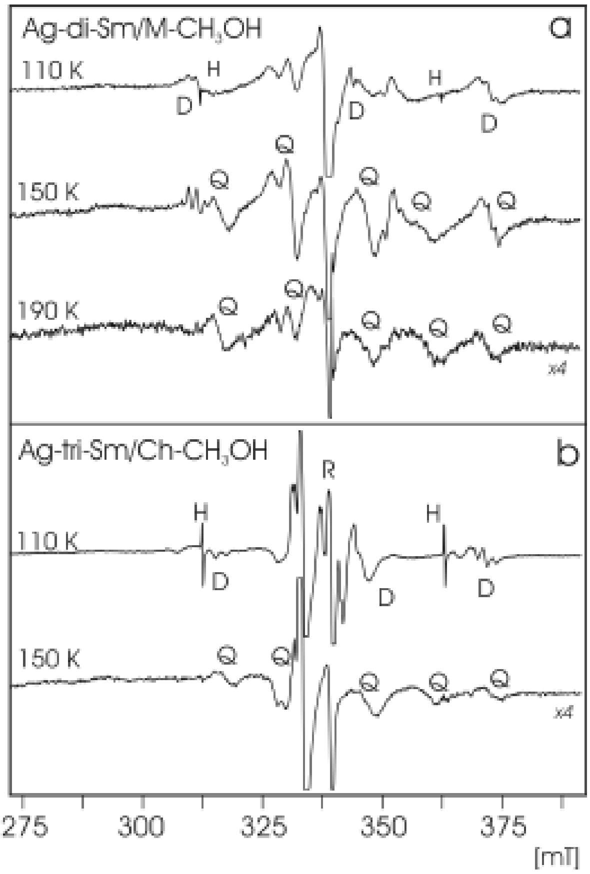

Fig.3. EPR spectra of interstratified clay minerals exposed to methanol irradiated at 77 K and annealed at different temperatures: (a) Ag-di-Sm/M and (b) Ag-tri-Sm/Ch.

When dehydrated Ag-tri-Sm/Ch and Ag-di-Sm/M samples are exposed to water vapor and then irradiated at 77 K the EPR spectra recorded just after the radiation treatment and in the course of annealing are similar to those of dehydrated samples.

On the contrary, the samples exposed to methanol vapor show completely different spectra after irradiation. In Figure 3, the lines related to silver species are denoted as D and Q. D lines observed at low temperature (110 K) constitute a triplet with hyperfine splitting 28.5 mT and g=1.979. The outer lines are additionally split to three components with intensity ratio 1:2:1 separated with 1.8 mT. We assigned the triplet D to Ag_2^+ dimer. At 110 K, besides the Ag_2^+ triplet, the singlet of framework defects, the doublet of hydrogen atoms and the triplet R of $^\bullet CH_2OH$ radicals ($A_{iso}=1.8$ mT and $g_{iso}=2.003$) are observed. At 150 K after the decay of Ag_2^+ and $^\bullet CH_2OH$ spectra, the quartet Q is only recorded. Its EPR parameters: $A_{iso}=13.9$ mT and $g_{iso}=1.979$ strongly support the view that it represents the Ag_4^{3+} cluster which was earlier observed in gamma-irradiated Ag-NaCs-rho zeolite even at room temperature. In the interstratified clays tetrameric clusters are less stable – in Ag-tri-Sm/Ch they decay above 170 K and in Ag-di-Sm/M above 200 K, respectively. The effective scavenging of positive holes by methanol molecules, which limits the geminate recombination and increases the number of Ag^0 atoms initiating the agglomeration process, is proposed to explain the formation of silver clusters with bigger nuclearity in the presence of methanol.

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PULSE RADIOLYSIS STUDY OF THE INTERMEDIATES FORMED IN IONIC LIQUIDS. INTERMEDIATE SPECTRA IN THE p-TERPHENYL SOLUTION IN THE IONIC LIQUID METHYLTRIBUTYLAMMONIUM BIS[(TRIFLUOROMETHYL)SULFONYL]IMIDE

Jan Grodkowski, Rafał Kocia, Jacek Mirkowski

Room temperature ionic liquids (IL) [1-3] are non-volatile and non-flammable and serve as good solvents for various reactions and have been proposed as solvents for green processing [3]. To understand the effect of these solvents on the chemical reactions, the rate constants of several elementary reactions in ionic liquids have been studied by the pulse radiolysis technique [4-9].

Fast kinetic measurements were carried out by pulse radiolysis using 10 ns, 10 MeV electron pulses from a LAE 10 linear electron accelerator [10] delivering the dose up to 20 Gy per pulse. The details of the computer controlled measuring system were described [9,11].

In this study, the formation of intermediates derived from p-terphenyl (TP) in the ionic liquid methyltributylammonium bis[(trifluoromethyl)sulfonyl]imide (R_4NNTf_2) solutions have been studied by pulse radiolysis as a part of our studies concerning CO_2 reduction. Conversion of CO_2 into organic compounds is a very important and permanent problem of chemistry. The ionic liquids as new type of solvent have also been used to study this subject.

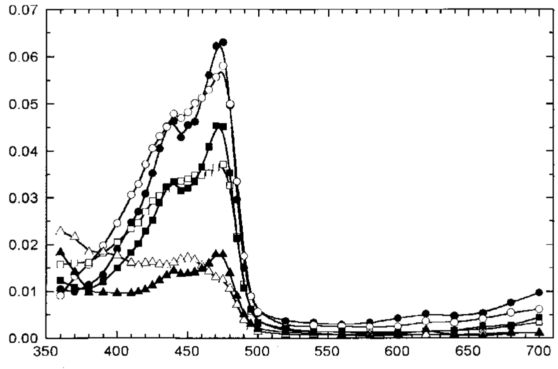

Fig.1. Transient optical spectra monitored by pulse radiolysis of deoxygenated R_4NNTf_2 containing 0.014 mol L^{-1} TP – open symbols, and addition (weight) 3% TEA – solid symbols. The spectra were taken at 400 ns (circles), 5 μs (squares), and 25 μs (triangles) after the pulse. Dose – 15 Gy.

TP was chosen because its radical anion ($TP^{\bullet-}$) has very strong reducing properties and was very useful in CO_2 reduction [12 and references therein]. In photochemical process, $TP^{\bullet-}$ is formed from excited states of TP* by reaction with electron donor triethylamine (TEA) or in radiolysis directly in the reaction with solvated electrons. The presence of solvated electrons is clearly seen in pulse radiolysis of R_4NNTf_2. The pulse radiolysis is always accompanied by Čerenkov light emission. It is then expected that formation of excited states of TP* can also take place.

The pulse radiolysis of TP solution in R_4NNTf_2 has been carried out as a function of TP concentration, TEA and under Ar, CO_2, O_2 and N_2O.

$TP^{\bullet-}$ under Ar is formed in two steps, one very fast already during the pulse and the second dependent on TP concentrations corresponding to the TP reaction with solvated electrons.

In Figure 1, there are presented spectra obtained in pulse radiolysis of Ar-saturated 14 mM TP solutions in R_4NNTf_2 and with 3% TEA added, measured at 400 ns, 5 μs, and 25 μs after the electron pulse. In the time zero only in the presence of TEA the spectra corresponded to the known spectrum of $TP^{\bullet-}$ [13]. Under the absence of TEA, for the measured spectra more transients are responsible. Besides $TP^{\bullet -}$, also cation radical and triplet excited state TP* are known to absorb in the same region. TEA is a scavenger for cation radical and excited states of TP. The occurrence of both species were confirmed also by the experiments under O_2 and N_2O. Kinetics of the absorption decay is quite complicated and the best fitting to the experimental results can be achieved taking an exponential decay equation with three different constants. In Figure 2, there are presented experimental traces of absorbencies at 475 nm *vs*. time in logarithmic scale for 14 mM TP in Ar-saturated samples in the absence and presence of TEA.

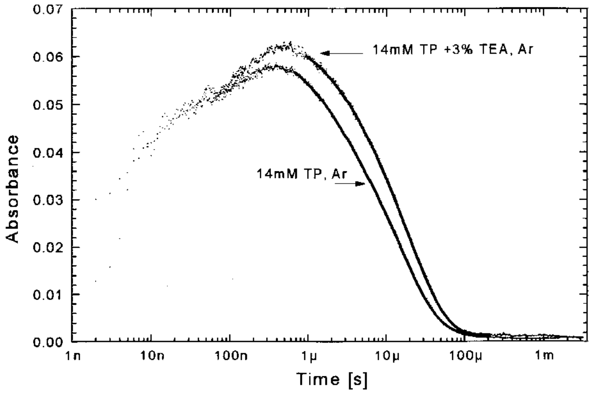

Fig.2. Experimental absorbance *vs*. time trace at 475 nm in 14 mM TP deoxygenated R_4NNTf_2 solution with and without 3% TEA added. Decaying parts of traces were fitted using equation: A(t)=A1*exp(-t*k1)+ A2*exp(-t*k2) + A3*exp(-t*k3) + A0. Dose – 15 Gy.

CO_2 saturation of 14 mM TP solution cut initial absorbance by about 50% and eliminates additional absorbance formation after the electron pulse. Only in the sample with TEA added some participation of $TP^{\bullet -}$ in the spectra can be distinguished. The effect can be explained by CO_2 reaction with solvated and dry electrons thus eliminating one path of $TP^{\bullet -}$ formation. Some $TP^{\bullet -}$ are formed by reaction of excited TP* states with TEA. Direct reactions involving TP, $TP^{\bullet -}$, CO_2 and $CO_2^{\bullet -}$ are too slow to be observed in pulse radiolysis time scale. The reactions involving metal complexes are underway.

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SINGLET OXYGEN-INDUCED OXIDATION OF ALKYLTHIOCARBOXYLIC ACIDS

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Singlet oxygen ($^1O_2$) could be generated in biological systems by endogenous and exogenous processes (*e.g*. enzymatic and chemical reactions, UV or visible light in the presence of a sensitizer) [1]. Numerous data show that proteins are the major targets of $^1O_2$-induced damage in the living cells. The primarily reactions occur here preferentially with residues of aromatic and sulphur containing amino acids [1].

In particular, reaction of $^1O_2$ with thioether sulphur of methionine (Met) leads to the formation of persulphoxide [2,3]:

$$^1O_2 + {>}S \rightarrow {>}S^{(+)}O\text{-}O^{(-)} \qquad (1)$$

which is in equilibrium with superoxide radical-anion ($O_2^{\bullet -}$) and respective sulphur-centered radical-cation:

$${>}S^{(+)}O\text{-}O^{(-)} = {>}S^{\bullet +} + O_2^{\bullet -} \qquad (2)$$

However, the major pathway of persulphoxide decay is bimolecular reaction with the second molecule of thioether that leads to the formation of respective methionine sulphoxide [2,3]:

$${>}S^{(+)}O\text{-}O^{(-)} + {>}S \rightarrow 2\ {>}S{=}O \qquad (3)$$

In this work, we have investigated the mechanisms of deprotonation and decarboxylation of sulphur-centered radical-cation (${>}S^{\bullet +}$) the irreversible processes, which compete with the formation of sulphoxide (reaction 3) by moving the equilibrium (2) to the right hand side. Importantly, efficiency of both decarboxylation and deprotonation could be influenced by various factors such as neighbouring group participation and environmental effects. These phenomena may be studied using thioethers diverse by the number and positions of carboxylate groups. Therefore, the experiments

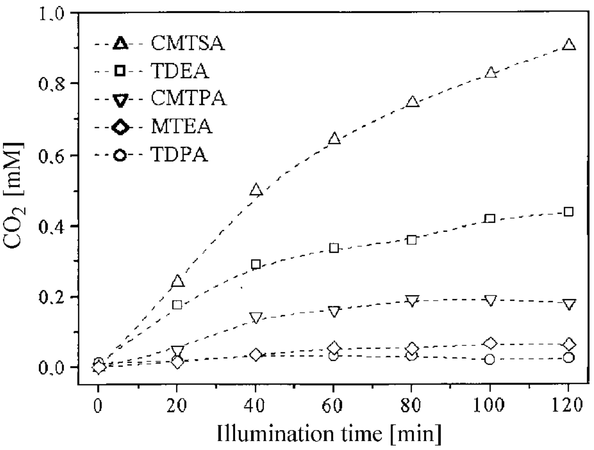

Fig.1. Efficiency of $^1O_2$-induced carbon dioxide formation *vs.* time of illumination in solutions containing 50 mM thioether, 22 μM RB, 1.045 mM oxygen at pH 6.

have been performed for the following model thioethers: 2,2'-thiodiethanoic acid (TDEA), 3,3'-thiodipropionic acid (TDPA), 2-(methylthio)ethanoic acid (MTEA), 3-(carboxymethylthio)propionic acid (CMTPA), 2-(carboxymethylthio)succinic acid (CMTSA). Singlet oxygen has been produced in aqueous, oxygen-saturated solutions of thioethers, illuminated by visible light in the presence of rose bengal (RB) as a photosensysbilizer [4]. Formation of carbon dioxide and respective sulphoxides has been monitored by means of head-space chromatography (GC) and high performance ion chromatography exclusion (HPICE), respectively.

For all investigated alkylthiocarboxylic acids, the $^1O_2$-induced oxidation leads to the release of carbon dioxide, and simultaneously to the formation of respective sulphoxide (Figs.1 and 2). However, the higher yield of decarboxylation has been observed for alkylthiocarboxylic acids containing carboxylate functionality in the α-position relative to the thioether sulphur, where such process leads to the formation of resonance stabilized α-alkylthioalkyl radicals (see example in Fig.1). The process of decarboxylation occurs most probably due to the intramolecular electron transfer from deprotonated carboxylic functionality to sulphur-centered radical-cation [5], since its efficiency depends on pH (Fig.3). It suggests that the formation of carbon dioxide may be catalyzed by the presence of Levis bases such as hydroxyl or chloride anions. It seems that the reaction (drafted for TDEA in Scheme 1 in [6]) can be described by nucleophilic substitution at the thioether sulphur, in which a weak nucleophile superoxide radical anion ($pK_A(HO_2^{\bullet}/O_2^{\bullet -})\approx 4.8$ [7]) is replaced by a much stronger nucleophile like hydroxide anion. In support, our DFT calculations [8] predict the possibility of the formation of the tetravalent transient product of hydroxide anion addition to persulphoxide. Therefore, the reaction may occur *via* two-step mechanism of nucleophilic addition – nucleophilic dissociation of (A_N+D_N)-type [9]. The observed influence of carboxylate groups in β-position relative to the sulphur on the efficiency of decarboxylation suggests furthermore that they may also catalyze decarboxylation of α-positioned carboxylate in a manner similar to hydroxide anion.

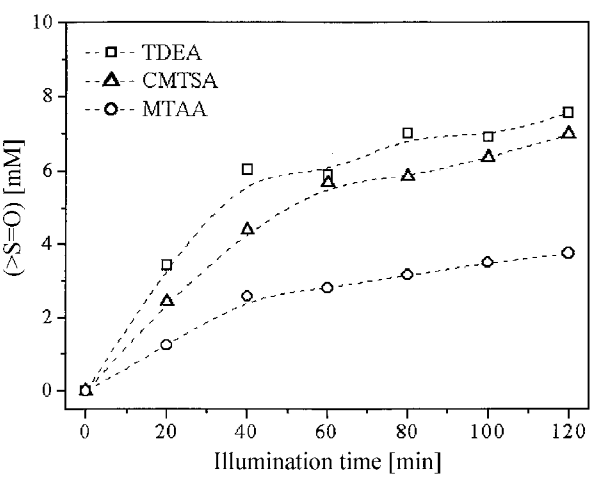

Fig.2. Efficiency of $^1O_2$-induced sulphoxide formation *vs.* time of illumination in oxygen-saturated solutions (1.045 mM oxygen) containing 22 μM RB and 50 mM of thioether at pH 6.

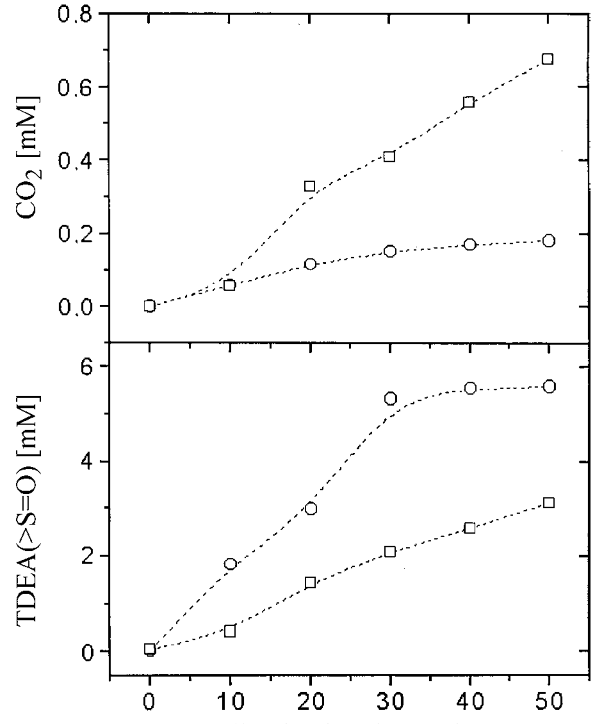

Fig.3. Efficiency of $^1O_2$-induced carbon dioxide and sulphoxides formation *vs.* time of illumination in oxygen-saturated solutions (1.045 mM oxygen) containing 50 mM TDEA, 22 μM RB at pH 9 (square points) and pH 6 (circle points).

This work described herein was supported by the Research Training Network SULFRAD (HPRN-CT-2002-00184) and the State Committee for Scientific Research (KBN) grant (No. 3 T09A 066 26). The computations were performed employing the computer resources of the Interdisciplinary Centre for Mathematical and Computational Modelling, Warsaw University (ICM G24-13).

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COMPUTATIONAL STUDY ON THE 1,2-HYDROGEN SHIFT IN THIYL, OXYL, AMINYL AND AMIDYL RADICALS

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The central issue of this paper are the reactions of the 1,2-hydrogen shift from the carbon atom to the adjacent heteroatom in thiyl, oxyl, aminyl and amidyl radicals. From the physiological point of view, thiols are one of the most important classes of sulphur-containing compound. The protective or antioxidant effects of thiols result from the fact that they can act as hydrogen or electron donors (pH dependent). One electron oxidation of thiols leads to the formation of thiyl radicals $RCH_2S^\bullet$. Therefore, $RCH_2S^\bullet$ are important intermediates in biological conditions of oxidative stress [1]. They are moderately good oxidants, having potential to abstract "activated" hydrogen from carbon atoms. This ability has been already experimentally demonstrated for several groups of biologically important compounds such as alcohols [2], carbohydrates [3], fatty acids [4-7], amino acids [8], and peptides

Table. G3MP2B3 calculated free energies [kcal mol^{-1}].

Reaction	ΔG	ΔG‡	ΔΔG$_{solv}$	ΔΔG$^‡_{solv}$
Thiyl radicals				
$CH_3S^\bullet \rightarrow {}^\bullet CH_2SH$	8.30	36.89	0.98	0.56
H_2O	9.35	8.99	-1.10	-2.67
$2H_2O$	10.13	0.89	-0.39	-0.01
$CH_3CH_2S^\bullet \rightarrow CH_3{}^\bullet CHSH$	6.97	33.82	-0.51	0.27
H_2O	7.72	33.78	-0.43	-1.82
$2H_2O$	8.21	3.08	0.44	1.05
$HOCH_2CH_2S^\bullet \rightarrow HOCH_2{}^\bullet CHSH$	4.26	32.48	-0.30	-0.34
H_2O	8.16	5.85	-3.60	-2.28
$2H_2O$	9.68	5.31	-0.26	-0.45
Oxyl radicals				
$CH_3O^\bullet \rightarrow {}^\bullet CH_2OH$	-8.73	29.83	-3.24	-0.44
H_2O	-11.45	29.49	-3.80	-1.86
$2H_2O$	-11.62	19.57	-0.95	-0.94
$CH_3CH_2O^\bullet \rightarrow CH_3{}^\bullet CHOH$	-11.77	26.44	-2.97	-1.06
H_2O	-12.25	27.67	-3.02	-1.01
$2H_2O$	-12.29	2.55	-0.53	0.13
Aminyl radicals				
$CH_3N^\bullet H \rightarrow {}^\bullet CH_2NH_2$	-6.00	36.96	-1.25	-10.64
H_2O	-3.89	37.25	1.30	0.30
$2H_2O$	-3.91	32.84	1.11	0.75
$CH_3CH_2N^\bullet H \rightarrow CH_3{}^\bullet CHNH_2$	-7.42	35.07	0.25	0.02
H_2O	-5.72	34.36	1.02	1.02
$2H_2O$	-6.16	31.06	1.80	0.95
Amidyl radicals				
$HC(=O)N^\bullet CH_2C(=O)H \rightarrow HC(=O)NH^\bullet CHC(=O)H$	-28.84	32.77	0.29	-3.82
H_2O	-26.99	16.57	0.55	-5.23
$CH_3C(=O)N^\bullet CH_2C(=O)CH_3 \rightarrow CH_3C(=O)NH^\bullet CHC(=O)CH_3$	-27.08	33.67	-0.08	-4.59
H_2O	-18.79	17.53	0.42	-4.06

[9]. In general, hydrogen atoms may be “activated”, and, therefore its abstraction can be facilitated, due to the quantum effects that may stabilize the carbon-centered radicals being the products of such abstraction. For example, Chhun *et al.* [10] have theoretically demonstrated that thiyl radical of homocysteine may intramolecularly abstract hydrogen from α-carbon of the amino acid, giving resonance-stabilized α-aminoalkyl radical. Also, the intramolecular rearrangements of the thiyl radicals from reduced glutathione (GSH) and 2-mercaptoethanol have been experimentally studied in detail (see review [1]). Therefore, it seems reasonable to assume that simple thiyl radical may be a subject of 1,2-hydrogen-atom shift leading to the formation of R-$^\bullet$CH-SH type radical, which should be stabilized by the resonance with electron pairs of the adjacent divalent sulphur. Importantly, Fernandez-Ramos and Zgierski [11] already demonstrated such a possibility for methoxyl and benzyloxyl radicals ($RCH_2O^\bullet$), which may rearrange to less reactive ketyl radicals R-$^\bullet CH_2OH$. Similarly, the question to what extend aminyl and amidyl radicals may suffer a 1,2-hydrogen shift and thus convert to more stable carbon-centered radical remains open [12,13]. Importantly, the biological consequence of such a rearrangement may directly concern the mechanism of (reactive oxygen species) ROS-related toxicity of amyloid β-peptide one of the major hallmarks of Alzheimer disease [13].

Our calculations were curried out for model pairs of radicals: $CH_3S^\bullet/^\bullet CH_2SH$, $CH_3CH_2S^\bullet/CH_3{}^\bullet CHSH$, $CH_3O^\bullet/^\bullet CH_2OH$, $CH_3CH_2O^\bullet/CH_3{}^\bullet CHOH$, $HOCH_2CH_2S^\bullet/HOCH_2{}^\bullet CHSH$, $CH_3N^\bullet H/^\bullet CH_2NH_2$, $CH_3CH_2N^\bullet H/CH_3{}^\bullet CHNH_2$, $HC(=O)N^\bullet CH_2C(=O)H/HC(=O)NH^\bullet CHC(=O)H$, and $CH_3C(=O)N^\bullet CH_2C(=O)CH_3/CH_3C(=O)NH^\bullet CHC(=O)CH_3$. For DFT (density functional theory) computations of open shell systems, we employed a commonly used, non-local hybrid functional, B3LYP, which appears to be particularly useful for the computation of optimized molecular geometries and radical spin densities. The DFT optimizations and energy calculations were done utilizing the standard 6-31G(d) basis set offering a reasonable compromise between proper description of the species with a good performance at a modest computational cost. The structures were fully optimized using the analytical gradient technique, and the nature of each located stationary point was checked by evaluating harmonic frequencies. To account for the effect of the solvent, the free energy of solvation was calculated for the gas-phase geometries of radicals applying the integral equation formalism model (IEFPCM). The search for the transition structures was performed using the quadratic synchronous transit (QST) method. The free energies of formation for the radicals and transient states were calculated applying the Gaussian-3/DFT theory. All the calculations were performed with the Gaussian’03 suite of programs, where detailed references to all methods applied here could be find [14]. The preparation of input file structures and the visualization of the computation results were done on a PC computer using the ChemCraft freeware program [15].

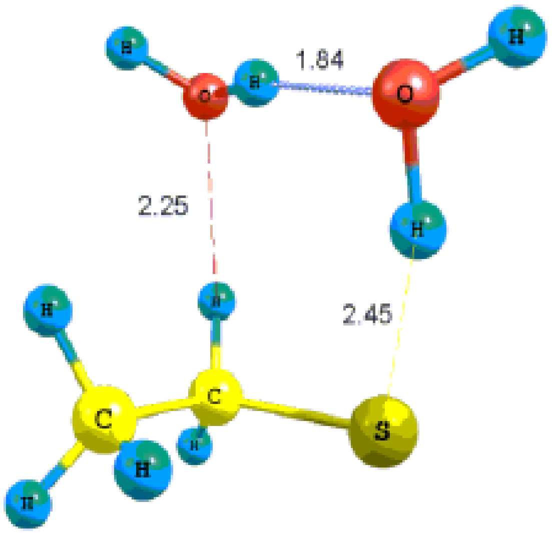

Fig. The B3LYP/6-31G(d) calculated geometry of transient state of the 1,2-hydrogen shift rearrangement in $CH_3CH_2S^\bullet$ radical, while assisted by the presence of two water molecules.

The computational results suggest that only for oxygen and nitrogen containing radicals the reaction of $RCH_2X^\bullet \rightarrow R^\bullet CHXH$ of 1,2-hydrogen shift is exergonic. For all investigated thiyl radical, this reaction is endergonic in nature. Moreover, the complexion of the radicals with one or two molecules of water additionally increases ΔG of the reaction. However, the reaction of 1,2-hydrogen shift benefits from the addition of water molecules, which results in a decrease of activation free energy ($\Delta G^\ddagger$). (The calculated free energies are summarized in Table.) Generally, it was confirmed that water may catalyze the 1,2-hydrogen shift by forming a bridge containing two water molecules (see an example in Fig.) that substantially decreases $\Delta G^\ddagger$ of the reaction.

This work described herein was supported by the Research Training Network SULFRAD (HPRN-CT-2002-00184), the State Committee for Scientific Research (KBN) grant (No. 3 T09A 066 26) and the International Atomic Energy Agency fellowship (C6/POL/03014). A part of the computation was performed employing the computing resources of the Interdisciplinary Centre for Mathematical and Computational Modelling, Warsaw University (ICM G24-13).

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DENSITY FUNCTIONAL THEORY STUDY OF $Na^+\cdots{}^\bullet CH_3$ COMPLEX STABILIZED IN DEHYDRATED Na-A ZEOLITE

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It is well-known that the porous nature of zeolite plays an important role in the separation and stabilization of various reactive intermediates as atoms, radicals, radical ions and metallic clusters [1,2]. Studies of these intermediates are very important for better understanding of the mechanisms of chemical reactions in heterogeneous catalysis as well as for photochemistry, radiation chemistry and environmental applications [3-5].

Recently, metal loaded zeolites were found to be promising catalysts in the decomposition of automotive and power plants exhaust emission. Synthetic zeolites play an important role in petrochemistry enabling catalytic conversion of hydrocarbons to liquid fuels.

One of the relatively simple, yet very important species stabilized in zeolites is methyl radical, for which its lifetime in the zeolites framework is extended to hours even at room temperature [6] compare to µs in liquid hydrocarbons.

The adsorption/stabilization of methyl radicals in zeolites has been studied by electron paramagnetic resonance (EPR) spectroscopy, where isotropic and anisotropic hyperfine coupling constants have provided an important insight into the electron structure/distribution in polyatomic radicals. The observed EPR spectrum of methyl radicals in zeolites usually exhibits isotropic quartet similar to those observed in the liquid phase or inert gas matrixes. However, line shape and finally hyperfine coupling constants depend on the nature of adsorption sites and activation of zeolite (dehydratation) [7].

Application of quantum chemistry methods can provide here important information on the nature of radical-zeolite interaction, particularly of the electronic and magnetic properties of the intermolecular adsorption complex. For example, the interpretation of hyperfine coupling constants of carried out by theoretical calculations applying even semiempirical methods can often help to rationally explain the experimental results.

However, due to the complexity of adsorbates-zeolite systems, calculations hyperfine coupling constants have been limited to rather simple systems [8] do not mention that the application of very sophisticated *ab initio* or density functional theory (DFT) methods require here quite substan-

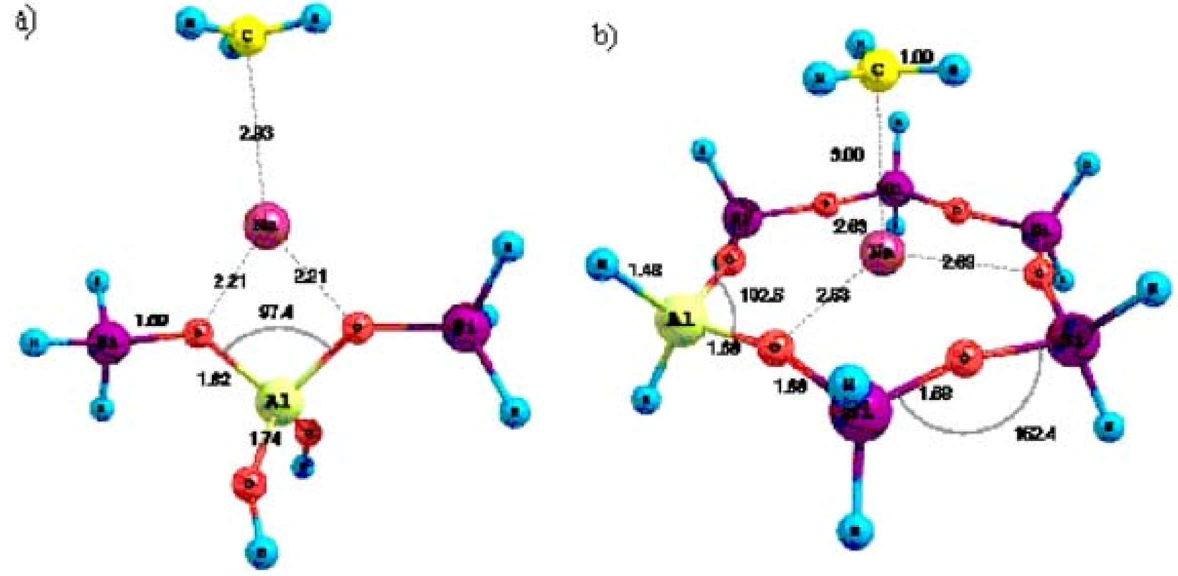

Fig. Two investigated models: a) 3T cluster and b) six-membered (6T) ring with sodium cation and methyl radical. Geometrics optimized with B3LYP/LANL2DZ theory level.

tial computational effort. Just recently, with the advent of new-generation computers, more accurate quantum chemical studies on such systems have started to appear in the literature. Since their enormous computational demand, such calculations are still performed rather for a small fragment of zeolite cages or channels.

The literature data univocally suggest that combination of hybrid functional DFT methods with Pöple basis sets gives appropriate information on the structure of examined molecules.

Especially, the B3LYP/6-31G(d) level calculations give geometries with sufficient quality for a broad range of chemical applications. Importantly, application of DFT methods for computing magnetic parameters of different type for organic radicals can give hyperfine couplings close to experimental data [9-13]. Particularly, application of the basis sets EPR-II and EPR-III designed by Barone [14] for calculation of magnetic properties of radicals in connection with B3LYP [15] functional, reproduce experimental hyperfine coupling constants for hydrogen, carbon and nitrogen in a number of radicals with an error of amplitude usually smaller than 10%.

In this study, we report structural and hyperfine coupling constants calculations of the $Na^{+}\cdots{}^{\bullet}CH_3$ complex (adduct) formed after gamma irradiation in Na-LTA zeolite containing methane adsorbed at low pressure.

Two different models have been applied to represent the zeolite framework; 6T (six-membered/six tetrahedral) ring, and 3T cluster ($H_3SiOAl(OH)_2OSiH_3$) remaining a fragment of octagonal window terminated with hydrogen atom with embedded sodium cation. Geometries of both model complexes have been fully optimized at a B3LYP level with LANL2DZ basis set. Calculations of hyperfine coupling constants have been carried out with DGDZVP and DGauss A1 Coulomb Fitting basis sets for sodium atom and EPR-III for methyl radical atoms. All calculations have been performed using Gaussian'03 suite of programs [16].

Table 1. Selected structural parameters for both investigated models [Å] obtained with B3LYP/LANL2DZ theory level.

Distance	3T cluster	6T ring
Na-O	2.21	2.64
O-Si	1.69	1.68
O-Al	1.82	1.68
Na-C	2.93	3.0
C-H	1.09	1.09

Geometries of both optimized fragments of zeolite (Fig.) are in pretty good agreement with the previous literature data [17,18]. The 6T rings has been optimized with silicon atoms then one silicon has been substituted by aluminium. Presence of one or two aluminium atoms instead of silicon in the six-membered ring could change the position of sodium cation. Here, sodium cation has remained in the centre of the 6T ring, with the coordination number close to zero. (Table 1 summarizes the most important parameters, representative for the investigated model of zeolite-framework $Na^{+}\cdots{}^{\bullet}CH_3$ interaction.) The latest crystallographic refinement of structure of LTA zeolite shows the possibility of sodium cation coordination with three oxygen atoms of 6T ring, but in spite of this sodium cation still occupies nearly central position – shifted out of the centre only by about 0.2 Å [18,19]. Van der Waals radius of sodium cation is approximately of the size of the 6T window, thus sodium cation can fit well insight, taking the advantage of the stabilization in the centre of hexagonal window [18].

A comparison of two applied models shows that the calculated distance between methyl radical and sodium cation in the 6T ring model is insignificantly longer than in the 3T cluster. This seems to be the reason why the presence of 6T ring does not affect the geometry of methyl radical, which is pyramidal with dihedral angle 10° in both cases (freely tumbling methyl radical has a flat or close to flat geometry).

Table 2. Calculated and experimental hyperfine coupling constants [G].

	3T cluster		6T ring		Experimental
	DGZVP	DGA1	DGZVP	DGA1	
A_{Na}	10.5	10.6	6.62	7.6	6.5
	EPR-III		EPR-III		
A_H	20.5	20.4	21.06	21.04	22.9

Calculated hyperfine coupling constants for optimized geometries (Table 2) are in good agreement with those obtained experimentally. (Since experimentally observed EPR spectra had isotropic nature, we do not present anisotropic coupling constants obtained in the calculations.) Specially, very good agreement has been obtained for A_{Na} in the 6T ring model, which seems to more adequately mimic real experimental conditions than the 3T cluster.

The successful modelling of the geometry of the $Na^{+}\cdots{}^{\bullet}CH_3$ complex evaluated by the comparison of calculated magnetic parameters with experimentally obtained data, we feel encouraged to use the approach outlined here in further studies on the adsorbate-zeolite systems.

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EFFECT OF HINDERED AMINE LIGHT STABILIZERS ON RADIATION RESISTANCE OF POLYPROPYLENE MEASURED BY DSC

Andrzej Rafalski, Grażyna Przybytniak

In many polymers, hindered amine light stabilizers (HALSs) are used as radical scavengers and antioxidants to protect material against photodegradation [1]. It is generally accepted that the decomposition of polyolefines initiated by ionizing radiation proceeds comparably to UV-induced degradation, *i.e. via* free radical mechanism [2,3], thus the application of amine stabilizer as a protecting agent against radio-degradation is fully entitled. Oxidative damage is the main reason for applying antioxidants as the radioprotective agents in polypropylene (PP). HALSs are well known radical scavengers that inhibit the propagation of free radicals acting as their scavengers.

Two various phases occur in isotactic polypropylene (iPP) – ordered domains of the crystalline phase and variety of amorphous sites [2]. Thus, there are two types of peroxyl radicals formed during irradiaton and situated in the totally different vicinity. Random orientation of macromolecules in the amorphous phase facilitates peroxyl radical mobility and involves their faster decay. Therefore, the amount of the radicals considerably decreases in presence of stabilizers. Defined rigid structure of crystal delays the combination of radicals and the unpaired electron is transferred into other sites inducing postirradiation damages for months. Assuming homogeneous distribution of modifiers added to polypropylene in melted state, we found unambiguously that radicals are scavenged by HALSs predominantly in amorphous phase as in presence of hindered amines a significant decrease in characteristic electron paramagnetic resonance (EPR) signal of peroxyl radical just in this phase was observed [4].

Differential scanning calorimetry (DSC) method was applied to characterize physical properties of isotactic polypropylene modified by selected HALSs before and after irradiation. Three types of amine stabilizers were applied: two derivatives of 1,2,2,6,6-pentamethyl piperidine of low and high molecular weight (Tinuvin 765 and Tinuvin 622, respectively) and one polymeric derivative of 2,2,6,6-tetramethyl piperidine (Chimassorb 944). In order to increase the compatibility of HALS – polymer macromolecules, maleic anhydride (MA) was added to the composites. Physical alternations were estimated comparing changes in phase transitions and crystallization temperatures before and after electron beam exposure.

Isotactic polypropylene (Malen P J601) was mixed with the following additives: Tinuvin 622 (T622), Tinuvin 675 (T675) and Chimassorb 944 (C944). Selected samples were mixed with maleic anhydride. Samples were prepared in a Brabender mixer at 180°C and subsequently compressed between two metal plates quenching with water. Concentration of additives is expressed as the parts per hundred resin (phr). Irradiation with a 10 MeV electron beam was performed using a linear accelerator LAE 13/9 in air at ambient temperature. All samples were irradiated to a dose of 25 kGy.

Thermal analysis was carried out using a TA Instruments differential scanning calorimeter (MDSC 2920). The measurements were performed under nitrogen at a heating rate of 10°C/min. About 5 mg samples were placed in aluminum pans and inserted in the cell. During the first cycle, the cell was heated from the ambient temperature to 200°C, then kept for 5 min at this temperature and gradually cooled. The second run was performed afterwards applying the same conditions as for the first cycle.

Phase transitions of polypropylene are influenced by electron beam irradiation. The melting behavior of polypropylene shown in Fig.1A indicates that the melting peak obtained during the first cycle at 163°C, in the second cycle becomes wider due to increase of low temperature endotherm. For irradiated polypropylene, a single peak detected during first heating splits in the second cycle and two distinct minima are observed. High temperature melting peak is less intensive, whereas the intensity of low temperature peak significantly increases indicating that ionizing radiation induces changes in morphology of the polymeric material. Multiple-peak endotherms reveal separation of different crystals that occurs during slow recrys-

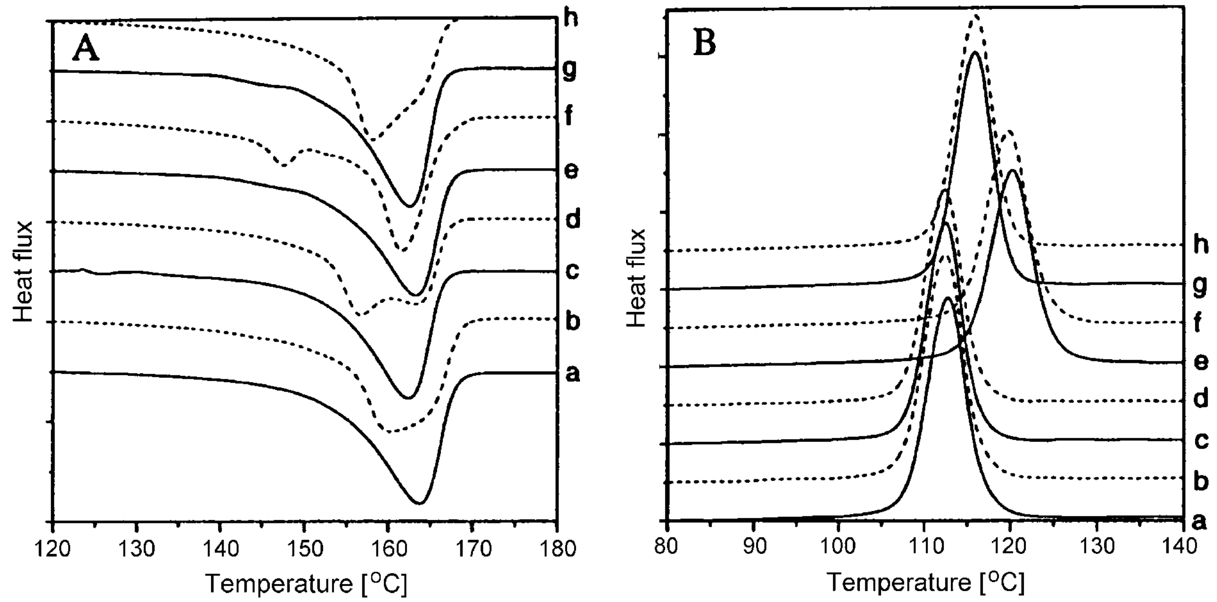

Fig.1. Phase transitions of polypropylene (a-d) and PP+0.5 phr T622 (e-h) before (a, b, e, f,) and after irradiation (c, d, g, h) with a dose of 25 kGy. Solid line – first cycles, doted lines – second cycle. (A) melting endotherms, (B) crystallization exotherms.

tallization in the second cycle [5]. The samples contain only α crystals, therefore two purely resolved melting endotherms correspond probably to the crystals of different orders.

In the presence of T622 single peak endotherm obtained in the first run splits after slow heating/cooling procedure in the second cycle, but this time the low temperature peak has a minimum at 147°C. The trace of peak at this temperature is detectable also in the irradiated sample. Character of main asymmetric peaks for both cycles is similar to that obtained for undoped samples and all these endotherms represent probably the same polymorph. It seems that the low temperature peak at 147°C represents β crystalline form [4]. Morphology of the sample is complex; the small area under the β peak shows that the content of this form is insignificant. The coexistence of various crystalline structures must be initiated by T622 stabilizer and results from complex polymorph transitions. Character of changes in polypropylene doped with other HALSs is similar.

The structure of crystals influences considerably crystallization transition [6]. The position of peaks during the first and second cycles for all samples is the same within the limits of experimental error ±0.5°C. The representative example of calorimetric measurement for T622 is plotted in Fig.1B. Although enthalpy of transition for all samples, both unirradiated and upon exposure to a dose of 25 kGy, varies in a narrow range from 87 to 89 J/g, the shape of curves changes – following exposure to ionizing radiation. The growth of peaks is observed simultaneously with reduction of their width. The maximum of crystallization temperature (T_c) recorded for polypropylene doped with stabilizers increases considerably. The crystallization temperature values determined from DSC curves for neat and modified polypropylene, both before and after irradiation, are collected in Table. For system PP+Tinuvins, the exothermic transitions are shifted even by about 10°C and crystallization is finished at the temperature corresponding to crystallization temperature of pure polypropylene. The observed changes clearly indicate that the stabilizers initially promote the conversion of melt to crystals and facilitate formation of crystal nuclei, what consequently determines the amount and distribution of microcrystals in the matrix. The increase of crystallization temperature results from the creation of large number of small nuclei leading to the shortening of the crystallization time. From industrial processing point of view, such effect is desired.

Table. Crystallization temperatures of neat and modified polypropylene, before irradiation and 72 days after irradiation.

Sample	Dose of irradiation [kGy]	T_c [°C]
PP	0	116.8
	25	116.4
PP+0.50phr T622	0	125.0
	25	119.7
PP+0.75phr T622	0	124,5
	25	119.8
PP+0.50phr T765	0	126.9
	25	115.1
PP+0.75phr T765	0	125.2
	25	115.6
PP+0.50phr C944	0	121.4
	25	115.5
PP+0.75phr C944	0	117.1
	25	114.6
PP+0.30phr MA	0	117.6
	25	115.3
PP+0.50phr MA	0	121.0
	25	114.9

The results obtained for polypropylene modified by amines show that crystallization temperature decreases by about 6-10°C upon exposure to ionizing radiation. Thus, upon irradiation the additives loss partly the nucleating properties, probably due to chemical changes of HALS stabilizers during the Denisov cycle that leads to decrease of crystallization temperature. It was found by Ahmed and Basfar that polypropylene in presence of nucleating agent is less resistant towards irradiation than without such admixture [7]. Therefore, considering the interaction of HALS with polypropylene one must take into account that amines, prompting formation of nuclei, increase imperfection of crystals, what results in easier and stronger stabilization of unpaired electrons in the crystal defects. In this way, amines strongly influence the radiosensitivity of crystalline phase, whereas their role as radical terminators in this phase is limited, contrary to the amorphous one as was confirmed earlier by EPR study.

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MODIFICATION OF MONTMORILLONITE FILLERS BY IONIZING RADIATION

Zbigniew Zimek, Grażyna Przybytniak, Andrzej Nowicki, Krzysztof Mirkowski

Nanofillers are a new class of particles that are applied to polymeric composites and other materials to improve some of their properties [1]. Elements, oxides, carbides, simple and composite salts, and other compounds can be used as the nanofillers. Manufacturing and investigation of properties of the composites have recently focused attention of many laboratories in polymer science.

The main problem in preparing composites from polymers and fillers is the incompatibility of components. Disperse phase is usually inorganic, hydrophilic compounds or minerals, while the main types of polymeric matrices are hydrophobic. For good mixing, the fillers should be modified to obtain hydrophobic layer on their surface. The modification is possible in many ways; the most popular is the impregnation of fillers with bifunctional molecules, containing in one molecule hydrophobic (*e.g.* long alkyl) and hydrophilic (*e.g.* ionic or polar) groups. Typical is the impregnation with ammonium salts having long alkyl chains. Such modified bentonites were mixed with commercially available polyolefines, *e.g.* polypropylene and polyethylene in molten state. For modification of the filler surface, other methods also are used, *e.g.* grafting of organophilic units on mineral particles.

As we reported earlier [2], the mineral fillers can be modified by using unsaturated compounds: styrene, methacrylic acid and maleic anhydride (MA), following by irradiation with high energy electron beam. Recently, we have used this method for compatibilization of montmorillonite (MMT) [3]. We selected maleic anhydride as a modifying agent because it does not undergo homopolymerization, is cheap and forms homogeneous mixtures with many polymers, for example, polypropylene. Now, we have used this method to change properties of bentonite "Specjal", containing about 70% of pure montmorillonite.

Acetone, maleic and phthalic anhydrides were obtained from P.O.Ch (Poland) while succinic anhydride was purchased from Fluka.

The samples were prepared by boiling bentonite with an acetone solution of suitable anhydride (10% w/w) for half an hour. The precipitate was filtered, dried at 30°C under low pressure, grinded and sieved to obtain a powder of particles below 70 μm. The concentration of adsorbed anhydride was about 5 to 8% w/w.

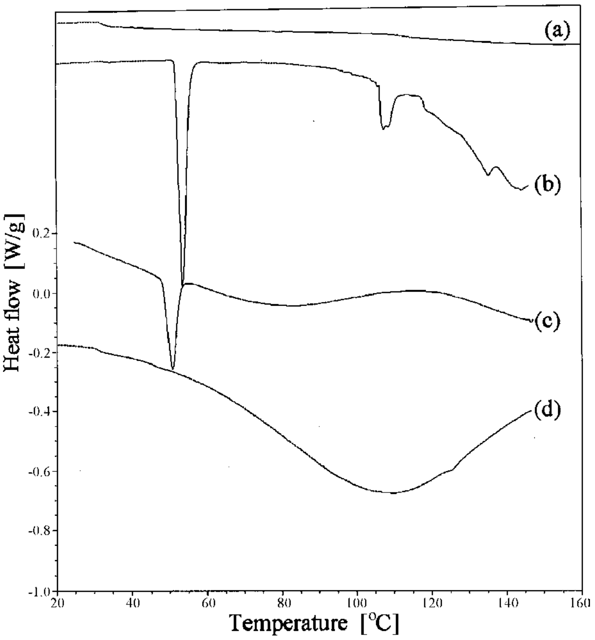

Fig.1. DSC results for bentonite "Specjal" (a), maleic anhydride (b), physical mixture of MMT/MA (c) and MMT/MA obtained *via* absorption from solution (d).

The samples were irradiated in an "Elektronika" accelerator using electron beam of energy 9 MeV and cumulative doses of 26, 52, 78 and 104 kGy.

After irradiation, the fraction of particles below 70 μm was selected.

The thermal properties of modified bentonite were tested using a differential scanning calorimeter MDSC2920CE in standard mode.

We used differential scanning calorimetry (DSC) measurements to determine the type of binding of maleic anhydride to bentonite. In Figure 1, are presented thermographs for: bentonite "Specjal" (a), maleic anhydride (b), physical mixture of bentonite "Specjal" with maleic anhydride (c) and sample of bentonite after absorption of maleic anhydride from acetone solution (d).

The thermograph (a) of unmodified bentonite does not confirm any exo- or endothermic process between 20 and 160°C. The diagram (b) indicates the melting point of maleic anhydride at 55°C and, additionally, at about 110°C peak belonging to the melting transition of maleic acid that could be present as an impurity. The physical mixture of bentonite with maleic anhydride shows the superposition of components, however the melting point of maleic anhydride is shifted slightly towards lower temperatures. The lowest thermograph (d) recorded for bentonite with the absorbed layer of anhydride reveals a different relationship. Lack of the signal at 55°C strongly suggest that the chemical reaction between maleic anhydride and active groups of bentonite takes place, leading to salt-type compounds that are responsible for the broad endotherm of minimum above 100°C. Additionally, it was confirmed that analogous DSC curves were obtained in the case of modification of bentonite with succinic or phthalic anhydrides (data not shown).

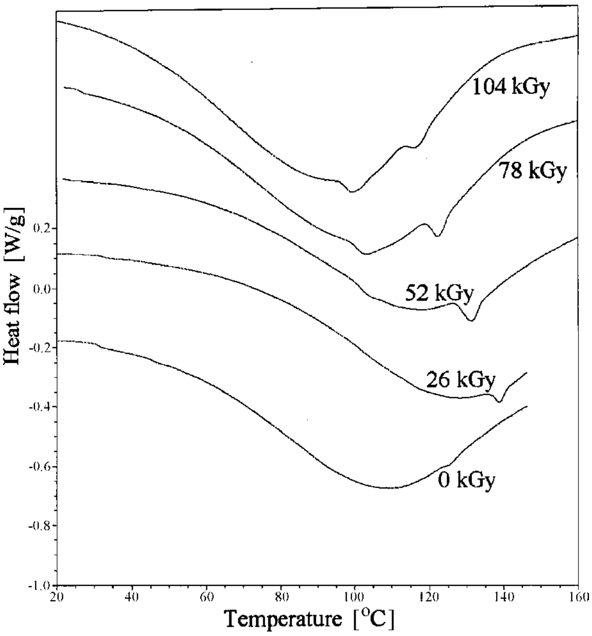

Fig.2. DSC thermographs for montmorillonite modified by maleic anhydride upon irradiation with electron beam with different doses.

Figure 2 shows the DSC results obtained for bentonite "Specjal" modified with maleic anhydride (MMT/MA) after ionizing radiation with the different doses. In comparison with previous results shown in Fig.1 new endothermic peaks appear what suggests that during irradiation a new phase of transition in the range 120-140°C is formed. The signal is strongly dose-dependent, the higher dose the greater is the shift towards lower temperatures. Futhermore, for doses above 50 kGy, a second low intensity peak is formed. It was also found that bentonites modified with succinic or phthalic anhydride upon irradiation do not reveal these additional DSC signals. The investigations indicate that the changes induced in the MMT/MA system by electron beam involve probably coupling between both components utilizing double bond of maleic anhydride.

Conclusion:

- Modification of the domestic bentonite "Specjal" by absorption of maleic anhydride, followed by irradiation with electron beam to the overall dose in the range 26-104 kGy, shows that the particles obtained in this process can be good fillers for the production of composites.
- Maleic anhydride reacts *via* anhydride group with active ionic sites of bentonite, forming a salt-like compound. Irradiation with electron beam leads to the breakage of double bond in maleic anhydride and to the production of new organic phases.

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STUDY OF THE PROPERTIES OF POLY(ESTER URETHANES) FOLLOWING IONIZING IRRADIATION

Ewa Maria Kornacka, Grażyna Przybytniak

Copolymers of polyurethanes and polyesters were found unsuitable for long-term implants because of fast hydrolysis of the ester soft segments. On the other hand, such properties make them valuable, gradually degradable biomaterial that might be used as scaffolds for tissue engineering [1-3]. The elastomeric polyurethanes are known to be radiation stable materials in sterilizing dose. Nevertheless, if additional components appear in the system, *e.g.* segments of polyesters, then the influence of irradiation is poorly recognized. Contrary to polyurethanes, polyesters are characterized by high oxidizability thus in their copolymers the oxidative processes are supposed to be at least partly limited.

The EPR spectrum of ethylene glycol (EG) at 77 K consists of dominant, asymmetric singlet and two low intensity peaks on both the sides of the central signal (Fig.1A). Upon gradual warming to 160-180 K, external lines grow and the sharp peak between them is revealed instead of diminishing broad singlet. We suggest that the alkoxyl radical formed in EG is a precursor of α-hydroxyl carbon-centered radical that exhibits usually slightly smaller hydrogen coupling than typical alkyl radicals. Therefore, detected triplet of $A(2H)_{iso}=1.93$ mT was attributed to $OHCH_2^\bullet$ radical. The intermediate subsequently undergoes oxidation since the newly-formed peak at g=2.0345, characteristic of peroxyl radicals, appears at elevated temperatures. The presence of other carbon-centered radical, $OHCH_2CH^\bullet OH$, was not confirmed since the overall width of spectrum, 4.25 mT, is too small to cover hyperfine splitting (hfs) of one α- and two β-protons.

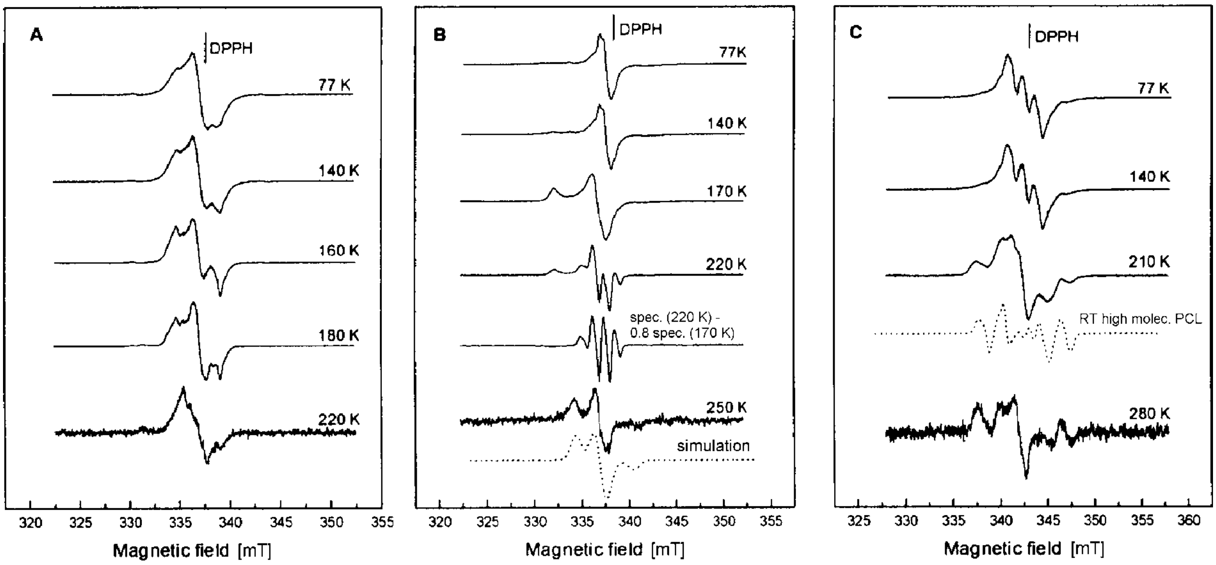

Fig.1. EPR spectra of PEU substrates irradiated at 77 K to a dose of 6 kGy upon annealing to indicated temperatures: (A) EG, (B) HMDI and (C) PCL.

Free radicals generated in the irradiated 4,4'-methylenebis(cyclohexyl isocyanate) (HMDI) show spectra collected in Fig.1B. Unresolved peak of $\Delta H_{pp}=1.19$ mT seems to correspond to radical formed upon abstraction of hydrogen at carbon atom bond to the isocyanate group. The strong influence of the substituent can prevent the interaction of unpaired spin with β-protons. Other possible intermediates would show typical of alkyl radicals hyperfine splittings. Moreover, in the range of temperatures 150-170 K, the product converts to peroxyl radical, a typical successor of carbon-centered radicals. Taking into account the above implications, we suggest that the most probable candidate for primary radical is $>C(NCO)^\bullet$. Quartet of proportion 1:2:2:1, selected at 220 K corresponds probably to $>CNH^\bullet$ radical.

Spectrum measured upon annealing to 250 K, showing two weak asymmetric external lines, must arise from the interaction between nitrogen and unpaired spin. The character of spectrum is comparable to simulated pattern of nitroxyl radical that was computed using the following parameters: $A(N)_{||}=3.0$ mT, $A(N)_\perp=0.5$ mT and $\Delta g=0.005$, thus the spectrum represent an oxidized form of radical whose spin interacts with nitrogen atom.

Spectrum detected at 77 K directly upon irradiation of poly(ε-caprolactane)diol (PCL) is a superposition of two components – triplet and wide signal comprising weak peaks both the sides of main absorption. The spectral range is comparable to that obtained for $OHCH_2^\bullet$ radical found in EG. Therefore, we interpret the triplet as the spectrum corresponding to species formed upon scission of C-C bond in the main chain. Hyperfine splitting, smaller than in typical alkyl radicals, indicates that the functional groups containing oxygen are involved, thus triplet might be assigned either to $OHCH_2^\bullet$ or $-OCH_2^\bullet$ radicals. The unambiguous interpretation of the singlet is not possible on the basis of obtained results, but we suggest that the peak represents radicals formed upon scission of the main chain, $-CH_2C(O)^\bullet$ and $^\bullet OCH_2-$. They are precursors of radicals situated in α-position to ether groups $-CH_2CH^\bullet OC(O)-$, whose fraction is already formed during irradiation at 77 K. To confirm unambiguously the above interpretation, a spectrum of high molecular weight PCL (80 kDa) measured at ambient temperature is shown in Fig.1C (dotted line). The signal corresponds to the radical characterized by the following EPR parameters: $A(H_\alpha)_{iso}=2.07$ mT, $A(H_{\beta 1})_{iso}=3.54$ mT, $A(2H_{\beta 2})_{iso}=2.60$ mT.

The resulting elastomers contain components of the following molar ratios HMDI:PCL:EG=4:1:3 for poly(ester urethanes)-1 (PEU1) and 2:1:1 for poly(ester urethanes)-2 (PEU2). PCL oligomers have various molecular weights – 1250 Da in PEU1 and 530 Da in PEU2. Free radical processes induced by ionizing irradiation might proceed in the entirely different way than in their substrates due to occurrence of totally different conditions for the dissipation of absorbed energy, for transfer of excitations and charges along macromolecules, and for localization of unpaired spin at newly formed functional groups, *e.g.* at urethane linkages. The unambiguous interpretation of PEUs spectra presented in Fig.2 is difficult as the primary species already above 170-180 K convert to peroxyl radicals of typical large, nearly axial g-anisotropy. At lower temperatures, two components could be distinguished. Except wide singlet that dominates at 160 K, the spectra measured directly upon irradiation and after annealing to temperatures below 160 K consist of six lines; two central peaks are of high intensity. The spectral distances among lines are consistent with alkyl radical that unpaired electron interacts with five equal hydrogen atoms $A(H_\alpha)= A(4H_\beta)=2.23$ mT. The intensity of two central peaks is too high for 1:5:10:10:5:1 ratio, thus sextet has to be overlapped by doublet of comparable hfs. Hence, contrary to radicals identified in components used for PEUs synthesis, radical centers in copolymers are localized also in hydrocarbon sequences, not only at α-position to heteroatom.

They combine inducing cross-linking or, upon oxidation, are precursors of polar groups in polymeric material. It was found that more than 70% of radicals detected directly upon irradiation convert at elevated temperatures to peroxyl radical.

Polar groups formed as stable products of oxidative degradation, *i.e.* hydroxyl, carbonyl and carboxyl groups, suppose to increase contact angle *vs.* water. Surprisingly, its value slightly increases upon irradiation from 84 to 95°C. It seems that ionizing radiation induces solid state reorganization of the segmented domains, leading to migration of soft segments towards the surface and to grow of hydrophobic properties.

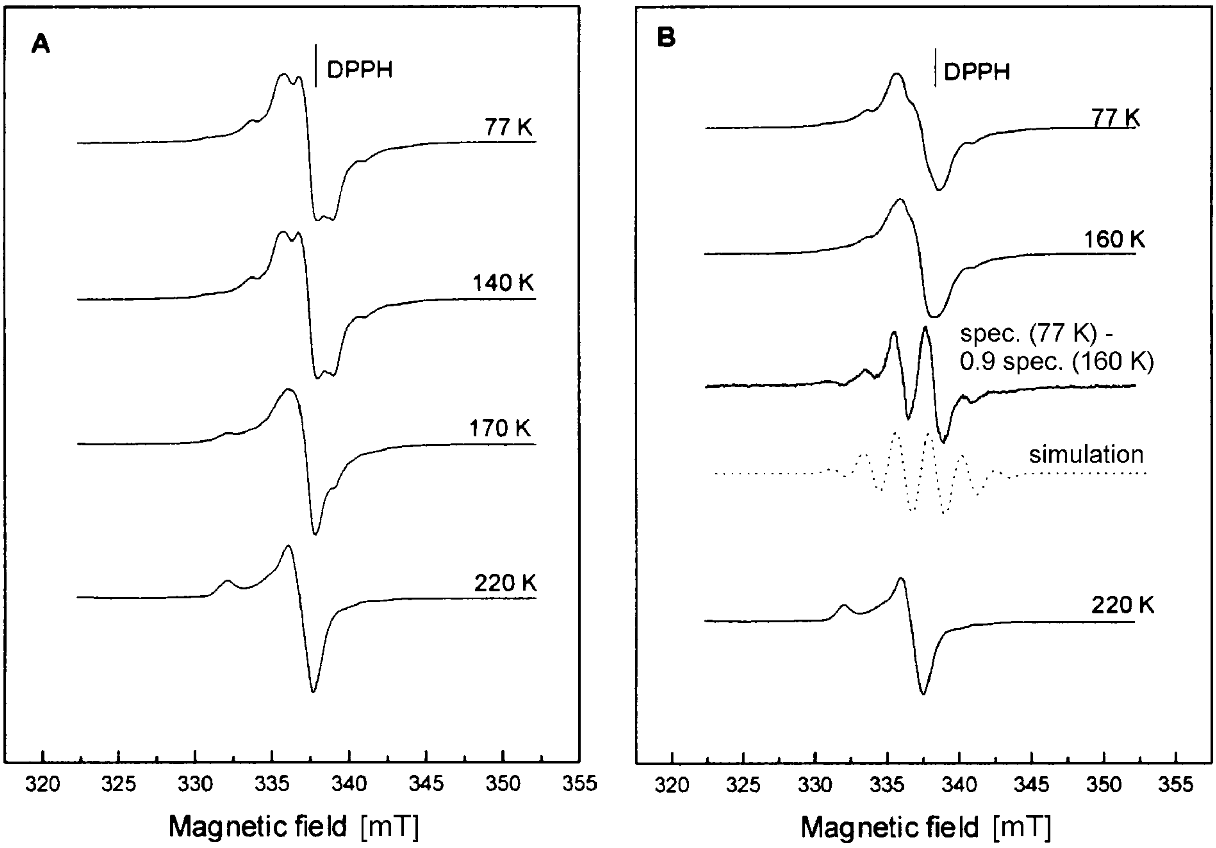

Fig.2. EPR spectra of PEU1 (A) and PEU2 (B) irradiated at 77 K to a dose of 6 kGy upon annealing to indicated temperatures.

Results confirmed that the urethane segments were more resistant towards ionizing irradiation and the presence of ester units facilitated generation of free radicals. It was also found that in PCL segments ionizing radiation induces radicals that are able to introduce cross-linking in macromolecules, and consequently reduce ability to biodegradation. Oxidation is a competitive reaction that refers to almost 70% of all initially generated radicals. The increased contact angle in water suggests that the surface of the irradiated materials might become more hydrophobic.

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BASIC RADIATION PHYSICS AND CHEMISTRY OF COMPOSITES

Grażyna Przybytniak, Zbigniew P. Zagórski

Until now, the radiation chemistry of composites, needed for effective radiation processing, has been not discussed. The survey of our research from that point of view is presented, starting with definition of a composite. Composites are more and more important in the applied and fundamental polymer science, and the participation of radiation processing of these systems will increase.

What is a composite? We have to answer the question before one can start the discussion of the radiation chemistry of the system. Polymeric composite is the combination of compositions that comprise two or more materials as separate phases, at least one of which is a polymer. On the other hand, polymeric compositions compounded with a plasticizer, stabilizer or very low proportions of pigments or processing aids are not ordinarily considered as composites. Typically, the goal of composites is to improve strength, stiffness or toughness, or dimensional stability by embedding particles or fibers in a matrix or binding phase. A second goal is to use inexpensive, readily available fillers to extend a more expensive or scarce resin. Such reason can be non-technical, like lowering the price of the product. In that sense the filler is categorized as a neutral additive to the polymer. However, in spite of to be composed for trivial reason, such material, when irradiated, it will behave like a composite.

The present attitude, especially nano-size oriented, treat composites as a hybrid material, which is a creation more or less different than the sum of constituents. The size, shape and chemical identity of the nanoparticle and interaction of the nanoparticles with the polymer matrix can affect significantly the final properties of a hybrid material. Radiation chemistry helps in fundamental understanding of hybrid materials containing inorganic nanoparticles embedded in an organic macromolecular matrix, in terms of the formation and intrinsic properties of the nanoparticles and the structure and properties inherent to the polymer. A composite from the point of view of radiation processing and radiation chemistry is any heterogeneous material in which the shortest size of a 3D, dispersed phase in the matrix is of the order of few nanometers. Shorter sizes do not qualify to the category of composites, because from the point view of radiation chemistry they form homogeneous material. Such small sizes are comparable with sizes of spurs, in looking into radiation chemistry on the molecular level [1]. Upper limit of size of the dispersed phase is not defined. The proposed definition of composites from the point of view of radiation physics and chemistry does not define the state of aggregation of both components of composites. Although the most common combination is solid-solid, *e.g.* polymer/clay combination, possible are systems solid-gas, *e.g.* porous plastics (prepared in the Department of Radiation Chemistry and Technology, Institute of Nuclear Chemistry and Technology, as scaffolds for growing cells [2]), polymers in the shape of pieces of medical devices with large volumes of air, *etc*. During radiation processing, the air gaps are also absorbing ionizing radiation, however with intensity by three orders of magnitude lower effect per volume.

Specific radiation chemistry of composites consists in:
- Different electron density of both substances results in different density of ionizations. This effect is not large, if both substances are chemical compounds of low Z number. However, the difference of electron density has to be taken into account.
- Different specific heat capacities of both phases, the dispersed and the main one, result in different temperatures reached in adiabatic irradiation, *i.e.* by electron beam.
- Large surface area of the interphase between two phases. It can reach enormous values with diminishing size of the dispersed phase. For instance, let us assume 1 kg of polymer composition with 30% content of dispersed phase (*e.g.* clay); the reduction of the diameter of particles from 1 μm, to 100 nm to 10 nm means an increase of the surface area respectively from 1800 m^2, to 18 000 m^2, to 180 000 m^2 (equivalent to 900 m x 200 m "lot"). These calculations are made for spheres, which show the smallest surface area for a given volume. Spheres occur in rather few composites, like latexes, and in most cases the shape of additional phase is far from the spherical. Therefore, any other shape means even higher surface area of the interface, with many consequences. In both phases independent radiation chemistries are running, with a variety of energy and material transfer in both directions. An important role is played by the quality of the interface. It is usually modified at the stage of preparation of a composite. Usually, the goal is to have the surface of dispersed phase as friendly to the host as possible, *e.g.* to make radiation-induced grafting possible, *i.e.* compatible. The consequences of enormous increase of the interphase, occurring with reduction of the size of dispersed phase, are well known in catalysis and adsorption, but are underestimated in radiation chemistry.

Any deviation from homogeneity, *i.e.* dealing with composites, introduces more or less disturbance into the depth dose curves. Keeping in mind the definition of the composite as the object with two or more bodies of different absorption characteristics towards interaction with radiation, one can start with a very common system of porous polymers, fibers, powders, *etc*. in which the second component of the system is air. Air is absorbing roughly by three orders of magnitude less per thickness than solid phase composed of low Z number. Therefore, the depth-dose curve shows a gap. The case of the same material, but divided into small particles gives the same basic curve for the same polymer, but of apparent lower density. Gaps between particles are too small to be reflected in details in the curve, but the apparent bulk density is lowered. In that case, the depth-dose curve is simply extended and the object is behaving like the original polymer "diluted" by air, which does not contribute much to the absorption of energy (but can have enormous effect on the final results of radiation processing from other reasons, for instance due to oxidation of the surface of dispersed phase). Composites with air, in other words porous polymers, are very important in the preparation and application of scaffolds for growing cells [2].

More complicate situations, as concerns depth dose curves occur, if the second phase in the composite of higher density material, *e.g.* clay. The depth dose curve is squeezed in that case, because the dispersed phase absorbs more energy than the polymer per volume. What is more, the clay particles radiate degraded, low energy quanta back in the direction of incoming radiation and forwards into the polymer. Behind the particle, the dose absorbed by the polymer is lower in comparison to basic depth-dose curve. The distance of optimum thickness, *i.e.* when the entrance and exit dose are equal, is shortened. The consequences of the presence of two phases of different interactions with ionizing radiation are many, but the principal one is the unfavorable increase of DUR (dose uniformity ratio). In the case of homogenous polymeric material in liquid state or solid in a block shape or as homogeneous porous material, or medical device, the DUR will not exceed the value of 2 in most favorable cases. In the case of composites, reaching of such excellent value is usually not possible.

Second important aspect of radiation processing of composites is the different temperature of both phases during high dose rate irradiation. Electron beam creates such a condition during adiabatic supply of energy, without the possibility of rapid equilibration of temperature, otherwise possible in gamma irradiation. Specific heats capacities of both phases are always different. Details connected with the heating of irradiated objects are collected in monographic chapter [3]. However, they do not take into consideration composites and the present paper draws attention to that fact.

This energy balance applies to most cases of radiation processing of homogeneous and composite materials which involve radiation-induced crosslinking, grafting, oxidation, controlled degradation. Radiation yields expressed as described by the change of single molecules or effects (*e.g.* formation of one double bond) per 100 eV absorbed energy usually are up to 5. The situation changes if a chemical chain reaction occurs. That is the case when a monomer is added as one of the composite and ionizing radiation acts as an initiator of reaction. The radiation yield jumps to 1000 and more in the case of gamma radiation. In the case of electron beam radiation, the yield is not so high, according to $I^{0.5}$ law (where I is the intensity of radiation, or dose rate). Even in the case of electron beam the rate of reaction is usually so high that the thermal effect is much larger than the heat effect of absorbed radiation. The jump of temperature can be so high that the system boils and direction of reactions runs in unexpected directions.

The knowledge of specific heat capacity of materials is important in planning the procedure of radiation processing, especially if very different compounds are involved in particular composites. The data of specific heats can be found in the literature, but not always, because demand for that information is limited. Very often the need arises to forecast the temperature reached by constituent of composites and for that purpose the application of differential scanning calorimetry (DSC) technique to determine specific heat capacity of any material occurring in the composite is useful. It is often a mixture, like a bentonite, which contains montmorillonite (MMT), for that the data in the literature is not likely to be found. Specific heat capacity depends on the substrate temperature. Simple dividing the energy evolved by the specific heat to give the temperature rise is precise enough only if the dose is low and the specific heat is high. Otherwise, one has to analyze the changes in heat capacity as a function of temperature [3].

The phenomenon of different temperatures reached in adiabatic conditions by the main constituent and the composite phase is well pronounced if the latter has micrometer dimensions. With diminishing size of the second phase, the heat transport is more and more effective and eventually the thermal equilibration is comparable to the supply of ionizing energy. Calculations of the heat transport are complicated, but simplified estimations show that composites in which the second phase has indeed dimensions of single nanometers, can be treated as thermally homogeneous. Strictly speaking, the equilibration of the temperature proceeds as fast as the equilibration of temperature in multi-ionization spurs *vs.* the body of the system.

Limited volume of the report allows discussion of one type of composite only, used in the Department. It belongs to the group dealing with incorporation of inorganics into polymeric base. The polymer phase of our composite is polypropylene, the second one is exfoliated silicate sheet minerals (montmorillonite). Earlier, we were using also polyolefine matrix composites with low molecular weight organics *e.g.* crystalline alanine in polyethylene matrix for spectrophotometric and electron paramagnetic resonance (EPR) dosimetry [4]. Polymer-clay composites attract considerable scientific and industrial interests, because they exhibit significant improvements in physical and mechanical properties over virgin polymers. From the applied perspective, determining the rheological properties of nanocomposites is vital to optimize processing during the manufacture and resulting properties. From the scientific research point of view, nanocomposites provide a nanoscale space to study confined polymers and examine the effect of nanoclays on the rheology of nanocomposites. Since nanoclays significantly affect the rheological properties of nanocomposites, the network formation would be related to the microstructure of nanocomposites and interaction between nano-clays and polymer matrix. Introduction of spectroscopic methods is improving the knowledge of the chemistry of montmorillonite/polymer. The intercalated polymer chains lie flat between the layers. There is not always a need to use clay of high montmorillonite content. In many cases the bentonite is sufficient. That composite is used in the Przybytniak group [5] in the paper on thermal stability of nanocomposites based on polypropylene and bentonite. A polycationic bentonite clay was modified with a quaternary organic salt and added to isotactic polypropylene. Compression moulded films were exposed to a thermal environment at 110°C to evaluate the thermal stability of polypropylene matrix after chemical modification of bentonite. Polypropylene with a modified clay has a higher thermal stability than with the natural clay. Work on radiation chemistry of composites was helped by experience gained on the investigation of blends with the help of electron beam [6,7].

There are many approaches to preparation of clays before combining with the polymer. There can be oligomerically modified clays for successful creation of a composite with styrenic, polyethylene and polypropylene matrix with sodium montmorillonite. The preparation of a nanocomposite is critical, if full advantages of the material have to be achieved. All clays are rather hydrophilic and combination with most hydrophobic popular polymers used as matrix, listed above is difficult, considering enormous surface area of contact of both phases, mentioned above. One can use organo-clay modified by organophilic surfactant. Going down to nanodimensions, the exfoliated nanocomposite shows a greatly improved modulus, higher glass transition temperature and better thermal stability compared to the neat polyethylene and the intercalated polypropylene/montmorillonite composites.

Already at the beginning of application of montmorillonite as the key constituent of clay/polymer composites, the observation was made that these materials show better properties when grafted with maleic anhydride as compatibilising agent. Considerable number of papers on composites with montmorillonite has created the base for radiation processing. The Laboratory of Radiation Modification of Polymers is working along that line, especially on radiation chemistry of polypropylene/montmorillonite composites.

In conclusion, although at present main experimental effort is directed towards the development of composites as such, and investigation of their specific properties, mechanical, physicochemical and physical, the radiation processing will enter the field on the wider scale, especially as concerns specialized plastics. It will happen under the acceptance of high cost of ionizing radiation. In medical applications any expenses are acceptable.

For the first time, in the field of radiation chemistry of polymers, at the initiative of the International Atomic Energy Agency (IAEA), there was a consultants meeting held at Sao Paulo, Brazil, August 2005, discussing specifics of radiation chemistry of composites [8,9].

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ABSTRACTION OF HYDROGEN FROM ORGANIC MATTER, CAUSED BY IONIZING RADIATION IN OUTER SPACE

Zbigniew P. Zagórski

In the continuation of research on radiation-induced dehydrogenation, work has been concentrated on simulation of radiolysis of live species transported presumably from the Cosmos to Earth (panspermia). The idea of panspermia started a century ago, when Svante Arrhenius, the chemist, faced the question of origin of life on Earth and has found difficulties to find an answer. As the best solution, he has invented the concept of extraterrestrial origin of life and of transportation to Earth from outer space, including even galaxies. The idea has attracted many followers and was a subject of extended interpretations. For instance, some preachers of panspermia have assumed the idea that life was always and everywhere present, from the beginning of the World, easily formed, and it was the transportation between different places only, which mattered. As there are still no plausible theories and chemical experiments proposed to explain spontaneous formation of pure enantiomers (homochiral compounds, called now "signature of life"), and preparations of minimal cell from ready, pure asymmetric blocks are at the very unsuccessful beginnings, there are numerable enthusiasts of panspermia. The idea of a very simple formation of life, prevailing 50 years ago after Miller's experiment of electric discharges in a reducing gas mixture, in which amino acids are formed, had to be also abandoned, because amino acids formed were racemates with no enantiomeric excess. However, those people not acquainted with elementary chemistry were thinking, that Miller "soup", easily formed everywhere, will breed quickly the life. The location "everywhere" included Mars and, therefore there was a certainty, that life, also intelligent must be there, and even the creator of radio, Guglielmo Marconi has announced in the twenties, that he got radio signals from there. Nowadays, the hope of any life on Mars has to be abandoned [1,2], therefore the distance fom Earth to a possible life has extended to light years.

There are many variations of panspermia concept, but neither takes into account the ionizing radiation damage, which inactivates any life, even of liofilized bacterial spores in vacuum, at temperatures close to absolute zero. Some people assumed that very low temperatures protect spores from radiation damage, but the interaction of ionizing radiation, neither of primary quanta nor of particles is not influenced by the temperature of the material. The temperature can modify slightly secondary chemical reactions of intermediate products formed in ionization spurs. The main factor of biological inactivation by radiation seems to be an irreversible detachment of hydrogen statistically, at random, from organic molecules.

The fundamental assumption of any type of panspermia hypothesis is the transportation of live species in the space, not disturbed by ionizing radiation. Nowadays, the average exposure to radiation in the space is known, as well as the shielding effect by the matter in which the object under consideration is transported. The intensity of exposure, divided by a shielding factor and multiplied by the time of travel, yields the absorbed radiation dose. Clark [3] has shown a diagram (adapted in Polish, corrected version in [4]) taking into considerations different size meteorites, that cosmic dust gives no chance as a vehicle for transportation of life, whereas thicker objects like meteoritic blocks secure a better shield in their very middle, but are extremely heated when entering the earth atmosphere. The absorbed energy initiates different chemical reactions leading to the inactivation of living processes, similar to used on Earth for sterilization by radiation large scale, commercial operations. We have concentrated on measurements of radiation yields of hydrogen abstraction from biopolymers, in particular from DNA. 10 MeV electrons from accelerators, applied in different dose rates are used to simulate the irradiation in space. Yields of hydrogen were measured by gas chromatography in function of dose, as described before [5].

The reaction of hydrogen abstraction is irreversible and results in killing of any form of life. Whereas the DNA in the living species, *i.e.* in aqueous system, when damaged slightly by ionizing radiation, can be repaired, the dry DNA in spores is effectively damaged by very first doses of radiation. The radiation-induced removal of hydrogen is only slightly influenced by temperature (reaction of close to zero activation energy) and, therefore the coldness of space does not function as the protection.

The G values of hydrogen abstraction are given for typical biopolimers. Typically, G_{H2}, *i.e.* the amount of H_2 molecules per 100 eV of absorbed energy, is *e.g.* from 0.10 for certain animal proteins to 0.37 for DNA. The maximum yield is 4.5 for non-biopolymers, in some polyolefines, when the reaction is connected to crosslinking. Similar radiation yields are observed for radiation-induced deamination and decarboxylations, also catastrophic for living systems or for bio-building blocks. Detection of amino acids in meteorites, announced in some publications means that either the object stayed for a short time only in the space or travelled in well shielded conditions. Trivial, but possible explanation is that such meteorites were contaminated on Earth, what is possible even in Arctic places, full of finely divided remains of plants and animals and/or their excrements. Pieces of solid volcanic exhaustes or coal containing conglomerates of carbonized organic matter formed in fire storm during forest fires, travelling high and deposited very far from places of origin, are sometimes taken as meteorites.

There is a need to support the real look on panspermia, especially concerning survival of living and prebiotic chemical structures in radiation fields of different linear energy transfer (LET) values, well known to prevail in outer space. According to popular modern myth, mutants like *Deinococcus radiodurans i.e.* bacterial strains of increased radiation resistance, are fully radiation resistant and would travel without any harm through the radiation impregnated space. According to our experience, such strains, like those investigated in the Department of Radiation Chemistry and Technology, Institute of Nuclear Chemistry and Technology (former the Department of Radiation Chemistry, Institute of Nuclear Research) *Micrococcus radiodurans* (common even in the dirt of radiological installations in hospitals) has a typical survival curve, shifted only for 10^{-6} survival from usual 20 to 40 kGy. After collection of sufficient dose, it will be killed anyway. Invocation of *Deinococcus radiodurans* as an argument for undisturbed travel of life through outer space (even in prestigious "Scientific American") has specially non-scientific character, because this bacterial strain does not form spores and dies simply in space, being rapidly dried.

In conclusion, the probability of survival of spores in the living condition in space is very low. Actual enthusiasm toward panspermia is basing on insufficient knowledge of radiation chemistry and radiobiology. Dissemination of hard facts will help to establish the negligible probability of transfer of life and slightly higher of building blocks of organics to Earth. It should promote concentration on looking for mechanisms of origin of life here on Earth [6].

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APPLICATION OF GAS CHROMATOGRAPHY TO THE INVESTIGATIONS ON POLYPROPYLENE RADIOLYSIS

Zbigniew P. Zagórski, Wojciech Głuszewski

Radiation-induced formation of gaseous produced at ambient and lower temperatures is unique in the field of chemistry of polymers. There is no form of energy, except ionizing radiation, to cause chemical reactions to produce a wide spectrum of low molecular weight compounds, starting with hydrogen.

After the report [1], showing the advantage of determination of radiation yield of hydrogen in the evaluation of mechanisms of radiolysis, we have refined our instrumental approach by acquiring a new gas chromatograph (type GC 2014 by Shimadzu, thermal conductivity detector, column packed with molecular sieves 5A), better adapted and more sensitive for our tasks of measuring not only hydrogen. Also methane and carbon dioxide can be measured by gas chromatography (GC) now, as well the consumption of oxygen which reacts with free radicals on the polypropylene chain. The purpose of investigation is basic research, but also development of a new kind of polypropylene blends, more suitable for the production of medical devices, radiation sterilized.

Phenomena connected with the deposition of ionizing radiation energy in the matter have non-homogeneous character and are described by the model of single- and multi-ionization spurs. The investigation of material properties of the polymer blend, necessary in applications is not sufficient to recognize the mechanism of reactions and to control them. The determination of product analysis is a basic procedure to the development of preparative procedures better than by trial and error, as it is still the praxis among the material science specialists not acquainted with radiation chemistry.

Samples of virgin polypropylene (F401) in powder form, obtained from the Orlen-Olefins production line, without additives, and also in the Department of Radiation Chemistry and Technology, Institute of Nuclear Chemistry and Technology, made blends with aromatics (naphthalene, polystyrene) were irradiated in dedicated special vessels to the dose from 10 to 100 kGy with electrons of 10 MeV energy and 6 kW power from the Elektronika-10 accelerator. Using the technique previously checked, the sample of gas was taken from the gas space over the sample with a micro-syringe and analyzed in a proper carrier gas (helium or argon, respectively). Whereas the equilibrium between the concentration of hydrogen in the polymer and the gas phase was reached immediately, the cases of methane, oxygen and carbon dioxide could prepare doubts. These were cleared by an experiment, involving gentle heating of the sample and analyzing the gas phase after determined lapses of time.

As concerns the radiation yield of hydrogen, it does not speak out about the ratio of single- and multi-ionization spurs, because H_2 is produced in all types of spurs, but in different mechanisms. The most important fact is the radiation yield of methane, which seems to be one of products entirely formed in multi-ionization spurs. Unfortunately, it is only one of products of multi-ionization spurs and the comfortable situation of alanine [2] is not repeated, where the carbon dioxide (0.95/100 eV) yield was responsible univocally for multi-ionization spurs (decarboxylation of alanine). In the case of methane, one has to introduce the concept of the participation of this product in the total yield of multi-ionization spur. If one can assume that the yield of multi-ionization spur is in the order of 1, as in all systems, then the participation of meth-

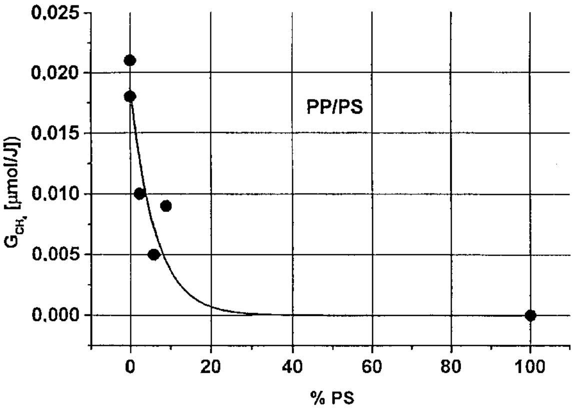

Fig.1. Relation between polystyrene concentration in polypropylene/polystyrene blends and radiation yield of methane.

ane is *ca.* 2% in all the products what sounds reasonably.

The next question connected with the yield of methane as an indicator of multi-ionization spur phenomena is the influence of energy transfer and resulting protection effect. It was shown for the first time that there is a typical, intensive protection effect in the system polypropylene/polystyrene (PP/PS) announced primarily in [3] (Fig.1). The explanation can be obvious: the energy transfer, *i.e.* the detached electrons and remaining positive holes formed in the polypropylene are effectively transferred to polystyrene in single ionizations of any generation, so that they prevent formation of secondary spurs at all.

Now, the question of oxygen reactions with polypropylene. Radiation chemistry of virgin polypropylene has been thoroughly investigated before and presented in a Ph.D. thesis by Andrzej Rafalski [4], however without determination of radiolytic gases. Already the investigation without gas determination has shown an important role played by oxygen in after-irradiation phenomena. The chain reaction of irradiated polypropylene with oxygen lasted for months. Therefore, determination of consumption of oxygen by irradiated polypropylene and formation of carbon dioxide has been incorporated in the new, this time gas-chromatographic investigation. It was supposed until now, that the chain of reactions evolves from peroxide (unpaired electron centered on carbon atom in the chain, combined with oxygen molecule O_2 forming peroxide of the characteristic electron paramagnetic resonance – EPR signal) to the keton group (detected by diffused reflection spectroscopy – DRS [5-7] method). Detection of carbon dioxide in our investigation shows that there is another, parallel path of reactions. Peroxide group located most probably on the carbon atom which is connected with the $-CH_3$ radical forms carbon dioxide, causing chain scission. The yield of carbon dioxide is unexpectedly high, 0.10/100 eV. Assuming basic total yield of radiolysis to 5.0, it means that 2% energy causes that reaction, which contributes also to the degradation (diminishment of the molecular weight) of propylene.

As in the methane case, the energy transfer in the carbon dioxide case was also investigated, and Fig.2 shows that again the protection effect exists.

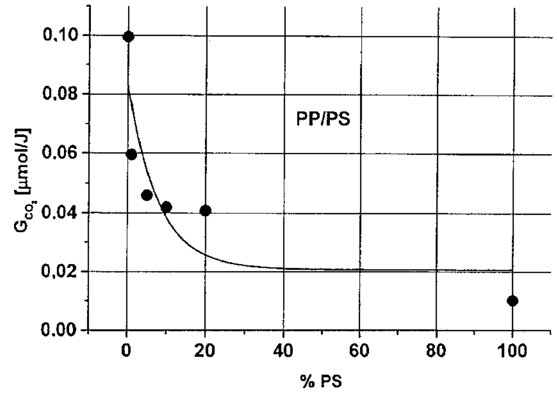

Fig.2. Relation between polystyrene concentration in polypropylene/polystyrene blends and radiation yield of carbon dioxide.

The explanation can be similar: Polystyrene is taking over effects of the first ionizations of most generations. Another explanations, *e.g.* deactivation of peroxide by polystyrene is less probable.

The method allows also the study of oxygen concentration over the irradiated polymer. Concentration of oxygen decays almost to zero in function of postirradiation time. Disappearance of oxygen is accompanied by the formation of carbon dioxide in the chain of reactions involving peroxide, described above. The work is in progress with the aim of identifying additional elements of the chain reactions, if any.

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RADIOLYTIC DEGRADATION OF HERBICIDE 4-CHLORO-2-METHYLPHENOXYACETIC ACID BY GAMMA RADIATION FOR ENVIRONMENTAL PROTECTION

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In spite of a large competition from many other methods and some sceptic opinions expressed of various reasons, the possibilities of application of ionizing radiation for treatment of natural waters

Table 1. The experimentally evaluated yield of radiolytic decomposition of MCPA in aqueous solutions of initial concentration 100 mg/l gamma-irradiated with a dose of 1 kGy.

Conditions of irradiation	Predominated products of radiolysis of water	Yield of decomposition [%]
Saturated with N_2O, pH 1.5	$OH^•$	64
Saturated with N_2O, pH 11.5	$OH^•$	64
Saturated with argon, pH 1.5	$OH^•$, $H^•$, e_{aq}^-	58
Saturated with argon, pH 11.5	$OH^•$, $H^•$, e_{aq}^-	61
Aerated, pH 1.5	$OH^•$, HO_2^-	44
Aerated, pH 11.5	$OH^•$, $O_2^{•-}$	43
Saturated with oxygen, pH 1.5	$OH^•$, HO_2^-	50
Saturated with oxygen, pH 11.5	$OH^•$, $O_2^{•-}$	42
Saturated with argon, pH 1.5 with 0.1% *t*-butanol	$H^•$	20
Saturated with argon, pH 11.5 with 0.1% *t*-butanol	e_{aq}^-	31
Saturated with argon, pH 1.5 with 1% *t*-butanol	$H^•$	20
Saturated with argon, pH 11.5 with 1% *t*-butanol	e_{aq}^-	28

and wastes are being investigated in numerous research groups in various countries. The objects of recent studies in this field are mainly organic compounds of anthropogenic origin, whose presence in natural waters and wastes is a significant environmental threat. In experimental laboratory studies, mostly gamma irradiation from cobalt sources is employed and the papers published in the last year deal with radiolytic degradation of numerous aromatic compounds such as p-chlorophenol [1], catechol [2], dihalobenzenes [3], p-nonylphenols [4], 2,3-dihydroxynaphthalene [5], benzophenone [6] and 2-chloroanisole [7]. The conditions of radiolytic decompositions have been also optimized for polycyclic aromatic hydrocarbons benzo[a]pyrene [8] and fluoranthene [9]. The electron beam (EB) irradiation was employed for radiolytic degradation of nonylphenol ethoxylates, carboxylates and nonylphenols [10], 2-chlorobiphenyl [11], and also for several metal ions from industrial wastes [12]. The decomposition of dyes has been reported with the use of EB in the presence of hydrogen peroxide [13], while methylene blue radiolysis with gamma radiation, protons and helium ions [14].

Several papers published recently have been devoted to radiolysis of pesticides. Gamma radiolysis was reported for herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) [15,16] and acetochlor [17]. The published results of our work dealt with EB degradation of herbicide dicamba [18].

The subject of the present studies is another chlorophenoxy pesticide – 4-chloro-2-methylphenoxyacetic acid (MCPA) Generally, chlorophenoxy herbicides, which have potential toxicity towards humans and animals, are suspected mutagenes and carcinogens, and are used worldwide on a large scale as plant growth regulator for agricultural and non-agricultural purposes. Among them, MCPA is used in amounts exceeding 2000 tons per year in West European countries. In the literature on degradation or removal of MCPA for environmental purposes mostly photodegradation methods have been reported. In our earlier studies on the decomposition of this pesticide with gamma radiation it

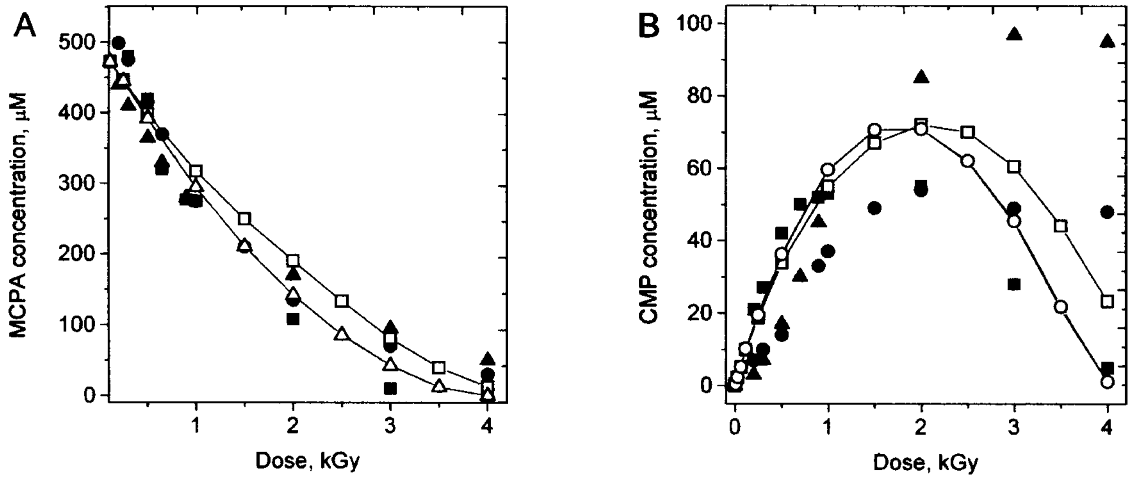

Fig.1. Comparison of experimental data with kinetic modeling for the yield of degradation of (A) MCPA of initial concentration 0.5 mM in aerated solutions of different pH, and (B) formation and decomposition of CMP in irradiated solutions of MCPA. Data for pH 1.5 – experimental (■) and calculated (□), data for pH 7.0 – experimental (●) and calculated (○), data for pH 11.5 – experimental (▲) and calculated (△).

was shown that complete decomposition at a concentration of 100 mg/l requires a dose of 3 kGy, and the main products of radiolysis are phenolic compounds and carboxylic acids [19].

In present studies, a yield of MCPA decomposition was compared in different conditions, where MCPA exists in acid or anion form, and where predominate particular, highly reactive products of radiolysis of water, which can react with MCPA. As it can be found from data in Table 1, obtained for an initial MCPA concentration of 100 mg/l at a 1 kGy dose, the effectiveness of decomposition is affected mostly by a kind of reactive species present, and not by the degree of protonation. The largest yield was observed in solutions saturated with nitrogen monoxide, what means that radiolytic decomposition of MCPA is a result of reaction with hydroxyl radicals.

The results of experimental data on the decomposition of MCPA and change of concentration of the main degradation product at low doses of radiation of 4-chloro-2-methylphenol (CMP) have been compared for different conditions used in the experiments with model kinetic calculations based on known rate constants of radical reactions. The calculations have been performed with the use of software KINETIC, which was used earlier, *e.g.* for modeling of a high temperature radiation-induced reduction of nitrogen oxide [20], and for the examination of decomposition mechanism of 1,1-dichloroethylene in humid air under EB irradiation [21]. The results of modeling obtained for processes carried out at different pH values are shown in Fig.1. The computer calculations have been carried out with the use of rate constants for MCPA and OH radical $k=6.6\text{x}10^9\ M^{-1}s^{-1}$ [22]. Similarly to experimental results, also well correlated with them model calculations (Fig.1A), indicate a minor effect of pH of irradiated solutions on yield of MCPA decomposition. No satisfactory correlation, however, has been observed between the experimental data and the results of kinetic modeling for decomposition of products of CMP for radiation doses above 2 kGy (Fig.1B), which means that some other processes take place, and not only those for which rate constants have been taken for modeling.

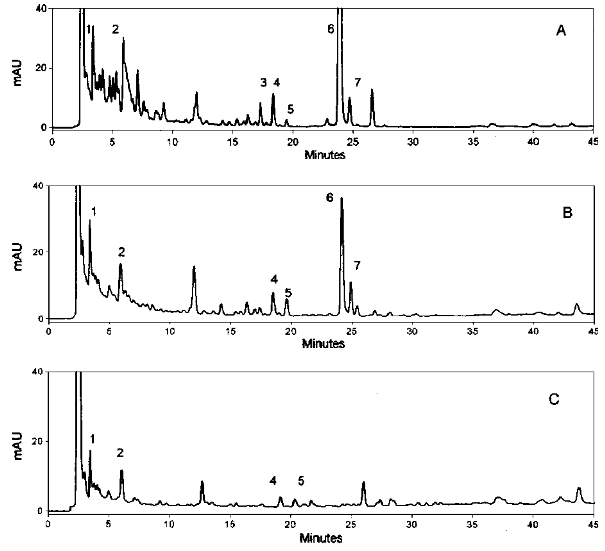

Fig.2. Chromatograms obtained for the sample of wastes from the process of chlorination of MPA in production of MCPA prior to the irradiation (A), after gamma irradiation with a 5 kGy dose (B), and after a 5 kGy dose irradiation in the presence of 39 mM (1.32 g/l) hydrogen peroxide in irradiated solutions (C). Gradient elution with a 2 g/l citric acid solution with 5% acetonitrile and mixed with pure acetonitrile. Peak assignment: 1 – hydroquinone, 2 – catchol, 3 – o-cresol, 4 – MPA, 5 – 4-chlorophenol, 6 – MCPA, 7 – CMP.

In investigations of radiolytic decomposition of several different organic pollutants based on reaction with hydroxyl radical, it has been shown that in some cases the effectiveness of decomposition can be improved by the addition of hydrogen peroxide to irradiated solutions. This effect was observed also in this study for irradiation of indus-

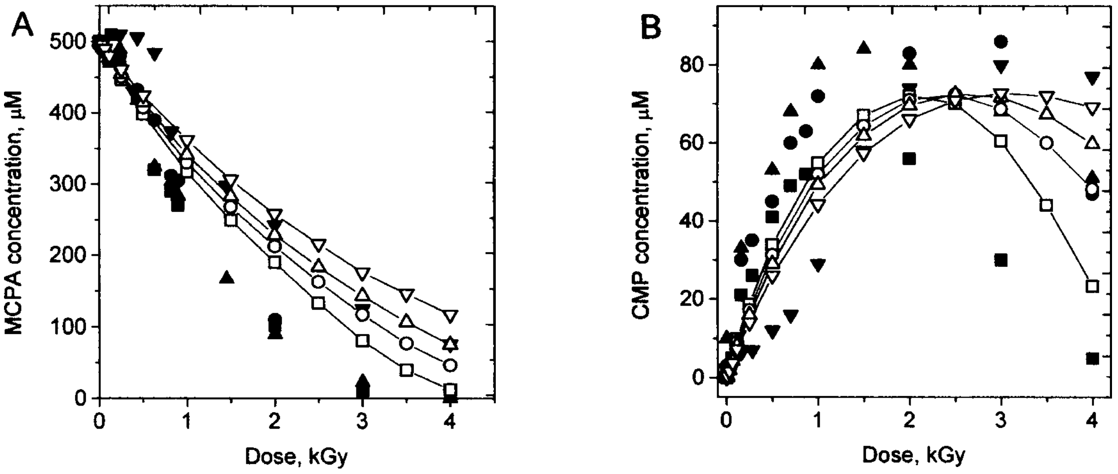

Fig.3. Comparison of experimental data with kinetic modeling for the yield of degradation of (A) MCPA of initial concentration 0.5 mM in aerated solutions of pH 1.5 and different concentration of hydrogen peroxide added to irradiated solutions, and (B) formation and decomposition of CMP in irradiated solutions of MCPA. Data for irradiation without hydrogen peroxide – experimental (■) and calculated (□), data for irradiation in the presence of 1.2 mM hydrogen peroxide – experimental (●) and calculated (○), data for added 2.4 mM hydrogen peroxide – experimental (▲) and calculated (△), data for added 4.8 mM hydrogen peroxide – experimental (▼) and calculated (▽).

trial wastes from production of MCPA (Fig.2). The irradiation of wastes with a 5 kGy dose at an initial MCPA content of 554 mg/l results in the decomposition of 89% MCPA. For irradiation with the same dose, but in the presence of added 39 mM hydrogen peroxide, the observed yield increased to 100%, and also much more effective removal of other organic compound has been found. Figure 3 shows the results of model calculations for processes carried out at pH 1.5 and various levels of hydrogen peroxide in irradiated solutions. A general course of calculated changes of MCPA and CMP concentrations in function of dose magnitude and hydrogen peroxide content is closed to those observed experimentally. The best correlation between the results of calculation and experimental data has been obtained for the largest amount of hydrogen peroxide added to irradiated solution (4.8 mM).

Table 2. The experimentally evaluated toxicity with a Microtox test for MCPA and considered potential products of its radiolytic degradation, expressed by EC_{50} (15 min).

Examined compound	EC_{50} (15 min) [mg/l]
4-chloro-2-methylphenoxyacetic acid	75.6
2-methylphenoxyacetic acid	300
Phenol	21.4 [23]
2-chlorophenol	21-34 [23]
4-chlorophenol	1.1-8.3 [23]
6-chloro-2-methylphenol	63.2
4-chloro-2-methylphenol	1.5
Hydroquinone	0.04-0.08 [23]
Methylhydroquinone	0.3
Chloroquinone	0.22
o-cresol	38.4
3-methylcatechol	9.6
Salicylic acid	408
5-chlorosalicylic acid	194

As it was shown in our earlier studies on radiolytic decomposition of chlorophenols, such processes, especially when low radiation doses are employed in order to be cost effective, may result, in formation of the products which are more toxic than the initial target compound. In order to examine this aspect in case of radiolysis of MCPA, with the use of bacterial, bioluminescence test Microtox, the toxicity of MCPA and the expected products of its radiolysis at low doses has been determined (Table 2). Although MCPA exhibits a low toxicity with Microtox, the main product of its radiolysis at low doses CMP shows toxicity about 50 times larger, while hydroquinone and its methyl- and chloro-derivatives show even one order of magni-

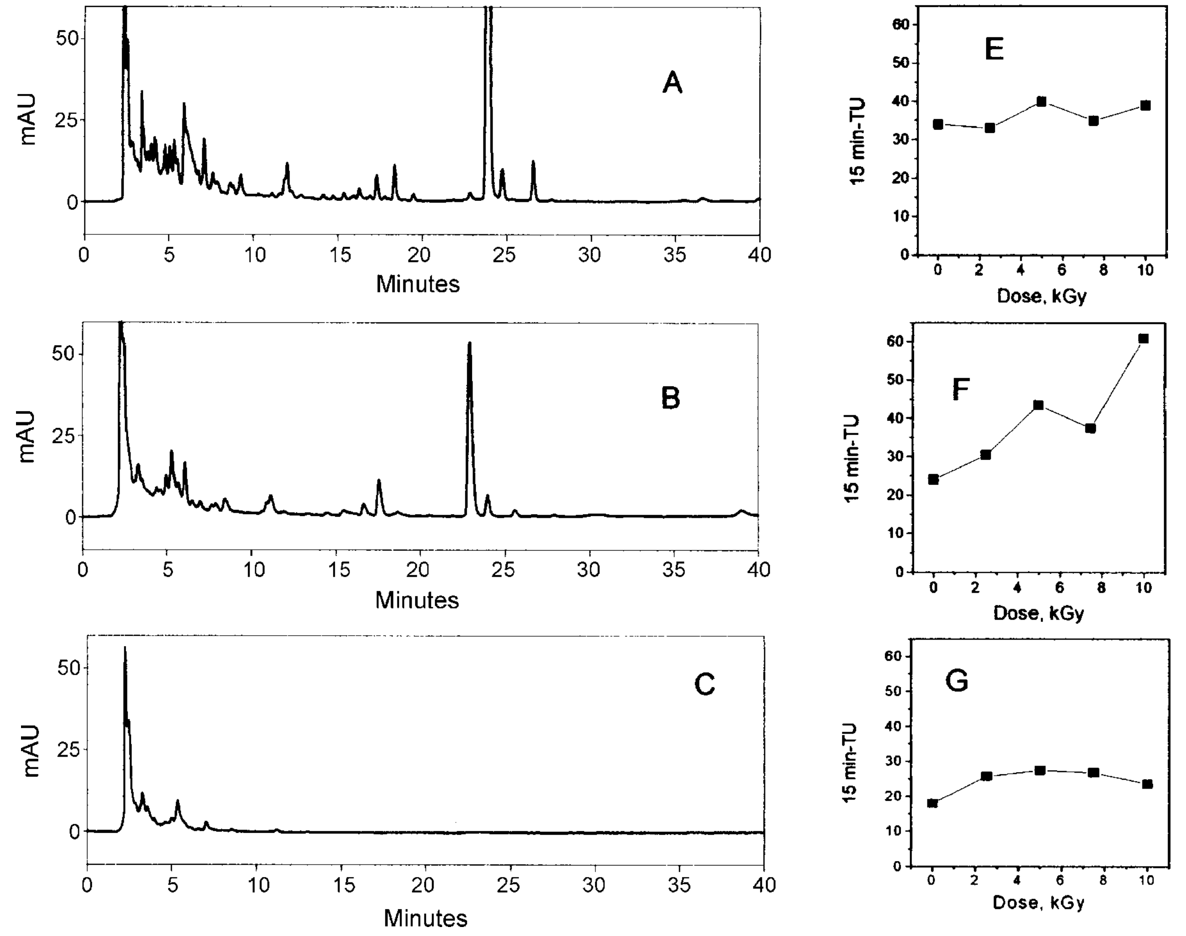

Fig.4. Chromatograms of the industrial waste samples from MCPA production prior to irradiation (A, B, C) and toxicity changes after gamma irradiation of each waste sample with different doses in aerated solutions of pH 1.5 (E, F, G). A – waste after chlorination of MPA, B – final waste from production line prior to adsorption on activated carbon, C – the same as B after adsorption on activated carbon.

tude larger toxicity. A larger Microtox toxicity has been also reported for products of photocatalytic decomposition of MCPA, than for the target compound [24]. Those data convincingly indicate the necessity of toxicity monitoring during carrying on such processes.

The measurements of toxicity have been carried out for three different waste samples from different stages of industrial production of MCPA in the Organika Sarzyna Chemical Company (Nowa Sarzyna, Poland), gamma-irradiated with a 10 kGy dose. They include raw waste after chlorination of 2-methylphenoxyacetic acid (MPA), a final waste from MCPA production line prior to the adsorption of its constituents on activated carbon, and the final waste after adsorption on activated carbon. As it is illustrated by the chromatograms of waste samples obtained prior to their irradiation (Fig.4A-C), the examined wastes differ significantly in content of organic compounds, but all them exhibit initial toxicity. Waste sample from chlorination of MPA exhibited about 75% higher initial toxicity than the two others (Fig.4E-G). This toxicity has not been reduced by gamma irradiation up to a 10 kGy dose, and in the same conditions for final waste before absorption on activated carbon even about a 3-fold increase of toxicity was observed (Fig.4E). The observed toxicity in case of final waste after adsorption on activated carbon suggests that a source of this behavior may be the presence of toxic polar or ionized inorganic compounds. They can include, for instance, chlorine-containing oxoanions. Their toxicity for different organisms was reported in the literature [25-28], and the least are considered perchlorates [28]. Chlorides are efficient scavengers of hydroxyl radicals [29], and oxoanions can be formed as a result of radical reactions. In further studies, ion-chromatographic studies of chlorine speciation is planned as well as total elemental analysis of examined wastes, including the content of heavy metals, for which Microtox toxicity is reported in the literature [30], together with synergistic interactions, when several metal ions are present simultaneously [31]. In order to reduce toxicity of the examine waste samples, the EB irradiation with higher doses, as well as gamma irradiation in the presence of ozone is planned.

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ANALYTICAL ACTIVITY OF THE LABORATORY FOR DETECTION OF IRRADIATED FOOD IN 2005

Wacław Stachowicz, Kazimiera Malec-Czechowska, Katarzyna Lehner, Grzegorz P. Guzik, Magdalena Laubsztejn

The activity of the Laboratory for Detection of Irradiated Foods, Institute of Nuclear Chemistry and Technology was focused in 2005 on the following topics:
- development and improvement of the methods for detection of irradiated food implemented and accredited earlier in the Laboratory,
- implementation of new standardised detection methods to be accredited in the Laboratory,
- analytical activity to fulfil the requirements of numerous firms and institutions from abroad and from the country. The purpose is to prove whether food products delivered for examination are or are not treated with ionising radiation.

In 2005, two detection methods adapted in the Laboratory have been implemented. One method is based on EPR (electron paramagnetic resonance) spectrometry, while its preparation and measuring procedures have their source in the European standard PN-EN 13708 [1]. The method is capable to detect all foods containing crystalline sugars *e.g.* dried fruits like dates, figs, resins *etc*. The second method employs photostimulated luminescence released from a sample proving its radiation treatment. The method was implemented after the installation of pulsed photostimulated luminescence (PPSL) system in the Laboratory this year. The corresponding European standard is numbered PN-EN 13751 [2]. This is a screening method but very useful for fast detection of irradiation in spices and herbs.

Actually, three detection methods have PCA (Polish Center for Accreditation) accreditation certificates and are routinely used for the examination of irradiation in food samples delivered from the clients. Two methods are based on EPR spectrometry, while the third one takes the advantage of thermoluminescence effect. The methods make it possible the detection of irradiation:
- in food containing bone, *e.g.* meat, poultry and fish according to European standard PN-EN 1786 [3];
- in food containing crystalline cellulose, *e.g.* in nuts and some spices (European standard PN-EN 1787) [4];
- in food from which silicate minerals are isolated, *i.e.* in spices, herbs and their blends, dried and fresh vegetables, shrimps (European standard PN-EN 1788) [5].

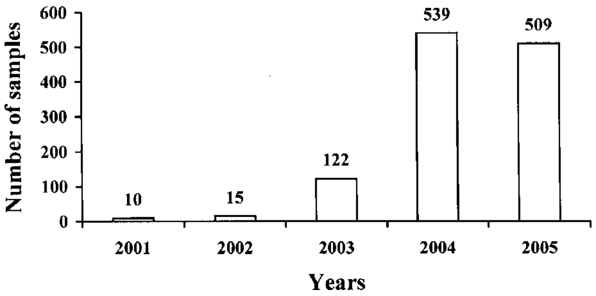

Fig.1. The number of samples analysed in the Laboratory for Detection of Irradiated Food in the period from 2001 to 2005.

The majority of 509 samples examined during the year 2005 (Fig.1) have been received from Germany and Italy, but some samples were also delivered from the United Kingdom, Denmark, and Sweden. Altogether 385 samples of various foodstuffs obtained from abroad have been examined. The number of samples delivered from the country is 124.

It has to be stressed, however, that only 4 samples have been received from private firms, while 120 were examined for the purpose of monitoring organised by the Chief Sanitary Inspector of Poland under supervision of the Ministry of Health (Fig.2).

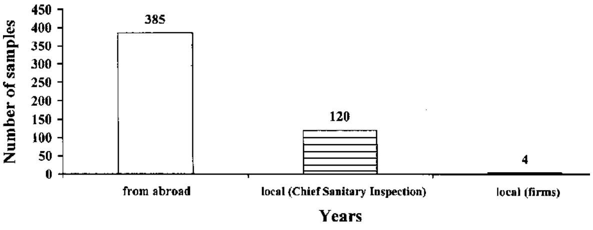

Fig.2. The origin of the orders for the examination of food samples in 2005.

The most of samples were examined by the thermoluminescence (TL) method (European standard PN-EN 1788 [5]). It is because the most of them contained spices as an ingredient. The products received were spices and their blends and/or foodstuffs or pharmacy composites containing spices, generally as flavour ingredients. About 7% of all samples have been examined by the EPR methods (European standards PN-EN 1786 [3] and PN-EN 1787 [4]).

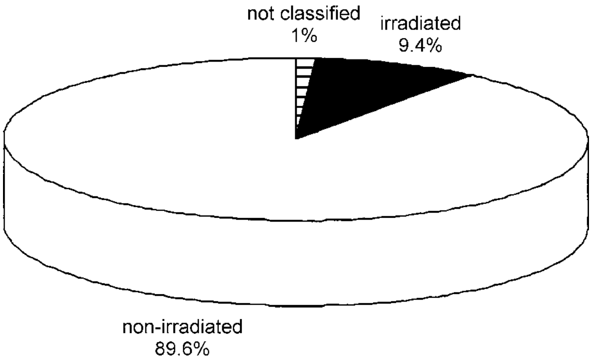

Fig.3. Classification of food samples undertaken to examination in 2005.

More and more frequently the Laboratory receives a lot of composed samples which have not been analysed earlier by the TL method in the Laboratory.

Under this new situation the Laboratory is faced today (a) how to analyse the complex samples to obtain reliable results and (b) how to treat those samples which cannot deliver reliable results and hence, will not undergo classification whether irradiated or non-irradiated according to standard PN-EN 1788 [5]. First problem finds very often its solution in the modification, if necessary, of the preparation technique leading to more effective isolation of mineral fraction and/or in an increase of the mass of a single sample to be examined. Sometimes, however, the separation of silicate minerals remains still unsuccessful. Under such a condition, the examination of a sample is not satisfactory and thus the test report cannot include the statement whether the sample was or was not irradiated. Usually, we inform our client in advance that such situation may appear and the receiving of reliable result of the analysis may be rather problematic. This year, only 5 samples remained unclassified.

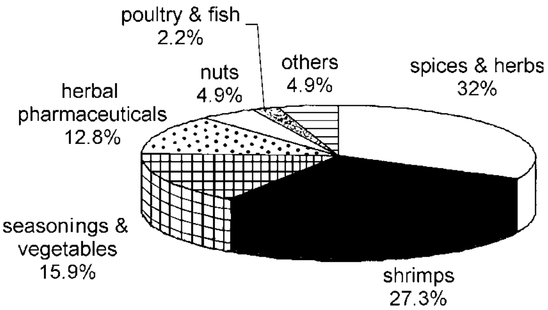

Fig.4. Assortment of foodstuffs examined in 2005.

Among the 509 food samples analysed in this year, 89.6% were found unirradiated, 9.4% – irradiated, while 1% samples remained not classified (Fig.3).

The assortment of foodstuffs that were examined in 2005 (Fig.4) compiles:

- spices, herbs and their blends that may contain a small admixture of irradiated spices as a flavour ingredient (32%);
- seasonings, fresh and dried vegetables (15.9%);
- shrimps (27.3%);
- herbal pharmaceuticals, herbal extracts (12.8%);
- foods containing bone – poultry, meat and fish (2.2%);
- nuts in shell (4.9%);
- others – instant soups, red fermented rice, all purpose savoury seasoning (4.9%).

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PPSL – THE NEWLY INSTALLED ANALYTICAL SYSTEM FOR THE DETECTION OF IRRADIATED FOOD

Grzegorz P. Guzik, Wacław Stachowicz

The pulsed photostimulated luminescence (PPSL) system has been installed in the Laboratory for Detection of Irradiated Food at the beginning of 2005. The system, composed of two modules, was manufactured by the Scottish Universities Research and Reactor Centre – SURRC (United Kingdom) in 2004.

The PPSL system has been developed to meet the requirement of European food market that needed a relatively simple and compact device for fast control of foodstuffs whether irradiated. Indeed, two Directives of the European Parliament, 1999/2/EC and 1999/3/EC established the requirement of labelling and control of irradiated foods in all EU countries [1-3].

The method of the detection of irradiated food using photostimulated luminescence has the status of European Standard EN 13751:2003 and is recommended for the use as a control method for the detection of irradiation in foods since 2003. The corresponding Polish replica of European standard is numbered PN-EN 13751:2003 (U).

The PPSL method is today successfully used for examination of the whole spices and herbs and some other food products to detect the earlier radiation treatment in them [3,4].

Currently, the research program with the use of PPSL system in the Institute of Nuclear Chemistry and Technology (INCT) is focused on the examination of archival samples of herbs and spices stored in the Laboratory. Basil, chilli, curry, tarragon, nutmeg, mustard, clove, juniper, dill, turmeric, lovage, oregano, black pepper and white pepper, sweet pepper and cayenne pepper, parsley and rosemary have been tested so far.

Principle of the PPSL method

Mineral debris of silicates and bioinorganic composites (calcite and hydroxyapatite) are the natural contaminants of most foods, *e.g.* of spices, herbs and seasonings that belong to most frequently irradiated food products. They are mainly composed of quartz and feldspar, as proved in earlier works [1-3]. This debris stores steadily the energy of ionising radiation in charge carriers trapped at structural, interstitial or impurity sites [4]. Charge carriers which are very stable at ambient temperatures are released from mineral debris with increasing temperature – thermoluminescence (TL)

Fig.1. Irradiated Food Screening System SURRC PPSL installed in this Laboratory. Placing of a Petri dish with a sample inside into a sample chamber by means of tweezers.

method and/or under illumination – optically stimulated luminescence (OSL) measurements [1,2,5,6] and PPSL method [4,7,8].

Methodology of the PPSL examination of food is simple. The analysed sample is dispensed into a Petri dish in a thin layer and then placed into a sample chamber (Fig.1). After switching on the system, the sample is exposed to pulsed laser infra-red light emitted by an array of diodes (IR LEDs). The PPSL signal produced in the system by luminescence released from photostimulated mineral debris of the sample is stored by a photomultiplier (PMT; bialcali cathode photomultiplier tube) and intensified. Numerical signal is transmitted to PC computer and printed by the use of PPSL DOS program delivered from the producer (Fig.1). Optical filtering of light is adapted to define both stimulation and detection wavebands [4]. Schematic diagram of the PPSL system is shown in Fig.2.

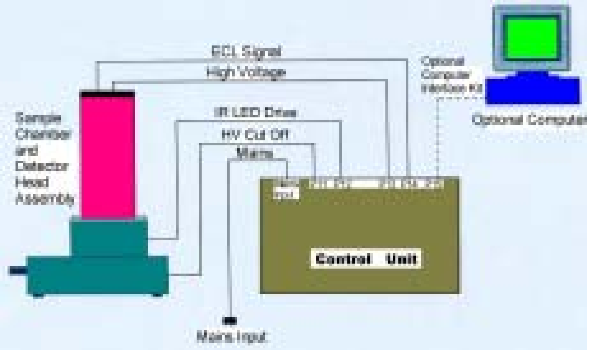

Fig.2. Block schematic and interconnection diagram [4].

Depending on the requirement two pathways of the PPSL examination are in use, screening or calibrated PPSL measurement.

Screening PPSL measurement

In screening measurement, signal intensity of luminescence produced by a sample is compared with two threshold values.

For herbs and spices as examined in the interlaboratory tests [9 – Part 10. Validation], the threshold settings of T_1=700 counts/60 s and T_2=5000 counts/60 s have been shown to be satisfactory. These thresholds refer to the use of 5 cm Petri dishes. This kind of dishes is also used now in the Laboratory.

For shellfish tested in an interlaboratory trial [9 – Part 10. Validation], slightly different threshold settings T_1=1000 counts/60 s and T_2=4000 counts/60 s have been shown to be better acceptable [4,10-12].

Typically, irradiated samples give rise to a strong signal much above the upper threshold level. The unirradiated ones, in turn, generate signals with the intensities below the lower threshold level. Samples that produce luminescence signals with the intensities between two thresholds cannot be classified by the PPSL method and should be investigated by means of the TL method according to the European Standard EN 1788, or, if suitable, by another validated method for the detection of irradiated food [12,13].

Fig.3. Irradiated Food Screening System SURRC PPSL installed in this Laboratory. From the right to the left: control unit and detector head assembly with sample chamber. Note three colour diodes (red, amber, green) on front panel of control unit.

Three diodes on the front panel of the apparatus indicate the actual status of a sample that undergoes examination: green light indicates negative result of examination, red light – positive result, while amber indicates intermediate result (Fig.3).

Calibrated PPSL measurement

Calibrated PPSL measurements deliver more adequate results and are carried out before and after exposing the sample to a defined dose of ionising radiation.

The recommended calibrating dose is 1-4 kGy or a dose comparable to that used for radiation treatment of food species examined [10]. Calibrating irradiation of samples is accomplished in the INCT with gamma rays from two ^{60}Co sources: "Issledovatel" (dose rate *ca*. 1.4 kGy/h) or "Mineyola" (dose rate *ca*. 0.6 kGy/h).

Irradiated samples indicate only a small increase of the PPSL signal, whereas with unirradiated ones the increase of the signal is significant.

Application and limitations of measures

The method of detection of irradiated food by means of PPSL has been positively tested in interlaboratory tests for samples of shellfish (*e.g.* prawns), herbs, spices and seasoning [9-11].

PPSL sensitivity depends on the quantity and type of minerals present in the individual sample. Signals of the intensity below the lower threshold (T_1) are generally associated with unirradiated material, but sometimes can be also derived from low sensitivity irradiated materials. In general, calibrated PPSL measurements are recommended for shellfish with low mineral contents and „clean" spices (*e.g.* nutmeg, white and black pepper) to avoid false negative results [9,14]. According to our experience, for the examination of any sample delivered from our clients the calibrated PPSL measurement should be always adapted.

Multicomponent food products like curry powder, for example, and blended seasonings may contain the debris of minerals of low PPSL sensitivities, in which case calibrated PPSL may also provide unclear results. In such a case it is necessary to turn to TL measurements.

Food products classified in the course of our investigation as such that may provide unclear results of PPSL measurements are: garlic powder, carrot pepper (leaves), sweet pepper (powder), black pepper (grains), black pepper (ground), clove (whole), dried dill (powder).

The presence of salt in a product given for examination intensifies so much the PPSL signal intensity that its contribution dominates to an extent which masks effectively signals from any irradiated ingredient. The dominance of the luminescence from crystalline salts in a product makes the signals from irradiated components undetectable. An admixture to a product of the following salts makes the examination of by PPSL method not rational: sodium chloride (domestic salt), natrium sorbitan, sodium benzoate, monosodium glutamate, Arabic gum.

It has to be strongly stressed that the examination of samples containing the above ingredients may also cause the damage of photomultiplier and is prohibited.

Sometimes hydration of a product leading to full dilution of salt and its elimination followed by drying and PPSL measurement can both identify and rectify this situation.

Conclusions

The PPSL method can be successfully used for the detection of irradiation in pure spices, herbs and seasonings as well as in most of multicomponent blends of spices, herbs and seasonings [6,14,15].

Screening by means of the PPSL apparatus is easy, effective and first and above all inexpensive. The method provides the fastest way to gain final results whether food product is irradiated. By comparison with the TL method, preparation of samples is simple, much quicker and takes not longer than one hour instead of few days by the TL method. However, in ambiguous results of PPSL, the validated TL method should be always used [16].

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DETECTION OF IRRADIATION IN CUTICLES OF COMMERCIAL SHRIMPS

Katarzyna Lehner, Wacław Stachowicz

The detection of stable EPR (electron paramagnetic resonance) signal produced by the action of ionising radiation in crustacea has been reported by several authors elsewhere [1,2]. The signal observed was identical with that used for detection of irradiation in bone and eggshell by the EPR method. This signal is specific for hydroxyapatite that appears in some extent in exoskeletons of shrimps and crabs. However, the results of model studies on these products were not reliable enough. For that reason, crustacea are not quoted until now in European Standard EN 1786 among food products that can be examined by EPR method to prove their irradiation [3]. The most reliable results have been obtained with lobsters [4]. The results of the examination of various crustacea species indicated that the EPR signal is more or less influenced by the variety, origin and age of crabs.

Nowadays, the Laboratory for Detection of Irradiated Food has more and more orders for detection of irradiation in shrimps. Part of them are delivered in cuticles. A method adapted to accomplish the detection of irradiation in shrimps is a thermoluminescence measure. However, the analytical procedure is much time-consuming and needs several days to receive the final result.

The aim of present study was to prove, whether the EPR examination of cuticles taken from shrimps could be used as a screening method for the detection of irradiation in this product. The earlier results obtained with irradiated cuticles of shrimps only seem promising [5].

In a model study commercial shrimps were irradiated in a ^{60}Co source with doses of 1, 3 and 7 kGy. The technological dose recommended for microbial decontamination of shrimps is between 3 and 7 kGy.

Cuticles taken from the shrimp body were cleaned, dried and subsequently crushed to small pieces to be measured by the EPR method. The resultant spectra recorded with cuticles irradiated with 3 and 7 kGy are shown in Fig.1. The positions of coefficient g (spectroscopic splitting factor), specific for irradiated hydroxyapatite, are marked with arrows. The signal is a singlet of axial symmetry with $g_x=2.0035$, $g_y=1.9973$ and $g_z=2.0017$, respectively.

The positions of all three g's in the magnetic field are easily distinguished in the spectrum of cuticle irradiated with 7 kGy (Fig.1b). However, in the spectrum of cuticle irradiated with 3 kGy the positions of g_z and g_x are not very well defined although the experienced EPR operator can establish them with a precision which could be perhaps satisfactory enough for identification of radiation treatment (Fig.1a).

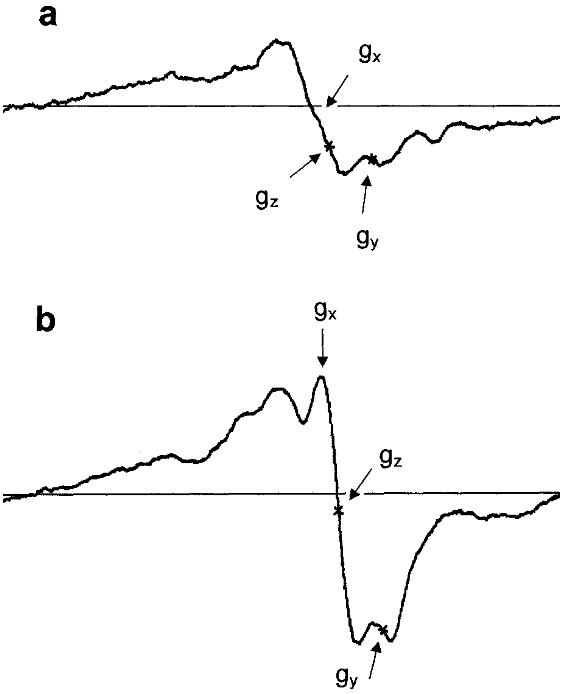

Fig.1. The EPR spectra (first derivatives) recorded with cuticles taken from shrimps irradiated with 3 kGy (a) and 7 kGy (b). The positions of g values specific for irradiated hydroxyapatite are marked with arrows: $g_x=2.0035$, $g_y=1.9973$, $g_z=2.0017$.

In conclusion, it can be postulated that the EPR measurement of cuticles of shrimps can be adapted in the Laboratory as preliminary, screening test proving the irradiation of shrimp. It has to be stressed, however, that the lack of a specific, hydroxyapatite born EPR signal in the spectrum cannot suggest that sample was not irradiated.

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DSC STUDIES OF RETROGRADATION AND AMYLOSE-LIPID TRANSITION TAKING PLACE IN GAMMA-IRRADIATED WHEAT STARCH

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The course of gelatinisation and retrogradation occurring during heating of starch and flour suspensions depend on the structure of starch granules. In the case of wheat flour, retrogradation depends additionally on the presence of lipids. In fact, binding of lipids to the polysaccharide chains was found to resist recrystallisation of starch gels.

Our previous studies have shown that degradation resulting from gamma irradiation induces a decrease in order of starch granules [1,2] and

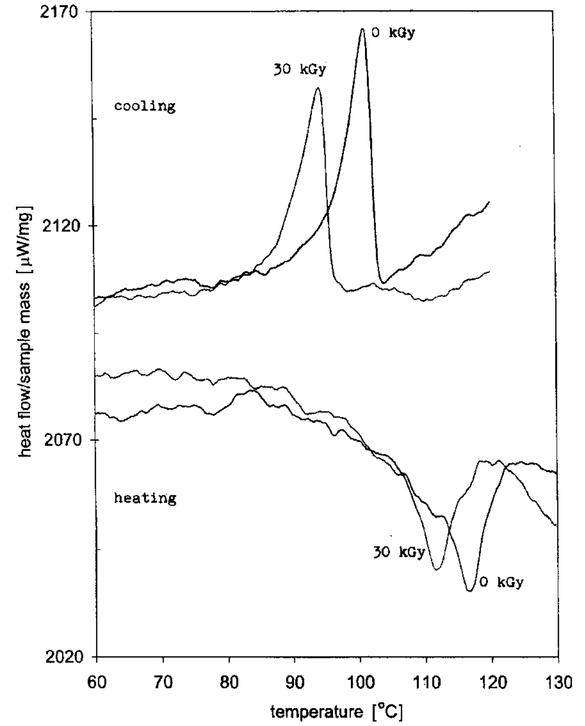

Fig. Comparison of the amylose-lipid transition endothermal effects recorded during the third heating and exothermal effects, observed during the third cooling in the case of the dense (50%) suspensions. Heating and cooling were performed with a rate of 10°C/min.

influences gelatinisation taking place during heating of starch and flour suspensions [3-7]. It was also found that modification in lipids surrounding brought about by gamma irradiation affect amylose-lipid complex transition taking place in wheat starch and wheat flour [3-6]. In particular, an essential decrease in transition temperature was found after irradiation performed with a dose of 30 kGy. Furthermore, our preliminary results have demonstrated that differences in storage effects on the irradiated and non-irradiated wheat starch and flour gels and might result in the expanded differences in the amylose-lipid structure formed in such gels.

At present, DSC (differential scanning calorimetry) studies were continued for wheat starch, non-irradiated and irradiated using doses in the range from 5 to 30 kGy. The influence of the conditions applied during DSC measurements on the possibility to observe differences between the amylose-lipid complex transition and retrogradation taking place in the non-irradiated and particularly irradiated starch samples was checked. Special interest was given to the influence of thermal treatment and further storage on the processes occurring in dense (*ca.* 50%) and watery (20-25%) starch gels.

Table 1. The values of peak temperature determined for themal effect of the amylose-lipid complex transition taking place in the non-irradiated samples and those irradiated with various doses obtained during heating at a rate of 10°C/min.

Dose [kGy]	Heating cycles			Cooling cycles		
	I	II	III	I	II	III
20% suspensions						
0	99.1	102.0	102.5	83.6	83.5	83.4
5	99.0	102.0	102.3	83.5	83.5	83.5
10	98.9	101.3	100.7	83.0	82.6	82.0
20	97.5	100.7	100.2	82.3	81.7	81.4
30	99.0	100.3	99.6	81.6	80.6	80.1
50% suspensions						
0	112.1	116.0	116.2	99.4	99.9	100.2
5	112.5	115.7	115.6	99.5	99.5	99.7
10	112.6	114.9	114.6	98.8	98.3	97.8
20	112.3	113.9	113.7	97.4	96.5	96.1
30	112.2	113.4	112.6	96.3	95.3	94.9

Wheat starch was a Sigma product. Irradiations were carried out with ^{60}Co radiation in a gamma cell "Issledovatel" in the Department of Radiation Chemistry, Institute of Nuclear Chemistry and Technology. DSC studies were carried out during heating-cooling-heating cycles (up to 3 heating processes) in the temperature range 10-150°C. The measurements were performed at heating and cooling rates of 10, 5 and 2.5°C/min. A Seiko DSC 6200 calorimeter installed at the University of Lund was used. Transition enthalpy (ΔH) as well as peak and onset temperature (T_p, T_{on}) were determined.

Modification of the amylose-lipid structure in wheat starch, in particular a decrease of the complex symmetry, can be concluded already after irradiation with a dose as high as 5 kGy. It is shown by a decreased temperature of the complex transition (Fig., Table 1), in particular observed during the successive heating and cooling cycles. The difference between the irradiated and the non-irradiated samples became more easily seen in each

Table 2. DSC results obtained for the non-irradiated and irradiated wheat starch gels (residues after the first DSC analysis, containing after the procedure *ca.* 60% of dry matter), carried out in the heating-cooling cycle after 13 days of storage.

Dose [kGy]	Retrogradation		Amylose-lipid complex transition					
	ΔH [Jg^{-1}]	R [%]	heating			cooling		
			T_p [°C]	T_{on} [°C]	ΔH [Jg^{-1}]	T_p [°C]	T_{on} [°C]	ΔH [Jg^{-1}]
0	9.51	80	110.5	112.4	1.92	127.1	122.3	-1.29
5	8.30	72	109.1	111.3	1.50	125.3	119.4	-0.85
10	7.60	67	107.0	109.7	1.33	124.2	116.7	-0.73
20	6.37	62	105.2	108.0	1.09	121.8	117.0	-0.66
30	6.14	56	104.4	107.3	0.71	110.8	109.2	-0.36

Table 3. DSC results obtained for the non-irradiated and irradiated wheat starch gels (residues after the first DSC analysis, containing *ca.* 25% of dry matter) carried out in the heating-cooling cycles after 7 days of storage. Nd – not detected.

Dose [kGy]	Retrogradation		Amylose-lipid complex transition				
			heating		cooling		
	ΔH [Jg^{-1}]	R [%]	T_p [°C]	ΔH [Jg^{-1}]	T_p [°C]	T_{on} [°C]	ΔH [Jg^{-1}]
0	Nd	0.0	102.7	1.46	84.3	86.5	-1.71
5	0.50	4	102.3	1.16	83.0	85.2	-1.15
10	1.11	9	101.1	1.27	82.3	84.1	-1.06
20	2.00	16	100.3	1.67	82.2	84.0	-1.79
30	3.26	28	99.5	1.21	79.9	82.2	-1.51

next cycle. It is because thermal treatment causes a decrease of transition temperature in all the irradiated samples (showing further deterioration of the complex structure under the influence of thermal treatment), with no effect or increase of transition temperature observed in the non-irradiated starch. The effect was observed for 50% (dense) suspensions/gels as well as for 20% (watery) suspensions/gels.

Retrogradation of wheat starch during storage occur more easily in dense suspensions than in watery ones. It was stated that irradiation hinders retrogradation taking place in dense suspension (Table 2, columns 2 and 3), but facilitates retrogradation taking place in watery ones (Table 3, columns 2 nad 3). In purpose of direct comparison of irradiation effect on retrogradation, the yield of retrogradation R was calculated as a percentage of the initial enthalpy of gelatinisation determined during the first heating. This parameter included the decrease in gelatinisation enthalpy brought about by irradiation.

Storage of the gels induces a decrease in the temperature of the amylose-lipid complex transition as compared to the last cycle of the first analysis (Tables 1-3), accordingly to the occurring recrystallisation of gels. This result differs from the increase in the transition temperature observed after irradiation for wheat flour [6]. That decrease was, however, more significant in the case of all the irradiated samples than in the case of the initial sample. As a result, the differences between the irradiated and non-irradiated samples are more easily detected after storage.

The better differentiation between the amylose-lipid complex transition taking place in particular samples accompanied by the better reproducity were obtained in the case of dense suspensions as compared to the watery suspensions as well as during the first analysis performed for the recrystallised gels.

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PHYSICOCHEMICAL CHANGES TAKING PLACE IN BOVINE GLOBULINS UNDER THE INFLUENCE OF GAMMA IRRADIATION STUDIED BY THERMAL ANALYSIS

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Recently, gamma irradiation became more and more often applied for modification of biopolymers. Radiation modification of protein based polymers as well as the present development of gamma irradiation techniques as a method of food sterilisation and preservation induces necessity of better recognition of the physicochemical changes occurring in proteins after gamma irradiation. Estimation of the applicability of particular physicochemical methods for detection of the structural modifications taking place under influence of gamma irradiation corresponds to that problem.

Chemical transformations of amino acids, breakdown of peptide bonds, and hydrogen and disulphide bridges, as well as crosslinking of the chains might occur under the influence of ionising radiation and affect the tertiary structure of proteins and their physicochemical properties. Nature of damage that result from radiation processes taking place in the solid state might differ from those carried out in the water environment.

During the last years, differential scanning calorimetry (DSC) became a useful method for life sciences and was applied widely in structural studies of proteins. Thermoanalytical methods (TG, DTG) applied for proteins pyrolysis were also found to be useful in characterisation of proteins structure and the properties of proteins containing tissues [1].

We have initiated studies of the processes occurring in the irradiated biochemicals (proteins, polysaccharides, foodstuffs) using thermal analysis methods. In our previous work, differences were described between denaturation processes taking place in gamma-irradiated and non-irradiated proteins [2]. At present, DSC and thermogravimetry (TG, DTG) were applied for investigation of the gamma irradiation influence on thermal decomposition of gamma and alpha globulins and the results were related to their structural modifications.

Two preparations of bovine globulins were G5009 and G8512 products of Sigma. These contain, respectively, Cohn fractions II, III (predominantly gamma globulins) and Cohn fraction IV-1 (predominantly alpha globulins). Irradiation were carried out in a gamma cell Mineyola installed in the Department of Radiation Chemistry and Technology, Institute of Nuclear Chemistry and Technology, using a dose rate of *ca.* 0.45 Gy s^{-1}. Irradiation of solid native proteins were performed at depressed temperature (in dry CO_2) with a dose of 24 kGy. 50% water suspensions of both gamma and alpha globulins placed in closed polymer capsules were irradiated at ambient temperature with doses of 2.5 and 24 kGy. Simultaneously, non-irradiated reference samples were submitted to the same treatment with water.

Thermal analysis was carried out at the University of Antwerp in an oxygen stream applying a heating rate of 3°C/min. DSC measurements were carried out in the temperature range from 120 to 670°C using a Perkin Elmer heat flow DSC-7 calorimeter. Thermogravimetry was carried out using a Mettler thermobalance. The measurements were performed within 120-800°C. The borders between the subsequent effect on differential curves (DTG) were determined and treated as the borders between the subsequent steps of thermal decomposition. Accordingly, the mass loss connected to the particular steps of thermal decomposition was calculated as the mass loss taking place within that selected temperature range. The mass loss was expressed in terms of the mass obtained after proteins dehydration (m_d).

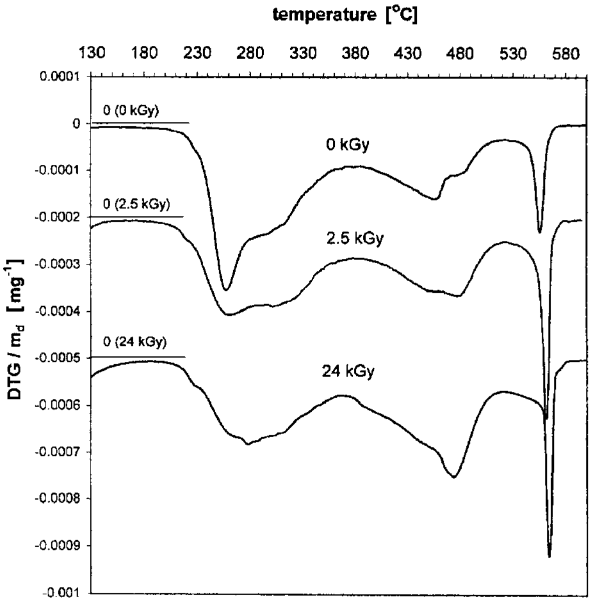

Fig.1. Comparison of DTG curves recorded for the reference gamma globulins (subjected to water treatment) and for the products irradiated with 2.5 and 24 kGy doses.

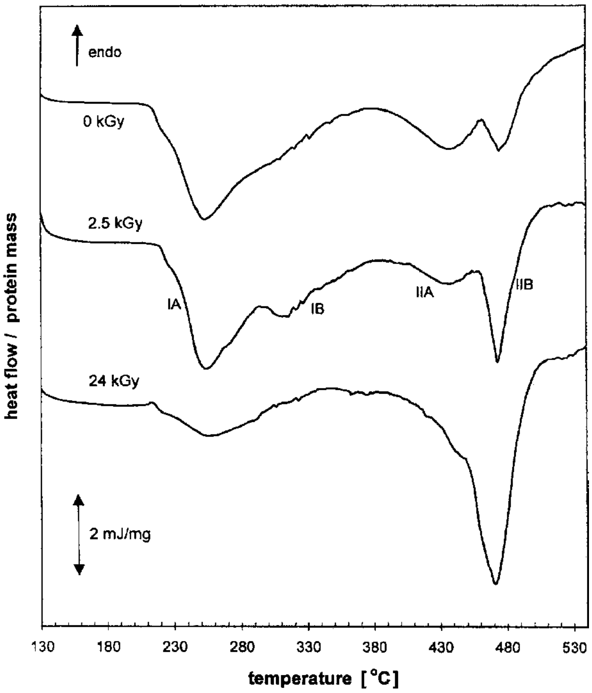

Fig.2. Comparison of DSC curves recorded within the range of the first and the second decomposition stages for the reference gamma globulins (subjected to water treatment) and for the products irradiated with 2.5 and 24 kGy doses.

Dehydration of proteins occur in the temperature range up to *ca.* 150°C. Several steps of thermal decomposition are observed at higher temperatures (Figs.1-3). Small amounts of non-volatile residues were still present after heating up to the temperature as high as 800°C. Three major temperature ranges of decomposition might be distinguished on the basis of thermoanalytical and DSC curves: the first till *ca.* 280°C, the second till *ca.* 520°C and the third till *ca.* 590°C. Two successive processes occur, however, in the first temperature range (marked IA and IB). Occurrence of two processes is evident in the second temperature range of decomposition of both gamma and alpha globulins treated with water, in contrary to the native proteins decomposition. It is shown by two exothermal effects recorded in this range on DSC curves (IIA, IIB) and two effects on DTG curves. Two processes were observed also in the third temperature range of alpha globulins decomposition (IIIA and IIIB).

Irradiation influences the course of decomposition of gamma and alpha globulins. Irradiation of solid native proteins result in decreased temperature of decomposition, especially decreased temperature of the last stage (Fig.4). The effects of irradiation performed for water suspensions

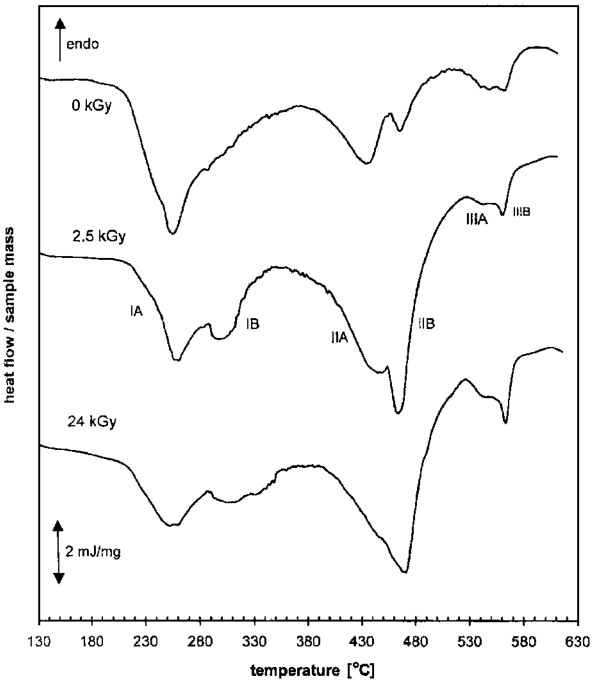

Fig.3. Comparison of DSC curves recorded for the reference alpha globulins (subjected to water treatment) and for the products irradiated with 2.5 and 24 kGy doses.

were clearly more significant. The bigger exothermal effects were thus accompanied by the second and the third stages of the irradiated samples decomposition as compared to the reference ones, while the smaler exothermal effects correspond to the first decomposition stage (Figs.2 and 3). Moreover, participation of IB, IIB and IIIB effects became more significant in DSC curves of the irradiated products. Results of thermogravimetry have shown that in the cases of irradiated products the mass loss was smaller in the first stage of decomposition and bigger in the second and third stages, in comparison to the reference samples. For example, in the case of the reference gamma globulins mass loss reach 59.98, 31.88 and 8.66% during the first, second and third decomposition stages. The appropriate values obtained for the sample irradiated with 2.5 kGy dose were equal to 52.29, 34.64 and 12.05% and those found for the sample irradiated with 24 kGy were equal to 40.00, 45.06 and 12.95%, respectively. Moreover, mass loss in the IB stage was also larger in relation to that obtained in IA stage in the cases of irradiated than in the case of non-irradiated samples. Therefore, the reference sample loses 50.65 and 9.33% of mass during the IA and IB stages, respectively, while the irradiated samples loses respectively 26.53 and 22.96% (irradiated with 2.5 kGy) and 19.75 and 20.25% (irradiated with 24 kGy). This was accompanied by the smaller DTG effect corresponding to the first decomposition stage and the bigger one corresponding to the second stage (Fig.1).

The results are related to the modification of amino-acid composition and modification of proteins tertiary structure. In particular, increase in the temperature of particular processes taking place during decomposition of the irradiated proteins demonstrates the occurring crosslinking processes. It is because that the first stage of decomposition consist on the cleavage of polypeptide linkages and shifts to the higher temperature in result of disulfide bridges formation [1]. On the contrary, decrease of decomposition temperature gives evidence of degradation induced by gamma irradiation performed for solid native proteins.

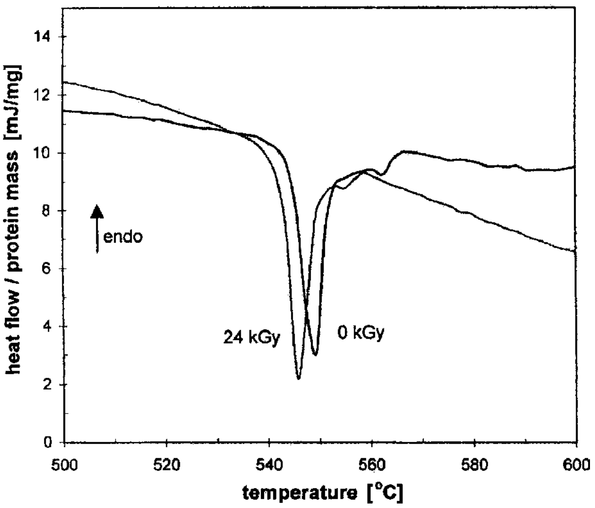

Fig.4. Comparison of DSC effects connected to the last fast stage of decomposition of the irradiated native dry globulins and the initial gamma globulins.

The relatively large differeces between decomposition of the irradiated and non-irradiated samples were detected by DSC and thermogravimetry already after irradiation of water suspensions with a dose of 2.5 kGy (Figs.1-3).

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RADIOCHEMISTRY
STABLE ISOTOPES
NUCLEAR ANALYTICAL METHODS
GENERAL CHEMISTRY

^{211}At-Rh(16-S4-diol) COMPLEX AS A PRECURSOR FOR ASTATINE RADIOPHARMACEUTICALS

Marek Pruszyński, Aleksander Bilewicz

^{211}At is one of the most promising radionuclides in α-radioimmunotherapy (α-RIT). Its 7.2 h half-life is sufficient for the radionuclide production, transportation, synthetic chemistry, quality control and biological application in the treatment of certain cancer diseases. The α particles with a mean energy of 6.4 MeV have a mean range in human tissue of 65 μm. Therefore, this nuclide may be useful for the treatment of small clusters of cells or single cells, micrometastatic diseases, leukemias, and lymphomas. Dosimetry calculations and preclinical therapeutic research with ^{211}At have demonstrated its highly toxic effects on tumor cells [1-5]. The short path length of the α particles also limits their toxicity to neighboring normal tissue. The additional electron capture (EC) decay gives rise to high intensity X-rays from the daughter ^{211}Po, making ^{211}At easy to follow with gamma-cameras [6].

^{211}At labeled immunoconjugates have been synthesized and evaluated for their therapeutic potential. Unfortunately, biomolecules labeled by direct electrophilic astatination are unstable due to the rapid loss of ^{211}At under both *in vitro* and *in vivo* conditions [7]. Better stabilization of the weak astatine-carbon bond is observed for proteins astatinated by acylation with a variety of astatobenzoic acid derivatives prepared from trialkylstannyl precursors [8,9].

The purpose of this work was to bind astatide anion At^-, the most stable oxidation state of astatine, with a biomolecule by attaching At^- to a metal cation in a chelate. It can be expected that At^-, similarly to iodide anion I^-, should demonstrate soft ligand properties and form strong complexes with soft metal cations, like Hg^{2+}, Pt^{2+}, Rh^{3+}, Ir^{3+}. In a previous work, we have shown that Hg^{2+} cations form strong complexes with At^-, much stronger than those with I^- [10]. The present paper describes the results of our studies on attaching At^- to the rhodium(III) complex with thioether ligand: 1,5,9,13-tetrathiacyclohexadecane-3,11-diol (16-S4-diol). Rh^{3+} was chosen as a moderately soft metal cation which should form very strong bonds with soft At^- anions, but first of all because of the kinetic inertness of low spin rhodium(III) d^6 complexes. The 16-S4-diol ligand was selected due to formation of stable complexes with Rh^{3+}, as reported in [11]. Additionally, this macrocyclic tetrathioether with the diol functionality offers a site for chemical modification in the synthesis of bifunctional chelating ligand.

Because the availability of ^{211}At is limited, the experiments related to optimization of the reaction conditions were performed with the ^{131}I, basing on a chemical similarity of I^- to At^-. The experiments with ^{211}At were then carried out under the conditions found optimal for I^-.

^{131}I-Rh(16-S4-diol) and ^{211}At-Rh(16-S4-diol) complexes were prepared by addition of $^{131}I^-$ or $^{211}At^-$ activity to the mixture of rhodium(III) nitrate and 16-S4-diol in water-ethanol solution. After adjusting pH to 4.0 by dropwise addition of 0.01-0.1 M nitric acid, the solution was heated for 1-2 h at 80°C. The syntheses were optimized to increase the yield of the obtained complexes with respect to time, temperature, pH, and the concentrations of rhodium(III) and the ligand. The complexes obtained were analyzed by thin-layer chromatography (TLC), paper electrophoresis and ion exchange chromatography (IC). The stability of the ^{131}I-Rh(16-S4-diol) complex was studied at different temperatures in phosphate-buffered saline (PBS) at pH 7.4.

In the complexes obtained, the sulfur donor atoms of the 16-S4-diol ligand occupy equatorial positions, whereas ^{211}At (^{131}I) and OH^- anions are in the axial positions (Fig.1). The formation of ^{131}I and ^{211}At rhodium complexes with thioether ligand was studied using mainly the electromigration method. As shown in Fig.2A, the ^{131}I-Rh(16-S4-diol) complex was a cation and migrated to the cathode, whereas uncomplexed $^{131}I^-$ migrated to the anode. The obtained results are consistent with the data on rhodium(III) chloride complexation with 16-S4-diol ligand, previously published [11].

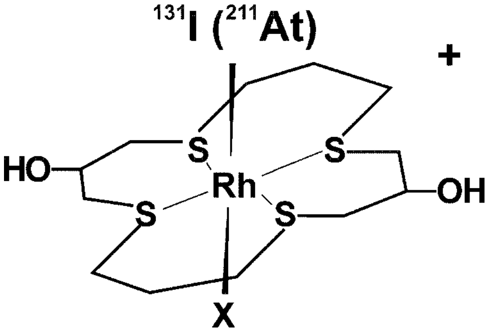

Fig.1. The proposed structure of the complexes, where $X=NO_3^-$, OH^- or H_2O.

The interaction of $^{131}I^-$ with Rh^{3+} cations in the absence of the 16-S4-diol ligand has been studied in control experiments. The products of the reaction between rhodium and iodide (Fig.2B) were neutral and remained at the starting point. These results indicate that $Rh(OH)_2I$ is probably formed under these conditions.

The results obtained by the TLC method confirm the formation of a complex between $^{131}I^-$ and Rh^{3+} with the macrocyclic thioether ligand. The experiments on cellulose plates gave the value $R_f=0.55-0.6$ for ^{131}I-Rh(16-S4-diol) complex, while for uncomplexed $^{131}I^-$ $R_f=1.0$. The rhodium-iodide species remained at the origin, when eluted with PBS or methanol-PBS (80-20%).

The kinetics of ^{131}I-Rh(16-S4-diol) formation was studied as a function of time (15-120 min) and temperature (30-90°C). The equilibrium was attained after 50 min heating the solution at 80°C. The kinetics of formation sharply increases at a temperature higher than 40°C. The high yields of the complex (>90%) can be obtained even when the complexation reaction was performed at a 1:1 stoichiometry ratio of rhodium(III) nitrate to 16-S4-diol at pH 4.0, but the rhodium concentration should not be less than 10^{-4} M; otherwise the yield decreases rapidly. The experiments under physiological conditions show that the complex obtained is stable for a long time. The complex was stable almost for 5 days of incubation at room temperature in 0.02 M PBS at pH 7.4. The experiment was performed by paper electrophoresis.

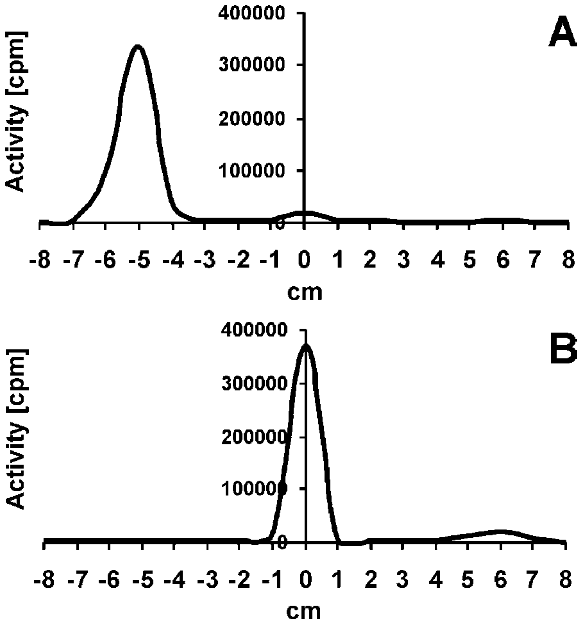

Fig.2. Electrophoretic analysis: (A) cationic complex ^{131}I-Rh(16-S4-diol), (B) mixture of rhodium(III) with ^{131}I, heated for 2 h at 80°C without the thioether ligand. Zero point on each chromatogram is the origin, while the directions of the cathode and anode are toward the -8 and +8 points, respectively.

Preliminary experiments on the synthesis of the ^{211}At-Rh(16-S4-diol) complex were performed using the same procedure as that elaborated with ^{131}I. Astatine was reduced to At^- by sodium sulfite or sodium borohydride in a methanol or water solution. The At^- solution was added to a mixture of rhodium(III) nitrate with 16-S4-diol in ethanol and acidified to pH=4.0, and heated for 1-2 h at 80°C. The synthesis products were analyzed by electrophoresis (Fig.3A). Control experiments were also performed to check whether any interactions occur between ^{211}At and rhodium(III) (Fig.3B).

The obtained results confirmed a similar behavior under the same conditions of the astatine compounds with that of the ^{131}I complexes. The ^{211}At-Rh(16-S4-diol) complex was also cationic (Fig.3A). Reaction of rhodium(III) with ^{211}At in the absence of 16-S4-diol gave the same results as with ^{131}I. The formed compound did not migrate to none of the electrodes (Fig.3B).

The preliminary results with ^{211}At are promising, and indicate a possibility for astatination of biomolecules by using the ^{211}At-Rh(16-S4-diol) complex. The future investigations will be related to stability studies of the astatide complex and to the possibility of linking the ^{211}At complex to biomolecule.

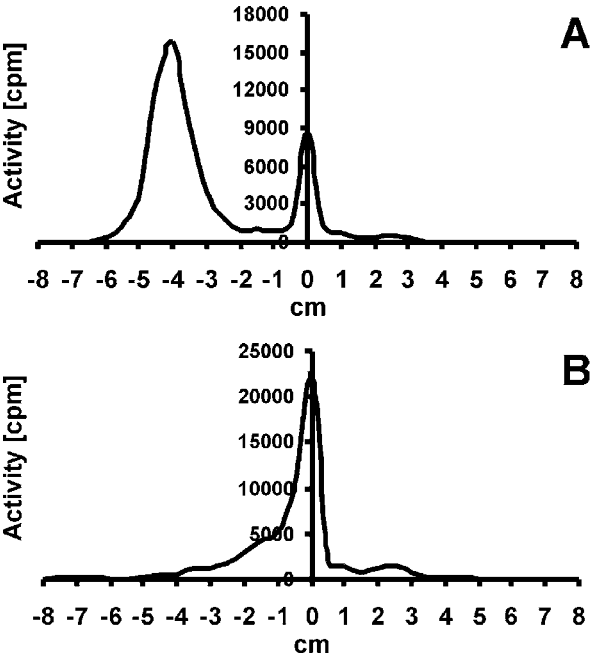

Fig.3. Electrophoretic analysis of ^{211}At-Rh(16-S4-diol) complex (A), and Rh(III)-^{211}At complex (B). Starting point on each chromatogram is the origin, while the directions to the cathode and anode are toward -8 and +8, respectively.

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THE STRUCTURES OF LEAD(II) COMPLEXES WITH TROPOLONE

Krzysztof Łyczko, Wojciech Starosta

Tropolone (2-hydroxy-2,4,6-cycloheptatriene-1-one), abbreviated as Htrop, is a non-benzenoid aromatic compound containing a seven-membered ring. Tropolonato ligand is a bidentate anionic species, which forms five-membered rings with metal ions [1]. The functional groups in tropolone (carbonyl and hydroxyl) make it possible its coordination to a number of various metal ions. There are many structural data on homoleptic complexes of metals with tropolonato ligands, *e.g.* Cu(trop)$_2$ [2], In(trop)$_3$ [3], Zr(trop)$_4$ [4]. Some dimeric species, such as [Tl^{III}(trop)Ph$_2$]$_2$ [5], [Bi^{III}(trop)$_2$(NO$_3$)]$_2$ [6], [Ni(trop)$_2$H$_2$O]$_2$ [7] and polymeric species of Zn^{2+} [8] and Hg^{2+} [9] with tropolone have also been obtained. In the dimeric and polymeric compounds the tropolone plays a bridging role.

Many structural data on coordination compounds of tropolone with *p*-block metal cations, such as gallium, indium [3], thallium(III) [5], tin(II) [8], tin(IV) [10], bismuth(III) [6] and bismuth(V) [11] have been reported. The methods of synthesis of bis(tropolonato)lead(II) and tetrakis(tropolonato)lead(IV) were described previously [12,13]. Apart from this information, there are no structural data on any tropolonato-lead compound.

The aim of this work was to determine the structure of complexes formed by the lead(II) ion and tropolone molecules. We presumed that the composition and the structure of the complexes may depend on the anion. For this purpose, we have used triflate, perchlorate, nitrate and acetate as counter ions. The reason was a good solubility of their lead(II) salts in a water/methanol mixture.

The reaction of tropolone with Pb(CF$_3$SO$_3$)$_2$, Pb(ClO$_4$)$_2$, Pb(NO$_3$)$_2$ and Pb(CH$_3$COO)$_2$ in solution led to the formation of four different lead(II) complexes: one dimeric and three polymeric. The structure of the [Pb(trop)(CF$_3$SO$_3$)(H$_2$O)]$_n$ (**1**), [Pb$_3$(trop)$_4$(ClO$_4$)$_2$]$_n$ (**2**), [Pb$_2$(trop)$_2$(NO$_3$)$_2$(CH$_3$OH)]$_n$ (**3**) and [Pb(trop)$_2$]$_2$ (**4**) compounds was determined by single crystal X-ray diffraction (Figs.1-4). A simple bis(tropolonato)lead(II) complex in the dimeric form was obtained only from the acetate salt. For the rest of salts, polymeric species were formed with the anions coordinated to lead atoms and acting as bridges. Each lead(II) ion in the polymeric compounds is chelated by one tropolonato ligand, apart from one type of lead atom in compound **2**, which is bound with two tropolone molecules. In the dimeric complex **4**, the metal ions are coordinated by two ligand molecules.

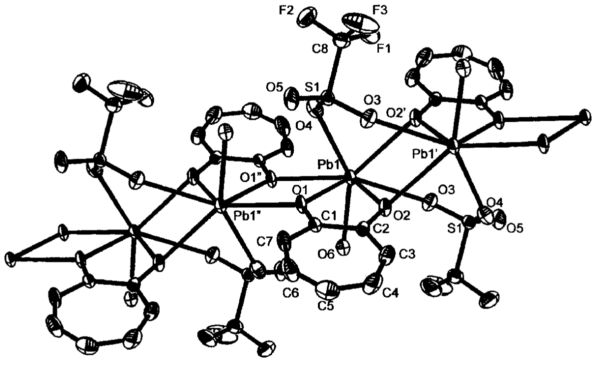

Fig.1. The structure of [Pb(trop)(CF$_3$SO$_3$)(H$_2$O)]$_n$ (**1**). Selected bond lengths [Å] and angles [°]: Pb1-O1 2.339(5), Pb1-O2 2.293(5), Pb1-O3 2.776, Pb1-O4 2.784, Pb1-O6 2.446(6), Pb1-O2' 2.853, Pb1-O1" 2.763, O1-C1 1.286(7), O2-C2 1.280(8), O1-Pb1-O2 68.38(16).

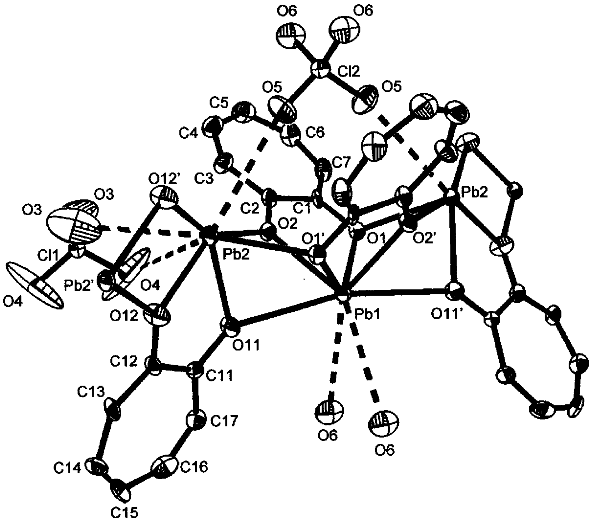

Fig.2. The structure of [Pb$_3$(trop)$_4$(ClO$_4$)$_2$]$_n$ (**2**). Selected bond lengths [Å] and angles [°]: Pb1-O1 2.455(12), Pb1-O2 2.344(13), Pb1-O11 2.838, Pb2-O11 2.297(14), Pb2-O12 2.362(14), Pb2-O1 2.436(12), Pb2-O2 2.606(12), Pb2-O12' 2.711(14), Pb1-O6 3.140, Pb2-O5 3.377, Pb2-O3 3.152, Pb2-O4 3.130, O1-C1 1.276(22), O2-C2 1.287(21), O11-C11 1.303(22), O12-C12 1.292(24), O1-Pb1-O2 65.01(42), O11-Pb2-O12 67.90(49).

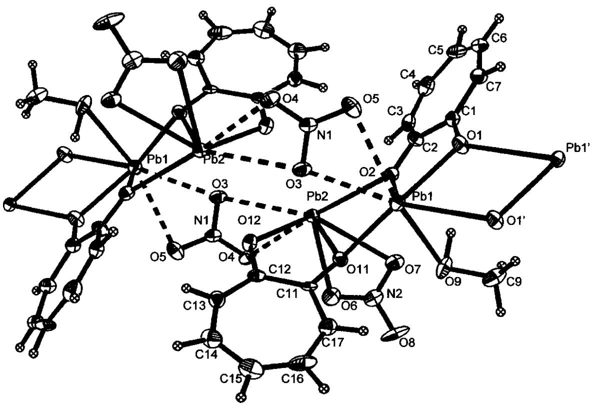

Fig.3. The structure of [Pb$_2$(trop)$_2$(NO$_3$)$_2$(CH$_3$OH)]$_n$ (**3**). Selected bond lengths [Å] and angles [°]: Pb1-O1 2.345(11), Pb1-O2 2.314(11), Pb1-O9 2.567(13), Pb1-O11 2.599(10), Pb1-O1' 2.770, Pb1-O3 2.677(12), Pb1-O5 2.806, Pb2-O11 2.369(12), Pb2-O12 2.327(11), Pb2-O3 3.007, Pb2-O4 2.871, Pb2-O6 2.789, Pb2-O7(14), Pb2-O2 2.760, O1-C1 1.306(18), O2-C2 1.287(19), O11-C11 1.277(18), O12-C12 1.319(19), O1-Pb1-O2 67.3(4), O11-Pb2-O12 67.2(4).

It is obvious that the counter anions play a decisive role in the formation of the studied compounds through entering (or not entering) the structure. In compounds **1** and **3**, the counter anions build bridges within the same polymeric chain, whereas in compound **2** they link two adjacent polymeric chains forming a three-dimensional lattice. A comparison of the respective Pb-O bond distances shows that perchlorate anions interact with metal atoms more weakly than the triflate and nitrate groups.

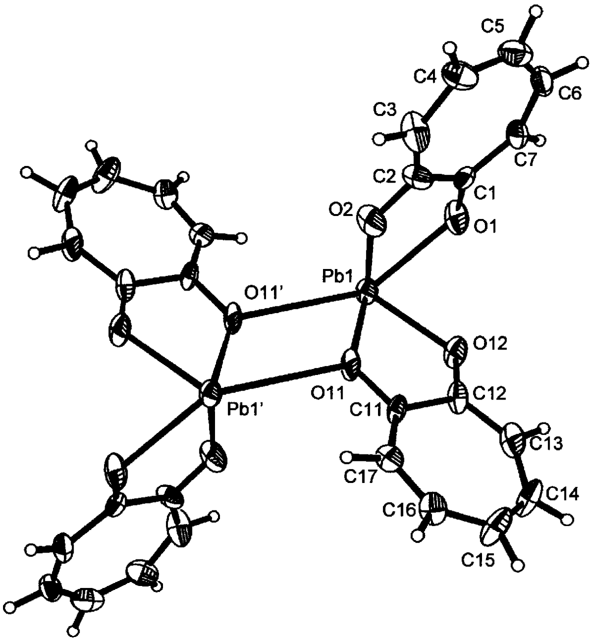

Fig.4. The structure of $[Pb(trop)_2]_2$ (**4**). Selected bond lengths [Å] and angles [°]: Pb1-O1 2.449(19), Pb1-O2 2.316(18), Pb1-O12 2.285(17), Pb1-O11 2.307(18), O1-C1 1.222(28), O2-C2 1.284(31), O11-C11 1.321(21), O12-C12 1.275(28), Pb1-O11' 2.912, O1-Pb1-O2 65.61(59), O11-Pb1-O12 67.95(54).

The formation of these four structures probably depends on the pH of the solution. Because of hydrolysis of the lead(II) salts, the pH of aqueous solutions of salts originating from strong acids ($Pb(CF_3SO_3)_2$, $Pb(ClO_4)_2$ and $Pb(NO_3)_2$) was lower (pH~3 or less) than that (pH>5) of $Pb(CH_3COO)_2$ – a salt of weak acid. In more acidic solutions, what is in the case of the first three salts, the formation of polymeric compounds followed the addition of tropolone. At higher pH value, as for the lead(II) acetate, we observed the precipitation of bis(tropolonato)lead(II).

Contrary to complexes **1** and **4**, which have only one kind of lead center, complexes **2** and **3** comprise two coordinatively different types of lead atoms. In all the complexes studied, tropolone chelates the lead(II) ion in an anisobidentate manner, with one shorter and one longer Pb-O bond. These Pb-O bond lengths are in the range 2.28-2.45 Å.

The C-O bond distances in the studied structures are intermediate between the C=O (1.26 Å) and C-O (1.33 Å) bond lengths, which are observed for the free tropolone molecule [14]. Only in the purely chelating tropolonato ligand in **4**, one of the C-O distances (1.22 Å) is surprisingly shorter than the C=O bond.

In the studied structures, the bridging $Pb\text{-}O_{(trop)}$ distances vary in the range 2.44-2.91 Å. For compounds **4** and **1**, we found one and two kinds of such bridges, respectively. The largest variety of side interactions between lead and tropolone appears in polymers **2** and **3**, where we have four and three different bridging $Pb\text{-}O_{(trop)}$ contacts, respectively, including the shortest one of 2.44 Å for compound **2**. Such an amazingly short bridge is comparable with some chelating $Pb\text{-}O_{(trop)}$ bonds, 2.455(12) Å (in **2**) and 2.449(19) Å (in **4**). The studied complexes demonstrate various total coordination numbers of lead(II) ions: from 5 in $[Pb(trop)_2]_2$, 7 in $[Pb(trop)(CF_3SO_3)(H_2O)]_n$ and $[Pb_2(trop)_2(NO_3)_2(CH_3OH)]_n$ to 8 in $[Pb_3(trop)_4(ClO_4)_2]_n$.

The nonspherical distribution of ligands surrounding the lead(II) ion (hemidirected geometry [15]) in the structures **1**, **3** and **4** results from the presence of the stereochemically active $6s^2$ lone electron pair. In compound **2**, we can consider a hemidirected geometry if we take into account only tropolonato ligands. The gap observed in this complex is filled, apart from the lone electron pair, with the weakly bonding ClO_4^- ions. The $6s^2$ lone electron pair on the lead(II) ions is stereochemically active in all the complexes studied. The active lone electron pair is common in lead(II) complexes with coordination number up to 8, and does not occur for higher coordination numbers [15].

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SYNTHESIS OF NOVEL “4+1” Tc(III)/Re(III) MIXED-LIGAND COMPLEXES WITH DENDRITICALLY MODIFIED LIGANDS

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Coordination chemistry of technetium and rhenium attracts a considerable interest due to the nuclear medicine applications of their radionuclides. Inert, so-called “3+1” [1] or “4+1” [2] technetium/rhenium mixed-ligand complexes open a new way to application of ^{99m}Tc/^{188}Re labeled compounds in tumor diagnosis and therapy. The “4+1” complexes of trivalent technetium and rhenium with tetradentate, NS_3, 2,2’,2”-nitrilotris(ethanethiol) and monodentate isocyanide ligands have been proved to be more stable than “3+1” complexes [3]. In addition, they do not undergo substitution reaction *in vivo* with SH-group-containing molecules such as cysteine or glutathione [4].

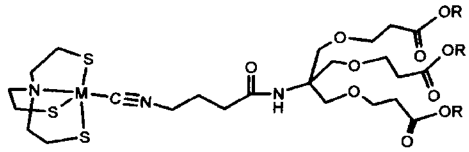
In the present paper, we describe the synthesis and study of novel ^{99m}Tc/^{188}Re complexes with dendritically functionalized tetradentate or monodentate ligands (Fig.1). To verify the identity of the prepared n.c.a. complexes, non-radioactive analogous “4+1” Re compounds were synthesized.

The tetradentate ligands: tripodal chelator 2,2’,2”-nitrilotris(ethanethiol), NS_3, [2] and carboxyl group-bearing ligand, $NS_3(COOH)_3$ [5,6], have been synthesized already in the Forschungszentrum Rossendorf e.V. (Germany). The monodentate isocyanide ligands: dendritically modified isocyanide, CN-R$(COOMe)_3$, and isocyanide-modified peptide, CN-GGY, were synthesized in the reaction of the aliphatic linker (CN-BFCA) and the dendritically functionalized amine H_2N-C(-CH_2-O-CH_2-CH_2-COO-Me$)_3$ (first generation “Newkome” type dendritic branch [5]) or model peptide Gly-Gly-Tyr, respectively.

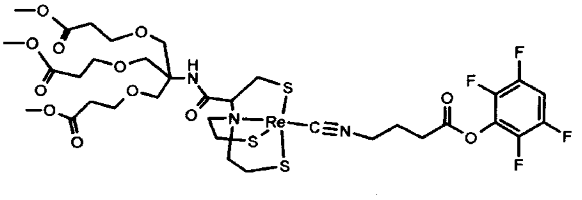
The reference “4+1” Re compound Re(NS_3)(CN-R$(COOMe)_3$) has been obtained in the ligand exchange reaction with Re$(NS_3)(PMe_2Ph)$ and dendritically modified isocyanide CN-R$(COOMe)_3$. For a convenient synthesis of the reference “4+1” Re compound, Re$(NS_3(COOH)_3)$(CN-GGY), the active ester Re$(NS_3(COOMe)_3)$(CN-BFCA) shown in Fig.1 was prepared starting from $NS_3(COOH)_3$, $[Re(tu\text{-}S)_6]Cl_3$ and PMe_2Ph followed by ligand exchange with CN-BFCA. Reaction of Re$(NS_3(COOMe)_3)$(CN-BFCA) with the model peptide and hydrolysis of the methyl ester gave the desired peptide derivative. The non-radioactive rhenium(III) reference compounds have been characterized by MS (mass spectrometry) and ^{1}H-NMR (nuclear magnetic resonance).

The n.c.a. synthesis of the “4+1” technetium/rhenium complex was carried out in two steps [6]. In the first step, a ^{99m}Tc- ^{188}ReEDTA-mannitol complex was formed (room temperature – 20 min) and the reaction progress was checked by the TLC (thin layer chromatography) analyses (Fig.2). In the second step the ^{99m}Tc-/^{188}ReEDTA-mannitol complex reacted with $NS_3/NS_3(COOH)_3$ and CN-R$(COOMe)_3$/CN-GGY ligands (50°C, 1 h) forming the desired “4+1” complex (Fig.1). Identification of the preparations obtained, as well as their stability and radiochemical purity studies were carried out by HPLC – high pressure liquid chromatography (Figs.3 and 4). To prepare the ^{99m}Tc/^{188}ReEDTA-mannitol complexes the kits formulation were used.

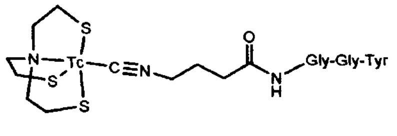
The experimental data show that a dendritic modification of the tetradentate/monodentate ligands changes the complex lipophilicity and does not influence its stability. The increase in hydrophilicity of ^{99m}Tc$(NS_3(COOH)_3)$(CN-GGY) complex in relation



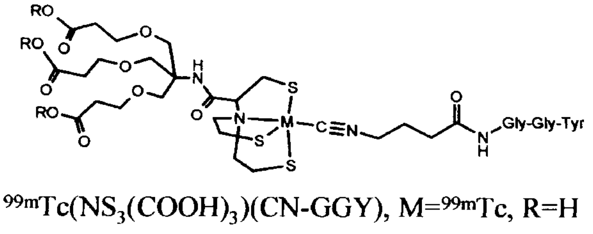
^{99m}Tc(NS_3)(CN-R$(COOMe)_3$), M=^{99m}Tc, R=Me
^{188}Re(NS_3)(CN-R$(COOMe)_3$), M=^{188}Re, R=Me
Re(NS_3)(CN-R$(COOMe)_3$), M=Re, R=Me



Re$(NS_3(COOMe)_3)$(CN-BFCA)



^{99m}Tc(NS_3)(CN-GGY)



^{99m}Tc$(NS_3(COOH)_3)$(CN-GGY), M=^{99m}Tc, R=H
Re$(NS_3(COOH)_3)$(CN-GGY), M=Re, R=H
Re$(NS_3(COOMe)_3)$(CN-GGY), M=Re, R=Me

Fig.1. Technetium(III)/rhenium(III) ”4+1” complexes used in this study.

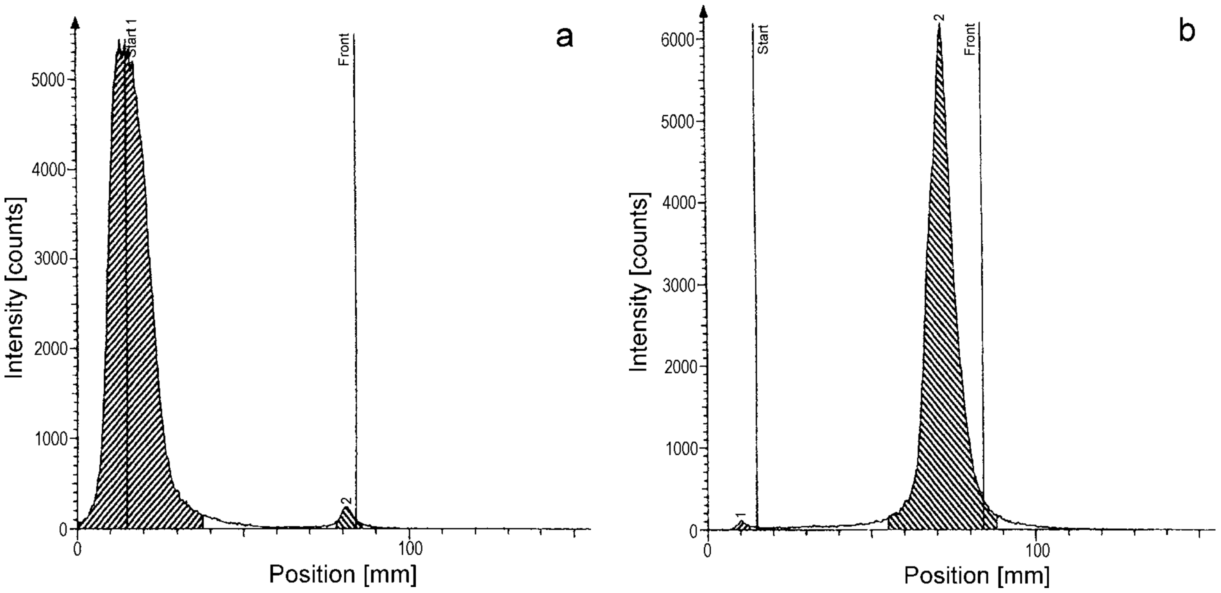


Fig.2. TLC chromatograms of ^{99m}Tc/^{188}ReEDTA-mannitol complex developed in acetone (a) and in water (b) (mobile phase; the strips, Silufol, Kavalier, were scanned with a Raytest Rita radioanalyzer).

to that of ^{99m}Tc(NS$_3$)(CN-GGY) has been shown by HPLC (Fig.4) and by determination of their partition coefficients, D. The logD values (n-octanol/PBS, pH 7.4) of the ^{99m}Tc(NS$_3$(COOH)$_3$) (CN-GGY) and ^{99m}Tc(NS$_3$)(CN-GGY) complexes are equal to -2.6±0.3 and -1.5±0.2, respectively.

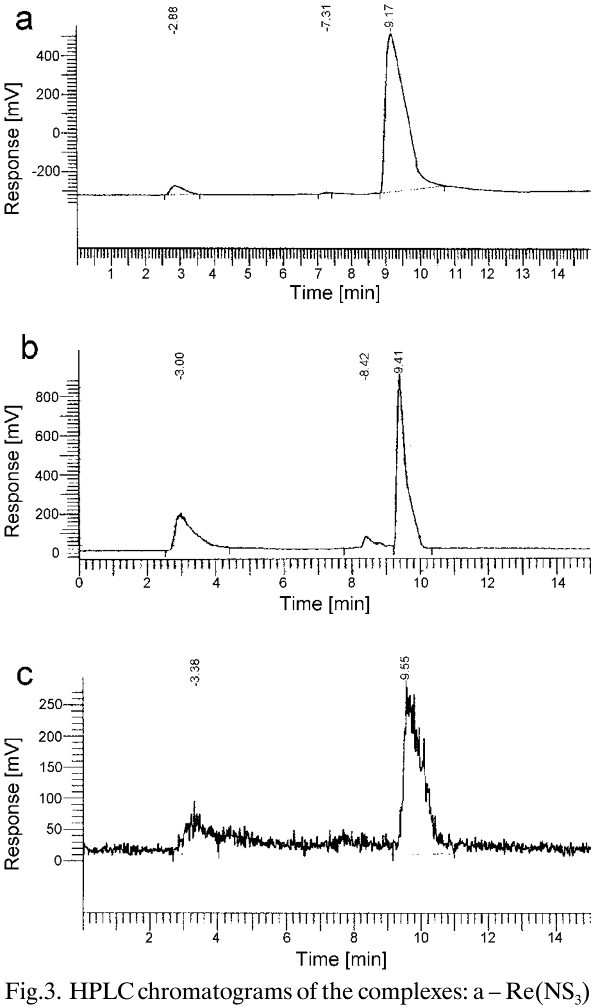


Fig.3. HPLC chromatograms of the complexes: a – Re(NS$_3$)(CN-R(COOMe)$_3$), R_T=9.17, UV-VIS detection at 220 nm; b – ^{99m}Tc(NS$_3$)(CN-R(COOMe)$_3$), R_T=9.41, gamma detection; c – ^{188}Re(NS$_3$)(CN-R(COOMe)$_3$), R_T=9.55, gamma detection; column – PRP 1, Hamilton, 250x4.1.

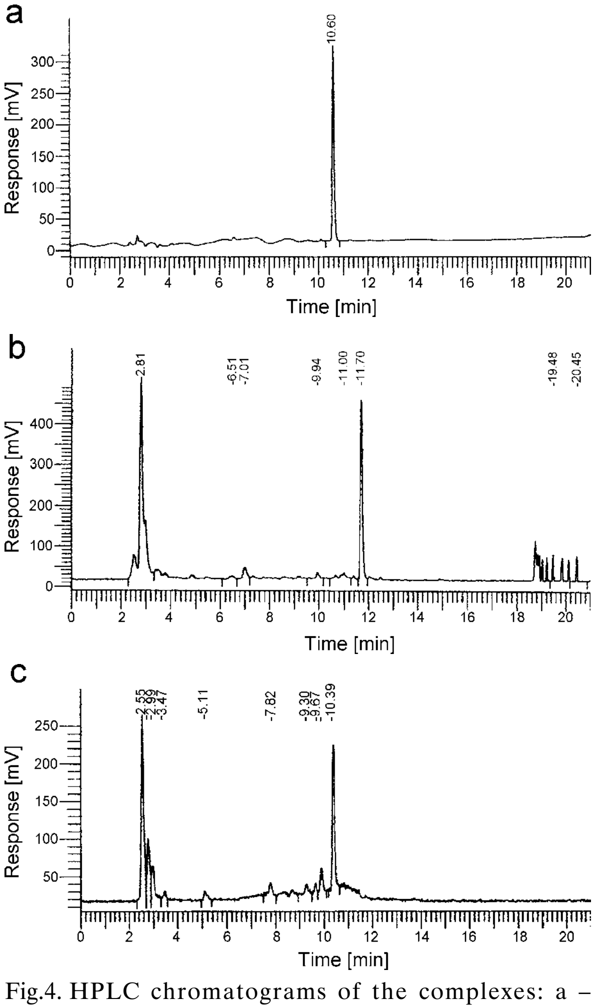


Fig.4. HPLC chromatograms of the complexes: a – Re(NS$_3$(COOH)$_3$)(CN-GGY), R_T=10.60, UV-VIS detection at 220 nm; b – ^{99m}Tc(NS$_3$)(CN-GGY), R_T=11.70, gamma detection; c – ^{99m}Tc(NS$_3$(COOH)$_3$) (CN-GGY), R_T=10.39, gamma detection; column – Jupiter 4u Proteo 90A, 250x4.6.

The conjugates of the ^{99m}Tc complexes with peptides exhibit a high stability *in vitro* (>90% in PBS after 24 h). As a next step, the new peptide-bearing "4+1" compounds will be evaluated in animal experiments.

The experiments have been done during the research stay of Ewa Gniazdowska at the Institute of Bioinorganic and Radiopharmaceutical Chemistry, Forschungszentrum Rossendorf e.V. in the frame of the project "Chemical Studies for Design and Production of New Radiopharmaceuticals" (No. MTKD-CT-2004-509224 (POL-RAD-PHARM)), supported by the European Community within the 6th Frame Programme Marie Curie: Host Fellowships for Transfer of Knowledge (ToK).

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TRANSITION METAL COMPLEXES WITH ALGINATE BIOSORBENT

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Alginate is one of the most extensively investigated biopolymers for metal ion removal from dilute aqueous solution [1-3]. It is a viscous gum present in the cell walls of brown algae. This linear copolymer contains homopolymeric blocks of covalently (1-4)-linked β-D-mannuronate (M) and its C-5 epimer α-L-guluronate (G) residues [4-7]. The length of each block and the total content of G and M residues depend on the source of the alginate.

Modern alginate biosorbents are usually prepared as calcium alginate-based ion-exchange resin (abbreviated as CA or CABIER) [1,8]. They exhibit extremely high sorption capacity and favorable kinetics for binding of heavy metal ions, and have been proven to be stable under various chemical and physical conditions. Adsorption capacity of the CA in relation to heavy metals can be as high as 3 mmol(M^{2+})/g(CA) [9,10], which is by one or two orders of magnitude more than that of activated carbons (being 0.05 to 0.15 mmol-metal per 1 g of carbon). Because the CA cannot be broken down by bile or saliva and cannot be absorbed by the body, it is excreted from the body together with the heavy metals and radioactive substances. Several attempts have been made to apply the CA as the human body remediation agent when the heavy or radioactive metal contamination occurred.

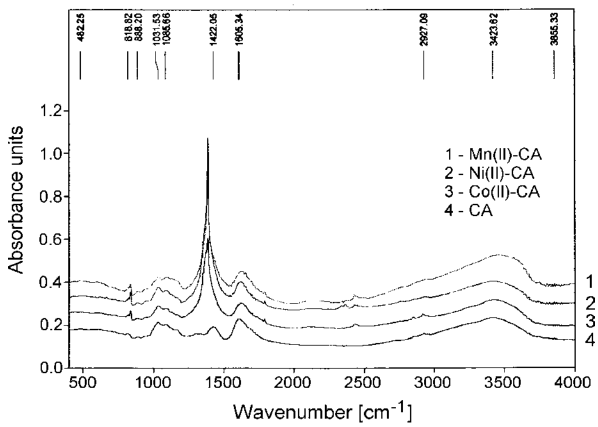

Fig.1. Vibrational spectra of the selected transition metal(II)-alginate complexes.

In general, process of biosorption of heavy metals can be explained by considering different kinds

Table 1. Assignments of main IR absorption bands for calcium alginate and selected metal complexes.

Assignment	Alginic acid*	CA	Mn(II)-CA	Co(II)-CA	Ni(II)-CA	Cu(II)-CA	Zn(II)-CA	Cd(II)-CA
$\nu(COO^-)_{sym}$	1738		1788	1788	1788			
$\nu(COO)_{sym}$	1620	1605	1621	1618	1617	1616	1617	1614
$\nu(COO)_{asym}$	1461	1421	1383	1384	1383	1384	1384	1429
δ(CCH)+δ(COH)	1248							
ν(CO)+ν(CC)	1175	1161		1170				
ν(CO)+ν(CCC)	1091	1085	1093	1086	1087	1087	1084	1087
ν(CO)+δ(CCO)+δ(CC)	1033	1033	1031	1033	1033	1033	1033	1031
δ(CO)+δ(CCH)		939	947		948		948	939
δ(CH) β-anomer	875	888	888	884	887	883	885	883
δ(CH) α-anomer	812	818	835	836	836	823	836	823

* Previously published data [16].

of chemical and physical interactions between the heavy metals present in solution and functional groups of the biosorbent: carboxylic, phosphate, sulfate, ammino, amidic or hydroxylic [10-12].

Divalent cation binding by calcium alginates was investigated using a number of techniques. Potentiometric titration revealed that CA exhibits two distinct pK_a values: (i) similar to that characteristic of carboxylic groups, and (ii) comparable to that of saturated alcohols. Esterification of the biosorbent species resulted in a significant reduction in metal sorption (up to 10 times), indicating that mainly carboxylic groups are responsible for the sorption. Also the ion-selective electrode (ISE) studies suggest that sorption of cadmium is mainly due to an ion exchange mechanism [13]. X-ray photoelectron spectroscopy (XPS) and the infrared (FTIR) results indicated that both alcoholic (-OH) and carboxylic ($-COO^-$) functional groups present in the carbohydrate moieties play an important role in the metal removal from aqueous solutions [14].

Because of the difficulties in direct X-ray investigations of the carbohydrate derivatives, FTIR absorption spectra of selected M(II)-alginate complexes and CA bed (Fig.1) were recorded as a continuation of our studies [15,16] on species formed by alginic biosorbent with different metal cations. Vibrational spectroscopy is the most widely used technique for studying natural products, being fast, non-destructive, and demanding small sample amounts. So, the aim of the presented work was to continue our studies on transition metal complexes with biosorbents on the alginate origin.

Main vibrational modes: IR spectra of the investigated species, especially in the fingerprint region, are rather complex and reflect the complex nature of the biomass. Analysis of the main features of the spectra shows that:

- In the fingerprint spectral window all spectra exhibit the absorbance bands at approximately 1605, 1420, 1085, 1030, 890 and 820 cm^{-1}. Proposed assignment of the bands forming the fingerprint spectral window has been revised since publication of the previous paper [16] and is presented in Table 1.
- The difference between the spectra of CA and M(II)-alginate is mainly in their absorbance intensities. While the band intensities of the metal-loaded CA in the region of the symmetric carboxylate stretching mode (1450-1300 cm^{-1}) are significantly higher than that of CA, in the asymmetric carboxylate stretching modes (about 1610 cm^{-1}) a slight decrease in the intensity can be observed for the transition metal cations upon the exchange of the calcium cation. The absorbance bands in pure alginic acid are 1740 and 1240 cm^{-1}.
- The distance between the ν_{sym} and ν_{asym} absorbance bands for CA is significantly smaller than those for M(II)-alginate. It can be related to the higher symmetry in CA in respect to other M(II)-alginates, which occurred due to complexation with metal cation.
- The ν_{asym}(COO) band of the M(II)-alginates are narrower and sharper than that in the CA spectrum. It could be linked with orthodox coordination spheres, wherein both oxygen-M(II) bonds have a very similar strength.
- Lack of displacement of the bands related to vibrations associated with the C-O (both alcoholic and ether groups) at 1085 and 1030 cm^{-1} is observed when calcium cation is replaced by another divalent cation. Such displacement could result from different coordination strengths of the metal and calcium cations to both alcoholic or ether groups.
- Broad absorption peaks in the region of 3250-3500 cm^{-1} indicate the existence of hydroxyl groups involved in H-bond network. The peak observed at 2930 cm^{-1} can be assigned as vibration of the CH group [17,18].

Table 2. Dependence of the $\nu(COO)_{sym}$ and $\nu(COO)_{asym}$ peak positions for the Mn(II)-CA on the equilibrium pH.

	pH				
	1.20	4.33	6.13	7.49	8.03
$\nu(COO)_{sym}$	1621	1619	1619	1619	1619
$\nu(COO)_{asym}$	1384	1383	1383	1383	1384

The dependence of the main peaks positions on the equilibrium pH has been analyzed for all the cations studied. The results are as follows:

- $\nu(COO)_{sym}$ and $\nu(COO)_{asym}$: Table 2 and Fig.2 present the data obtained for the Mn(II)-alginate. The complexation mode does not change within the whole pH range studied [19]. All other cations behave similarly – neither position nor shape of both main peaks describing the complexation mode depends on the solution acidity. So, the results obtained for other cations are not shown neither in Table 2, nor in Fig.2.

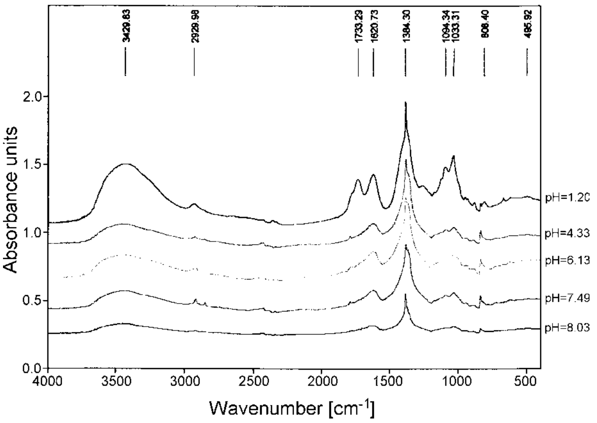

Fig.2. Spectra of the CA loaded with manganese(II) of different pH.

- The significant decrease in the intensity of the 3429 cm^{-1} peak may be explained in terms of decreasing number of H-bonds, caused by the dissociation of the hydroxyl groups present in the uronic moieties.

Because the carboxylate group in the alginate resin plays an important role in binding metal ions, the percentage of ionic bonding (PIB) was introduced to characterize qualitatively the cation-anion bond formed by the biosorbents [14]:

Table 3. Percentage of the ionic bonding estimated for the transition metal cations relatively to the calcium(II).

Cation	Ca(II)	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
$R_{ion}/(R_{ion}^{-1})$ [pm]	$99/1.010\cdot10^{-2}$	$80/1.235\cdot10^{-2}$	$72/1.389\cdot10^{-2}$	$69/1.449\cdot10^{-2}$	$72/1.408\cdot10^{-2}$	$74/1.351\cdot10^{-2}$	$95/1.037\cdot10^{-2}$
PIB [%]*	100.0	195.0	192.5	195.0	192.5	192.5	102.5

* Relatively to the Ca(II)-alginate.

$$\mathrm{PIB} = \frac{\nu_{\mathrm{COOH}} - \nu_{\mathrm{COOM}}}{\nu_{\mathrm{COOH}} - \nu_{\mathrm{COONa}}}$$

where ν is the frequency of the asymmetric vibration of the carboxylate group. The denominator is the IR frequency shift of the asymmetric C-O vibration from the typical covalent bonding (carboxylic acid) to the typical ionic bonding (sodium carboxylate), whereas the numerator is the frequency shift of the same vibration when a particular metal ion is bound. On the basis of the frequencies found in the FTIR spectra (Table 1), the relative PIB values for the divalent transition metal cations *vs.* that for calcium(II) were calculated (Table 3 and Fig.3). These values are independent of the cation and for the first transition metals row – significantly greater than unity. The observation may be related to the inversed ionic radii, which determine the ionic charge density being proportional to the cation hardness. Value for cadmium(II) (of the radius similar to this of calcium(II)) appears to be close to that for calcium(II).

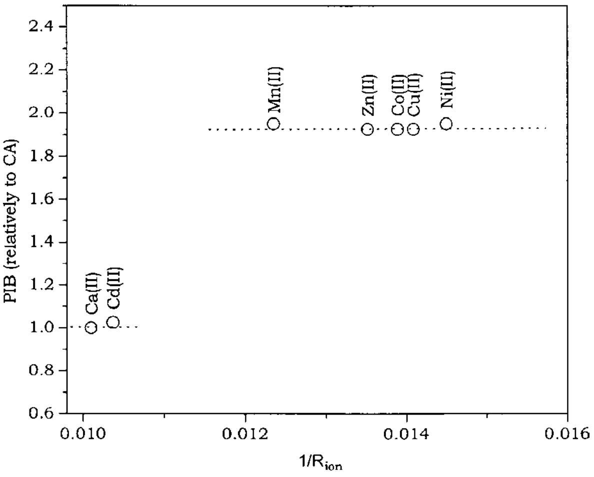

Fig.3. PIB values for the investigated species relatively to the CA.

The observed lack of PIB dependence on the cationic radius for the manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes may be explained in terms of the cation hydration. In the outer-sphere complexes, the cation radii of the hydrated species are close to each other within the group and different from those of calcium(II) and cadmium(II). The latter may probably form the inner-sphere complexes.

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STRUCTURAL STUDIES AND CYTOTOXICITY ASSAYS OF PLATINUM(II) CHLORIDE COMPLEXED BY (TETRAHYDROTHIOPHENE)THIOUREA

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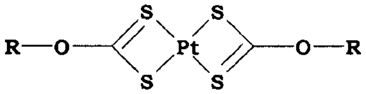
At present, chemotherapy is indispensable for the treatment of numerous kinds of cancer. Despite advances in surgery and radiotherapy, the mortality caused by cancer remained practically unchanged until the *cis*platin (*cis*-diamminedichloroplatinum(II), CDDP) has been discovered. The introduction of platinum-based chemotherapy has significantly improved the efficiency of therapeutic regimens. Most of the platinum compounds used today are the derivatives of CDDP, with two amino groups in the *cis* position [1,2].



In 2000, a novel platinum complex based on sulfur as complex-forming donor atoms – bis(*O*-ethyldithiocarbonato)-platinum(II), named thioplatin – a tumor targeting platinum-based drug was developed by the German Cancer Research Centre and licensed by Antisoma [3]. At present, it is called the "gold standard" and forms the cornerstone of cancer treatments against a range of solid tumors resistant to *cis*platin, including lung, ovarian and testicular cancers. On the basis of our previous studies [4], a question arises if the $\mathbf{M}(R_1R_2\mathbf{tu})_x^{2+}$, where $(R_1R_2\mathbf{tu})$ denotes various derivatives of thiourea, might exhibit the desired biological activity. The main objective of the present work was to modify the **tu** molecule in order to obtain other platinum(II) complexes which exhibit the antitumor activity. In details, the N-(2-methyltetrahydrothiophene)thiourea, derivative of simple thiourea containing the moiety able to link to the DNA and its platinum(II) complex were prepared and tested for antitumor properties. The biological activity was checked using the standard L1210 murine leukemia cell line.

The title complex, was synthesized according to the following reaction:

$$K_2Pt^{II}Cl_4 + L \rightarrow Pt^{II}LCl_2 + 2KCl$$

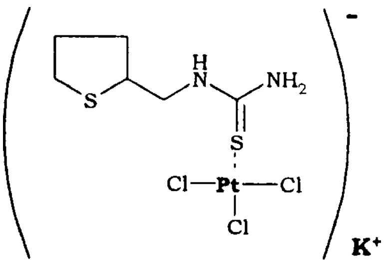
by dropwise adding, at room temperature, an ethanolic solution of the ligand to the aqueous solution of K_2PtCl_4 until the molar ratio 1:1 was achieved [4].

It is well known, that the structure of the investigated platinum(II) complexes strongly influences their biological properties. This might be of importance for their interactions with numerous biochemical targets, *e.g.* with DNA. However, because of the severe difficulties in obtaining crystals suitable for X-ray diffraction investigations, the registered IR spectra accompanied by quantum-chemical calculations appeared to be main source of the structural information. We have already shown that the calculations performed sufficiently well reflect the main structural features of platinum(II) complexes with the thiourea derivatives [4,5].

Structural investigations

It has been already demonstrated that the MPW1PW one-parameter density-functional approach is a reliable method for predicting molecular structures and vibrational spectra of the therapeutically important platinum(II) coordination compounds: *cis*platin and carboplatin. The MPW1PW/LanL2DZ method yielded the geometry and vibrational frequencies in better agreement with the experimental data, than those obtained with other functionals and using the MP2 routine [6]. It also generated the geometry and vibrational frequencies, describing complexes of the divalent platinum and palladium cations with thiourea, very similar to the experimental data [4].

Calculations for the title compound have been performed by two consecutive quantum-chemical methods: semi-empirical PM3 and MPW1PW/LanL2DZ procedure. The LanL2DZ basis set of Hay and Wadt [7-9], takes into account relativistic effects. All calculations were performed using SPARTAN Pro 5.0 (PC version) [10] and Gaussian 98 package [11] running on the Silicon Graphics IRIS Indigo work station with the processor RISC 10000. Application of the semi-empirical PM3 method resulted in several dozens of conformers of the complex. However, during quantum-chemical calculations only one structure could be optimized.



Under the assumption of the analytically found Pt:Cl mol ratio close to 3, analogously to our previous work [5], three hypothetic structures were examined. The species containing monodentately bound ligand has been chosen as the most probable structure because of its lowest energy. Two projections of the structure are shown in Fig.1.

From Fig.1b, it can easily be seen that within the entire molecule two hydrogen bonds between the hydrogen and chloride atoms can be formed (2.119 and 2.795 Å). Thiophene ring of the ligand exists in the C_s twisted conformation, which is characterized by the coplanarity of three adjacent ring atoms and the midpoints of the opposite bonds [12]. The computation has revealed its similarity to these of the isolated thiophene and 1-methylthiophene rings. The result obtained seems to be interesting and important for further studies, be-

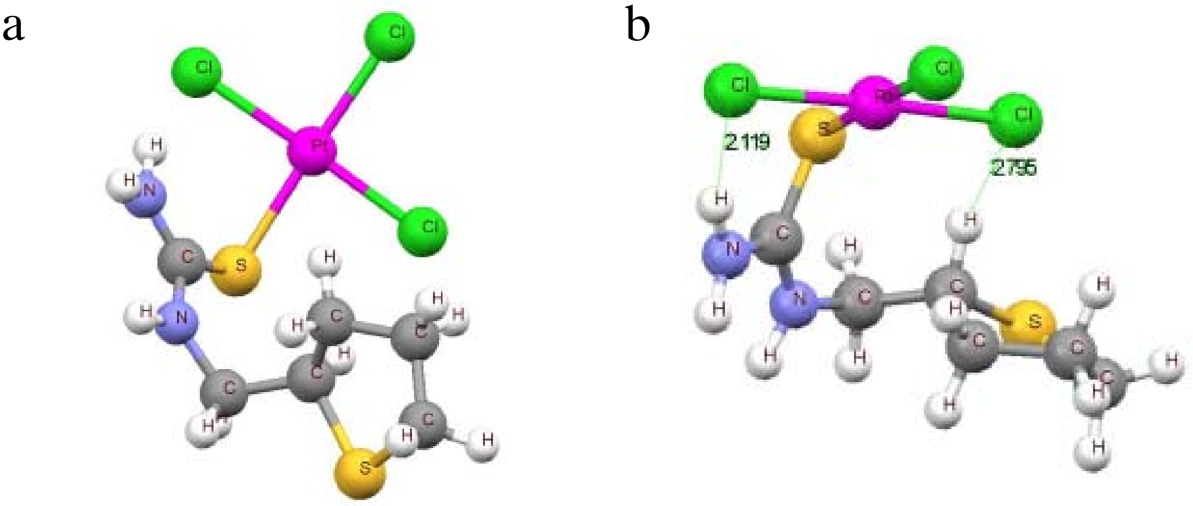


Fig.1. Linear (a) and seven-membered (b) structures of the platinum(II) complex; possible hydrogen bonds are shown.

cause the most stable conformation of its oxygen analog – tetrahydrofuran – appeared to be different. The results published already of *ab initio* calculations [13] suggest that the equilibrium conformation of tetrahydrofuran is an envelope C_s structure. On the contrary, the calculations performed in our group for the 1-methyltetrahydrofuran ring suggest that the lowest-energy is associated to even the most low (C_1) symmetry of the ring.

Biological investigations

Cytotoxicity of the studied complex was estimated *in vitro* by means of the relative growth test with 1 hour exposure to the drug, as described elsewhere [14]. Studies were performed with the mouse lymphoma cell line L1210. The 50% inhibition dose (ID_{50}) was determined by extrapolation of the steep part of survival curves obtained. Concentration range of the investigated species was 0.01-0.150 $mg \cdot cm^{-3}$. Precision of the calculated ID_{50} value was estimated using the propagation of measuring uncertainty technique, and the error limits of the estimates for the slope and intercept of survival curves.

If the toxicity of the reference CDDP was found to be $ID_{50}=5$ μM [15], the ID_{50} of the species investigated in the presented work appeared to be about 313.8 ± 10.8 and 10.63 ± 1.31 μM for the ligand and complex, respectively (Fig.2). The latter value, being comparable to that for CDDP, suggests the necessity of determining the therapeutic index of the complex ($TI=LD_{50}/ID_{90}$; TI of the CDDP being 8.1 [16]) as well as of checking its toxicity against other tumor lines.

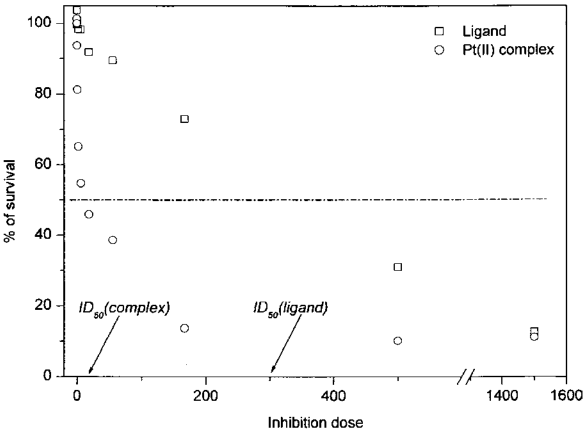


Fig.2. Cytotoxicity of the studied ligand and platinum(II) complex.

We thank Prof. Adam Krówczyński (Department of Chemistry, Warsaw University) for synthesizing the ligand.

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INTERLABORATORY COMPARISON OF THE DETERMINATION OF ^{137}Cs AND ^{90}Sr IN WATER, FOOD AND SOIL

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Reliable measurements of radioisotope concentrations are of primary importance for the laboratories dealing with radioactivity determinations. Only reliable analytical results can serve as a basis of meaningful evaluation and protection of the environment against radioactive contaminants. Laboratories should demonstrate their ability to produce reliable results. This can be done by the participation in interlaboratory comparisons (ILC). The participation is also recommended by ISO/IEC 17025 standard [1]. According to the Polish regulations [2], since 2002 it is obligatory to organize every two years national ILC on the determination of various radionuclides in food and environmental samples. First such ILC on the determination of ^{137}Cs and ^{90}Sr in water, food and soil was organized by the National Atomic Energy Agency of Poland in 2004 with the participation of fourteen laboratories from Polish research institutes and universities. The ILC was conducted by the Institute of Nuclear Chemistry and Technology.

The following testing materials have been prepared by spiking appropriate raw materials with a known amount of ^{137}Cs and ^{90}Sr: two types of water (surface and potable), wheat flour and soil. Certificated aqueous nitrate solutions of ^{137}Cs and ^{90}Sr radioisotopes (Amersham, Braunschweig) were used. In order to determine the moisture content, samples of the solid materials were dried to constant mass at 105°C for 1 h or 70°C for 20 h, for soil or flour, respectively. For ^{137}Cs measurements, the samples were placed in a 0.5 dm^3 Marinelli vessel and analyzed using a γ-ray spectrometer. Liquid samples were measured in the same way. The measuring time varied from 24 h to 7 days, depending on the specific radioactivity of the samples. The detection limit was 0.01 Bq kg^{-1} at a 95% confidence level. Wheat flour samples for ^{90}Sr measurements were burned to ashes, dissolved in concentrated nitric acid and analyzed using the liquid scintillation (LSC) measurements after separation. The scheme of analysis is presented in Fig.1.

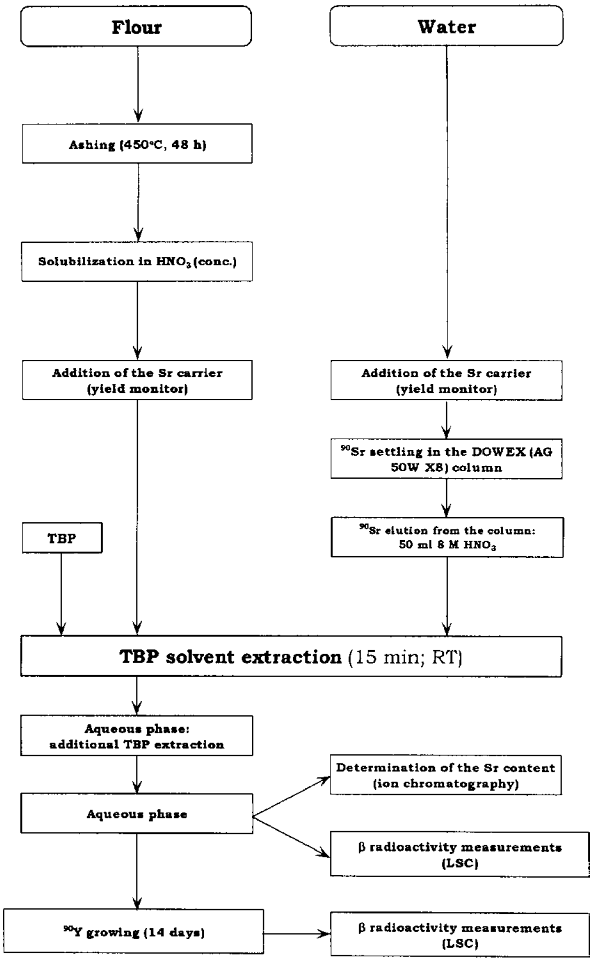

Fig.1. Scheme of ^{90}Sr analytical procedure.

Radioactivity measurements of the defined volumes of the tributyl phosphate (TBP) extract (usually: 5 cm^3) containing the ^{90}Y isotope were performed using the LSC method with the ULTIMA GOLD (Packard) or RIAFLUOR (NEN) scintillation cocktails. 96% efficiency of the detection has been achieved. Measurement times varied from

Table. Assigned values of ^{90}Sr and ^{137}Cs*.

Material	Sample	^{90}Sr	^{137}Cs
Potable water	reference sample	below the detection limit	below the detection limit
	low activity sample	0.020±0.002	0.031±0.002
	high activity sample	0.102±0.008	0.115±0.008
Surface water	reference sample	below the detection limit	below the detection limit
	low activity sample	0.101±0.007	0.157±0.010
	high activity sample	0.501±0.033	0.498±0.033
Wheat flour	low activity sample	0.150±0.005	0.285±0.008
	high activity sample	0.479±0.017	0.537±0.019
Sand	low activity sample	-	6.15±0.25
	high activity sample	-	31.6±1.07

* Water in [Bq dm^{-3}], solid samples in [Bq kg^{-1}].

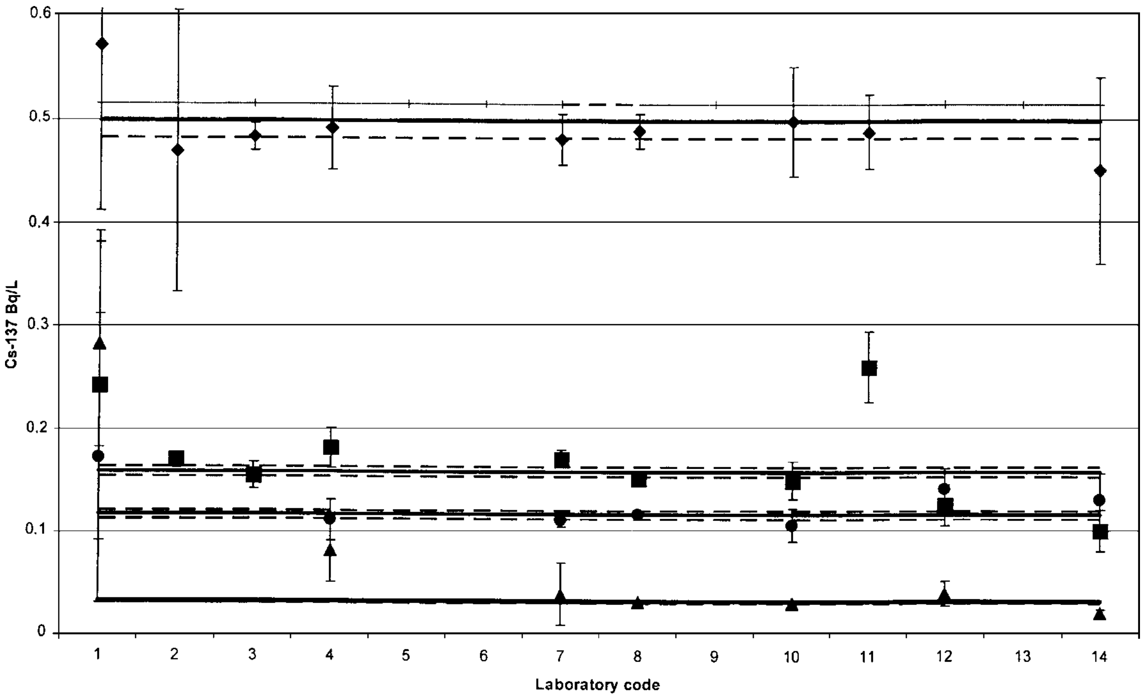

Fig.2. An example presenting results obtained by the laboratories participating in the ILC: determination of ^{137}Cs in water.

600 to 1200 min and a correction factor for the isotope decay during the measurement period was applied. Chemical and radiochemical efficiency of strontium and yttrium determination (on the basis of non-radioactive carrier determination) has been examined using ion chromatography. Detection limit for yttrium determination appeared to be 0.01 mg dm^{-3}. Six samples of water and four solid samples containing both radioisotopes were prepared and distributed to fourteen laboratories participating in the ILC.

Homogeneity of test materials is of crucial importance for the comparability of the results, and, consequently, for a successful assessment of laboratory performance. A consensus value is often used to determine the assigned values. However, if the test materials used for the studies have traceable assigned values, then ILC provides the accuracy of results in the participating laboratories. The prepared test materials were spiked using certified radionuclide solutions traceable to SI. Target values of the ^{137}Cs and ^{90}Sr radioactivity concentration have been assigned considering the way the test materials were prepared. The uncertainties of the assigned values were evaluated taking into account all possible sources of uncertainty using ISO Guide to the Expression of Uncertainty in Measurements (GUM) [3] and EURACHEM Guides [4]. The assigned values are summarized in Table.

Figure 2 presents, as an example, a comparison of the results reported by the participating laboratories with the assigned value. A plot of normal curve with a maximum at the assigned value is obtained. It can be concluded that the procedures of assigning value and preparation of homogeneous material have been done properly.

The main conclusion drawn from the ILC is that the majority of the determinations remain in good agreement with the assigned values and with the results obtained by other laboratories. Such agreement means that the performance of the laboratories is good and also that the samples are equivalent.

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TRICARBONYLTECHNETIUM(I) COMPLEXES WITH NEUTRAL BIDENTATE LIGANDS: N-METHYL-2-PYRIDINECARBOAMIDE AND N-METHYL-2-PYRIDINECARBOTHIOAMIDE

Monika Łyczko, Jerzy Narbutt

Chemistry of tricarbonyltechnetium(I) complexes, the derivatives of organometallic aqua-ion *fac*-$[Tc(CO)_3(H_2O)_3]^+$ (**1**), with a chelating ligand in the molecule, is being quickly developed in the last years [1]. These thermodynamically stable and kinetically inert ^{99m}Tc chelates are good candidates for radiopharmaceuticals or their precursors. Due to the softness (HSAB) of the technetium(I) centre, chelators with soft donor atoms are preferred as the ligands. Widely studied in this respect are bi- and tridentate derivatives of pyridine and/or imidazole (aromatic N donors) in combination with other donor atoms, in particular sulphur. The aim of the present work is to select ligands that form very stable tricarbonyl complexes of technetium(I), and after further functionalization can be precursors for radiopharmaceuticals of the second generation.

Two kinds of $[Tc(CO)_3LB]$ complexes were obtained and studied, where L is a neutral chelating ligand with either N,S donor atoms, N-methyl-2-pyridinecarbothioamide, L_{NS}, or its analog with N,O donor atoms, N-methyl-2-pyridinecarboamide, L_{NO}, while B is a monovalent anion or H_2O. The complexes were prepared both with ^{99m}Tc at n.c.a. level ($B=OH^-$ or H_2O) and with ^{99}Tc in mg quantities ($B=Cl^-$). The ^{99m}Tc complexes were investigated by HPLC and those of ^{99}Tc – by IR measurements.

$Na[^{99m}TcO_4]$ was eluted from a ^{99}Mo/^{99m}Tc generator using 0.9% saline. Synthesis of precursor **1** in water was carried out according to Alberto's low-pressure method [2,3] and/or by using potassium boranocarbonate [4]. The complexes in n.c.a concentrations were obtained from **1** by adding a methanol solution of L to the precursor solution in a phosphate-buffered saline (PBS) to reach $[L]=10^{-3}$ M, followed by heating the mixture at 37 or 75°C for 10-60 min. The complexes of ^{99}Tc were prepared in water-methanol solution by adding little excess of the ligand to the precursor solution and heating the mixture at 50°C, then recrystallized from a mixture of dichloromethane-hexane. The IR spectra were carried out in KBr pellets using a Perkin Elmer 16 PC FT-IR spectrophotometer.

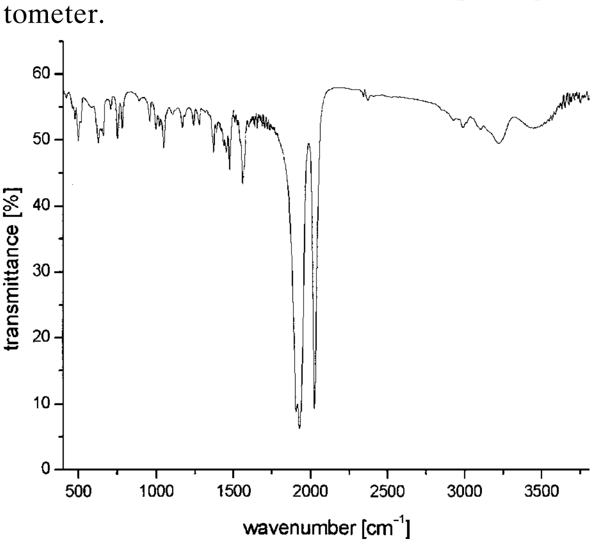

Fig.1. IR spectrum of $[Tc(CO)_3L_{NS}Cl]$; L_{NS}=N-methyl-2-pyridinecarbothioamide.

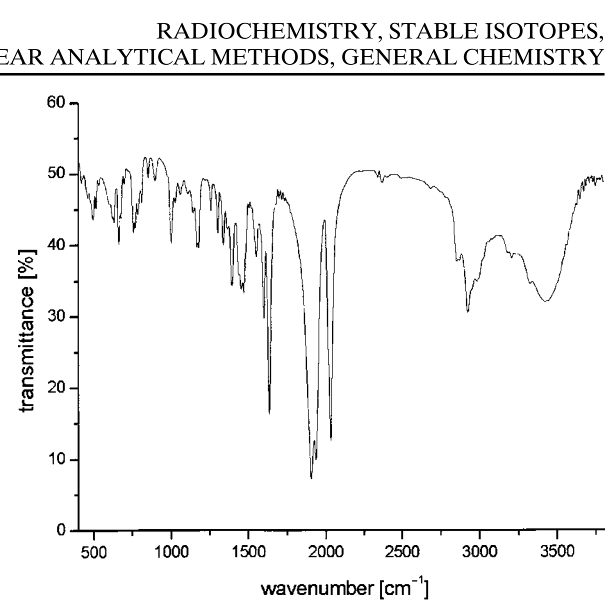

Fig.2. IR spectrum of $[Tc(CO)_3L_{NO}Cl]$ (contaminated with some L_{NO}); L_{NO}=N-methyl-2-pyridinecarboamide.

We expect that each ligand coordinates the metal center bidently *via* the pyridine nitrogen and the X atom (X=O or S), forming a five-membered chelate ring. This conclusion is supported by the similarity of IR spectra of the ^{99}Tc complexes studied (Figs.1 and 2) to those of their rhenium analogs [5,6]. Two characteristic peaks of CO vibrations (2026 and 1928 cm^{-1}) confirm the existence of the $^{99}Tc(CO)_3$ core in the complexes studied.

The yield of the $[^{99m}Tc(CO)_3L_{NX}B]$ complexes ($B=H_2O$ and/or OH^-) was studied by HPLC [7]. After 40 min incubation at 75°C, the $[^{99m}Tc(CO)_3L_{NS}B]$ complex was obtained with the nearly 100% yield (Fig.3), while the yield of $[^{99m}Tc(CO)_3L_{NO}B]$ was lower (53 to 84% depending on pH of the complex formation, Fig.4). Two forms of the complexes were observed: cationic ($B=H_2O$), eluted as the peak No.2 on the chromatograms (Figs.3 and 4), and neutral ($B=OH^-$), eluted as the peak No.3. The equilibrium between these two forms depended on the complex and on pH of the complex formation. It was shifted to over 90% of the neutral form at pH>7 for $[^{99m}Tc(CO)_3L_{NS}B]$ (Fig.3), but for $[^{99m}Tc(CO)_3L_{NO}B]$ the cationic form predominated (from 50% at pH 3 to 64% at pH 10 (Fig.4). The coexistence of the two forms of the complexes, cationic and neutral, was also confirmed by paper electrophoresis. Under the appropriate experimental conditions (*e.g.* proper pH) two ^{99m}Tc peaks appeared on the electropherograms: that remaining at the starting point corresponded to the neutral form, while that moving to the cathode corresponded to the cationic form.

The easier hydrolysis of the $[^{99m}Tc(CO)_3L_{NS}H_2O]^+$ complex can hardly be discussed in terms of easier deprotonation of the H_2O molecule coordinated to the technetium atom more strongly than in the analogous $[^{99m}Tc(CO)_3L_{NO}H_2O]^+$ complex. The stronger coordination of the L_{NS} than L_{NO} ligand reflected by the greater yield (and stability) of the former complex, and the smaller positive charge on the technetium atom calculated for the former (0.14 e) than for the latter (0.31 e) [8] lead to the conclusion on the weaker bonding of the H_2O molecule in the former species. Therefore, the hydrolysis proceeds most probably *via* the ligand exchange, *i.e.* the exchange of the coordinated H_2O molecule for an OH^- ion from the aqueous solution.

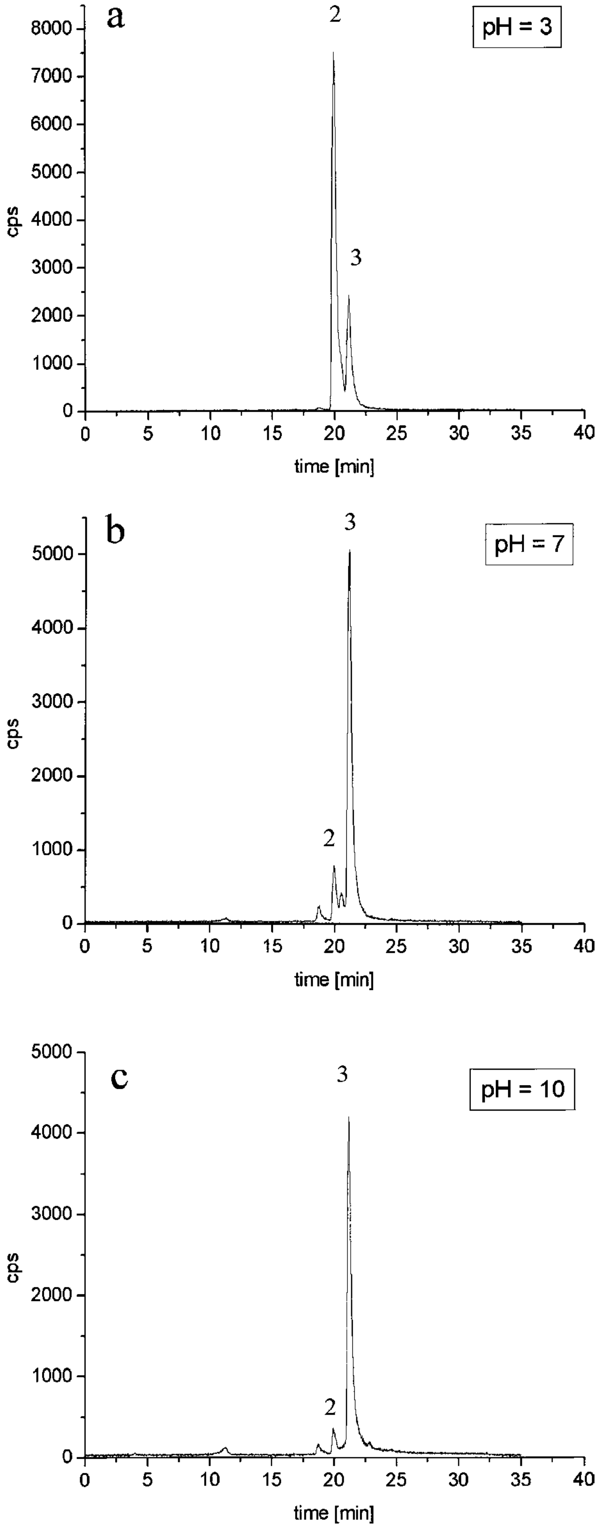

Fig.3. HPLC chromatograms of the [$^{99m}Tc(CO)_3L_{NS}B$] complexes obtained at different pH: (a) pH 3, (b) pH 7 and (c) pH 10. Peak 2 – [$^{99m}Tc(CO)_3L_{NS}(H_2O)]^+$, peak 3 – [$^{99m}Tc(CO)_3L_{NS}(OH)$].

The work was supported by the State Committee for Scientific Research (KBN) – grant No. 4 TO9A 11023. Part of the work (^{99}Tc complexes), carried out during the stay of Monika Łyczko at Paul Scherrer Institute (Switzerland), was financed from the European Commission under Marie Curie Actions for the Transfer of Knowledge – contract No. MTKD-CT-2004-509224.

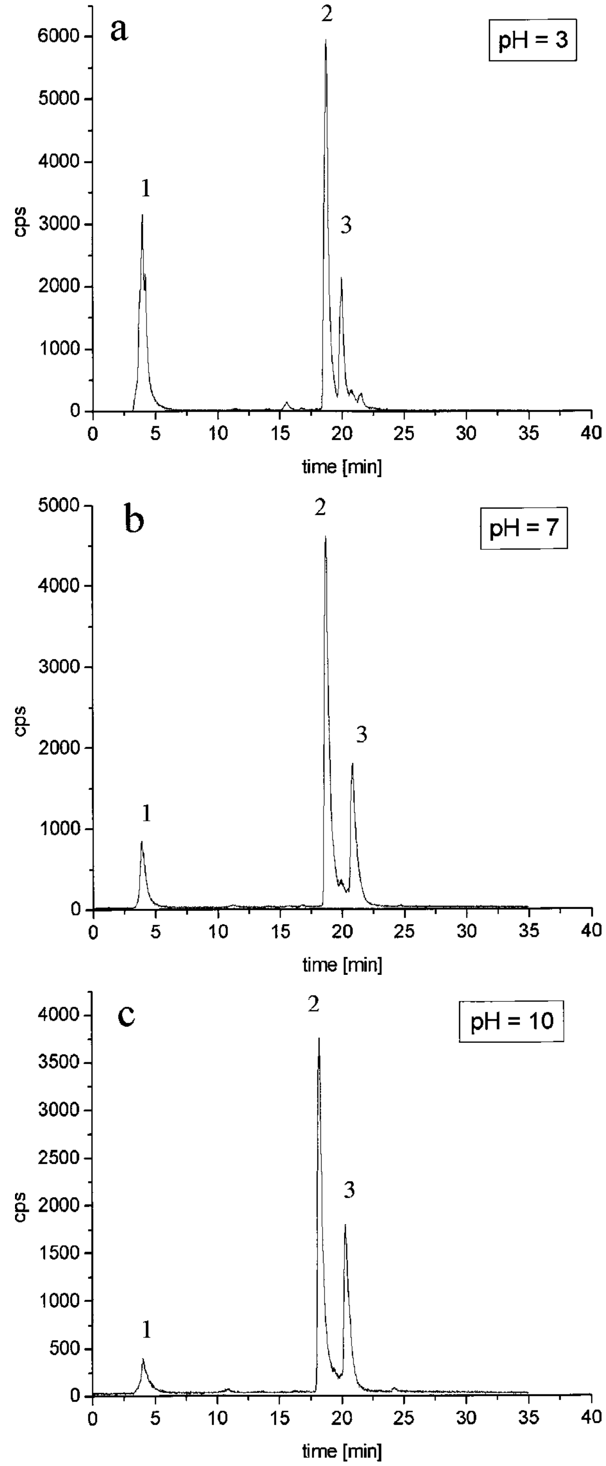

Fig.4. HPLC chromatograms of the [$^{99m}Tc(CO)_3L_{NO}B$] complexes obtained at different pH: (a) pH 3, (b) pH 7 and (c) pH 10. Peak 1 – precursor **1**, peak 2 – [$^{99m}Tc(CO)_3L_{NO}(H_2O)]^+$, peak 3 – [$^{99m}Tc(CO)_3L_{NO}(OH)$].

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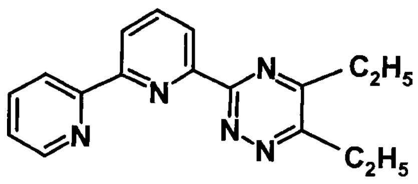
SEPARATION OF Am(III) FROM Eu(III) BY MIXTURES OF TRIAZYNYLBIPYRIDINE AND BIS(DICARBOLLIDE) EXTRACTANTS. THE COMPOSITION OF THE METAL COMPLEXES EXTRACTED

Jerzy Narbutt, Jadwiga Krejzler

Reprocessing of spent nuclear fuels by the PUREX process leads to the formation of high active raffinates which contain nuclear wastes, *i.e.* fission products and minor actinides (MAs). In the future, the wastes will be vitrified and disposed of into deep underground repositories. The most important radiotoxicity of the waste, still significant even after more than 10^4 years, is related to the presence of MAs. Therefore, the elimination of these MAs from the nuclear wastes will simplify the selection of geological sites for the underground repositories. After partitioning from the fission products, the MAs can be transmuted into stable or short-lived fission products, using, for example, the future Accelerator Driven System facility. The research in Partitioning & Transmutation domain is an important programme in Europe and in several nuclear countries in the world [1]. The partitioning processes of MAs are the subject of an integrated project (IP) EUROPART realized in the 6th Framework Programme of EU within EURATOM [2]. The team from the Institute of Nuclear Chemistry and Technology (INCT) is one of 25 partners participating in the realization of the project.

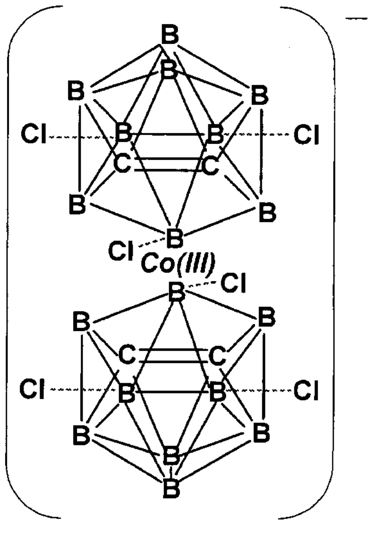
The separation of trivalent actinides, in particular americium and curium, from lanthanides is an important step in an advanced partitioning process for future reprocessing of spent nuclear fuels. Since the trivalent actinides and lanthanides have similar chemistries, it is rather difficult to separate them from each other. The use of soft donor (N and S) ligands makes it possible to separate the two groups of elements, probably because of the more covalent character in the complexes with actinides compared to the lanthanides [3].

Very efficient polyheterocyclic extractants containing pyridine and triazine rings have been proposed for the partitioning of minor actinides from lanthanides [4,5]. Numerous extractants of this type were synthesized [6]. One of them, 6-(5,6-diethyl-1,2,4-triazin-3-yl)-2,2'-bipyridine (diethyl*hemi*-BTP; Scheme 1), is the extractant studied in the present work. The diethyl*hemi*-BTP was already tested as an extractant of Am(III) and Eu(III) from nitric acid solutions, separating the metals in the presence of a co-extractant, 2-bromodecanoic acid [7]. Large hydrophobic anions of the carboxylic acid and neutral diethyl*hemi*-BTP molecule(s) form extractable heteroleptic complexes with the metal ions. However, the rather high pK_a of this carboxylic acid (3.7) [8] requires its high concentration (1 M) to reach a significant extraction of Am(III) at higher acidities.



Scheme 1.

The aim of our work was to study solvent extraction of Am(III) and Eu(III) in a similar system with diethyl*hemi*-BTP and COSAN: protonated bis(chlorodicarbollido)cobalt(III) or commo-3,3-cobalta-bis(8,9,12-trichlora-1,2-dicarbaclosododecaborane)ic acid (Scheme 2) – another hydrophobic



Scheme 2.

synergent of anionic character, more acidic than 2-bromodecanoic acid. The salts of chloroprotected COSAN – extremely hydrophobic, highly soluble in organic solvents, of high chemical and radiation stability, and completely dissociated in polar solutions – are able to co-extract the metals at low pH and at much lower concentrations [9]. The heterocyclic (pyridine/triazine) extractants with the chloroprotected COSAN were already tested for solvent extraction of alkaline earths [10], but the extraction of Am(III) and Eu(III) in systems of this type was not studied yet.

The present research was focused on both the determination of conditions for the separation of ^{241}Am(III) from ^{152}Eu in aqueous nitrate solution by using a synergistic extraction system diethyl-*hemi*-BTP–COSAN, and on the modelling of the process by slope analysis. The knowledge of the composition of the extracted metal species is crucial both for understanding the phenomena involved and for optimizing the process conditions. In order to conclude on the composition of the extracted complexes, we systematically studied the dependence of the distribution ratio, D, of Am(III) and Eu(III) on the concentration of diethyl*hemi*-BTP (**B**) and of COSAN-H (**HA**) in the organic phase (1-octanol), the aqueous phase being 1 M $NaNO_3$ pH≈4, at 25.0°C. The initial organic-phase concentration of **B** varied from 0.010 to 0.025 M (series with the same initial [**B**] values were used), while that of **HA** was always lower. The D_{Am} and D_{Eu} values were determined for the same aqueous solutions, pre-equilibrated with the proper organic phase. The drop in pH of the initial aqueous phase, caused by **HA** present in the organic phase, was balanced by adding small amounts of dilute NaOH solution. The final pH was in the range of 3.8÷4.2, so the effect of pH on D had to be considered as well. The details of the experiment and the numerical data are available from the EUROPART reports [11,12].

Strong interactions between the co-extractants were observed: a yellow **BHA** adduct (1:1) precipitated upon contacting the liquid phases. This precipitate was removed, and the total concentrations of the co-extractants in the organic phase at equilibrium, $[\mathbf{B}]_{t,o}$ and $[\mathbf{A}^-]_{t,o}$, were determined by UV spectrophotometry [11,12]. The distribution ratios of both metal ions increased with increasing $[\mathbf{B}]_{t,o}$ and $[\mathbf{A}^-]_{t,o}$, and also changed with minute changes in pH, but the separation factor, $SF_{Am/Eu}=D_{Am}/D_{Eu}$, remained nearly constant, equal to 30÷40, within the whole range of the concentrations studied. These interactions made the common slope analysis difficult, because we were not able to study the dependence of D on one parameter (concentration) at fixed values of the other parameters. This lack of full slope analyses in other studies on similar systems [7,10] was probably due to the same reason. To overcome this difficulty, multi-regression analysis of the solvent extraction data was carried out.

Thermodynamic activities of the extractants (**B** and **HA**), necessary for the slope analysis, can be replaced by the concentrations of their free molecules in a given phase, but even the latter could not be directly determined under the conditions of the experiment. Therefore, we assumed that total concentrations in the organic phase, $[\mathbf{B}]_{t,o}$ and $[\mathbf{HA}]_{t,o}$, were good estimates.

The following function

$$\log D = b_0 + b_1 \cdot pH + b_2 \cdot \log[\mathbf{B}]_{t,o} + b_3 \cdot \log[\mathbf{HA}]_{t,o} \qquad (1)$$

was fitted to 45 data points for Am(III) and 45 data points for Eu(III). The results are shown in Table. For all the data points: $|\log D_{i,calc} - \log D_{i,exp}| < 0.3$.

Table. The "best fit" parameters in Eq. (1), $b_i \pm s(b_i)$ (standard deviation).

Parameter	b_0	b_1	b_2	b_3
Am(III)	6.28±1.03	0.70±0.25	2.02±0.27	1.99±0.27
Eu(III)	4.53±1.03	0.59±0.24	1.98±0.13	1.77±0.13

Figure 1 shows the distribution of the experimental $\log D_{Am}$ values (recalculated for pH=4) around the "best fit" plane (Eq. (1) pH=4). For a better clarity, the distribution has also been shown in the form of 2D graphs, *i.e.* as functions of the concentration of only one extractant at a fixed concentration of the other (Fig.2). Similar graphs for the $\log D_{Eu}$ values are not shown.

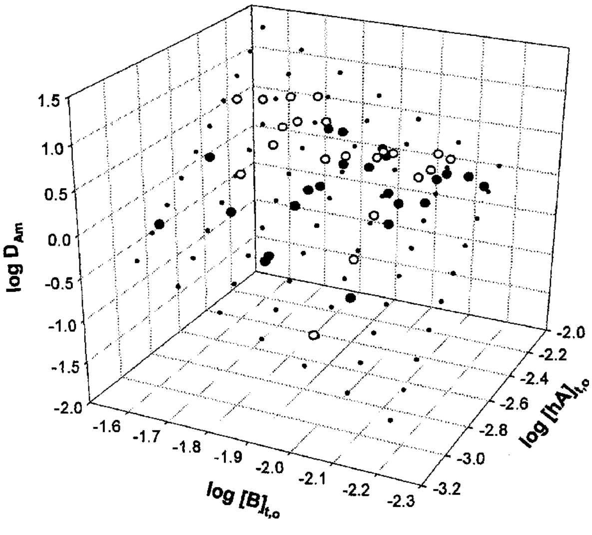


Fig.1. 3D dependence of $\log D_{Am}$ on the equilibrium total concentrations of the extractants, $\log[\mathbf{B}]_{t,o}$ and $\log[\mathbf{A}^-]_{t,o}$ for pH=4. Circles denote the pH-corrected experimental values and dots – the calculated "best fit" values. Open circles denote the values above the "best fit" plane, closed circles – the values below the plane.

Both stoichiometric coefficients b_2 and b_3 are close to the integer 2. It is noteworthy that b_3 is not equal to 3 as could be expected for the trivalent cations. In order to have the total charge zero on the extracted complexes with the two $\mathbf{A}^-$ anions only, which is an important condition for their efficient extraction, we assumed that one nitrate anion enters the coordination sphere of each metal ion. Similar structures were observed elsewhere [7].

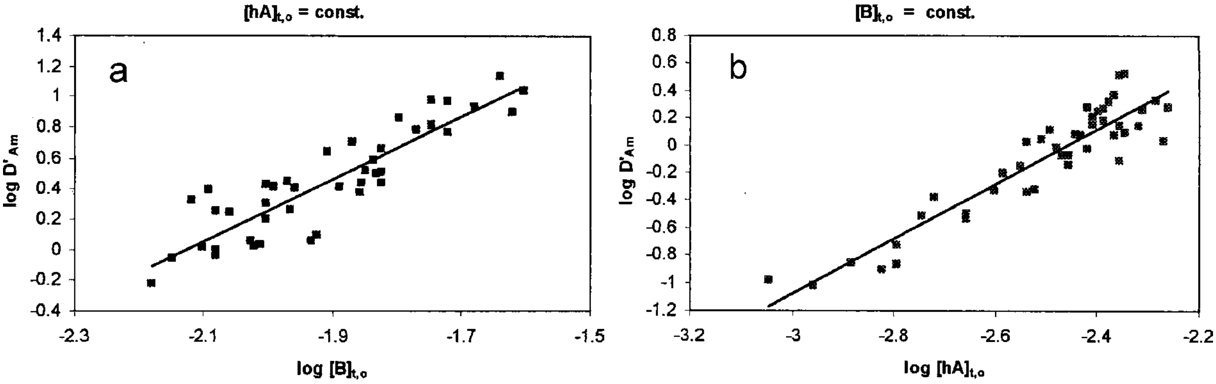


Fig.2. 2D dependences of $\log D_{Am}$ values: (a) on $[\mathbf{B}]_{t,o}$ at $[\mathbf{A}^-]_{t,o}=0.004$ M and pH=4, (b) on $[\mathbf{A}^-]_{t,o}$, at $[\mathbf{B}]_{t,o}=0.015$ M and pH=4. The points denote the experimental values corrected for: (a) pH and [HA], (b) pH and [**B**]. Straight lines are the calculated "best fit" functions.

Assuming tridentate coordination by the **B** ligands, and bidentate – by NO_3^-, we can expect that with $CN_{Am,Eu} \approx 9$ no more than one molecule of solvent (water or octanol) enters the inner coordination sphere of the metal (M) ions, and the two large $\mathbf{A}^-$ anions remain in the outer sphere. The composition of the M(III) complexes extracted to the organic phase is $[MB_2(NO_3)S_x]^{2+} \cdot 2A^-$, where S denotes the solvent, and x=0 or 1.

The following equation describes extraction of the M(III) ions from the aqueous nitrate (aq) to the organic (org) phase:

$$M^{3+}_{aq} + 2B_{org} + NO^-_{3,aq} + 2A^-_{org} + xS \xleftrightarrow{K_{ex}} [MB_2(NO_3)S_x]^{2+} \cdot 2A^-_{org} \quad (2)$$

In the presence of strong acid, HA, fully dissociated in the organic phase the base, **B**, in the same phase becomes protonated to a certain extent. This explains why the pH affects the equilibrium (2), therefore it also influences the D values as expected from Eq. (1). The detailed analysis of this problem will be done elsewhere.

In the synergistic system diethyl*hemi*-BTP–2-bromodecanoic acid [7], the distribution ratio, D, of the M(III) ions in the two-liquid-phase system decreased with the third power of HNO_3 concentration and increased with increasing concentration of **B**, and the observed $SF_{Am\text{-}Eu}$ values at the concentration of **B** comparable to those studied in this work were about 18. Hudson *et al.* concluded that the extracted Am(III) and Eu(III) complexes contained three 2-bromodecanoate anions and one **B** molecule in the inner coordination sphere of the metal ion [7]. On the contrary, in the present system, the COSAN anion, $\mathbf{A}^-$, does not enter the inner coordination sphere and acts only as a counter anion – the phase transfer reagent which neutralizes the charge of cationic complex(es) by formation of ion-pair species. We conclude that the higher $SF_{Am\text{-}Eu}$ values in the system studied than those observed in the system with the three inner-sphere carboxylate ligands, which allow only one **B** ligand to coordinate the metal ions, are due to the greater number of the specific diethyl*hemi*-BTP ligands in the inner coordination sphere of the metal ions in the extracted complexes.

The work was carried out within the European Commission project EUROPART (contract No. FI6W-CT-2003-508854) and was co-financed by the Polish Ministry of Education and Science (619/E-76/SPB/6). The authors thank their EUROPART partners – Dr. M.R.St.J. Foreman and Dr. B. Casensky for delivering the extractants: diethyl*hemi*-BTP and COSAN-Cs.

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INDIUM ISOTOPE EFFECT IN THE Dowex 50-X8/HCl SYSTEM – COMPARISON WITH THE ISOTOPE EFFECT OF GALLIUM

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In the framework of our studies on the fractionation of gallium, indium and thallium by chemical methods the indium isotope effect ($^{113/115}$In) has been discovered in the chromatographic system: strong cation exchanger/HCl.

Previously, we observed the gallium isotope effect ($^{69/71}$Ga) in a similar system. The fractionation of heavy isotope into the resin phase and the lighter isotope into the complexes in the solution was revealed. The value of unit separation factor for gallium was found to be $\varepsilon=(2\div3)\mathrm{x}10^{-5}$ in the acid concentration range 1.5÷3.0 M [1,2].

For the separation of indium isotopes, the same experimental method as for gallium was applied. It was the merry-go-round elution of the band from a column 100 cm high and 0.5 cm in inner diameter, filled with Dowex 50-X8, 200-400 mesh. The flow rate of effluent (HCl) was 0.11 ml/min. The only significant difference was that the concentration of acid was decreased to 0.5 M in order to maintain the value of $K_d\approx4$. For gallium, as follows from Fig.1, the same value of K_d was reached at 2.5 M HCl.

The indium content in the consecutive fractions was followed qualitatively by spot tests with Rhodamine B [3], and then determined quantitatively by atomic absorption analysis with flame atomisation.

The ratio (R) of the isotopes, $^{113/115}$In, in selected fractions was determined by an inductively-coupled-plasma mass spectrometer (ICP-MS) Perkin Elmer Elan 6000. Prior to the analysis, chlorides were removed from the samples by evaporation with 4 M HNO_3 to dryness and dissolving the residue in 0.1 M HNO_3. The relative standard deviation of measurements was usually 0.05%.

The local separation factors defined as $q_i=R_i/R_{feed}$ or the local separation gain defined as $\varepsilon_i=\ln(q_i)$ were calculated from the data.

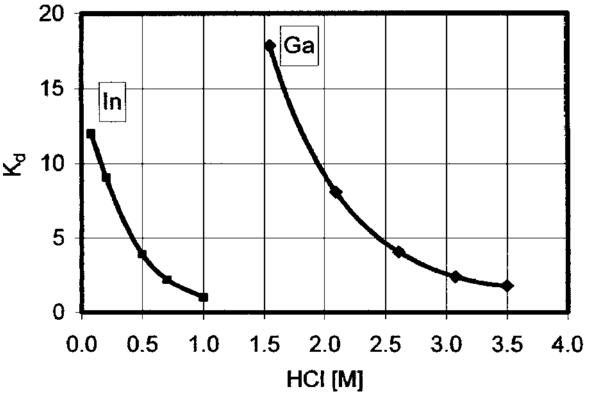

Fig.1. K_d of indium and gallium *vs.* acid concentration in Dowex 50-X8/HCl system.

The results of the indium separation experiments, performed with 0.5 M HCl, are shown in Fig.2, together with the data for gallium taken from our previous work [2]. The opposite slopes of the S-shape curves demonstrate the opposite turn of indium and gallium isotope effects. In fact, the light isotope of indium was fractionated into the resin phase, whereas the heavy isotope into the complexes in the solution.

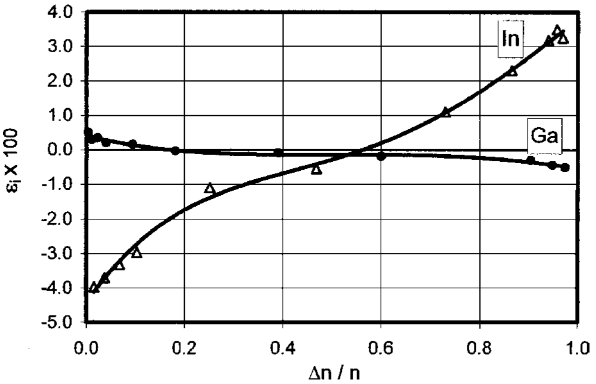

Fig.2. Local isotope separation gain of indium (N=10 000) and gallium (N=3200) *vs.* eluted fraction.

The unit separation factor was calculated by the Glueckauf approximation, under the assumption that the shape of the eluted band resembles the normal distribution [4,5]. According to this theory ε is equal to $S/N^{0.5}$, where S is the slope of linear function of ε_i *vs.* the eluted fraction (Δn/n) at X-axis scaled in standardized differences (Z) of normal distribution (Fig.3) and N is the number of theoretical plates. The same result could be obtained by plotting ε against Δn/n on a probability graph paper.

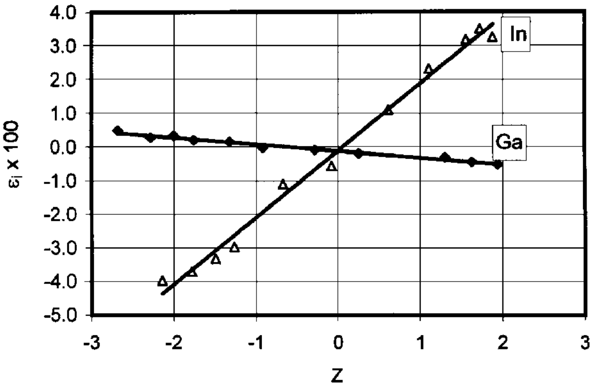

Fig.3. Local isotope separation gain of indium and gallium *vs.* eluted fraction. X-axis in Z units.

The value of unit separation factor for indium was found to be $\varepsilon=-2.0\mathrm{x}10^{-4}$, that is one order of magnitude higher than that for gallium, but of opposite sign.

The opposite signs of isotope effects reflect the difference in the stability constants of the complex species involved in the Me/HCl system. These are

$\beta_1=0.01$ for gallium and $\beta_1=2.32$, $\beta_2=3.6$, $\beta_3=4.0$ for indium.

It seems justified to assume that the much stronger complexes of indium fractionate the heavy isotope to the solution, according to the general rule of vibrational approximation of Bigeleisen. For gallium, which is weekly coordinated, the different mechanism should be taken into account. We suggest that the differences in the composition of the hydration spheres of the complexes in both phases are mainly responsible for gallium isotope fractionation.

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INSTRUMENTAL NEURON ACTIVATION ANALYSIS FOR CERTIFICATION OF STAINLESS STEEL MATERIALS

Halina Polkowska-Motrenko

Neutron activation analysis (NAA) is extremely valuable for development of reference materials. Because of non-destructive nature, it is free from blank and does not depend on the chemical form of elements. Moreover, it has been shown that instrumental NAA (INAA) can comply with the definition of primary ratio method of measurements [1-3]. Analytical techniques used mostly for the certification of CRMs (certified reference materials) for the iron and steel industry are optical emission spectrometry (OES) and X-ray fluorescence spectrometry (XRF). The use of INAA may contribute to improve the certification, especially in the case of minor and trace elements. The INAA method of analysis of stainless steel materials has been elaborated. The obtained results are compared with those of common analytical techniques.

Table 1. Radionuclides, cooling times and energy of gamma rays used.

Element	Radionuclide	Cooling time, d	E_γ used [keV]
Fe	^{59}Fe	30-90	1098.6, 1291.5
Cr	^{51}Cr	30-90	320.0
Co	^{60}Co	30-90	1332.4
Ni	^{58}Co	30-90	810.3
Mn	^{56}Mn	1	846.9
Mo	^{99m}Tc	5	140.6
Cu	^{64}Cu	1-3	1345.5
W	^{187}W	5	134.3
As	^{76}As	3-5	559.2
Sb	^{124}Sb	30-90	1690.7

Samples of steel of 60 to 120 mg were weighed into polyethylene vials. Elemental standards were prepared from appropriate amounts of spectral purity elements or oxides by weighing and dissolution in *aqua regia* or nitric acid of high purity and weighing the obtained solutions. Aliquots of the standard solutions (10-50 µg) were weighed into polyethylene vials and air-dried in a laminar flow

Tabele 2. Results of analysis of ECRM 379-1, Highly Alloyed Steel by INAA, OES and XRF methods.

Element	Unit	Obtained results – mean ± standard deviation (number of determinations)		
		this laboratory	other laboratories	
		INAA	INAA	non nuclear thechniques[a]
Fe	wt%	37.00±1.40 (6)	37.46±2.98 (5)	36.66±2.01 (6)
Ni	wt%	31.76±0.90 (6)	30.15±1.61 (3)	30.10±1.83 (19)
Cr	wt%	25.67±1.03 (6)	25.74±0.56 (4)	26.80±0.57 (18)
Mo	wt%	3.24±0.12 (6)	3.08±0.22 (4)	3.29±0.09 (19)
Mn	wt%	1.90±0.07 (6)	1.82±0.04 (4)	1.84±0.06 (17)
Cu	wt%	0.95±0.09 (6)	0.99±0.06 (4)	0.94±0.079 (17)
Co	wt%	0.038±0.001 (6)	0.039±0.001 (4)	0.035±0.011 (16)
W	wt%	0.011±0.003 (6)	0.015±0.008 (5)	0.025±0.017 (12)
As	mg kg^{-1}	27.3±1.8 (6)	33.5±4.7 (4)	20±20 (5)
Sb	mg kg^{-1}	5.6±0.3 (6)	5.3±0.1 (4)	24±10 (3)

[a] OES and XRF.

box. The package containing samples sandwiched by standards, CRMs and blank were irradiated for 5 min in the nuclear reactor "Maria" (Świerk, Poland) at a neutron flux of $2x10^{13}$ n cm^{-2} s^{-1}. A gamma-ray spectrometer consisting of 255 cm^3 well type HPGe detector (Canberra) well, diameter 16 mm and depth 40 mm, resolution 2.4 keV for the 1332.4 keV peak of ^{60}Co, relative efficiency 24% with GENIE-2000 Canberra Gamma Spectroscopy System was used. Different cooling times were selected to determine the radionuclides with different half-lives. Gamma-ray energies used and cooling times are shown in Table 1.

The elaborated method was applied for the certification of Euronom Certified Reference Material CRM 379-1, Highly Alloyed Steel within the framework of European Committee for Iron and Steel Standardisation. In Table 2, the obtained results are compared with those obtained by the other laboratories participating in the certification campaign using other analytical techniques as well as INAA [4,5].

Generally, the results agree well. The mean values with their confidence limits overlap. The only difference is in the case of antimony determination. The INAA results for antimony agree well but disagree with the results obtained by OES and XRF methods. Taking into account the level of antimony content, it seems that the results obtained by INAA should be more correct as INAA detection limit for antimony determination is much more favorable than those of OES and XRF.

The precision of INAA determination for all elements determined can be considered better than those of OES and XRF determinations especially taking into account the smaller number of INAA determinations.

The presented results show the usefulness of the INAA method for the certification of CRMs for the iron and steel industry.

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A STUDY ON THE MECHANISM OF BAND SPREADING DURING THE PROCESS OF RARE EARTH ELEMENTS SEPARATION BY ION CHROMATOGRAPHY

Rajmund Dybczyński, Krzysztof Kulisa

This work is a continuation of our previous studies on the mechanism of zone spreading and the effect of temperature on cation-exchange separation of rare earth elements (REEs). An improved version of gradient cation-exchange separation procedure of 14 REE as well as Y^{3+} and Sc^{3+} has been proposed with the use of temperature as an additional factor improving the quality of separation [1,2]. In order to optimize the method, several isocratic elutions of REE, as Y^{3+} and Sc^{3+} were performed at different temperatures, and during the experiments some interesting observations on the mechanism of band spreading in this system were made indicating the contribution of longitudinal diffusion in the resin phase to total zone spreading was provided. Because of significant differences between retention factors (k) of REEs separated in isocratic elutions and substantial changes of k with changing temperature (10-65°C), experiments were conducted on two groups of REEs. The first comprised scandium, yttrium and heavy lanthanides from terbium to lutetium (eluent 80 mmol·L^{-1} α-hydroxyisobutyric acid – α-HIBA) and the second – the light lanthanides from europium to lan-

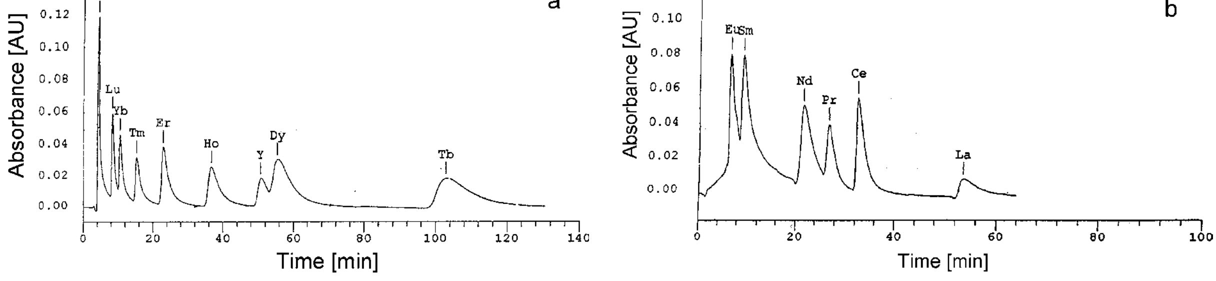

Fig.1. Elution curves of REE cations obtained during isocratic elution at 35°C: a) Sc^{3+}, Lu^{3+}, Yb^{3+}, Tm^{3+}, Er^{3+}, Ho^{3+}, Y^{3+}, Dy^{3+} and Tb^{3+} (Column – Ion Pac CS3+CG3, eluent – 80 mmol·L^{-1} α-HIBA, flow rate – 1 mL·min^{-1}. Sample: Sc^{3+} – 5 mg·L^{-1}; Lu^{3+}, Yb^{3+}, Tm^{3+} and Y^{3+} – 10 mg·L^{-1}; Er^{3+} and Ho^{3+} – 20 mg·L^{-1}; Dy^{3+} – 30 mg·L^{-1}; Tb^{3+} – 40 mg·L^{-1}.). b) Eu^{3+}, Sm^{3+}, Nd^{3+}, Pr^{3+}, Ce^{3+} and La^{3+} (Column – Ion Pac CS3+CG3, eluent – 220 mmol·L^{-1} α-HIBA, flow rate – 1 mL·min^{-1}. Sample: Eu^{3+} – 10 mg·L^{-1}; Sm^{3+}, Nd^{3+} and Pr^{3+} – 20 mg·L^{-1}; Ce^{3+} – 40 mg·L^{-1}; La^{3+} – 50 mg·L^{-1}.).

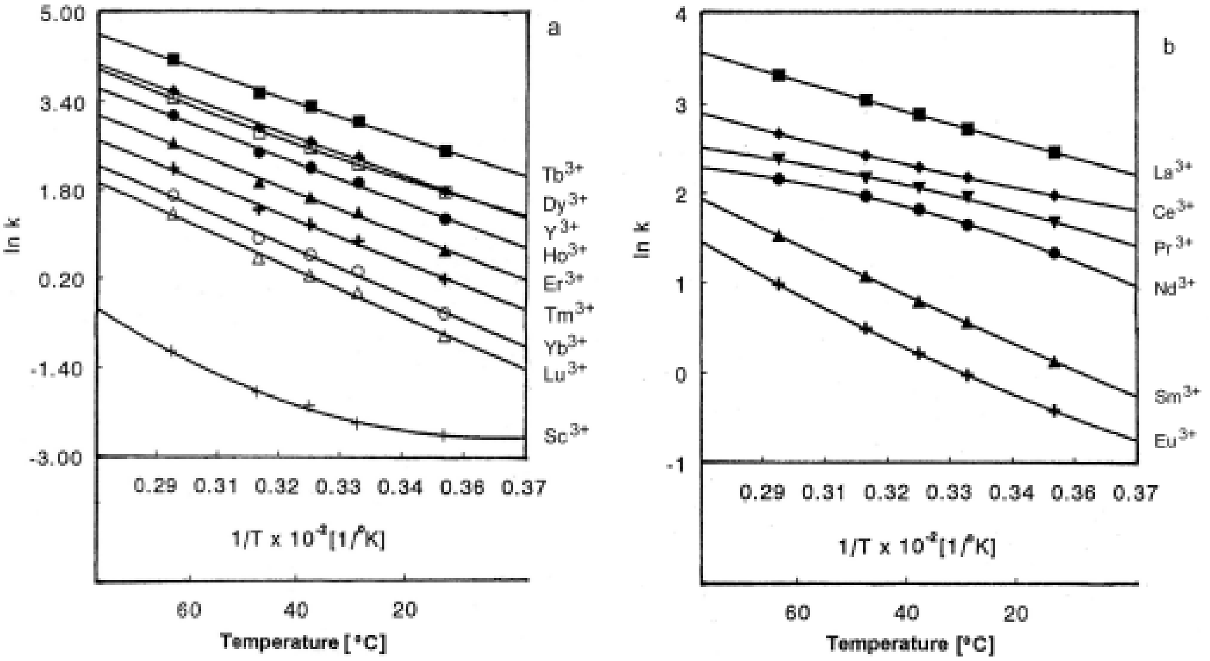

Fig.2. Van't Hoff plots of: a) Sc^{3+}, Lu^{3+}, Yb^{3+}, Tm^{3+}, Er^{3+}, Ho^{3+}, Y^{3+}, Dy^{3+} and Tb^{3+} (Column – Ion Pac CS3+CG3, eluent – 80 mmol·L^{-1} α-HIBA, flow rate – 1 mL·min^{-1}, temperature range – 10-65°C. Sample: Sc^{3+} – 5 mg·L^{-1}; Lu^{3+}, Yb^{3+}, Tm^{3+} and Y^{3+} – 10 mg·L^{-1}; Er^{3+} and Ho^{3+} – 20 mg·L^{-1}; Dy^{3+} – 30 mg·L^{-1}; Tb^{3+} – 40 mg·L^{-1}.). b) Eu^{3+}, Sm^{3+}, Nd^{3+}, Pr^{3+}, Ce^{3+} and La^{3+} (Column – Ion Pac CS3+CG3, eluent – 220 mmol·L^{-1} α-HIBA, flow rate – 1 mL·min^{-1}, temperature range – 10-65°C. Sample: Eu^{3+} – 10 mg·L^{-1}; Sm^{3+}, Nd^{3+} and Pr^{3+} – 20 mg·L^{-1}; Ce^{3+} – 40 mg·L^{-1}; La^{3+} – 50 mg·L^{-1}.).

thanum (eluent 220 mmol·L^{-1} α-HIBA). Gadolinium was not included because of its interference with europium under these conditions. Ion Pac CS3 column with Ion Pac CG3 guard were used in the experiments. Details concerning the elution method were published previously [1,2]. Chromatograms were obtained in all experiments as a function of column temperature in the range 10-65°C when separating the cations in isocratic elution mode and in the range 10-70°C when gradient elution was used. As examples, separations of heavy lanthanides, scandium and yttrium as well as light lanthanides at 35°C are shown in Fig.1. The increase of the temperature from 10 up to 65°C caused a significant increase in retention factors of all REEs studied including scandium and yttrium. The relationship between ln k of REEs and inverse absolute temperature (van't Hoff plots) is shown in Fig.2. As one can see from the plots, the overall ion exchange-complexation revealed endothermic character for all REEs investigated. The changes of enthalpy (ΔH) given by the van't Hoff isochore:

$$\Delta H = -R\frac{d\ln k}{d(1/T)} \tag{1}$$

where: T – absolute temperature, R – gas constant (1.987 cal·K^{-1}·mol^{-1}), are clearly not constant for several elements, particularly scandium, yttrium, praseodymium, neodymium and europium but are a function of temperature, *i.e.*:

$$\Delta H = \Delta H_0 + \Delta C_p T \tag{2}$$

where: ΔC_p is heat capacity.

For the other REEs, changes of enthalpy is constant or almost constant in the temperature range studied. The relationship between changes of enthalpy and ionic radius of heavy REE at 5°C is presented in Fig.3. The relationship between changes of enthalpy and ionic radius for heavy lanthanides is represented by a smooth curve with yttrium lying distinctly below it.

Values of plate height (H), determined from isocratic runs at 35°C are shown as a function of reciprocal of the weight distribution coefficient (1/λ) for heavy (Fig.4a) and light (Fig.4b) REEs.

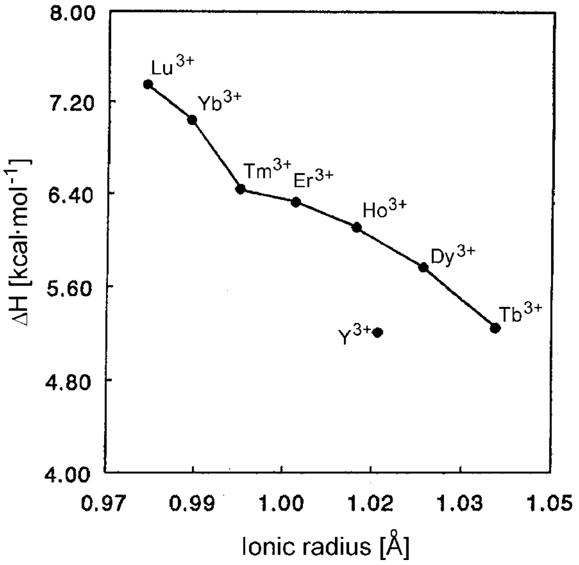

Fig.3. Enthalpy changes derived from van't Hoff isochore for the process of elution of REE from an Ion Pac CS3 column at 5°C for Lu^{3+}, Yb^{3+}, Tm^{3+}, Er^{3+}, Ho^{3+}, Y^{3+}, Dy^{3+} and Tb^{3+}. Eluent – 80 mmol·L^{-1} α-HIBA, flow rate – 1 mL·min^{-1}. Sample: Lu^{3+}, Yb^{3+}, Tm^{3+} and Y^{3+} – 10 mg·L^{-1}; Er^{3+} and Ho^{3+} – 20 mg·L^{-1}; Dy^{3+} – 30 mg·L^{-1}; Tb^{3+} – 40 mg·L^{-1} as a function of ionic radius of REE.

It is apparent that for elements with relatively low values of distribution coefficients plate height increases with 1/λ. For elements more strongly retained by the resin, however, the opposite trend was observed, *i.e.* plate height increased with increasing λ. In addition, for the elements most strongly retained by the resin (cerium, lanthanum) the plate height increased with increasing temperature. Such behaviour is inconsistent with the Van Deemter and Glueckauf-Hamilton equations, because these equations contain no terms in which the distribution coefficient is in the numerator. Similar phenomenon was observed earlier when separating several anions [3] as well as alkali and alkaline earth cations [4] by ion chromatography. The behaviour seems to be quite general. Increasing plate height with increasing distribution coefficient has also been observed in classical ion exchange chromatography of REE ethylenediaminetetraacetates on anion-exchange resins with different cross-linking [5] and in analogous experiments with alkali and alkaline earth metals on sulfonic cation exchangers with different cross-linking [6]. Dybczyński [5] proposed modifying the Glueckauf-Hamilton equation by incorporating a fifth term taking into account the contribution of longitudinal diffusion in the stationary phase to the total plate height. The possibility that longitudinal diffusion in the stationary phase may contribute substantially to the total plate height was originally foreseen by Giddings [7].

So, in its final form the equation for plate height is:

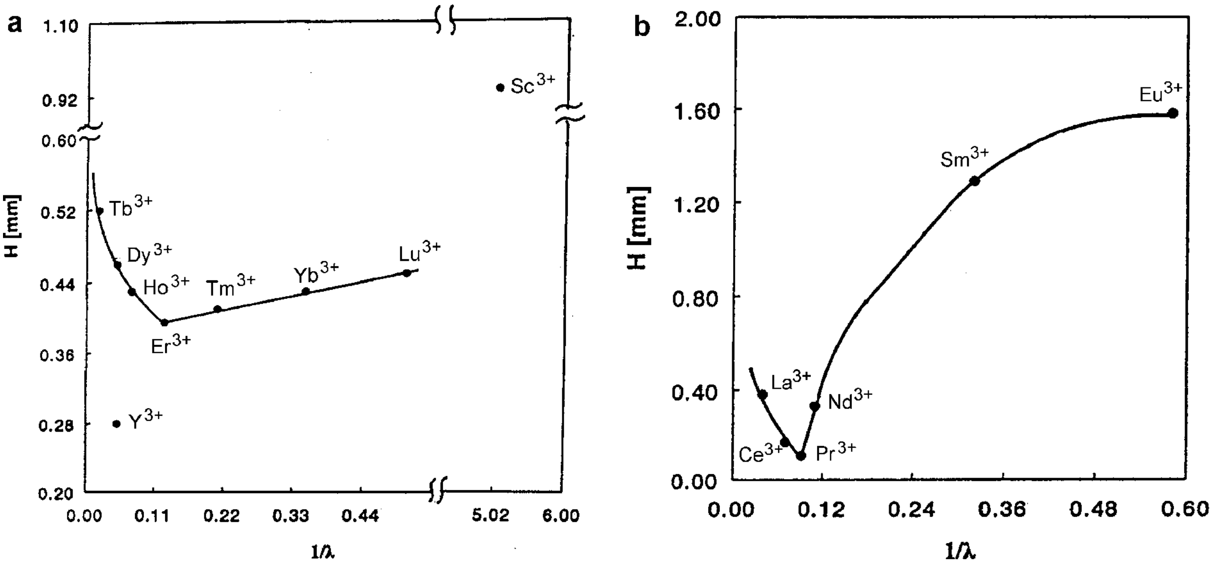

Fig.4. Plate heights calculated from elution curves of REE cations obtained on Ion Pac CS3+CG3 column at 35°C; a) Sc^{3+}, Lu^{3+}, Yb^{3+}, Tm^{3+}, Er^{3+}, Ho^{3+}, Y^{3+}, Dy^{3+} and Tb^{3+} (Eluent – 80 mmol·L^{-1} α-HIBA, flow rate – 1 mL·min^{-1}. Sample: Sc^{3+} – 5 mg·L^{-1}; Lu^{3+}, Yb^{3+}, Tm^{3+} and Y^{3+} – 10 mg·L^{-1}; Er^{3+} and Ho^{3+} – 20 mg·L^{-1}; Dy^{3+} – 30 mg·L^{-1}; Tb^{3+} – 40 mg·L^{-1}.). b) Eu^{3+}, Sm^{3+}, Nd^{3+}, Pr^{3+}, Ce^{3+} and La^{3+} (Eluent – 220 mmol·L^{-1} α-HIBA, flow rate – 1 mL·min^{-1}. Sample: Eu^{3+} – 10 mg·L^{-1}; Sm^{3+}, Nd^{3+} and Pr^{3+} – 20 mg·L^{-1}; Ce^{3+} – 40 mg·L^{-1}; La^{3+} – 50 mg·L^{-1} as a function of reciprocal of the distribution coefficient.).

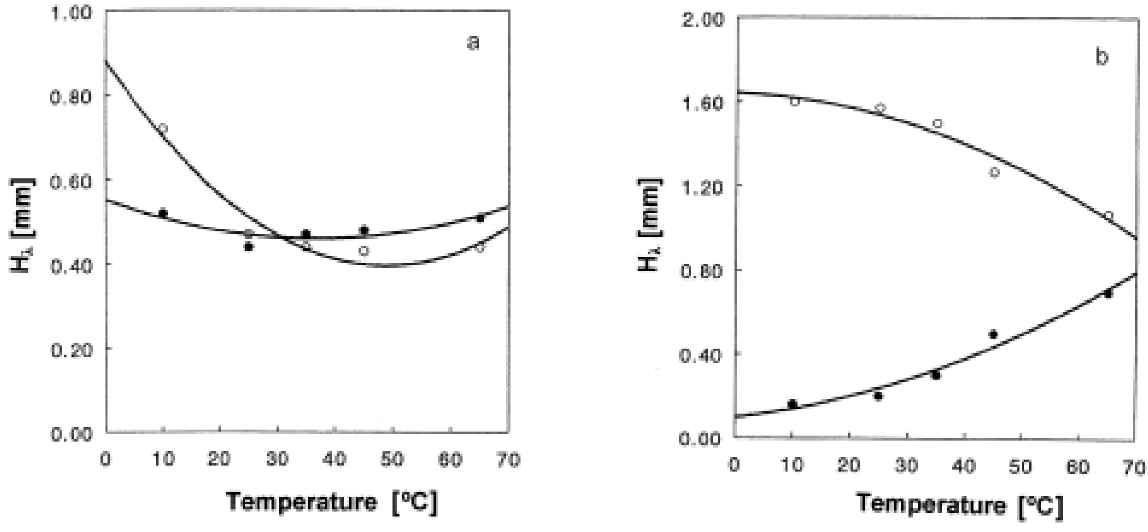

Fig.5. Temperature dependence of the plate height (normalized with respect to individual values of the weight distribution coefficient values) as a function of temperature: a) Lu^{3+}, Yb^{3+}, Tm^{3+}, Er^{3+}, Ho^{3+}, Dy^{3+} and Tb^{3+}. Column – Ion Pac CS3+CG3, flow rate – 1 mL·min^{-1}, eluent – 80 mmol·L^{-1} α-HIBA; open circles – λ=2, full circles – λ=20). b) Eu^{3+}, Sm^{3+}, Nd^{3+}, Pr^{3+}, Ce^{3+} and La^{3+}. Column – Ion Pac CS3+CG3, flow rate – 1 mL·min^{-1}, eluent – 220 mmol·L^{-1} α-HIBA; open circles – λ=2, full circles – λ=20.

$$H = \omega r_0 + \frac{\lambda' 0.142 r_0^2 u}{(\lambda' + i)^2 \bar{D}} + \frac{(\lambda')^2 0.266 r_0^2 u}{(\lambda' + 1)^2 (1 - i) D (1 + 70 r_0 u)} + \frac{D i \sqrt{2}}{u} + \frac{2\gamma_s \bar{D} \lambda'}{u i} \qquad (3)$$

where: r_0 – particle radius; $\bar{D}$, D – diffusion coefficients in the resin phase and in solution, respectively; $\lambda' = \lambda\, d_z$ – bed distribution coefficient (d_z – bed density); u – linear flow rate; i – fractional void volume of the bed; ω, γ_s – constants.

In Eq. (3), the five terms represent, respectively, the contributions of Eddy diffusion, diffusion within resin particles, diffusion within the liquid film adhering to the resin particles, and longitudinal diffusion in the mobile and resin phases. Because the distribution coefficient in the term describing the contribution of longitudinal diffusion in the resin phase is in the numerator, this equation rationally explains the unusual shapes of plots of plate height against $1/\lambda$ (*cf.* Fig.4). It also explains why the plate height, which is usually expected to diminish with increasing temperature (owing to the predominant effect of the mass-transfer term) can occasionally increase (for a fixed value of λ) with the increase of temperature (*cf.* Fig.5) because of the fourth and fifth terms of Eq. (3) in which diffusion coefficients in the mobile and stationary phases are directly proportional to plate height.

The position of yttrium within the lanthanide series is of special interest. In the ion exchange system studied in this work yttrium elutes before dysprosium, *i.e.* has an apparent atomic number 66.5 (*cf.* Fig.1a) in agreement with its IR=1.019 Å for CN=8 (for dysprosium IR=1.027 Å, for holmium IR=1.015 Å). Interestingly, the plate height for yttrium (*cf.* Fig.4a) is much lower than it would be expected from its distribution coefficient. So, the efficiency of the chromatographic column, *i.e.* the value of the number of theoretical plates (N), is better during elution of yttrium than it is not only for its immediate neighbours (dysprosium and holmium), but also for all the other lanthanides. A possible explanation is that *f*-electrons contribute to the complex formation reaction and the bond between the lanthanides and the ligands is more covalent than the analogous bond for the lighter III group element (yttrium) which has no *f*-orbitals. From the random walk model [7] it follows that:

$$\lambda^2 = l^2 n \qquad (4)$$

where: σ – standard deviation (“quarter width“) of the chromatographic zone, l – average step length in the sorption-desorption processes when the molecules are travelling down the column, n – number of steps.

With increasing covalency of the bond between REE cation and the ligand(s), the average step length in the sorption-desorption processes occurring when REE are travelling down the column, is expected to increase. This fact would account for larger plate height for the lanthanides than for yttrium because of the relationship:

$$H = \sigma^2/L \qquad (5)$$

where L is column length.
This phenomenon creates also better prospects for the separation of yttrium from the neighboring lanthanides by the proper temperature adjustment.

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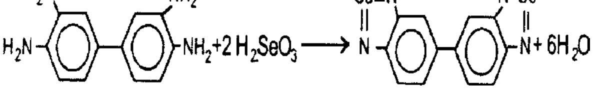
VERY ACCURATE DETERMINATION OF TRACE AMOUNTS OF SELENIUM IN BIOLOGICAL MATERIALS BY RADIOCHEMICAL NEUTRON ACTIVATION ANALYSIS

Ewelina Chajduk, Halina Polkowska-Motrenko, Rajmund Dybczyński

Selenium is both a toxic and an essential trace element for humans and animals. Because of the wide range of biologically relevant, selenium concentration and its many chemical forms, the reliability of selenium determination in biological samples has been problematic, leading to many specialized methods suitable for specific sample types. The purpose of this work was to elaborate a very accurate (“definitive”) method for the determination of selenium traces in different types of biological materials. The devised method is based on a combination of neutron activation and quantitative and very selective radiochemical separation of selenium by ion-exchange and extraction chromatography, followed by gamma-spectrometric measurement of ^{75}Se.

Aromatic o-diamines are known as selective organic reagents for Se(IV). In acidic solutions, selenium is treated with an appropriate compound and the corresponding piazselenol is formed:



Three amines: 2,3-diaminonaphtalene, 3,3’-diaminobenzidine and 4-nitro-phenyldiamine supported on Bio Beads SM-2 or Amberlite XAD-4 were chosen to batch experiments. Determined mass distribution coefficients λ (mass of analyte per g of dry ion exchanger) indicated that 4-nitro-phenyldiamine on SM-2 in 7 M HCl solution (λ =1180), 2,3-diaminonaphtalene on SM-2 in 0.5 M HCl solu-

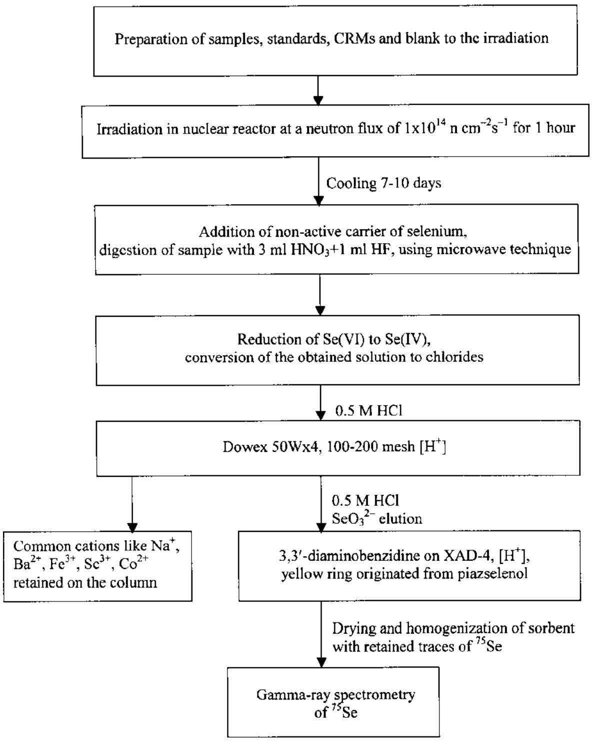


Fig. Scheme of elaborated procedure for the determination of selenium traces in biological samples by radiochemical neutron activation analysis (RNAA).

tion (λ=1240) and 3,3'-diaminobenzidine on SM-2 in 0.5 M HCl solution (λ=320) as the most perspective to the isolation of selenium from many accompanying elements. The above conclusions were verified by series of column experiments; obtained data showed that for quantitative retention of selenium the most beneficial column filling is 3,3'-diaminobenzidine supported on Amberlite XAD-4. Final scheme of the elaborated method is presented in Fig. The irradiation package containing 4 samples, 6 standards and blank wrapped in an aluminium foil, was irradiated in the MARIA reactor at the neutron flux 1x10^{14} n cm^{-2} s^{-1} for 1 h. After *ca.* ten days of cooling, the samples were quantitatively transferred into special teflon vessels. Then, 50 μg carrier, 3 ml of concentrated HNO_3 and 1 ml of concentrated HF were added. Digestion of the sample was carried out in a microwave system under controlled conditions. After digestion, Se(VI) was reduced to Se(IV). The resulting solution was transferred into a teflon evaporating dish and evaporated to wet salts. The residue was dissolved in concentrated HCl and evaporated near to dryness. Dissolution in concentrated HCl and evaporation was repeated two times. Finally, the sample was dissolved in 10 ml of 0.5 M HCl and introduced onto a column with Dowex 50Wx4, 100-200 mesh [H^+], equilibrated previously with 0.5 M HCl. The column was washed with 20 ml of 0.5 M HCl; cationic radionuclides like sodium, iron, and cobalt stayed on the ion exchanger, while selenium in the form of SeO_3^{2-} passed into the eluate. This solution was quantitatively transferred onto the column with 3,3'-diaminobenzidine on XAD-4. Selenium was retained on the column as a clearly-visible yellow ring originated as a result of formation of piazselenol. After drying, the column filling with ^{75}Se was transferred into a polyethylene test-tube, and after homogenization was measured by gamma-ray spectrometry. Selenium content was determined *via* the 136 and 400 keV lines. Blank and 1-2 standards were processed identically as the samples. One of the irradiated standards was measured directly after dissolution and dropping onto resin. Activity of two standards, which one was processed in the same way as the samples and the other one was measured directly did not differ by more than 5%.

Tracer experiments carried out with the unirradiated biological samples, proved that the whole radiochemical separation procedure is quantitative. Gamma-ray spectrum of the selenium fraction practically did not show any other activities except background peaks. Accuracy of the method was demonstrated by analyzing several certified reference materials (CRMs). The obtained results, presented in Table, demonstrate good agreement of results obtained by our new "definitive" method for the determination of selenium with the certified values.

Table. Results of selenium determination in the CRMs.

Certified reference material	Certified value and its confidence limits [ng/g]	Arithmetic mean* and its confidence limits [ng/g]
Spinach NBS 1570	47±10	56±18 (n=5)
Peach Leaves NBS 1547	120±10	129±20 (n=7)
Oriental Tobacco Leaves INCT-OTL-1	153±18	132±23 (n=4)
Rice Flour NBS 1568	370±40	369±34 (n=5)
Oyster Tissue NBS 1566 A	2.17±0.20 [μg/g]	2.18±0.17 [μg/g] (n=3)

* Results are presented as: $\bar{X} \pm t_{0.05} \cdot s/\sqrt{n}$, where: $\bar{X}$ – arithmetic mean, s – standard deviation, $t_{0.05}$ – parameter of t-Student's distribution for significance level α=0.05 and n-1 degrees of freedom, n – number of determinations.

DETERMINATION OF CADMIUM, LEAD, COPPER AND BISMUTH IN HIGHLY MINERALIZED WATERS BY ATOMIC ABSORPTION SPECTROMETRY AFTER SEPARATION BY SOLID PHASE EXTRACTION

Jadwiga Chwastowska, Witold Skwara, Elżbieta Sterlińska, Jakub Dudek, Leon Pszonicki

In the last time, the consumption of mineral waters in Poland grows very quickly and its average value is equal to 50 L per person and year. It is expected a farther increase of this value in the nearest years. In this situation the quality control of the commercially available mineral waters becomes necessary. Among many tests applied for this control, the determination of heavy metals concentration plays a very important role.

There exist many analytical methods for the determination of trace amounts of metals in water; however, most of them are not adequate to be used for analysis of mineral waters, particularly, for waters with high concentration of mineral salts. We prepared a method that enables a relatively simple separation of the trace amounts of cadmium, copper, lead and bismuth from the mineral matrix contained in the water and their preconcentration by solid phase extraction before determination by graphite furnace atomic absorption spectrometry.

Looking for the optimal sorbents for separation of the heavy metals from mineral waters we tested a dithizone sorbent (H_2Dz-MM) and a mercaptobenzothiazole sorbent (MBT-MM), both of them prepared in our laboratory by fixation of the chelating agents on a polymethacrylic resin (Diaion HP-2MG) and applied already for the separation and preconcentration of platinum and palladium in the analysis of environmental samples [1] and for mercury speciation in waters [2]. Thiol cotton (TC), obtained by chemical reaction of the cotton gauze with thioglycolic acid, was the third tested sorbent. It was chosen on the basis of the literature data [3,4] that point out very good sorption properties of the cotton with the thiol groups. For comparison of the sorbents, their sorption curves, *i.e.* sorption efficiency as a function of pH, were estimated in hydrochloric acid medium for all determined elements. These curves are presented in Figs.1-3. It results from this comparison that the mercaptobenzothiazole sorbent is not adequate for group separation of the investigated metals (Fig.2).

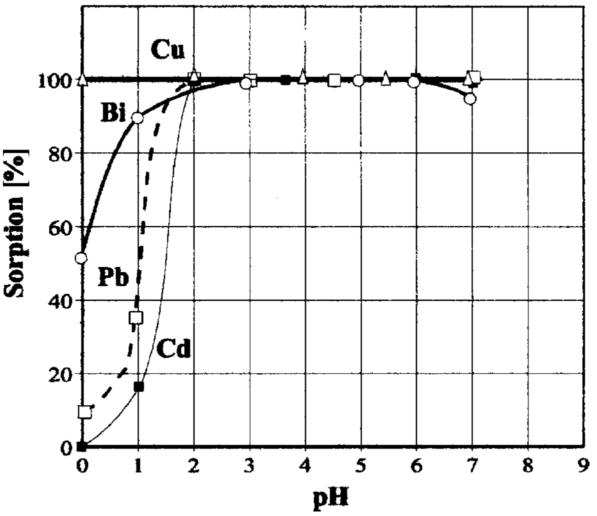


Fig.1. Sorption curves for dithizone sorbent.

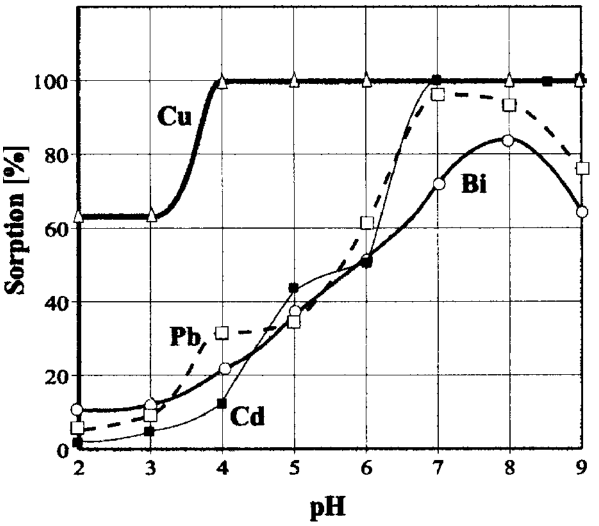


Fig.2. Sorption curves for mercaptobenzothiazole sorbent.

One observes a good sorption in a large range of pH only for copper. Cadmium is adsorbed at pH above seven and the sorption for lead and bismuth is insufficient. Dithizone sorbent and thiol cotton enable the group separation of all the metals; however, the first of them is more versatile. It works correctly in a very large range of pH values from 2 to 6 (Fig.1), whereas this range for thiol cotton is limited to the pH values between 3 and 5 (Fig.3).

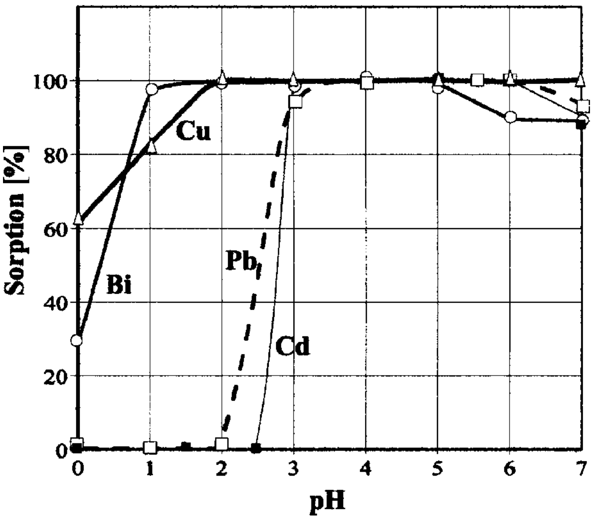


Fig.3. Sorption curves for thiol cotton sorbent.

Therefore, the dithizone sorbent was chosen as optimum for our method. The efficiency of sorption in the column process does not change in the flow rate range between 1-5 ml min^{-1}.

Table. Results of analysis of some commercially available mineral waters (volume of water sample – 200 ml).

Name of water		Determined concentration of element [μg l^{-1}]			
		Cu	Pb	Cd	Bi
Drinking waters	Nałęczowianka	0.4	0.01	<0.005	<0.05
	Galicjanka	0.8	0.01	<0.005	<0.05
	Maksymilian	<0.007	<0.02	<0.005	<0.05
	Żywiec Zdrój	<0.007	0.09	<0.005	<0.05
Therapeutic waters	Józef	2.5	0.13	0.01	<0.05
	Zuber	0.4	<0.02	0.06	<0.05
	Henryk	10.0	<0.02	0.005	<0.05

2 M nitric acid was applied as an effective desorbing agent for all the metals. After desorption they were determined in the nitric acid medium by graphite furnace atomic absorption spectrometry using a pyrolytic coated graphite tube without platform and Zeeman background correction. Copper and bismuth were atomized without modifier and cadmium and lead were atomized in the presence of a mixed palladium-magnesium modifier preliminary thermolized in the tube.

The accuracy of the method was tested by determination of the recovery of the individual metals in various mineral waters spiked with known amounts of these metals. All obtained results were between 90 and 100% and indicated that the accuracy is satisfactory.

The results of analysis of some commercially available drinking and therapeutic mineral waters are presented in Table. We did not find the recommended maximum concentration values for the determined elements in mineral waters, however, they can be compared with the values recommended by WHO in 1993 for drinking waters that are as follows: copper – 2 mg l^{-1}, lead – 10 μg l^{-1}, cadmium – 3 μg l^{-1} and bismuth – 5 μg l^{-1}. All concentration values determined in the tested waters are significantly lower.

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INFLUENCE OF ELECTRON BEAM IRRADIATION ON SOME PROPERTIES OF POLYPROPYLENE MEMBRANE

Marek Buczkowski, Danuta Wawszczak, Wojciech Starosta

Polymeric membranes are often being used as separators in arrangements for electrochemical processes which are important for galvanic cells or batteries. Polypropylene (PP) membranes can be very important in the above arrangements because of their high chemical resistance and good mechanical strength [1,2]. For the above application, modification of surface or bulk properties usually becomes necessary. This work has been focused on changing some properties of a PP membrane by the influence of electron beam irradiation.

In case of PP material during electron irradiation outweighed degradation processes of polymeric chains and formation of radicals should be taken into account that stimulate another changes. From the point of view of increasing hydrophilic property, the formation of oligomers of polarity type is important [3,4].

For experiments, samples of the PP membrane Celgard® 3500 type have been taken (supplied by the Central Laboratory of Batteries and Cells, Poznań, Poland). Radiation processing has been carried out at the Institute of Nuclear Chemistry and Technology (Department of Radiation Chemistry and Technology) using a linear electron accelerator LAE 13/9 type with energy of electrons 10 MeV. Seven samples were treated by electron beam with doses: 5, 10, 14, 20, 25 and 35 kGy (accuracy of dose determination was in the range from ±2 up to ±5% – for bigger doses).

Table. Wetting angle values for irradiated (at different doses) samples of Celgard® membrane.

Dose [kGy]	Wetting angle [°]	Wetting angle [°]
I	II	III
5	105.2	105.1
10	100.5	93.0
14	92.0	105.8
20	99.4	102.1
25	87.0	102.2
30	96.5	93.9
35	87.1	100.1

Immediately after irradiation the wetting angle had been determined; similar measurements were carried out after the period of seven months (samples were stored at room temperature in the dark package). Results are given in Table where column II concerns the measurements immediately after irradiation and column III – after storage.

Value of the wetting angle in case of virgin membrane was equal to 110.7°.

Permeability of a membrane is an important parameter responsible for the behaviour of a given membrane as a semi-permeable barrier. Permeability was determined by an indirect method. A disc of the membrane (2.5 cm diameter) were placed in a holder and then by decreasing air pressure properly big volumes were registered *vs.* time. Results are given in Fig. for the virgin membrane and three irradiated samples at different doses. Practically, there is no difference for all samples. Value of permeability was equal to 5.2 L/min·cm^2 at a pressure difference of 1 bar.

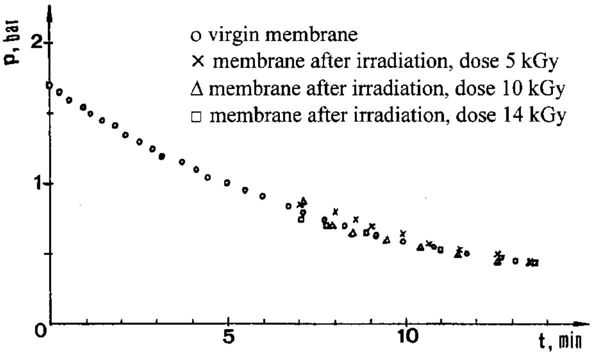

Fig. Decreasing of air pressure in measuring volume *vs.* time, for virgin sample of PP Celgard® membrane and samples of such a membrane after irradiation by 10 MeV electron beam.

Burst pressure is a parameter that characterizes mechanical strength of membrane samples. A disc of the membrane sample was placed in a special holder between aluminium plates with rubber seals. Air under pressure was introduced by a needle valve and then burnt pressure was registered by using a precise manometer. In case of the virgin membrane, burnt pressure was equal to 2.5 bar. After irradiation at a dose of 5 kGy burnt pressure was 1.4 bar at doses 10 and 14 kGy – 1 bar and only – 0.2 bar at the highest dose of 35 kGy.

Summarizing, we can conclude that radiation treatment by swift electron beam (10 MeV energy) at doses up to 35 kGy causes significant changes in bulk and on the surface of PP Celgard® membrane samples. Increasing hydrophilic property was observed. For a dose of 14 kGy, the wettability angle decreased by 17% and for a dose of 35 kGy – by 21% (immediately after irradiation). After the storage time of seven months, this property has ceased in essential stage for bigger doses.

Radiation treatment does not change permeability in case of air stream, but causes a decrease of mechanical strength. Burst pressure for the virgin membrane sample was equal to 2.5 bar and at a dose of 5 kGy it decreased by 44% and at a dose of 14 kGy – by 60%.

Practical conclusions concerning the application of PP Celgard® membrane after irradiation by swift electron beam as the barrier for electrochemical processes are the following: membrane samples should be taken immediately for further attempts or treatment (*e.g.* by plasma method) and irradiation dose should not be higher than about 14 kGy (because of mechanical strength maintaining).

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PREPARATION OF TITANIUM OXIDE AND METAL TITANATES AS POWDERS, THIN FILMS, AND MICROSPHERES BY COMPLEX SOL-GEL PROCESS

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Titanium oxide (TiO_2) and titanates based on Ba, Sr and Ca were prepared from commercial solutions of $TiCl_4$ and HNO_3. The main preparation steps for the sols consisted of elimination of Cl^- by distillation with HNO_3 and addition of metal hydroxides for the titanates. Resulting sols were gelled and used to:

- prepare irregularly shaped powders by evaporation;
- produce by a dipping technique thin films on glass, Ag or Ti supports;
- produce spherical powders (diameters <100 µm) by solvent extraction.

Results of thermal and X-ray-diffraction analyses indicated that the temperatures required to form the various compounds were lower than those necessary to form the compounds by conventional solid-state reactions and comparable to those required with use of organometallic based sol-gel methods. Temperatures of formation could be further reduced by addition of ascorbic acid (ASC) to the sols.

Titanium oxide, for many years an important pigment, has recently been applied widely as a photocatalyst or as supports for metallic catalysts, gas sensors, photovoltaic solar cells, and water and air purification devices. Titanates are being studied as materials for advanced technologies such as tritium breeders for fusion reactors [1-3], cathodes for Li-based batteries [4], and pH sensors [1-10]. $BaTiO_3$ and its alloys are widely used in a variety of electronic applications and interest is growing for other ferroelectric titanates such as $CaTiO_3$ [11] and $SrTiO_3$ [10,12,13], and for alkali titanates as photocatalysts, reinforcements in composites, and ion exchange materials [10-15].

All of the above compounds were first fabricated by solid-state reaction of oxides and/or metallic salts. Wet processing, advantages of which derive from precise compositional control and homogeneity on a molecular scale, has been applied successfully to synthesis of many titanates. Following the pioneering work of Mazdyiasni *et al.* [16] on synthesis of $BaTiO_3$, many papers have described sol-gel processes to produce TiO_2 and titanates [17-21]. Because of homogeneity on a nanometer scale, sol-gel-derived powders generally allow for decreased processing temperatures. Problems associated with sol-gel methods include deleterious formation of $BaCO_3$ during thermal conversion of gels [22-24] and high costs of substrates and precursor chemicals [20]. A key question in processing titanates well and inexpensively is the source of Ti. Our work reported here focuses on use of inexpensive commercial $TiCl_4$ (its cost is approximately 10% or less than those of competing sol-gel sources for Ti) and on methods to reduce processing temperatures and minimize $BaCO_3$ formation. These advances can allow to produce very high quality materials at substantially reduced cost.

The primary goals of this work were to use concentrated Ti-O nitrate sols to produce irregularly shaped and spherical particles of TiO_2 and various titanates and to produce films on commercial substrates. We applied a strong complexing agent, ASC, to stabilize the sols. This proprietary procedure (IChTJ) has been patented [25] and successfully applied to the synthesis of materials, such as high-temperature superconductors and various Li-based electronic ceramics [1-3,25-28]. We synthesized by sol-gel processing highly pure powders and other forms of TiO_2, Li_2TiO_3, $Li_4Ti_5O_{12}$, $BaTiO_3$, $SrTiO_3$, $CaTiO_3$, Na_2TiO_3, and K_2TiO_3. In this paper, we shall discuss only TiO_2, $BaTiO_3$, $SrTiO_3$, and $CaTiO_3$.

For all compositions, anhydrous $TiCl_4$ was combined to concentrated HNO_3, in contrast to our previous work based on HCl solutions [1]. Excess of HCl was exhausted, resulting in a solution of high Ti concentration (*ca.* 4 M). The main processing steps consisted of chloride elimination by distillation with HNO_3 (Rotavapor equipment, Büchi, Switzerland), and for the titanates addition of metal hydroxides or carbonates, evaporation of sols to dry powders, comminution, and thermal treatment [1-3]. To obviate a sol concentration step, we carried out distillation after adding every portion of HNO_3. We found that complete removal of the Cl^- from each $TiCl_4$ solution was required only five distillation steps.

Spherical gelled particles with diameters of <100 μm were produced by our IChTJ variant of the sol-gel process [2,3,26]. They were synthesized by extraction of H_2O from inorganic hydroxyl sol emulsion drops in ethylhexanol, followed by thermal treatment. During this process, the Me:Ti molar ratios decreased markedly because of extraction of metal nitrates. To prepare stoichiometric gels, required quantities of MeOH solutions were introduced into the gel microspheres that were placed into the Rotavapor.

The coatings were prepared by a technique [27,28] that employed a motor-driven dip-coating unit, with an immersion time of 20 s and a withdrawal rate of 2 cm/s. Covered substrates were stored for 24 h, then soaked for 48 h at 200°C, and finally fired for 1 h at 500°C. All thermal treatments were performed in air in a programmable furnace.

Gels and final products were characterized by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in a Hungarian MOM Derivatograph (sample weight – 200 mg, heating rate – 10°C/min), X-ray diffraction (XRD) by Cu Kα radiation in a Philips Diffraction System, and scanning electron microscopy (SEM) in a Zeiss DSM 942.

During the initial processing, in which the distillation temperature was 70°C, a white milky solution formed; it tended to agglomerate and form sediments. We surmised that formation of stable colloidal titanic acid induced repulsion of Cl^- from the colloidal particles. Based on our experience [1], we added ASC before the dechlorination step to prevent precipitation. The resulting sols were transparent, pale yellow, and stable. During the dechlorination steps, we observed decomposition and vigorous evolution of gas due to oxidation of the ASC by the nitrates. The stable Ti sol was used to produce various compositions and forms.

TiO_2

TG traces revealed systematic escape of volatiles without defined thermic effects. Weight loss was slightly lower for ASC-containing gel, presumably

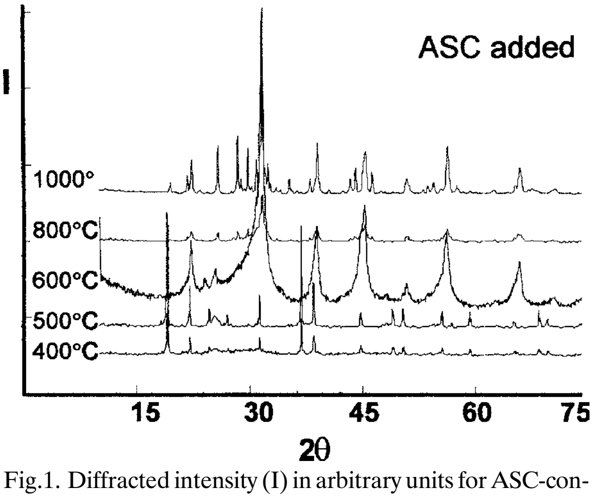

Fig.1. Diffracted intensity (I) in arbitrary units for ASC-containing TiO_2 sols heated for 2 h at the temperatures shown.

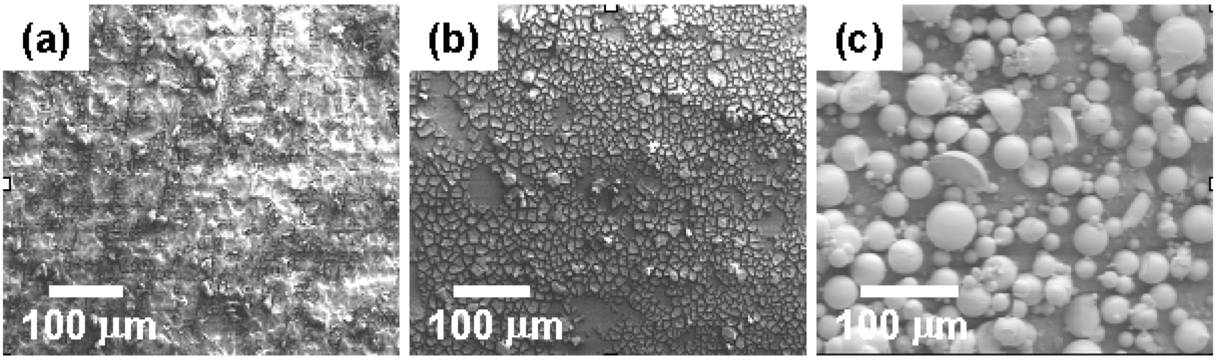

Fig.2. SEM photomicrographs of TiO_2 films on glass derived from (a) ASC-containing sol and (b) conventional sol; (c) spherical powder from ASC-containing sol.

because of lower content of nitrates, many of which decomposed during an earlier, low-temperature preparation step:

$$TiO(OH)_a\text{-}3.5NO_3\text{-}H_2O + ASC \rightarrow$$
$$TiO(OH)_{a+x}\text{-}(3.5\text{-}y)NO_3\text{-}H_2O\text{-}CO_2$$

Figure 1 shows XRD patterns of titania gels calcined for 2 h at various temperatures. Formation of crystalline phases of titania and transformation anatase to rutile phases took place at lower temperatures when ASC was added. Temperatures to complete reaction were similar to those reported when organometallic precursors have been used [16-20]. SEM of the TiO_2 films (1-5 µm thick) coated onto glass substrates revealed that the ASC-containing sols produced better morphologies and improved adhesion (Fig.2a,b). There was no significant difference in spherical powders prepared from both types of sol, but it seemed that ASC-based spheres (Fig.2c) were slightly finer and more regular. All products exhibited excellent phase purity.

$BaTiO_3$

For preparation of $BaTiO_3$, a key was to maintain sols without precipitation of Ba nitrates. Thermal analysis of two gels prepared with addition of $Ba(NO_3)_2$ and $Ba(OH)_2$ are shown in Fig.3a. For all gels, the dominant endotherm, observed at *ca.* 600°C, could be attributed to melting; smaller endotherms were attributed to decomposition of Ba nitrates. Addition of ASC induced melting at lower temperature. XRD analyses of powders treated to various temperatures indicated that addition of ASC promoted formation of the desired crystalline phase. Nitrates were present from 500 to 570°C; at 600°C, all nitrates decomposed over a 2 h period and formation of crystalline $BaTiO_3$ began. The temperature of formation and crystallization temperatures (Fig.3b) were comparable to what has been reported when organometallic reagents have been used [23].

$BiTiO_3$ films were prepared on glass and Ag substrates by a dip-coating technique. XRD confirmed good phase purities. SEM revealed various morphologies. The films were generally smooth, but examinations at magnifications of 5000x or above indicated microscopic irregularities. As was found with the TiO_2 films on glass substrates, addition of ACS resulted in minimization of cracks. One presumes lower shrinkage upon firing to be the cause of the improvement.

Following our success with production of medium-sized Li_2TiO_3 spherical particles [1-3], we prepared particles by a similar method from the

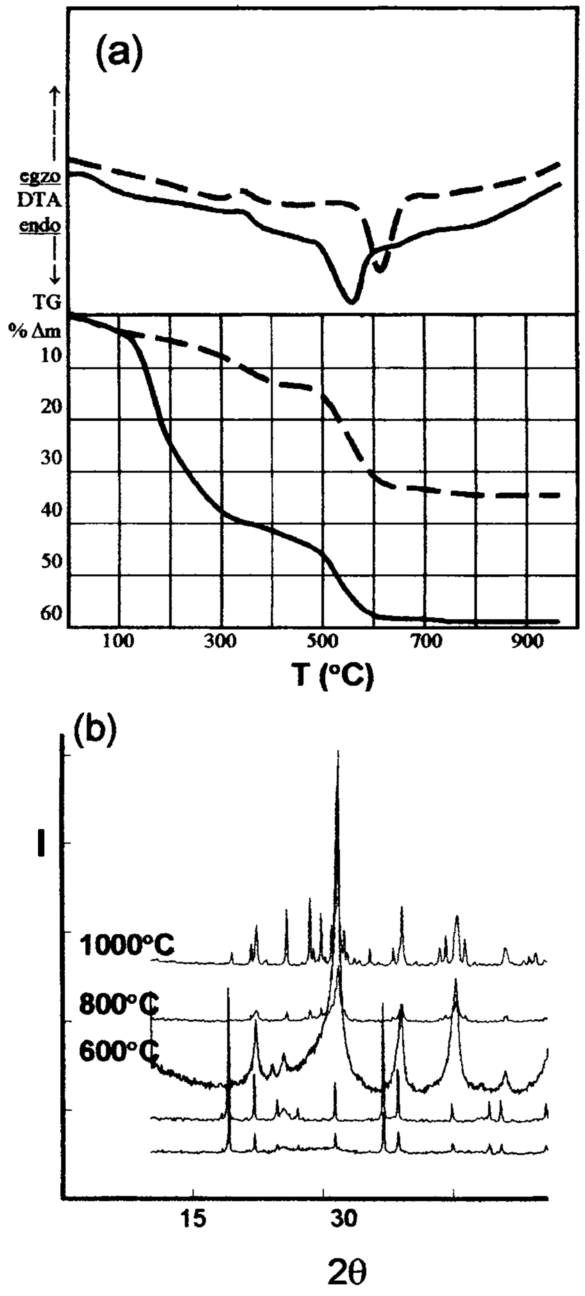

Fig.3. (a) DTA traces of $BaTiO_3$ sols with (dashed line) and without (solid line) ASC; (b) XRD patterns after 2 h at various temperatures for ASC-derived $BaTiO_3$.

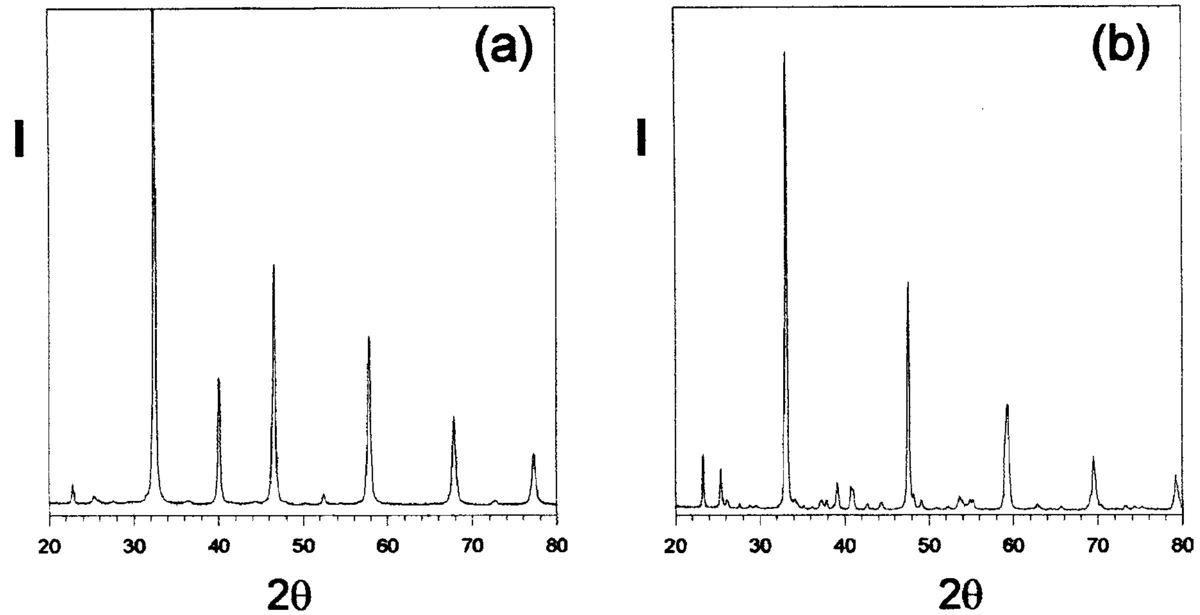

Fig.4. XRD spectra, intensity (I) in arbitrary units, of (a) $SrTiO_3$ and (b) $CaTiO_3$ fired to 800°C, 24 h.

Ba-Ti/OH-NO_3 sol. We initially obtained Ba-Ti gel spheres of diameter 1-80 μm, but with Ba loss and a final molar ratio of Ba:Ti=0.2. Per previous successes [1-3], we therefore impregnated the gels with $Ba(OH)_2$ in a hot solution (90°C, 25 g Ba/l), followed by vacuum drying, and final thermal treatment. With impregnation, we obtained medium-sized spherical powders (most spheres were 15-30 μm). We have not been able to identify $BaTiO_3$ spheres of such size in the literature: although fine (diameter <1 μm [20,29] and <10 μm [30]) $BaTiO_3$ particles have been obtained previously. Our larger spheres, which should be free-flowing, should be useful in, for example, plasma-spraying techniques.

$SrTiO_3$ and $CaTiO_3$

We have to date completed less work on the perovskites $SrTiO_3$ and $CaTiO_3$ than we have on TiO_2 or $BaTiO_3$, but the results have been quite encouraging. Use of the simple, $TiCl_4$-based sol-gel method has produced powders of good phase purity. Gels have been fired to various temperatures. With firing at 800°C, XRD patterns for $SrTiO_3$ indicated presence of a cubic phase; the cell parameter, calculated with the program Unitcell, was that found in the literature (a=3.90 Å) [31]. A small amount (1-2%) of anatase was present in the best sample (Fig.4a).

The XRD patterns of the $CaTiO_3$ indicated a monoclinic phase and 7-8% of anatase (Fig.4b). The cell parameters calculated with the Unitcell program were a=7.64 Å, b=7.60 Å, c=7.54 Å, which is in good agreement with those of literature [31]. For both $SrTiO_3$ and $CaTiO_3$, phase purity was independent of use of ASC, but use of ASC tended to the lower reaction temperatures (Table).

Powders, films, and spheres were produced from TiO_2 and $BaTiO_3$ sols, and powders were produced from $SrTiO_3$, and $CaTiO_3$ sols. All sols were based on use of inexpensive $TiCl_4$ as the Ti source. Formation of stable, concentrated Ti-nitrate sols (>170 g of Ti/cm^3) was favored by presence of ASC. Gels prepared from stable, transparent Ti-nitrate sols, in which ASC was incorporated, formed crystalline titanate phases at lower temperatures than did gels without this additive. ASC promoted higher quality in the dip-coated films: minimal cracking and good adhesion. Formation crystalline phases occurred at lower temperatures than required for solid-state processes and at temperatures comparable to those of other sol-gel techniques, in which more-expensive organometallic precursors are used.

Table. DTA and TGA data summary for the various titanates.

Compound	Mass stabilization [°C]	Endotherm of phase formation [°C]
$BaTiO_3$ (with ASC)	600	560
$BaTiO_3$	650	620
$SrTiO_3$ (with ASC)	610	590
$SrTiO_3$	650	590
$CaTiO_3$ (with ASC)	520	550
$CaTiO_3$	590	580

Stoichiometry was maintained during preparation of irregularly shaped powders of the various titanates. Correction of Me:Ti molar ratios during preparation of medium-sized spherical particles by an emulsion-extraction process could be effected by impregnation with metal hydroxides. No formation of metal carbonates was observed because of the very high acidity of the parent sols.

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STUDY OF GLUCOFURANOSE-BASED GEL NANOSTRUCTURE USING THE SAXS METHOD

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The glucofuranose-based gels were synthesized by the method described in [1]. The gelator of chemical formula: 1,2-O-(1-ethylpropylidene)-α-D-glucofuranose is built of furanose ring and contains three unprotected -OH groups. Its concentrations of 3, 1, 0.5 and 0.1% in toluene were chosen. The measurements were carried out with a ULTRA-SAXS BW-4 wiggler beamline of the HASYLAB synchrotron. The obtained data were subjected to pie integration and, after normalization, to subtraction of the background which was the SAXS curve of the solvent. For each sample, two measurements with sample-detector distances of 4 and 12 m were performed and joined using OTOKO program [2] to get a bigger range of the data. The complex method of SAXS data processing was applied, to find structural parameters of the gelator in gel, such as: the mass fractal, d_m, and surface fractal, d_s, dimensions, radius of gyration, R_g, distance distribution function, $p(r)$, and dummy atom models [3-5].

The results (Table and Figs.1 and 2) of all methods make it possible to assume that two types of aggregates exist in the gel. The differences between them are: the first type (for 3% gel) – the aggregate is smaller, compact, of well-defined smooth surface and a rod-like shape, and the second type (for 0.1% gel) – aggregate is bigger, looser, of rough surface and a disk-like shape. The aggregate change at in-

Table. Structural parameters *vs.* gelator concentration.

Concentration [%g/mL]	Mass fractal dimension, d_m	Surface fractal dimension, d_s	Radius of gyration, R_g [nm]
3	2.8	2.2	49.7
1	2.6	2.2	57.4
0.5	2.7	2.2 and 2.7	60.7
0.1	-	2.9	61.9

termediate concentration is gradual and there, especially for 0.5%, a mix of both types is detected. The results suggest the appearance of structural transformation caused by the change of gelator concentration. The transition acts gradually with concentration change. The process of glucofuranose-based gels formation occurred not caused by the same kind of self-assembly of aggregates but its course is dependent on the concentration of the gelator molecules in solvent.

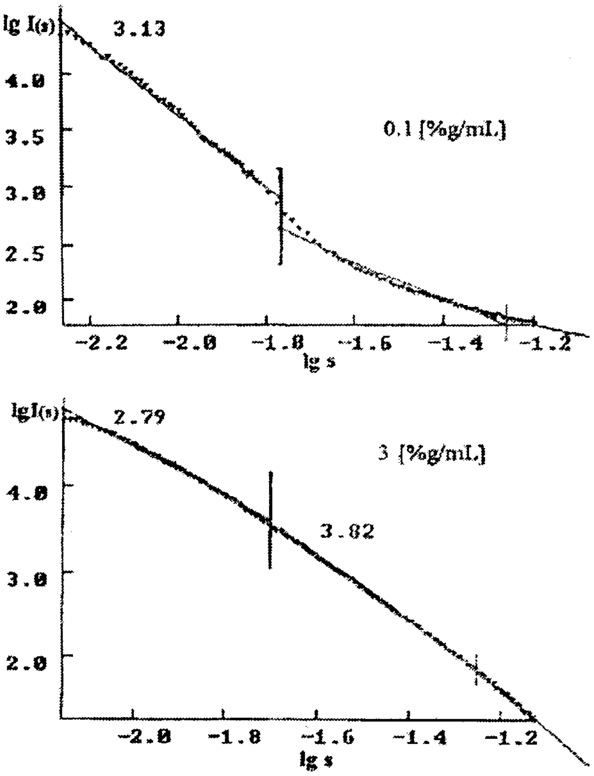

Fig.1. Fractal analysis, log-log curves with fitted straight-line segments.

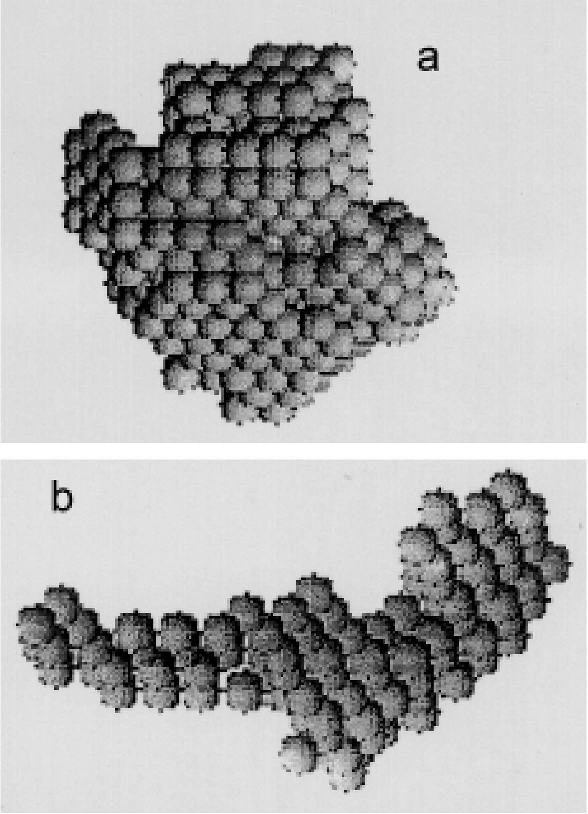

Fig.2. Model aggregate for (a) 0.1% gel and (b) 3% gel.

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CRYSTAL CHEMISTRY OF COORDINATION COMPOUNDS WITH HETEROCYCLIC CARBOXYLATE LIGANDS. PART LIV. THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS[HEXAQUAMAGNESIUM(II)] PYRAZINE-2,3,5,6-TETRACARBOXYLATE TETRAHYDRATE

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Triclinic unit cell [space group P1(bar)] of the title compound contains two hexaquamagnesium(II) cations, one fully deprotonated pyrazine-2,3,5,6-tetracarboxylate (2,3,5,6-PZTC) anion with its geometrical centre situated at the inversion centre and four solvation water molecules. Figure 1 shows the relevant ions with atom numbering scheme, Fig.2 – the content of the unit cell. The magnesium(II) ion is sorrounded by six water molecules with their oxygen atoms located at the apices of a fairly regular octahedron. Mg-O bond distances range from 2.036(1) to 2.115(1) Å (mean 2.065 Å). The pyrazine ring of the anion is planar (rms 0.0001 Å), the carboxylate groups are inclined to the pyrazine ring by 22.8 and 99.1°. A three-dimensional network of hydrogen bonds with d(O-H...O)>2.70 Å is operating between the coordinated water molecules and carboxylate oxygen atoms.

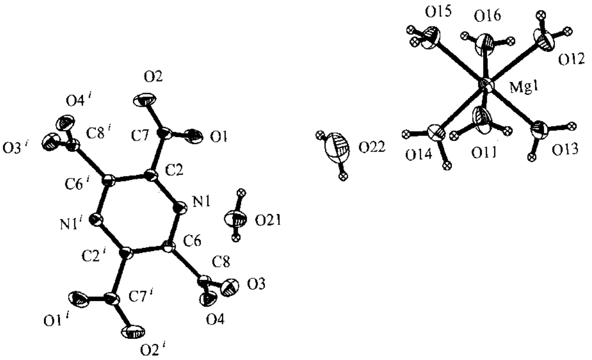

Fig.1. Atom labelling scheme for bis[hexaquamagnesium(II)] pyrazine-2,3,5,6-tetracarboxylate tetrahydrate. Non-hydrogen atoms are shown at 50% probability displacement ellipsoids. Symmetry code: (I) -x+2, -y, -z.

X-ray diffraction data collection was carried out on a KUMA KM4 four circle diffractometer at the Institute of Nuclear Chemistry and Technology. Structure solution and refinement was performed using SHELXL programme package.

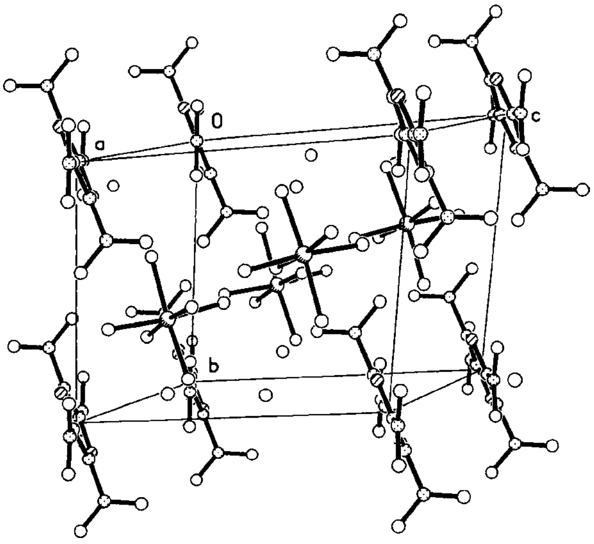

Fig.2. Packing of molecules in the unit cell of bis[hexaquamagnesium(II)] pyrazine-2,3,5,6-tetracarboxylate tetrahydrate. Hydrogen atoms have been omitted.

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CRYSTAL CHEMISTRY OF COORDINATION COMPOUNDS WITH HETEROCYCLIC CARBOXYLATE LIGANDS. PART LV. THE CRYSTAL AND MOLECULAR STRUCTURE OF A MAGNESIUM(II) COMPLEX WITH PYRIDAZINE-3-CARBOXYLATE AND WATER LIGANDS

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The crystal structure of bis(aqua-O)di(*trans*-pyridazine-3-carboxylato-*N*,*O*)magnesium(II) dihy-

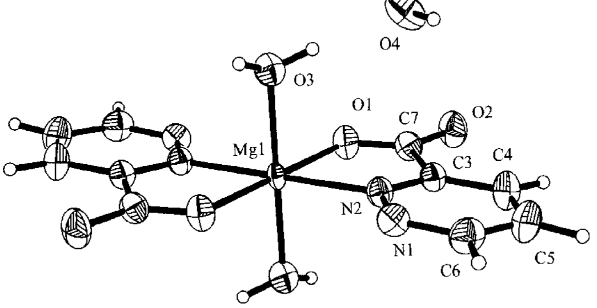

Fig.1. The molecule of $Mg[(C_5H_3N_2O_2)(H_2O)]_2{\cdot}2H_2O$ with atom labelling scheme. Unlabelled atoms are related by symmetry code (x-1, y-1, z-1). Displacement ellipsoids are drawn at the 50% probability level.

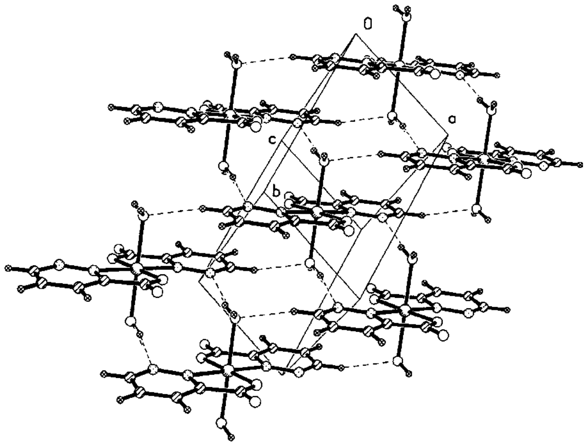

Fig.2. Packing of $Mg[(C_5H_3N_2O_2)(H_2O)]_2$ and solvation water molecules in the crystal structure. Dashed lines indicate hydrogen bonds.

drate ($\mathrm{Mg}[(C_5H_3N_2O_2)(H_2O)]_2\cdot 2H_2O$) is composed of monomeric molecules in which the magnesium(II) ion at the centre of symmetry is coordinated by two ligand molecules, each *via* its N,O bonding moiety [Mg-N 2.177(2) Å, Mg-O 2.041(1) Å]. The ligand molecules and the metal ion form a *trans*-planar configuration (rms 0.0001 Å). Two water oxygen atoms [Mg-O 2.091(1) Å], above and below the plane, complete a slightly distorted octahedron (Figs.1 and 2). A network of hydrogen bonds operating between the solvation water molecules acting as donors and unbonded carboxylate oxygen atoms and unbonded hetero-ring nitrogen atoms holds the monomers together.

X-ray diffraction data collection was carried out on a KUMA KM4 four circle diffractometer at the Institute of Nuclear Chemistry and Technology. Structure solution and refinement was performed using SHELXL programme package.

CRYSTAL CHEMISTRY OF COORDINATION COMPOUNDS WITH HETEROCYCLIC CARBOXYLATE LIGANDS. PART LVI. THE CRYSTAL AND MOLECULAR STRUCTURES OF TWO CALCIUM(II) COMPLEXES WITH IMIDAZOLE-4,5-DICARBOXYLATE AND WATER LIGANDS

Wojciech Starosta, Janusz Leciejewicz, Thathan Premkumar[1/], Subbian Govindarajan[1/]

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The structure of *poly*-diaqua(μ-imidazole-4,5-dicarboxylato-N,O;O'; -O", O"')calcium(II) monohydrate ($[Ca(C_5H_2N_2O_4)(H_2O)_2\cdot H_2O]$) is built of molecular sheets in which imidazole-4,5-dicarboxylate ligand molecules (4,5-IDA) bridge the metal ions using both their carboxylate groups, each acting in a bidentate mode. Figure 1 shows the structural unit with atom labelling scheme, Fig.2 – the packing diagram. Calcium(II) ion is coordinated by six oxygen atoms and one hetero-ring nitrogen atom distributed at the apices of a capped trigonal pyramid. The basal plane of the prism is formed by two carboxylate oxygen atoms [d(Ca-O2=2.374(1) Å, d(Ca-O4)=2.412(1) Å] and two water oxygen atoms [d(Ca-O5)=2.384(1) Å, d(Ca-O6)=2.455(1) Å], the capped position is occupied by the carboxylate oxygen atom O3 [d(Ca-O3)=2.325(1) Å], the hetero-ring nitrogen atom [d(Ca-N2)=2.523(1)Å]

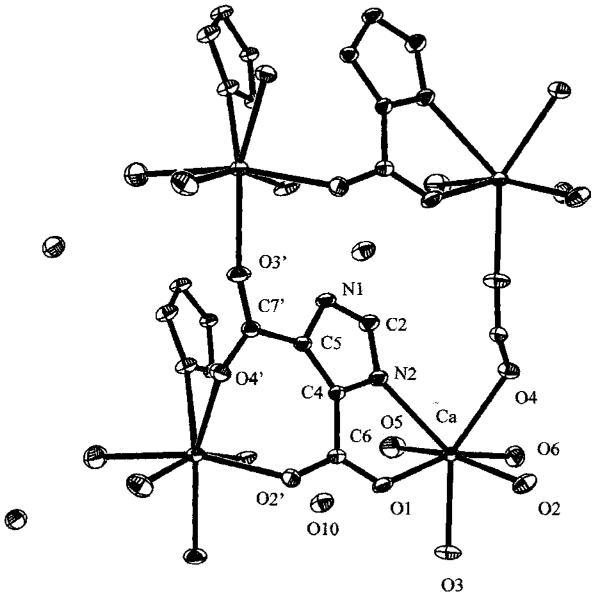

Fig.1. A fragment of the molecular sheet constituting the structure of $Ca(4,5\text{-IDA})(H_2O)_4\cdot H_2O$ with atom labelling scheme. Non-hydrogen atoms are drawn at the 50% probability level. For clarity, hydrogen atoms are not shown.

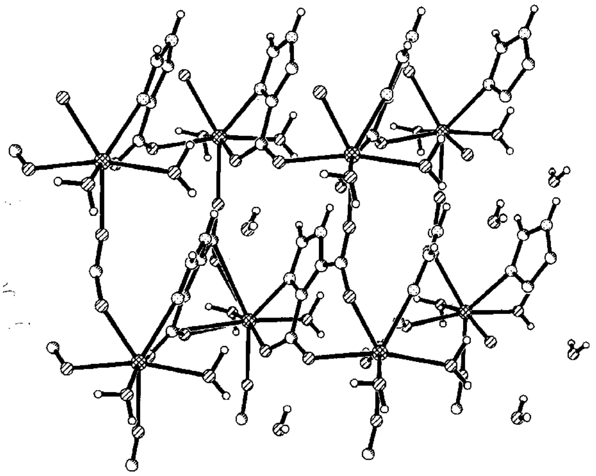

Fig.2. The packing diagram of $Ca(4,5\text{-IDA})(H_2O)_4\cdot H_2O$ showing the alignment of the molecular layers along the *c* axis.

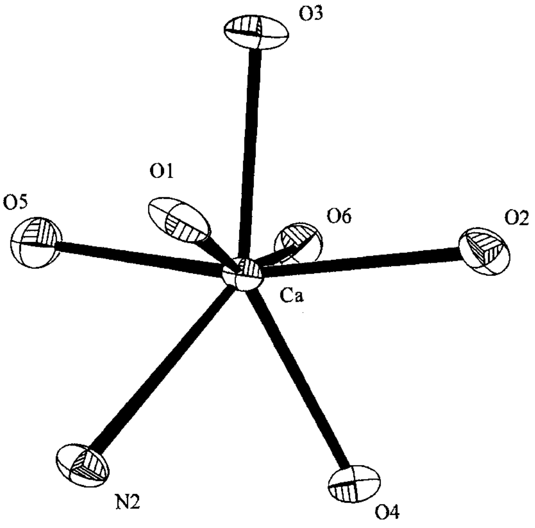

Fig.3. The coordination the calcium(II) ion in the structure of $Ca(4,5\text{-IDA})(H_2O)_4\cdot H_2O$.

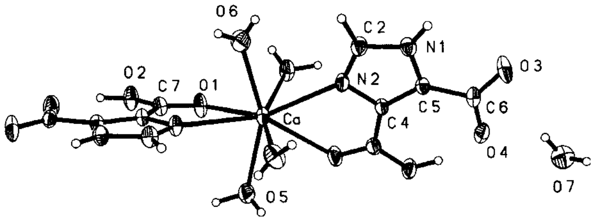

Fig.4. A molecule of $Ca[H(4,5\text{-}IDA)]_2(H_2O)_4$ with numbering of atoms. Non-hydrogen atoms are drawn at the 50% probability level.

and the carboxylate oxygen atom O4 [d(Ca-O2)= 2.412(1) Å] form the apices of the prism (Fig.3). The solvation water molecule plays a significant role in the framework of hydrogen bonds responsible for the stability of the crystal.

The structure of tetraquadi(*trans*-*H*imidazole-4,5-dicarboxylato-N,O) calcium(II) hydrate ($Ca(C_5H_3N_2O_4)_2(H_2O)_4{\cdot}H_2O$) consists of monomers in which the calcium(II) ion is located on a centre of symmetry. Figure 4 shows a monomer with atom labelling scheme, Fig.5 – a fragment of the molecular pattern. The coordination around the calcium(II) ion is a strongly deformed pentagonal bipyramidal with the imidazole-4,5-dicarboxylate ligand molecules in the *trans* arrangement forming a dihedral angle of 68.3°. An imidazole-ring nitrogen atom [d(Ca-N)=2.632(2) Å] and one carboxylate oxygen atom [d(Ca-O)=2.531(2) Å] from each ligand coordinate to the metal ion. The coordination is completed by four water oxygen atoms [d(Ca–O)= 2.393(2) Å] and [d(Ca-O)=2.367(2) Å]. The coordinated water molecules act as hydrogen bond donors and acceptors to the unbonded carboxylate oxygen atoms in adjacent monomers giving rise to a three-dimensional molecular network.

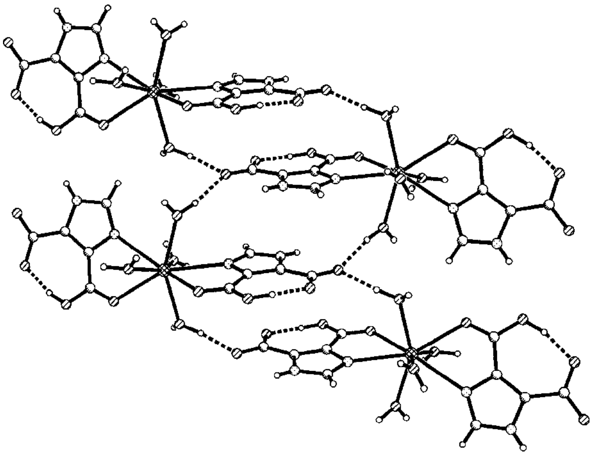

Fig.5. A fragment of the molecular pattern in the structure of $Ca[H(4,5\text{-}IDA)]_2(H_2O)_4{\cdot}H_2O$. Hydrogen bonds are shown as dashed lines.

X-ray diffraction data collection was carried out on a KUMA KM4 four circle diffractometer at the Institute of Nuclear Chemistry and Technology. Structure solution and refinement was performed using SHELXL programme package.

CRYSTAL CHEMISTRY OF COORDINATION COMPOUNDS WITH HETEROCYCLIC CARBOXYLATE LIGANDS. PART LVII. THE CRYSTAL AND MOLECULAR STRUCTURE OF A CALCIUM(II) COMPLEX WITH IMIDAZOLE-4-CARBOXYLATE AND WATER LIGANDS

Wojciech Starosta, Janusz Leciejewicz

The structure of *catena*-monoaqua(μ-imidazole-4-carboxylato-N,O',-O',O'')(μ-imidazole-4-carboxylato-O''',O'''',-O''')calcium(II) is composed of molecular ribbons in which calcium(II) ions are bridged by two crystallographically independent imidazole-4-carboxylate ligand molecules ($Ca(4\text{-}IMC)_2(H_2O)$). Each calcium(II) ion is coordinated by the N,O bonding moiety of one ligand molecule [d(Ca-N)=2.508(1) Å; d(Ca-O11)= 2.384(1) Å], two carboxylate oxygen atoms of the other ligand molecule [d(Ca-O21)=2.527(1) Å; d(Ca-O22)=2.465(1) Å], an oxygen atom of a coordinated water molecule [d(Ca-O31)=2.412(1) Å] and three carboxylate oxygen atoms donated by the adjacent ligand molecules, acting in bridging mode [d(Ca-O11^{II})=2.512(1) Å; d(Ca-O12= 2.452(1) Å; d(Ca-O22^{I})=2.530(1) Å]. Figure 1 shows a fragment of the molecular chain with atom numbering scheme, Fig.2 – two views of the ribbon. The coordination number of the calcium(II) ion is eight, the coordination polyhedron – a bicapped pentagonal bipyramid with a strongly deformed equatorial plane (rms 0.3401 Å). Molecu-

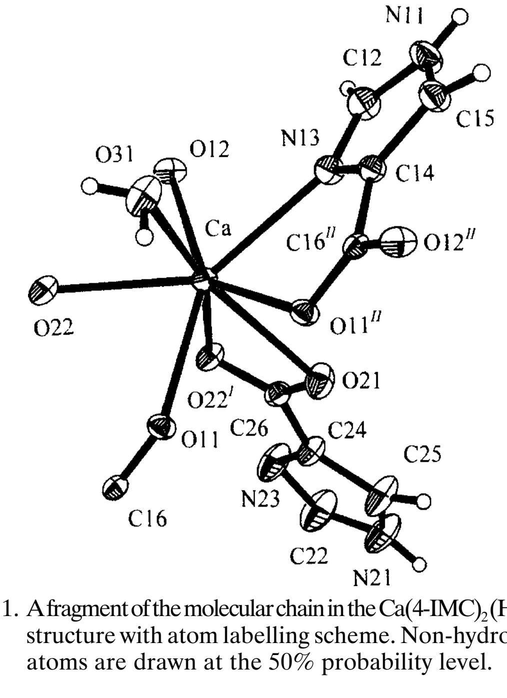

Fig.1. A fragment of the molecular chain in the $Ca(4\text{-}IMC)_2(H_2O)$ structure with atom labelling scheme. Non-hydrogen atoms are drawn at the 50% probability level.

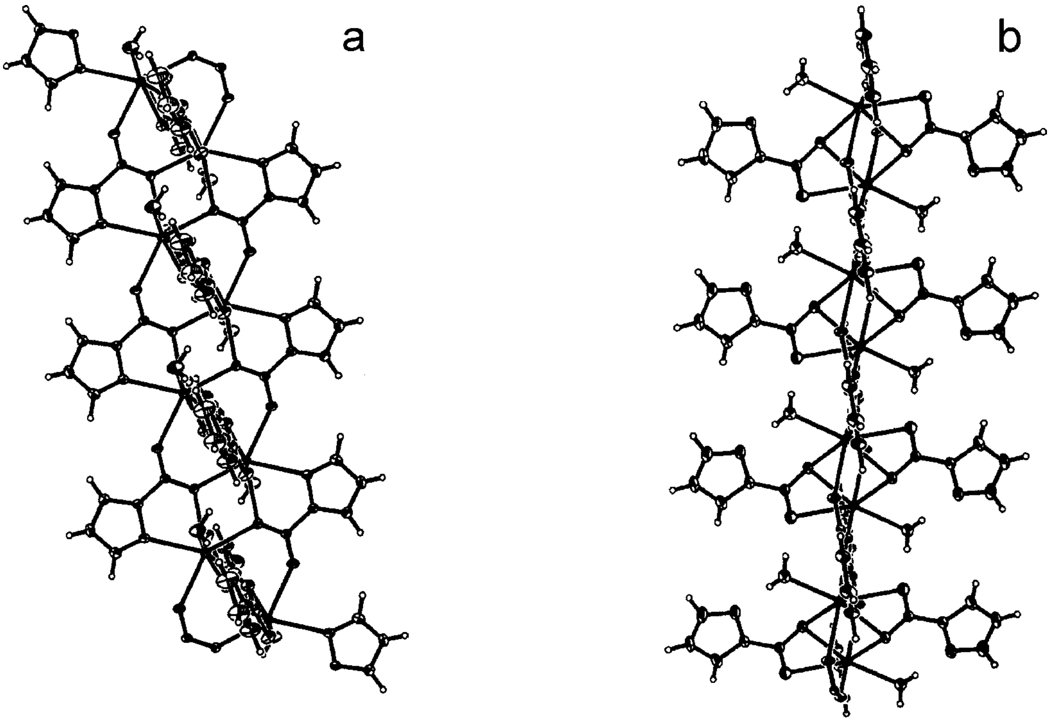

Fig.2. A molecular ribbon in the structure of $Ca(4\text{-}IMC)_2(H_2O)$ viewed (a) along the *b* axis and (b) along the *c* axis.

lar ribbons are held together by a system of hydrogen bonds.

X-ray diffraction data collection was carried out on a KUMA KM4 four circle diffractometer at the Institute of Nuclear Chemistry and Technology. Structure solution and refinement was performed using SHELXL programme package.

CRYSTAL CHEMISTRY OF COORDINATION COMPOUNDS WITH HETEROCYCLIC CARBOXYLATE LIGANDS. PART LVIII. THE CRYSTAL AND MOLECULAR STRUCTURE OF A BARIUM(II) COMPLEX WITH IMIDAZOLE-4,5-DICARBOXYLATE AND WATER LIGANDS

Wojciech Starosta, Janusz Leciejewicz, Thathan Premkumar[1/], Subbian Govindarajan[1/]

[1/] Department of Chemistry, Bharathiar University, Coimbatore, Tamilnadu, India

The structure of *poly*-tetraaquabis(μ-*H*imidazole-4,5-dicarboxylato-N,O;-O') barium(II) dihydrate ($Ba(C_5H_3N_2O_4)_2(H_2O)_4{\cdot}2H_2O$) is built of molecular sheets in which singly deprotonated imidazole-4,5-dicarboxylate ligand molecule [H(4,5-IDA)] bridges metal ions using its N,O bonding moiety and one oxygen atom of its second carboxylate group. Each barium(II) ion is coordinated by N,O bonding moieties of two ligand molecules, two carboxylate oxygen atoms of two another ligand molecules and four water oxygen atoms. The coordination number of a barium(II) ion is ten, the coordination polyhedron contains fourteen faces. Figure 1 shows a molecular unit of the structure with atom labelling system, Fig.2 –

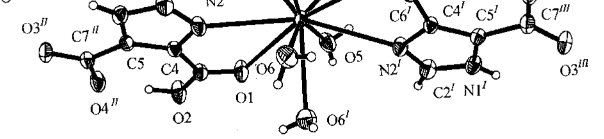

Fig.1. A fragment of the molecular sheet constituting the structure of $Ba[H(4,5\text{-}IDA)]_2(H_2O)_4{\cdot}2H_2O$ with atom labelling scheme. Non-hydrogen atoms are drawn at the 50% probability level.

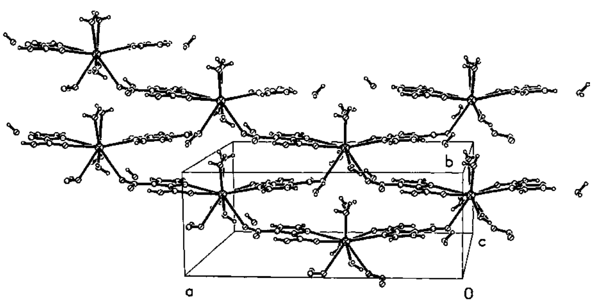

Fig.2. A molecular layer in the structure of $Ba[H(4,5\text{-}IDA)]_2(H_2O)_4{\cdot}2H_2O$. For clarity, hydrogen atoms are not shown.

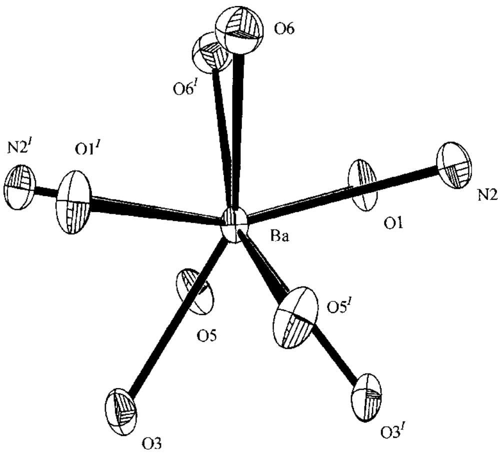

Fig.3. The coordination around the barium(II) ion in the structure of $Ba[H(4,5\text{-}IDA)]_2(H_2O)_4 \cdot 2H_2O$.

the packing diagram, Fig.3 – the coordination around the barium(II) ion. A network of hydrogen bonds is responsible for the stability of the crystal.

X-ray diffraction data collection was carried out on a KUMA KM4 four circle diffractometer at the Institute of Nuclear Chemistry and Technology. Structure solution and refinement was performed using SHELXL programme package.

CRYSTAL CHEMISTRY OF COORDINATION COMPOUNDS WITH HETEROCYCLIC CARBOXYLATE LIGANDS. PART LIX. THE CRYSTAL STRUCTURE OF A CALCIUM(II) COMPLEX WITH PYRIDAZINE-3-CARBOXYLATE AND WATER LIGANDS

Wojciech Starosta, Janusz Leciejewicz

The crystals of bis[(μ_2-pyridazine-3-carboxylato-N,O, O')-trisaqua-calcium(II)] are monoclinic, space group $P2_1/n$ with a=9.173(1) Å, b=10.539(2) Å, c=14.984(3) Å, β=99.43(3)° and Z=4. The structure contains centrosymmetric dimeric molecules composed of two calcium(II) ions, each coordinated by two pyridazine-3-carboxylate ligand molecules ($Ca_2(C_5H_3N_2O_2)_4(H_2O)_6$) *via* their N,O bonding moieties [Ca-O11 2.432(1) Å, Ca-N11 2.585(1) Å; Ca-O21 2.404(1) Å, Ca-N21 2.606(1) Å] and three water molecules [mean Ca-O 2.389(1) Å]. The calcium ions are bridged by two carboxylate oxygen atoms, each acting in a bidentate mode donated by ligand molecules coordinated to different metal ions forming a bridging path Ca-O11-Ca^{I} (Fig.). The coordination number of the calcium(II) ion is eight, the coordination polyhedron is a strongly deformed decahedron. Coordinated water molecules participate in a hydrogen bond network linking the dimers.

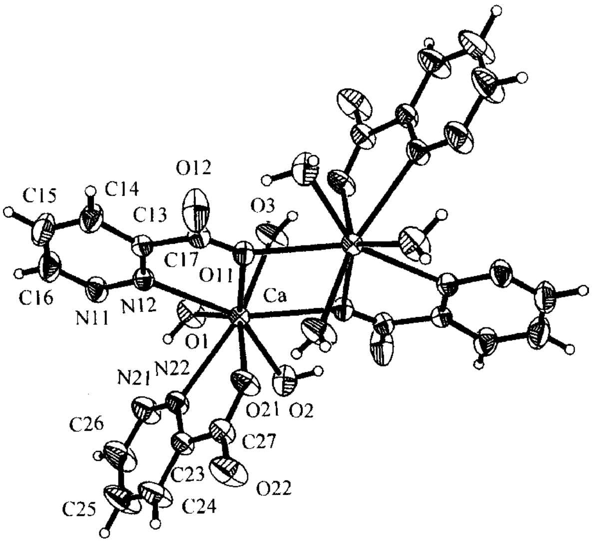

Fig. The centrosymmetrical dimeric molecule of $Ca_2(C_5H_3N_2O_2)_4(H_2O)_6$ with atom labelling scheme. Unlabelled atoms are related by the symmetry code: -x+1, -y+2, -z+1. Displacement ellipsoids are drawn at the 50% probability level.

X-ray diffraction data collection was carried out on a KUMA KM4 four circle diffractometer at the Institute of Nuclear Chemistry and Technology. Structure solution and refinement was performed using SHELXL programme package

RADIOBIOLOGY

DNA DAMAGE IN SUBFRACTIONS OF HUMAN LYMPHOCYTES IRRADIATED WITH LOW DOSES OF X-RADIATION

Marcin Kruszewski[1,2], **Maria Wojewódzka**[1], **Teresa Iwaneńko**[1], **Aneta Goździk**[3], **Tomasz Ołdak**[2,3], **Eugeniusz K. Machaj**[2,3], **Zygmunt Pojda**[2,3]

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[3] Military Institute of Hygiene and Epidemiology, Warszawa, Poland

The aim of this study was to find a reliable, sensitive, fast and relatively cheap method to estimate radiation-induced DNA damage in human lymphocytes during a short time period after irradiation. We compared three methods: comet assay, micronucleus test and formation of phosphorylated histone H2AX foci.

Human peripheral blood lymphocytes were collected by vein puncture and fractionated using T Cell Isolation Kit II and B Cell Isolation Kit II (Miltenyi Biotec), according to the manufacturer recommendations. Homogeneity of both T and B cell populations was 97-99%, as estimated by flow cytometry. Cells were irradiated with low doses of X-rays (0-1 Gy, 180 kV, 18 mA, 1 mm Cu filter) using Stabilipan X-ray machine (Siemens). Dose rate was 1.2 Gy/min. DNA damage was assessed by standard alkaline comet assay [1], micronucleus test [2] and from the number of phosphorylated histone H2AX foci estimated by immunofluorescence [3] (Figs.1 and 2).

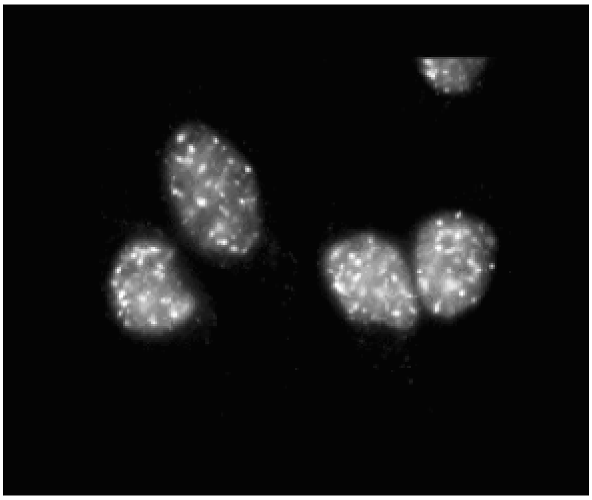

Fig.1. Microscopic image of nuclei from X-irradiated (1 Gy) human lymphocytes with repair foci visualised with anti-H2AX histone monoclonal antibody.

The results indicate that all tests have similar sensitivity, approximately 0.3 Gy. All methods also reveal slightly higher induction of DNA damage in B lymphocytes as compared with T cells. The highest ratio of damage marker in irradiated cells (1 Gy) to control cells was obtained for formation of γH2AX foci; it was equal to 8.3, whereas for comet assay and micronucleus test, it was 4.0 and 4.1, respectively. The repair of DNA estimated by the γH2AX foci scoring was much slower as compared to the repair of total DNA damage measured by the comet assay.

In summary, our study indicates that γH2AX foci assay is an advantageous alternative for micronucleus test and comet assay for radiation dose estimation in irradiated individuals. Long time of repair of DNA damage and high irradiated/control ratio make this assay more convenient than the other two methods applied.

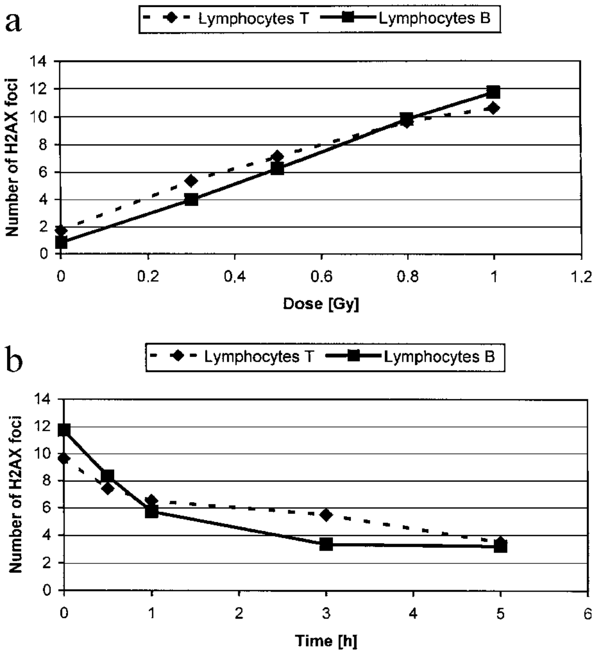

Fig.2. Formation of phosphorylated histone H2AX foci upon irradiation (a) and repair of DNA damage (b) induced by 1 Gy of X-rays, reflected as disappearance of phosphorylated histone H2AX foci.

The work was supported by the Polish Ministry of Scientific Research and Information Technology statutory grant for the INCT.

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THE ROLE OF LYSOSOMAL IRON IN NITRIC OXIDE SIGNALLING

Sylwia Męczyńska, Hanna Lewandowska-Siwkiewicz, Marcin Kruszewski

A considerable amount of cellular iron remains in the form of complexes with low molecular mass ligands, labile enough to enter the Fenton reaction. This pool has been called the labile iron pool (LIP). It plays a role, among others, in cellular iron transport, expression of iron regulatory genes, control of the activity of iron containing proteins, and catalysis of the Fenton reactions. It was proposed (*e.g.* [1,2]) that a part of the cellular pool of labile iron is confined within the acidic vacuolar compartment (lysosomes).

Our previous results [3] show that LIP plays a role in the regulation of nitric oxide-dependent biochemical pathways, forming dinitrosyl iron complexes (DNIC), a group of physiologically important transducers of nitric oxide. Formation of nitrosyl iron complexes, known as 2.03 complexes due to the g value of their characteristic EPR spectra, has been found by several groups of researchers in many kinds of bacteria, plants and animals. It is postulated that DNIC are important factors in nitric oxide-dependent regulation pathways in the cell (*e.g.* [4,5]). The low molecular-weight DNIC have been shown to modulate redox properties of the cellular interior through the inhibition of glutathione-dependent enzymes, such as glutathione reductase, transferase and peroxidase. The sources of iron forming DNIC *in vivo* are still not precisely defined, one of the putative sources being the LIP and another – iron proteins. Neither are defined the cellular compartments, in which DNIC are formed.

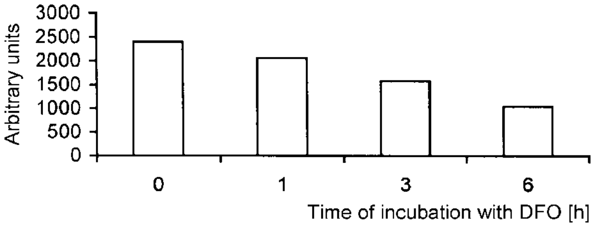

Fig.1. EPR (electron paramagnetic resonance) signal intensity in K-562 cells incubated with DFO prior to the treatment with nitric oxide donor. Cells were treated with 1 mM DFO and incubated at 37°C for 1, 3 or 6 h. After that time, nitric oxide donor was added to generate DNIC.

In the present report, we show that depletion of lysosomal LIP by either chelation with deferoxamine (DFO) or lysis inhibition (by treatment with 10 mM ammonium chloride) in K-562, human myelogenous leukemia cells leads to a considerable decrease (down to 50%, depending on the incubation time) of DNIC forming in the cells treated with 70 μM nitric oxide donor (DEANO). The EPR spectra were recorded on Bruker ESP 300 at 77 K, microwave power – 1 mW, microwave frequency – 9.31 GHz, modulation amplitude – 3.027 G and time constant – 41 ms. In order to estimate the values of g coefficients, computer simulation was performed on SimFonia 1.25 software (Bruker Analytische Messtechnik, DE).

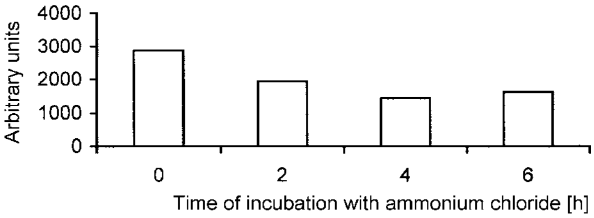

Fig.2. EPR signal intensity in K-562 cells incubated with ammonium chloride prior to the treatment with nitric oxide donor. Cells were treated with 10 mM ammonium chloride and incubated at 37°C for 2, 4 or 6 h. After that time, nitric oxide donor was added to generate DNIC.

The results presented in Figs.1 and 2 indicate a vital role of lysosomal labile iron in DNIC formation. Taken together, our present and previous results are consistent with the thesis on the considerable contribution of lysosomal iron to the total LIP in the cell.

The work was supported by the Polish Ministry of Scientific Research and Information Technology statutory grant for the INCT.

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RADIOSENSITIVITY OF HUMAN CHROMOSOMES 2, 8 AND 14. PART 1. PRIMARY BREAKS

Sylwester Sommer, Iwona Buraczewska, Maria Wojewódzka, Irena Szumiel, Andrzej Wójcik

A number of studies have been performed with the aim of verifying if the inter-chromosomal distribution of radiation-induced aberrations is proportional to the DNA content of the chromosome (reviewed in [1,2]). While deviations from randomness have been observed for a number of chromosomes, no consensus exists as to which chromosomes are repeatedly more or less sensitive than expected. A factor that has been suggested to contribute is donor variability [1,2]. However, the extent of donor variability has never been investigated thoroughly. We have, therefore, compared the frequencies of radiation-induced aberrations in chromosomes 2, 8 and 14 analyzed in lymphocytes of seven donors. Peripheral blood lymphocytes were collected from seven healthy donors and exposed to different doses of gamma rays (approximate range – 0.2-2.8 Gy). Chromosomes 2, 8 and 14 were painted in different colors and aberrations scored with the help of an image-analysis system.

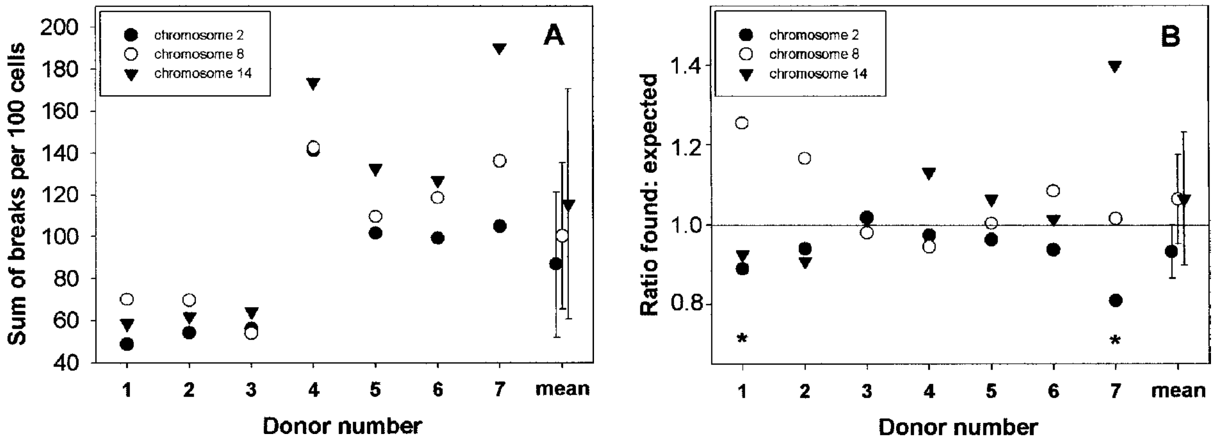

Fig. Primary breaks observed in the painted chromosomes of donors 1-7. Breaks calculated from aberrations (including complexes) observed after all doses of radiation were summed up and scaled to the whole genomic frequencies. The absolute numbers are shown in panel A and the ratios of found to expected are shown in panel B. Error bars represent the standard deviations from the mean values of all donors for each painted chromosome. * – difference between the observed and expected frequencies significant with $p<0.05$.

In order to assess the overall radiosensitivity of the painted chromosomes, chromosomal aberrations including complexes were transformed into primary breaks. The break frequencies were summed up for all doses of radiation and scaled to the whole genomic frequencies. The results are presented in Fig. In the case of most donors the lowest frequency of breaks was observed in chromosome 2 and the highest – in chromosome 14. The ratio of found to expected breaks deviated significantly only in lymphocytes of donors 1 and 7. A separate analysis of exchanges is presented in the following report. Altogether, the data indicate that inter-donor variability may explain some of the controversies regarding the inter-chromosomal distribution of radiation-induced aberrations.

The work was supported by the Polish Ministry of Scientific Research and Information Technology – project No. 6 P05A 119 20.

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RADIOSENSITIVITY OF HUMAN CHROMOSOMES 2, 8 AND 14. PART 2. 2A AND 2B EXCHANGES

Sylwester Sommer, Iwona Buraczewska, Irena Szumiel, Andrzej Wójcik

In order to compare the frequencies of exchanges in the painted chromosomes, the total 2A and 2B exchange frequencies scored after all doses of radiation were summed up and scaled to the whole genomic frequencies. The frequency of aberrations in lymphocytes of donors 1-3 was lower than that in lymphocytes of donors 4-7 because lymphocytes of donors 1-3 were exposed to a higher number of doses in the low-dose range. Generally, the lowest frequencies of exchanges were scored in chromosome 2. This effect is prominent for total 2B exchanges as well as for the sum of 2B and 2A, and less so for total 2A exchanges. The highest level of exchanges was generally observed in chromosome 14, however, not in lymphocytes of all donors. For example, in lymphocytes of donors 1 and 2 the highest level of 2B exchanges were observed in chromosome 8. In the case of total 2B exchanges, the levels of aberrations deviated significantly from the expected values in lymphocytes of donors 2, 4, 6 and 7. In the case of total 2A exchanges, a significant deviation from the expected levels was only observed in lymphocytes of donor 7. For the sums of total 2B and 2A, a significant deviation was observed in lymphocytes of donors 4-7.

We also checked whether the ratios of total 2B to total 2A aberrations in the painted chromosomes are individually variable. The results are presented in Fig. It is evident that individual differences do exist. On average, the ratio was below 1 for chromosome 2 and above 1 for chromosomes 8 and 14. For all painted chromosomes the ratio was close to 1.

Controversy exists in the literature with respect to the ratio of 2B to 2A exchanges. While an equal ratio has been reported by some authors (*e.g.* [1,2]), many found the ratio to be higher than unity (*e.g.* [3,4]). Our results indicate that this ratio may also be donor-specific, although in none of the cases were the deviations from unity strong enough to be statistically significant. The mean ratio for all chromosomes and donors was found to be close to 1.

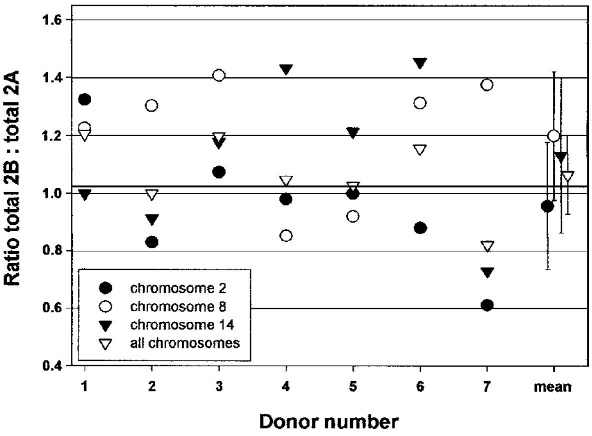

Fig. Ratios of total 2B-type to total 2A-type exchanges. Exchanges observed after all doses of radiation (approximate range – 0.2-2.8 Gy) were summed up.

The results presented in this and the preceding report indicate that inter-donor differences do exist, however, not with respect to all chromosomes. Our observations very well agree with the data published by others in that chromosome 2 is less radiosensitive than expected with minimal inter-donor variability. Chromosome 14 is more sensitive than expected and the sensitivity of chromosome 8 corresponds to its DNA content, however, this trend is individually variable. It appears that inter-donor variability is an important factor in the radiosensitivity of individual chromosomes and may explain some of the controversies regarding the inter-chromosomal distribution of radiation-induced aberrations. The implication of this conclusion for biological dosimetry is that the inter-donor variability is a potential source of error in calculating the dose absorbed by one individual on the basis of a calibration curve generated with lymphocytes of a different individual. This error can be minimized by choosing chromosome 2 for analysis.

The work was supported by the Polish Ministry of Scientific Research and Information Technology – project No. 6 P05A 119 20.

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THE EFFECT OF TEMPERATURE ON THE FREQUENCY OF RADIATION-INDUCED MICRONUCLEI IN HUMAN PERIPHERAL BLOOD LYMPHOCYTES

Kinga Brzozowska, Andrzej Wójcik

The impact of temperature on the frequency of radiation-induced chromosome aberrations in the human lymphocytes was first described by Bajerska and Liniecki [1]. We have performed experiments to analyze the impact of blood temperature at irradiation *in vitro* on the level of radiation-induced micronuclei. Blood samples were drawn from two healthy male donors aged 24 and 45 years and irradiated at 0, 20 and 37°C with X-rays (200 kVp, 5 mA, 3 mm Cu filter). The doses were: 0, 1 and 2 Gy for the first donor, and 0, 1.35 and 2.7 Gy for the second donor. Twenty minutes before irradiation as well as during irradiation, the blood samples were incubated at 0, 20 or 37°C. After irradiation, blood samples (0.5 ml) were transferred into 4.5 ml RPMI 1640 medium supplemented with 25%

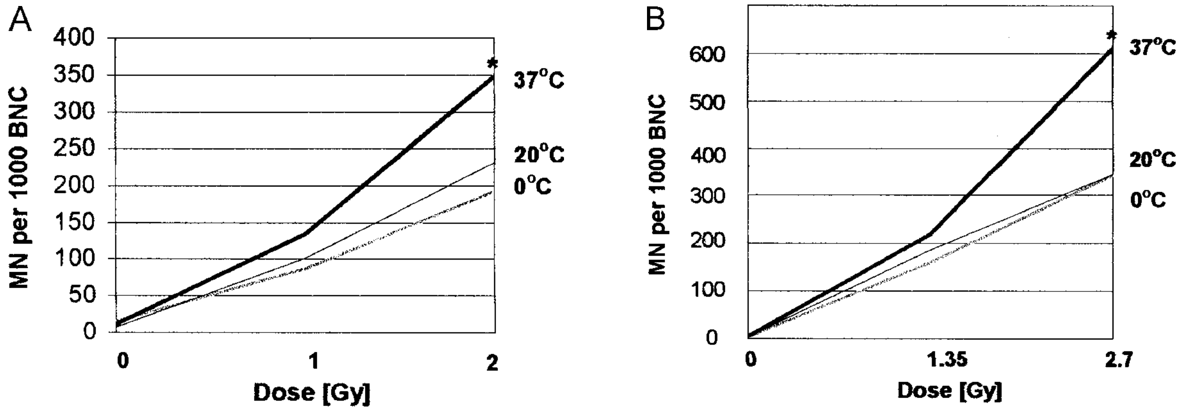

Fig. The dose-response curves for micronuclei (MN) in binucleated cells (BNC) in lymphocytes of the first (A) and second (B) donor. * – the difference significant with $p<0.05$ (Fisher's test for Poisson distribution events).

calf serum, 2.5% PHA (phytohaemagglutinin), anibiotic solution and incubated for 72 h at 37°C and 5% CO$_2$. Lymphocyte preparations for micronuclei analysis were prepared according to the standard method of Fenech [2].

As shown in Fig., temperature of pre-irradiation incubation as well as that during exposure exerts an effect on the frequency of radiation-induced micronuclei in human peripheral blood lymphocytes. The highest frequency of micronuclei is observed for blood samples incubated at 37°C before and during irradiation *in vitro* with doses of 2 and 2.7 Gy. Further work is aimed at elucidation of the mechanism of this effect.

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EGF RECEPTOR KINASE ACTIVITY IS REQUIRED FOR EFFICIENT DOUBLE STRAND BREAK REJOINING IN X-IRRADIATED HUMAN GLIOMA M059 CELLS

Iwona Grądzka, Barbara Sochanowicz, Irena Szumiel

The epidermal growth factor (EGF) receptor (EGFR) is a mediator of both proliferative and survival signals in mammalian cells (reviewed in [1]). Nuclear translocation of EGFR was observed after the ligand binding as well as following the ligand-independent activation. The latter was always linked to exposure to genotoxic stress and it was speculated that it is important for regulation of DNA repair processes [2]. We investigated the effect of EGF and X-irradiation on EGFR activation and translocation to the nuclei in two related human glioma cell lines M059 K and M059 J, the latter highly sensitive to X-radiation due to the lack of a catalytic subunit of DNA-dependent protein kinase (DNA-PK$_{cs}$). Tyrphostin AG 1478 was used as a specific inhibitor to block EGFR tyrosine kinase activity.

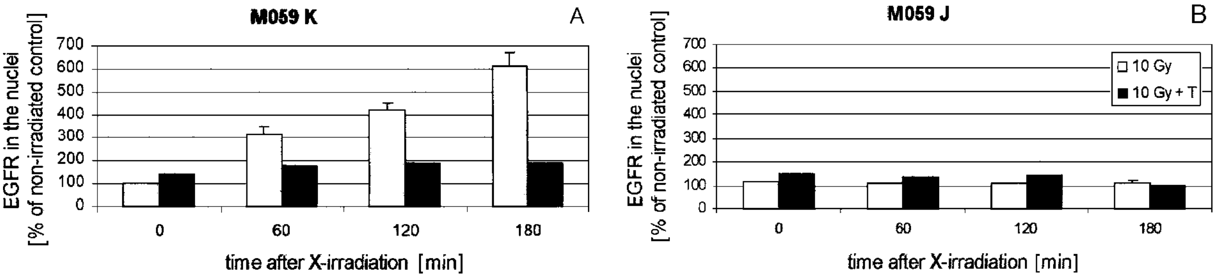

Fig.1. Accumulation of EGFR in the nuclei of M059 K (A) and M059 J (B) cells after X-irradiation with 10 Gy and the effect of tyrphostin AG 1478 (T) on this process.

We found that the total cellular level of EGFR is 3-fold higher in M059 J than in M059 K cells. This correlates with higher resistance of M059 J to tyrphostin AG 1478. Addition of EGF to the cell cultures results both in the increase of phosphorylation status of EGFR (at the position Y1068) and in the receptor translocation to the nuclei. In HeLa cells the EGFR autophosphorylation is the main effect of the stimulation with the ligand. On the contrary, in M059 K and J cells, EGFR translocation to the nuclei prevails over autophosphorylation. Tyrphostin AG 1478 prevents the EGF-induced receptor accumulation in the nuclei of M059 K and J cells (not shown). Thus, the kinase activity of EGFR enables the receptor translocation to the nuclei in the gliomas. In accordance with the results of Dittmann *et al.* [4], in M059 K cells X-irradiation induces EGFR translocation to the nuclei. This process can be prevented by tyrphostin AG 1478 (Fig.1A). In M059 J cells no accumulation of EGFR in the nuclei is observed following X-irradiation (Fig.1B). The data indicate that the kinase activity of EGFR and the presence of DNA-PK$_{cs}$, lacking in M059 J cells, are required for EGFR translocation to the nuclei following the DNA damage.

Double strand break (DSB) rejoining after X-irradiation is faster in M059 K than in M059 J cells because of a defect in a nonhomologous DNA end-joining (NHEJ) in the latter cell line (lack of an important NHEJ component – DNA-PK$_{cs}$) [3]. Tyrphostin AG 1478 slows down the DSB rejoining in M059 K and has no effect in M059 J cells. This suggests a direct link between EGFR kinase activity and DNA-PK-dependent DSB rejoining and is consistent with observation of other authors [3].

The work was supported by the Polish Ministry of Scientific Research and Information Technology – grant No. 3 P05A 013 23.

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DNA INTER-STRAND CROSSLINKS ARE INDUCED IN CELLS PRE-LABELLED WITH 5-BROMO-2'-DEOXYURIDINE AND EXPOSED TO UVC RADIATION

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It has been observed previously that 5-bromo-2'-deoxyuridine (BrdU) potentiates the effect of UVC radiation on the level of sister chromatid exchanges. It is not known which type of DNA damage is responsible for this enhancing effect and we have proposed this to be the DNA inter-strand crosslink (ICL) [1] which, theoretically, may arise in cells that are labelled with BrdU for one round of replication and exposed to UVC radiation. This notion was based on the fact that irradiation of BrdU-labelled DNA with UV leads not only to the formation of a uracilyl radical but also of a bromine atom which can oxidise a purine base of the DNA strand opposed to the uracilyl radical. Thus, two radicals at opposing strands are formed and this can easily lead to the formation of an ICL.

The aim of the present investigation was to verify if ICLs are indeed formed in this irradiation scenario. CHO-K1 cells were pre-labelled with BrdU and exposed to UVC. ICLs were detected by the modified version of the comet assay that relies on the reduction of induced DNA migration in the agarose gel. Carboplatin was used as a positive control. The results fully supported this hypothesis: exposure to BrdU+UVC reduced the level of damage induced by gamma radiation and measured in the comet assay in a manner similar to carboplatin, a platinum compound which is a potent inducer of both ICLs and intra-strand crosslinks.

In order to confirm the results of the comet assay in a different system, we have tested the sensitivity of CL-V4B cells towards BrdU+UVC. These cells have a mutated Rad51C paralog, a key enzyme in the homologous recombination repair [2,3]. Due to this, they are highly sensitive to ICLs [4]. The observation of a high level (as compared to the wild type cells) of chromosomal damage in CL-V4B cells exposed to BrdU+UVC and mitomycin C, but not to UVC alone, substantiates the results obtained with the comet assay (*cf.* Fig.).

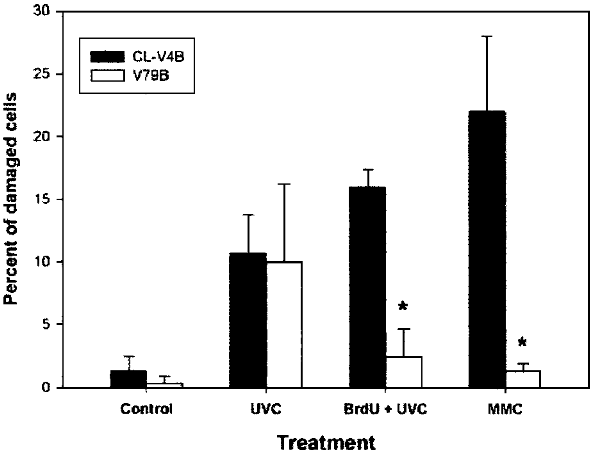

Fig. Percent of cells with chromosomal aberrations following treatment with UVC (60 J m^{-2}), BrdU+UVC (3 J m^{-2}) and mytomycin C – MMC (0.2 μM) in the Rad51C mutants (CL-V4B) and wild type cells (V79B). Error bars represent standard deviations from the results of three independent experiments. * – difference between cell lines significant with $p<0.05$.

Taken together these results clearly show that ICLs are formed in DNA that is pre-labelled with BrdU and exposed to UVC radiation.

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NONHOMOLOGOUS END-JOINING DEFICIENCY OF L5178Y-S CELLS IS NOT ASSOCIATED WITH MUTATION IN THE ABCDE AUTOPHOSPHORYLATION CLUSTER

Kamil Brzóska, Marcin Kruszewski, Irena Szumiel

Recent studies by Block *et al.* [1] indicated that cells expressing DNA-dependent protein kinase (DNA-PK) catalytic subunit (DNA-PK$_{cs}$) with mutated autophosphorylation sites in the so-called ABCDE cluster of serine and threonine residues in the central part of the molecule are defective in the repair of ionising radiation-induced double strand breaks (DSB). The purified mutated DNA-PK proteins, however, had shown in an *in vitro* test the same protein kinase activity as the wild type enzyme and were able to undergo ATP-dependent autophosphorylation and inactivation. Thus, the properties of mutants corresponded with those of L5178Y-S (LY-S) cells (review in [2,3]) which show both phenotypic features that are characteristic of cells with a defective nonhomologous end-joining (NHEJ): a slown down DSB repair and a pronounced G1 phase radiosensitivity. However, in spite of the functional impairment in LY-S cells, the same level of DNA-PK activity is present in total cell extracts of both LY cell lines [4].

It seemed plausible that such an autophosphorylation defect which does not affect kinase activity but is a cause of failure in DNA end-joining is the cause of impaired NHEJ in LY-S cells. Therefore, we examined the Prkdc gene fragment coding the cluster of autophosphorylation sites (ABCDE casette) in search for possible mutations that would affect autophosphorylation the DNA-PK in LY-S cells. LY-R cells served as reference cells. In spite of phenotypic features suggesting the existence of such mutations, no differences were found in size of RT-PCR product (not shown). This, however, does not exclude a point mutation that might cause the loss of autophosphorylation sites. So, we sequenced the region of interest. Again, no differences were found in the sequence of RT-PCR product obtained from LY-R and LY-S cells (Fig.). These results indicate that the defect in NHEJ in the latter cells is not related to the structure of the ABCDE casette.

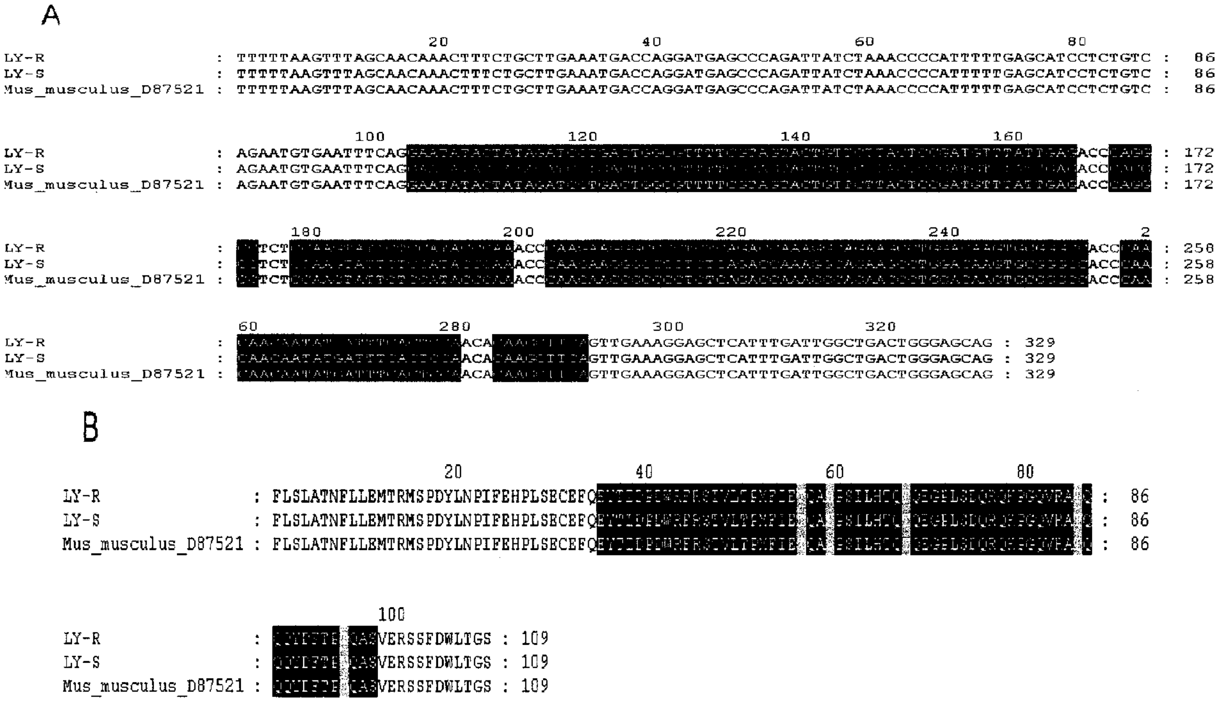

Fig. Nucleotide (A) and predicted amino acid (B) sequences of DNA-PK$_{cs}$ region containing ABCDE autophosphorylation cluster of LY-S and LY-R cells compared with sequence of murine DNA-PK$_{cs}$ ABCDE autophosphorylation cluster (GenBank accesion No. D87521). Exon 58 of DNA-PK$_{cs}$ is highlighted by black background colour, five phosphorylation sites present in murine ABCDE cluster are shown in gray. Nucleotide sequences of DNA-PK$_{cs}$ region containing ABCDE autophosphorylation cluster of LY-S and LY-R cells were deposited in GenBank under the accesion Nos. DQ235257 and DQ235258, respectively.

The work was supported by the Polish Ministry of Scientific Research and Information Technology statutory grant for the INCT.

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SIRTUIN INHIBITION INCREASES THE RATE OF DNA DOUBLE STRAND BREAK REPAIR IN xrs6 CELLS

Maria Wojewódzka, Marcin Kruszewski, Irena Szumiel

Histone deacetylases (HDAC) are an important member of a group of enzymes that modify chromatin conformation. Homologues of the yeast gene *SIR2* (silent information regulator) in mammalian cells code type III histone deacetylases (HDAC III, sirtuins), dependent on NAD$^+$ and inhibited by nicotinamide. It is assumed that in mammalian cells with damaged DNA, HDAC, including certain sirtuins, may modify chromatin structure and thus, alter the accessibility of the damaged sites for repair enzymes [1]. So far, however, there were no data directly confirming the effect of sirtuin inhibition on double strand break (DSB) repair processes in mammalian cells. We investigated the role of sirtuins in DSB repair using two Chinese hamster cell lines: wild type – CHO-K1 and radiation sensitive – DSB repair defective mutant line, xrs6. The latter is defective in DNA-dependent protein kinase (DNA-PK)-mediated nonhomologous end-joining (D-NHEJ) due to the deficiency in Ku80 protein. Here, we present the results of experiments with a specific sirtuin inhibitor – GPI 19015.

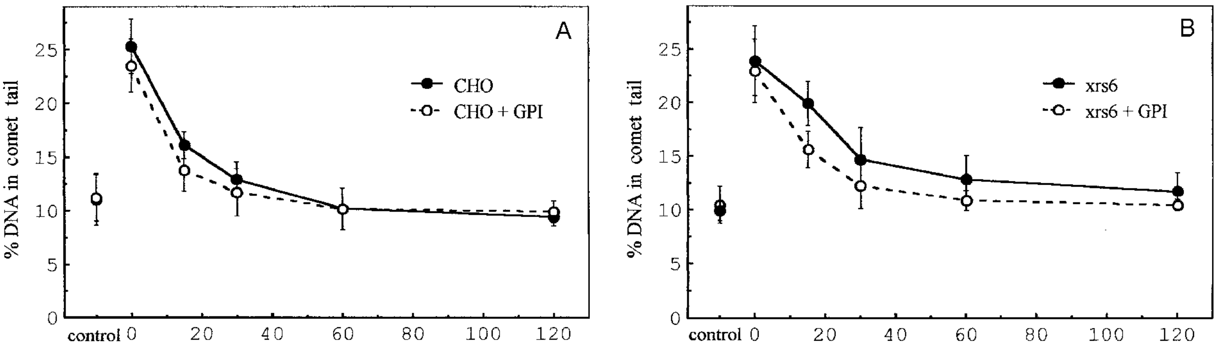

Fig. DSB repair in CHO-K1 (A) and xrs6 (B) cells, untreated or incubated with sirtuin inhibitor, 20 μM GPI 19015, at 37°C for 1 h and X-irradiated with 10 Gy without medium change.

The cells were treated with sirtuin inhibitor 20 μM GPI 19015 at 37°C for 1 h and X-irradiated with 10 Gy without medium change. Using a recently validated neutral comet assay [2], we observed a relatively weak effect of GPI 19015 treatment on the repair kinetic in CHO-K1 cell line, as shown in Fig. In the DSB repair defective mutant cell line, xrs6, the increase in the rate of DSB repair was more pronounced although statistically significant only at the 15 min repair interval ($P=0.048$, $n=3$).

The work was supported by the Polish Ministry of Scientific Research and Information Technology statutory grant for the INCT.

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SHORT-TERM SIRTUIN INHIBITION DOES NOT AFFECT SURVIVAL OF CHO AND xrs6 CELLS

Iwona Buraczewska, Maria Wojewódzka

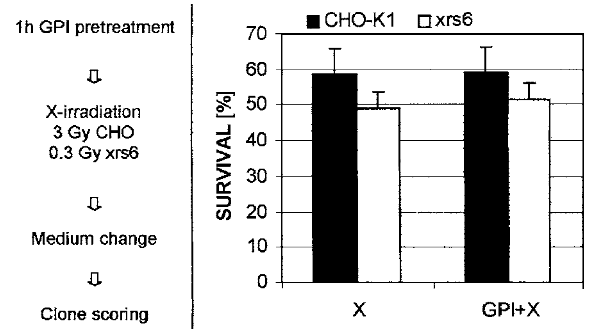

Fig. No effect on clonogenic ability of CHO and xrs6 cells treated with sirtuin inhibitor GPI 19015 20 μM at 37°C for 1 h, X-irradiated with 3 or 0.3 Gy (CHO and xrs6 cells, respectively) and cloned in fresh culture medium.

In the preceding report, we described the effect of sirtuin inhibitor, GPI 19015 treatment on the repair of DNA double strand breaks (DSB) in CHO-K1 and xrs6 cells. In CHO-K1 cells, a relatively weak effect was noted at a 15 min repair interval. In contrast, in the DSB repair defective mutant cell line, xrs6, the increase in the rate of DSB repair was more pronounced. The cells were treated with sirtuin inhibitor 20 μM GPI 19015 at 37°C for 1 h and X-irradiated with 10 Gy without medium change. Applying the same experimental schedule, we determined survival. Here, the cells were cloned in fresh culture medium. This experimental schedule has been targeted on differentiation between effects on DSB repair and the late post-irradiation processes such as pro-apoptotic signalling which is known to depend on sirtuins (reviews in [1,2]). We found that the short treatment with GPI 19015 before and during X-irradiation did not significantly alter survival, as shown in Fig. Prolongation of the treatment until clone scoring, however, did markedly enhance the lethal effect of irradiation (not shown).

The work was supported by the Polish Ministry of Scientific Research and Information Technology statutory grant for the INCT.

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BACKUP NONHOMOLOGOUS END-JOINING IS THE TARGET OF SIRTUIN INHIBITOR

Maria Wojewódzka, Marcin Kruszewski, Irena Szumiel

In the preceding reports, we described the effect of sirtuin inhibitor, GPI 19015 treatment on the repair of DNA double strand breaks (DSB) and survival in CHO-K1 and xrs6 cells. In CHO-K1 cells, a relatively weak effect was noted at a 15 min repair interval. In contrast, in the DSB repair (nonhomologous end-joining – NHEJ) defective mutant cell line, xrs6, the increase in the rate of DSB repair was more pronounced. The cells were treated with sirtuin inhibitor 200 µM GPI 19015 at 37°C for 1 h and X-irradiated with 10 Gy without medium change. Applying the same experimental schedule, we determined survival and found that the short term treatment did not alter the clonogenic ability of both cell lines.

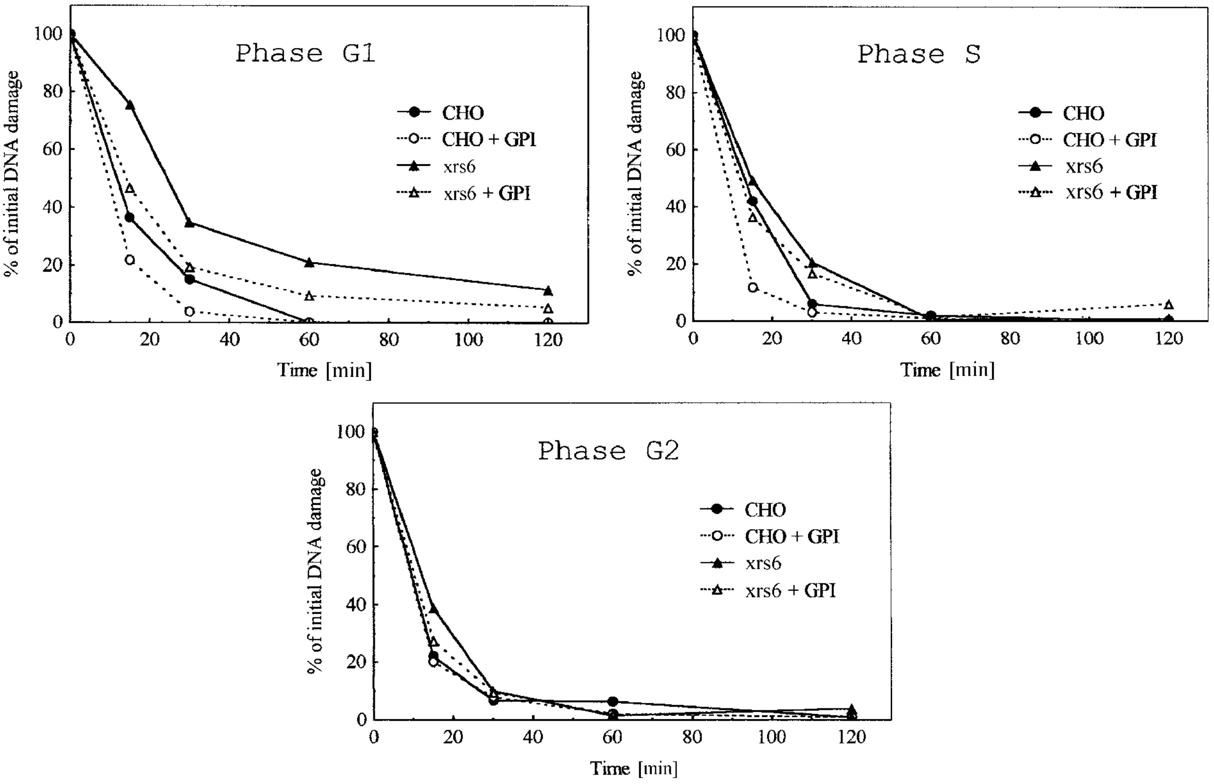

Fig. DSB repair in CHO-K1 and xrs6 cells, untreated or incubated with sirtuin inhibitor, 20 µM GPI 19015, at 37°C for 1 h and X-irradiated with 10 Gy without medium change. The results obtained for single cells in all experiments were pooled and grouped according to the distribution in the cell cycle.

The difference between CHO-K1 (wild type) and xrs6 cells (deficient in DNA-dependent protein kinase – DNA-PK subunit Ku86 and hence, in dependent nonhomologous end-joining – D-NHEJ repair system) became more evident when we evaluated DSB rejoining in different phases of the cell cycle. The results obtained for single cells in each experiment were grouped according to the distribution in the cell cycle. The results shown in Fig. show that at the 15 min repair interval in CHO-K1 the increase in rejoining was most marked in G1 and S phases. Predictably, untreated D-NHEJ-deficient xrs6 cells in G1 phase rejoined DSB much more slowly than the wild type CHO-K1 cells. Nevertheless, sirtuin inhibitor accelerated the repair of DSB in G1 phase at early repair intervals, with the most pronounced effect at 15 min. In xrs6 cells in S and G2 phases the rejoining was improved at 15 min; at later intervals the difference between inhibitor-treated and untreated cells was lost. At these intervals, also the differences between wild type and mutant cells in S and G2 phases disappeared.

The possible reason of this effect may lay in the impaired DNA-PK D-NHEJ in xrs6 cells: DSB repair in these cells has to rely on the homologous recombination repair or DNA-PK independent (backup) B-NHEJ. The latter system is active in cells with impaired DNA-PK dependent rejoining system, D-NHEJ. It was reported by Wang and co-workers [1-3] that B-NHEJ is active in the G1 phase, supressed by DNA-PK, and involves ligase III instead of ligase IV. We conclude that the alternative (backup) route of DSB repair, B-NHEJ, is the DSB repair system affected by sirtuin inhibition to a greater extent than other DSB repair systems.

The work was supported by the Polish Ministry of Scientific Research and Information Technology statutory grant for the INCT.

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NUCLEAR TECHNOLOGIES
AND
METHODS

PROCESS ENGINEERING

SULPHUR ISOTOPE RATIO δ^{34}S IN THE DESULPHURIZATION PROCESSES

Małgorzata Derda, Andrzej G. Chmielewski, Janusz Licki

Major environmental impact of atmospheric sulphur compounds is related to rain acidity, human health, climate, visibility and material corrosion. Very important is the evaluation of economic responsibility for emitted pollution. Therefore, scientists look for a suitable marker which could be used as environmental tracer.

A literature review shows that there are a few data on sulphur isotope ratio in Polish coals and on fractionation of sulphur isotopes in process of coal combustion. Results of preliminary investigations concerning characteristics of the Polish coals are presented [1].

On the basis of this study an investigation was performed for desulphurization process in the Electric Power Station (EPS) Bełchatów [2]. The study concluded that the phenomena which occur during desulphurization process play a major role in the change of sulphur isotopic composition in the outlet gases. This confirms that during the desulphurization process, a fractionation of sulphur isotopes occurs. The sulphur in the outlet gases is depleted in the heavy isotope and the by-product from this process is enriched in the isotope ^{34}S (fractionation factor is lower than 1). This fractionation may suggest that the main process runs in heterogenic conditions (gas-liquid). Therefore, most likely the equilibrium and kinetic processes are responsible for the sulphur isotope fractionation. The condensed phase (liquid, solid) is enriched in the heavier isotope ^{34}S [3].

The desulphurization process was tested at an electron beam/ammonia experimental installation. Sulphur dioxide from the outlet gas was absorbed in hydrogen peroxide solution:

$$SO_{2(gas)} + H_2O \longrightarrow H_2SO_3 \xrightarrow{H_2O} H_2SO_4$$

The sulphate ions produced in this way were quantitatively recovered as barium sulphate by precipitation with barium chloride solution [4].

The product is a mixture of sulphates and nitrogen from ammonium with fly ash. This mixture has been formed as a consequence of irradiation of outlet gases. The product is removed as by-product in the desulphurization process. The obtained results are presented in Table.

Table. Sylphate sulphur in flue gas and the product from desulphurization process [‰].

$\delta^{34}S_{CDT}$ [‰]			α
inlet	product	outlet	
2.59 ± 0.02	3.05 ± 0.04	-5.88 ± 0.02	0.992

The sulphur from the outlet gas was also absorbed to determine sulphur isotope fractionation in the desulphurization process. The sulphates from outlet gases are enriched in the light isotope ^{32}S in comparison to coal which is the fuel in the studied power plants. However, in the case of solid products from the investigated process (gypsum and ammonium sulphate), ^{34}S is enriched in this phase in both desulphurization processes. This method may also be applied to investigate different air pollution control technologies, for example, the method can be used to establish further fate of the by-products *e.g.* elution of gypsum from landfill waste, monitoring of water and investigation of ash leaching.

However, introduction of desulphurization units has changed the isotopic ratio of sulphur in the outlet gas streams. Normally, sulphur dioxide retained in this flue gas is depleted in the heavy isotope 34. These phenomena should be taken into account during the preparation of sulphur balance for the country and region.

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1-CHLORONAPHTHALENE DECOMPOSITION IN AIR USING ELECTRON BEAM IRRADIATION

Andrzej G. Chmielewski, Yongxia Sun, Sylwester Bułka, Zbigniew Zimek

Polychlorinate naphthalenes (PCNs) are persistent and bioaccumulative, some of them are very toxic. 1-Chloronaphthalene was widely used in Xylamits as a wood preservative with fungicidal and insecticidal properties in the past in Poland [1]. 2-Chloronaphthalene was produced and used as a solvent in Poland, some of PCNs were found in polychlorinated biphenyls (PCBs) congeners. Chlorinated hydrocarbons are emitted into atmosphere from medical waste incinerators, waste oil combustion power plants, metallurgical factories, *etc.*

Certain pesticides, PCBs and dioxins are listed as persistent organic pollutants (POPs) based on Stockholm convention. They were banned on usage and will be destroyed in a long term. Electron beam (EB) process was demonstrated as a promising technology to remove chlorinated aliphatic and aromatic compounds from gas phase [2], dioxins [3] and polyacrylic aromatic hydrocarbons (PAHs) from industrial off-gases [4]. Because chemical and physical properties of PCNs are similar to those of PCBs, we selected 1-chloronaphthalene as a studied object. Different gas mixtures influencing the decomposition efficiency of 1-chloronaphthalene were studied in order to examine PCBs' degradation in the future.

A method for the preparation of model gas containing 1-chloronaphthalene can be referred to 1,1-DCE (dichloroethene) [5].

A pulsed electron beam accelerator ILU-6 (2.0 MeV max., 20 kW max.) was used as an irradiation source. Pyrex glass vessels were placed under scan horn of the accelerator for irradiation. Irradiation conditions were the following: pulse repetition rate – 2 Hz, energy – 2 MeV and pulse current – 54 mA. An average absorbed dose rate inside the glass vessel was measured by an N_2O gas dosimeter. The absorbed dose rate inside the glass vessel was 10.835 kGy/min. Total absorbed dose was adjusted by changing irradiation time of the Pyrex glass vessels.

1-Chloronaphthalene concentration was analyzed using gas-chromatography (Perkin Elmer 8700) with a flame ionizing detector (GC-FID) before and after irradiation, respectively. A capillary column (SPB-5, 30 m x 0.32 mm x 0.25 μm, Supelco Company, USA) was used. Stack solution of 1-chloronaphthalene (2000 μg/ml) was used for a calibration curve (Supelco Company, USA). Experiments were carried out at ambient temperature conditions and under atmospheric pressure.

Figure 1 shows the 1-chloronaphthalene decomposition efficiency in air as a function of dose under EB irradiation. Concentration of 1-chloronaphthalene in air decreases with increasing dose. Over 80% 1-chloronaphthalene is decomposed in air at 57.9 kGy dose when the initial concentration of 1-chloronaphthalene was 12-30 mg/Nm^3. In order to investigate whether different gas mixtures have influence on organic compound decomposition under EB irradiation, we studied 1-chloronaphthalene decomposition in N_2 under EB irradiation and the results are shown in Fig.2. Similar to 1-chloronaphthalene decomposition in air, concentration of 1-chloronaphthalene in N_2 decreases with increasing absorbed dose. Over 50% 1-chloronaphthalene was decomposed in N_2 when initial concentration of 1-chloronaphthalene was 15-42 mg/Nm^3. Decomposition efficiency of 1-chloronaphthalene in air was higher than that in N_2, this phenomenon was different from that observed by Kim [6], who claimed that the order of decomposition efficiency of toluene in different gas mixtures was: N_2 > air.

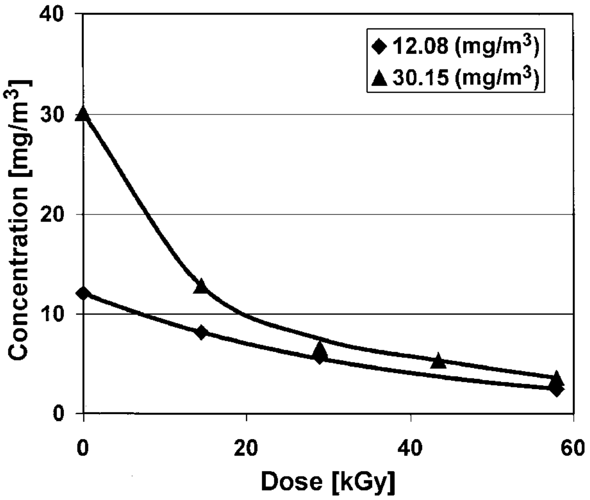

Fig.1. 1-Chloronaphthalene decomposition in air under EB irradiation.

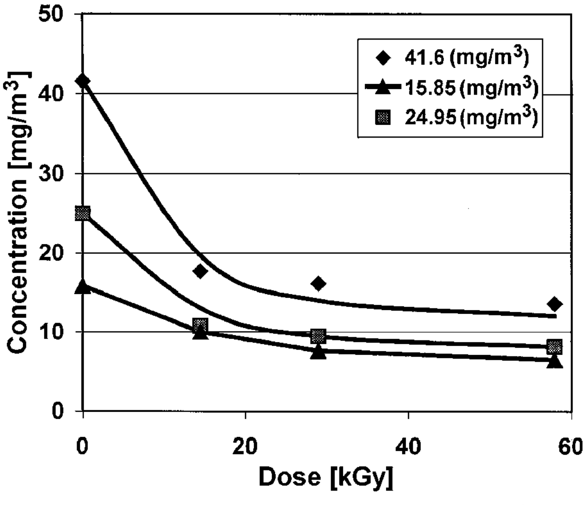

Fig.2. 1-Chloronaphthalene decomposition in N_2 under EB irradiation.

1-Chloronaphthalene can be decomposed in air or N_2 using EB irradiation. Decomposition efficiency of 1-chloronaphthalene in air is higher than that in N_2. Positive charge transfer reactions and OH radicals' reaction may play a main role in 1-chloronaphthalene decomposition process.

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INVESTIGATION OF CATALYSTS FOR CRACKING OF POLYETHYLENE WASTES INTO LIQUID HYDROCARBONS

Bogdan Tymiński, Krzysztof Zwoliński, Renata Jurczyk, Andrzej Darkowski

Plastic wastes contain 65 to 70% polyolefines. Part of them is recycled, but in Poland most of them is dumped in landfill sites. In other countries plastic wastes are burned in incinerators, but this needs very expensive methods for control of pollutant emission in flue gas. Very perspective is the transformation of polyolefines into liquid hydrocarbons, which can be used as a fuel like gasoline and diesel or heating oil. The liquid hydrocarbons can be produced from polyolefines by thermal or thermocatalytic cracking. Thermocatalytic cracking with the use of proper catalyst gives a lower content of gas and coke in the products of decomposition. In our work 11 aluminosiliate catalysts were tested in a laboratory batch reactor connected with a distillation column (Fig.). List of catalysts is given in Table 1. The reactor was loaded with 800 g of polyethylene wastes and 200 g of catalyst. Decomposition products in the form of a gas-vapor mixture separated in the distillation column. Uncondensed gas is burned in a burner. The five side fractions are taken from the distillation column. The reflux from the distillation column containing heavy hydrocarbon is returned to the reactor for decomposition. Solidification point, viscosity, density and normal distillation curves were determined for all fractions. In experiments, temperatures were measured at points of withdrawal of distillates in the distillation column and in the bottom of the reactor in the layer of catalyst and in the top of the reactor in gas phase over the layer of the melted polyethylene wastes. Distillates from the distillation column during the normal distillation process were separated into 3 fractions: gasoline with the boiling temperature up to 200°C, light oil with the boiling temperature ranging from 200 to 350°C and heavy oil with the boiling temperature above 350°C. The properties of the gasoline and light oil fractions are presented in Tables 2 and 3.

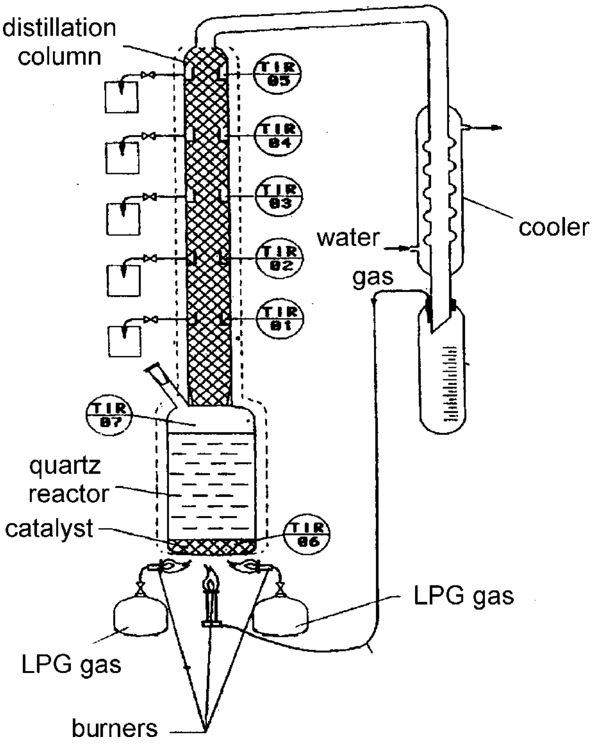

Fig. Scheme of apparatus for waste polyolefines cracking.

Table 1. List of tested catalysts.

Exp. No	Catalyst	Temperature of decomposition [°C]	Fractions [%]			
			gas	gasoline	light oil	heavy oil
1	Without catalyst	400-420	10.2	17.2	43.3	29.3
2	Molecular sieves 4A, balls	398-435	16.0	13.7	48.1	22.0
3	Molecular sieves 5A, Carl Roth	395-410	-	16.7	58.0	25.3
4	$SiO_2 + Al_2O_3$, powder	400-440	11.6	19.5	33.0	35.9
5	Diatomite CECA, powder	370-420	13.6	9.6	40.5	36.3
6	Diatomite polish, powder	420-429	15.2	15.9	27.4	41.5
7	Molecular sieves H-4A, balls	400-412	5.8	13.0	36.7	41.6
8	H-G5, 0,9 nm, X, balls	404-433	34.7	25.2	27.9	10.7
9	H-NK10, 0,4 nm, powder	390-420	15.5	16.1	42.5	26.0
10	Catalyst from Orlen	390-415	-	32.3	41.9	25.8
11	Molecular sieves 5A, extrudes from Mątwy	405-420	-	14.9	61.3	23.8

Table 2. Gasoline fraction.

	% of charge	Sulphur content [mg/kg]	Octane number research	Density [kg/m^3]	Distillation [%]					Olefine content [%]	Content of aromatic hydrocarbons [%]
					to 70°C	to 100°C	to 150°C	end of distillation [°C]	residue after distillation [%]		
Gasoline fraction	20÷26	10÷55	75÷92	736÷747	0÷4.1	1.3÷21.1	41÷81.5	236÷270	1.3÷1.5	40÷66	12÷17
Standard requirements PN-EN 228:2003	-	150	95	720÷775	20÷48	46÷71	min. 75	max. 210	max. 2	max. 18	max. 42

Table 3. Light oil fraction.

	% of charge	Sulphur content [mg/kg]	Cetane index	Density [kg/m^3]	Distillation [%]			Ignition temperature [°C]	Viscosity [mm^2/s]
					to 250°C	to 350°C	95% distillation at a temperature [°C]		
Light oil fraction	39÷49	11÷21	61÷71	796÷809	13÷47	89÷97	337÷370	69÷71	2.9
Standard requirements for diesel oil PN-EN 590:2002	-	max. 350	over 46	820÷845	max. 65	min. 85	max. 360	over 65	2.0÷4.5 at 40°C
Standard requirements for heating oil EKOTERM	-	max. 2000	-	below 860	max. 65	min. 85	-	56	below 6.00 at 20°C

A NEW-TYPE MEMBRANE MODULE REDUCING THE FOULING AND BOUNDARY LAYER PHENOMENA

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Membrane processes become common techniques in nuclear technologies nowadays. Various membrane methods were applied in nuclear centers in the world, including full-scale installations operated in continuous mode and cleaning different kinds of radioactive waste. One of the serious problems of pressure driven membrane processes is the permeate flux decline that occurs in time of operation of filtration systems. The phenomena responsible for this are concentration polarization and progressive fouling of the membranes that implicate the regular cleaning of the membranes and interrupting the processing. One of the effective methods of fouling minimization is the regulation of hydrodynamic conditions in the module. This can be attained by the use of special baffles in the apparatus, which improve mass exchange conditions or by the application of pulse flow. The application of Taylor flow creating the vortices by the use of movable parts that results in self-cleaning effect of the membrane surface, was considered, as well. The SpinTek Membrane Technology based on rotating membrane discs was successfully tested in the Los Alamos Nuclear Laboratory and its implementation for the processing of the U.S. Department of Energy (DOE) tank radioactive waste was considered [1,2].

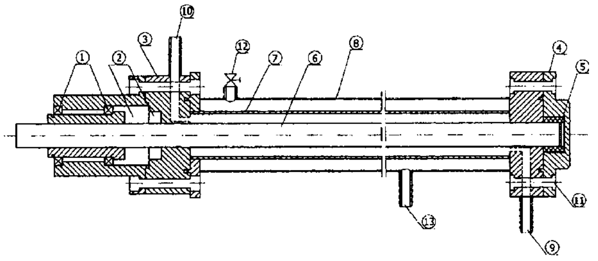

Fig. A scheme of the helical membrane apparatus for radioactive waste processing: 1 – ball bearings, 2 – seal gap, 3 – front shield, 4 – shield with the socket, 5 – socket, 6 – rotor, 7 – tubular membrane, 8 – housing, 9 – feed inlet, 10 – retentate outlet, 11 – clamping screw, 12 – vent, 13 – permeate outlet.

A new membrane contactor with helical Couette-Taylor flow (CTF) in the annular space between the tubular membrane and the surface of rotating shaft (Fig.) was applied to separate radioactive compounds after precipitation or complexation by macromolecular ligands. CTF is a combination of the axial Poiseuille flow and the rotating Couette flow with axisymmetric Taylor vortices. Such a combination results in limited axial dispersion coefficients in relation with dispersion coefficients in other directions, independence of intensity of mixing on residence time in the apparatus and good transport parameters.

The new construction of the membrane apparatus that changes the hydrodynamic conditions in the module and promotes turbulence, allows increasing efficiency of separation and reduction of the membrane fouling. The advantages of helical apparatus with porous tubular membrane are expected in:

- simplicity of the construction in comparison with dynamic filtration by use of rotating discs;
- high mass transfer coefficients to the membrane surface;
- good effects of mixing, especially when the rotor is asymmetrically assembled or pulse flow is applied;
- the possibility of replacement of the rotating shaft by spiral insert creating helical flow.

The experiments with suspensions of different concentration were carried out in static and dynamic conditions. The apparatus can be used as a filtration stage after formation of precipitate or metal complexes, as well as a membrane contactor in the process of solvent extraction used for radioactive waste processing [3].

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GROUNDWATER MONITORING IN THE AREA OF OPENCAST BEŁCHATÓW

Robert Zimnicki, Wojciech Sołtyk, Małgorzata Derda, Andrzej G. Chmielewski, Andrzej Owczarczyk

Groundwater analyses in the area of the opencast lignite mine Bełchatów and Szczerców have been continued since 2000. The field work contains analyses of macro- and microion concentrations as well as measurements of tritium, radon-222 and mean radioactivity (^{40}K). Complementary to these analyses, isotope ratios of $\delta^{34}S/^{32}S$ and $\delta^{18}O/^{16}O$ in SO_4^{2-} ion and δD in water have been investigated.

Table 1. Changes of tritium concentration during investigated exploitation period.

Year	2000	2001	2002	2003	2004
Groundwater layers	Tritium concentrations [TU/dm^3]				
Below-coal layers	4.6	3.96	2.99	2.98	3.1
Above-coal layers		3.1	2.43	7.68	4.7

In 2005, the groundwater properties and quality in the area of Szczerców opencast have been investigated. Samples of water from boreholes and drains were taken and analyzed. It was found that the groundwater was not polluted, its quality and purity being in agreement with the approved groundwater purity standards. The drain system work forced the groundwater flow, this being the reason for decreasing of tritium concentrations (Table 1) (the water age is increasing) also the radon-222 concentration is decreasing (Table 2) (this being an effect of ascense flow through fissures in the above-coal layer) [1,2]. The locally redox properties were changed (Fig.). Isotope ratios in SO_4^{2-} ion confirms that these processes are running in the above-coal layers, without any contact with atmospheric oxygen, causing simultaneous changes in tritium activity (layer flow indicator).

Table 2. Mean radon-222 concentration changes in groundwater during investigated exploitation period.

Year	Number of analysis	Mean activities [Bq/dm^3]
2000	13	7.5 ± 2.4
2001	24	8.2 ± 5.3
2002	24	12.7 ± 12.0
2003	24	13.5 ± 13.3
2004	31	12.6 ± 10.6

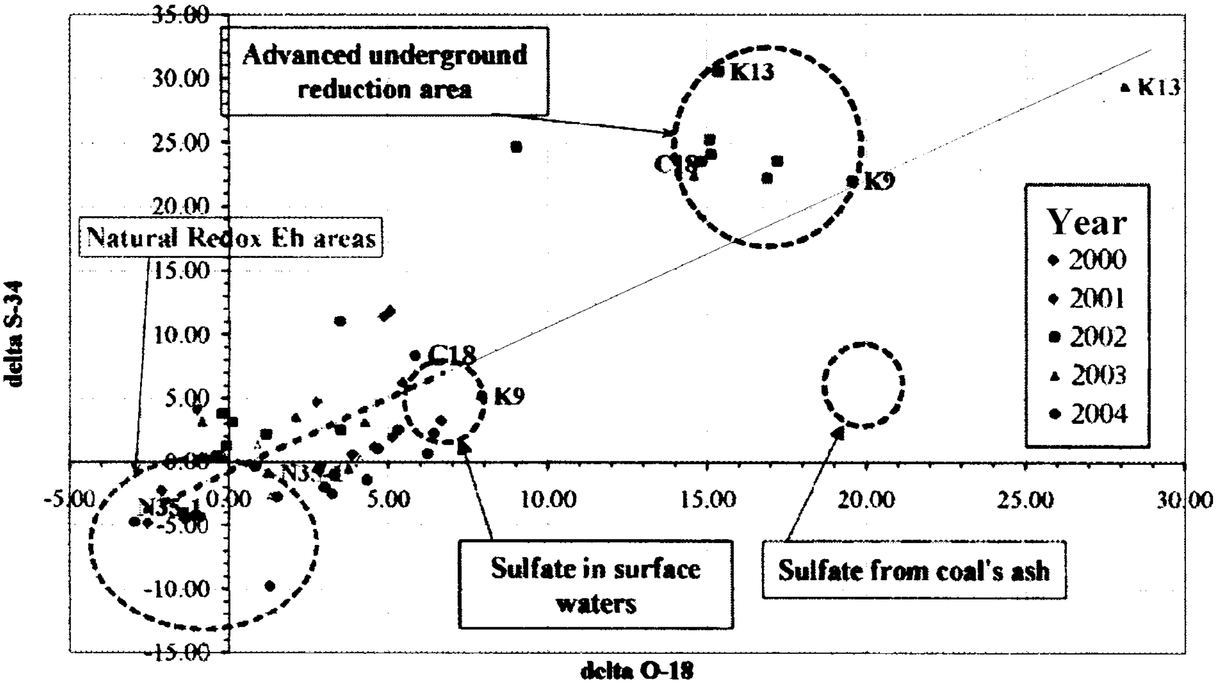

Fig. Relationship of $\delta^{34}S$ and $\delta^{18}O$ in SO_4^{2-} ion concentration in groundwater in exploitation area.

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WATER ISOTOPE COMPOSITION AS A TRACER FOR STUDY OF MIXING PROCESSES IN RIVERS. PART II. DETERMINATION OF MIXING DEGREES IN THE TRIBUTARY-MAIN RIVER SYSTEMS

Andrzej Owczarczyk, Ryszard Wierzchnicki, Robert Zimnicki, Sylwia Ptaszek, Jacek Palige, Andrzej Dobrowolski

Two river-tributary systems have been chosen for the investigation of mixing processes. These are: the Narew River-the Bug River-Zegrzynski Reservoir and the Bugo-Narew River-the Vistula River.

Fig.1. Localization of measuring profiles in the Vistula River down to the Bug-Narew confluence profile.

Preliminary results of water isotope compositions in each river exhibit a significant differences in δD and $\delta^{18}O$. The observed differences were, an average in the measuring season (May-October), 0.5±0.1 and up to 6±0.5 for $\delta^{18}O$ and δD, respectively. Because the error/value ratio is better for δD measurement, we decide to use this parameter (not $\delta^{18}O$) as a tracer.

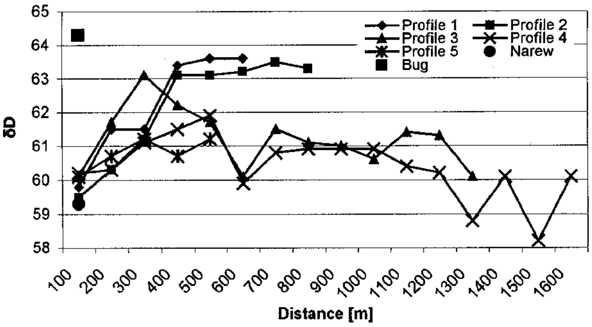

Fig.2. δD distribution as a function of distance from the right bank of Zegrzynski Reservoir (down to Bug and Narew rivers confluent line) (07.09.2004).

Table 1. Mixing degrees in the Bug River-Narew River system.

Bug and Narew rivers	Date					
	08.07.2004		07.09.2004		21.10.2004	
Profile – distance from injection	Distance from injection [m]	M ($Q=145.1\ m^3/s$)	Distance from injection [m]	M ($Q=155.3\ m^3/s$)	Distance from injection [m]	M ($Q=165.2\ m^3/s$)
Profile I	2831	0.1497	2738	0.2475	2801	0.5419
Profile II	5062	0.5558	5130	0.2667	5003	0.6691
Profile III	8065	0.7881	7809	0.7142	7553	0.7718
Profile IV	9803	0.752	10124	0.764	9482	0.904
Profile V	10456	0.703	10800	0.871	11154	0.945

In both river systems, several profiles have been selected down to the tributary confluent line (Fig.1). The water samples have been taken 1.5 m below the water table every 25 m across each profile. A sampling pump was connected to the measuring boat. Each sample position has been precisely determined by means of GPS. Then, the δD_i have been measured in IRMS (isotope ratio mass spectroscopy). The δD distributions in selected profiles have been shown in Figs.2 and 3 for both investigated river systems.

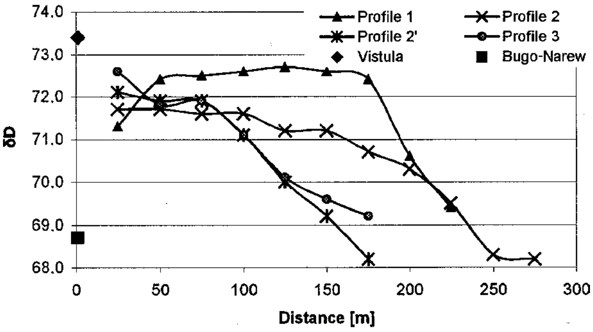

Fig.3. δD distribution as a function of distance from the right Vistula River bank (13.07.2005).

On the basis of the obtained data the mixing degree of river water has been calculated as

$$M = 1 - \left[\frac{1}{N-1} \sum_{i=1}^{N} \left(1 - \frac{C_i}{\bar{C}} \right)^2 \right]^{1/2}$$

Table 2. Mixing degrees in the Bugo-Narew River-Vistula River system.

Bugo-Narew and Vistula rivers	Date			
	14.06.2005		13.07.2005	
Profile – distance from injection	Distance from injection [m]	M ($Q=1083\ m^3/s$)	Distance from injection [m]	M ($Q=487.3\ m^3/s$)
Profile Ia	498	0.0963	-	-
Profile Ib	497	0.1912	673	0.2604
Profile Ic	503	0.2149	-	-
Profile II	1515	0.4983	1920	0.5370
Profile II'	2490	0.5204	3875	0.5566
Profile III	3930	0.7104	8765	0.7587

where: M – mixing degree (1 means the entire mixing across the profile); i=1, 2, 3...N; $\bar{C}$ – mean value of C_i for given profile; $C_i=\Delta\delta D_0 - \Delta\delta D_i$ ($\Delta\delta D_0=|\delta D_M - \delta D_T|$, $\Delta\delta D_i=|\delta D_M - \delta D_i|$, δD_i – means isotope composition δ in the i point at measuring profile).

δD_M and δD_T means isotope composition expressed as

$$\delta D = \left[\frac{(D/H)_{sample} - (D/H)_{standard}}{(D/H)_{standard}}\right] \times 1000$$

for main river and tributary, respectively, where $(D/H)_{standard}$=SMOW (standard mean ocean water).

The values of mixing degrees calculated for both investigating river systems have been shown in Tables 1 and 2.

Presented results will be applied for the verification of the mathematical model for transport and mixing in river systems. They could also be a basis for forecasting a pollutant transport and for the evaluation of ecological hazard, for example, for potable water intakes localized in the area of their interaction. Modeling and simulations of mixing and transport processes will be supported by GAMBIT software.

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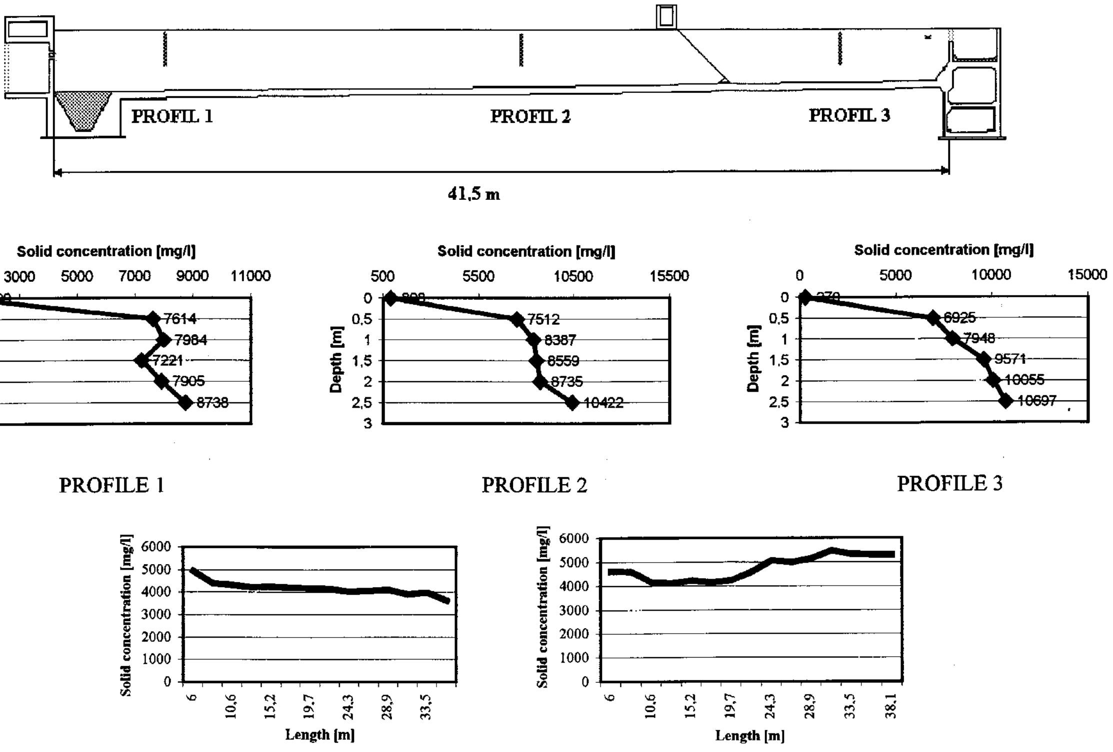
CFD AND RTD METHODS FOR WASTEWATER TREATMENT PLANTS APPARATUS INVESTIGATION

Jacek Palige, Andrzej Owczarczyk, Andrzej Dobrowolski, Sylwia Ptaszek

Two methods, residence time distributions (RTD) and computational fluid dynamics (CFD) are most effective for solid and wastewater phases investigations of flow dynamics.

Many apparatus of wastewater treatment plants such as equalizers, clarifiers, settlers, aeration tanks and equalizer-mixers were investigated using the tracer method with application of Br-82, Tc-99 and fluoresceine as tracers. On the basis of measured (in tracer experiment) RTD function, the model of flow can be proposed for the unit under investigation. The experimental and numerical RTD functions were compared for different technological parameters values of processes (apparatus geometry, flow rate, location and construction of input and output). Numerical RTD function was obtained by DRW (discrete random walk) technique – determination of residence times of many liquid particles.

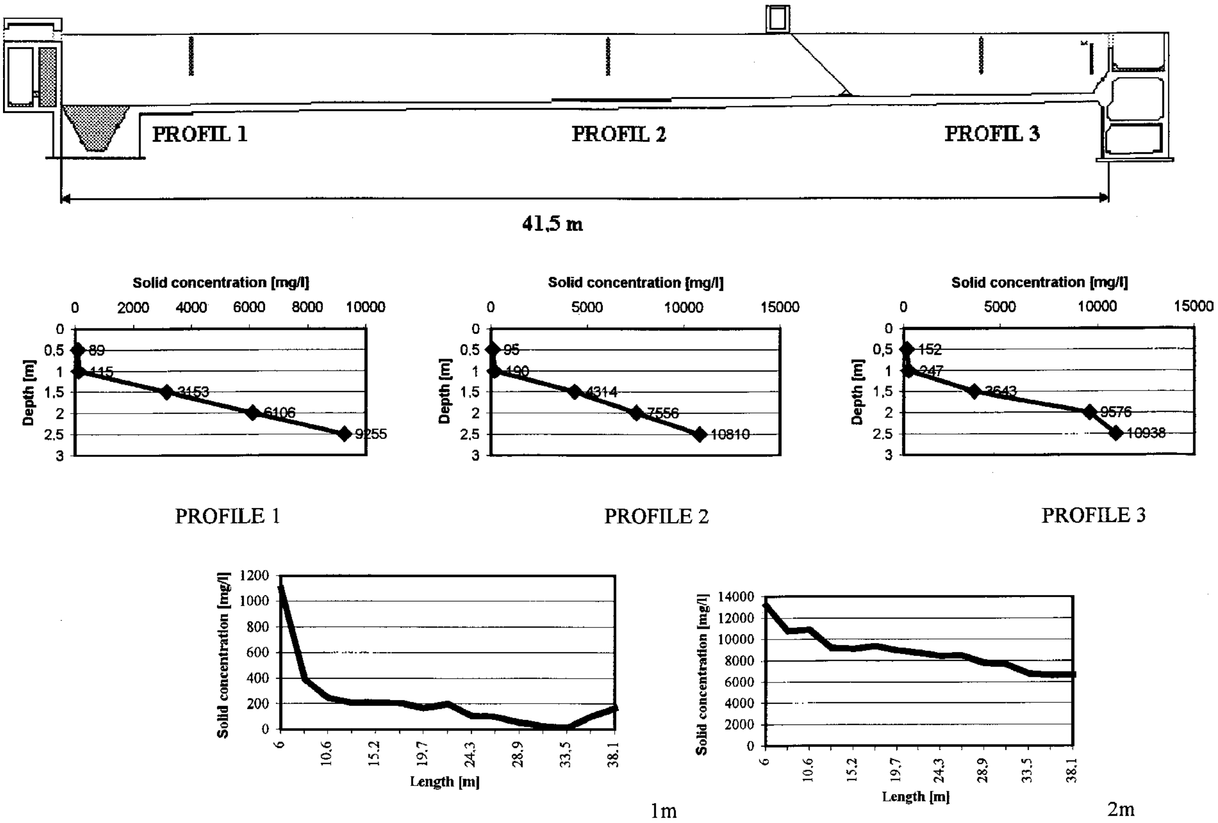
Two types of input flow organization in settling tanks – immersed multitubing system and surface overflow – are operating at industrial wastewater



1m 2m

Fig.1. Distribution of solids concentration in profiles at 7, 23, 38 m from the wastewater input as a function of depth and in the axis of settler on the depth 1 and 2 m below water table – settling tank with immersed multitubing input system.

treatment plants. Our task was to decide which one generates a flow structure assuring better sedimentation conditions and ensure a higher sediment removal efficiency. For this reason, the sediment concentrations in both types of settlers have been measured (1 and 2 m below water table in the axis of the settler and in profiles at 7, 23, 38 m from the wastewater input as a function of depth), Figs.1 and 2. The best results have been obtained for overflow input where no stream constituents were observed disturbing the sedimentation in the vicinity of sediment collecting funnel, for removing the settled particles, contrary to the immersed input. Visualization of the observed flow structure in the settler with immersed input is presented in Fig.3. Taking into account a real flow pattern, the optimal inlet organization geometry has been proposed on the basis of CFD calculations (using numerical code of FLUENT software).



PROFILE 1 PROFILE 2 PROFILE 3

1m 2m

Fig.2. Distribution of solids concentration in profiles at 7, 23, 38 m from the wastewater input as a function of depth and in the axis of settler on the depth 1 and 2 m below water table – settling tank with surface overflow.

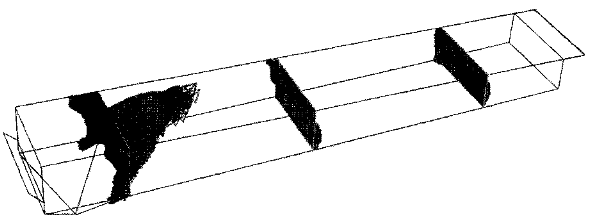


Fig.3. Visualization of the flow structure in settling tank with immersed multitubing input system.

The usefulness of these techniques was checked on a large scale laboratory model of settler. Satisfactory agreement of the data obtained by both methods – tracer and CFD – was observed. A comparison of experimental and numerical RTD functions is presented in Fig.4.

The presented above methods have also been used for checking the operation correctness of equalizer-mixer. Its task was to equalize the pollutants load (delivered from the factory with four tubing collectors) and sending equal portions to each of the parallel operated sections of wastewater treatment plant. Tracer methods have been used for apparatus examination. Different inlet stream were selectively investigated by fluoresceine injection as a tracer. The uncorrected apparatus operation has been stated. CFD simulation for flow hydrodynamic improvement in equalizer-mixer was

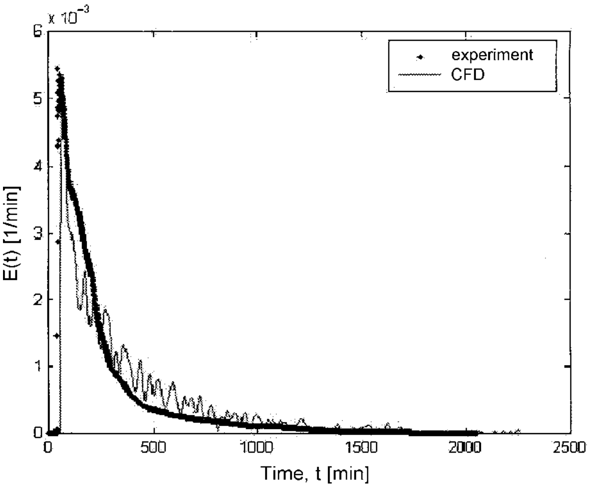


Fig.4. The comparison of experimental and numerical RTD functions for settling tank with surface overflow.

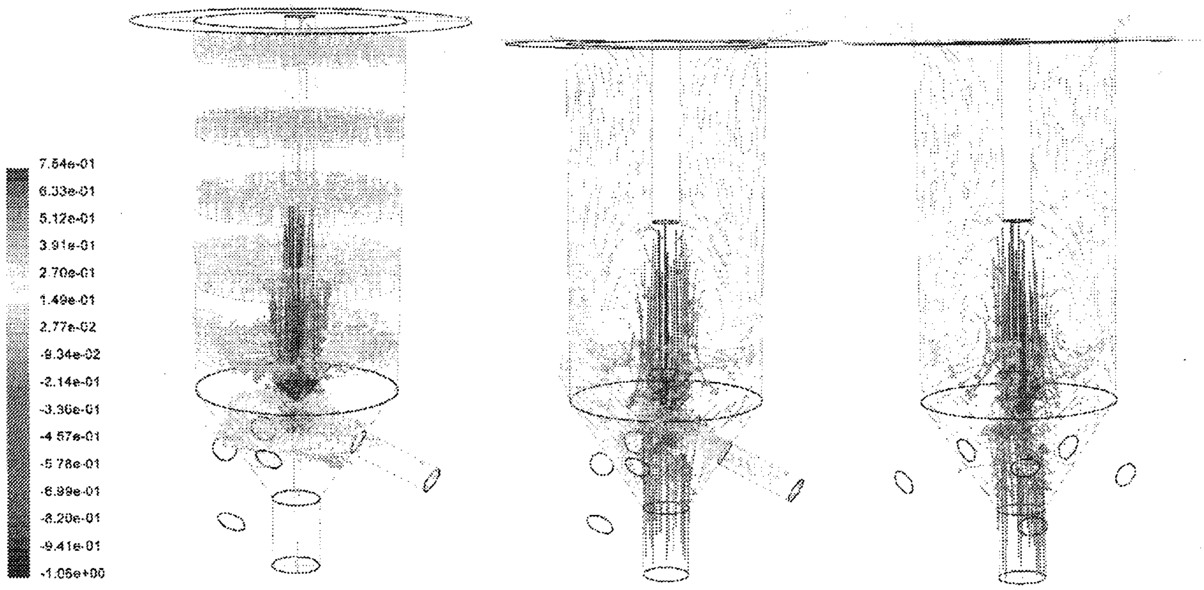


Fig.5. The final results of flow hydrodynamic modeling in equalizer-mixer (CFD simulations).

done. The final results of wastewater flow structure optimization in the mixer, proposed for industrial realization, are presented in Fig.5.

Both the RTD and CFD methods are complementary. The numerical simulation of complex system by CFD is a powerful tool for visualization of processes. But obtained results should be always validated by the tracer RTD measurements. Application of both techniques to solution of problems arised in industry, especially connected with construction optimization significance of apparatus is important and very often of decisive.

MATERIAL ENGINEERING, STRUCTURAL STUDIES, DIAGNOSTICS

APPLICATION OF INAA TO IDENTIFY LEAD WHITE IN ICONS FROM THE 15th-18th CENTURIES FROM SOUTH-EASTERN POLAND

Ewa Pańczyk, Jarosław Giemza[1/]**, Lech Waliś**

[1/] The Castle Museum in Łańcut, Poland

The purpose of the work was to analyse lead white from icons of the 15th-18th centuries, collected in the Orthodox Art Department at the Castle Museum in Łańcut, using the neutron activation analysis (NAA) method. These tests allowed to identify concentration of trace elements in collected samples. The achieved results provided a basis for the conclusion that lead white from analysed icons demonstrates specific common characteristic features and differs from lead white from panel paintings from the Małopolska and Silesia regions. Identifying similarities and differences in the applied lead white would allow to create a "map" of its common features and in the future would support the territory identification of the pigment, as well as the age, origin and authenticity of an object under examination.

Lead white is a pigment most frequently used for determining trace elements. This is due to its features; having been varnished, lead white is resistant to degradation and additionally, it is one of the most frequently used pigments for the last twenty centuries. Also, in the case of icon painting, lead white is the only known white pigment used until the 19th century [1-3].

The lead production process changed over time and the analysis of impurities in the pigment can be used to identify approximate date of its production.

There are three potential methods for physical and chemical classification of lead white:

- test of changes in the level of impurities by analysing concentration of elements,
- test of changes in ^{206}Pb/^{204}Pb isotope ratio,
- analysis of crystal structure modification.

The crystal structure and the level of main impurities are typical of the production method, while the isotope ratio and trace impurities are related to the origin of the mineral. Consequently, the analysis of trace elements allows to determine the time of the painting creation and its origin. Additionally, it is possible to identify repainting and conservation activities, which is of key importance to historians of art.

Based on to date quantitative analysis of trace elements in lead white collected from paintings from the 15th-19th century, it can be concluded that lead white from regions south to Alps, found, inter alia, in Venetian paintings, shows a higher content of copper and manganese and lower content of sliver and antimony than lead white from regions north to Alps, applied in northern Europe [4-6].

The analysis included selected icons dated from the 15th-18th century from the Orthodox Art Department at the Castle Museum in Łańcut. Eighteen icons were selected for the analysis, from which samples of lead white were collected. Table includes the description of the collected samples. Collecting a sample including pure lead white in the case of paintings such as icons is very difficult due to the lavish gilding. 1-3 samples from each object, with a mass from 0.1 to 1 mg were collected after removing the varnish, from the top lights, in order to ensure that they include pure lead white without other pigment additives.

The analysis of lead white samples was carried out using the instrumental NAA (INAA) method without chemical separation, using standards of analysed elements. After weighing and sealing in quartz ampoules, samples were packed in packages including seven samples each together with 47 standards of determined elements such as Na, K, Sc, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga ,Ge, As, Se, Br, Rb, Sr, Zr, Mo, Ru, Ag, Cd, Sn, Sb, Te, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Yb, Lu, Hf, Ta, W, Ir, Au, Hg, Th and ^{238}U. Small volumes (0.001 ml) of solutions of appropriately grouped elements were placed in quartz ampoules, evaporated to dryness and sealed. Zinc (1 mg), tin (10 mg), iron (10 mg) and nickel (1 mg) standards were additionally wrapped in an aluminium film. Additionally, scandium and gold standards were attached to every sample series, to act as the monitor of thermal neutron flux.

Samples were irradiated in the MARIA reactor in Świerk, in a channel with a 8×10^{13} n/cm^{2}s thermal neutron flux. Samples were irradiated for 24 h and cooled for 8 h. Irradiated samples after taking out from the package were washed with an HCl 1:1 solution and then with alcohol to remove surface contaminations. Standards were washed out from ampoules or, in the case of scandium and gold, dissolved together with the aluminium film

Table. Description of the analysed samples.

Sample number	Catalogue number	Author	Icon	Dating
I	S.12011	unknown	Mandylion, Owczary	15th century
II	D.990 MŁ	unknown	St. Paraskevi Tyrnowska, Korytniki	end of 15th century
III	S.12296 MŁ	unknown	Pantocrator, Świątkowa Wielka	15th-16th century
IV	MZŁ-SZR-1026	unknown	Archangel Michael and St. George, Wola Wielka	15th-16th century
V	MZŁ-SZR-819	unknown	Hodigitria, Świątkowa Wielka	about 1550
VI	WS-2193	unknown	Tsar's Gate, Krościenko	16th century
VII	MZŁ-SZR-821	unknown	Pantocrator, Świątkowa Wielka	about 1550
VIII	MZŁ-SZR-987	unknown	The Christ Baptism, Korytniki	16th century
IX	MZŁ-SZR-979	unknown	The Last Judgment, Korytniki	16th century
X	MZŁ-SZR-849	unknown	St.Nicolas, Łodyna	16th century
XI	S.12191 MŁ	unknown	Archangel Michael, Brzeżawa	16th century
XII	MZŁ-SZR-813	unknown	Pantocrator, Tyniowice	17th century
XIII	MZŁ-SZR-1551	Jacenty Rybotycki	St. Cosmas and Damian, Kotań	1691
XIV	MZŁ-SZR-1570	Jacenty Rybotycki	Pantocrator/Tsar's Gate, Kotań	1689
XV	MZŁ-SZR-1567	Tymotej Rybotycki	Deesis (The Apostles), Kotań	1673
XVI	MZŁ-SZR-908	Ioan malarz Hyrowski	Deakon's Gate, Pielgrzymka	1660
XVII	S.12061 MŁ	unknown	St. Paraskevi Piatnica, Surochów(?)	17th-18th century(?)
XVIII	MZŁ-SZR-2185	unknown	Deesis (The Apostles), Smolnik	

and then predefined volumes from obtained solutions (0.01-0.1 ml) were drawn to glass flat measuring vessels and evaporated to dryness.

Measurements of activity of the samples and standards prepared in such a way were carried out using an HP germanium detector with an active volume of 80 cm^3 and an energy resolving of 1.95 keV for 1333 keV ^{60}Co. The detector cooperates with a S100 Canberra analyser, controlled by IBM/PS-2. The analysis of complex gamma radiation spectra was carried out using a micro-SAMPO program. Eight measurements for each sample were performed. Forty elements were identified and determined in the analysed samples.

Ultimately, 28 elements were selected for a multi-parameter statistical analysis aimed at identifying the degree of similarity of analysed icons. The clustering analysis using STATISTICA (StatSoft) program was carried out to identify the similarity degree of analysed objects. Distances between objects in the characteristic space (space dimension equals the number of characteristic features) are a direct point of entry for the clustering analysis. Every object can be described using some features that can be presented as real numbers – in our case it was the concentration of elements in the particular lead white sample. Similarity between the analysed samples can be determined based on the distribution of points in multidimensional space. Hierarchical object clustering methods are used most frequently. This allows to obtain a structure arranged in a hierarchy, with increasing distance corresponding to decreasing similarity. The result is presented in form of a dendrogram (clustering tree). The clustering analysis was carried out for standardised variables.

The clustering analysis for all the tested 18 icons was carried out. Results of this analysis are presented in Fig., which clearly shows division into groups closely related to chronology of tested icons. Icons from the 15th and 16th centuries are much more alike than icons from the 17th and 18th centuries. Probably, the applied lead white was obtained from different sources that had changed over time. Icons from the workshop of Jacenty and Tymotej Rybotyccy (St. Cosmas and Damian – marked as XIII on the diagram, Pantocrator – marked as XIV and Deesis – marked as XV) are much the same, which indicates that they used lead white from the same source.

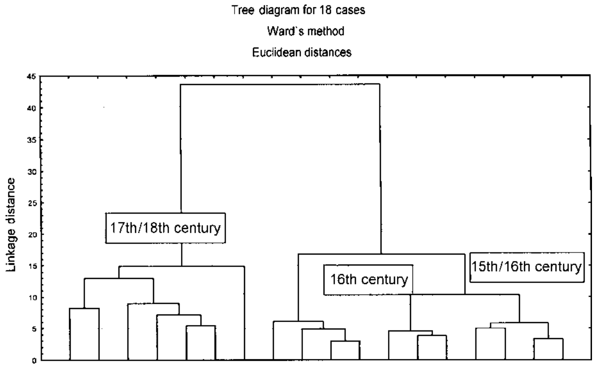


Fig. Cluster analysis of 18 analysed icons described 28 features (feature number = determined element number); standardised variables.

The aforementioned comparisons indicate that lead white used in the analysed icon paintings, constituting a unified, very typical group that had undergone changes with time. Further qualification will be feasible after obtaining the database from lead white analysis of icons from other centres, such as the Ukraine or Slovakia. As a result, it would allow to compare characteristic features of lead white used in important regions of icon paintings.

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TITANIUM DIOXIDE AND OTHER MATERIALS COATED WITH SILICA-QATS COMPOUNDS AND METALLIC SILVER AS POTENTIAL BIOCIDES AND PHOTOCATALYTIC BIOCIDES

Andrzej Łukasiewicz, Dagmara K. Chmielewska, Jacek Michalik

The photochemical and photocatalytic properties of TiO_2 have been the subject of intensive investigations in recent years [1-3]. One of the methods applied in order to enhance the efficiency of photocatalytic properties is coating or dopping the material with noble and transition metals [4,5].

Silica materials elaborated by coating of TiO_2 or other carriers (*e.g.* dolomite) with salt of water glass (WG) and quaternary N-alkylammonium compound (QAC) were described previously [6]. In course of this research it was found out that TiO_2-WG·QAC materials bind Ag^+ from aqueous solutions and after UV irradiation reduction of silver takes place. Photochemical reduction of Ag^+ in these materials is much faster than for pure TiO_2, what suggests strong photochemical properties of TiO_2-WG·QAC. Silver is also an antibacterial agent with an exceptionally broad spectrum of bacteria, so due to additional binding of silver in the material a synergic effect occurs and a higher antibacterial activity of the materials can be obtained.

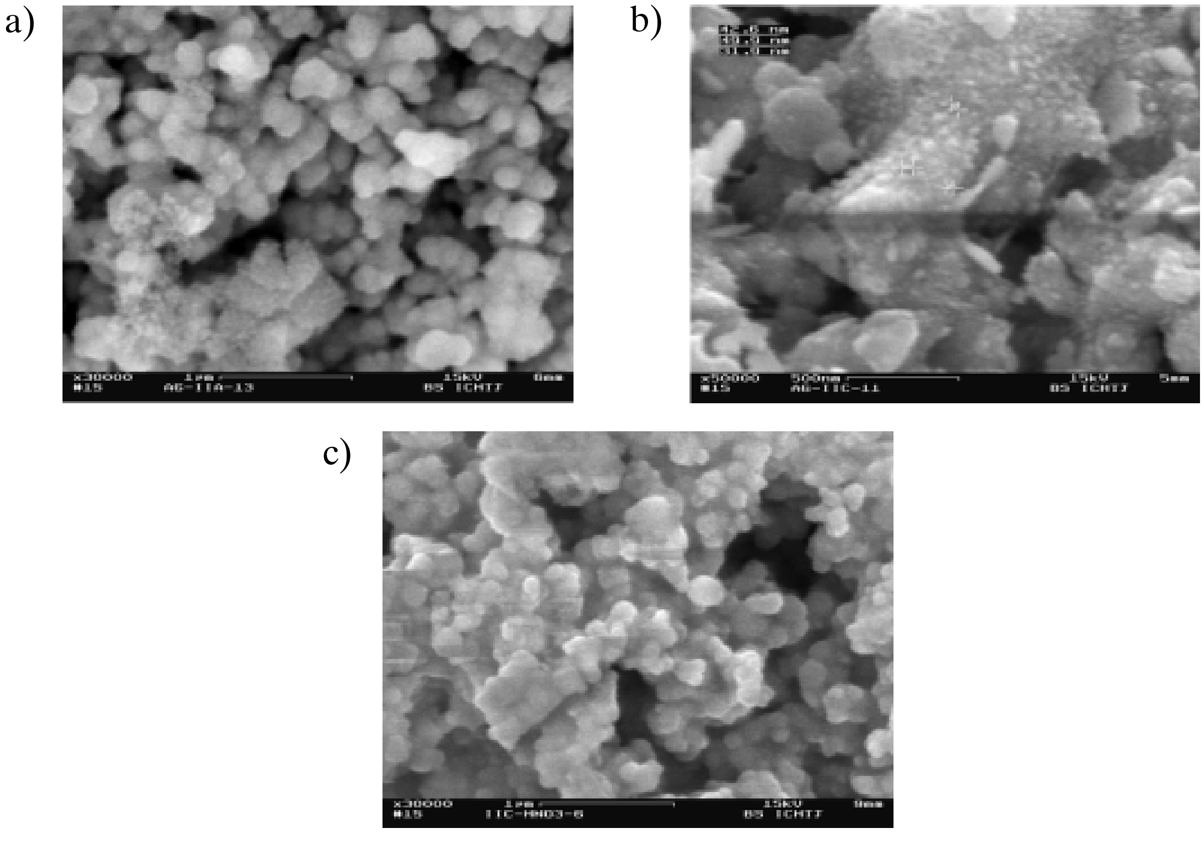

Fig. SEM photomicrograph of: TiO_2-WG·QAC material (a), TiO_2-WG·QAC material with silver coating after UV irradiation (b), TiO_2-WG·QAC material with silver coating after UV irradiation and HNO_3 treatment (c).

Preliminary electron paramagnetic resonance (EPR) spectroscopy and scanning electron microscopy (SEM) investigation of the materials were carried out. SEM investigations suggest that metallic silver creates 30-50 nm particles on the biocidal materials grains. Three SEM images for non-modified TiO_2-WG·QAC material, the material with silver coating and UV irradiation and the same material after HNO_3 treatment that caused silver coating dissolution, are presented in Fig.

The combined system TiO_2 photocatalyst–WG-QAC photocatalyst demonstrates particularly interesting effects. TiO_2-WG·QAC in comparison to pure TiO_2 significantly accelerates the reduction of Cr^{6+} to Cr^{3+}, it suggests photochemical synergism of TiO_2 bound with WG-QAC. Taking into account preliminary results, TiO_2 materials coated with WG-QAC seem to be very perspective to be applied as photocatalysts and photobiocatalysts.

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METALLIC AND/OR OXYGEN ION IMPLANTATION INTO AlN CERAMICS AS A METHOD OF PREPARATION FOR ITS DIRECT BONDING WITH COPPER

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Direct bonding (DB) process is recently getting an increasing interest as a method for producing high quality joints between aluminum nitride (AlN) ceramics and copper. Beneficial features of AlN as a substrate material for AlN-Cu joints in high power semiconductor devices are: high thermal conductivity (about 10 times higher than that for Al_2O_3 and only about 17% lower than for toxic BeO ceramic), good electrical insulation, thermal expansion similar to silicon and non-toxicity. To form AlN-Cu joint, two prerequisites must be satisfied. Firstly, oxygen must be present in the system to allow the formation of Cu/Cu_2O eutectic liquid (about 0.4 wt% oxygen in copper) with melting point 1065°C, *i.e.* slightly below the melting point of copper. Secondly, since the surface of pure AlN is not wettable by this eutectic, this surface must be suitably modified to ensure sufficiently strong bond. Conventionally, AlN is oxidized in a furnace to convert its surface into Al_2O_3 type, *e.g.* [1,2], which is wettable by Cu/Cu_2O eutectic. Recently, we undertook a new approach to AlN pretreatment prior to DBC using ion implantation technique to form an intermediate layer between the joined elements. In the present work, we summarize the results of systematic experiments in which with such ion elements as: O, Ti, Fe, Cr and Cu were implanted in four versions into the commercial AlN substrates. For each of them, the calculations of the Gibbs free energy ΔG^{o} was performed to facilitate the prediction of the formation of a given compound. The results are as follows:

(i) Oxygen implantation

$$\langle AlN\rangle + 3/2\,(O) \rightarrow 1/2\,\langle Al_2O_3\rangle + (N)$$
$$\Delta G^{o}_{298K} = -396.89\ \text{kJ/mol}$$
$$\langle AlN\rangle + 3/2\,(O) \rightarrow 1/2\,Al_2O_3 + 1/2\,(N_2)$$
$$\Delta G^{o}_{298K} = -852.56\ \text{kJ/mol}$$
$$\langle AlN\rangle + (O) \rightarrow \langle AlN\rangle + (O)$$
$$\Delta G^{o}_{298K} = 0\ \text{kJ/mol}$$
$$\langle AlN\rangle + (O) \rightarrow \langle AlN\rangle + 1/2\,(O_2)$$
$$\Delta G^{o}_{298K} = -262.45\ \text{kJ/mol}$$

(ii) Titanium implantation

$$\langle AlN\rangle + (Ti) \rightarrow \langle AlN\rangle + \langle Ti\rangle$$
$$\Delta G^{o}_{298K} = -425.57\ \text{kJ/mol}$$

In addition, it is likely that the presence of titanium in AlN substrate can lead to creation of TiN. The value of ΔG^{o}_{298K} computed for such reaction seems to confirm this possibility:

$$\langle AlN\rangle + (Ti) \rightarrow \langle TiN\rangle + \langle Al\rangle$$
$$\Delta G^{o}_{298K} = -445.91\ \text{kJ/mol}$$

(iii) O+Ti implantation

Assuming that oxygen implantation may lead to Al_2O_3 as in (i), one can expect the formation of TiO, which is well wettable by copper. Then, the calculation of Gibbs free energy gives:

$$\langle Al_2O_3\rangle + 3\,\langle Ti\rangle \rightarrow 3\,\langle TiO\rangle + 2\,\langle Al\rangle$$
$$\Delta G^{o}_{298K} = -1232.66\ \text{kJ/mol}$$

From these calculations, it appears that the probability of formation of titanium lean oxides, which are not wettable, is 2 to 3 times smaller. Obviously, the formation of TiN is also possible as it was shown in (ii).

(iv) Ti+O implantation

In the fourth approach we intended to check whether the sequence of implantation of titanium and oxygen influences the quality of the joints. The reasoning behind this approach stems from considering case (ii), where titanium implantation leads to the formation of TiN and hence oxygen implantation as the second step will promote the formation of TiO according to the reactions:

$$\langle TiN\rangle + (O) \rightarrow \langle TiO\rangle + (N)$$
$$\Delta G^{o}_{298K} = 18.26\ \text{kJ/mol}$$
$$\langle TiN\rangle + (O) \rightarrow \langle TiO\rangle + (N_2)$$
$$\Delta G^{o}_{298K} = -195.39\ \text{kJ/mol}$$

The metallic ions were implanted using an MEVVA type TITAN implanter with unseparated beam, described in detail elsewhere. Oxygen ions were implanted using a semi-industrial ion implanter without mass separation equipped with a gaseous ion source. The substrate temperature did not exceed 200°C. Ions were implanted at two acceleration voltages, *i.e.* 15 and 70 kV. The fluence range was between 1E16 and 1E18 cm^{-2}. The base pressure in the vacuum chamber was about (2-5)E-4 Pa.

After implantation, some of the samples were characterized by the Rutherford backscattering (RBS) method (SIMNRA 5.0 30 days trial version computer code was used).The metallic component of the joint, *i.e.* oxygen-free copper in the form of strips of 30x3x0.3 mm^3 was first annealed at 600°C for about 40 min in flowing nitrogen containing 1.5 ppm of oxygen. Subsequently the copper component was oxidized in air at 380°C for 3 min. A controlled-atmosphere tube furnace was used for oxidation procedure.

Direct bonding process was carried at 1075±5°C in a conveyor type furnace with a nitrogen flow of 60 l/min, for about 10 min. This procedure was previously adopted for the Cu-Al_2O_3 system. After completing the joining procedure, the samples were subjected to shear strength measurements using a Hackert test apparatus. Both components (Cu and AlN sides) were then examined with the use of a stereoscopic optical microscope (OM).

The following regularity is observed, as regards the shear strength, the sequence of ions implanted into AlN in the direction of diminishing values is: Ti, O+Ti, O, Ti+O (*i.e.* 73, 54, 40 and 34 kG/cm^2, respectively). As seen, in all cases listed above, the values of shear strength are greater than the average value obtained after conventional (oxidation) pretreatment processes, which amounts to 14 kG/cm^2. In view of the RBS results, it may be concluded that the optimum treatment of AlN ceramics is to form a thin TiN surface layer and that the presence of oxygen is detrimental to the joint quality.

In conclusion: The investigations performed in the present work confirm our assumption that ion implantation is a very promising technique as a pretreatment of AlN ceramics for the formation of the joints with copper in direct bonding process.

It has been shown that titanium implantation gives the best results in comparison to other metals examined (Fe, Cr, Cu) but also in comparison to double Ti+O and O+Ti implantations. However, as regards the potential improvement in the joint quality, oxygen implantation deserves further study.

The sequence of titanium and oxygen implantation has a marked effect on the joint quality, O+Ti giving significantly better results than Ti+O.

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ION IMPLANTATION OF MAGNESIUM IONS INTO BORON AND TRANSIENT PLASMA TREATMENT IN FORMATION OF SUPERCONDUCTING REGION OF INTERMETALLIC MgB_2 COMPOUND

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Since the discovery [1] of superconductivity in the intermetallic compound MgB_2 with transition temperature as high as 39 K, several successful attempts have been made to fabricate superconducting thin films of this material. The main reasons for this interest are: low price of the component elements, simplicity of the synthesis, relatively high values of transition temperature T_c and critical current density J_c, broad perspectives of applications in various industries including the power industry and microelectronic application.

In papers published thus far, the synthesis of films occurs in a conventional process of annealing of the Mg-B system in the presence of magnesium vapor. The values of T_c reported in the literature are in the 22-35 K range, and J_c in the $3x10^4$-$2x10^6$ A/cm^2 range. Recently we have undertaken an attempt to synthesize superconducting phase of MgB_2 from the liquid state using a transient melting process without necessity of annealing in magnesium vapor.

The ion implantation technique is combined with the use of high intensity pulsed plasma beam (HIPPB) irradiation. In our preliminary experiments, we obtained encouraging results using boron implanted magnesium substrates (B→Mg) [2]. In the present work the magnesium implanted boron substrates are adopted (Mg→B).

The substrates were cut out from a commercial (Goodfellow) cast boron ingot of 99.6 wt% purity in the form of mirror-like polished discs of 3.8 mm in diameter and 2 mm thick. In the first step, the samples were implanted with magnesium ions using the MEVVA type TITAN implanter with unseparated ion beam, described in detail elsewhere. Ions were implanted at acceleration voltages between 20 to 67 kV which, at the average ionization multiplicity of magnesium ions equal to about 1.5, correspond to energies of about 30 to 100 keV, respectively. The implantation processes were carried out up to three ion fluences of $5x10^{17}$, $7x10^{17}$ and $1x10^{18}$ cm^{-2}. In the second step, the three HIPPB argon pulses were applied to melt the top layer of the Mg-B system. The plasma pulses were generated in a rod plasma injector (IBIS) type of accelerator described elsewhere. In the present experiments, the energy density of plasma were in the range of 0.8-3 J/cm^2. Pulse duration in the μs range corresponds to irradiance in the MW/cm^2 range. Scanning electron microscopy (SEM) was used to examine the changes of processed sample morphology with magnification ranging from 100 to 5000 times.

In order to get insight into the composition of the processed layer, the selected samples were subjected to the Rutheford backscattering (RBS) technique. The spectra were recorded using 1.7 MeV He^+ ion beam at normal incident to the sample. The backscattered particles were detected at an angle of 170° using a Si(Li) detector with the 15 keV energy resolution. The RBS spectra were fitted using a RUMP computer code.

In order to detect superconducting state of processed material three methods were used: magnetic measurements, magnetically modulated microwave absorption (MMMA) and four probe electric conductivity measurements.

The results of the sample characterization can be summarized as follows: Even as low pulse energy density, as 0.78 J/cm^2, is sufficient to melt the near surface layer of the substrate. After pulse treatment, the surface becomes relatively smooth, the edges of the craters (created as a result of chipping during surface polishing) are rounded. At higher energy densities, the morphology becomes rich of topographical features and the microcracks are also clearly visible. In spite of poor morphology, unexpectedly the sample treated with pulses of average energy density of 2.38 J/cm^2 appeared to be the best with respect to superconductive properties. The measured retained fluence in the as-implanted sample equal to $7x10^{17}$ cm^{-2} and decreases down to $6.4x10^{17}$ cm^{-2} after plasma pulses. RBS spectra exhibit that both process steps, especially pulse plasma treatment introduce excessive amount oxygen. The depth distribution profiles of magnesium atoms extracted from the spectra shows that. The depth distribution profiles of magnesium atoms extracted from the RBS spectra show that after pulse treatment, the magnesium to boron concentration ratio is closest to the stoichiometry of MgB_2 at about 100 nm thick surface layer. MMMA signals *vs.* temperature and external magnetic field are almost one order of magnitude stronger than that in the previous (B→Mg) [2] case. The T_c for the best samples is slightly above 25 K. At this temperature, also a sharp drop of electric resistively was observed. In spite of the presence of the substantial amount of the superconducting phase as confirmed by MMMA and resistivity measurements, no full macroscopic percolation occurred. This may be due to the two main reasons:

- microcracks at the top layer caused by rapid solidification;
- excessive amount of oxygen in the system, which may form MgO films insulating the superconductive regions.

Further experiments will be aimed at reduction of these two flaws.

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STRUCTURAL AND TRIBOLOGICAL PROPERTIES OF CARBON STEELS MODIFIED BY PLASMA PULSES

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When steel is exposed to nitrogen incorporation at elevated temperature by such techniques as ion implantation, plasma immersion ion implantation (PI^3) and plasma nitriding, several nitrides are formed depending on the process conditions. Among all phases formed in this way an expanded austenite attracts a special interest of many authors [1-4]. Nitrogen expanded austenite ($\gamma_{N,}$) and carbon ex-

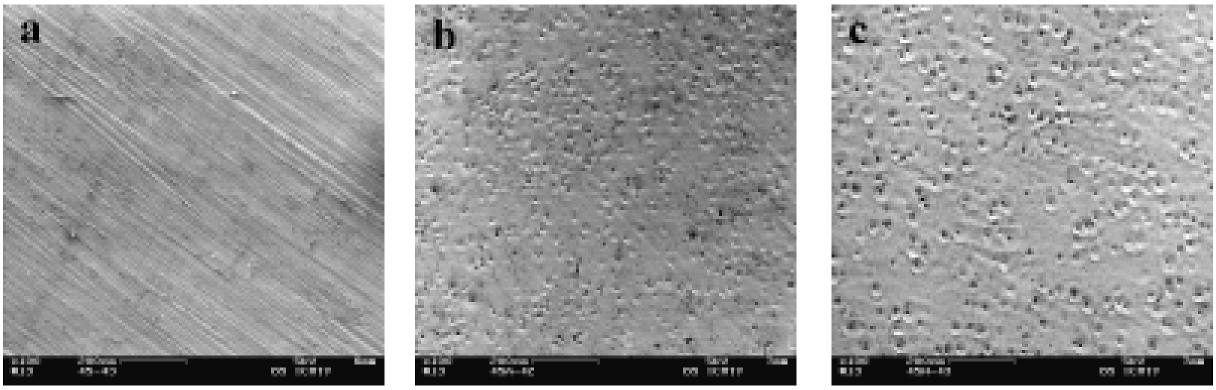

Fig.1. Surface morphology of steel 45: (a) untreated, modified with (b) argon and (c) nitrogen intense pulsed plasma beams.

panded austenite (γ_C) combine high hardness, good wear and corrosion resistance in austenitic stainless steels.

If the process of transient melting and recrystallization of the near surface layer of the substrate is applied, then the γ_N can be formed even in pure iron [5]. The expanded austenite is an interstitial solution of nitrogen or carbon where the nitrogen or carbon atoms are in octahedral interstitial sites in the fcc (face centered cubic) crystal lattice of the austenite. Increase of fcc structure lattice parameter depends on the contents of interstitials. Nitrogen atoms having the smaller radius compared to carbon, but cause a higher dilatation being dissolved in the fcc lattice. Nitrogen atoms in austenite increase the concentration of free electrons, *i.e.* enhance the metallic component of atomic interactions. Carbon atoms are expected to contribute to the localized electrons, *i.e.* to enhance covalent bonds [6].

Carbon steels with different concentration of carbon and heat treated according to the standard procedures were used: Armco-iron, steels 20, 45, 65 and N9. The samples were irradiated with five intense (about 5 J/cm^2), short (μs range) argon or nitrogen plasma pulses generated in a rod plasma injector (RPI) type of plasma generator.

Samples were characterized by the following methods: nuclear reaction analysis (NRA) $^{14}N(d,\alpha)^{12}C$, scanning electron microscopy (SEM), conversion electron Mössbauer spectroscopy (CEMS), X-ray diffraction analysis (GXRD) with grazing incidence angle between 0.5 and 2° and Amsler wear tests.

Of all nitrogen plasma treated samples only those were selected in which the retained dose of nitrogen is equal to $1.2\text{x}10^{17}\pm2\text{x}10^{16}$ N/cm^2.

Table. Content of phases [vol.%] identified at the surface layer of initial and modified carbon steels.

Material		Argon				Nitrogen				
Steel	%C	α-Fe	α'	γ_0	γ_C	α-Fe	γ_0	γ_C	γ_N	ε-Fe_3N
Armco	0.018	100				68.04	11.85	1.35	11.06	7.71
20	0.28	78.1	12.58	6.22	3.1	35.24	33.5	11.39	14.99	4.87
45	0.52	71.33	13.19	10.56	4.91	27.76	39.12	8.87	20.34	3.91
65	0.63	54.48	10.22	22.89	12.41	27.01	35.23	10.54	17.85	9.37
N9	0.93	47.91	6.61	27.83	17.65	26.6	36.73	17.25	13.67	5.64

SEM observations shown that the morphology of the pulse treated samples, both argon and nitrogen plasma are identical. The craters and droplets are uniformly distributed over the surface, which is typical of melted and rapidly recrystallized top layers (Fig.1). The thickness of the modified layers is in the range of 1.2-1.6 μm.

Combined computer fitting of the CEMS spectra taken on full and reduced velocity scale enabled us to determine the contribution of each of the identified phase (Table). The general observation is that nitrogen is much more efficient than argon in ausenitization of carbon steel. For example, 15.5 vol.% of fcc phases was detected in steel 45 (containing 2.2 at.% C) treated with argon pulses, whereas 60% of fcc phases were detected in steel 20 which after nitrogen plasma treatment contains 1.0 at.% C and 1.5 at.% N.

Figure 2 shows the GXRD patterns taken at the incidence angle between 0.5 and 2° for martensitic α'-Fe: initial, argon and nitrogen pulse plasma treated. Only reflections characteristic of α'-Fe are observable in untreated sample. After argon pulses treatment, two additional γ reflections: at $2\theta\approx50.5^\circ$ and 74.4° are clearly seen. Unfortunately, at such small content of carbon it is impossible to resolve γ into γ_0 and γ_C, as it was possible with CEMS. After nitrogen plasma treatment, the γ reflections are much stronger than for argon ones although resolution of γ into γ_0, γ_C and γ_N is also impossible. From the shift of γ(111) toward the smaller 2θ, it was estimated that lattice expansion of fcc by about 0.8% occurs. Comparing the intensities of α'(111) and γ(111) in the range of $2\theta=43\text{-}46^\circ$ one can see that for incident angle 2° the α'(111) peak is stronger that that of γ(111), and for lower angles the situation is reverse. This

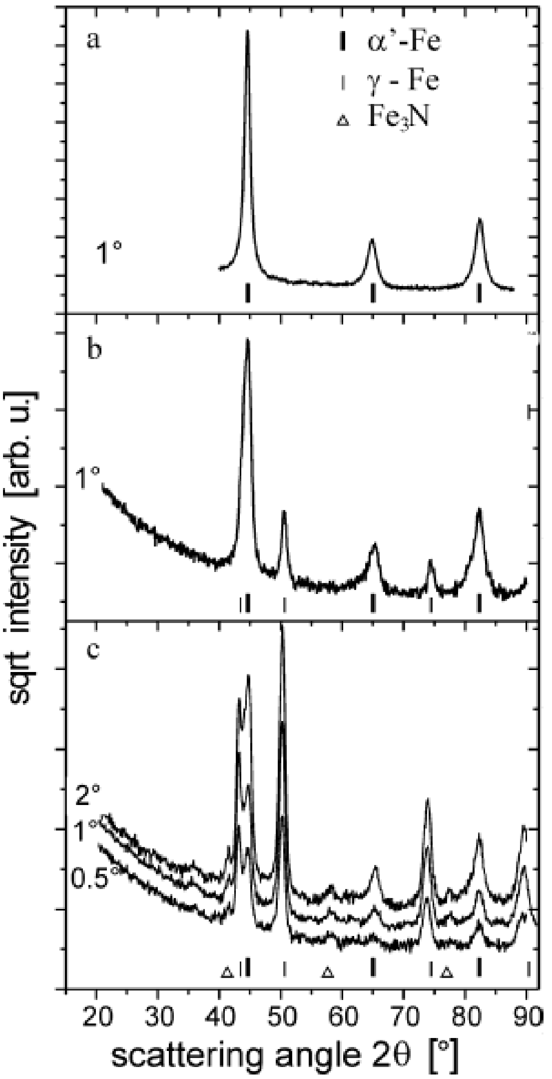

Fig.2. GXRD spectra for steel 65: (a) initial modified with (b) argon and (c) nitrogen intense pulsed plasma beams.

suggests that the top layer is composed of a mixture of this two phases. GXRD pattern shows also the presence of ε-Fe_3N by peaks at 41.2, 57.8 and 77.5°. In general, GXRD confirms at least qualitatively the results derived from the CEMS data.

Figure 3 shows the results of the linear wear measurements on initial, argon and nitrogen plasma treated samples of carbon steels. The wear was lower for all the modified samples as compare with the initial material. Substantial improvement of wear for argon and nitrogen treated samples is observed only for lower carbon steels. Results obtained for high carbon steel – N9 – show a significantly lower linear wear than for low carbon steels. Greater improvement of tribological properties occurs for nitrogen than for argon treatment, which can be explained by the presence of nitrogen phases (γ_N and ε). SEM observations of the wear tracks morphology show the parallel grooves and scratches in the direction of sliding and allowed us to state that the microcutting together with the plastic deformation was the main wear mechanism existing here.

In contrast to γ'-Fe_4N which yields the most wear resistant surfaces, the ε-Fe_3N is not identified as a phase that improves tribological properties of nitrided steels [1,7]. No γ'-phase was detected in our samples, therefore improvement of wear resistant in our case we ascribe as being due mainly to the presence of γ_N phase.

In conclusions: The nitrogen expanded austenite – γ_N phase was detected in the near-surface region of Armco and carbon steels in the case of nitrogen plasma modification. Significant increase of the hardness and tribological properties of modified surfaces occurs for nitrogen treatment, which can be explained by the presence of γ_N phase.

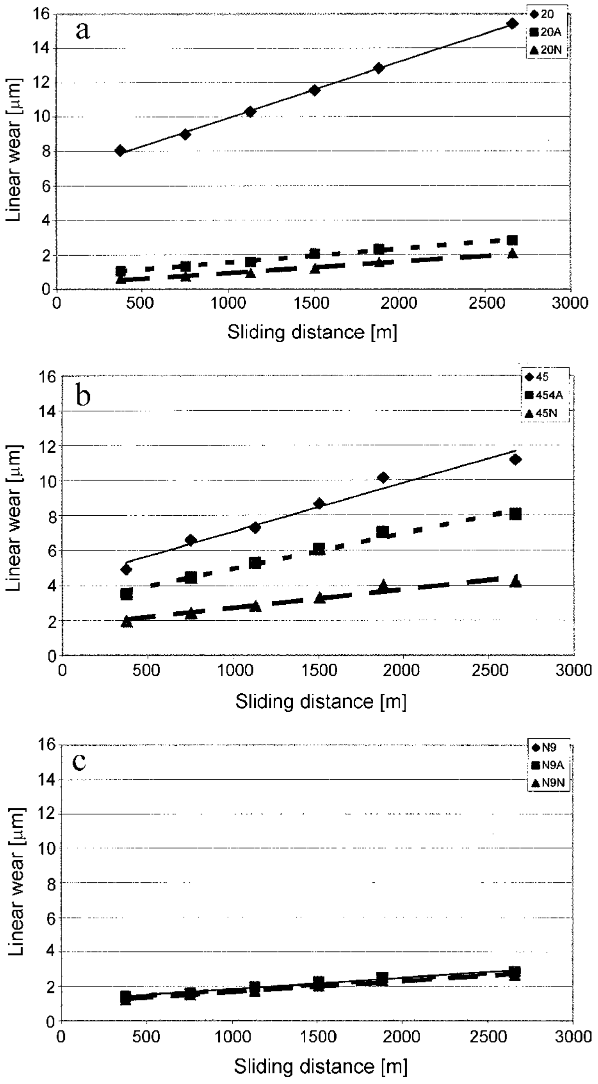

Fig.3. Linear wear of untreated and modified with intense plasma pulses: steel 20 (a), steel 45 (b) and steel N9 (c).

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UV IRRADIATION OF TRACK MEMBRANES AS A METHOD FOR OBTAINING THE NECESSARY VALUE OF BRITTLENESS FOR GOOD FRACTURES OF SAMPLES FOR SEM OBSERVATIONS

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Synthesis of nano- and microstructures of materials inside the pores of specific template-track membranes can be used to obtain nano- and microwires or nano- and microtubes [1]. It is important for these applications to know the inner geometry of the pores like sizes, shape and surface morphology [2,3]. Scanning electron microscopy technique (SEM) was used for this kind of membrane characterisation. The proper preparation of samples for SEM observations is very important in order to prevent destruction of the structure of membrane during the fracture preparation. The breaking membranes samples at the liquid nitrogen temperature (77 K) did not allow us to obtain undistorted cross-section. The use of other methods of sample preparation as electron, gamma rays or UV irradiation allows us to make them more brittle [4-6]. The preliminary results of tensile measurements of membranes after UV irradiation are presented here.

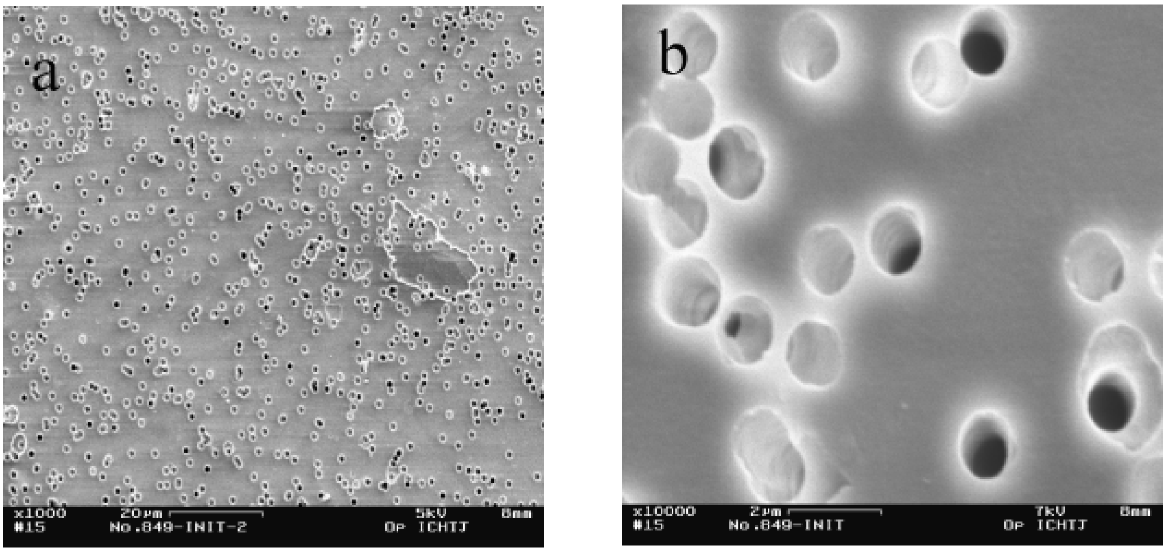

Fig.1. Surface morphology of PET investigated membrane: a) x1000 magnification and b) x10 000 magnification.

Poly(ethylene terephthalate) (PET) membrane 10 µm thick with pore diameter 1.0 µm were prepared at the Joint Institute for Nuclear Research (Dubna, Russia) using the standard procedure [3]. Then, the samples were irradiated with UV light with energy flux 2.8 W/cm^2 during different periods of time. The tensile measurements of the initial and irradiated materials were carried out using a tensile machine Instron 5565 (Instron Co., England) in the Institute of Nuclear Chemistry and Technology. Membranes surface and fracture observations were made using SEMs: JSM 840 (Jeol, Japan), DSM 942 (Zeiss, Germany) and LEO 1530 GEMINI (Zeiss, Germany) with low accelerating.

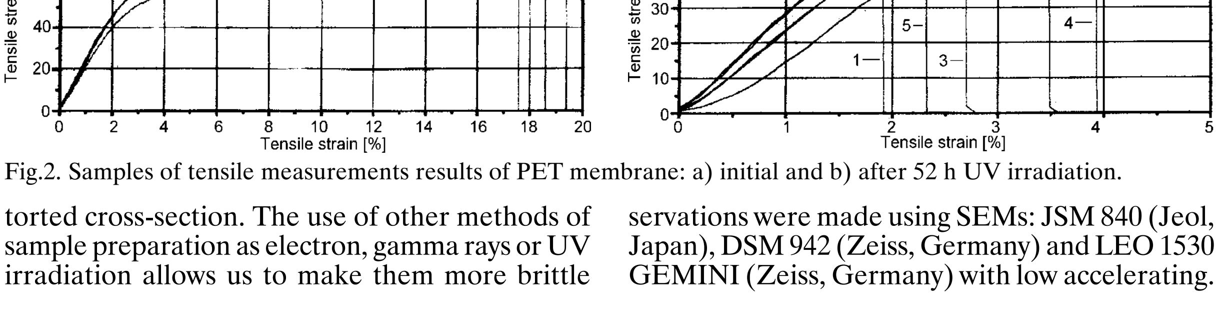

Fig.2. Samples of tensile measurements results of PET membrane: a) initial and b) after 52 h UV irradiation.

The samples were fixed using a conductive glue and then coated with a thin layer of gold to reduce the charging which takes place during SEM observations [4].

Figure 1 presents the surface morphology of the investigated membrane. Average pore diameter measured by the use of SEM was 1.14±0.20 µm. In the majority of cases they have a round shape. Multiple pores can be seen.

Figure 2 presents the results of tensile measurements for initial material (three samples signed 1-3) and for irradiated material (five samples signed 1-5). According to these diagrams we can determine the main parameters of material tensile properties: strain at brake [%], tensile stress [MPa] for each sample and average values for the investigated material.

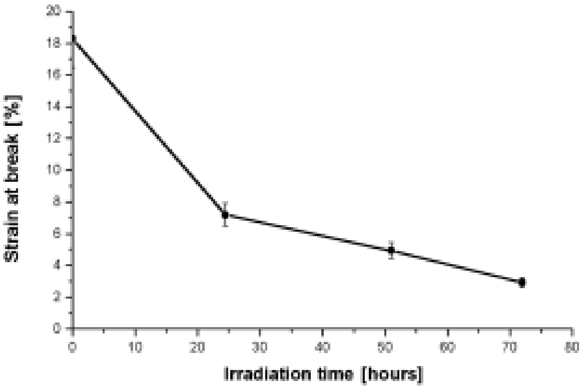

Fig.3. The strain at break of PET membrane – results of the tensile measurements *vs*. the UV irradiation time.

The dependence of the UV irradiation dose on the strain at brake is presented in Fig.3. The strength of the membrane decreases with increasing irradiation time, *i.e*. with increasing dose. This means that the investigated material became significantly more brittle. The degradation of PET was provoked by absorbed UV light with wavelengths in the range of 310-320 nm. In the case when the time of UV irradiation increases up to 90 h under the same conditions, the membrane breaks without distortion of its channel structure and we obtain the cleavage without elastic deformations.

Figure 4 illustrates the cross-section of a PET membrane with asymmetric pores subjected to oxidative photodegradation under the UV irradiation in air during 90 h. The structure of selecting the layer near the membrane surface as well as the shape and sizes of channels are clearly seen. In the bulk of membrane, the high porosity can be seen at the same time. We can say that this membrane has a good productivity, dirt capacity and selectivity.

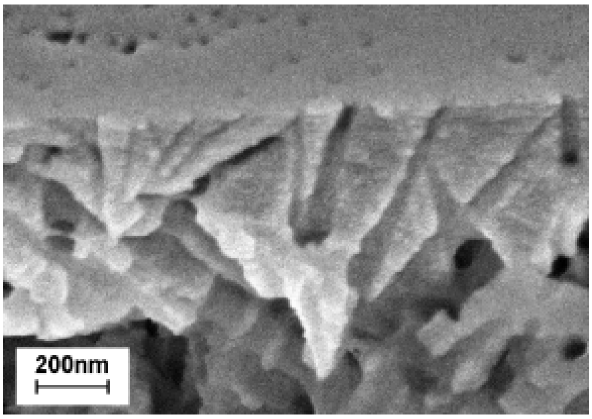

Fig.4. The fractures of PET asymmetric membrane after 90 h UV irradiation.

In conclusion, we can find the dose of UV irradiation that ensures the fracture without elastic deformation. In the case when the time of UV irradiation increases up to 90 h, the PET membrane breaks without distortion of its channel structure.

Thanks to Dr. Pavel Apel (Joint Institute for Nuclear Research, Dubna) for present samples and Dr. Adam Presz (Unipress, Warszawa) for the help in SEM observations.

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NUCLEONIC CONTROL SYSTEMS AND ACCELERATORS

LUCAS CELL AS A DETECTOR OF RADON DAUGHTERS IN AIR

Bronisław Machaj, Jakub Bartak

Radon daughters concentration in air is a direct indicator of the radiological hazard to human beings due to radon existence in the air. The knowledge on radon daughters concentration in the air is thus of vital importance. Radon as a natural radioactive marker existing in the air is used in investigations of movement and mixing of atmospheric air. Radon concentration in atmospheric air is much lower (5-15 Bq/m^3) than in dwellings and much higher sensitivity of measurement can be achieved by measuring radon daughters than radon itself. Standard procedure in measuring radon daughters is the deposition of radon progeny attached to dust aerosols on an air filter and then measurement of alpha radiation of deposited decay products.

A new approach was made to measure radon decay products with a Lucas cell [1]. Lucas cell is a sensitive detector of alpha radiation. It is known that radon daughters easily attach to the walls of a measuring cell. Radon progeny are positively charged thus connecting a photocathode of the photomultiplier tube to negative voltage and grounding the anode, helps to deposit radon daughter inside the Lucas cell. The Lucas cell for radon daughter measurement was modified as shown in Fig.1. Small active part ϕ54x10 mm for radon progeny measurement is limited by plate, window, and wall. The cell was installed in a radon monitor equipped with a photomultiplier tube with a photocathode connected to high voltage of negative polarity (-820 V, anode grounded). The radon monitor was then placed in a radon cham-

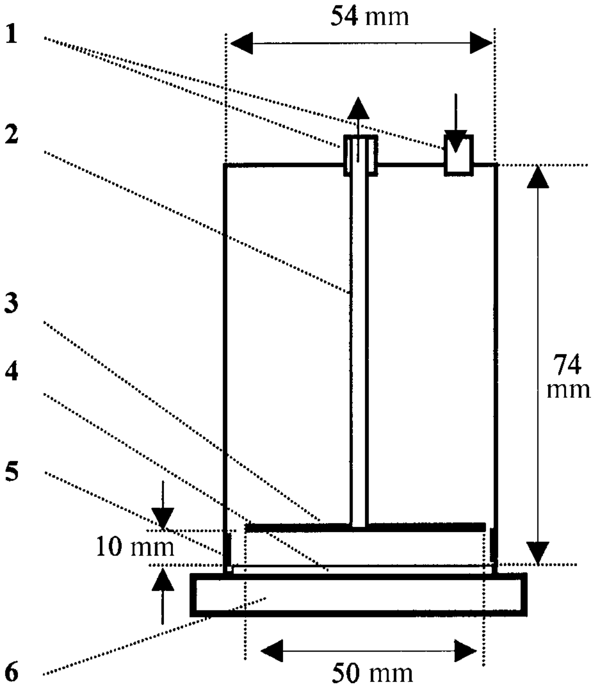

Fig.1. Lucas cell for measurement of radon progeny: 1 – air inlet and outlet, 2 – pipe, 3 – plate covered with ZnS(Ag), 4 – cell transparent windows, 5 – wall covered with ZnS(Ag), 6 – flange.

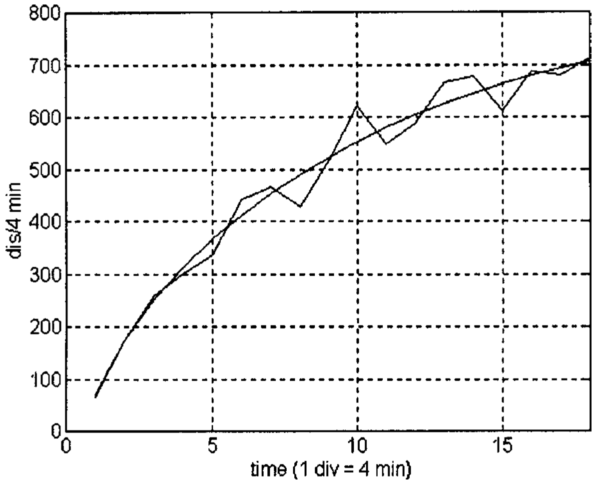

Fig.2. Count rate, measured (broken line) and simulated (continuous line) on the same time scale. Count numbers at time intervals t_1=1-12 min, t_2=13-28 min and t_3=29-40 min from broken curve processed gave the activities ^{218}Po=5.027, ^{214}Pb=0.5263 and ^{218}Bi=4.8845 dpm. Continuous curve corresponds to the above activities.

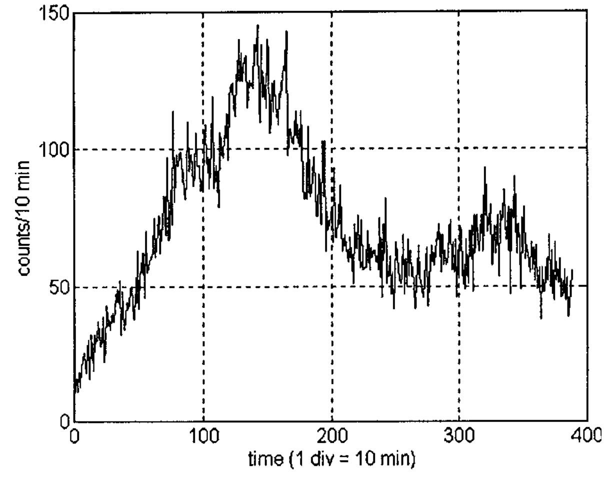

Fig.3. Count rate of Lucas cell shown in Fig.1 at an airflow of 1.1 dm^3/min.

ber and after radiation equilibrium was reached, the airflow 1.1 dm^3/min was forced (sucked) through the Lucas cell and count rates were measured. The results of measurement and simulation are shown in Fig.2. The simulation was done employing radioactive series decay equations [2] and three interval count processing. The activities of radon progeny deposited inside the Lucas cell achieved from three interval data processing are: ^{218}Po=5.027, ^{214}Pb=0.5263 and ^{214}Bi=4.8845 dpm (dis per min) or 76.2, 7.9 and 74 Bq/m^3 for ^{218}Po, ^{214}Pb and ^{214}Bi, correspondingly. Estimated radon progeny in the air was 1540 Bq/m^3, thus the efficiency of deposition and detection of ^{218}Po was estimated to be $\eta=76.2/1540=0.05$.

Figure 3 shows the count rate at 10 min intervals from total radon progeny measured in a laboratory room at ground level within 65 h during weekend days. The count rate up to 130 counts/10 min was registered indicating a good sensitivity of the detector.

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A GAUGE FOR THE MEASUREMENT OF WOOD DENSITY MGD-05

Jakub Bartak, Bronisław Machaj, Piotr Urbański, Jan P. Pieńkos

Wood density is an important parameter determining several properties of wood as: wood quality, mechanical resistance, charcoal production, transport cost, *etc*. [1]. General relations and definitions of density, specific gravity, moisture influence on wood density, density variation and chemical composition of wood are given in [2]. A short review of different methods for the measurement of wood density is given in [1]. Radiometric methods are based on attenuation of ^{241}Am gamma radiation, or measurement of backscattered ^{241}Am radiation [3,4]. Attenuation of gamma radiation is preferred as the attenuation is proportional to the density across the total wood thickness, whereas in backscattered geometry the surface layer has higher influence on density signal. Block diagram of the gauge in transmission geometry illustrating its principle of operation is shown in Fig.

The gauge is designed for non routine measurements of board and plank wood in the field environment. Radiation source ^{241}Am (370 MBq) and a scintillation detector with NaI(Tl) (ϕ25x12 mm) are collimated with a 40 mm thick Pb collimator. Diameter of the collimator can be set at 5, 10 and 15 mm. The measuring head containing radiation source and scintillation probe fixed in a C form frame can be moved across the measured board up to 250 mm wide. The measuring head and measured wood are supported by a folding measuring table. Pulses from the scintillation probe after amplification and discrimination in E1 discriminator are counted in a pulse counter PL1 and are processed to get the density of wood and error of measurement. Up to 1000 measuring results are stored in the gauge memory. The measuring results stored in the memory are sent to an external laptop for computations of density contours.

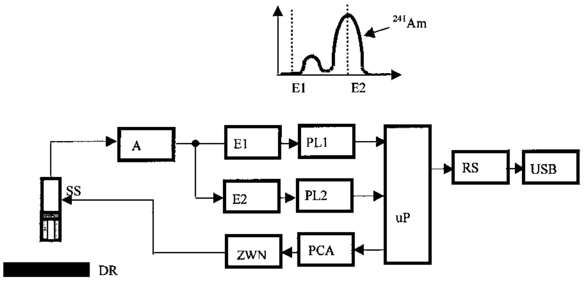

Fig. Block diagram of wood density gauge. At the top, discrimination levels E1 and E2 against ^{241}Am differential spectrum are shown: Z – radiation source ^{241}Am, DR – wood sample, SS – scintillation probe, A – pulse amplifier, E1 – discrimination level of measuring channel, E2 – discrimination level of automatic gain control, PL1 – measuring channel pulse counter, PL2 – automatic gain control pulse counter, uP – microprocessor, PCA – digit-to-analog converter, ZWN – high voltage power supply, ZNN – low voltage power supply, RS – serial port RS232, USB – RS232 to USB converter, AK – battery, PAK – battery charger.

To control the gain of photomultiplier tube (PMT), count rate n1 and n2 is measured at E1 and E2 discrimination level and the ratio n2/n1 is checked. If the ratio is lower or higher than the value corresponding to the nominal gain, the gain of PMT is corrected by a decrease or increase in the PMT high voltage. The gain is automatically controlled by a microprocessor and a digit-to-analog converter.

Wood density (ρ) and relative random error (s(ρ)/ρ) due to fluctuations of count rate are computed from the relations:

$$\rho = \frac{\ln(n_o / n)}{\mu d}$$

$$\frac{s(\rho)}{\rho} = \frac{\sqrt{[1/n_o + 1/n]/t}}{\mu d \rho}$$

where: n_o – count rate when no wood is placed between the source and detector; n – count rate when wood is between the source and detector (The n_o and n are corrected for detector background and dead time of measuring channel.); μ – wet wood attenuation coefficient, $\mu=\mu_d+w(\mu_w-\mu_d)$; μ_d – dry wood attenuation coefficient; μ_w – water attenuation coefficient; d – thickness of wood; t – counting time.

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APPLICATION OF THE BOOTSTRAP FOR ASSESSMENT OF RESULTS FROM INTERLABORATORY COMPARISON

Ewa Kowalska, Piotr Urbański

Investigations performed by some authors [1] have shown that statistical distribution of the results taken from interlaboratory comparisons often cannot be approximated by the normal probability function. In some cases, attempts to approximate them by other distribution functions (*e.g.* Weibull) also failed [2]. In such situations nonparametric [3] or bootstrap method [4] for results evaluation should be used. Both the methods have been applied for interlaboratory comparisons of data obtained for the determination of iron in the reference material: Mixed Polish Herbs and Tea Leaves. Preparation of the material and organization of the interlaboratory comparison were performed by the Department of Analytical Chemistry (Institute of Nuclear Chemistry and Technology) [5,6].

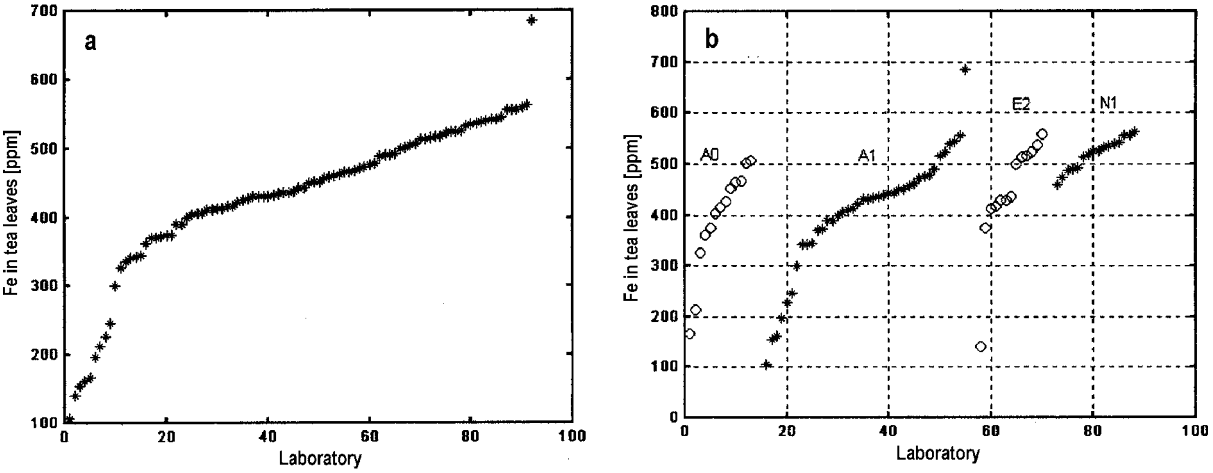

Fig.1. Cumulative distribution of the results of iron content in tea leaves: a – the whole set of 92 results; b – results for particular analytical methods: A0 – AAS general, A1 – AAS flame technique, E2 – AES (ICP), N1 – INAA (thermal neutrons).

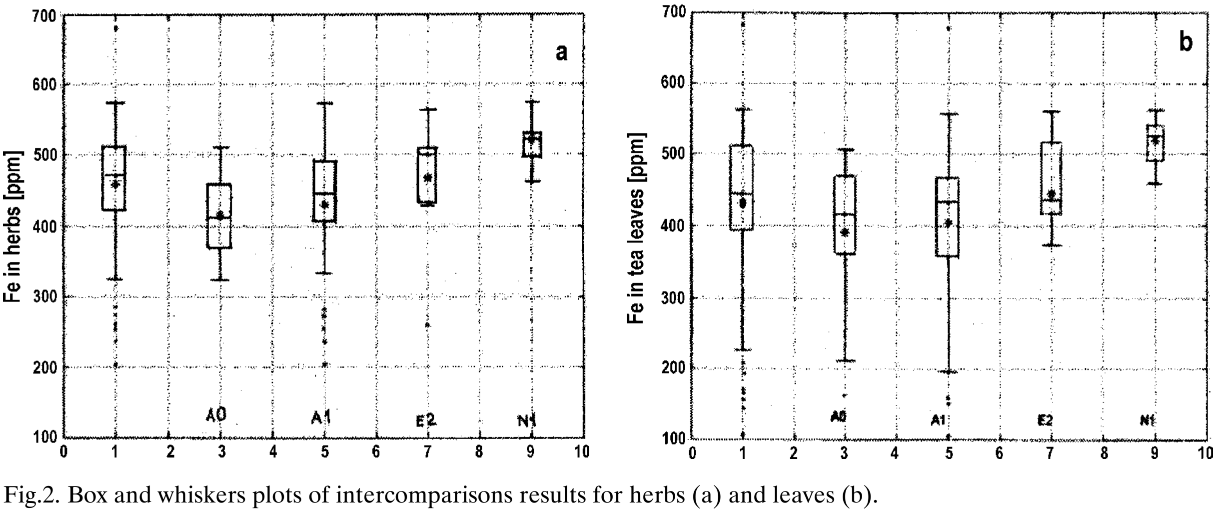

Fig.2. Box and whiskers plots of intercomparisons results for herbs (a) and leaves (b).

In Figure 1, there are shown the data obtained for the determination of iron in the tea leaves. Since the attempt to approximate its distribution

Table. Distribution parameters [ppm] computed by bootstrap for particular analytical methods.

Reference material	Parameter	All results	A0	A1	E2	N1
Tea Leaves	N	92	13	40	13	16
	Mean	431.61	391.08	404.31	445.25	519.23
	Median	445.03	414.4	426.85	460.01	524.17
	IQR	114.02	125.69	111.04	107.51	44.5
	Std	105.8	97.6	115.62	97.97	29.35
Mixed Polish Herbs	N	90	11	39	13	17
	Mean	459.71	415.38	430.86	468.33	521.39
	Median	473.38	414.57	446.55	483.82	523.14
	IQR	84.13	94.66	92.73	73.45	38.05
	Std	81.42	58.79	85.36	67.59	27.81

by the normal probability function failed [2], the results were evaluated using nonparametric method box and whiskers (Fig.2). More detailed evaluation is presented in [2].

The results of application of the bootstrap methodology for treatment of this data set are shown in Table and Fig.3. The computations were performed using MATLAB package with Statistics Toolbox [7]. Estimated number of bootstrap simulation was 5000.

It is seen that using the bootstrap methodology, not only mean values of the all interesting parameters can be computed, but also the shape of their own distributions may be found.

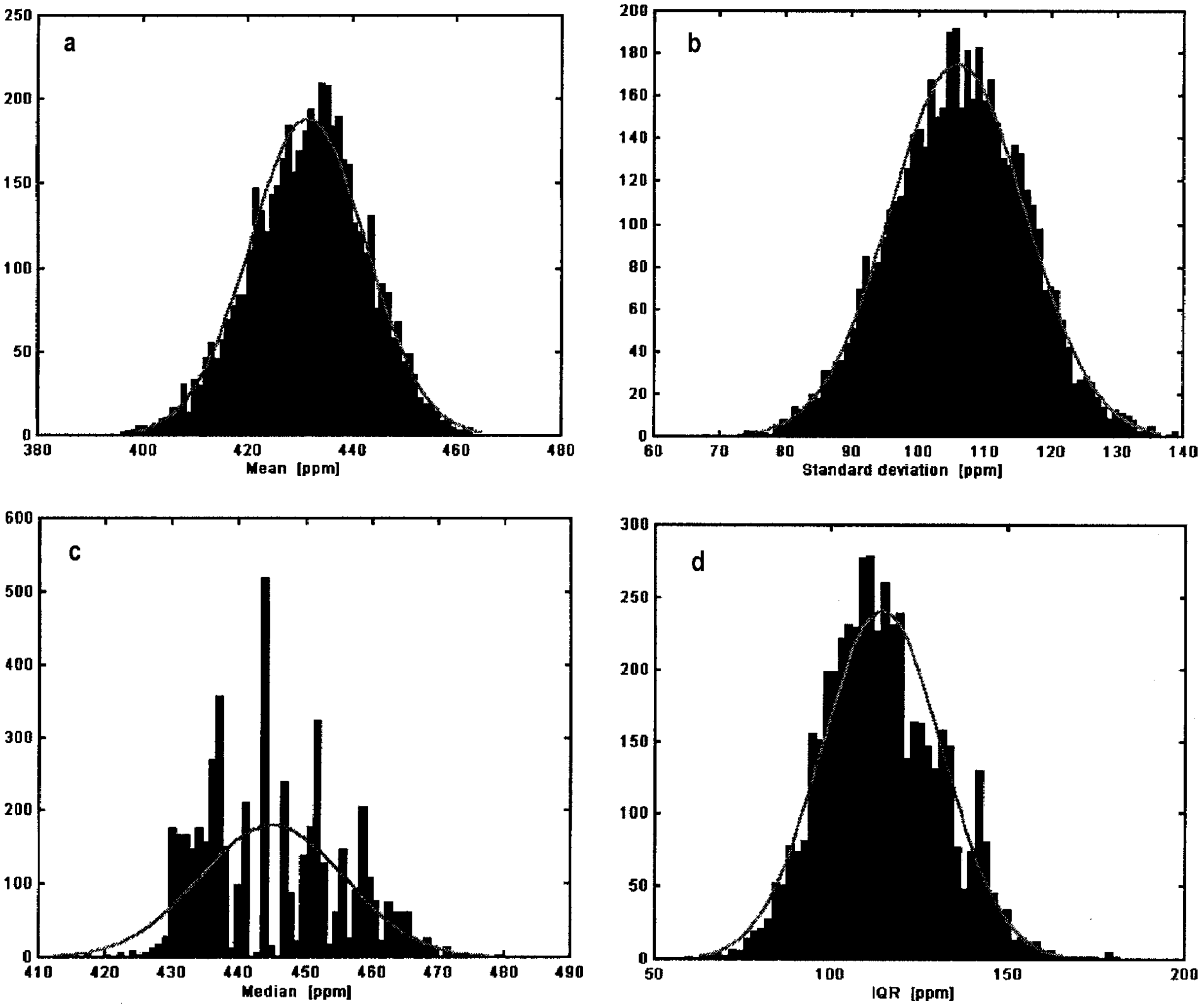

Fig.3. Distributions of mean (a), standard deviation (b), median (c) and IQR (d) computed using bootstrap for results obtained for iron determination in leaves.

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ASSESSMENT OF SMOOTHED SPECTRA USING AUTOCORRELATION FUNCTION

Piotr Urbański, Ewa Kowalska

Recently, data and signal smoothing became almost standard procedures in the spectrometric and chromatographic methods. In radiometry, the main purpose to apply smoothing is minimisation of the statistical fluctuation and avoid distortion.

Every procedure of smoothing leads to some distortions of the smoothed spectra. However, it is difficult to find an objective measure of the degree to which the smoothed spectrum was distorted, because the shape of "ideal" spectrum is unknown. Most of the smoothing and denoising procedures are based on the assumption of the additive noise model:

$$\mathbf{w} = \mathbf{w}_p - \mathbf{v} \qquad (1)$$

where: **w**, $\mathbf{w}_p$ – vectors of the raw and "ideal" spectrum respectively; **v** – vector of noise.

In practice, if a smoothing procedure is applied to a spectrum, the experimentator knows, beside the raw spectrum, the smoothed spectrum only (vectors of **w** and $\mathbf{w}_s$), and can compute the vector of removed part assuming the linear model:

$$\mathbf{v}_s = \mathbf{w} - \mathbf{w}_s \qquad (2)$$

The aim of this work was to find a qualitative parameter, which could be used, as a figure of merit for detecting distortion of the smoothed spectra, based on the above linear model.

It is assumed that as long as the part of the raw spectrum removed by the smoothing procedure ($\mathbf{v}_s$) will be of random nature, the smoothed spectrum can be considered as undistorted. To detect the random nature of the $\mathbf{v}_s$ one can use its autocorrelation function $\mathbf{r}_{vs}$ [1]:

$$\mathbf{r}_{vs} = \frac{\operatorname{cov}\left[\mathbf{v}_s(i),\ \mathbf{v}_s(i+p)\right]}{\sigma^2(\mathbf{v}_s)} \qquad (3)$$

where: p – shift (lag), $\sigma^2(\mathbf{v}_s)$ – variance of removal noise, i – 1...k, k – number of channels.

If the vector $\mathbf{v}_s$ is of random nature (*e.g.* white noise) its autocorrelation function has a zero value at all lags except a value of unity at lag zero, to indicate that the removed noise is completely uncorrelated. A correlated noise on the other hand

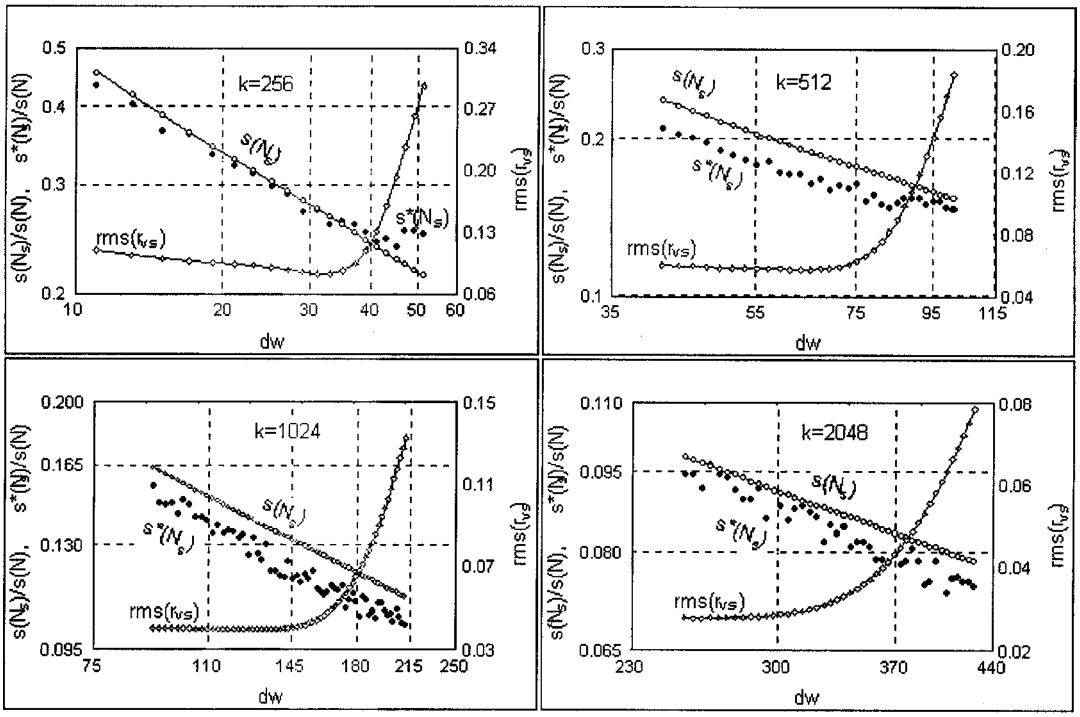

Fig. Root mean square error of total counts for the smoothed and raw spectra and *rms* of the autocorrelation function of the removed noise *vs*. filter width for simulated spectra smoothed with the Savitsky-Golay procedure.

will produce non-zero values at lags other than zero to indicate a correlation between different lagged observation. Thanks to this feature of the autocorrelation function, drifts of the mean value in the removed noise $\mathbf{v}_s$ as well as its periodicity can be more easily detected from the autocorrelogram than from the original data. As a measure of the random nature of the removed noise, the root mean square value of the correlation function $rms(\mathbf{r}_{vs})$ was used:

$$rms(\mathbf{r}_{vs}) = \sqrt{\frac{1}{p}\sum_{i=1}^{p}\left|\mathbf{r}_{vs}(i)\right|^2} \tag{4}$$

The above considerations were checked on simulated spectra consisting of k channels and corrupted with Poisson distributed noise and then smoothed with the Savitsky-Golay procedure using second order polynomial and variable filter width dw [2]. As a measure of the smoothing quality, the ratio of the root mean square error (RMSE) of the total counts for the smoothed and raw spectra $s(N_s)/s(N)$ was applied [3]. The $s^*(N_s)/s(N)$ ratio was computed using bootstrap method [4] for a single spectrum. The both ratios and $rms(\mathbf{r}_{vs})$ *vs.* filter width were plotted and are shown in Fig.1.

It is seen that with increasing filter width, the quality of the smoothing also increases (RMSE ratio is lower), however, beginning from a certain channel, the $rms(\mathbf{r}_{vs})$ also increases sharply indicating that in the removed noise some non-random component appear. If the goal of the optimization is to minimise distortion and maximise smoothing quality, the filter width should be chosen for the $rms(\mathbf{r}_{vs})$ lying on the flat part of the plot and in "safe" distance left from the observed knee of the plot.

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WIRELESS AIR MONITORING NETWORK WITH NEW AMIZ-2004G DUST MONITORS

Adrian Jakowiuk, Bronisław Machaj, Jan P. Pieńkos, Edward Świstowski

Since many years, MIZA and AMIZ dust monitors are used for the measurement of airborne dust concentration. The principle of operation of the monitor is based on determination of dust mass deposited on an air filter from a known volume of air sample. The dust mass is determined from radiation attenuation of a Pm-147 beta source. Additionally, relative humidity, atmospheric pressure and temperature of the air are measured [1].

Usually, the dust monitors are installed in places where wire communication not always is secured. In such a case, direct collection of measuring results is impossible and requires that personnel of the environment protection units has to go frequently to the monitors to collect the measured data. In case the measurements are made in a few different places, such situation restricts the measurements from economical reasons.

To solve the problem, a new version of dust monitor AMIZ-2004G was developed (Fig.1). The monitor, after a general reconstruction, is equipped with a GSM modem enabling communication with a central computer that is also equipped with such a modem. Thanks to the new construction not only a remote wireless communication with AMIZ is possible, but also a monitoring network containing a higher number of dust monitors can be made. The measuring data from all the monitors in the network can now be collected in one central computer equipped with the GSM modem and a proper acquisition program [2,3].

At the beginning of the year 2005, dust monitoring network was put into operation in the Kielce

Fig.1. Airborne dust concentration gauge AMIZ-2004G.

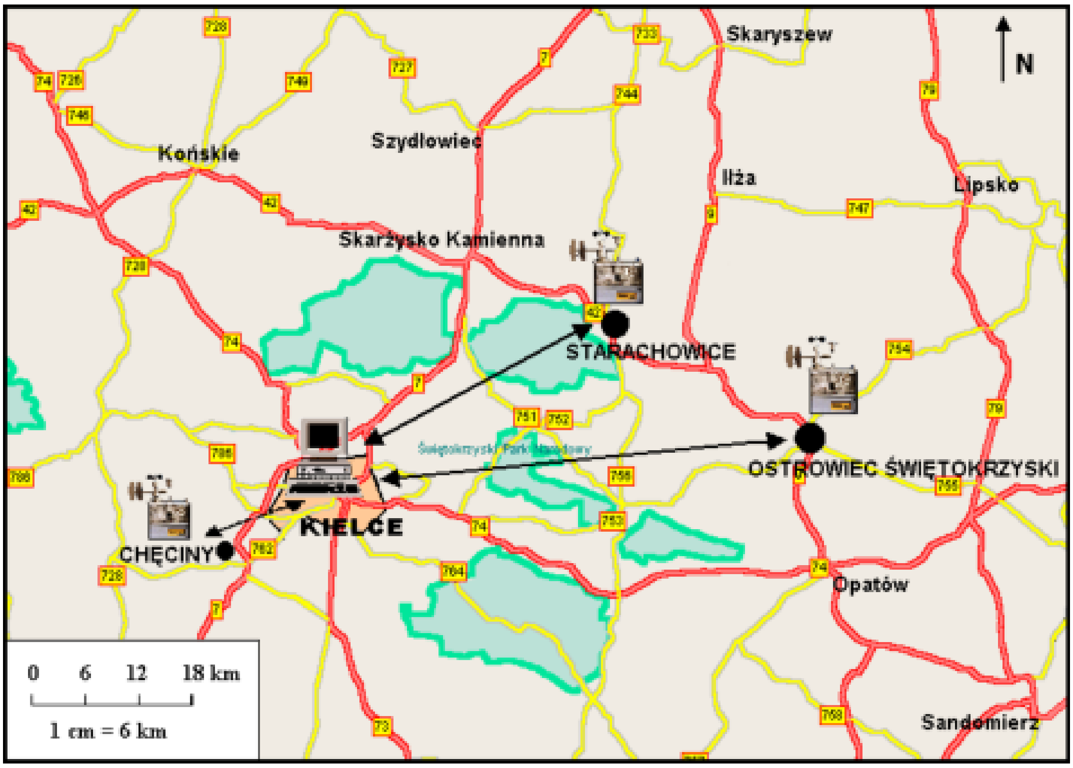

Fig.2. Dust monitoring network in the neighborhood in Kielce.

Voivodeship. Two dust monitors AMIZ-2004G were installed, one at Starachowice the other one at Ostrowiec Świętokrzyski (Fig.2). The measured data from the monitors are collected in a central computer of the Voivodeship Inspectorate of Environment Protection at Kielce. Apart from measured data collection from the AMIZ-2004G monitors, the network offers additionally data collection from two other monitoring stations containing two older AMIZ monitors at Chęciny and Kielce and from monitors of NO_X, NO_2, NO and SO_2 [4].

In the second half of 2005, the Institute of Nuclear Chemistry and Technology received an order for an installation of dust monitoring network in

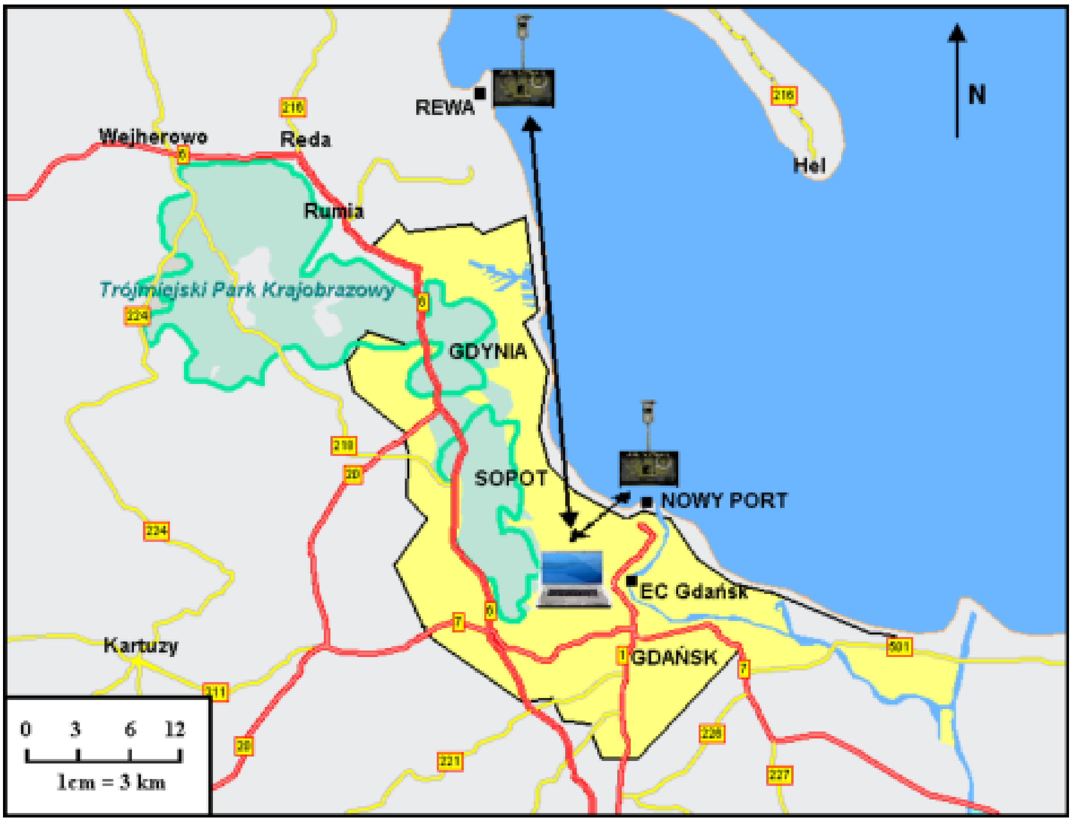

Fig.3. Dust monitoring network in the neighborhood of Gdańsk.

the neighborhood of Gdańsk (Fig.3). The first monitor AMIZ-2004G was installed at Rewa, approximately 60 km from the central computer located in the Environment Management Board of Electro-Power Station Gdańsk. In the coming year, an installation of air dust monitoring is foreseen at New Port in Gdańsk.

The developed and installed software in the monitors AMIZ enables the following functions [5]:
- data acquisition by means of GSM network from AMIZ-2004G monitors,
- data acquisition from a number of monitoring stations,
- readout of data from all the gauges (monitors) located in the monitoring station,
- review of measuring results from different gauges (monitors),
- review of measuring results in external database,
- readout and programming new measuring parameters,
- readout and setting new alarm messages – SMS,
- readout air pump temperature.

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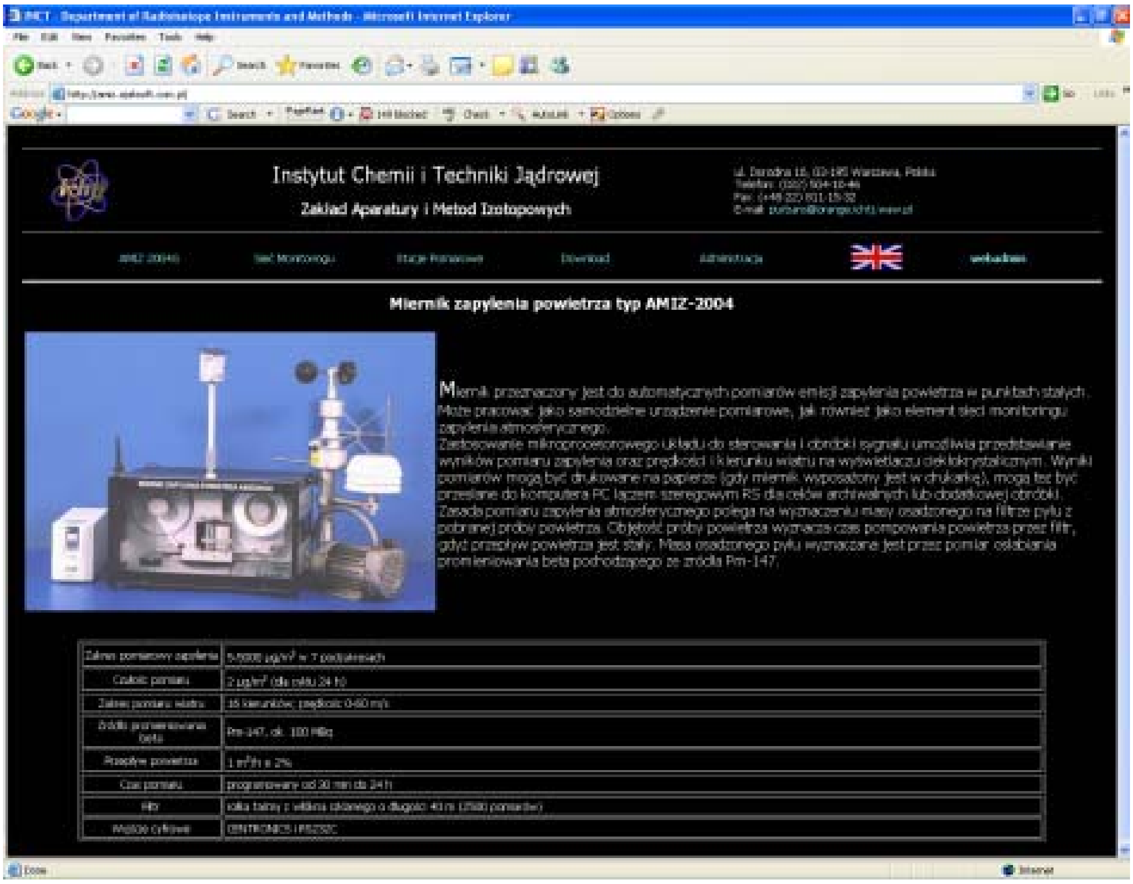
DEVELOPMENT OF INTERNET SERVICE FOR AIRBORNE DUST MONITOR

Adrian Jakowiuk

During use of the system for acquisition and presentation of measuring data from dust monitors AMIZ-2004G [1], it became evident that creation of an internet service should be very useful. The task of such a service would be presentation of the idea of dust monitoring system that was put into operation, as well as presentation of measuring results from already existing measuring stations.



Instytut Chemii i Techniki Jądrowej

Zakład Aparatury i Metod Izotopowych

Miernik zapylenia powietrza typ AMIZ-2004

Fig.1. Web page containing information of AMIZ-2004G.

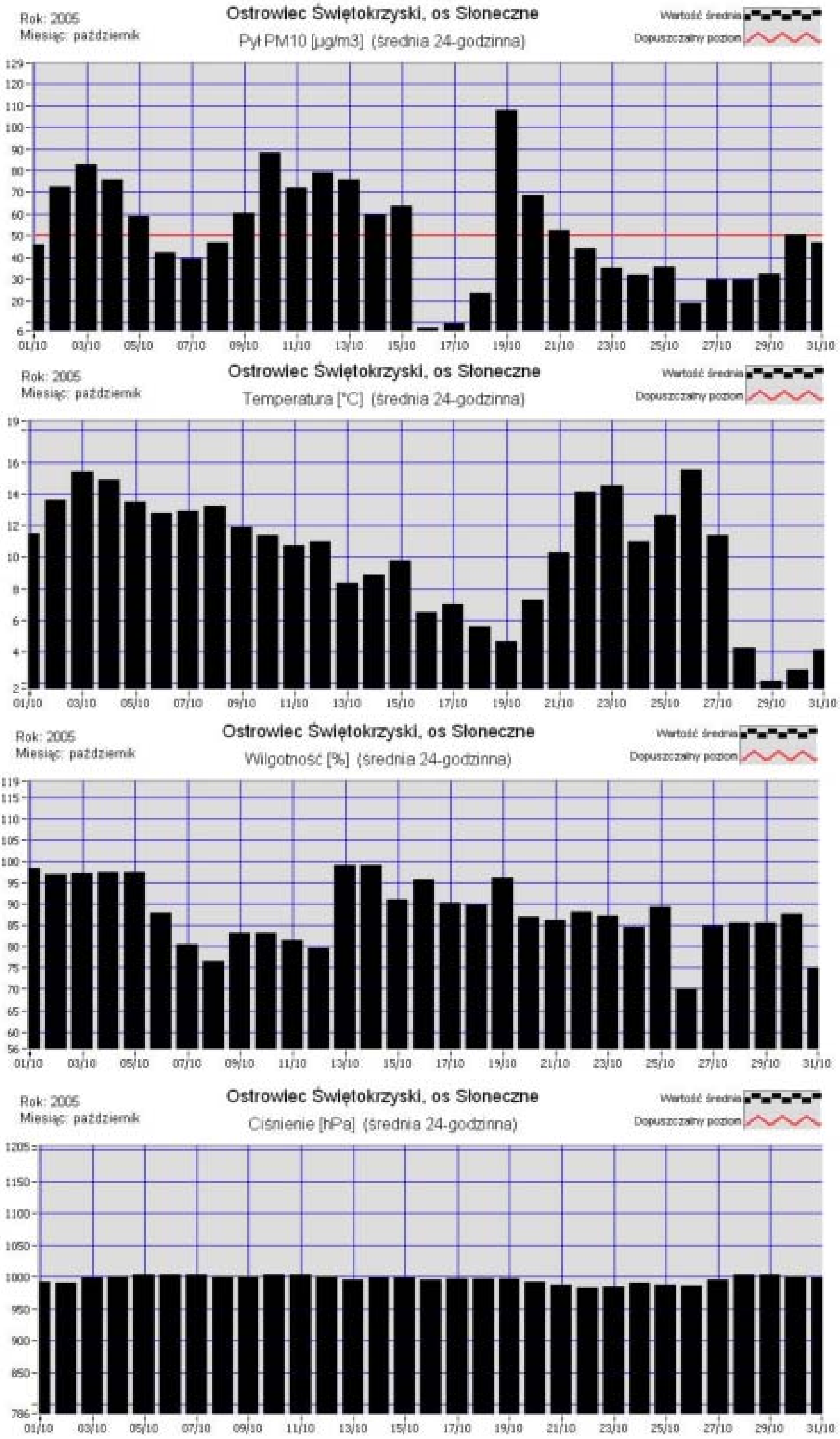


Fig.2. Example diagrams with measured data.

Such an internet service was created and is accessible now on web page www.amiz.ajaksoft.com.pl (Fig.1). Information concerning dust monitor AMIZ-2004G and its basic technical data are now given in the service. Description of the dust monitoring system, instruction how to operate the program for acquisition of measured data, operating instruction of the monitor AMIZ-2004G, and leaflets of the system can also be found there.

The main task of the created service, apart from the presentation of the dust monitor AMIZ-2004G, is the presentation of measured results from already existing measuring stations. Three measuring stations are put presently into operation. Two of them are located in the neighborhood of Kielce (one at Ostrowiec Świętokrzyski, the other at Starachowice). The third station is located at Rewa near Gdańsk. Measured data from two stations in the neighborhood of Kielce are presented on the web page. The data are: airborne dust concentration, air temperature and pressure and relative humidity measured by the stations. Example diagrams with measured data are shown in Fig.2. The diagrams presented in the page are generated by the program servicing AMIZ-2004G and then they are sent to a server. The diagrams show the real dust concentration measured by two stations.

Creation of internet service presenting an airborne dust monitor is necessary also from marketing reasons – easiness to reach potential clients. Such a service enables to show that such monitors are already in operation. This is also the first step in the development of internet page database containing measuring results of all installed monitors.

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FIBER-OPTIC CONTROL SYSTEM FOR LAE 10 ACCELERATOR AND PULSE RADIOLYSIS EXPERIMENTAL SET

Zygmunt Dźwigalski, Zbigniew Zimek

The LAE 10 accelerator is used in nanosecond pulse radiolysis experiments as a source of 10 ns pulses of high energy electrons [1-4]. The accelerator system was elaborated in the years 1991-1993 [5]. Block diagram of the optic trigger system with later modifications is presented in Fig.1. Inseparable connections of the optical fiber marrow with E/O and O/E converters (executed in welding technique) ensured a high stability of the optical parameters at a very long time. The preparation of connections needed adoption of expensive instrumentation from an optoelectronic laboratory in Warsaw.

However, time jitter of the pulses of electron delivered by the accelerator was too big for pulse radiolysis experiments. The total accelerator jitter

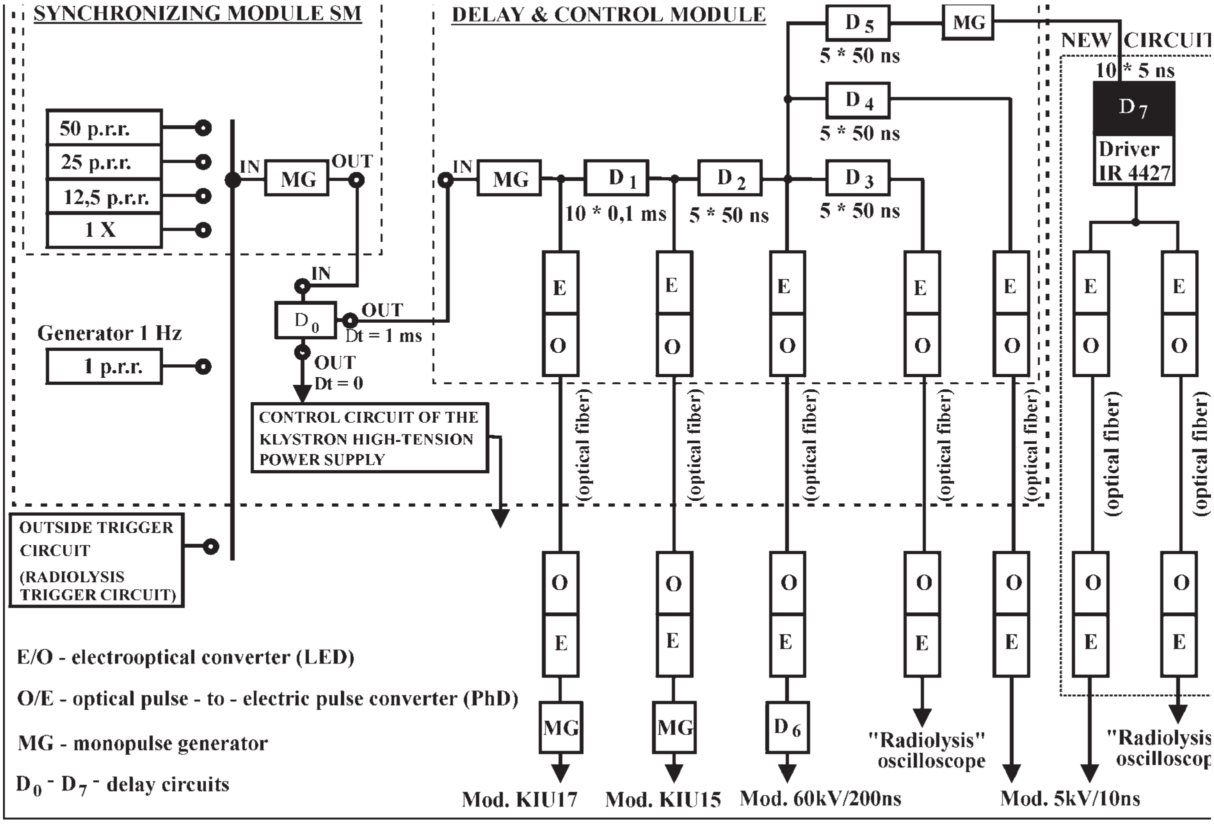

Fig.1. Timing and trigger circuits of the LAE 10 accelerator.

is practically the same as the jitter of a nanosecond modulator (5 kV/10 ns) of the electron gun grid [6]. A detailed consideration of the problem revealed that the applied electronic circuits in trigger line of the nanosecond modulator and in trigger line of the oscilloscopes have too long pulse leading edges (turn-on rise times). The pulse rise time is about 100 ns. The "speed" of thyristors, BTP128 type (commercially available), determined the jitter level. Completely new trigger lines were designed and realized. The new trigger lines of jitter level should ensure less than or equal to ±5 ns.

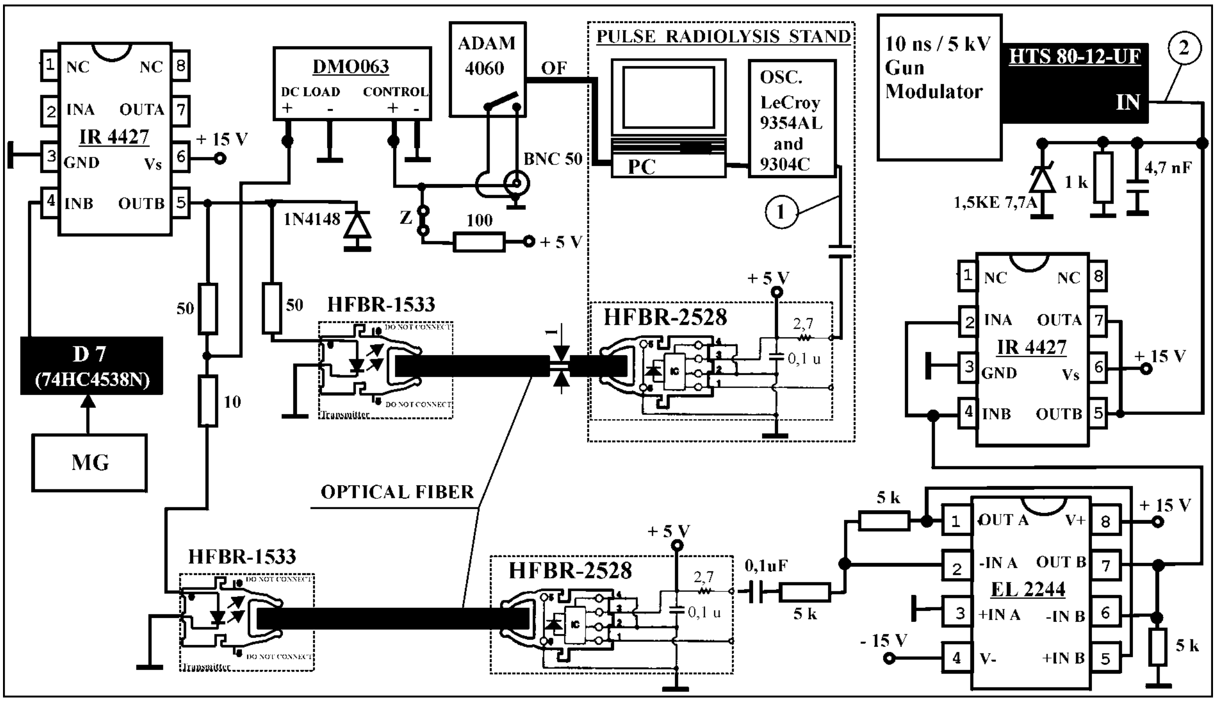

Fig.2. Simplified scheme of the fiber-optic trigger circuits for the nanosecond electron gun modulator and radiolysis oscilloscopes.

Figure 2 shows the simplified schematic drawing of the new trigger circuits with fiber-optic channels of the nanosecond modulator and radiolysis oscilloscopes. Highly speedy electronic subassemblies and E/O and O/E converters (HFBR-1533 "transmitters" and HFBR-2528 "receivers" made by Hewlett Packard) were applied in the trigger lines. A nylon optical fiber which to get along with the converters has a diameter of 1 mm. Advantages of the new circuits are the following:

- rise time of each subassembly is repeatedly lower,
- low cost of subassemblies and elements,
- connections HFBR-1533 "transmitters" and HFBR-2528 "receivers" with the nylon optical fiber are possible (in own range) without very expensive instrumentation,
- precise and repeated shift possibility on the time axis (as about 5 ns) to allow on adjustment pulse of the nanosecond modulator in proportion to anode modulator (60 kV/200 ns) of the gun. Digital potentiometer (with decimal controller) 3683 type Bourns firm was applied in D7 delay circuit [7] to achieve precise adjustment.

Another interesting feature of the accelerator is the possibility of the control of pulse pedestal [8] while running the experiment. This can be carried out during analyzing a light adjustment procedure (after each change of wavelength), it requires triggering all accelerator pulse devices except the nanosecond modulator of the accelerator electron gun grid. Triggered pulse of the HFBR-1533 "transmitter" in the trigger line of the nanosecond modulator is shorted to "ground" by an electronic relay, DMO063 type. The short-circuit is executed on the

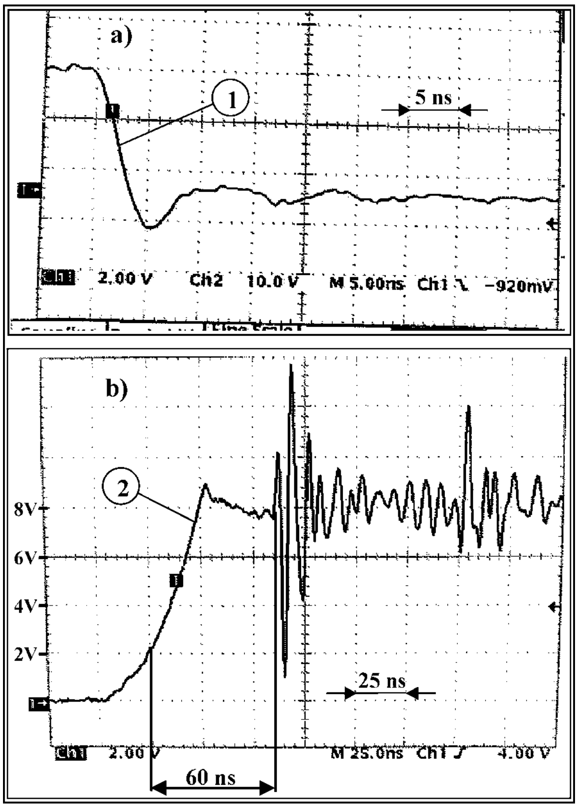

Fig.3. Pulse leading edges in selected places of fiber-optic trigger circuits.

signal from the pulse radiolysis experimental set. The signal is transfer by the optical fiber "FO" and Adam-4060 couple module (Fig.2).

Figure 3 shows the pulse leading edges in selected places (see Fig.2) of the new trigger circuits. The pulse leading edges was recorded by a digital Tektronix oscilloscope, TDS620 type, and the oscillograms were taken by QV-100 Casio digital camera and computer processed. We can state that the pulses on the output of the HFBR-2528 "receiver" (Fig. 3a) can be obtained with rise time less than 5 ns. It was a significant achievement because own rise time of the HFBR-2528 receiver is 12 ns typically. Radiolysis oscilloscopes can be, therefore triggered with jitter below 1 ns. Trigger circuit of the nanosecond modulator is more complicated. Additional electronic subassemblies and elements are inserted between the output of the HFBR-2528 "receiver" and the input HTS 80-12-UF high voltage transistor switch of the nanosecond modulator. The amplifier built-up, inter alia, from the EL2244 integrated circuit and IR4427 driver are the subassemblies. Resistor (1 kΩ), capacitor (4.7 nF – relatively big capacity in this case) and 1.5KE7.7A diode to overvoltage protection are the elements set up in parallel to the switch input. It was necessary to reduce – to value less than noise-margin – the amplitude of the disturbing pulse on the input of the HTS 80-12-UF switch. Anode modulator (60 kV/200 ns) of the accelerator gun [6] is the source of the disturbing pulse. So, therefore considerable reduction occurred of the pulse rate-of-rise from about 1 V/ns on the output of the HFBR-2528 receiver to about 0.1 V/ns on the input of the HTS 80-12-UF switch. Delay time of the switch is 60 ns with an effect from the moment of time in which the voltage on the input of the switch achieved an adequate value. Amplitude of the trigger pulse ought to range from 2 to 10 V. The start action of the switch can be recognized by the occurrence of characteristic pulse ripple (Fig.3b).

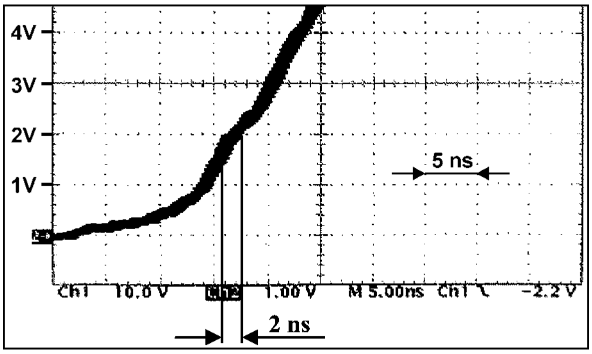

Fig.4. Part of 30 pulse leading edges.

Essential fragments of the successive 30 pulses on the HTS 80-12-UF switch input is shown in Fig.4. We can state that jitter of the trigger line of the nanosecond modulator is not more than 2 ns even for the most disadvantageous case *i.e.* for least rate-of-rise the voltage range from 2 to 3 V. Jitter of the nanosecond modulator is practically the same because own jitter of the switch is only 100 ps.

A series of accelerator pulses in radiolysis experiments as a rule is less than or equal to 10 pulses. In conclusion, we can state that the new trigger lines assure the operation jitter of the LAE 10 accelerator less than 5 ns. Successive results from numerous recent pulse radiolysis experiments confirm this conclusion.

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Badania składu izotopowego żywności – aspekty poznawcze i utylitarne (Investigations of isotopic composition of foodstuff – basic study and applications).

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1. Foreword
   G. Bystrzejewska-Piotrowska
2. Short review: the mechanisms of radiocaesium uptake by Arabidopsis roots
   C.R. Hampton, M.R. Broadley, P.J. White
3. Cationic interactions in caesium uptake by king oyster mushroom (*Pleurotus eryngii*)
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9. Plutonium isotopes ^{238}Pu, $^{239+240}$Pu and ^{241}Pu in the Baltic Sea ecosystem
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10. Bioaccumulation of ^{137}Cs and ^{60}Co by *Helianthus annuus*
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12. Platinum bioaccumulation by mustard plants (*Sinapis alba* L.)
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13. Preliminary study of platinum accumulation in the fruitbodies of a model fungal species: king oyster mushroom (*Pleurotus eryngii*)
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   E. Szajdzińska-Piętek, M. Wolszczak
2. Application of ionizing radiation in studies of biomarkers of individual susceptibility
   A. Cebulska-Wasilewska
3. The influence of fractionated radiation on proliferation, cell cycle and apoptosis of normal human dermal fibroblasts
   A. Adamczyk, A. Gasińska
4. Stimulatory effects of single low-level irradiations with X-rays on functions of murine peritoneal macrophages
   A. Cheda, J. Wrembel-Wargocka, E.M. Nowosielska, M.K. Janiak
5. Pro-angiogenic effects of X-rays on murine endothelial cells
   E. Lisiak, M. Dziekiewicz, V. Meineke, M. Bilski, M.K. Janiak
6. Low-level exposures to ionising radiation modulate the anti-tumour activity of murine NK cells
   E.M. Nowosielska, J. Wrembel-Wargocka, A. Cheda, E. Lisiak, M.K. Janiak
7. Influence of frequent magnetic field on chlorophyll content in leaves of sugar beet plants
   M. Rochalska
8. The mechanism and kinetics of ozone formation in a pulse radiolysis study of the Ar-O_2 system
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9. Formation of $Br_2^{\bullet-}$, $BrSCN^{\bullet-}$ and $(SCN)_2^{\bullet-}$ intermediates in the ionic liquid methyltributylammonium bis[(trifluoromethyl)sulfonyl]imide. Pulse radiolysis study
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SUPPLEMENT No. 3/2005

Proceedings of the Jubilee Symposium for the 50th anniversary of the foundation of the Institute of Nuclear Research "Atomic Science in the XXI Century", 16 June 2005, Warsaw, Poland

Information

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1. **Wojciech Migdał**
   Solska J.: Promień pierwszej świeżości (A ray of early freshness). Polityka, 31 (2515), (2005).
2. **Zbigniew P. Zagórski**
   Jabłoński R.: Korea Północna czeka na wybuch (North Korea is waiting for burst). Życie Warszawy, 11-12.06.2005, p.17.

THE INCT PATENTS AND PATENT APPLICATIONS IN 2005

PATENTS

1. Sposób wytwarzania termotopliwej kompozycji klejowej z kopolimerów octanu winylu z etylenem (Method for obtaining thermomeltable glue composition from copolymers of vinyl acetate with ethylene)
   I. Legocka, Z. Zimek, A. Woźniak, K. Mirkowski
   Polish Patent No. 190634

PATENT APPLICATIONS

1. Sposób otrzymywania nanobiokompozytu bioceramiczno-polimerowego (Method for obtaining the bioceramic-polymer nanobiocompound material)
   W. Łada, D. Wawszczak, A. Deptuła, A. Ignaciuk, W. Zieliński, T. Olczak
   P 373689
2. Sposób topienia odpadów termoplastycznych tworzyw sztucznych oraz urządzenie do realizacji tego sposobu (Method and melter for melting thermoplastic wastes)
   B. Tymiński, R. Jurczyk, K. Zwoliński
   P 373853
3. Sposób modyfikowania pigmentów mineralnych (Method for modification of mineral pigments)
   A. Łukasiewicz, D. Chmielewska, L. Waliś, J. Michalik
   P 375801

CONFERENCES ORGANIZED AND CO-ORGANIZED BY THE INCT IN 2005

1. MINI-SYMPOSIUM "FREE RADICALS AND NEURODEGENERATION", 24 JANUARY 2005, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Organizer: Prof. K. Bobrowski, Ph.D., D.Sc.

LECTURES

- Molecular mechanisms of neurodegeneration
  D. Elbaum (Nencki Institute of Experimental Biology, Polish Academy of Sciences, Warszawa, Poland)
- One-electron oxidation of β-amyloid peptide and related peptides
  Ch. Houée-Levin (Université Paris-Sud XI, Orsay, France)
- How α-helical β-amyloid peptide could be a source of free radicals? Some molecular modeling attempts to β-amyloid mystery
  D. Pogocki (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)

2. FIRST PLANNING AND COORDINATING MEETING IN THE FRAME OF THE TECHNICAL COOPERATION PROJECT RER/8/010 "QUALITY CONTROL METHODS AND PROCEDURES FOR RADIATION TECHNOLOGY", 21-25 FEBRUARY 2005, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology, International Atomic Energy Agency

Organizing Committee: Z. Zimek, Ph.D., I. Kałuska, M.Sc., S. Bułka, M.Sc.

LECTURES

- Technical and training aspects of program implementation
  A.G. Chmielewski (International Atomic Energy Agency, Vienna, Austria)
- TC program and its requirements, Program Coordination
  A. Chupov (International Atomic Energy Agency, Vienna, Austria)
- Validation and routine control of radiation sterilization process
  I. Kałuska (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- The role of dosimetry in facility qualification and process validation with respect to the recent sterilization standard
  A. Miller (Risoe National Laboratory, Denmark)
- Dosimetry systems, calibration and traceability according to recent developments
  A. Kovacs (Institute of Isotopes and Surface Chemistry, Budapest, Hungary)
- Requirements for an industrial irradiation center – acceptance and possibility of irradiation in Germany
  A. Zyball (Beta-Gamma Service GmbH & Co, Germany)
- Electron accelerators for radiation processing
  Z. Zimek (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Radiation crosslinking of cable isolation; QA and QC at irradiation centers. Radiation processing in Switzerland
  H.J. Hartmann (Studer AG Werk Hard, Switzerland)
- Control system for dose and process data registration
  S. Bułka (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Radiation processing in Hungary
  A. Kovacs (Institute of Isotopes and Surface Chemistry, Budapest, Hungary)
- Radiation processing in Spain
  J.I.M. Galan (Electron Servic Line, Madrid, Spain)

- Radiation processing in Ukraine
  G. Popov (Kharkov State University, Ukraine)
- Radiation processing in Republic of Moldova
  A. Buzdugan (Centre for Metrology and Automation of Scientific Research, Republic of Moldova), I. Bahnarel (Ministry of Health, Republic of Moldova)
- Radiation technologies in Serbia, present status and prospects
  D. Babic (Vinča Institute of Nuclear Sciences, Belgrade, Serbia and Montenegro)
- Radiation processing in Montenegro
  S. Jovanovic (University of Montenegro, Podgorica, Serbia and Montenegro)
- Radiation processing in Albania
  A. Dodbiba (Institute of Nuclear Physics, Tirana, Albania)
- Radiation processing in Poland
  Z. Zimek (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)

3. FUTURE INCT RESEARCH PROGRAMMES – PREPARATION OF IAEA COUNTRY PROGRAMME FRAMEWORK (CPF) FOR POLAND 2006-2012, 28 APRIL 2005, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology, International Atomic Energy Agency, National Atomic Energy Agency

Organizers: J. Michalik, J. Niewodniczański, J. Zlatansky, A. Cardoso, P.R. Danesi

LECTURES

- INCT research programmes
  J. Michalik (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Electron beam facilities for radiation processing
  S. Bułka (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Nuclear technologies for environment protection
  G. Zakrzewska-Trznadel (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Nuclear analytical methods for quality assurance, food safety and environment protection
  H. Polkowska-Motrenko (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- 40 years of radiation sterilization and tissue banking in Poland
  A. Dziedzic-Gocławska (Medical University of Warsaw, Poland)

Visit to the INCT departments: Department of Radiation Chemistry and Technology, Department of Nuclear Methods of Process Engineering, Department of Analytical Chemistry

4. IV KRAJOWA KONFERENCJA „RADIOCHEMIA I CHEMIA JĄDROWA" (FOURTH NATIONAL CONFERENCE ON RADIOCHEMISTRY AND NUCLEAR CHEMISTRY), 9-11 MAY 2005, KRAKÓW-PRZEGORZAŁY, POLAND

Organized by the Institute of Nuclear Chemistry and Technology, the Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences with the participation of the Committee of Nuclear and Radiation Chemistry of the Council for Atomistics

Organizing Committee: L. Fuks, Ph.D. (Chairman), Ewa Gniazdowska, Ph.D., Barbara Kubica, Ph.D., Assoc. Prof. Jerzy W. Mietelski, Ph.D., D.Sc.

PLENARY LECTURES

- Kierunki rozwoju radiochemii na początku XXI wieku (Trends in radiochemistry at the beginning of the 21th century)
  J. Narbutt (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Technetium and rhenium in radiopharmacy
  R. Alberto (University of Zürich, Switzerland)
- Wykorzystanie metod radiochemicznych w badaniach środowiska naturalnego (Some applications of environmental radiochemical analysis)
  H. Bem (Technical University of Łódź, Poland)

LECTURES

Session 1

- INAA w badaniach ikon z Polski południowo-wschodniej (INAA in the studies of icons originating from south-eastern Poland)

  E. Pańczyk (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), J. Giemza (The Łańcut Castle Museum, Poland), L. Waliś (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Międzynarodowe ćwiczenia interkalibracyjne ruchomych laboratoriów spektrometrycznych „Turawa 2003" (International mobile spectrometric laboratory; intercomparison exercise "Turawa 2003")

  K. Isajenko (Central Laboratory for Radiological Protection, Warszawa, Poland), P. Lipiński (Central Laboratory for Radiological Protection, Warszawa, Poland)
- Badanie zależności oceny narażenia radonowego w budynkach od rozkładu wielkości cząstek związanych z pochodnymi (Investigation of the dependence of the radon risk assessment in dwelling on the radon progeny size distribution)

  K. Mamont-Cieśla (Central Laboratory for Radiological Protection, Warszawa, Poland), O. Stawarz (Central Laboratory for Radiological Protection, Warszawa, Poland)
- Rozmieszczenie ^{137}Cs, ^{239,240}Pu, ^{238}Pu i ^{90}Sr w osadach dennych Bałtyku południowego w latach 2001-2004 (Distribution of ^{137}Cs, ^{239,240}Pu, ^{238}Pu and ^{90}Sr in bottom sediments from the southern Baltic Sea in the years 2001-2004)

  M. Suplińska (Central Laboratory for Radiological Protection, Warszawa, Poland), Z. Pietrzak-Flis (Central Laboratory for Radiological Protection, Warszawa, Poland), A. Adamczyk (Central Laboratory for Radiological Protection, Warszawa, Poland)
- Badania adsorpcji konkurencyjnej jonów Sr^{2+} i Y^{3+} na granicy faz SiO_2/roztwór elektrolitu metodą radioizotopową (A study of the coadsorption of Sr^{3+} and Y^{3+} ions at the silica/electrolyte solution interface)

  W. Janusz (The Maria Curie-Skłodowska University, Lublin, Poland)
- Migracja pionowa ^{129}I i ^{137}Cs w glebach (Vertical migration of ^{129}I and ^{137}Cs in soils)

  Z. Pietrzak-Flis (Central Laboratory for Radiological Protection, Warszawa, Poland), I. Radwan (Central Laboratory for Radiological Protection, Warszawa, Poland), P. Krajewski (Central Laboratory for Radiological Protection, Warszawa, Poland)

Session 2

- Poprawki na samoabsorpcję i koincydencyjne sumowanie w dokładnych pomiarach próbek środowiskowych metodą spektrometrii gamma (Self-absorption and coincidence-summing corrections in precise gamma-ray spectrometry of environmental samples)

  P. Jodłowski (AGH University of Science and Technology, Kraków, Poland)
- Klasyfikacja i ocena materiałów budowlanych w Polsce w świetle nowych przepisów (Classification and evaluation of building materials in Poland from the point of view of new regulations)

  A. Żak (Central Laboratory for Radiological Protection, Warszawa, Poland), M. Biernacka (Central Laboratory for Radiological Protection, Warszawa, Poland)
- Pionowy transport izotopów plutonu w glebach uprawnych Pojezierza Łęczyńsko-Włodawskiego (Vertical migration of plutonium isotopes in cultivated soils of the Łęczna-Włodawa lake district)

  A. Komosa (The Maria Curie-Skłodowska University, Lublin, Poland), S. Chibowski (The Maria Curie-Skłodowska University, Lublin, Poland), J. Orzeł (The Maria Curie-Skłodowska University, Lublin, Poland)
- Zastosowanie kompleksów zawierających mostek metal-^{211}At jako nowej metody otrzymywania radiofarmaceutyków astatowych (Use of metal-^{211}At complexes as a new method for preparation of astatine radiopharmaceuticals)

  M. Pruszyński (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), A. Bilewicz (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), B. Wąs (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), B. Petelenz (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland)
- Metoda wytwarzania i badanie stabilności L-α-metylotyrozyny znakowanej jodem-123 stosowanej do diagnostyki nowotworów mózgu (Production method and determination of stability of ^{123}I labelled L-α-methylthyrosine for the brain cancer diagnosis)

  E. Zakrzewska (Radioisotope Centre POLATOM, Świerk, Poland), R. Mikołajczak (Radioisotope Centre POLATOM, Świerk, Poland), A. Markiewicz (Radioisotope Centre POLATOM, Świerk, Poland), A. Korsak (Radioisotope Centre POLATOM, Świerk, Poland)
- Przedkliniczna ocena *in vitro* peptydu DOTATATE znakowanego ^{177}Lu lub ^{90}Y, radiofarmaceutyku do radioterapii nowotworowej (*In vitro* pre-clinic trials of the ^{177}Lu or ^{90}Y labelled peptide DOTATATE, radiopharmaceutical used in the cancer radiotherapy)

  D. Pawlak (Radioisotope Centre POLATOM, Świerk, Poland), A. Korsak (Radioisotope Centre POLATOM, Świerk, Poland), R. Mikołajczak (Radioisotope Centre POLATOM, Świerk, Poland)

- Synteza związków znakowanych ^{18}F stosowanych w diagnostyce PET (Synthesis of ^{18}F-labelled compounds used in PET diagnosis)
  M. Kańska (Warsaw University, Poland)
- Wpływ inhibitorów na wartości kinetycznych efektów izotopowych w reakcji katalizowanej przez enzym fenololiazę tyrozynową (Impact of competitive inhibitors on kinetic isotope effects in reaction catalyzed by enzyme tyrosine phenol-lyase)
  W. Augustyniak (Warsaw University, Poland), M. Kańska (Warsaw University, Poland)
- Zastosowanie ^{210}Pb i ^{137}Cs do oceny szybkości sedymentacji w zbiornikach wodnych (Application of ^{210}Pb and ^{137}Cs for assessment of sedimentation rate in aquatic reservoirs)
  M. Olszewski (Technical University of Łódź, Poland), H. Bem (Technical University of Łódź, Poland)

Session 3

- Chemia radiacyjna odpadów radioaktywnych, na podstawie doświadczeń WIPP – Los Alamos National Laboratory (Radiation chemistry of radioactive waste, experience of WIPP – Los Alamos National Laboratory)
  Z.P. Zagórski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Rozmieszczenie Pb, Zn, Cd, Fe i K oraz radionuklidów ^{137}Cs i ^{40}K w wybranych glebach Tatr (Location of Pb, Zn, Cd, Fe, K and radionuclides ^{137}Cs and ^{40}K in some soil samples from the Tatra mountains (southern Poland))
  M. Stobiński (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), B. Kubica (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland; AGH University of Science and Technology, Kraków, Poland), J. Gołaś (AGH University of Science and Technology, Kraków, Poland), S. Skiba (Jagiellonian University, Kraków, Poland), W.M. Kwiatek (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), M. Skiba (Jagiellonian University, Kraków, Poland), E.M. Dutkiewicz (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), J. Górecki (AGH University of Science and Technology, Kraków, Poland)
- Rozmieszczenie skażeń izotopem ^{90}Sr na terenie Polski (Distribution of the ^{90}Sr contamination in Poland)
  P. Gaca (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), B. Skwarzec (University of Gdańsk, Poland), J.W. Mietelski (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland)
- Występowanie radonu w środowisku na obszarze polskiej części Sudetów: stan wiedzy i przyszłe wyzwania (Radon presence in the environment of the Polish part of the Sudety mountains: the state of knowledge and future challenges)
  T.A. Przylibski (Wrocław University of Technology, Poland)
- Stanowisko do kalibracji radonowych detektorów śladowych w Politechnice Wrocławskiej (Appointment for the calibration of radon trace detectors at Wrocław University of Technology)
  A. Żebrowski (Wrocław University of Technology, Poland), T.A. Przylibski (Wrocław University of Technology, Poland)
- Radionuklidy żelaza (^{55}Fe), niklu (^{63}Ni), polonu (^{210}Po), uranu (^{234}U, ^{235}U, ^{238}U) i plutonu (^{238}Pu, $^{239+240}$Pu, ^{241}Pu) w środowisku naturalnym Polski i Morza Bałtyckiego (Radionuclides of iron (^{55}Fe), nickel (^{63}Ni), polonium (^{210}Po), uranium (^{234}U, ^{235}U, ^{238}U) and plutonium (^{238}Pu, $^{239+240}$Pu, ^{241}Pu) in Poland and the Baltic Sea environment)
  B. Skwarzec (University of Gdańsk, Poland), D. I. Strumińska (University of Gdańsk, Poland), A. Boryło (University of Gdańsk, Poland)
- Pluton w ekosystemie południowego Bałtyku (Plutonium in the southern Baltic Sea ecosystem)
  D.I. Strumińska (University of Gdańsk, Poland), B. Skwarzec (University of Gdańsk, Poland)
- Badania migracji pionowej w glebach uprawnych i współczynników przeniesienia (gleba-roślina) izotopu strontu ^{90}Sr (Studies of vertical migration of strontium ^{90}Sr in arable soils and soil to plant transfer factor of this isotope)
  J. Solecki (The Maria Curie-Skłodowska University, Lublin, Poland)
- Sztuczne pierwiastki promieniotwórcze w kościach dzikożyjących zwierząt z terenów Polski wschodniej (Artificial radionuclides in bones of wild animals from eastern Poland)
  J.W.Mietelski (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), P. Gaca (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), I. Kitowski (The Maria Curie-Skłodowska University, Lublin, Poland), E. Tomankiewicz (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), S. Grabowska (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland)
- Nagromadzenie polonu (^{210}Po), uranu (^{234}U, ^{238}U) i plutonu (^{238}Pu, $^{239+240}$Pu) w tkankach i narządach jeleniowatych (*Cervidae*) z Polski północnej (Bioaccumulation of polonium (^{210}Po), uranium (^{234}U, ^{238}U) and plutonium (^{238}Pu, $^{239+240}$Pu) in tissues and organs of deer (*Cervidae*) from northern Poland)
  M. Prucnal (University of Gdańsk, Poland), B. Skwarzec (University of Gdańsk, Poland)

POSTERS

- Prace nad konstruowaniem metody definitywnej dla oznaczania selenu w materiałach biologicznych za pomocą radiochemicznej neutronowej analizy aktywacyjnej (Studies on the elaboration of the definite method of the analysis of selenium in biological materials using RNAA)

  E. Chajduk-Maleszewska (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), H. Polkowska-Motrenko (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), R. Dybczyński (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Rozdzielenie jonów Am(III) i Eu(III) metodą ekstrakcji z roztworów azotanowych mieszaniną nowego heterocyklicznego liganda *N*-polidentnego i chlorowanego dikarbolidu kobaltu (Separation of Am(III) from Eu(III) by solvent extraction from nitrate solution using a new heterocyclic *N*-polydentate ligand and chlorinated cobalt dicarbollide)

  J. Krejzler (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), J. Narbutt (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Analiza bieli ołowiowej w tablicowym malarstwie gdańskim z II połowy XV wieku z wykorzystaniem neutronowej analizy aktywacyjnej (The examination of lead white from Gdańsk panel paintings of the fifteenth century by means of neutron activation analysis)

  J. Olszewska-Świetlik (The Nicolaus Copernicus University, Toruń, Poland), E. Pańczyk (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Analiza materiałów opakowaniowych metodą instrumentalnej neutronowej analizy aktywacyjnej (Instrumental neutron activation analysis of wrapping materials)

  Z. Szopa (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), K. Kulisa (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), R. Dybczyński (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Radiochemiczna metoda oznaczania wiązania jonów przez heparynę (Radiochemical method of determination of metal binding by heparine)

  I. Kijewska (Technical University of Łódź, Poland), E. Hawlicka (Technical University of Łódź, Poland)
- Kinetyczne efekty izotopowe trytu w enzymatycznym rozkładzie L-tryptofanu (Kinetic isotope effects on enzymatic decomposition of L-tryptophan)

  E. Boroda (Warsaw University, Poland), R. Kański (Warsaw University, Poland), M. Kańska (Warsaw University, Poland)
- Enzymatyczna synteza tyraminy znakowanej izotopami wodoru (Enzymatic synthesis of tyramine labelled with isotopes of hydrogen)

  E. Panufnik (Warsaw University, Poland), R. Kański (Warsaw University, Poland), M. Kańska (Warsaw University, Poland)
- Synteza znakowanej w pierścieniu [1'-^{14}C]-L-tyrozyny (Synthesis of ring labelled [1'-^{14}C]-L-tyrosine)

  R. Kański (Warsaw University, Poland), W. Augustyniak (Warsaw University, Poland), M. Kańska (Warsaw University, Poland)
- Wpływ podstawienia izotopowego H/D na właściwości fizykochemiczne nitrometanu, pentanolu i ich roztworu (The influence of H/D isotope substitution on physicochemical properties of nitromethane, pentanol and their mixture)

  A. Makowska (Warsaw University, Poland), J. Szydłowski (Warsaw University, Poland)
- Wpływ podstawienia izotopowego H/D na mieszalność układu anilina/cykloheksan (Influence of H/D isotope substitution on miscibility of aniline/cyclohexane system)

  A. Siporska (Warsaw University, Poland), E. Starościak (Warsaw University, Poland), J. Szydłowski (Warsaw University, Poland)
- Cs-137 w środowisku naturalnym Gorców – wartości i rozkłady skażeń, zmienność lokalna (The deposition of Cs-137 and its spatial variability over the Gorce mountains in Poland)

  P. Jodłowski (AGH University of Science and Technology, Kraków, Poland)
- Czasowa zmienność stężenia radonu w jednorodzinnych domach północno-wschodniej Polski (Time changeability in radon concentration in one-family dwelling houses in the north-eastern region of Poland)

  M. Karpińska (Medical University of Białystok, Poland), Z. Mnich (Medical University of Białystok, Poland), J. Kapała (Medical University of Białystok, Poland)
- Analiza czynników wpływających na depozycję radiocezu w jeziorach północno-wschodniej Polski (Parameters determining the deposition of radiocaesium in the lakes of north-eastern Poland)

  J. Kapała (Medical University of Białystok, Poland), M. Karpińska (Medical University of Białystok, Poland), Z. Mnich (Medical University of Białystok, Poland)
- Migracja pionowa ^{129}I i ^{137}Cs w glebach (Vertical migration of ^{129}I and ^{137}Cs in soils)

  Z. Pietrzak-Flis (Central Laboratory for Radiological Protection, Warszawa, Poland), I. Radwan (Central Laboratory for Radiological Protection, Warszawa, Poland), P. Krajewski (Central Laboratory for Radiological Protection, Warszawa, Poland)

- System wczesnego wykrywania skażeń promieniotwórczych w Polsce (Early detection system of radioactive contamination in Poland)

  K. Isajenko (Central Laboratory for Radiological Protection, Warszawa, Poland), P. Lipiński (Central Laboratory for Radiological Protection, Warszawa, Poland)

- Metoda oznaczania ^{228}Ra w próbkach środowiskowych z wykorzystaniem pomiaru promieniowania beta ^{228}Ac (Method for ^{228}Ra determination in environmental samples by the measurement of ^{228}Ac beta activity)

  I. Kamińska (Central Laboratory for Radiological Protection, Warszawa, Poland), E. Chrzanowski (Central Laboratory for Radiological Protection, Warszawa, Poland), P. Roos (Central Laboratory for Radiological Protection, Warszawa, Poland)

- Interkalibracja przyrządów do pomiaru radonu i jego pochodnych w komorze CLOR w roku 2003 (Intercomparison of instruments for radon and radon progeny measurements in the CLOR chamber in 2003)

  K. Mamont-Cieśla (Central Laboratory for Radiological Protection, Warszawa, Poland), O. Stawarz (Central Laboratory for Radiological Protection, Warszawa, Poland)

- Badanie wpływu wysokiej wilgotności względnej i czasu ekspozycji na wynik pomiaru stężenia radonu za pomocą detektorów węglowych (Studies of influence of high relative humidity and exposure time on the results of radon concentration measured by means of charcoal detectors)

  O. Stawarz (Central Laboratory for Radiological Protection, Warszawa, Poland), M. Karpińska (Medical University of Białystok, Poland), K. Mamont-Cieśla (Central Laboratory for Radiological Protection, Warszawa, Poland)

- Badania środowiskowe materiału zgromadzonego na hałdach pouranowych w Radoniowie (Environmental assessment of the material deposited on the former uranium mining disposal dumps in Radoniów)

  A. Żak (Central Laboratory for Radiological Protection, Warszawa, Poland), M. Biernacka (Central Laboratory for Radiological Protection, Warszawa, Poland), K. Isajenko (Central Laboratory for Radiological Protection, Warszawa, Poland), P. Lipiński (Central Laboratory for Radiological Protection, Warszawa, Poland), T.J. Sibiga (MOSTOSTAL-Warszawa S.A., Poland)

- Test biegłości laboratoriów oznaczających izotopy promieniotwórcze w materiałach środowiskowych i w żywności (Proficiency testing of the laboratories determining radionuclides in environmental and food samples)

  L. Fuks (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), H. Polkowska-Motrenko (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)

- Rozmieszczenie Pb, Zn, Cd, Fe i K oraz radionuklidów ^{137}Cs i ^{40}K w wybranych glebach Tatr (Location of Pb, Zn, Cd, Fe, K and radionuclides ^{137}Cs and ^{40}K in some soil samples from the Tatra mountains)

  M. Stobiński (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), B. Kubica (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland; AGH University of Science and Technology, Kraków, Poland), J. Gołaś (AGH University of Science and Technology, Kraków, Poland), S. Skiba (Jagiellonian University, Kraków, Poland), W.M. Kwiatek (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), M. Skiba (Jagiellonian University, Kraków, Poland), E.M. Dutkiewicz (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), J. Górecki (AGH University of Science and Technology, Kraków, Poland)

- Badanie procesów akumulacji ^{137}Cs i ^{40}K w osadach dennych Zbiornika Dobczyckiego (Investigations on ^{137}Cs and ^{40}K accumulation processes in sediments from the Dobczyce reservoir)

  B. Kubica (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland; AGH University of Science and Technology, Kraków, Poland), J. Gołaś (AGH University of Science and Technology, Kraków, Poland), W.M. Kwiatek (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), M. Skiba (Jagiellonian University, Kraków, Poland), W. Reczyński (AGH University of Science and Technology, Kraków, Poland; Jagiellonian University, Kraków, Poland), M. Stobiński (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland)

- Właściwości akumulacyjne świerka wobec różnych radionuklidów (Accumulation properties of Norway spruce for different radionuclides)

  E. Tomankiewicz (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), J.W. Mietelski (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), P. Gaca (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), S. Grabowska (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland)

- Sezonowe zmiany ^{22}Na, ^{7}Be i ich stosunku w przyziemnej warstwie atmosfery (Seasonal variation of ^{22}Na and ^{7}Be activity and their ratio in ground level air)

  S. Grabowska (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), J.W. Mietelski (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland)

- Badania międzylaboratoryjne poziomu izotopów antropogennych w glebie torfowisk węglanowych i kłoci wiechowatej (*Cladium mariscus*) w okolicach Chełma (Interlaboratory studies of anthropogenic radionuclide level in calcareous peat soil and the saw sedge (*Cladium mariscus*) in the Chełm-town region)

  A. Komosa (The Maria Curie-Skłodowska University, Lublin, Poland), S. Chibowski (The Maria Curie-Skłodowska University, Lublin, Poland), I. Kitowski (The Maria Curie-Skłodowska University, Lublin, Poland), M. Reszka (The Maria Curie-Skłodowska University, Lublin, Poland), J. Orzeł (The Maria Curie-Skłodowska University, Lublin, Poland), J.W. Mietelski (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), R. Kierepko (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), P. Gaca (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), S. Grabowska (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), E. Tomankiewcz (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland)
- ^{137}Cs, $^{238,239+240}$Pu oraz ^{90}Sr w bezkręgowcach z Białorusi (^{137}Cs, $^{238,239+240}$Pu and ^{90}Sr in invertebrates from Belarus)

  J W. Mietelski (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), S. Maksimova (Institute of Zoology, National Academy of Sciences of Belarus, Mińsk, Belarus), K. Wnuk (AGH University of Science and Technology, Kraków, Poland), S. Grabowska (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), P. Gaca (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), E. Tomankiewicz (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland)
- ^{137}Cs, $^{238,239+240}$Pu oraz ^{90}Sr w próbkach biologicznych z ekosystemu antarktycznego (^{137}Cs, $^{238,239+240}$Pu and ^{90}Sr in biological samples from the Antarctic ecosystem)

  J.W. Mietelski (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), M.A. Olech (Jagiellonian University, Kraków, Poland), P. Gaca (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), K. Sobiech (Jagiellonian University, Kraków, Poland), M. Zwolak (Jagiellonian University, Kraków, Poland), S. Grabowska (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), E. Tomankiewicz (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland)
- Izotopy plutonu w powietrzu w latach 1990-1993 (Plutonium isotopes in air during the years 1990-1993)

  J.W. Mietelski (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), P. Gaca (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland)
- ^{238}Pu, $^{239+240}$Pu, ^{241}Am i ^{90}Sr w próbkach gleby z Tatrzańskiego Parku Narodowego (^{238}Pu, $^{239+240}$Pu, ^{241}Am and ^{90}Sr in soil samples from the Tatra National Park)

  J.W. Mietelski (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), P. Gaca (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), E. Tomankiewicz (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), S. Grabowska (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), B. Kubica (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland)
- Sorpcja ^{67}Ga na trudnorozpuszczalnych sześciocyjanożelazianach (II,III) metali przejściowych z roztworów kwasów mineralnych (Sorption of ^{67}Ga on insoluble hexacyanoferrates (II, III) transition metals from mineral acids solutions)

  M. Tuteja-Krysa (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), B. Kubica (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland; AGH University of Science and Technology, Kraków, Poland), E. Ochab (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland)
- Zmiany skażenia środowiska Bałtyku promieniotwórczym cezem – ^{137}Cs w latach 2000-2004 (Changes of the Baltic Sea contamination with caesium – ^{137}Cs in the years 2000-2004)

  T. Zalewska (Institute of Meteorology and Water Management, Gdynia Branch, Poland), J. Lipska (Institute of Meteorology and Water Management, Gdynia Branch, Poland)
- Tło hydrogeochemiczne radonu w wodach podziemnych na przykładzie intruzji granitoidowej kłodzko-złotostockiej i metamorfiku Lądka-Śnieżnika (Hydrogeochemical background from radon in underground water studied in the Kłodzko-Złoty Stok granite intrusion and the Lądek-Śnieżnik metamorphics)

  A. Adamczyk-Lorenc (Wrocław University of Technology, Poland)
- Wody radonowe Sudetów: przyrodnicze, radiologiczne oraz balneologiczne i górnicze aspekty ich występowania (Radon waters of the Sudety mountains: environmental, radiological, balneological and mining aspects of their presence)

  T.A. Przylibski (Wrocław University of Technology, Poland)
- Nagromadzanie polonu ^{210}Po w ptakach morskich (Bioaccumulation of polonium ^{210}Po in marine birds)

  J. Fabisiak (Academy of the Navy, Gdynia, Poland), B. Skwarzec (University of Gdańsk, Poland)

- Spływ polonu (^{210}Po) z dorzecza Wisły (The inflow of polonium ^{210}Po with Vistula river catchment area)
  A. Jahnz (University of Gdańsk, Poland), B. Skwarzec (University of Gdańsk, Poland)
- Specjacja plutonu w osadach dennych południowego Bałtyku (The speciation of plutonium in southern Baltic sediments)
  M. Mazurek (University of Gdańsk, Poland), B. Skwarzec (University of Gdańsk, Poland)
- Spływ polonu ^{210}Po z dorzecza Odry (The inflow of polonium ^{210}Po with Odra river catchment area)
  A. Tuszkowska (University of Gdańsk, Poland), B. Skwarzec (University of Gdańsk, Poland)
- Badanie przechodzenia wybranych metali ciężkich i izotopów promieniotwórczych z gleby torfowisk węglanowych wschodniej Polski do kłoci wiechowatej (*Cladium mariscus*) (Study on selected heavy metal and radioisotope transfer from calcareous peat soil to the saw sedge (*Cladium mariscus*) in eastern Poland)
  A. Komosa (The Maria Curie-Skłodowska University, Lublin, Poland), S. Chibowski (The Maria Curie-Skłodowska University, Lublin, Poland), I. Kitowski (The Maria Curie-Skłodowska University, Lublin, Poland), R. Krawczyń (The Maria Curie-Skłodowska University, Lublin, Poland), J. Orzeł (The Maria Curie-Skłodowska University, Lublin, Poland), M. Reszka (The Maria Curie-Skłodowska University, Lublin, Poland)
- Pionowa migracja ^{137}Cs w glebach uprawnych Pojezierza Łęczyńsko-Włodawskiego (Vertical migration of ^{137}Cs in cultivated soils of the Łęczna-Włodawa lake district)
  A. Komosa (The Maria Curie-Skłodowska University, Lublin, Poland), M. Reszka (The Maria Curie-Skłodowska University, Lublin, Poland), S. Chibowski (The Maria Curie-Skłodowska University, Lublin, Poland)
- Badania adsorpcji ^{85}Sr na frakcjach ziarnowych gleb (Studies of ^{85}Sr adsorption on grain fraction of soil)
  J. Solecki (The Maria Curie-Skłodowska University, Lublin, Poland), S. Michalik (The Maria Curie-Skłodowska University, Lublin, Poland)
- Badania zawartości metali ciężkich oraz izotopów strontu ^{90}Sr i cezu ^{137}Cs w osadach dennych wybranych jezior Pojezierza Łęczyńsko-Włodawskiego (Studies on concentration of some havy metals and strontium ^{90}Sr and cesium ^{137}Cs isotopes in bottom sediments of selected lakes of the Łęczna-Włodawa lake district)
  J. Solecki (The Maria Curie-Skłodowska University, Lublin, Poland), M. Reszka (The Maria Curie-Skłodowska University, Lublin, Poland), S. Chibowski (The Maria Curie-Skłodowska University, Lublin, Poland)
- Przestrzenny rozkład ^{137}Cs w glebie leśnej (Spatial distribution ^{137}Cs in forest soil)
  A. Dołhańczuk-Śródka (Opole University, Poland), T. Majcherczyk (Opole University, Poland), M. Smuda (Opole University, Poland), M. Wacławek (Opole University, Poland)
- Synteza nowych „4+1" Tc(III)/Re(III) mieszanych kompleksów z dendrimerowo zmodyfikowanym ligandem monodentnym (The synthesis of novel "4+1" Tc(III)/Re(III) mixed-ligand complexes with a dendritically modified monodentate ligand)
  E. Gniazdowska (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), H. Stephan (Forschungszentrum Rossendorf e.V., Dresden, Germany), H.-J. Pietzsch (Forschungszentrum Rossendorf e.V., Dresden, Germany)
- Znaczniki ^{73}As, ^{69}Ge i ^{67}Ga – otrzymywanie, wydzielanie i kontrola jakości (Production, separation and quality control of ^{73}As, ^{69}Ge and ^{67}Ga tracers)
  M. Bartyzel (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), M. Kłos (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), R. Misiak (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), E. Ochab (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), B. Petelenz (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland)
- Otrzymywanie i wydzielanie selenu-75 z tarczy germanowej aktywowanej cząstkami α (Production and separation of ^{75}Se from germanium target bombarded with α-particles)
  B. Wąs (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), M. Bartyzel (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), B. Petelenz (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland)
- Synteza L-DOPA znakowanej izotopami węgla i wodoru (Synthesis of L-DOPA labelled with isotopes of carbon and hydrogen)
  M. Kozłowska (Warsaw University, Poland), J. Lepa (Warsaw University, Poland), R. Kański (Warsaw University, Poland), M. Kańska (Warsaw University, Poland)
- Synteza DOPAMINY znakowanej trytem (Synthesis of tritium labelled dopamine)
  M. Pająk (Warsaw University, Poland), M. Kańska (Warsaw University, Poland)
- Efekty izotopowe galu i indu w układach chromatograficznych wymieniających kationy i aniony (Gallium isotopic effects in cation- and anion-exchange chromatography)
  I. Herdzik (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), W. Dembiński (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), W. Skwara (Institute of Nuclear Chemistry

and Technology, Warszawa, Poland), E. Bulska (Warsaw University, Poland), A. Wysocka (Warsaw University, Poland)

- Termochromatograficzne wydzielanie ^{206,208}Po z metalicznej tarczy bizmutowej aktywowanej protonami (Thermochromatographic separation of ^{206,208}Po from a bismuth target bombarded with protons)
  B. Wąs (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), R. Misiak (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), M. Bartyzel (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland)
- Objętości molowe pochodnych ksantyny w H_2O i D_2O (Molar volumes of the xantine derivatives in H_2O and D_2O)
  M. Jelińska-Kazimierczuk (Warsaw University, Poland), J. Szydłowski (Warsaw University, Poland)
- Interkalibracja przyrządów do pomiaru radonu i jego pochodnych w komorze CLOR w roku 2003 (Intercomparison of instruments for radon and radon progeny measurements in the CLOR chamber in 2003)
  K. Mamont-Cieśla (Central Laboratory for Radiological Protection, Warszawa, Poland), O. Stawarz (Central Laboratory for Radiological Protection, Warszawa, Poland)
- Stężenie ^{137}Cs i ^{40}K w próbkach gleby oraz roślin pobranych z terenu Tatrzańskiego Parku Narodowego (Concentration of ^{137}Cs and ^{40}K in samples of soil and flora taken from the Tatra National Park)
  B. Kubica (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland)

5. EUROPEAN YOUNG INVESTIGATOR CONFERENCE 2005 (EYIC 2005), 7-12 JUNE 2005, GNIEZNO, POLAND

Organized by the Institute of Nuclear Chemistry and Technology, the Adam Mickiewicz University

Organizing Committee: Prof. K. Bobrowski, Ph.D., D.Sc. (Chairperson), M. Celuch, M.Sc., P. Filipiak, Ph.D., Assoc. Prof. J. Grodkowski, Ph.D., D.Sc., G. Kciuk, M.Sc., R. Kocia, M.Sc., O. Mozziconacci, M.Sc., Assoc. Prof. D. Pogocki, Ph.D., D.Sc., G. Strzelczak, Ph.D., P. Wiśniowski, Ph.D., Prof. B. Marciniak, Ph.D., D.Sc. (SULFRAD Coordinator)

Opening of the Conference

Chairman: K. Bobrowski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)

B. Marciniak (The Adam Mickiewicz University, Poznań, Poland)
A. Mikołajczak (Collegium Europaeum Gnesnense, Gniezno, Poland)
J. Michalik (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)

I scientific session

Chairman: K.-D. Asmus (The Adam Mickiewicz University, Poznań, Poland)

- Carbon nanotubes and molecular wires – new opportunities for radiation-chemical and photo-chemical investigations
  D.M. Guldi (Friedrich-Alexander-Universität, Erlangen-Nürnberg, Germany)

II scientific session

Chairman: N. Mason (The Open University, Milton Keynes, United Kingdom)

- Absorption spectrum of solvated electrons paired with nonreactive metal cations
  J. Bonin (Université Paris-Sud XI, Orsay, France), I. Lampre (Université Paris-Sud XI, Orsay, France), M. Mostafavi (Université Paris-Sud XI, Orsay, France)
- Free electron transfer involving naphtylamines
  A. Baidak (University of Leipzig, Germany)
- Free electron transfer in benzyltrimethylsilane and derivative molecules
  N. Karakostas (University of Leipzig, Germany)

III scientific session

Chairman: E. Andrzejewska (Poznań University of Technology, Poland)

- Sol-Gel-techniques and photocatalytic applications
  M. Königs (University of Hannover, Germany), D.W. Bahnemann (University of Hannover, Germany)
- Porous poly(epsilon-caprolactone) structures for tissue engineering prepared by a solvent casting/particulate leaching technique
  L. Olah (Technical University of Łódź, Poland; Budapest University of Technology and Economics, Hungary), K. Filipczak (Technical University of Łódź, Poland), P. Ulański (Technical University of Łódź, Poland), T. Czigany (Budapest University of Technology and Economics, Hungary), L. Borbas (Budapest University of Technology and Economics, Hungary), J.M. Rosiak (Technical University of Łódź, Poland)

- Surface properties of KrF laser irradiated collagen films
  M. Wiśniewski (The Nicolaus Copernicus University, Toruń, Poland), A. Sionkowska (The Nicolaus Copernicus University, Toruń, Poland), H. Kaczmarek (The Nicolaus Copernicus University, Toruń, Poland), S. Lazare (Université de Bordeaux I, Talence, France), V. Tokarev (Université de Bordeaux I, Talence, France)
- Irradiation of yeast cell monolayer
  R. Plukienė (Institute of Physics, Vilnius, Lithuania), Š. Vaitekonis (Institute of Physics, Vilnius, Lithuania), B. Remeikytė (Institute of Physics, Vilnius, Lithuania)

IV scientific session

Chairman: O. Brede (University of Leipzig, Germany)

- Thioanalogs of nucleobases as photoprobes for nucleic acid and protein studies
  B. Skalski (The Adam Mickiewicz University, Poznań, Poland)

V scientific session

Chairman: J. Pączkowski (University of Technology and Agriculture, Bydgoszcz, Poland)

- Influence of irradiation sterilization on poly(epsilon-caprolactone). Surface properties and biocompatibility of PCL matrix
  K. Filipczak (Technical University of Łódź, Poland), P. Ulański (Technical University of Łódź, Poland), R. Olkowski (Medical University of Warsaw, Poland), M. Lewandowska-Szumieł (Medical University of Warsaw, Poland), J.M. Rosiak (Technical University of Łódź, Poland)
- Sonolysis of polymers in aqueous solution
  B. Rokita (Technical University of Łódź, Poland), P. Ulański (Technical University of Łódź, Poland), J.M. Rosiak (Technical University of Łódź, Poland)
- Complexation and aggregation of oligo(acrylic acid) with polylactams in aqueous solution
  A. Henke (Technical University of Łódź, Poland), V. Boyko (Dresden University of Technology, Germany), T. Schmidt (Dresden University of Technology, Germany), P. Ulański (Technical University of Łódź, Poland), K.-F. Arndt (Dresden University of Technology, Germany), J.M. Rosiak (Technical University of Łódź, Poland)
- Radiation-induced synthesis of hydrogels based on Pluronic F127
  R. Gottlieb (Dresden University of Technology, Germany; Technical University of Łódź, Poland), A. Henke (Technical University of Łódź, Poland), P. Ulański (Technical University of Łódź, Poland), K.-F. Arndt (Dresden University of Technology, Germany), J.M. Rosiak (Technical University of Łódź, Poland)

VI scientific session

Chairman: C. von Sonntag (The Max Planck Institute for Bioinorganic Chemistry, Mülheim an der Ruhr, Germany)

- Photochemistry of carboxylic acids containing the phenyl and thioether groups. Steady-state and laser flash photolysis studies
  P. Filipiak (The Adam Mickiewicz University, Poznań, Poland), G.L. Hug (University of Notre Dame, USA), K. Bobrowski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), B. Marciniak (The Adam Mickiewicz University, Poznań, Poland)
- Photooxidation of methionine and tyrosine containing peptides: a competition study
  G. Hörner (The Adam Mickiewicz University, Poznań, Poland), A. Lämmermann (The Adam Mickiewicz University, Poznań, Poland), B. Marciniak (The Adam Mickiewicz University, Poznań, Poland)
- Degradation of p-chlorophenol in water solution with Fenton reagent using a photocatalytic system
  V.M. Menéndez (University of Hannover, Germany), D.W. Bahnemann (University of Hannover, Germany), C. Durán-Domínguez (Ciudad Universitaria, Mexico)
- Reactions of flavonoids with α-hydroxyl-containing carbon-centered radicals of various structures
  I.B. Hryntsevich (Belarussian State University, Minsk, Belarus)

VII scientific session

Chairman: B. Marciniak (The Adam Mickiewicz University, Poznań, Poland)

- Rediscovering bimolecular homolytic substitution reactions with time-resolved electron spin resonance: H-atom reactions with α-(alkylthio)-carbonyl compounds
  G.L. Hug (University of Notre Dame, USA), P. Wiśniowski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland; University of Notre Dame, USA), K. Bobrowski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), P. Filipiak (University of Notre Dame, USA), I. Carmichael (University of Notre Dame, USA)

VIII scientific session

Chairman: Ch. Houée-Levin (Université Paris-Sud XI, Orsay, France)

- Radiation-induced radical processes in enkephalin peptides
  O. Mozziconacci (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), J. Mirkowski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), K. Bobrowski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Radical cation $ABTS^{+\bullet}$ in pulse radiolysis studies of radical products of aliphatic amino acids oxidation in homogeneous and microhetereogeneous systems
  M. Maciejewska (Technical University of Łódź, Poland), J.L. Gębicki (Technical University of Łódź, Poland)
- β-Amyloid peptide oxidation by reactive oxygen species: a steady-state γ-radiolysis study
  M. Voicescu (Université Paris-Sud XI, Orsay, France; "I.G. Murgulescu" Institute of Physical Chemistry, Romanian Academy, Bucharest, Romania), V. Kadlčik (Université Paris-Sud XI, Orsay, France), F. Rusconi (Plateforme de Spectrométrie de masse et de Protéomique du Muséum, Paris, France), C. Sicard-Roselli (Université Paris-Sud XI, Orsay, France), Ch. Houée-Levin (Université Paris-Sud XI, Orsay, France)
- Reaction of carbonate radical anion with heme proteins
  J. Didik (Technical University of Łódź, Poland), L. Gębicka (Technical University of Łódź, Poland)

IX scientific session

Chairman: P. Wardman (Gray Cancer Institute, Northwood, United Kingdom)

- Reaction of nitrogen monoxide with glutathione thiyl radical – a kinetic study
  D. Hofstetter (The Swiss Federal Institute of Technology – ETH Zürich, Switzerland), Th. Nauser (The Swiss Federal Institute of Technology – ETH Zürich, Switzerland), W.H. Koppenol (The Swiss Federal Institute of Technology – ETH Zürich, Switzerland)
- Transient reactions in the system thiol/pyrimidine
  A. Wójcik (University of Leipzig, Germany)
- Cyclic voltammetry studies of redox indicators for thiyl radicals
  E. Madej (Gray Cancer Laboratory, Northwood, United Kingdom), P. Wardman (Gray Cancer Laboratory, Northwood, United Kingdom)
- Solvent effects on the redox properties of thioethers
  K. Taras-Goślińska (Royal Institute of Technology – KTH, Stockholm, Sweden), M. Jonsson (Royal Institute of Technology – KTH, Stockholm, Sweden)

X scientific session

Chairman: R. Hermann (University of Leipzig, Germany)

- Dynamics of electron solvation in ethylene glycol
  M. Mostafavi (Université Paris-Sud XI, Orsay, France)

XI scientific session

Chairman: M. Jonsson (Royal Institute of Technology – KTH, Stockholm, Sweden)

- Formation and interactions of dinitrosyl iron complexes in living cells
  H. Lewandowska (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), M. Kruszewski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Vibrational spectroscopy and radiobiological assays of HaCaT keratinocytes post exposure to ionising radiation
  A.D. Meade (Dublin Institute of Technology, Ireland), H.J. Byrne (Dublin Institute of Technology, Ireland), F.M. Lyng (Dublin Institute of Technology, Ireland)
- Spectroelectrochemical studies of redox behaviour and cardiotoxicity of some anti-tumoral drugs
  M. Enache ("I.G. Murgulescu" Institute of Physical Chemistry, Romanian Academy, Bucharest, Romania; Institute of Nuclear Chemistry and Technology, Warszawa, Poland), E. Volanschi (University of Bucharest, Romania)

XII scientific session

Chairman: W. Knolle (Leibniz-Institut für Oberflächenmodifizierung e.V., Leipzig, Germany)

- 1,4-dichlorobenzene decomposition in different gas mixture using electron beam irradiation
  A.G. Chmielewski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), Y. Sun (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), S. Bułka (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), Z. Zimek (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Mechanistic studies of oxidative dissolution of UO_2
  O. Roth (Royal Institute of Technology – KTH, Stockholm, Sweden), E. Ekeroth (Royal Institute of Technology – KTH, Stockholm, Sweden), T. Bönnemark (Royal Institute of Technology – KTH, Stockholm,

Sweden), S. Nilsson (Royal Institute of Technology – KTH, Stockholm, Sweden), M. Jonsson (Royal Institute of Technology – KTH, Stockholm, Sweden)

- A popular liquid, rich in antioxidants and radical scavengers, and flavoured with more than 4000 aromatic ingredients: Some reflections on wine
  Ch. Asmus (Metshop, Berlin, Germany)

Poster session (I)

Chairman: S.P. Naumov (Leibniz-Institut für Oberflächenmodifizierung e.V., Leipzig, Germany; University of Leipzig, Germany)

- Photochemistry of the benzophenone-carboxylic acid tetraalkylammonium salt system
  J. Bartoszewicz (The Adam Mickiewicz University, Poznań, Poland), H. Kozubek (The Adam Mickiewicz University, Poznań, Poland), A. Wrzyszczyński (University of Technology and Agriculture, Bydgoszcz, Poland), G.L. Hug (University of Notre Dame, USA), J. Pączkowski (University of Technology and Agriculture, Bydgoszcz, Poland), B. Marciniak (The Adam Mickiewicz University, Poznań, Poland)
- Radiolytic decomposition of pesticide MCPA in various condtions – comparison of experimental data and calculated kinetic model
  A. Bojanowska-Czajka (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), P. Drzewicz (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), M. Trojanowicz (Institute of Nuclear Chemistry and Technology, Warszawa, Poland; Warsaw University, Poland), G. Nałęcz-Jawecki (Medical University of Warsaw, Poland), J. Sawicki (Medical University of Warsaw, Poland), Cz. Kozyra (Organika Sarzyna S.A., Nowa Sarzyna, Poland)
- Reactive intermediates generated by one-electron oxidation of 2-thiouridine
  M. Czerwińska (Technical University of Łódź, Poland), J. Zielonka (Technical University of Łódź, Poland), A. Marcinek (Technical University of Łódź, Poland), I. Frątczak (Technical University of Łódź, Poland), E. Sochacka (Technical University of Łódź, Poland)
- Formation and reactions of halogenated peroxyl and alkoxyl radicals derived from halogenated methanes
  R. Flyunt (Leibniz-Institut für Oberflächenmodifizierung e.V., Leipzig, Germany; Institute of Physico-Chemistry, National Academy of Sciences of Ukraine, Lviv, Ukraine), O. Makogon (Institute of Physico-Chemistry, National Academy of Sciences of Ukraine, Lviv, Ukraine), S. Naumov (Leibniz-Institut für Oberflächenmodifizierung, Leipzig, Germany), K.-D. Asmus (The Adam Mickiewicz University, Poznań, Poland)
- Photopolymerization kinetics of bis-GMA/poly(ethylene-glycol) blends
  M. Janaszczyk (Poznań University of Technology, Poland), A. Sobczyk (Poznań University of Technology, Poland), E. Andrzejewska (Poznań University of Technology, Poland)
- Oxidation of TYR-MET and MET-TYR dipeptides: a pulse radiolysis study
  G. Kciuk (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), G.L. Hug (University of Notre Dame, USA), J. Mirkowski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), K. Bobrowski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Formation of p-terphenyl radical anion in the ionic liquid methyltributylammonium bis[(trifluoromethyl)-sulfonyl]imide
  R. Kocia (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), J. Grodkowski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), J. Mirkowski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Development of new dyeing photoinitiators based on dibenzo[a,c]phenazine skeleton
  A. Kosobucka (University of Technology and Agriculture, Bydgoszcz, Poland), Z. Kucybała (University of Technology and Agriculture, Bydgoszcz, Poland), J. Pączkowski (University of Technology and Agriculture, Bydgoszcz, Poland)
- Investigation of molecular dynamics and photopolymerization kionetics of a two-monomer system
  A. Maciejewska (Poznań University of Technology, Poland), E. Andrzejewska (Poznań University of Technology, Poland), M. Mazurewicz (Poznań University of Technology, Poland), P. Ziobrowski (Poznań University of Technology, Poland), M. Drozdowski (Poznań University of Technology, Poland)
- Laser IMS for sensing of volatile organic compounds
  T. Pędziński (The Adam Mickiewicz University, Poznań, Poland), R. Schultze (Optimare GmbH, Wilhelmshaven, Germany), H.-G. Loehmannsroeben (University of Potsdam, Germany)
- Radiation damage in biomolecular systems by low energy electrons
  S. Ptasińska (Leopold-Franzens-Universität Innsbruck, Austria), S. Denifl (Leopold-Franzens-Universität Innsbruck, Austria), V. Grill (Leopold-Franzens-Universität Innsbruck, Austria), E. Illenberger (Leopold-Franzens-Universität Innsbruck, Austria), P. Scheier (Leopold-Franzens-Universität Innsbruck, Austria), T.D. Märk (Leopold-Franzens-Universität Innsbruck, Austria)
- Novel media for characterization of radical cations based on ionic liquids
  A. Sikora (Technical University of Łódź, Poland), M. Czerwińska (Technical University of Łódź, Poland), A. Marcinek (Technical University of Łódź, Poland)

- Transient species in oxidation and reduction processes of ethidine
  P. Szajerski (Technical University of Łódź, Poland), A. Marcinek (Technical University of Łódź, Poland)
- Paramagnetic silver clusters in analcime
  J. Turek (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), J. Sadło (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), J. Michalik (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Chemistry and programming together. A new tool in modern science?
  P. Wiśniowski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland; University of Notre Dame, USA), J. Mirkowski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), G.L. Hug (University of Notre Dame, USA), R.W. Fessenden (University of Notre Dame, USA), K. Bobrowski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- The kinetics of the radical reactions in gaseous chloro- or fluoroalkanes
  K. Wnorowski (University of Podlasie, Siedlce, Poland), A. Jówko (University of Podlasie, Siedlce, Poland)

Poster session (II)

Chairman: R. Flyunt (Leibniz-Institut für Oberflächenmodifizierung e.V., Leipzig, Germany; Institute of Physico-Chemistry, National Academy of Sciences of Ukraine, Lviv, Ukraine)

- Photoinduced electron transfer reaction in the 10-methylacridinium perchlorate – benzyltrimethylsilane system
  A. Bednarek (The Adam Mickiewicz University, Poznań, Poland), T. Pędzinski (The Adam Mickiewicz University, Poznań, Poland), B. Marciniak (The Adam Mickiewicz University, Poznań, Poland)
- Single oxygen-induced oxidation of carboxylate substituted thioethers
  M. Celuch (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), M. Enache (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), D. Pogocki (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Integrating carbon nanotubes into donor-acceptor nanohybrides
  D.M. Guldi (Friedrich-Alexander-Universität, Erlangen-Nürnberg, Germany), G.M. Aminur Rahmen (Friedrich-Alexander-Universität, Erlangen-Nürnberg, Germany), Ch. Ehli (Friedrich-Alexander-Universität, Erlangen-Nürnberg, Germany)
- Formation of $Br_2^{\bullet -}$, $BrSCN^{\bullet -}$ and $(SCN)_2^{\bullet -}$ intermediates in the ionic liquid methyltributylammonium bis[(trifluoromethyl)-sulfonyl]imide. Pulse radiolysis study
  J. Grodkowski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), M. Nyga (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), J. Mirkowski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Two-stage radiation synthesis of polymeric nanogels
  S. Kadłubowski (Technical University of Łódź, Poland), P. Ulański (Technical University of Łódź, Poland), J.M. Rosiak (Technical University of Łódź, Poland)
- Intramolecular transformation of radical cations of unsaturated amines. A low temperature EPR study
  W. Knolle (Leibniz-Institut für Oberflächenmodifizierung e.V., Leipzig, Germany), S. Naumov (Leibniz-Institut für Oberflächenmodifizierung e.V., Leipzig, Germany), Ff. Williams (University of Tennessee, Knoxville, USA), I. Janovský (Leibniz-Institut für Oberflächenmodifizierung e.V., Leipzig, Germany)
- Measurement of small air-ions at various Rn^{222} concentrations near the ground
  P. Kolarz (Institute of Physics, Belgrade, Serbia and Montenegro), B. Marinkovič (Institute of Physics, Belgrade, Serbia and Montenegro), D.M. Filipovič (University of Belgrade, Belgrade, Serbia and Montenegro)
- On the behaviour of radiocesium in organic-rich sediments of Lake Juodis, Lithuania
  N. Tarsiuk (Institute of Physics, Vilnius, Lithuania), E. Koviazina (Institute of Physics, Vilnius, Lithuania), V. Kubarevičienė (Institute of Physics, Vilnius, Lithuania)
- The dynamical behaviour of radical cation of s-trioxane: quantum chemical calculations and low-temperature EPR results
  S.S. Naumov (Leibniz-Institut für Oberflächenmodifizierung e.V., Leipzig, Germany; University of Leipzig, Germany), W. Knolle (Leibniz-Institut für Oberflächenmodifizierung e.V., Leipzig, Germany), I. Janovský (Leibniz-Institut für Oberflächenmodifizierung e.V., Leipzig, Germany), S.P. Naumov (Leibniz-Institut für Oberflächenmodifizierung e.V., Leipzig, Germany), A. Pöppl (University of Leipzig, Germany)
- Computational DFT study on the 1,2-hydrogen shift in thiyl and oxyl radicals
  D. Pogocki (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), M. Celuch (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), A. Rauk (University of Calgary, Canada)
- Reinvestigation of the mechanism of the free radical polymerization photoinitiation process by camphorquinone-coinitiator systems
  I. Pyszka (University of Technology and Agriculture, Bydgoszcz, Poland), Z. Kucybała (University of Technology and Agriculture, Bydgoszcz, Poland), J. Pączkowski (University of Technology and Agriculture, Bydgoszcz, Poland)

- EPR study of radicals in aromatic carboxylic acids containing sulfur
  G. Strzelczak (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), A. Korzeniowska-Sobczuk (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), K. Bobrowski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- AFM visualization of the UV-induced damage in plasmid DNA
  M. Śmiałek (The Open University, Milton Keynes, United Kingdom), N. Mason (The Open University, Milton Keynes, United Kingdom), S. Moore (The Open University, Milton Keynes, United Kingdom), D. Jaksch (The Open University, Milton Keynes, United Kingdom)
- Self-assembled monolayer interface for yeast *Saccharomyces Cerevisiae* cells irradiation
  Š. Vaitekonis (Institute of Physics, Vilnius, Lithuania), R. Plukienë (Institute of Physics, Vilnius, Lithuania), V. Remeikis (Institute of Physics, Vilnius, Lithuania)
- Low energy electron attachment by haloalkanes
  J. Wnorowska (University of Podlasie, Siedlce, Poland), I. Szamrej (University of Podlasie, Siedlce, Poland)
- Reactivity of leuco dyes and their oxidized forms towards free radicals. Properties of radical intermediates derived from fluoresceins
  M. Wrona (Mount Vernon Hospital, Northwood, United Kingdom), P. Wardman (Mount Vernon Hospital, Northwood, United Kingdom)

6. KRAJOWE SYMPOZJUM „TECHNIKA JĄDROWA W PRZEMYŚLE, MEDYCYNIE, ROLNICTWIE I OCHRONIE ŚRODOWISKA" (NATIONAL SYMPOSIUM ON NUCLEAR TECHNIQUE IN INDUSTRY, MEDICINE, AGRICULTURE AND ENVIRONMENTAL PROTECTION), 7-9 SEPTEMBER 2005, KRAKÓW, POLAND

Organized by the Faculty of Physics and Applied Computer Science, AGH University of Science and Technology; Institute of Nuclear Chemistry and Technology; National Atomic Energy Agency; Polish Nuclear Society

Organizing Committee: Prof. K. Różański, Ph.D., D.Sc. (Chairman), Z. Stęgowski, Ph.D., Prof. M. Lankosz, Ph.D., D.Sc., Prof. M. Wasilewska-Radwańska, Ph.D., D.Sc., Prof. P. Urbański, Ph.D., D.Sc., J. Siwiński, M.Sc., Z. Zimek, Ph.D., P. Wachniew, Ph.D., M. Zimnoch, Ph.D., J. Chwiej, E. Nowak, Ł. Chmura, S. Wójcik

PLENARY LECTURES

- Nowe trendy w zastosowaniach technik jądrowych i radiacyjnych (New trends in application of nuclear and radiation technologies)
  A.G. Chmielewski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Zagadnienie biologicznego działania małych dawek promieniowania i jego znaczenie w różnych rodzajach ekspozycji ludzi na promieniowanie jonizujące (Biological interaction of low doses of ionising radiation on the human body)
  J. Liniecki (Medical University of Łódź, Poland)
- Perspektywy energetyki jądrowej w Polsce i na świecie (Development of nuclear power in Poland and worldwide)
  S. Chwaszczewski (Institute of Atomic Energy, Świerk, Poland)
- Techniki jądrowe w badaniach środowiskowych (Nuclear techniques in environmental research)
  K. Różański (AGH University of Science and Technology, Kraków, Poland)

LECTURES AND POSTERS

Session I: Ochrona środowiska, nauki o Ziemi, ochrona dziedzictwa kulturowego (Environmental protection, earth science, cultural heritage)

- Skład izotopowy siarki jako znacznik środowiskowy (Sulfur isotope composition as an environmental tracer)
  M. Derda (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), A.G. Chmielewski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Przyczyny zmienności składu izotopowego tlenu i siarki w jonie siarczanowym jezior w Polsce (Causes of changeability of isotopic composition of oxygen and sulpur in the sulphate ion of lakes in Poland)
  M.O. Jędrysek
- Tryt jako znacznik przepływu w hydrofitowych oczyszczalniach ścieków (Tritium as a tracer of flow in constructed wetlands)
  P. Wachniew (AGH University of Science and Technology, Kraków, Poland), P. Czupryński (AGH University of Science and Technology, Kraków, Poland), P. Małoszewski (Institut für Grundwasserökologie – GSF, Neuherberg, Germany)

- Wymywanie naturalnych izotopów promieniotwórczych pod działaniem wody o różnym składzie chemicznym (Leaching of technologically enhanced naturally occurring radioactive materials (TENORM) under interaction of various aqueous chemical solutions)

  N.D. Chau (AGH University of Science and Technology, Kraków, Poland), E. Chruściel (AGH University of Science and Technology, Kraków, Poland)
- Badanie skażeń promieniotwórczych likwidowanych osadników wód dołowych (Studies of radioactive contamination of disposed decanters of tailwaters)

  M. Wysocka (Central Mining Institute, Katowice, Poland), S. Chałupnik (Central Mining Institute, Katowice, Poland)
- Badania właściwości sorpcyjnych iłowców solnych wieku cechsztyńskiego przy pomocy izotopów promieniotwórczych $^{90}Sr+^{90}Y$ i $^{152,154}Eu$ (Investigations of sorption properties of salt-mudstones of the Zechstein age by means of $^{90}Sr+^{90}Y$ and $^{152,154}Eu$)

  J. Gilewicz-Wolter (AGH University of Science and Technology, Kraków, Poland), J. Dudała (AGH University of Science and Technology, Kraków, Poland), A. Ochoński (AGH University of Science and Technology, Kraków, Poland), K. Przewłocki (AGH University of Science and Technology, Kraków, Poland), K. Ślizowski (Mineral and Energy Economy Research Institute, Polish Academy of Sciences, Kraków, Poland)
- Detektor wychwytu elektronów w analizach śladowych (Electron capture detector in trace analysis)

  J. Śliwka (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), J. Lasa (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland)
- Ocena wielkości emisji CO_2 i CH_4 na terenie Krakowa na podstawie pomiaru aktywności atmosferycznego ^{222}Rn (Assessment of CO_2 and CH_4 emission in Kraków from ^{222}Rn measurements)

  Ł. Chmura (AGH University of Science and Technology, Kraków, Poland), J. Nęcki (AGH University of Science and Technology, Kraków, Poland), K. Różański (AGH University of Science and Technology, Kraków, Poland), M. Zimnoch (AGH University of Science and Technology, Kraków, Poland)
- Studia sezonowych zmian składu powietrza atmosferycznego w kościołach zabytkowych w kontekście doboru i modyfikacji metod konserwacji obiektów zabytkowych (Study of the winter and summer changes of the composition of the air in the historical churches related to the conservation)

  L. Samek (AGH University of Science and Technology, Kraków, Poland), A. Worobiec (University of Antwerp, Belgium), Z. Spolnik (University of Antwerp, Belgium), R. Van Grieken (University of Antwerp, Belgium)
- Biel ołowiowa zidentyfikowana metodą neutronowej analizy aktywacyjnej, w gdańskim malarstwie tablicowym 2 poł. XV wieku, na tle innych warsztatów w Polsce (Identification and comparison of lead white of the 15th century Gdańsk panel paintings by neutron activation analysis)

  J. Olszewska-Świetlik (The Nicolaus Copernicus University, Toruń, Poland), E. Pańczyk (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Próba ustalenia proweniencji bieli ołowiowej stosowanej w XV-XVIII-wiecznym malarstwie weneckim z wykorzystaniem technik jądrowych (An attempt of establishing lead white provenance of the 15th-18th Venetian paintings by nuclear analytical techniques)

  E. Pańczyk (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), L. Waliś (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Wpływ promieniowania jonizującego na wybrane pigmenty występujące w obiektach zabytkowych (Influence of ionizing radiation on specific pigments appearing in antique objects)

  J. Perkowski (Technical University of Łódź, Poland), B. Karpińska (Technical University of Łódź, Poland), M. Kaźmierska (Institute of Dyes and Organic Products, Zgierz, Poland), J. Zajączkowska-Kło-da (Firma Zajączkowska-Kłoda Sp. z o.o., Łódź, Poland), S. Kuberski (Technical University of Łódź, Poland)
- Promieniowanie rtg, UV i IR w badaniach dzieł sztuki (Radiography, ultraviolet induced luminescence photography and infrared reflectography in the study of paintings)

  A. Baran (AGH University of Science and Technology, Kraków, Poland), J. Rutkowski (AGH University of Science and Technology, Kraków, Poland)
- Próby identyfikacji żelaza otrzymywanego w starożytnym procesie dymarskim (Attempts of iron identification smelt in an ancient bloomery process)

  E. Pańczyk (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), W. Weker (National Archeological Museum, Warszawa, Poland), Zs. Kasztovszky (Chemical Research Center, Hungarian Academy of Sciences, Budapest, Hungary)
- Metoda datowania izotopem ^{14}C jako narzędzie do konstruowania chronologii prehistorycznych (^{14}C dating as a tool of construction of prehistoric chronologies)

  M. Fogtman (The Silesian University of Technology, Gliwice, Poland), A. Pazdur (The Silesian University of Technology, Gliwice, Poland)

- Izotopy plutonu ^{238}Pu, $^{239+240}$Pu i ^{241}Pu w środowisku Morza Bałtyckiego (Plutonium ^{238}Pu, $^{239+240}$Pu and ^{241}Pu isotopes in the Baltic Sea environment)
  D.I. Strumińska (University of Gdańsk, Poland), B. Skwarzec (University of Gdańsk, Poland)
- Procedura odzysku uranu z wód mineralnych o wysokiej zawartości dwutlenku węgla (A procedure for uranium extraction from mineral waters with high content of dissolved carbon dioxide)
  B. Michalec (AGH University of Science and Technology, Kraków, Poland), M. Duliński (AGH University of Science and Technology, Kraków, Poland)
- Metodyka oznaczania form chemicznych plutonu w środowisku morskim (An analytical procedure for determination of plutonium chemical forms in the marine environment)
  D.I. Strumińska (University of Gdańsk, Poland), B. Skwarzec (University of Gdańsk, Poland), M. Mazurek (University of Gdańsk, Poland)
- Zastosowanie metody ^{210}Pb do wyznaczania tempa sedymentacji rzecznych osadów pozakorytowych (Use of ^{210}Pb dating method to investigate rates of sediment deposition on floodplains)
  E. Łokas (AGH University of Science and Technology, Kraków, Poland), P. Wachniew (AGH University of Science and Technology, Kraków, Poland), N.D. Chau (AGH University of Science and Technology, Kraków, Poland), B. Ostachowicz (AGH University of Science and Technology, Kraków, Poland)
- Analiza izotopowa azotanów rozpuszczonych w wodzie: aspekty metodyczne (Isotopic analysis of nitrates dissolved in water: methodological aspects)
  W.M. Chmura (AGH University of Science and Technology, Kraków, Poland), K. Różański (AGH University of Science and Technology, Kraków, Poland), T. Kuc (AGH University of Science and Technology, Kraków, Poland), M. Chmiel (Agricultural University of Cracow, Poland), A. Żurek (AGH University of Science and Technology, Kraków, Poland)
- Modelowanie zmian składu izotopowego wody w procesie parowania (Modelling of isotopic changes of water during evaporation)
  Ł. Chmura (AGH University of Science and Technology, Kraków, Poland), K. Różański (AGH University of Science and Technology, Kraków, Poland)
- Wykorzystanie naturalnie istniejących różnic w składzie izotopowym wód rzecznych jako znacznika procesów mieszania w systemach rzeka-dopływ (Application of naturally existed differences in stable isotope composition of river waters as a tracer of mixing processes in main river-tributary systems)
  A. Owczarczyk (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), R. Wierzchnicki (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), A. Dobrowolski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), J. Palige (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), S. Ptaszek (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Pomiar stężenia radonu w wodzie (Measurement of radon concentration in water)
  B. Machaj (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), J. Bartak (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), J. Pieńkos (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Narażenie radiacyjne mieszkańców Krakowa związane z promieniotwórczością naturalną aktualnie produkowanych materiałów budowlanych (Radiation hazard of inhabitants of the Cracow neighborhood connected with natural radioactivity of the currently produced building materials)
  M. Kiszka (AGH University of Science and Technology, Kraków, Poland), S.J. Kalita (AGH University of Science and Technology, Kraków, Poland), P. Jodłowski (AGH University of Science and Technology, Kraków, Poland)
- Zastosowanie programu analizatora Tukan 8k do pomiarów skażeń środowiskowych i analizy „on-line" (Application of Tukan 8k program for environmental contamination measurements and "on-line" analysis)
  K. Traczyk (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), M. Płomiński (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), S. Borsuk (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), Z. Guzik (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), R. Marcinkowski (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), I. Obstój (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland)

Session II: Zastosowania przemysłowe (Industrial applications)

- Ekonomiczne i społeczne aspekty zastosowań radioizotopowej aparatury pomiarowej (Economic and social aspects of application of radioisotope gauges)
  P. Urbański (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), E. Kowalska (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Kierunki rozwoju metod radioizotopowych stosowanych w badaniach procesów przepływowych (Development of radioisotope application in investigation of flow processes)
  L. Petryka (AGH University of Science and Technology, Kraków, Poland)
- Ekonomiczne aspekty oczyszczania spalin metoda radiacyjną (Economical aspects of electron beam flue gas treatment)
  A. Pawelec (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), B. Tymiński (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)

- Usuwanie lotnych zanieczyszczeń organicznych i WWA z gazów odlotowych przy użyciu wiązki elektronów z akceleratora (Removal of volatile organic compounds and PAHs from exhaust gases using electron beam from accelerator)

  A.G. Chmielewski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), A. Ostapczuk (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), Z. Zimek (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), S. Bułka (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), J. Licki (Institute of Atomic Energy, Świerk, Poland)
- Techniki membranowe w przerobie ciekłych odpadów radioaktywnych (Membrane technologies for processing of liquid radioactive waste)

  G. Zakrzewska-Trznadel (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Połączenie symulacji pracy hydrocyklonu z radioznacznikowymi danymi doświadczalnymi (Combining the simulation of hydrocyclone's working with the radiotracer experimental data)

  Z. Stęgowski (AGH University of Science and Technology, Kraków, Poland), E. Nowak (AGH University of Science and Technology, Kraków, Poland)
- Numeryczna metoda otrzymywania funkcji rozkładu czasu przebywania RTD układów działających w warunkach zmiennego natężenia przepływu (Computational RTD evaluation for processes under variable flow)

  L. Furman (AGH University of Science and Technology, Kraków, Poland), Z. Stęgowski (AGH University of Science and Technology, Kraków, Poland), A. Bartyzel (AGH University of Science and Technology, Kraków, Poland)
- Analiza przepływu zawiesin okrzemkowo-iłowych w laboratoryjnym kanale otwartym (Analysis of diatomite-clayey suspensions flow in a laboratory flume)

  L. Petryka (AGH University of Science and Technology, Kraków, Poland), M. Zych (AGH University of Science and Technology, Kraków, Poland), W. Mastej (AGH University of Science and Technology, Kraków, Poland), J. Kępiński (AGH University of Science and Technology, Kraków, Poland), G. Rzepa (AGH University of Science and Technology, Kraków, Poland)
- Detektor nadążny do radioizotopowej kontroli szczelności i lokalizacji miejsc nieszczelnych w rurociągach podziemnych Φ>600 mm wyposażonych w komory czyszczakowe (Follow-up detector to radioisotopic leak proof control underground pipelines Φ>600 mm with a cleaning chamber)

  J. Kraś (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), S. Myczkowski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Unikalna instalacja oczyszczania wód dołowych z radu – doświadczenia i perspektywy (A unique installation for cleaning tailwaters from Ra – experiments and perspectives)

  S. Chałupnik (Central Mining Institute, Katowice, Poland), M. Wysocka (Central Mining Institute, Katowice, Poland)
- Wpływ oczyszczania wód kopalnianych na stężenie radu w produktach procesu odsalania (Effect of cleaning mine waters on the concentration of Ra i the products of desalination process)

  S. Chałupnik (Central Mining Institute, Katowice, Poland)
- Badania znacznikowe i CFD przemysłowych osadników prostokątnych (Tracer and CFD investigation of industrial rectangular settlers)

  J. Palige (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), A. Owczarczyk (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), A. Dobrowolski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), S. Ptaszek (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Przetwarzanie wyników z eksperymentów radiometrycznych metodami wielowymiarowej analizy statystycznej (Processing data collected from radiometric experiments by multivariate technique)

  P. Urbański (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), E. Kowalska (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), B. Machaj (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), A. Jakowiuk (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Modyfikacja warstw wierzchnich stali węglowych poprzez oddziaływanie z intensywnymi impulsami plazmy (Modification of near surface layer of carbon steels as a result of interaction with intense plasma pulses)

  B. Sartowska (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), J. Piekoszewski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland; The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), L. Waliś (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), J. Stanisławski (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), L. Nowicki (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), R. Ratajczak (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), M. Kopcewicz (Institute of Electronic Materials Technology, Warszawa, Poland), J. Kalinowska (Institute of Electronic Materials Technology, Warszawa, Poland), A. Barcz (Institute of Physics, Polish Academy of Sciences, Warszawa, Poland)
- Bezprzewodowe sieci monitoringu z radioizotopowymi czujnikami zapylenia powietrza AMIZ 2004G (Wireless dust concentration monitoring network based on the radioisotope gauge AMIZ 2004G)

A. Jakowiuk (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), B. Machaj (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), J. Pieńkos (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), E. Świstowski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)

Session III: Zastosowania w medycynie, aparatura medyczna (Nuclear medicine, instrumentation)

- Badanie procesów neurodegeneracyjnych z wykorzystaniem technik opartych na promieniowaniu synchrotronowym (Investigations of neurodegenerative processes with the use of techniques based on synchrotron radiation)

  J. Chwiej (AGH University of Science and Technology, Kraków, Poland), M. Szczerbowska-Boruchowska (AGH University of Science and Technology, Kraków, Poland), M. Lankosz (AGH University of Science and Technology, Kraków, Poland), S. Wójcik (AGH University of Science and Technology, Kraków, Poland), Z. Stęgowski (AGH University of Science and Technology, Kraków, Poland), D. Adamek (Jagiellonian University Medical College, Kraków, Poland), A. Krygowska-Wajs (Jagiellonian University Medical College, Kraków, Poland), B. Tomik (Jagiellonian University Medical College, Kraków, Poland), S. Bohic (European Synchrotron Radiation Facility, Grenoble, France), D. Eichert (European Synchrotron Radiation Facility, Grenoble, France), J. Susini (European Synchrotron Radiation Facility, Grenoble, France), G. Falkenberg (Hamburger Synchrotronstrahlungslabor HASYLAB at DESY, Hamburg, Germany)

- Wpływ zanieczyszczeń chemicznych na wydajność znakowania ^{90}Y i ^{177}Lu DOTA pochodnych peptydów (The influence of metallic impurities on the ^{90}Y or ^{177}Lu labelling yield of DOTA-derivatised peptides)

  D. Pawlak (Radioisotope Centre POLATOM, Świerk, Poland), A. Korsak (Radioisotope Centre POLATOM, Świerk, Poland), R. Mikołajczak (Radioisotope Centre POLATOM, Świerk, Poland)

- Częstość aberracji chromosomowych w limfocytach krwi obwodowej chorych na nowotwór krtani (Chromosome aberrations frequencies in peripheral blood lymphocytes from patients with larynx cancer)

  H. Lisowska (Świętokrzyska Academy, Kielce, Poland), A. Lankoff (Świętokrzyska Academy, Kielce, Poland), A. Banasik (Świętokrzyska Academy, Kielce, Poland), A. Padjas (Holycross Cancer Center, Kielce, Poland), A. Wieczorek (Holycross Cancer Center, Kielce, Poland), T. Kuszewski (Holycross Cancer Center, Kielce, Poland), S. Góźdź (Holycross Cancer Center, Kielce, Poland), A. Wójcik (Świętokrzyska Academy, Kielce, Poland; Institute of Nuclear Chemistry and Technology, Warszawa, Poland)

- Znaczenie prognostyczne tempa proliferacji komórek na podstawie testu AgNOR u chorych na nowotwory mózgowia leczonych pooperacyjnie napromieniowaniem (Prognostic significance of proliferative potential based on AgNOR technique in patients with brain tumours treated with postoperative radiotherapy)

  A. Baran (AGH University of Science and Technology, Kraków, Poland), J. Niemiec (Centre of Oncology – Maria Skłodowska-Curie Memorial Institute, Kraków, Poland), A. Adamczyk (Centre of Oncology – Maria Skłodowska-Curie Memorial Institute, Kraków, Poland)

- Wiązanie jodu-125 na powierzchni srebra w aspekcie wykonania rdzenia aktywnego I-125 do ziaren jodowych stosowanych w brachyterapii (Fixing of iodine-125 on silver backing in aspect of prepared source core of I-125 seeds used in brachytherapy)

  I. Cieszykowska (Radioisotope Centre POLATOM, Świerk, Poland), M. Mielcarski (Radioisotope Centre POLATOM, Świerk, Poland), A. Piasecki (Radioisotope Centre POLATOM, Świerk, Poland)

- Modelowe badanie procesu perfuzji w sercu metodą SPECT (Experimental model of the haemoperfusion in heart using SPECT technique)

  M. Wasilewska-Radwańska (AGH University of Science and Technology, Kraków, Poland), K. Natkaniec (AGH University of Science and Technology, Kraków, Poland), A. Stępień (5th Military Clinical Hospital with Polyclinic, Kraków, Poland), J. Pawlus (5th Military Clinical Hospital with Polyclinic, Kraków, Poland)

- Wpływ jonów rtęci na naprawę radiacyjnych uszkodzeń DNA (Mercury ions influence on repair of the radiation induced DNA damage)

  A. Panek (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), A. Cebulska-Wasilewska (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), Jin Kyu Kim (Korean Atomic Energy Research Institute, Taejon, South Korea)

- Radioizotopowe i termograficzne obrazowanie obrzęku kończyn dolnych – porównanie technik diagnostycznych (Radioisotopic and thermographic imaging of the lower limbs oedema – comparison diagnostic techniques)

  A. Stępień (5th Military Clinical Hospital with Polyclinic, Kraków, Poland), J. Pawlus (5th Military Clinical Hospital with Polyclinic, Kraków, Poland), E. Nowak (AGH University of Science and Technology, Kraków, Poland), J. Kulka (AGH University of Science and Technology, Kraków, Poland), J. Giełżecki (AGH University of Science and Technology, Kraków, Poland), O. Kraft (University Hospital, Ostrava, Czech Republic), T. Puto (5th Military Clinical Hospital with Polyclinic, Kraków, Poland), G. Klauz (5th Military Clinical Hospital with Polyclinic, Kraków, Poland)

- Detektory rekombinacyjne dla terapii borowo-neutronowej (Recombination detectors for BNCT beam dosimetry)

  P. Tulik (Warsaw University of Technology, Poland), N. Golnik (Institute of Atomic Energy, Świerk; Warsaw University of Technology, Poland), M. Zielczyński (Institute of Atomic Energy, Świerk, Poland)
- Półprzewodnikowa, pozycjoczuła sonda promieniowania gamma do śródoperacyjnej lokalizacji węzłów wartowniczych (Semiconductor, position-sensitive gamma probe to intraoperative sentinel lymph nodes localization)

  E. Nowak (AGH University of Science and Technology, Kraków, Poland), J. Kulka (AGH University of Science and Technology, Kraków, Poland)
- Morfologiczna analiza obrazu (Morphological images analysis)

  A. Jakowiuk (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- System obrazowania cyfrowego dla potrzeb mammografii wykorzystującej promieniowanie X o dwóch różnych energiach (System of numerical imaging for mammography applying X-radiation of two different energies)

  K. Świentek (AGH University of Science and Technology, Kraków, Poland), W. Dąbrowski (AGH University of Science and Technology, Kraków, Poland), P. Gryboś (AGH University of Science and Technology, Kraków, Poland), P. Wiącek (AGH University of Science and Technology, Kraków, Poland), A.E. Cabal Rodrigez (Centro de Aplicaciones Tecnológicas y Desarrollo Nuclear – CEADEN, Havana, Cuba), C. Ceballos Sanchez (Centro de Aplicaciones Tecnológicas y Desarrollo Nuclear – CEADEN, Havana, Cuba), M. Gambaccini (Universita di Ferrara and INFN, Ferrara, Italy), J. Lopes Gaitan (Universidad de los Andes, Bogota, Colombia), F. Prino (INFN, Torino, Italy), L. Ramello (Universita degli Studi del Piemonte Orientale and INFN, Alessandria, Italy)
- Liczniki gamma do analiz radioimmunologicznych (Gamma counters for radioimmuno- and immunoradiometric assay)

  B. Machaj (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), J. Bartak (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), A. Jakowiuk (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Zastosowanie metody całkowitego odbicia promieniowania X (TXRF) do analizy składu pierwiastkowego płynu mózgowo-rdzeniowego oraz osocza u chorych na stwardnienie boczne zanikowe (Application of the TXRF method for the elemental analysis of the cerebrospinal fluid (CSF) and serum in amyotrophic lateral sclerosis (ALS))

  B. Ostachowicz (AGH University of Science and Technology, Kraków, Poland), M. Lankosz (AGH University of Science and Technology, Kraków, Poland), B. Tomik (Jagiellonian University Medical College, Kraków, Poland), D. Adamek (Jagiellonian University Medical College, Kraków, Poland), P. Wobrauschek (Vienna University of Technology, Austria), Ch. Streli (Vienna University of Technology, Austria), P. Kregsamer (Vienna University of Technology, Austria)
- Polska igła fotonowa (Polish photon needle)

  M. Słapa (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), W. Straś (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), A. Fronczak (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), M. Snopek (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), M. Talejko (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), M. Traczyk (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), K. Wincel (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), B. Zaręba (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), H. Roguszczak (Zakład Usług Elektronicznych, Wrocław, Poland), T. Zawada (Zakład Usług Elektronicznych, Wrocław, Poland), T. Kotowski (ZRK Color, Zambrów, Poland), R. Gutowski (Uniquant, Warszawa, Poland), J. Dora (Power Dora System, Wrocław, Poland)
- ^{99m}Tc-HYNIC-TOC, ^{99m}Tc-HYNIC-TATE – znakowane technetem-99m analogi somatostatyny wykorzystywane w diagnostyce medycznej (^{99m}Tc-HYNIC-TOC, ^{99m}Tc-HYNIC-TATE – somatostatin analogs labelled with technetium-99m useful in medical diagnosis)

  B. Janota (Radioisotope Centre POLATOM, Świerk, Poland), R. Mikołajczak (Radioisotope Centre POLATOM, Świerk, Poland), E. Zakrzewska (Radioisotope Centre POLATOM, Świerk, Poland)
- Technologia otrzymywania beznośnikowego Re-188 w postaci sterylnego i izotonicznego nadrenianu (VII) sodu (Production technology of carrier – free ^{188}Re in the form of sterile, isotonic solution of sodium perrhenate(VII))

  K. Sawlewicz (Radioisotope Centre POLATOM, Świerk, Poland), Z. Zelek (Radioisotope Centre POLATOM, Świerk, Poland), M. Konior (Radioisotope Centre POLATOM, Świerk, Poland), E. Iller (Radioisotope Centre POLATOM, Świerk, Poland), U. Kaczmarczyk (National Institute of Public Health, Warszawa, Poland)
- Ocena zjawiska radiofobii wśród pacjentów poddawanych terapii izotopowej (Evaluation of radiophoby phenomenon among patients undergoing radioisotope therapy)

  M. Stępień (5th Military Clinical Hospital with Polyclinic, Kraków, Poland), A. Stępień (5th Military Clinical Hospital with Polyclinic, Kraków, Poland), J. Pawlus (5th Military Clinical Hospital with Polyclinic, Kraków, Poland), M. Wasilewska-Radwańska (AGH University of Science and Technology, Kraków, Poland)

- Metoda wyznaczania składowych dawki w polach gamma-neutronowych za pomocą wysokociśnieniowej komory jonizacyjnej (Method for determination of gamma and neutron dose components in mixed radiation fields using a high-pressure ionization chamber)

  M.A. Gryziński (Warsaw University of Technology, Poland), N. Golnik (Warsaw University of Technology; Institute of Atomic Energy, Świerk, Poland), M. Zielczyński (Institute of Atomic Energy, Świerk, Poland)

Session IV: Metody pomiarowe, symulacje, planowanie eksperymentów (Measurements, simulations, experiments design)

- Pozycja NAA wśród innych metod nieorganicznej analizy śladowej w przeszłości i obecnie (The position of NAA among the methods of inorganic trace analysis in the past and now)

  R.S. Dybczyński (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Zastosowanie spektrometrii alfa w badaniach przyrody i ochronie środowiska (Application of alpha spectrometry in environment studies and environmental protection)

  B. Skwarzec (University of Gdańsk, Poland), D.I. Strumińska (University of Gdańsk, Poland), A. Boryło (University of Gdańsk, Poland)
- Wybrane zastosowania detektorów śladowych (Selected applications of nuclear track detectors)

  T. Horwacik (AGH University of Science and Technology, Kraków, Poland; The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), W. Pohorecki (AGH University of Science and Technology, Kraków, Poland), J. Janczyszyn (AGH University of Science and Technology, Kraków, Poland), S. Taczanowski (AGH University of Science and Technology, Kraków, Poland), G. Domańska (AGH University of Science and Technology, Kraków, Poland), P. Bilski (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), P. Olko (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland)
- Badania składu izotopowego żywności – aspekty poznawcze i utylitarne (Investigations of isotopic composition of foodstuff – basic study and applications)

  R. Wierzchnicki (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Radiometryczna głowica do pomiaru *in situ* składu gleb i skażeń powierzchniowych metodą fluorescencji rentgenowskiej (Portable, radiometric head for *in situ* X-ray fluorescence analysis of soils and thin layer contamination)

  M. Bielewski (AGH University of Science and Technology, Kraków, Poland), M. Lankosz (AGH University of Science and Technology, Kraków, Poland), B. Ostachowicz (AGH University of Science and Technology, Kraków, Poland), J. Ostachowicz (AGH University of Science and Technology, Kraków, Poland), A. Ostrowski (AGH University of Science and Technology, Kraków, Poland), D. Węgrzynek (AGH University of Science and Technology, Kraków, Poland)
- Zawartość popiołu w węglu a jego naturalna promieniotwórczość gamma (Ash concentration in hard coal and its natural gamma radioactivity)

  B. Czerw (EMAG, Katowice, Poland), T. Sikora (EMAG, Katowice, Poland), E. Chruściel (AGH University of Science and Technology, Kraków, Poland), P. Jodłowski (AGH University of Science and Technology, Kraków, Poland), S.J. Kalita (AGH University of Science and Technology, Kraków, Poland), A. Bolewski (AGH University of Science and Technology, Kraków, Poland)
- Akcelerator z systemem detekcyjnym do radiograficznych badań nieniszczących w czasie rzeczywistym (Accelerator with imaging system for non-destructive testing)

  J. Harasimowicz (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), E. Jakubowska (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), S. Wronka (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), J. Wysokiński (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland)
- Autonomiczne miniaturowe urządzenie z magistralą USB do analizy amplitud impulsów spektrometrycznych i przebiegów czasowych (TUKAN-8K-USB) (Autonomous miniaturised device with USB interface for pulse height analysis and multi-channel scaling (TUKAN-8K-USB))

  Z. Guzik (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), S. Borsuk (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), M. Płomiński (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), K. Traczyk (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland)
- Elektrolityczne wzbogacanie izotopowe próbek wody w pomiarach ciekłoscyntylacyjnych trytu (Electrolytic enrichment of isotopes in water samples for liquid scintillation measurement of tritium concentration)

  T. Kuc (AGH University of Science and Technology, Kraków, Poland), J. Grabczak (AGH University of Science and Technology, Kraków, Poland)
- Zastosowanie detektora jonizacyjnego do monitoringu profilu wiązek ciężkich jonów (Application of the ionization detector to monitoring of a profile of heavy ion beams)

  G. Kamiński (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), S. Myalski (AGH University of Science and Technology, Kraków, Poland), K. Malarz

(AGH University of Science and Technology, Kraków, Poland), Y. Teterev (Joint Institute for Nuclear Research, Dubna, Russia), Phi Thanh Huong (Joint Institute for Nuclear Research, Dubna, Russia), A. Soloviev (Joint Institute for Nuclear Research, Dubna, Russia)

- Symulacje komputerowe transportu neutronów jako narzędzie projektowania układów pomiarowych na przykładzie urządzenia do kontroli czystości grafitu (Computer simulations of neutron transport as a tool for designing measurement systems shown by an example of the instrument for graphite purity testing)

  A. Dydejczyk (AGH University of Science and Technology, Kraków, Poland), A. Bolewski (AGH University of Science and Technology, Kraków, Poland), M. Ciechanowski (AGH University of Science and Technology, Kraków, Poland), A. Kreft (AGH University of Science and Technology, Kraków, Poland)
- Zastosowanie zintegrowanego systemu MCB (Monte-Carlo Continous Energy Burnup) do projektowania eksperymentów oraz systemów jądrowych (Applications of integrated system MCB (Monte Carlo Continous Energy Burnup) in designs of experiments and nuclear systems)

  J. Cetnar (AGH University of Science and Technology, Kraków, Poland)
- Przestrzenny rozkład produkcji izotopów promieniotwórczych w modelu tarczy spalacyjnej (Spatial distribution of residual nuclei production inside a spallation target)

  W. Pohorecki (AGH University of Science and Technology, Kraków, Poland), J. Janczyszyn (AGH University of Science and Technology, Kraków, Poland), S. Taczanowski (AGH University of Science and Technology, Kraków, Poland), T. Horwacik (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), I.V. Mirokhin (Joint Institute for Nuclear Research, Dubna, Russia), A.G. Molokanov (Joint Institute for Nuclear Research, Dubna, Russia)
- Urządzenie do aktywacji tarcz wiązką wewnętrzną cyklotronu AIC-144 (The internal target assembly for the cyclotron AIC-144)

  B. Petelenz (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), L. Źródłowski (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), M. Szałkowski (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), J. Halik (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), B.N. Gikał (Joint Institute for Nuclear Research, Dubna, Russia), S. Knapek (Lurgi Polska S.A., Poland)
- Niskomocowe generatory promieniowania X (Low power X-ray generators)

  M. Talejko (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), W. Straś (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), M. Kisieliński (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), A. Fronczak (The Andrzej Sołtan Institute for Nuclear Studies, Świerk, Poland), T. Kotowski (ZRK Color, Zambrów, Poland)
- Nowy modulator impulsowy klistronu dla akceleratora elektronów Elektronika 10/10 (New pulse modulator for electron accelerator Elektronika 10/10)

  Z. Dźwigalski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), Z. Zimek (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Nowe urządzenia do pomiaru promieniowania i kontroli zagrożenia (New devices for radiation measurement and hazard control)

  B. Machaj (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), J. Mirowicz (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), E. Świstowski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), J. Pieńkos (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Neutronowa analiza aktywacyjna w zastosowaniu do badania wybranych produktów żywnościowych (Neutron activation analysis for investigation of chosen food products)

  B. Danko (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), H. Polkowska-Motrenko (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), A. Koster-Ammerlaan (Delft University of Technology, the Netherlands; Świętokrzyska Academy, Kielce, Poland)

Session V: Techniki radiacyjne (Radiation technologies)

- Higienizacja radiacyjna – możliwości i perspektywy (Radiation hygienization possibility and perspectives)

  W. Migdał (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), O. Tomasiński (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Ekonomiczne i społeczne korzyści wykorzystania techniki radiacyjnej w przemyśle, ochronie środowiska, rolnictwie i medycynie (Economical and social benefits of radiation processing applied in industry, environment protection, agriculture and medicine)

  Z. Zimek (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Wpływ promieniowania jonizującego na własności materiałów opakowaniowych (The influence of ionization radiation on properties of packaging materials)

  P.P. Panta (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), W. Głuszewski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), H. Kubera (Poznań University of Economics, Poland)

- Zastosowanie promieniowania gamma do modyfikacji właściwości biodegradowalnych materiałów opakowaniowych otrzymywanych na bazie białek (Application of gamma irradiation for modification of the properties of biodegradable packaging materials based on proteins)
  K. Cieśla (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Wpływ procesów rodnikowych na odporność radiacyjną polimerów (Effect of radical processes on radiation resistance of polymers)
  G. Przybytniak (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), E. Kornacka (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), K. Mirkowski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), I. Legocka (Industrial Chemistry Research Institute, Warszawa, Poland)
- Czy radiacyjna modyfikacja elastomerów odniesie podobny sukces jak sieciowanie polietylenu promieniowaniem jonizującym? (EB-crosslinking of elastomers, how does it compare with radiation crosslinking of other polymers?)
  Z.P. Zagórski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), W. Głuszewski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Wykrywanie napromieniowania żywności metodą luminescencji stymulowanej światłem (Detection of irradiated food using photostimulation luminescence)
  K. Malec-Czechowska (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), W. Stachowicz (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- System kontroli i rejestracji dawki akceleratorowej w procesie napromieniowania żywności (Control and monitoring system of EB dose in food irradiation process)
  M. Strupiechowski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), W. Migdał (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), P. Tomasiński (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), I. Norwa (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Czytnik dawki CD-02 (Dose Reader CD-02)
  A. Jakowiuk (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), I. Kałuska (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), B. Machaj (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Nanożele do celów biomedycznych otrzymywane poprzez radiacyjne sieciowanie kompleksów międzypolimerowych (Nanogels for biomedical purposes based on radiation induced cross-linking of interpolymer complexes)
  A. Henke (Technical University of Łódź, Poland), P. Ulański (Technical University of Łódź, Poland), J.M. Rosiak (Technical University of Łódź, Poland)

Session VI: Laboratoria, metrologia (Laboratories and radiation metrology)

- Laboratorium metrologiczne w OBRI POLATOM (Metrological laboratory in RC POLATOM)
  R. Broda (Radioisotope Centre POLATOM, Świerk, Poland), K. Maletka (Radioisotope Centre POLATOM, Świerk, Poland), A. Muklanowicz (Radioisotope Centre POLATOM, Świerk, Poland), A. Listkowska (Radioisotope Centre POLATOM, Świerk, Poland)
- Akredytowane Laboratorium Pomiarów Dozymetrycznych Instytutu Energii Atomowej (Certificated Radiation Protection Laboratory of Institute of Atomic Energy)
  T. Pliszczyński (Institute of Atomic Energy, Świerk, Poland), B. Filipiak (Institute of Atomic Energy, Świerk, Poland), Z. Haratym (Institute of Atomic Energy, Świerk, Poland), E. Józefowicz (Institute of Atomic Energy, Świerk, Poland), K. Józefowicz (Institute of Atomic Energy, Świerk, Poland)
- Akredytowane Laboratorium Identyfikacji Napromieniowania Żywności IChTJ (Accredited Laboratory for Detection of Irradiated Food)
  W. Stachowicz (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), K. Malec-Czechowska (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), K. Lehner (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Serwis dozymetryczny akredytowanego Laboratorium Pomiarów Dawek Technologicznych Instytutu Chemii i Techniki Jądrowej w Warszawie (Dosimetry service offered by accredited Laboratory for Measurements of Technological Doses, Institute of Nuclear Chemistry and Technology)
  Z. Peimel-Stuglik (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Wzorcowanie aparatury dozymetrycznej w akredytowanym Laboratorium Pomiarów Dozymetrycznych Instytutu Energii Atomowej (Calibration of dosimetric instruments in accredited Radiation Protection Measurements Laboratory of Institute of Atomic Energy)
  K. Józefowicz (Institute of Atomic Energy, Świerk, Poland), B. Filipiak (Institute of Atomic Energy, Świerk, Poland)
- Ocena narażenia wewnętrznego na podstawie pomiarów „in vivo” i „in vitro” (Assessment of internal exposure based on “in vivo” and “in vitro” measurements)
  T. Pliszczyński (Institute of Atomic Energy, Świerk, Poland), J. Ośko (Warsaw University of Technology, Poland)

- Charakterystyka aktualnego stanu Międzynarodowego Systemu Informacji Jądrowej INIS, wkład Polski do tego systemu i możliwości korzystania z tego systemu przez polskich użytkowników (Present state of the International Nuclear Information System INIS, the input of Poland to this system and possibilities to use this system by Polish users)

  T. Urbański (National Atomic Energy Agency, Warszawa, Poland)

7. VI INTERNATIONAL COMET ASSAY WORKSHOP, 22-24 SEPTEMBER 2005, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Scientific Committee: Prof. A. Collins, M. Dusinska, Ph.D., A. Gábelová, Ph.D., Assoc. Prof. M. Kruszewski, Ph.D., D.Sc., Prof. B. Pool-Zobel, Prof. G. Speit, M. Wojewódzka, Ph.D.

Organizing Committee: H. Lewandowska-Siwkiewicz, M.Sc., S. Męczyńska, M.Sc., M. Wojewódzka, Ph.D., Assoc. Prof. M. Kruszewski, Ph.D., D.Sc.

LECTURES

Session I: Technical aspects and new applications

Chairman: A. Collins (University of Oslo, Norway)

- RET, cAbl, and TP53 gene fragmentations detected in Comet-FISH assay act as bio-markers of radiation exposure in two inbred strain of mice *in vivo*

  R. Amendola (ENEA, Rome, Italy), E. Basso (ENEA, Rome, Italy), P. Pacifici (ENEA, Rome, Italy), E. Piras (ENEA, Rome, Italy), A. Giovanetti (ENEA, Rome, Italy), G. Romeo (University of Bologna, Italy)
- Atypical comet assay as a useful tool to evidence flavonoids-DNA complexes in Caco2 cells

  M. Renis (University of Catania, Italy), M.L. Calandra (University of Catania, Italy), C. Scifo (University of Catania, Italy), M. Zingale (University of Catania, Italy), V. Cardile (University of Catania, Italy), A. Vanella (University of Catania, Italy), F. Galvano (University of Reggio Calabria, Italy)
- A modified comet-assay to assess nucleotide excision repair

  S.A.S. Langie (Maastricht University, the Netherlands), A.M. Knaapen (Maastricht University, the Netherlands), K.J.J. Brauers (Maastricht University, the Netherlands), F.J. Van Schoote (Maastricht University, the Netherlands), R.W.L. Godschalk (Maastricht University, the Netherlands)
- Validation of the comet assay for use as a biomarker in human population studies

  A. Collins (University of Oslo, Norway), T. Langleite (University of Oslo, Norway), T. Veggan (University of Oslo, Norway)
- The plant comet assay

  I. Žnidar (University of Ljubljana, Slovenia), M. Camloh (National Institute of Biology, Ljubljana, Slovenia), B. Vilhar (University of Ljubljana, Slovenia), M. Ravnikar (National Institute of Biology, Ljubljana, Slovenia), R. Marinšek-Logar (University of Ljubljana, Slovenia)
- Use of the multi-colour Comet-FISH assay to measure preferential DNA repair in TCR-deficient cell lines

  D.J. McKenna (University of Ulster, Coleraine, United Kingdom), B.A. Doherty (University of Ulster, Coleraine, United Kingdom), G. McKerr (University of Ulster, Coleraine, United Kingdom), S.R. McKeown (University of Ulster, Coleraine, United Kingdom), V.J. McKelvey-Martin (University of Ulster, Coleraine, United Kingdom)
- Application of the Comet Assay, Comet FISH and 24-colour-FISH to detect genotoxic effects of uranyl nitrilotriacetate and related environmental samples in human primary colon cells and colon adenoma cells

  Y. Knöbel (Friedrich Schiller University, Jena, Germany), A. Weise (Friedrich Schiller University, Jena, Germany), M. Glei (Friedrich Schiller University, Jena, Germany), W. Sendt (Friedrich Schiller University, Jena, Germany), U. Clausse (Friedrich Schiller University, Jena, Germany), B.L. Pool-Zobel (Friedrich Schiller University, Jena, Germany)

Session II: Genotoxicity testing

Chairman: V. McKelvey-Martin (University of Ulster, Coleraine, United Kingdom)

- Genotoxicity assessment of three trichothecene mycotoxins in the Caco-2 human cell line

  S. Bony (UMR INRA-DGER, Ecole Nationale Vétérinaire de Lyon, France), A. Devaux (INRA-EFPA, ENTPE, France)
- Quantification of initial DNA damage after alpha-irradiation measured *via* comet-assay

  U. Rößler (Federal Office for Radiation Protection – BfS, Oberschleissheim, Germany), C. Seidl (Technische Universität München, Germany), M. Gomolka (Federal Office for Radiation Protection – BfS, Oberschleissheim, Germany), E. Müller-Laue (Federal Office for Radiation Protection – BfS, Oberschleissheim, Germany), S. Hornhardt (Federal Office for Radiation Protection – BfS, Oberschleissheim, Germany), A. Morgenstern (Institut für Transurane, Karlsruhe, Germany), R. Senekowitsch-Schmidtke (Technische Universität München, Germany)

- Genotoxicity testing of arsenic and platinum compounds in the comet assay

  E. Guillamet (Universitat Autònoma de Barcelona, Spain), A. Creus (Universitat Autònoma de Barcelona, Spain), R. Marcos (Universitat Autònoma de Barcelona, Spain)
- Comparison of DNA damage induced by MH and NMH in plant and human cells in acellular comet assay

  J. Juchimiuk (University of Silesia, Katowice, Poland), A. Gnys (University of Silesia, Katowice, Poland), J. Maluszynska (University of Silesia, Katowice, Poland)
- Evaluation of rosiglitazone genotoxicity in rats

  A. Bedir (Ondokuz Mayis University, Samsun, Turkey), Y. Aliyazýcýoglu (Ondokuz Mayis University, Samsun, Turkey), Z. Yurdakul (Ondokuz Mayis University, Samsun, Turkey), M. Uysal (Ondokuz Mayis University, Samsun, Turkey), D. Erol Suvac (Ondokuz Mayis University, Samsun, Turkey), A. Okuyucu (Ondokuz Mayis University, Samsun, Turkey), H. Kahram (Ondokuz Mayis University, Samsun, Turkey), M. Hökelek (Ondokuz Mayis University, Samsun, Turkey), M. Alvur (Ondokuz Mayis University, Samsun, Turkey)

Session III: Human health

Chairman: A. Gábelová (Cancer Research Institute, Slovak Academy of Sciences, Bratislava, Slovakia)

- Evaluation the significance of initial, residual and oxidative DNA damage levels and DNA repair kinetics as biomarkers of cervical cancer patient responsiveness to radiotherapy

  A. Gábelová (Cancer Research Institute, Slovak Academy of Sciences, Bratislava, Slovakia), T. Farkašová (Cancer Research Institute, Slovak Academy of Sciences, Bratislava, Slovakia), S. Gurská (Cancer Research Institute, Slovak Academy of Sciences, Bratislava, Slovakia), Z. Macháčková (National Cancer Institute, Bratislava, Slovakia), P. Lukačko (National Cancer Institute, Bratislava, Slovakia)
- The role of genetic polymorphism in hOGG1 in radiosensitivity of cervical cancer cell lines

  S. Gurská (Cancer Research Institute, Slovak Academy of Sciences, Bratislava, Slovakia), T. Farkašová (Cancer Research Institute, Slovak Academy of Sciences, Bratislava, Slovakia), A. Gábelová (Cancer Research Institute, Slovak Academy of Sciences, Bratislava, Slovakia)
- Is the comet assay a useful tool for detecting smoking-related DNA damage?

  H. Hoffmann (Universitätsklinikum Ulm, Germany), G. Speit (Universitätsklinikum Ulm, Germany)
- Effect of aging, sun exposure and smoking on repair of H_2O_2-induced DNA damage by human fibroblasts measured using the comet assay

  S. Sauvaigo (CEA Grenoble, France), M. Bonnet-Duquennoy (GIE LVMH Recherche, Saint Jean de Braye, France), F. Odin (CEA Grenoble, France), F. Hazane (CEA Grenoble, France), N. Lachmann (GIE LVMH Recherche, Saint Jean de Braye, France), F. Bonté (GIE LVMH Recherche, Saint Jean de Braye, France), R. Kurfürst (GIE LVMH Recherche, Saint Jean de Braye, France), A. Favier (CEA Grenoble, France)
- Analysis of DNA repair in lymphocytes of breast cancer patients and healthy donors

  A. Padjas (Holycross Cancer Center, Kielce, Poland), A. Lankoff (Świętokrzyska Academy, Kielce, Poland), A. Banasik (Świętokrzyska Academy, Kielce, Poland), H. Lisowska (Świętokrzyska Academy, Kielce, Poland), A. Wieczorek (Holycross Cancer Center, Kielce, Poland), T. Kuszewski (Holycross Cancer Center, Kielce, Poland), S. Góźdź (Holycross Cancer Center, Kielce, Poland), A. Wójcik (Institute of Nuclear Chemistry and Technology, Warszawa, Poland; Świętokrzyska Academy, Kielce, Poland)

Session IV: Diet and DNA damage

Chairman: M. Kapiszewska (Jagiellonian University, Kraków, Poland)

- Modulation of oxidative DNA damage and other oxidant markers by apple juice phenolics/extracts in human colon cells

  S. Schäfer (Technical University of Kaiserslautern, Germany), T. Weisel (Technical University of Kaiserslautern, Germany), M. Baum (Technical University of Kaiserslautern, Germany), H. Dietrich (Research Institute Geisenheim, Germany), F. Will (Research Institute Geisenheim, Germany), G. Eisenbrand (Technical University of Kaiserslautern, Germany), C. Janzowski (Technical University of Kaiserslautern, Germany)
- Reduction of oxidative DNA damage by a flavonoid/polyphenolic rich fruit juice in an intervention study with healthy probands

  T. Weisel (Technical University of Kaiserslautern, Germany), S. Schäfer (Technical University of Kaiserslautern, Germany), M. Baum (Technical University of Kaiserslautern, Germany), H. Dietrich (Research Institute Geisenheim, Germany), F. Will (Research Institute Geisenheim, Germany), G. Eisenbrand (Technical University of Kaiserslautern, Germany), C. Janzowski (Technical University of Kaiserslautern, Germany)

- Orange juice *versus* vitamin C: effect on lymphocyte DNA resistance to oxidative damage
  S. Guarnieri (University of Milan, Italy), P. Riso (University of Milan, Italy), A. Brusamolino (University of Milan, Italy), M. Porrini (University of Milan, Italy)
- Protective effect of xanthohumol against genotoxicity of benzo(a)pyrene in HepG2 cells
  J. Plazar (National Institute of Biology, Ljubljana, Slovenia), T. Lah-Turnšek (National Institute of Biology, Ljubljana, Slovenia), M. Filipič (National Institute of Biology, Ljubljana, Slovenia)

Session V: Environmental and occupational exposure

Chairman: M. Kruszewski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)

- Assessment of genotoxic damage in nurses occupationally exposed to antineoplastic agents. Influence of genetic polymorphisms
  T. Cornetta (Universita degli Studi di Roma Tre, Italy), A. Testa (ENEA C.R. Casaccia, Italy), M. Giachelia (ENEA C.R. Casaccia, Italy), E. Ievoli (ENEA C.R. Casaccia, Italy), S. Palma (ENEA C.R. Casaccia, Italy), M. Appolloni (ENEA C.R. Casaccia, Italy), G. Spagnoli (Italian Institute for Occupational Prevention and Safety, Rome, Italy), G. Tranfo (Italian Institute for Occupational Prevention and Safety, Rome, Italy), R. Cozzi (Universita degli Studi di Roma Tre, Italy)
- Imatinib mesylate (STI571) inhibits DNA reapir in BCR/ABL – expressing cells exposed to environmental agents
  I. Majsterek (University of Łódź, Poland), A. Czechowska (University of Łódź, Poland), M. Arabski (University of Łódź, Poland), T. Wysocki (University of Łódź, Poland), J. Blasiak (University of Łódź, Poland)
- Influence of extremely low frequency magnetic fields on DNA damage in young mouse brain
  M. Villarini (Universita degli Studi di Perugia, Italy), G. Mariucci (Universita degli Studi di Perugia, Italy), I.C. Zampini (Universita degli Studi di Perugia, Italy; Universidad Nacional de Tucumán, Argentina), L. Dominici (Universita degli Studi di Perugia, Italy), M. Tantucci (Universita degli Studi di Perugia, Italy), S. Monarca (Universita degli Studi di Perugia, Italy), M.V. Ambrosini (Universita degli Studi di Perugia, Italy), M. Moretti (Universita degli Studi di Perugia, Italy)
- DNA damage and apoptosis in HepG2 cells following treatment with Cylindrospermopsin
  A. Lankoff (Świętokrzyska Academy, Kielce, Poland), W.W. Carmichael (Wright State University, Dayton, USA), J. Bialczyk (Jagiellonian University, Kraków, Poland), D. Dziga (Jagiellonian University, Kraków, Poland), J. Sochacki (Świętokrzyska Academy, Kielce, Poland), H. Lisowska (Świętokrzyska Academy, Kielce, Poland), A. Wójcik (Institute of Nuclear Chemistry and Technology, Warszawa, Poland; Świętokrzyska Academy, Kielce, Poland)
- Effects of chemical contaminants on genetic diversity, DNA integrity and fitness traits in feral fish populations
  V. Larno (INRA-EFPA, ENTPE, France), A. Devaux (INRA-EFPA, ENTPE, France)
- Assessment of DNA strand breakage on marine organisms for environmental monitoring
  E. Maran (University of Trieste, Italy), P. Barbieri (University of Trieste, Italy), M. Doz (P.S.C.P. Lisert, Trieste, Italy), E. Reisenhofer (University of Trieste, Italy)
- Soil and water soil leachates genotoxicity evaluations using comet assay and other bioassays
  B. Lah (University of Ljubljana, Slovenia), R. Marinšek-Logar (University of Ljubljana, Slovenia)

POSTERS

- Predictive significance of tumour cells radiosensitivity assessed on the basis of comet assay in cervical cancer patients treated with radiotherapy
  B. Biesaga (Centre of Oncology – Maria Skłodowska-Curie Memorial Institute, Kraków, Poland), A. Adamczyk (Centre of Oncology – Maria Skłodowska-Curie Memorial Institute, Kraków, Poland), M. Klimek (Centre of Oncology – Maria Skłodowska-Curie Memorial Institute, Kraków, Poland), A. Gasińska (Centre of Oncology – Maria Skłodowska-Curie Memorial Institute, Kraków, Poland)
- Comparative response to comet test between the wood mouse (*apodemus sylvaticus*) and the laboratory mouse (*mus musculus*) exposed to polar or lipophilic xenobiotics
  J. de Lapuente (Parc Científic de Barcelona, Spain), J. González-Linares (Parc Científic de Barcelona, Spain), M. Acosta (Parc Científic de Barcelona, Spain), M. Borràs (Parc Científic de Barcelona, Spain)
- Improving the comet assay
  G. Brunborg (Norwegian Institute of Public Health, Oslo, Norway), A. Collins (University of Oslo, Norway)
- Comet assay in somatic and germ cells of mice treated with dibutyl (DBP) and butylbenzyl (BBP) phthalates
  M. Dobrzyńska (National Institute of Hygiene, Warszawa, Poland), U. Mikulska (National Institute of Hygiene, Warszawa, Poland), E. Tyrkiel (National Institute of Hygiene, Warszawa, Poland)
- Genotoxic effect of benzophenanthridine alkaloids on human leukemia (HL60) cells
  M. Dvořák (Masaryk University in Brno, Czech Republic), M. Matejovičová (Masaryk University in Brno, Czech Republic), I. Slaninová (Masaryk University in Brno, Czech Republic), Z. Slunská (Masaryk University in Brno, Czech Republic), E. Táborská (Masaryk University in Brno, Czech Republic)

- Effect of T-2 toxin on DNA fragmentation in broiler chickens
  V. Rezar (University of Ljubljana, Slovenia), T. Frankic (University of Ljubljana, Slovenia), A. Levart (University of Ljubljana, Slovenia), T. Pajk (University of Ljubljana, Slovenia), J. Salobir (University of Ljubljana, Slovenia)
- Mice exposed to different doses of X-rays: persistence of genetic damage and *in vitro*-irradiation test
  A. Giovanetti (ENEA C.R. Casaccia, Italy), T. Deshpande (Goa University, India), E. Basso (ENEA C.R. Casaccia, Italy), R. Amendola (ENEA C.R. Casaccia, Italy), P. Ninova (Institute of Molecular Biology, Bulgarian Academy of Sciences, Sofia, Bulgaria)
- Double strand break induction by blue light at 420 nm and detection of DNA fragmentation by the protein-based neutral comet immunoassay
  P. Grigaravicius (Leibniz Institute for Age Research – Fritz Lippmann Institute, Jena, Germany), A. Rapp (Leibniz Institute for Age Research – Fritz Lippmann Institute, Jena, Germany), K.O. Greulich (Leibniz Institute for Age Research – Fritz Lippmann Institute, Jena, Germany)
- The effect of phenolic phytochemicals on the DNA damage in polymorphonuclear neutrophils upon oxidative burst
  E. Ignatowicz (Poznań University of Medical Sciences, Poland), A. Kniewel (Poznań University of Medical Sciences, Poland), W. Baer-Dubowska (Poznań University of Medical Sciences, Poland)
- The extent of DNA oxidative damage induced by hydrogen peroxide in HL-60 cells and its repair measured by the 8-OHdG ELISA and comet assay
  M. Kalemba (Jagiellonian University, Kraków, Poland), G. Zając (Jagiellonian University, Kraków, Poland), M. Kapiszewska (Jagiellonian University, Kraków, Poland)
- Assessment of DNA damage in children environmentally exposed to lead with the comet assay and the Micronucleus test
  L. Kapka (Institute of Occupational Medicine and Environmental Health, Sosnowiec, Poland), E. Siwińska (Institute of Occupational Medicine and Environmental Health, Sosnowiec, Poland), M. Kruszewski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), D. Miełżyńska (Institute of Occupational Medicine and Environmental Health, Sosnowiec, Poland)
- Modification of comet assay for detection of DNA cross-links and their repair
  J. Kozak (Institute of Experimental Botany, Academy of Sciences of Czech Republic), H. Puchta (Universität Karlsruhe, Germany), K.I. Angelis (Institute of Experimental Botany, Academy of Sciences of Czech Republic, Prague)
- DNA damage and its repair in subpopulations of peripheral blood lymphocytes
  B. Lubecka (Centre of Oncology – Maria Skłodowska-Curie Memorial Institute, Gliwice, Poland), M. Wideł (Centre of Oncology – Maria Skłodowska-Curie Memorial Institute, Gliwice, Poland), Z. Wołosza (Centre of Oncology – Maria Skłodowska-Curie Memorial Institute, Gliwice, Poland), J. Rzeszowska-Wolny (Centre of Oncology – Maria Skłodowska-Curie Memorial Institute, Gliwice, Poland)
- Use of Multicolour-Comet FISH to investigate preferential repair in wild-type and thymidine kinase deficient Raji cells
  K. McAllister (University of Ulster, Coleraine, United Kingdom), A. Yasseen (University of Ulster, Coleraine, United Kingdom), C.S. Downes (University of Ulster, Coleraine, United Kingdom), V.J. McKelvey-Martin (University of Ulster, Coleraine, United Kingdom)
- Influence of mercury vapors on lymphocytes *in vivo* and on their susceptibility to UV-C and X-rays, and repair efficiency *in vitro*
  A. Panek (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland), A. Cebulska-Wasilewska (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland; Jagiellonian University Medical College, Kraków, Poland), Z. Żabiński (International Institute of Universalistic Medicine, Tarnów, Poland), P. Moszczyński (International Institute of Universalistic Medicine, Tarnów, Poland)
- Diverse activity of dietary polyphenols on cancer cells in *in vitro* study
  M. Schmidt (The August Cieszkowski Agricultural University of Poznań, Poland), A.M. Olejnik (The August Cieszkowski Agricultural University of Poznań, Poland), A. Nakoneczna (The August Cieszkowski Agricultural University of Poznań, Poland), R. Krysiak (The August Cieszkowski Agricultural University of Poznań, Poland), K. Czajka (The August Cieszkowski Agricultural University of Poznań, Poland), A. Przybyłowicz (The August Cieszkowski Agricultural University of Poznań, Poland), P. Fijak (The August Cieszkowski Agricultural University of Poznań, Poland), M. Kawka (The August Cieszkowski Agricultural University of Poznań, Poland), A. Franas (The August Cieszkowski Agricultural University of Poznań, Poland), W. Grajek (The August Cieszkowski Agricultural University of Poznań, Poland)
- Radiation-induced DNA damage in whole blood of cancer patients subjected to chemotherapy
  N.P. Sirota (Institute of Theoretical and Experimental Biophysics, Russian Academy of Sciences, Pushchino, Russia), E.A. Kuznetsova (Institute of Theoretical and Experimental Biophysics, Russian Academy of Sciences, Pushchino, Russia), N.A. Gouliaeva (Institute of Theoretical and Experimental Biophysics, Russian Academy of Sciences, Pushchino, Russia), M.A. Popkova (Hospital of Pushchino Research Center, Russia), I.G. Zakharova (Hospital of Pushchino Research Center, Russia), L.N.

Kochmeneva (Hospital of Pushchino Research Center, Russia), V.I. Bruskov (Institute of Theoretical and Experimental Biophysics, Russian Academy of Sciences, Pushchino, Russia), A.I. Gaziev (Institute of Theoretical and Experimental Biophysics, Russian Academy of Sciences, Pushchino, Russia)

- Inhalation of air ions produced no damage to leukocyte DNA in peripheral blood of rats

  N.P. Sirota (Institute of Theoretical and Experimental Biophysics, Russian Academy of Sciences, Pushchino, Russia), B.G. Safronova (Institute of Cell Biophysics, Russian Academy of Sciences, Pushchino, Russia), V.N. Maltseva (Institute of Cell Biophysics, Russian Academy of Sciences, Pushchino, Russia), E.A. Kuznetsova (Institute of Theoretical and Experimental Biophysics, Russian Academy of Sciences, Pushchino, Russia), V.A. Yanin (Institute of Cell Biophysics, Russian Academy of Sciences, Pushchino, Russia), T.V. Sirota (Institute of Theoretical and Experimental Biophysics, Russian Academy of Sciences, Pushchino, Russia)
- Observations made during in-house validation of the comet assay

  C.C. Smith (AstraZeneca, United Kingdom), M.R. O'Donovan (AstraZeneca, United Kingdom), E.A. Martin (AstraZeneca, United Kingdom)
- Assessing DNA damage at points peripheral and distal to the treatment field during therapeutic radiation delivery

  M.L. Tassotto (Thunder Bay Regional Health Sciences Centre, Canada), B. Arjune (Thunder Bay Regional Health Sciences Centre, Canada), J. Th'ng (Thunder Bay Regional Health Sciences Centre, Canada)
- Sirtuins inhibition can be an important modulator of DNA repair

  M. Wojewódzka (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), A. Goździk (Military Institute of Hygiene and Epidemiology, Warszawa, Poland), I. Szumiel (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- DNA damage in subfractions of human lymphocytes irradiated with low doses of X-radiation

  E.K. Machaj (Military Institute of Hygiene and Epidemiology, Warszawa, Poland; Centre of Oncology – Maria Skłodowska-Curie Memorial Institute, Warszawa, Poland), A. Goździk (Military Institute of Hygiene and Epidemiology, Warszawa, Poland), M. Wojewódzka (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), T. Iwaneńko (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), T. Ołdak (Military Institute of Hygiene and Epidemiology, Warszawa, Poland; Centre of Oncology – Maria Skłodowska-Curie Memorial Institute, Warszawa, Poland), M. Kruszewski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland; Centre of Oncology – Maria Skłodowska-Curie Memorial Institute, Warszawa, Poland), Z. Pojda (Military Institute of Hygiene and Epidemiology, Warszawa, Poland; Centre of Oncology – Maria Skłodowska-Curie Memorial Institute, Warszawa, Poland)
- The formation of inter-strand DNA cross-links in the pig skin treated with sulphur mustard *in vivo*

  R. Štětina (University of Defence, Faculty of Military Health Sciences, Hradec Králové, Czech Republic), F. Opluštil (Military Technical Institute for Protection, Brno, Czech Republic)
- Increased DNA repair capacity in individuals exposed to oxidative stress: results with styrene-exposed workers and patients with type 1 diabetes mellitus

  R. Štětina (University of Defence, Faculty of Military Health Sciences, Hradec Králové, Czech Republic), P. Vodička (Institute of Experimental Medicine, Academy of Sciences of Czech Republic, Prague, Czech Republic), J. Varvařovská (Charles University, Plzen, Czech Republic)
- Bioindicators to monitor genotoxic damage by accidential release of toxic substances

  E. Sturchio (National Institute of Occupational Safety and Prevention, Rome, Italy), P. Boccia (National Institute of Occupational Safety and Prevention, Rome, Italy), L. Casorri (National Institute of Occupational Safety and Prevention, Rome, Italy), R. Ficociello (National Institute of Occupational Safety and Prevention, Rome, Italy), S. Marconi (Istituto Sperimentale per lo Studio e la Difesa del Suolo, Rieti, Italy), C. Beni (Experimental Institute for Plant Nutrition, Rome, Italy), P. Ferrazza (Opera research), R. Aromolo (Experimental Institute for Plant Nutrition, Rome, Italy), B. Felici (Experimental Institute for Plant Nutrition, Rome, Italy), M. Pezzella (Universita degli Studi di Roma "La Sapienza", Rome, Italy)

Panel discussion: Everything you always wanted to know about comet assay, but were afraid to ask (moderators: A. Collins, M. Kruszewski)

8. 2nd POLAND-JAPAN WORKSHOP ON MATERIALS SCIENCE "MATERIALS FOR SUSTAINABLE DEVELOPMENT IN 21st CENTURY", 12-15 OCTOBER 2005, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology, National Institute for Materials Science

Organizing Committee: Prof. J. Michalik, Ph.D., D.Sc., H. Yamada, Ph.D., J. Sadło, Ph.D., T. Mori, Ph.D.

LECTURES

Session I

Chairman: J. Michalik (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)

- International strategy of NIMS
  T Fujita (National Institute for Materials Science, Tsukuba, Japan)
- Structure and properties of nano-materials produced by severe plastic deformation
  Z. Pakieła (Warsaw University of Technology, Poland), K.J. Kurzydłowski (Warsaw University of Technology, Poland)

Session II

Chairman: H. Yamada (National Institute for Materials Science, Tsukuba, Japan)

- Recent development and issues on ecomaterials
  K. Halada (National Institute for Materials Science, Tsukuba, Japan)
- Worldwide developments in the field of radiation processing of materials in the dawn of 21st century
  A.G. Chmielewski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Consolidation of eutectic materials having nano-size structure
  K. Kakegawa (Chiba University, Japan), M. Nagata (Chiba University, Japan), T. Kojima (Chiba University, Japan), N. Uekawa (Chiba University, Japan)

Session III

Chairman: G. Zakrzewska-Trznadel (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)

- Properties of novel hydrides derived from AB_2 Laves phases and other intermetallics by using high hydrogen pressure technique
  S.M. Filipek (Institute of Physical Chemistry, Polish Academy of Sciences, Warszawa, Poland)
- Fabrication and processing of high-strength magnesium alloys with ductility
  T. Mukai (National Institute for Materials Science, Tsukuba, Japan), H. Somekawa (National Institute for Materials Science, Tsukuba, Japan), Y. Osawa (National Institute for Materials Science, Tsukuba, Japan), K. Hono (National Institute for Materials Science, Tsukuba, Japan)

Session IV

Chairman: S.M. Filipek (Institute of Physical Chemistry, Polish Academy of Sciences, Warszawa, Poland)

- Structural characterization of room-temperature synthesized fullerene nanowhiskers
  K. Miyazawa (National Institute for Materials Science, Tsukuba, Japan), J. Minato (National Institute for Materials Science, Tsukuba, Japan), T. Mashino (Kyoritsu University of Pharmacy, Tokyo, Japan), S. Nakamura (Kyoritsu University of Pharmacy, Tokyo, Japan), M. Fujino (University of Tokyo, Japan), T. Suga (University of Tokyo, Japan)
- Polyurethane-based materials as scaffolds for tissue engineering
  G. Przybytniak (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)

Session V

Chairman: J. Ye (National Institute for Materials Science, Tsukuba, Japan)

- Properties of novel silicon nitride-based materials
  K. Itatani (Sophia University, Tokyo, Japan)
- Synthesis of nanostructured t-ZrO_2 of enhanced thermal stability
  Z. Sojka (Jagiellonian University, Kraków, Poland), A. Adamski (Jagiellonian University, Kraków, Poland), P. Jakubus (Szczecin University of Technology, Poland)
- Design of high quality solid oxide electrolyte with nano-hetero structure
  T. Mori (National Institute for Materials Science, Tsukuba, Japan), J. Drennan (University of Queensland, Brisbane, Australia), D.R. Ou (National Institute for Materials Science, Tsukuba, Japan), J. Zou (University of Queensland, Brisbane, Australia)

Session VI

Chairman: Z. Sojka (Jagiellonian University, Kraków, Poland)

- Metal clusters in zeolites
  J. Michalik (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), J. Sadło (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), M. Danilczuk (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), J. Turek (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Novel visible light sensitive photocatalysts for environmental purification and hydrogen generation
  J. Ye (National Institute for Materials Science, Tsukuba, Japan; Japan Science and Technology Agency,

Kawaguchi, Japan), T. Kako (National Institute for Materials Science, Tsukuba, Japan), D. Wang (National Institute for Materials Science, Tsukuba, Japan), J. Tang (National Institute for Materials Science, Tsukuba, Japan)

- Preparation of catalysts and sorbents by sol-gel method
  A. Deptula (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), W. Łada (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), T. Olczak (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), D. Wawszczak (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), J. Chwastowska (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), A.G. Chmielewski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)

Session VII

Chairman: K. Halada (National Institute for Materials Science, Tsukuba, Japan)

- Lead-free solder as an eco-material. Production of fine spherical lead-free solder powder
  K. Minagawa (National Institute for Materials Science, Tsukuba, Japan), H. Kakisawa (National Institute for Materials Science, Tsukuba, Japan), S. Takamori (National Institute for Materials Science, Tsukuba, Japan), Y. Osawa (National Institute for Materials Science, Tsukuba, Japan), K. Halada (National Institute for Materials Science, Tsukuba, Japan)
- Polyolefine wastes degradation into liquid fuels
  B. Tymiński (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), K. Zwoliński (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), R. Jurczyk (Zakład Usług Technicznych, Warszawa, Poland)
- Development of environmental purification materials with smart functions
  H. Yamada (National Institute for Materials Science, Tsukuba, Japan), Y. Watanabe (Kanazawa Institute of Technology, Nonoichi, Japan), K. Tamura (National Institute for Materials Science, Tsukuba, Japan)
- Membrane processes for environmental protection
  G. Zakrzewska-Trznadel (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)

Session VIII

Chairman: A.G. Chmielewski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)

- Biological and synthetic hydroxyapatites
  J. Sadło (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), J. Michalik (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), W. Stachowicz (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Silica materials with biocidal activity
  A. Łukasiewicz (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), D.K. Chmielewska (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), K.J. Krajewski (Warsaw Agricultural University, Poland), J. Michalik (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Advanced processing for recycling of iron scrap with impurities
  Y. Osawa (National Institute for Materials Science, Tsukuba, Japan), S. Takamori (National Institute for Materials Science, Tsukuba, Japan), K. Minagawa (National Institute for Materials Science, Tsukuba, Japan), H. Kakisawa (National Institute for Materials Science, Tsukuba, Japan), K. Halada (National Institute for Materials Science, Tsukuba, Japan)
- Template synthesis of nanostructures in track-etched membranes
  M. Buczkowski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), W. Starosta (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), D. Wawszczak (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Radiation processing of polymers and semiconductors
  Z. Zimek (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), G. Przybytniak (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), I. Kałuska (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)

Discussion on the Polish-Japanese cooperation in 2006-2007

9. VIII SZKOŁA STERYLIZACJI I HIGIENIZACJI RADIACYJNEJ (VIII TRAINING COURSE ON RADIATION STERILIZATION AND HYGIENIZATION), 20-21 OCTOBER 2005, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology, National Atomic Energy Agency, Polish Nuclear Society

Organizing Committee: Z. Zimek, Ph.D. (Chairman), I. Kałuska, M.Sc., W. Głuszewski, M.Sc.

LECTURES

- Sterylizacja radiacyjna na tle innych metod wyjaławiania (Radiation sterilization as compared with other sterilization methods)
  W. Stachowicz (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Podstawy oddziaływania promieniowania jonizującego z materią (Fundamentals of interaction of ionizing radiation with matter)
  P.P. Panta (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Akceleratory elektronów stosowane w technice radiacyjnej (Electron accelerators used for radiation processing)
  Z. Zimek (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Mikrobiologiczne aspekty sterylizacji radiacyjnej (Microbiological aspects of radiation sterilization)
  M. Żak (Toruńskie Zakłady Materiałów Opatrunkowych S.A., Poland)
- Określanie dawki sterylizacyjnej (Establishing of sterilization dose)
  I. Kałuska (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Wykorzystanie promieniowania hamowania do sterylizacji radiacyjnej (X-rays (bremsstrahlung) application for radiation sterilization)
  Z. Zimek (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Izotopowe źródła promieniowania w sterylizacji radiacyjnej (Isotopic sources of radiation used for radiation sterilization)
  W. Bogus (Technical University of Łódź, Poland)
- Walidacja procesu napromieniowania w stacji sterylizacji radiacyjnej (Validation of sterilization process at a radiation sterilization plant)
  I. Kałuska (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Kontrola dozymetryczna przemysłowej sterylizacji wyrobów medycznych (Dosimetric control of industrial sterilization process of medical devices)
  W. Głuszewski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Napromieniowanie żywności w Unii Europejskiej i w Polsce (Ford irradiation in the European Union and in Poland)
  W. Migdał (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Samodzielne Laboratorium Identyfikacji Napromieniowania Żywności (Laboratory for Detection of Irradiated Food)
  W. Stachowicz (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), K. Malec-Czechowska (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Wpływ promieniowania jonizującego na materiały polimerowe stosowane w medycynie (Influence of ionizing radiation on polymeric materials used in medicine)
  G. Przybytniak (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Sztuczne materiały implantacyjne – rola biomateriałów w inżynierii tkankowej (Artificial implant materials – role of biomaterials in tissue engineering)
  M. Lewandowska-Szumieł (Medical University of Warsaw, Poland)
- Aktualne kierunki rozwoju metodyki badań leków sterylizowanych radiacyjnie (Actual trends in investigation methods for radiation sterilized pharmaceuticals)
  B. Marciniec (Poznań University of Medical Sciences, Poland)
- Dobre praktyki stosowane w farmacji (Good practices used in pharmacy)
  D. Prokopczyk (POLFA S.A., Warszawa, Poland)
- Przegląd różnych zakresów praw obowiązujących wytwórców produktów leczniczych (Review of different range of laws obligatory for the manufacturers of pharmaceuticals)
  D. Prokopczyk (POLFA S.A., Warszawa, Poland)
- Wyroby medyczne – rejestracja, klasyfikacja, ocena zgodności, nadzór (Medical devices – registration, classification, evaluation of consistence, inspection)
  A.I. Lasocka (Office for Registration of Medicinal Products, Medical Devices and Biocides, Warszawa, Poland)
- Radiacyjna inżynieria biomedyczna (Radiation biomedical engineering)
  J.M. Rosiak (Technical University of Łódź, Poland)
- Zastosowanie promieniowania jonizującego do wyjaławiania przeszczepów tkankowych (Use of ionizing radiation for radiation sterilization of tissue grafts)
  A. Dziedzic-Gocławska (National Centre for Tissues and Cell Banking, Warszawa, Poland), A. Kamiński (National Centre for Tissues and Cell Banking, Warszawa, Poland), I. Uhrynowicz-Tyszkiewicz (National Centre for Tissues and Cell Banking, Warszawa, Poland), J. Michalik (Institute of Nuclear Chemistry

and Technology, Warszawa, Poland), W. Stachowicz (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)

- Sterylizacja radiacyjna allogenicznych, biostatycznych przeszczepów kostnych zamrożonych celem klinicznego ich zastosowania (Radiation sterilization of biostatic freezed bone allografs for clinical use)
  W. Marczyński (Military Institute of the Health Services, Warszawa, Poland)
- Z archiwum sterylizacji radiacyjnej (From the archives of radiation sterilization)
  Z.P. Zagórski (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Biologiczne działanie i ryzyko promieniowania jonizującego (Biological effects and risk of ionizing radiation)
  A. Wójcik (Institute of Nuclear Chemistry and Technology, Warszawa, Poland), I. Szumiel (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
- Akredytowane Laboratorium Pomiarów Dawek Technologicznych Instytutu Chemii i Techniki Jądrowej w Warszawie (Accreditated Laboratory for Measurement of Technological Doses at the Institute of Nuclear Chemistry and Technology)
  Z. Peimel-Stuglik (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)

10. III KONFERENCJA „PROBLEMY UNIESZKODLIWIANIA ODPADÓW" (III CONFERENCE ON PROBLEMS OF WASTE DISPOSAL), 21 NOVEMBER 2005, WARSZAWA, POLAND

Organized by the Warsaw University of Technology, Plant for Utilization of Solid Municipal Wastes (Warszawa), Institute of Nuclear Chemistry and Technology, Gdańsk University of Technology

Organizing Committee: M. Obrębska, Ph.D., S. Sobera-Madej, M.Sc.

Session IA. NAUKOWO-TECHNICZNA (SCIENCE AND TECHNOLOGY)

Chairman: A.G. Chmielewski (Warsaw University of Technology; Institute of Nuclear Chemistry and Technology, Poland)

- Funkcjonowanie barier aktywnych ograniczających migrację zanieczyszczeń (Functioning of active barriers limiting the migration of pollutants)
  A. Adach (Warsaw University of Technology, Poland), S. Wroński (Warsaw University of Technology, Poland)
- Wykorzystanie ogrzewania mikrofalowego do procesu karbonizacji odpadów rolniczych (Using the microwave heating for the process of agricultural waste carbonization)
  K. Bratek (Wrocław University of Technology, Poland), W. Bratek (Wrocław University of Technology, Poland), M. Kułażyński (Wrocław University of Technology, Poland)
- Charakterystyka produktów otrzymywanych podczas krakingu odpadów polietylenu (Characterization of products received during cracking of polyethylene waste)
  B. Tymiński (Institute of Nuclear Chemistry and Technology, Poland), K. Zwoliński (Institute of Nuclear Chemistry and Technology, Poland), R. Jurczyk (Institute of Nuclear Chemistry and Technology, Poland), A. Darkowski (Warsaw University of Technology, Poland)
- Recykling poliuretanów (Recycling of polyurethanes)
  Z.K. Brzozowski (Central Institute for Labour Protection – National Research Institute, Warszawa; Warsaw University of Technology, Poland)

Session IB. SAMORZĄDOWO-EKONOMICZNO-PRAWNA (MUNICIPAL-ECONOMIC-LAWFULL)

Chairman: M. Obrębska (Warsaw University of Technology, Poland)

- Problemy unieszkodliwiania odpadów medycznych w ocenie Inspekcji Ochrony Środowiska (Problems of medical waste neutralizing in the assessment of the Environmental Preservation Inspection)
  M. Suchy (Voivodeship Inspectorate of Environment Protection, Rzeszów, Poland)
- Termiczne przekształcanie odpadów komunalnych w aspekcie wypełnienia przyjętych zobowiązań akcesyjnych (Thermal transforming of municipal waste from the accession obligations point of view)
  T. Pająk (AGH University of Science and Technology, Kraków, Poland)
- Spalarnie odpadów w krajach Unii Europejskiej (Incinerators of waste in the EU countries)
  G. Wielgosiński (Technical University of Łódź, Poland)
- Instalacje monitoringu emisji spalin w ZUSOK (Installations for the emission monitoring of the exhaust fumes in ZUSOK)
  P. Nadulski (Plant for Utilization of Solid Municipal Wastes, Warszawa, Poland)

Session IIA. NAUKOWO-TECHNICZNA (SCIENCE AND TECHNOLOGY)

Chairman: A. Biń (Warsaw University of Technology, Poland)

- Termiczne przekształcanie odpadów metodą pirolizy na przykładzie zużytych opon samochodowych (Thermal transforming of the waste by the pyrolysis method on the example of used car tyres)
  A. Sobolewski (Institute for Chemical Processing of Coal, Zabrze, Poland), S. Stelmach (Institute for Chemical Processing of Coal, Zabrze, Poland), R. Wasilewski (Institute for Chemical Processing of Coal, Zabrze, Poland)
- Recykling termiczno-katalityczny poliolefin i polistyrenu (Thermal-catalytic recycling of polyolefines and polystyrene)
  J. Sokołowski (Warsaw University of Technology, Poland), G. Rokicki (Warsaw University of Technology, Poland), M. Baranowska (Warsaw University of Technology, Poland)
- Ocena adsorbentów węglowych stosowanych w układach oczyszczania spalin instalacji termicznego unieszkodliwiania odpadów (na wybranych przykładach) (Assessment of coal adsorbents application in purifying the exhaust fumes arrangements of thermal neutralizing waste installations (on chosen examples))
  A. Świątkowski (WAT Military University of Technology, Warszawa, Poland)
- Techniczne środki oceny czynników niebezpiecznych w gospodarce odpadami (Technical remedies for the assessment of dangerous factors occurring in waste management)
  K. Pawłowski (Warsaw University of Technology, Poland)

Session IIB. SAMORZĄDOWO-EKONOMICZNO-PRAWNA (MUNICIPAL-ECONOMIC-LAWFULL)

Chairman: T. Pająk (AGH University of Science and Technology, Kraków, Poland)

- Problem warszawskich osadów z oczyszczalni ścieków w aspekcie unijnych procedur realizacji inwestycji o dużym oddziaływaniu na środowisko (Problems of sludge from a Warsaw sewage treatment plant from the point of view of EU procedures fro the realization of investments of great environmental impact)
  J. Kaznowski (Plant for Utilization of Solid Municipal Wastes, Warszawa, Poland)
- Przykłady technologii do unieszkodliwiania osadów ściekowych (Examples of technology to rendering sediments deposits)
  J. Kaznowski (Plant for Utilization of Solid Municipal Wastes, Warszawa, Poland)
- Określenie możliwości pozyskania PET na rynku krajowym (Defining the possibility of PET recruiting on the domestic market)
  P. Grzybowski (Warsaw University of Technology, Poland)
- Techniczne środki oceny czynników niebezpiecznych w gospodarce odpadami (Technical remedies for the assessment of dangerous factors occurring in waste management)
  K. Pawłowski (Warsaw University of Technology, Poland)

Session IIIA. NAUKOWO-TECHNICZNA (SCIENCE AND TECHNOLOGY)

Chairman: B. Kawalec-Pietrenko (Gdańsk University of Technology, Poland)

- Zastosowanie wysokoefektywnych procesów utleniania do podczyszczania odcieków ze składowisk odpadów komunalnych (Application of high-effective oxidizing processes for municipal wastewater stockpiles purification)
  I. Prokurat (Warsaw University of Technology, Poland), J. Naumczyk (Warsaw University of Technology, Poland)
- Badanie możliwości podczyszczania odcieków z kompostowania odpadów komunalnych (Research on the purification possibility of wastewater from composting of municipal waste)
  M. Obrębska (Warsaw University of Technology, Poland), A.G. Chmielewski (Warsaw University of Technology, Poland), W. Piątkiewicz (Warsaw University of Technology, Poland), R. Czykwin (Warsaw University of Technology, Poland), A. Polak (Warsaw University of Technology, Poland)
- Elektrochemiczne oczyszczanie odcieków ze składowisk odpadów komunalnych (Electrochemical purification of wastewater from stockpiles of municipal waste)
  A. Dmochowska (Warsaw University of Technology, Poland), J. Naumczyk (Warsaw University of Technology, Poland)
- Ceramiczne tworzywa porowate do separacji zanieczyszczeń organicznych z drobno zdyspergowanych emulsji wodnych (Ceramic porous materials for the separation of organic pollutants from finely dispersed aqueous emulsions)
  K. Perkowski (Warsaw University of Technology, Poland), J. Sokołowski (Warsaw University of Technology, Poland), M. Szafran (Warsaw University of Technology, Poland)

Session IIIB. SAMORZĄDOWO-EKONOMICZNO-PRAWNA (MUNICIPAL-ECONOMIC-LAWFULL)

Chairman: J. Kaznowski (Plant for Utilization of Solid Municipal Wastes, Warszawa, Poland)

- Akumulatory i baterie jako odpady niebezpieczne (Batteries as dangerous waste)
  A. Czerwieński (Industrial Chemistry Research Institute, Warszawa, Poland), Z. Rogulski (Industrial Chemistry Research Institute, Warszawa, Poland)

- Co robić· ze zużytymi i przeterminowanymi akumulatorami i bateriami? (What to do with used and overdue batteries?)
  Z. Rogulski (Industrial Chemistry Research Institute, Warszawa, Poland), A. Czerwieński (Industrial Chemistry Research Institute, Warszawa, Poland)
- Termiczne unieszkodliwianie zużytego koksu aktywnego z adsorbera przeciwprądowego WKV w ZUSOK (Thermal neutralizing of used coke from a counter-current adsorber WKV in ZUSOK)
  K. Stańczak (Plant for Utilization of Solid Municipal Wastes, Warszawa, Poland)
- Wysokotemperaturowa technologia utylizacji osadów ściekowych (High-temperature recycling technology of sewage deposits)
  H. Karcz (Wrocław University of Technology, Poland), W. Sitkowski (ZBUS Combustion Głowno, Poland), K. Folga (ZBUS Combustion Głowno, Poland), A. Kozakiewicz (TKW Combustion Głowno, Poland)

Session IVA. NAUKOWO-TECHNICZNA (SCIENCE AND TECHNOLOGY)

Chairman: P. Grzybowski (Warsaw University of Technology, Poland)

- Kinetyka biodegradacji ketonów i alkoholi w obecności bakterii w zawiesinie oraz bakterii unieruchomionych w warstwie fluidalnej (Biodegradation kinetics of ketones and alcohols in the presence of bacteria in suspension or immobilized in a fluidized bed)
  B. Kawalec-Pietrenko (Gdańsk University of Technology, Poland), M. Łazarczyk (Gdańsk University of Technology, Poland)
- Zastosowanie preparatów bakterii kwasu mlekowego do konserwowania produktów ubocznych przemysłu piwowarskiego (Use of lactic acid bacteria for preservation of by-products of the brewing industry)
  E. Baca (Institute of Agricultural and Food Biotechnology, Warszawa, Poland)
- Ocena energetycznych i ekologicznych własności osadów ściekowych (Assessment of energy and ecological properties of sewage deposits)
  H. Karcz (Wrocław University of Technology, Poland), D. Maciejak (Wrocław University of Technology, Poland), M. Charusta (Wrocław University of Technology, Poland)

Session IVB. SAMORZĄDOWO-EKONOMICZNO-PRAWNA (MUNICIPAL-ECONOMIC-LAWFULL)

Chairman: M. Obrębska (Warsaw University of Technology, Poland)

- Energetyczna i ekologiczna przydatność·odpadów zwierzęcych (Energetical and ecological usefulness of animal waste)
  H. Karcz (Wrocław University of Technology, Poland), A. Kozakiewicz (TKW Combustion Głowno, Poland), A. Kotulski (TKW Combustion Głowno, Poland)
- Technologia termicznej utylizacji mączki mięsno-kostnej i tłuszczu zwierzęcego (Thermal recycling technology of flour meat-bone and animal fats)
  H. Karcz (Wrocław University of Technology, Poland), M. Krzysztof (ZBUS Combustion Głowno, Poland), M.J. Michalak (ZBUS Combustion Głowno, Poland)
- System sterowania instalacji do utylizacji odpadów organicznych na przykładzie układu do spalania mączki kostnej w Struga S.A. (The installation controlling system to the organic waste recycling on an example of burning bone meal in the Struga S.A.)
  K. Cisak (TKW Combustion Głowno, Poland), Z. Kaczmarek (TKW Combustion Głowno, Poland), H. Karcz (Wrocław University of Technology, Poland)
- Rozwój technologii perkolacji odpadów komunalnych (Development of technology for percolation of municipal waste)
  A. Jędrczak (University of Zielona Góra, Poland)

Ph.D./D.Sc. THESES IN 2005

Ph.D. THESES

1. Małgorzata Derda, M.Sc.
   Oznaczanie stosunków izotopowych siarki w procesie spalania węgla (Determination of sulphur isotope ratios in coal combustion process)
   supervisor: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.
   Institute of Nuclear Chemistry and Technology, 15.12.2005
2. Ewa Kornacka, M.Sc.
   Badanie wpływu jonów niektórych metali przejściowych oraz substancji ochronnych na proces radiolizy DNA (Influence of some transition metal ions and protective agents on DNA radiolysis)
   supervisor: Assoc. Prof. Hanna Ambroż, Ph.D., D.Sc.
   Institute of Nuclear Chemistry and Technology, 15.12.2005
3. Joanna Perlińska, M.Sc.
   Paramagnetyczne centra generowane radiacyjnie w sodalitach (Paramagnetic centers generated radiolytically in sodalites)
   supervisor: Prof. Jacek Michalik, Ph.D., D.Sc.
   Institute of Nuclear Chemistry and Technology, 14.04.2005
4. Wojciech Starosta, M.Sc.
   Krystalochemia kompleksów wapnia z ligandami azynodwukarboksylowymi (Crystal chemistry of calcium complexes with azinedicarboxylate ligands)
   supervisor: Prof. Janusz Leciejewicz, Ph.D., D.Sc.
   Institute of Nuclear Chemistry and Technology, 06.10.2005
5. Yongxia Sun, M.Sc.
   Radiation induced decomposition of selected chlorinated hydrocarbons in gaseous phase
   supervisor: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.
   Institute of Nuclear Chemistry and Technology, 06.10.2005

D.Sc. THESES

1. Grażyna Przybytniak, Ph.D.
   Rodniki powstające w DNA i jego nukleotydach pod wpływem promieniowania jonizującego (Radicals of DNA and DNA nucleotides generated by ionising radiation)
   Institute of Nuclear Chemistry and Technology

EDUCATION

Ph.D. PROGRAMME IN CHEMISTRY

The Institute of Nuclear Chemistry and Technology holds a four-year Ph.D. degree programme for graduates of chemical, physical and biological departments of universities, for graduates of medical universities and to engineers in chemical technology and material science.

The main areas of the programme are:

- radiation chemistry and biochemistry,
- chemistry of radioelements,
- isotopic effects,
- radiopharmaceutical chemistry,
- analytical methods,
- chemistry of radicals,
- application of nuclear methods in chemical and environmental research, material science and protection of historical heritage.

The candidates accepted for the mentioned programme can be employed in the Institute. The candidates can apply for a doctorial scholarship. The INCT offers accommodation in 10 rooms in the guesthouse for Ph.D. students not living in Warsaw.

During the four-year Ph.D. programme the students participate in lectures given by senior staff from the INCT, Warsaw University and the Polish Academy of Sciences. In the second year, the Ph.D. students have teaching practice in the Chemistry Department of Warsaw University. Each year the Ph.D. students are obliged to deliver a lecture on topic of his/her dissertation at a seminar. The final requirements for the Ph.D. programme graduates, consistent with the regulation of the Ministry of Education and Science, are:

- submission of a formal dissertation, summarizing original research contributions suitable for publication;
- final examination and public defense of the dissertation thesis.

In 2005, the following lecture series were organized:

- "Radiobiology" – Assoc. Prof. Andrzej Wójcik, Ph.D., D.Sc. (Institute of Nuclear Chemistry and Technology);
- "Chemometrics" – Prof. Piotr Urbański, Ph.D., D.Sc. (Institute of Nuclear Chemistry and Technology);
- "Nuclear chemistry" – Assoc. Prof. Aleksander Bilewicz, Ph.D., D.Sc. (Institute of Nuclear Chemistry and Technology);
- "Coordination chemistry" – Prof. Jerzy Narbutt, Ph.D., D.Sc. (Institute of Nuclear Chemistry and Technology).

The qualification interview for the Ph.D. programme takes place in the mid of October. Detailed information can be obtained from:

- Head: Assoc. Prof. Aleksander Bilewicz, Ph.D., D.Sc.
  (phone: (+4822) 504 13 57, e-mail: abilewic@ichtj.waw.pl);
- Secretary: Dr. Ewa Gniazdowska
  (phone: (+4822) 504 10 74 or 504 11 78, e-mail: studium@ichtj.waw.pl).

TRAINING OF STUDENTS

Institution	Country	Number of participants	Period
AGH University of Science and Technology	Poland	12	2 weeks
European Union (FP5)	France	1	1 year

Institution	Country	Number of participants	Period
European Union (FP5)	Romania	1	8.5 month
International Atomic Energy Agency	Indonesia	1	3 months
International Atomic Energy Agency	Iran	1	4 months
International Atomic Energy Agency	Libya	1	1 month
International Atomic Energy Agency	Tunisia	1	1 month
Technical School of Chemistry	Poland (Warszawa)	3	1 month
Technical University of Łódź Faculty of Chemistry	Poland	1	7 days
Warsaw University of Technology Faculty of Chemical and Process Engineering	Poland	2	1 month
		12	one-day practice
Warsaw University of Technology Faculty of Chemistry	Poland	8	1 month
Warsaw University of Technology Faculty of Materials Science and Engineering	Poland	3	1 month
Warsaw University of Technology Faculty of Physics	Poland	3	1 month
		23	one-day practice

RESEARCH PROJECTS AND CONTRACTS

RESEARCH PROJECTS GRANTED BY THE MINISTRY OF EDUCATION AND SCIENCE IN 2005 AND IN CONTINUATION

1. **Tricarbonyl technetium(I) and rhenium(I) complexes with chelating ligands as radiopharmaceutical precursors.**
   supervisor: Prof. Jerzy Ostyk-Narbutt, Ph.D., D.Sc.
2. **Neutron activation analysis and ion chromatography as a tool for reliable lanthanides determination in the biological and environmental samples.**
   supervisor: Bożena Danko, Ph.D.
3. **The chemical isotope effects of gallium, indium and thallium in ligand exchange and red-ox reactions.**
   supervisor: Wojciech Dembiński, Ph.D.
4. **Comparative analysis of telomere length, chromosomal aberration frequency and DNA repair kinetics in peripheral blood lymphocytes of healthy donors and cancer patients.**
   supervisor: Assoc. Prof. Andrzej Wójcik, Ph.D., D.Sc.
5. **Baroque glass in Polish collections (provenance verification).**
   supervisor: Jerzy Kunicki-Goldfinger, Ph.D.
6. **The role of PARP-1 in DNA double strand breaks repair.**
   supervisor: Maria Wojewódzka, Ph.D.
7. **Sodium and silver clusters in gamma irradiated sodalites.**
   supervisor: Prof. Jacek Michalik, Ph.D., D.Sc.
8. **Radiation induced decomposition of selected chlorinated hydrocarbons in gaseous phase.**
   supervisor: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.
9. **Oxidation of thioether by organic complexes of copper. Processes of potential importance for pathogenesis of some neurodegenerative diseases.**
   supervisor: Assoc. Prof. Dariusz Pogocki, Ph.D., D.Sc.
10. **New methods of the study and reduction of fouling in processes of micro- and ultrafiltration of liquid radioactive waste.**
    supervisor: Grażyna Zakrzewska-Trznadel, Ph.D.
11. **Modelling of the dispersion of pollutants and studying their transport in natural water receivers using stable isotopes as tracers.**
    supervisor: Andrzej Owczarczyk, Ph.D.
12. **Influence of gamma irradiation on starch properties: starch interaction with water and lipids, starch-lipid films.**
    supervisor: Krystyna Cieśla, Ph.D.
13. **Changes of sulphur isotope ratio in the products of coal combustion and flue gas desulphurization processes.**
    supervisor: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.
14. **Process of nanostructure formation of small-molecule organic gels using synchrotron methods.**
    supervisor: Assoc. Prof. Helena Grigoriew, Ph.D., D.Sc.
15. **Analytical studies of products of degradation of selected chlorophenols and pesticides caused by ionizing radiation.**
    supervisor: Prof. Marek Trojanowicz, Ph.D., D.Sc.

16. **Studies of coordination of magnesium and zinc ions in their complexes with the azine dicarboxylate ligands.**
    supervisor: Prof. Janusz Leciejewicz, Ph.D., D.Sc.
17. **Stable isotope applications to quality and origin control of milk and milk products.**
    supervisor: Ryszard Wierzchnicki, Ph.D.
18. **Protection phenomena in radiation chemistry of polypropylene.**
    supervisor: Prof. Zbigniew P. Zagórski, Ph.D., D.Sc.
19. **Modification of the near surface layer of carbon steels with intense argon and nitrogen plasma pulses.**
    supervisor: Prof. Jerzy Piekoszewski, Ph.D., D.Sc.

IMPLEMENTATION PROJECTS GRANTED BY THE MINISTRY OF EDUCATION AND SCIENCE IN 2005 AND IN CONTINUATION

1. **Polish certified reference materials: maize meal and soia flour for the quality control of laboratories analyzing food.**
   06 P06 2002C/05899
   supervisor: Halina Polkowska-Motrenko, Ph.D.

RESEARCH PROJECTS ORDERED BY THE MINISTRY OF EDUCATION AND SCIENCE IN 2005

1. **Radiation processing application to modify and sterilize polymer scaffolds.**
   PBZ-KBN-082/T08/2002
   supervisor: Grażyna Przybytniak, Ph.D., D.Sc.
2. **Radiation processing application to form nanofillers with different structure including hybrid and functionalized.**
   PBZ-KBN-095/T08/2003
   supervisor: Zbigniew Zimek, Ph.D.
3. **Mutual interactions between nutritional components in steering of development of the intestinal immunological system.**
   PBZ-KBN-093/P06/2003
   supervisor: Assoc. Prof. Marcin Kruszewski, Ph.D., D.Sc.

IAEA RESEARCH CONTRACTS IN 2005

1. **Application of ionizing radiation for removal of pesticides from ground waters and wastes.**
   12016/RO
   principal investigator: Prof. Marek Trojanowicz, Ph.D., D.Sc.
2. **Radiation resistant polypropylene for medical applications and as component of structural engineering materials.**
   12703/RO
   principal investigator: Zbigniew Zimek, Ph.D.
3. **Electron beam for VOCs treatment emitted from oil combustion process.**
   13136/Regular Budget Fund
   principal investigator: Anna Ostapczuk, M.Sc.
4. **Electron beam for VOCs treatment emitted from oil combustion process.**
   13136/RO
   principal investigator: Anna Ostapczuk, M.Sc.

IAEA TECHNICAL CONTRACTS IN 2005

1. **Accredited laboratory for the use of nuclear and nuclear-related analytical techniques.**
   POL/2/014
2. **Mobile detector for leakproof control and location of leaks in underground pipelines: elaboration of method, installation and delivery of instrumentations.**
   TC RAF0014-90533L

EUROPEAN COMMISSION RESEARCH PROJECTS IN 2005

1. FP6 Integrated Project **European research program for the partitioning of actinides from high active wastes issuing the reprocessing of spent nuclear fuels (EUROPART).**
   FP6-508854
2. FP5 Research Training Network: **Sulfur radical chemistry of biological significance: the protective and damaging roles of thiol and thioether radicals (SULFRAD).**
   principal investigator: Prof. Krzysztof Bobrowski, Ph.D., D.Sc.
   RTN-2001-00096 under FP5
3. FP6 Marie Curie Host Fellowships for the Transfer of Knowledge: **Advanced methods for environment research and control (AMERAC).**
   principal investigator: Grażyna Zakrzewska-Trznadel, Ph.D.
   MTKD-CT-2004-509226
4. FP6 Marie Curie Host Fellowships for the Transfer of Knowledge: **Chemical studies for design and production of new radiopharmaceuticals (POL-RAD-PHARM).**
   principal investigator: Prof. Jerzy Ostyk-Narbutt, Ph.D., D.Sc.
   MTKD-CT-2004-509224
5. European cooperation in the field of scientific and technical research. COST D27 – **Prebiotic chemistry and early evolution. Role of radiation chemistry in the origin of life on Earth.**
   supervisor: Prof. Zbigniew Zagórski, Ph.D., D.Sc.
6. European cooperation in the field of scientific and technical research. COST P9 – **Radiation damage in biomolecular systems (RADAM). Mechanisms of radiation damage transfer in polypeptide molecules.**
   supervisor: Prof. Krzysztof Bobrowski, Ph.D., D.Sc.

OTHER FOREIGN CONTRACTS IN 2005

1. **Laboratory scale experimental analysis of electron beam treatment of flue gases from combustion of liquid petroleum oils**
   Contract with King Abdulaziz City for Science and Technology, Atomic Energy Research Institute, Saudi Arabia

LIST OF VISITORS TO THE INCT IN 2005

1. **Aksenov Nikolay**, Joint Institute for Nuclear Research, Dubna, Russia, *10-14.01*.
2. **Alharbi Hamoud H.**, King Abdulaziz City for Science and Technology, Saudi Arabia, *14-17.08*.
3. **Alshahrani Ahmed Alis**, King Abdulaziz City for Science and Technology, Saudi Arabia, *05.03-04.04*.
4. **Amara Rugia**, Biotechnology Research Center, Libya, *19.11-19.12*.
5. **Azizova Elena**, Navoi Mining and Metallurgical Combinat, Uzbekistan, *11-22.09*.
6. **Babic Dragan**, Vinča Institute of Nuclear Sciences, Belgrade, Serbia and Montenegro, *24-25.02*.
7. **Bahnarel Ion**, Ministry of Health, Republic of Moldova, *24-25.02*.
8. **Banu Juliana**, University "Dunarea de Jos" of Galati, Romania, *05.04-05.07*.
9. **Basfar Ahmed Alia**, King Abdulaziz City for Science and Technology, Saudi Arabia, *09-15.04*.
10. **Bergès Jacqueline**, Rene Descartes University, Pierre and Marie Curie University, Paris, France, *19-25.01*.
11. **Boshnakova Neli**, Sopharma Ltd., Sofia, Bulgaria, *24-25.02*.
12. **Buzdugan Artur**, Centre for Metrology and Automation of Scientific Research, Academy of Sciences of Moldova, Chisinau, Republic of Moldova, *24-25.02*.
13. **Chigrinov Sergey**, Scientific and Technical Center "Sosny", National Academy of Sciences of Belarus, Belarus, *24-25.02*.
14. **Dalivelya Olga**, Institute of Genetics and Cytology, National Academy of Sciences of Belarus, Belarus, *26.07-24.08*.
15. **Dodbiba Andon**, Institute of Nuclear Physics, Tirana, Albania, *24-25.02*.
16. **Enache Mirela**, Institute of Physical Chemistry "I.G. Murgulescu", Romanian Academy, Bucharest, Romania, *14.04-31.12*.
17. **Erizal**, National Nuclear Energy Agency, Indonesia, *15.05-16.08*.
18. **Fuochi P.**, Instituto per la Sintesi Organica e la Fotoreattività – Consiglio Nazionale delle Ricerche (ISOF-CNR), Bologna, Italy, *24-25.02*.
19. **Galan Jose Ignacio Martin**, Electron Service Line (ESERLINE) S.L., Madrid, Spain, *24-25.02*.
20. **Garibov Adil**, Institute of Radiation Problems, Azerbaijan Academy of Sciences, Azerbaijan, *24-25.02*.
21. **Gaurish Y.N.**, Scientific Institute of Nuclear Equipment, St. Petersburg, Russia, *18-22.07*.
22. **Gharbi Foued**, National Center for Nuclear Sciences and Technologies, Tunisia, *30.06-31.07*.
23. **Gryzlov Anatolij**, State Research and Production Corporation TORIJ, Russia, *03-12.02*.
24. **Hartmann Hans** J., c/o Struder AG Werk Hard, Switzerland, *24-25.02*.
25. **Hasegava Yuko**, Science University of Tokyo, Japan, *10-11.04*.
26. **Houeé-Levin Chantal**, Université Paris-Sud, France, *17-25.01*.
27. **Ionila Maria**, Institute of Nuclear Research, Romania, *24-25.02*.
28. **Jovanovic Slobodan**, University of Montenegro, Serbia and Montenegro, *24-25.02*.
29. **Kasztovszky Zsolt**, Institute of Isotope and Surface Chemistry, Budapest, Hungary, *02-07.11*.
30. **Knyazev Mikhail**, St. Petersburg Instruments Ltd., Russia, *19-23.04*.
31. **Kovacs Andras**, Institute of Isotope and Surface Chemistry, Budapest, Hungary, *24-25.02*.
32. **Kunnummal Noushaud**, Saudi Arabian Oil Company, Saudi Arabia, *03-09.04*.
33. **Lazurik Vladymyr**, Kharkiv National University, Ukraine, *21-25.02*.
34. **Lyssukhin Sergey**, National Nuclear Centre of the Republic of Kazakhstan, Kazakhstan, *24-25.02*.
35. **Miljević Nada**, Vinča Institute of Nuclear Sciences, Belgrade, Serbia and Montenegro, *03.05-03.08*.

36. **Miller Arne**, Risoe National Laboratory, Denmark, *24-25.02*.
37. **Mozziconazzi Oliver**, France, *01.01-31.12*.
38. **Nedealcov Semion**, Republican Center of Applies of Soil Science, Chisinau, Republic of Moldova, *09-16.10*.
39. **Nichipor Henrietta**, Institute of Radiation Physical-Chemical Problems, National Academy of Sciences of Belarus, Minsk, Belarus, *10-25.11*, *13-25.12*.
40. **Norseev Jurij**, Joint Institute for Nuclear Research, Dubna, Russia, *10.05-10.06*, *27.10-26.11*.
41. **Okyar Halil Burcin**, Turkish Atomic Energy Authority (TAEK), Ankara, Turkey, *24-25.02*.
42. **Orelovitch Oleg**, Joint Institute for Nuclear Research, Dubna, Russia, *04-23.06*.
43. **Othman Mohd Nahar**, Malaysian Institute for Nuclear Technology Research (MINT), Malaysia, *27.08-02.09*.
44. **Persson Ingmar,** Swedish University of Agricultural Science, Uppsala, Sweden, *17-18.10*.
45. **Pietzsch Hans Jungen**, Institute of Bioinorganic and Radiopharmaceutical Chemistry, Forschungszentrum Rossendorf e.V., Germany, *05-09.11*.
46. **Placek Vit**, Nuclear Research Institute, Řež, Czech Republic, *24-25.02*.
47. **Politovskij Fiodor**, State Research and Production Corporation TORIJ, Moscow, Russia, *03-12.02*.
48. **Ponta Corneliu Catalin**, National Institute of Research and Development for Physics and Nuclear Engineering "Horia Hulubei", Bucharest, Romania, *24-25.02*.
49. **Popov Gennadiy**, Kharkiv State University, Ukraine, *24-25.02*, *06-09.06*.
50. **Sahafipour Fard Mohammad Hassan**, Teheran Nuclear Research Center, Iran, *31.07-01.12*.
51. **Savina Natalya**, Institute of Genetics and Cytology, National Academy of Sciences of Belarus, Belarus, *26.07-24.08*.
52. **Shinkarev Sergey**, Institute of Biophysics, State Research Center of Russia, Russia, *24-25.02*.
53. **Shishin Sergey**, Joint Institute for Nuclear Research, Dubna, Russia, *10-14.01*.
54. **Spies Hartmunt**, Institute of Bioinorganic and Radiopharmaceutical Chemistry, Forschungszentrum Rossendorf e.V., Germany, *01-11.11*.
55. **Stefanova Maja**, Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria, *01.03-31.05*.
56. **Taroyan Sargis**, Yerevan Physics Institute, Yerevan, Armenia, *24-25.02*.
57. **Tran Thac An**, Research and Development Center for Radiation Technology, Vietnam, *09-10.11*.
58. **Tsrunchev Tsvetelin**, National Centre of Radiobiology and Radiation Protection, Sofia, Bulgaria, *24-25.02*.
59. **Usaćov Aleksiej**, State Research and Production Corporation TORIJ, Moscow, Russia, *03-12.02*.
60. **Villaneal Angela**, Electron Service Line (ESERLINE) S.L., Madrid, Spain, *24-25.02*.
61. **Zyball Z.**, BGS Geta Gamma Service GmbH+Co. KG, Wiehl, Germany, *24-25.02*.

THE INCT SEMINARS IN 2005

1. Anna Bojanowska-Czajka, M.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
   Analityczne badania przebiegu procesów rozkładu wybranych pestycydów przy użyciu promieniowania jonizującego prowadzonych na potrzeby ochrony środowiska (Analytical control of decomposition of selected pesticides using gamma irradiation for environmental protection)
2. Dr. Małgorzata Derda (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
   Przygotowywanie próbek stałych do bezpośredniej analizy EA-MS (Solid samples preparation for on-line EA-MS analysis)
3. Dr. Nada Miljević (Vinča Institute of Nuclear Sciences, Belgrade, Serbia and Montenegro)
   Environmental isotope investigation of the river catchments
4. Dr. Halina Polkowska-Motrenko (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
   Organizacja badań biegłości i przygotowanie materiałów atestowanych (Training course on organization of proficiency tests and preparation of reference materials)
5. Marek Pruszyński, M.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
   Kompleksy ^{211}At jako prekursory radiofarmaceutyków (Complexes of ^{211}At as precursors of radiopharmaceuticals)
6. Dr. Maya Stefanova (Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria)
   Biologic and anthropogenic markers in Bulgarian neogene coals and their combustion wastes
7. Prof. Juan Eduardo Vargas (University of South Caroline; Academic Relations Manager for Microsoft, USA)
   Recent trends on sensors and sensor networks at Microsoft
8. Robert Zimnicki, M.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
   Próba zastosowania uproszczonych modeli matematycznych w celu przewidywania składu chemicznego i kompozycji izotopowej wód podziemnych w rejonach narażonych na działalność przemysłową (An attempt of applying simplified mathematical models in the purpose to predict chemical and isotopic composition of underground waters in areas exposed to industrial activity)

LECTURES AND SEMINARS DELIVERED OUT OF THE INCT IN 2005

LECTURES

1. **Brzozowska K.**
   Influence of temperature on radiation-induced micronuclei in human peripheral blood lymphocytes.
   Third International Summer Student School "Nuclear Physics Methods and Accelerators in Biology and Medicine", Dubna, Russia, 29.06-12.07.2005.
2. **Chmielewski A.G.**
   Electron beam irradiators.
   Regional (AFRA) IAEA Training Course on General Process Control, QC/QA, Radiation Dosimetry, Safety Procedures and New Engineering Developments in Industrial Irradiators, Cairo, Egypt, 15-18.05.2005.
3. **Chmielewski A.G.**
   Gamma irradiators.
   Regional (AFRA) IAEA Training Course on General Process Control, QC/QA, Radiation Dosimetry, Safety Procedures and New Engineering Developments in Industrial Irradiators, Cairo, Egypt, 15-18.05.2005.
4. **Chmielewski A.G.**
   Radiation sterilization centres worldwide.
   Regional (AFRA) IAEA Training Course on General Process Control, QC/QA, Radiation Dosimetry, Safety Procedures and New Engineering Developments in Industrial Irradiators, Cairo, Egypt, 15-18.05.2005.
5. **Chmielewski A.G.**
   Strategy for AFRA program on radiation technology implementation.
   Regional (AFRA) IAEA Training Course on General Process Control, QC/QA, Radiation Dosimetry, Safety Procedures and New Engineering Developments in Industrial Irradiators, Cairo, Egypt, 15-18.05.2005.
6. **Chmielewski A.G.**
   Metody jądrowe w ochronie środowiska (Nuclear technologies in environment protection).
   Jubileuszowe Sumpozjum „Atomistyka w XXI wieku", Warszawa, Poland, 16.06.2005.
7. **Chmielewski A.G.**
   Electron beam systems.
   European School of Advanced Studies – Nuclear and Ionizing Radiation Technology, Pavia, Italy, 20.06.2005.
8. **Chmielewski A.G.**
   Flue gas treatment by electron beam.
   European School of Advanced Studies – Nuclear and Ionizing Radiation Technology, Pavia, Italy, 20.06.2005.
9. **Chmielewski A.G.**
   Gamma irradiators.
   European School of Advanced Studies – Nuclear and Ionizing Radiation Technology, Pavia, Italy, 20.06.2005.
10. **Chmielewski A.G.**
    Environmental applications of radiation.
    Round Table "Sustainable development and radiation: possible alliance", Bologna, Italy, 21.06.2005.
11. **Chmielewski A.G.**
    Electron beam flue gas treatment – basics.
    IAEA/RCA Regional Training Course on Clean Water and Air (Radiation Processing Advanced Processes for Air, Water and Soil Pollution Control), Beijing, China, 27.06.-01.07.2005.

12. **Chmielewski A.G.**

    IAEA programs in the field of radiation technology application for environment protection.

    IAEA/RCA Regional Training Course on Clean Water and Air (Radiation Processing Advanced Processes for Air, Water and Soil Pollution Control), Beijing, China, 27.06.-01.07.2005.

13. **Chmielewski A.G.**

    Pilot and industrial plants for EBFGT worldwide.

    IAEA/RCA Regional Training Course on Clean Water and Air (Radiation Processing Advanced Processes for Air, Water and Soil Pollution Control), Beijing, China, 27.06.-01.07.2005.

14. **Chmielewski A.G.**

    The economic aspects of EBFGT.

    IAEA/RCA Regional Training Course on Clean Water and Air (Radiation Processing Advanced Processes for Air, Water and Soil Pollution Control), Beijing, China, 27.06.-01.07.2005.

15. **Chmielewski A.G.**

    Worldwide situation regarding air pollution.

    IAEA/RCA Regional Training Course on Clean Water and Air (Radiation Processing Advanced Processes for Air, Water and Soil Pollution Control), Beijing, China, 27.06.-01.07.2005.

16. **Chmielewski A.G.**

    Radiation technologies for environment protection.

    International Nuclear Atlantic Conference, Santos, Brazil, 28.08.-02.09.2005.

17. **Chmielewski A.G.**

    Electron beam flue gas treatment.

    First Symposium on Nuclear Sciences and Technology (ISTN-2005), Hammanet, Tunisia, 08-10.12.2005.

18. **Machaj B.**

    Film Dose Reader CD-02.

    First Planning and Coordinating Meeting in the frame of Technical Cooperation Project RER/8/010/ “Quality control methods and procedures for radiation technology”, Warszawa, Poland, 21-25.02.2005.

19. **Pszonicki L.**

    Opis statystyczny – obraz rzeczywisty czy odbicie w krzywym zwierciadle? (Statistical description – real image or reflection in distorting mirror?)

    IX Konwersatorium Spektrometrii Atomowej, Ustroń, Poland, 19-21.09.2005.

20. **Sun Y.**

    Conventional analytical techniques for halogenated organic pollutants analysis.

    Consultant’s Meeting on Nuclear Analytical Techniques for Determination of Halogenated Organic Pollutants, Vienna, Austria, 20-23.09.2005.

21. **Wójcik A.**

    Dozymetria biologiczna w wypadkach radiacyjnych (Biological dosimetry in radiation accidents).

    Konferencja naukowa „Nukleonika na początku XXI wieku”, Warszawa, Poland, 16.04.2005.

22. **Wójcik A.**

    Badania osobniczej promieniowrażliwości pacjentów poddawanych radioterapii (Investigations of the individual radiosensitivity of patients subjected to radiotherapy).

    Seminarium poświęcone pamięci profesora Sławomira Chojnackiego „Fizyka w medycynie”, Kielce, Poland, 06-07.05.2005.

23. **Wójcik A.**

    Biological basis of radiotherapy.

    Third International Summer Student School “Nuclear Physics Methods and Accelerators in Biology and Medicine”, Dubna, Russia, 02-06.07.2005.

24. **Wójcik A.**

    Model liniowo-kwadratowy – spojrzenie radiobiologa (The linear-quadratic model – the perspective of a radiobiologist).

    Szkoła Radioterapii, Kielce, Poland, 19-22.09.2005.

25. **Wójcik A.**

    Promieniowrażliwość komórek – podstawy radiobiologiczne radioterapii (Radiosensitivity of cells – radiobiological basis of radiotherapy).

    Szkoła Radioterapii, Kielce, Poland, 19-22.09.2005.

26. **Wójcik A.**
    Cytogenetic damage in lymphocytes of patients exposed to radiation for the purpose of diagnosis or treatment.
    III International Conference "Genetic consequences of extremal radiation situations", Dubna, Russia, 04-07.10.2005.

SEMINARS

1. **Andrzej G. Chmielewski**
   Recent developments in radiation processing.
   Research Institute for Food Industry (IIIA), Havana, Cuba, 31.01.2005.
2. **Andrzej G. Chmielewski**
   Recent developments in radiation processing.
   National Centre for Plant and Animal Health (CENSA), Havana, Cuba, 01.02.2005.
3. **Andrzej G. Chmielewski**
   Recent developments in radiation processing.
   Centre for Technological Applications and Nuclear Development (CEADEN), Havana, Cuba, 01.02.2005.
4. **Andrzej G. Chmielewski**
   Recent developments in radiation processing.
   Institute of Nuclear Energy and Research – IPEN, São Paulo, Brazil, 04.02.2005.
5. **Andrzej G. Chmielewski**
   Recent developments in radiation processing.
   Comisión Nacional de Energía Atómica – CNEA, Buenos Aires, Argentina, 07.02.2005.
6. **Andrzej G. Chmielewski**
   Recent progress in the radiation technology.
   Vietnam Atomic Energy Commission, Hanoi, Vietnam, 14.02.2005.
7. **Andrzej G. Chmielewski**
   Present status of the radiation processing technology (in Russian).
   Academy of Sciences of Moldova, Kishinev, Moldova, 03.05.2005.
8. **Andrzej G. Chmielewski**
   Commercial application of radiation processing.
   Industrial Technology Institute (ITI), Colombo, Sri Lanka, 27.07.2005.
9. **Marian Harasimowicz**
   Membrane separation of gaseous mixtures: A summary of work performed at INCT.
   Complutense University of Madrid, Spain, 28.09.2005.
10. **Iwona Kałuska**
    Dozymetria procesów radiacyjnych (Dosimetry of radiation processing).
    Poznań University of Medical Sciences, Poland, 18.01.2005.
11. **Iwona Kałuska**
    Dozymetria procesów radiacyjnych (Dosimetry of radiation processing).
    Poznań University of Medical Sciences, Poland, 29.11.2005.
12. **Iwona Kałuska**
    Zastosowanie promieniowania jonizującego w technologii żywności (Use of ionizing radiation in food processing).
    Warsaw Agricultural University, Poland, 01.12.2005.
13. **Marcin Kruszewski**
    Rola puli labilnego żelaza w powstawaniu uszkodzeń DNA i odpowiedzi na stres tlenowy (Role of labile iron pool in induction of DNA damage and cellular response to oxidative stress).
    Warsaw University, Poland, 21.03.2005.

14. **Halina Polkowska-Motrenko**
Organizacja i prowadzenie testów biegłości (Conducting of proficiency testing schemes).
Klub Polskich Laboratoriów Badawczych POLLAB, Warszawa, Poland, 03.06.2005.

15. **Halina Polkowska-Motrenko**
Przygotowanie i certyfikacja materiałów odniesienia (Preparation and certification of reference materials)
Warsaw University, Poland, 04.12.2005.

16. **Halina Polkowska-Motrenko**
Testy biegłości przeprowadzone przez Sekcję Laboratoriów Chemicznych POLLAB w roku 2005 (Proficiency tests coordinated by POLLAB in 2005).
Klub Polskich Laboratoriów Badawczych POLLAB, Warszawa, Poland, 06.12.2005.

17. **Andrzej Wójcik**
Cytogenetic markers of individual radiosensitivity.
Institute of Radiation Protection and Nuclear Safety – IRSN, Fontenay-aux-Roses, France, 11.01.2005.

18. **Andrzej Wójcik**
Historia radioterapii (History of radiotherapy)
Holycross Cancer Center, Kielce, Poland, 08.03.2005.

19. **Andrzej Wójcik**
Mechanizmy powstawania wymian chromatyd siostrzanych (Mechanism of sister chromatid exchange induction).
Warsaw University, Poland, 14.03.2005.

20. **Andrzej Wójcik**
Rad, radon i zdrowie (Radium, radon and health).
Katolicki Zespół Edukacyjny im. ks. Piotra Skargi, Warszawa, Poland, 18.03.2005.

21. **Andrzej Wójcik**
Genetic basis of the immune system.
Universita degli Studi della Tuscia, Viterbo, Italy, 26.06.2005.

22. **Andrzej Wójcik**
Genetic basis of the immune system.
Universita degli Studi della Tuscia, Viterbo, Italy, 27.06.2005.

23. **Andrzej Wójcik**
Wpływ promieniowania jonizującego na człowieka (The effect of ionising radiation on human organism).
Polskie Sieci Energetyczne, Warszawa, Poland, 08.11.2005.

AWARDS IN 2005

1. Method for obtaining hollow spherical particles from ceramic and metallic materials reduced by hydrogen

   A. Deptuła, A.G. Chmielewski, W. Łada, T. Olczak

   Gold medal at the VIII Moscow International Salon of Industrial Property ARCHIMEDES-2005, Moscow, Russia, 15-18.03.2005

2. Method for obtaining calcium phosphate layers, especially hydroxyapatite

   A. Deptuła, W. Łada, T. Olczak, R.Z. LeGeros, J.P. LeGeros

   Bronze medal at the 33rd International Exhibition of Inventions, New Techniques and Products of Geneva, Switzerland, 06-10.04.2005

3. Catalytic cracking of polyolefine wastes into liquid fuels

   B. Tymiński, K. Zwoliński, A.G. Chmielewski, R. Jurczyk

   Gold medal with a distinction at the 54th World Exhibition of Innovation, Research and New Technologies "BRUSSELS EUREKA 2005", Belgium, 16-20.11.2005 and the Cup of the Polish Minister of Economy

4. Dr. J. Fijałkowski's prize for investigations in the field of spectral atomic analysis conferred by the Commission of Analytical Atomic Spectrometry, the Committee of Analytical Chemistry, Polish Academy of Sciences

   Leon Pszonicki

5. First degree group award of Director of the Institute of Nuclear Chemistry and Technology for a series of papers concerning radiation and photochemically induced radical processes in thioether compounds

   Krzysztof Bobrowski, Dariusz Pogocki, Grażyna Strzelczak, Paweł Wiśniowski, Anna Korzeniowska-Sobczuk

6. Second degree group award of Director of the Institute of Nuclear Chemistry and Technology for the contribution to a series of papers concerning fundamental studies and relativistic effects and their influence on cations of the heavy elements of the sixth period

   Aleksander Bilewicz, Krzysztof Łyczko

7. Third degree individual award of Director of the Institute of Nuclear Chemistry and Technology for the contribution to a series of papers concerning the application of inelastic scattering of thermal neutrons as well as Raman spectroscopy and infrared methods for studying the structure of organic charge transfer (CT) compounds

   Andrzej Pawlukojć

INSTRUMENTAL LABORATORIES AND TECHNOLOGICAL PILOT PLANTS

I. DEPARTMENT OF NUCLEAR METHODS OF MATERIALS ENGINEERING

1. Laboratory of Materials Research

Activity profile: Studies of the structure and properties of materials and historical art objects. Modification of surface properties of materials by means of intense plasma pulses and ions beams. Synthesis and studies of new type of materials with predetermined properties (biocidal, fungicidal, sorptional). Characterization of structural properties of materials using SEM (scanning electron microscopy), X-ray fiffraction (powder and single crystal). Determination of elemental content of environmental and geological samples, industrial waste materials, historic glass objects and other materials by energy dispersive X-ray fluorescence spectrometry using a radioisotope excitation source as well as a low power X-ray tube and using a 2 kW X-ray tube in total reflection geometry. Determination of radioactive isotope content in environmental samples and historical glass objects by gamma spectrometry.

- Scanning electron microscope

DSM 942, LEO-Zeiss (Germany)

Technical data: spatial resolution – 4 nm at 30 kV, and 25 nm at 1 kV; acceleration voltage – up to 30 kV; chamber capacity – 250x150 mm.

Application: SEM observation of various materials such as metals, polymers, ceramics and glasses. Determination of characteristic parameters such as molecule and grain size.

- Scanning electron microscope equipped with the attachment for fluorescent microanalysis

BS-340 and NL-2001, TESLA (Czech Republic)

Application: Observation of surface morphology and elemental analysis of various materials.

- Vacuum evaporator

JEE-4X, JEOL (Japan)

Application: Preparation of thin film coatings of metals or carbon.

- Gamma radiation spectrometer

HP-Ge, model GS 6020; Canberra-Packard (USA)

Technical data: detection efficiency for gamma radiation – 60.2%, polarization voltage – 4000 V, energy resolution (for Co-60) – 1.9 keV, analytical program “GENIE 2000”.

Application: Neutron activation analysis, measurements of natural radiation of materials.

- Gamma spectrometer in low-background laboratory

EGG ORTEC

Technical data: HPGe detector with passive shield; FWHM – 1.9 keV at 1333 keV, relative efficiency – 92%.

- Total reflection X-ray spectrometer

Pico TAX, Institute for Environmental Technologies (Berlin, Germany)

Technical data: Mo X-ray tube, 2000 W; Si(Li) detector with FHWM 180 eV for 5.9 keV line; analysed elements – from sulphur to uranium; detection limits – 10 ppb for optimal range of analysed elements, 100 ppb for the others.

Application: XRF analysis in total reflection geometry. Analysis of minor elements in water (tap, river, waste and rain water); analysis of soil, metals, raw materials, fly ash, pigments, biological samples.

- X-ray spectrometer

SLP-10180-S, ORTEC (USA)

Technical data: FWHM – 175 eV for 5.9 keV line, diameter of active part – 10 mm, thickness of active part of detector – 5.67 mm.

Application: X-ray fluorescence analysis.

- Coulter Porometer II

Coulter Electronics Ltd (Great Britain)

Application: Pore size analysis in porous media.

- Vacuum chamber for plasma research

POLVAC Technika Próżniowa

Technical data: dimensions – 300x300 mm; high voltage and current connectors, diagnostic windows.
Application: Studies on plasma discharge influence on physicochemical surface properties of polymer films, particularly TEM (track-etched membranes).

2. Laboratory of Diffractional Structural Research

Activity profile: X-ray diffraction structural studies on metal-organic compounds originating as degradation products of substances naturally occurring in the environment. Röntgenostructural phase analysis of materials. Studies on interactions in a penetrant-polymer membrane system using small angle scattering of X-rays, synchrotron and neutron radiation. Studies of structural changes occurring in natural and synthetic polymers under influence of ionising radiation applying X-ray diffraction and differential scanning calorimetry.

- KM-4 X-ray diffractometer
KUMA DIFFRACTION (Poland)
Application: 4-cycle diffractometer for monocrystal studies.

- CRYOJET - Liquid Nitrogen Cooling System
Oxford Instruments
Application: Liquid nitrogen cooling system for KM-4 single crystal diffractometer.

- HZG4 X-ray diffractometer
Freiberger Präzisionsmechanik (Germany)
Application: Powder diffractometers for studies of polycrystalline, semicrystalline and amorphous materials.

- URD 6 X-ray diffractometer
Freiberger Präzisionsmechanik (Germany)
Application: Powder diffractometers for studies of polycrystalline, semicrystalline and amorphous materials.

3. Sol-Gel Laboratory of Modern Materials

Activity profile: The research and production of advanced ceramic materials in the shape of powders, monoliths, fibres and coatings by classic sol-gel methods with modifications – IChTJ Process or by CSGP (Complex Sol-Gel Method) are conducted. Materials obtained by this method are the following powders: alumina and its homogeneous mixtures with Cr_2O_3, TiO_3, Fe_2O_3, $MgO+Y_2O_3$, MoO_3, Fe, Mo, Ni and CaO, CeO_2, Y_2O_3 stabilized zirconia, β and β" aluminas, ferrites, $SrZrO_3$, ceramic superconductors, type YBCO (phases 123, 124), BSCCO (phases 2212, 2223), $NdBa_2Cu_3O_x$, their nanocomposites, Li-Ni-Co-O spinels as cathodic materials for Li rechargeable batteries and fuel cells MCFC, $BaTiO_3$, $LiPO_4$, Li titanates: spherical for fusion technology, irregularly shaped as superconductors and cathodic materials, Pt/WO_3 catalyst. Many of the mentioned above systems, as well as sensors, type SnO_2, were prepared as coatings on metallic substrates. Bioceramic materials based on calcium phosphates (*e.g.* hydroxyapatite) were synthesized in the form of powders, monoliths and fibres.

- DTA and TGA thermal analyser
OD-102 Paulik-Paulik-Erdey, MOM (Hungary)
Technical data: balance fundamental sensitivity – 20-0.2 mg/100 scale divisions, weight range – 0-9.990 g, galvanometer sensitivity – $1x10^{-10}$ A/mm/m, maximum temperature – 1050°C.
Application: Thermogravimetric studies of materials up to 1050°C.

- DTA and TGA thermal analyser 1500
MOM (Hungary)
Technical data: temperature range – 20-1500°C; power requirements – 220 V, 50 Hz.
Application: Thermal analysis of solids in the temperature range 20-1500°C.

- Research general-purpose microscope
Carl Zeiss Jena (Germany)
Technical data: General purpose microscope, magnification from 25 to 2500 times, illumination of sample from top or bottom side.

- Metallographic microscope
EPITYP-2, Carl-Zeiss Jena (Germany)
Technical data: magnification from 40 to 1250 times.
Application: Metallographic microscope for studies in polarized light illumination and hardness measurements.

- Laboratory furnace
CSF 12/13, CARBOLITE (Great Britain)
Application: Temperature treatment of samples in controlled atmosphere up to 1500°C with automatic adjustment of final temperature, heating and cooling rate.

II. DEPARTMENT OF RADIOISOTOPE INSTRUMENTS AND METHODS

Laboratory of Industrial Radiometry

Activity profile: Research and development of non-destructive methods and measuring instruments utilizing physical phenomena connected with the interaction of radiation with matter: development of new methods and industrial instruments for measurement of physical quantities and analysis of chemical composition; development of measuring instruments for environmental protection (dust monitors, radon meters); implementation of new methods of calibration and signal processing (multivariate models, artificial neural networks); designing, construction and manufacturing of measuring instruments and systems; testing of industrial and laboratory instruments.

- Multichannel analyser board with software for X and γ-ray spectrometry

Canberra

- Function generator

FG-513, American Reliace INC

III. DEPARTMENT OF RADIOCHEMISTRY

1. Laboratory of Coordination and Radiopharmaceutical Chemistry

Activity profile: Preparation of novel complexes, potential radiopharmaceuticals, *e.g.* derivatives of tricarbonyltechnetium(I) (^{99m}Tc) with chelating ligands mono- and bifunctional. Studying of their hydrophilic-lipophilic properties, structure and their interactions with peptides. Also rhenium(VI) complexes with dendrimeric ligands are synthesised and studied. Novel platinum and palladium complexes with organic ligands, analogs of *cis*platin, are synthesised and studied as potential antitumor agents. Solvent extraction separation of trivalent actinides from lanthanides is studied, directed towards nuclear waste treatment. Studies in the field of isotope chemistry of middle and heavy elements in order to find correlations between isotope separation factor and the structure of species which exchange isotopes in chemical systems, as well as to select the methods suitable for isotope enrichment. (For the research equipment, common for both Laboratories, see below.)

2. Laboratory of Heavy Elements

Activity profile: Synthesis and studies of the structure of heavy p-block elements in the solid state and in solution. Elaboration of new methods for binding of ^{211}At, ^{47}Sc and $^{103m/105}$Rh to biomolecules. Elaboration of new medically important radionuclide generators, *e.g.* ^{82}Sr/^{82}Rh, ^{103}Ru/^{103m}Rh, ^{44}Ti/^{44}Sc.

- Spectrometric set

ORTEC
Multichannel analyser, type 7150, semiconductor detector
Application: Measurements and identification of γ- and α-radioactive nuclides.

- Spectrometric set

TUKAN, IPJ (Świerk, Poland)
Multichannel analyser, type SILENA with a PC card type TUKAN
Application: Measurements and identification of γ-radioactive nuclides.

- Gas chromatograph

610, UNICAM (England)
Application: Analysis of the composition of mixtures of organic substances in the gas and liquid state.

- High Performance Liquid Chromatography system

Gradient HPLC pump L-7100, Merck (Germany) with γ-radiation detector, INCT (Poland)
Application: Analytical and preparative separations of radionuclides and/or various chemical forms of radionuclides.

- Capillary electrophoresis system

PrinCE Technologies with a UV-VIS detector (Bischoff Lambda 1010) and a radiometric detector Activity Gauge type Tc-99m (INCT, Poland)
Application: Analytical separation of various radiochemical and chemical species, in particular charged.

- UV-VIS spectrophotometer

DU 68, Beckman (Austria), modernized and computerized
Application: Recording of electronic spectra of metal complexes and organic compounds in solution. Analytical determination of the concentration of these compounds.

- FT-IR spectrophotometer

EQUINOX 55, Bruker (Germany)
Application: Measurements of IR spectra of metal complexes and other species in the solid state and in solution.

IV. DEPARTMENT OF NUCLEAR METHODS OF PROCESS ENGINEERING

1. Laboratory for Flue Gases Analysis

Activity profile: Experimental research connected with elaboration of removal technology for SO_2 and NO_x and other hazardous pollutants from flue gases.

- Ultrasonic generator of aerosols

TYTAN XLG

- Gas chromatograph

Perkin-Elmer (USA)

- Gas analyser LAND

Application: Determination of SO_2, NO_x, O_2, hydrocarbons, and CO_2 concentrations.

- Impactor MARK III

Andersen (USA)
Application: Measurement of aerosol particle diameter and particle diameter distribution.

2. Laboratory of Stable Isotope Ratio Mass Spectrometry

Activity profile: Study of isotope ratios of stable isotopes in hydrogeological, environmental, medical and food samples.

- Mass spectrometer DELTA^{plus}

Finnigan MAT (Bremen, Germany)
Technical data: DELTA^{plus} can perform gas isotope ratio measurements of H/D, $^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{18}O/^{16}O$, $^{34}S/^{32}S$.
Application: For measurements of hydrogen (H/D) and oxygen ($^{18}O/^{16}O$) in water samples with two automatic systems: H/Device and GasBench II. The system is fully computerized and controlled by the software ISODAT operating in multiscan mode (realtime). The H/Device is a preparation system for hydrogen from water and volatile organic compounds determination. Precision of hydrogen isotope ratio determination is about 0.5‰ for water. The GasBench II is a unit for on-line oxygen isotope ratio measurements in water samples by “continuous flow” techniques. With GasBench II, water samples (0.5 ml) can be routinely analyzed with a precision and accuracy of 0.05‰. The total volume of water sample for oxygen and hydrogen determination is about 2 ml.

- Elemental Analyzer Flash 1112 NCS

Thermo Finnigan (Italy)
Application: For measurement of carbon, nitrogen and sulfur contents and their isotope composition in organic matter (foodstuff and environmental samples).

- Gas chromatograph mass spectrometer

GC MS-QP 5050A, GC-17A, Shimadzu (Japan)
Technical data: capillary column – SPB 5, HP-5MS, SUPELCOWAX™-10.

3. Radiotracers Laboratory

Activity profile: Radiotracer research in the field of: environmental protection, hydrology, underground water flow, sewage transport and dispersion in rivers and sea, dynamic characteristics of industrial installations and waste water treatment stations.

- Heavy lead chamber (10 cm Pb wall thickness) for up to $3.7x10^{10}$ Bq (1 Ci) radiotracer activity preparations in liquid or solid forms
- Field radiometers for radioactivity measurements
- Apparatus for liquid sampling
- Turner fluorimeters for dye tracer concentration measurements
- Automatic devices for liquid tracers injection
- Liquid-scintillation counter

Model 1414-003 ”Guardian”, Wallac-Oy (Finland)
Application: Extra low-level measurements of α and β radionuclide concentrations, especially for H-3, Ra-226, Rn-222 in environmental materials, *e.g.* underground waters, surface natural waters; in other liquid samples as waste waters, biological materials, mine waters, *etc*.

4. Membrane Laboratory

Activity profile: Research in the field of application of membranes for radioactive waste processing and separation of isotopes.

- Membrane distillation plant for concentration of solutions

Technical data: output ~0.05 m^3/h, equipped with spiral-wound PTFE module G-4.0-6-7 (SEP GmbH) with heat recovery in two heat-exchangers.

- Multi-stage MD unit (PROATOM) with 4 chambers equipped with flat sheet membranes for studying isotope separations
- US 150 laboratory stand (Alamo Water) for reverse osmosis tests

Technical data: working pressure – up to 15 bar, flow rate – 200 dm^3/h, equipped with two RO modules.

- Laboratory stand with 5 different RP spiral wound modules and ceramic replaceable tubular modules
- Laboratory set-up for small capillary and frame-and-plate microfiltration and ultrafiltration module examination (capillary EuroSep, pore diameter 0.2 µm and frame-and-plate the INCT modules)
- The system for industrial waste water pretreatment

Technical data: pressure – up to 0.3 MPa; equipped with ceramic filters, bed Alamo Water filters with replaceable cartridge (ceramic carbon, polypropylene, porous or fibrous) and frame-and-plate microfiltration module.

- The set-up for chemically agressive solutions (pH 0-14), high-saline solutions (~50 g/l) in the whole pH range, and of radioactive solutions treatment

Technical data: equipped with TONKAFLO high pressure pump, up to 7 MPa, chemically resistant Kiryat Weizmann module (cut-off 400 MW), and high-pressure RO module.

- Gas separation system

V. DEPARTMENT OF RADIATION CHEMISTRY AND TECHNOLOGY

1. Laboratory of Radiation Modified Polymers

Activity profile: Modification of polymers by ionising radiation. Radiation-induced radicals in polymers. Optimization of mechanical and chemical properties of biocompatible materials following electron beam and gamma irradiation, biological application of polymers. Nanocomposites and nanofillers modified by ionising radiation.

- Extruder

PLV-151, BRABENDER-DUISBURG (Germany)

Technical data: Plasti-Corder consists of: driving motor, temperature adjustment panel, thermostat, crusher, mixer, extruder with set of extrusion heads (for foils, rods, sleevs, tubes), cooling tank, pelleting machine, collecting device.

Application: Preparation of polymer samples.

- Equipment for mechanical testing of polymer samples

INSTRON 5565, Instron Co. (England)

Technical data: high performance load frame with computer control device, equipped with Digital Signal Processing and MERLIN testing software; max. load of frame is 5000 N with accuracy below 0.4% in full range; max. speed of testing 1000 mm/min in full range of load; total crosshead travel – 1135 mm; space between column – 420 mm; the environmental chamber 319-409 (internal dimensions 660x230x240 mm; temperature range – from -70 to 250°C).

Application: The unit is designed for testing of polymer materials (extension testing, tension, flexure, peel strength, cyclic test and other with capability to test samples at low and high temperatures).

- Viscosimeter

CAP 2000+H, Brookfield (USA)

Technical data: range of measurements – 0.8-1500 Pa*s, temperature range – 50-235°C, cone rotation speed – 5-1000 rpm, sample volume – 30 µl. Computer controlled *via* Brookfield CALPCALC® software.

Application: Viscosity measurements of liquids and polymer melts.

- Differential scanning calorimeter

MDSC 2920 CE, TA Instruments

Technical data: equipped with liquid nitrogen cooling adapter (LNCA) for 60 l of liquid nitrogen and sample encapsulating press for open or hermetically sealed pans. Module for Modulated DSC™ is included. Working temperature – from -150°C with the LNCA to 725°C.

Application: Determines the temperature and heat flow associated with material phase transitions as a function of time and temperature. It also provides quantitative and qualitative data on endothermic (heat absorption) and exothermic (heat evolution) processes of materials during physical transitions that are caused by phase changes, melting, oxidation, and other heat-related changes.

- Processor tensiometer K100C

Technical data: supplied with the thermostatable sample vessel. Working temperature is from -10 to +100°C. The height of the sampler carrier is adjusted with the help of a high-precision motor. The balance system is automatically calibrated by a built-in reference weight with a high precision. Resolutions of measurement is 0.01 mN/m.

Application: Surface and interfacial tension measurement of liquids – Du Noüy Ring method and Dynamic Wilhelmy method with range 1-1000 mN/m; dynamic contact angle measurements; surface energy calculations on solids, powders, pigments, fibers, *etc.*; sorption measurements with the Washburn method for determining the surface energy of a powder-form solid. Controlled by LabDesk™ software.

- Spectrophotometer UV-VIS

UNICAM SP 1800 with linear recorder UNICAM AR 25

Technical data: Wavelength – 190-850 nm.

- Equipment for gel electrophoresis

System consists of: horizontal electrophoresis apparatus SUBMINI Electrophoresis Mini-System, transilluminator UV STS-20M JENCONS (United Kingdom), centrifuge EBA 12 Hettich/Zentrifugen, microwave oven KOR 8167 Daewoo.

- Melt flow tester

ZWICK 4105, Zwick GmbH (Germany)

Technical data: temperature of measurements – 150, 190 and 230°C; press load – 2.16 and 5.00 kg; manual operating.

Application: Determination of standard values of melt-mass flow rate (MFR) of the thermoplastic materials (polymers) under specified conditions of temperature and load (according to standards: PN-EN ISO 1133:2005, ASTM 1328); comparison of rheological properties of polymers, including filled materials; comparison of degree of degradation; testing of catalogue data.

- Transiluminator UV

STS-20M, JENCONS (United Kingdom)

Technical information: six 15 W bulbs, emitted 312 nm wavelength, which corresponds to the fluorescence excitation maximum of ethidium bromide. Product description: For visualisation of ethidium bromide – stained nucleic acids fluorescence detection systems. Fluorescence intensity is enhanced, while photobleaching and photonicking of stained nucleic acids are reduced.

2. Radiation Sterilization Pilot Plant of Medical Devices and Tissue Grafts

Activity profile: Research and development studies concerning new materials for manufacturing single use medical devices (resistant to radiation up to sterilization doses). Elaboration of monitoring systems and dosimetric systems concerning radiation sterilization processing. Introducing specific procedures based on national and international recommendations of ISO 9000 and PN-EN 552 standards. Sterilization of medical utensils, approx. 70 million pieces per year.

- Electron beam accelerator

UELW-10-10, NPO TORIJ (Moscow, Russia)

Technical data: beam energy – 10 MeV, beam power – 10 kW, supply power – 130 kVA.

Application: Radiation sterilization of medical devices and tissue grafts.

- Spectrophotometer UV-VIS

Model U-1100, Hitachi

Technical data: wavelength range – 200-1100 nm; radiation source – deuterium discharge (D_2) lamp, and tungsten-iodine lamp.

- Spectrophotometer UV-VIS

Model SEMCO S/EC

Technical data: wavelength range – 340-1000 nm, radiation source – halogen lamp.

Application: Only for measurements of dosimetric foils.

- Bacteriological and culture oven with temperature and time control and digital reading

Incudigit 80L

Technical data: maximum temperature – 80°C, homogeneity – ±2%, stability – ±0.25%, thermometer error – ±2%, resolution – 0.1°C.

3. Laboratory of Radiation Microwave Cryotechnique

Activity profile: Radiation processes in solids of catalytic and biological importance: stabilization of cationic metal clusters in zeolites, radical reactions in polycrystalline polypeptides, magnetic properties of transition metals in unusual oxidation states; radical intermediates in heterogeneous catalysis.

- Electron spin resonance X-band spectrometer (ESR)

Bruker ESP-300, equipped with: frequency counter Hewlett-Packard 5342A, continuous flow helium cryostat Oxford Instruments ESR 900, continuous flow nitrogen cryostat Bruker ER 4111VT, ENDOR-TRIPLE unit Bruker ESP-351.

Application: Studies of free radicals, paramagnetic cations, atoms and metal nanoclusters as well as stable paramagnetic centers.

- Spectrophotometer UV-VIS

LAMBDA-9, Perkin-Elmer

Technical data: wavelength range – 185-3200 nm, equipped with 60 nm integrating sphere.

4. Pulse Radiolysis Laboratory

Activity profile: Studies of charge and radical centres transfer processes in thioether model compounds of biological relevance in liquid phase by means of time-resolved techniques (pulse radiolysis and laser flash photolysis) and steady-state γ-radiolysis.

- Accelerator LAE 10 (nanosecond electron linear accelerator)

INCT (Warszawa, Poland)

Technical data: beam power – 0.2 kW, electron energy – 10 MeV, pulse duration – 7-10 ns and about 100 ns, repetition rate – 1, 12.5, 25 Hz and single pulse, pulse current – 0.5-1 A, year of installation 1999.

Application: Research in the field of pulse radiolysis.

- Gas chromatograph

GC-14B, Shimadzu (Japan)

Specifications: two detectors: thermal conductivity detectors (TCD) and flame ionization detector (FID). Column oven enables installation of stainless steel columns, glass columns and capillary columns. Range of temperature settings for column oven: room temperature to 399°C (in 1°C steps), rate of temperature rise varies from 0 to 40°C/min (in 0.1°C steps). Dual injection port unit with two lines for simultaneous installation of two columns.

Application: Multifunctional instrument for analysis of final products formed during radiolysis of sulphur and porphyrin compounds and for analysis of gaseous products of catalytic reactions in zeolites.

- Dionex DX500 chromatograph system

Dionex Corporation

Specifications: The ED40 electrochemical detector provides three major forms of electrochemical detection: conductivity, DC amperometry and integrated and pulsed amperometry. The AD20 absorbance detector is a dual-beam, variable wavelength photometer, full spectral capability is provided by two light sources: a deuterium lamp for UV detection (from 190 nm) and a tungsten lamp for VIS wavelength operation (up to 800 nm). The GP40 gradient pump with a delivery system designed to blend and pump mixtures of up to four different mobile phases at precisely controlled flow rates. The system can be adapted to a wide range of analytical needs by choice of the chromatography columns: AS11 (anion exchange), CS14 (cation exchange) and AS1 (ion exclusion).

Application: The state-of-the-art analytical system for ion chromatography (IC) and high-performance liquid chromatography (HPLC) applications. Analysis of final ionic and light-absorbed products formed during radiolysis of sulphur compounds. The system and data acquisition are controlled by a Pentium 100 PC computer.

- Digital storage oscilloscope

9354AL, LeCroy

Specifications: Bandwidth DC to 500 MHz; sample rate – 500 Ms/s up to 2 Gs/s (by combining 4 channels); acquisition memory – up to 8 Mpt with 2 Mpt per channel; time/div range – 1 ns/div to 1000 s/div; sensitivity – 2 mV/div to 5 V/div; fully variable, fully programmable *via* GPIB and RS-232C.

Application: Digital storage oscilloscope (DSO) with high speed and long memory controls pulse radiolysis system dedicated to the nanosecond electron linear accelerator (LAE 10). The multiple time scales can be generated by a computer from a single kinetic trace originating from DSO since the oscilloscope produces a sufficient number of time points (up to 8 M points record length).

- Digital storage oscilloscope

9304C, LeCroy

Specifications: Bandwidth DC to 200 MHz; sample rate – 100 Ms/s up to 2 Gs/s (by combining 4 channels); acquisition memory – up to 200 kpt per channel; time/div range – 1 ns/div to 1000 s/div; sensitivity – 2 mV/div to 5 V/div; fully variable.

Application: Digital osciloscope (DO) is used in pulse radiolysis system dedicated to the nanosecond electron linear accelerator (LAE 10).

- Nd:YAG laser

Surelite II-10, Continuum (USA)

Specifications: energy (mJ) at 1064 nm (650), 532 nm (300), 355 nm (160) and 266 nm (80); pulse width – 5-7 ns (at 1064 nm) and 4-6 ns (at 532, 355 and 266 nm); energy stability – 2.5-7%; can be operated either locally or remotely through the RS-232 or TTL interface.

Application: A source of excitation in the nanosecond laser flash photolysis system being currently under construction in the Department.

- Potentiostat/Galvanostat VersaStat II

Princeton Applied Research (USA)

Specifications: Power amplifier compliance voltage single channel – ±20 V, maximum current – ±200 mA, rise time – 100 µs, slew rate – 1 V/µs; system performance: minimum timebase – 100 µs, minimum potential step – 250 µV, noise and ripple <50 µV rms typically, minimum current range – 1 µA (hardware), minimum current range – 100 nA (software), minimum current resolution – 200 pA, drift – *vs*. time <50 µV/°C *vs*. time: <200 µV/week. iR compensation: current interrupt 12-bit potential error correction total int. time <50-2000 µs. Accuracy: applied potential – 0.2% of reading ±2 mV, applied current – 0.2% of full-scale current. Computer interface: GPIB IEEE-488, RS-232. Differential electrometer: input bias current <50 pA at 25°C, typically <20 pA at 25°C. Max. voltage range – ±2 V, max. input voltage differential – ±10 V. Bandwidth – -3 dB at>4 MHz. Offset voltage <100 µV. Offset temperature stability <5 µV/°C. Common mode rejection >70 dB at 100 Hz and >60 dB at 100 kHz. Input impedance >1010 Ω, typically 1011 Ω in parallel with <50 pF.

5. Research Accelerator Laboratory

Activity profile: Laboratory is equipped with accelerators providing electron beams which make capable to perform the irradiation of investigated objects within wide range of electron energy from 100 keV to 13 MeV and average beam power from 0.1 W do 20 kW, as well as with Co-60 gamma sources with activity 1.9x10^{10} to 1.3x10^{14} Bq and dose rate from 0.03 to 1.8 kGy/h. The described above irradiators are completed in a unique in world scale set of equipment which can be applied in a wide range of electron beam and gamma-ray research and radiation processing.

- Accelerator ILU-6

INP (Novosibirsk, Russia)
Technical data: beam power – 20 kW, electron energy – 0.7-2 MeV.
Application: Radiation processing.

- Linear electron accelerator

LAE 13/9, Institute of Electro-Physical Equipment (Russia)
Technical data: electron energy – 10-13 MeV; electron beam power – 9 kW.
Application: Radiation processing.

- Cobalt source I

Issledovatel (Russia)
Technical data: 32 sources with an actual activity of 9.2x10^{13} Bq.
Application: Radiation research.

- Cobalt source II

Mineyola 1000, INR (Świerk, Poland)
Technical data: 8 rods with an initial activity of 2.66x10^{13} Bq; the actual activity is 1.07x10^{13} Bq.
Application: Radiation research.

- Electron accelerator

AS-2000 (the Netherlands)
Technical data: energy – 0.1-2 MeV, max. beam current – 100 µA.
Application: Irradiation of materials.

- Spectrometer

DLS-82E, SEMITRAP (Hungary)
Application: Research in radiation physics of semiconductors.

- Argon laser

ILA-120, Carl Zeiss (Jena, Germany)
Application: Measurements of optical properties.

- Spectrometer

DLS-81 (Hungary)
Application: Measurements of semiconductor properties.

- Argon laser

LGN-503 (Russia)
Application: Measurements of optical properties.

VI. DEPARTMENT OF ANALYTICAL CHEMISTRY

1. Laboratory of Spectral Atomic Analysis

Activity profile: atomic absorption and emission spectroscopy, studies on interference mechanisms, interpretation of analytical signals, service analysis.

- Atomic absorption spectrometer

SH-4000, Thermo Jarrell Ash (USA); equipped with a 188 Controlled Furnace Atomizer (CTF 188), Smith-Heftie background correction system and atomic vapor (AVA-440) accessory.
Application: For analyses of samples by flame and furnace AAS.

- Atomic absorption spectrometer

SP9-800, Pye Unicam (England); equipped with SP-9 Furnace Power Supply, PU-9095 data graphics system, PU-9095 video furnace programmer and SP-9 furnace autosampler.
Application: For analyses of samples by flame and furnace AAS.

- Atomic absorption spectrometer

SOLAR M6 MK II (Thermo Electron Corporation), equipped with: graphite furnace GF 95 with D_2 and Zeeman background correction system, autosampler FS 95 and hydride and cold vapour generator.
Application: For analyses of samples by flame and furnace AAS.

2. Laboratory of Neutron Activation Analysis

Activity profile: The sole laboratory in Poland engaged for 40 years in theory and practice of neutron activation analysis in which the following methods are being developed: reactor neutron activation analysis (the unique analytical method of special importance in inorganic trace analysis), radiochemical separation methods, ion chromatography. The laboratory is also the main Polish producer of CRMs and the provider for Proficiency Testing exercises.

- Laminar box

HV mini 3, Holten (Denmark)
Technical data: air flow rate 300 m^3/h.
Application: Protection of analytical samples against contamination.

- Ion chromatograph

2000i/SP, Dionex (USA)
Technical data: data evaluating program AI-450, ion exchange columns of type Dionex Ion Pac, conductivity detector, UV/VIS detector.
Application: Analyses of water solutions, determination of SO_2, SO_3 and NO_x in flue gases and in air, determination of metals in biological and environmental samples.

- HPGe detector, well-type

CGW-3223, Canberra, coupled with analog line (ORTEC) and multichannel gamma-ray analyzer TUKAN
Application: Instrumental and radiochemical activation analysis.

- Coaxial HPGe detector

POP-TOP, ORTEC (USA), coupled with analog line (ORTEC) and multichannel gamma-ray analyzer TUKAN

- HPGe detector, well-type

CGW-5524, Canberra, coupled with multichannel gamma-ray analyzer (hardware and software) Canberra
Application: Instrumental and radiochemical activation analysis.

- Analytical balance

Sartorius BP2 215
Application: For weighing sample of mass >10 mg to 220 g.

- Analytical micro-balance

Sartorius MC5
Application: Preparation of mono- and multi-elemental standards as well as for weighing small mass samples, less than 10 mg.

- Balance

WPX 650, RADWAG (Poland)
Application: For weighing sample of mass >10 mg to 650 g.

- Liquid Scintillation Analyzer

TRI-CARB 2900TR, Packard BioScience Company
Application: α- and β-ray measurements.

- Planetary Ball Mill

PM 100, Retsch
Application: Grinding and mixing: soft, medium hard to extremly hard, brittle or fibrous materials.

- Balance-drier

ADS50, AXIS (Poland)
Application: Determination of mass and humidity of samples.

- Microwave digestion system

Uniclever^{TM}II, PLAZMATRONIKA (Poland)
Application: Microwave digestion of samples.

- Microwave digestion system

BM-1S/II, PLAZMATRONIKA (Poland)
Application: Microwave digestion of samples.

- Homogenizer

INCT (Poland)
Application: Homogenization of the material used for preparation of CRMs.

- Peristaltic pump

REGLO ANALOG MS-4/6-100, ISMATEC (Switzerland)
Application: Regulation of flow of eluents during elution process.

3. Laboratory of Chromatography

Activity profile: Development of HPLC methods for determination of environmental pollutants, application of HPLC and ion-chromatography monitoring of degradation organic pollutants in waters and wastes using ionizing radiation, development of chromatographic methods, preconcentration of organic environmental pollutants, development of chromatographic methods of identification of natural dyes used for ancient textiles.

- Apparatus for biological oxygen demand determination by respirometric method and dissolved oxygen measurement method

WTW-Wissenschaftlich-Technische Wersttätten (Germany)
Application: Analyses of water and waste water samples.

- Apparatus for chemical oxygen demand determination by titrimetric method

Behr Labor-Technik (Germany)
Application: Analyses of water and waste water samples.

- Set-up for solid phase-extraction (vacuum chamber for 12 columns and vacuum pump)

Application: Analyses of water and waste water samples.

- Shimadzu HPLC system consisting of: gradient pump LC-10AT, phase mixer FCV-10AL, diode-array detector SPD-M10A, column thermostat CTO-10AS

Application: Analyses of natural dyes, radiopharmaceuticals, water and waste water samples.

- Laboratory ozone generator

301.19, Erwin Sander Elektroapparatebau GmbH (Uetze-Eltze, Germany)
Application: Ozone production for degradation of pollutants in waste water samples.

4. Laboratory of General Analysis

Activity profile: Preparation and application of new chelating sorbents to the separation of metal traces from environmental materials for their determination by atomic absorption spectrometry, speciation analysis, service analysis.

- Spectrophotometer

PU8625 Series UV/Visible, Philips
Technical data: wavelength range – 200-1100 nm.
Application: Measurements of absorbance in spectrophotometric analysis.

- Spectrophotometer

UV-160, Shimadzu (Japan)
Technical data: wavelength range – 200-1100 nm, with automatic baseline correction and graphic printer.
Application: Routine spectrophotometric analysis and research works.

VII. DEPARTMENT OF RADIOBIOLOGY AND HEALTH PROTECTION

- Equipment for electrophoretic analysis of DNA

CHEF III, BIO-RAD (Austria)
Application: Analysis of DNA fragmentation as a result of damage by various physical and chemical agents.

- Microplate reader

ELISA, ORGANON TEKNICA (Belgium)
Application: For measurement of optical density of solutions in microplates.

- Hybridisation oven

OS-91, BIOMETRA (Germany)
Technical data: work temperatures from 0 to 80°C; exchangeable test tubes for hybridisation.
Application: For polymerase chain reaction (PCR).

- Spectrofluorimeter

RF-5000, Shimadzu (Japan)
Application: For fluorimetric determinations.

- Transilluminator for electrophoretic gels

Biodoc, BIOMETRA (Great Britain)
Application: For analysis of electrophoretic gels.

- Laminar flow cabinet

NU-437-400E, Nu Aire (USA)
Application: For work under sterile conditions.

- Liquid scintillation counter

LS 6000LL, BECKMAN (USA)
Application: For determinations of radioactivity in solutions.

- Research microscope universal

NU, Carl Zeiss Jena (Germany)
Application: For examination of cytological preparations.
Comments: Universal microscope for transmission and reflected light/polarised light. Magnification from 25x to 2500x. Possibility to apply phase contrast.

- Incubator

T-303 GF, ASSAB (Sweden)
Technical data: 220 V, temperature range – 25-75°C.
Application: For cell cultures under 5% carbon dioxide.

- Incubator

NU 5500E/Nu Aire (USA)
Technical data: 220 V, temperature range from 18 to 55°C.
Application: For cell cultures under 0-20% carbon dioxide.

- Laminar flow cabinet

V-4, ASSAB (Sweden)
Application: For work under sterile conditions.

- Image analysis system

Komet 3.1, Kinetic Imaging (Great Britain)
Application: For comet (single cell gel electrophoresis) analysis.

- ISIS 3

Metasystem (Germany)
Application: Microscopic image analysis system for chromosomal aberrations (bright field and fluorescence microscopy).

VIII. LABORATORY FOR DETECTION OF IRRADIATED FOOD

Activity profile: Detection of irradiated food. European standards (CEN) adapted as analytical methods to be routinely used in the Laboratory are based on electron paramagnetic resonance (EPR/ESR) spectroscopy, pulsed photo-stimulated luminescence (PPSL) and thermoluminescence measurements (TL). The research work is focused on the development of these methods as well as on validation and implementation of other detection methods as gas chromatographic determination of volatile hydrocarbons in fats, DNA comet assay (observation of single cells destruction) and statistical germination study. The quality assurance system is adapted in the Laboratory in agreement with the PN-EN 150/IEC 17025:2001 standard and fully documented. Laboratory possesses Accreditation Certificate of Testing Laboratory AB 262 issued by the Polish Centre for Accreditation valid from 25.10.2002 to 25.10.2006.

- Thermoluminescence reader

TL-DA-15 Automated, Risoe National Laboratory (Denmark)
Technical data: turntable for 24 samples, heating range – 50÷500°C, heating speed – 0.5÷10.0°C/s, optical stimulated luminescence (OSL) system.
Application: Detection of irradiated foods containing silicate minerals, *e.g.* spices, vegetables shrimps tc, research work on irradiated foods.

- Fluorescence microscope

OPTIPHOT Model X-2, NIKON (Japan)
Technical data: halogen lamp 12 V-100 W LL; mercury lamp 100 W/102 DH; lenses (objectives) CF E Plan Achromat 4x, CF E Plan Achromat 40x, CF FLUOR 20x.
Application: Detection of irradiated foods by the DNA comet assay method, research work on apoptosis in mammalian cells, biological dosimetry, analysis of DNA damage in mammalian cells.

- Compact EPR spectrometer

EPR 10-MINI, St. Petersburg Instruments Ltd. (Russia)

Technical data: sensitivity – $3x10^{10}$, operating frequency (X band) – 9.0-9.6 GHz, max. microwave power – 80 mW, magnetic field range – 30-500 mT, frequency modulation – 100 kHz.

Application: Detection of irradiated foods, bone and alanine dosimetry, research work on irradiated foods and bone tissues.

- Pulsed photo-stimulated luminescence system

SURRC (United Kingdom)

Technical data: pulsed light source – diodes IR LED; detector – photomultiplier ETL; pulse on and off periods – 15 µs; sample holder – 50 mm diameter disposable Petri dishes; set up – sample chamber and detector head assembly, contol unit, on line computer, optional.

Application: Irradiated food screening system.

IX. EXPERIMENTAL PLANT FOR FOOD IRRADIATION

1. Microbiological Laboratory

Activity profile: optimization of food irradiation process by microbiological analysis.

- Sterilizer

ASUE, SMS (Warszawa, Poland)

Application: Autoclaving of laboratory glass, equipment, and microbiological cultures.

- Fluorescence microscope

BX, Olimpus (Germany)

Application: Quantitative and qualitative microbiological analysis.

2. Experimental Plant for Food Irradiation

Activity profile: Development of new radiation technologies for the preservation and hygienization of food products. Development and standarization of the control system for electron beam processing of food. Development of analytical methods for the detection of irradiated food. Organization of consumer tests with radiation treated food products.

- Accelerator ELEKTRONIKA (10 MeV, 10 kW)

UELW-10-10, NPO TORIJ (Moscow, Russia)

Application: Food irradiation.

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