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GENERAL INFORMATION

Poland decided to start a national nuclear energy programme 55 years ago and the Institute of Nuclear Research (IBJ) was established. Research in nuclear and analytical chemistry, nuclear chemical engineering and technology (including fuel cycle), radiochemistry and radiation chemistry, and radiobiology were carried out mainly in the Chemistry Division, located at Warsaw Żerań, which became the interdisciplinary Institute of Nuclear Chemistry and Technology (INCT) in 1983.

The INCT is Poland's most advanced institution in the fields of radiochemistry, radiation chemistry, nuclear chemical engineering and technology, application of nuclear methods in material engineering and process engineering, radioanalytical techniques, design and production of instruments based on nuclear techniques, environmental research, cellular radiobiology, *etc*. The results of work at the INCT have been implemented in various branches of the national economy, particularly in industry, medicine, environmental protection and agriculture. Basic research is focused on: radiochemistry, chemistry of isotopes, physical chemistry of separation processes, cellular radiobiology, and radiation chemistry, particularly that based on the pulse radiolysis method. With its nine electron accelerators in operation and with the staff experienced in the field of electron beam application, the Institute is one of the most advanced centres of science and technology in this domain. The Institute has four pilot plants equipped with six electron accelerators: for radiation sterilization of medical devices and transplantation grafts; for radiation modification of polymers; for removal of SO_2 and NO_x from flue gases; for food hygiene. The electron beam flue gas treatment in the EPS Pomorzany with the accelerators power over 1 MW is the biggest radiation processing facility ever built.

The Institute trains many of IAEA's Fellows and plays a leading role in agency regional projects. Because of its achievements, the INCT has been nominated the IAEA's Collaborating Centre in Radiation Technology and Industrial Dosimetry.

The INCT has been implementing several projects in the programme "Innovative Economy" POIG, granted on the basis of high evaluation of the Institute's achievements:

- Centre of Radiochemistry and Nuclear Chemistry – meeting the needs of nuclear power and nuclear medicine (completed in August 2012);
- Analysis of thorium usage effects in a power nuclear reactor (coordinated by the Institute of Atomic Energy);
- Analysis of the possibilities of uranium extraction from indigenous resources (in cooperation with the Polish Geological Institute – NRI);
- New generation of intelligent radiometric tools with wireless data transmission;
- Development of a multi-parametric triage approach for an assessment of radiation exposure in a large-scale radiological emergency;
- New generation of electrical wires modified by radiation.

The INCT is the leading institute in Poland regarding the implementation of nuclear energy related EU projects. Its expertise and infrastructure was the basis for participation in FP7-EURATOM grants:

- ACSEPT: Actinide Recycling by Separation and Transmutation;
- ADVANCE: Ageing Diagnostics and Prognostics of Low-voltage I&C Cables;
- IPPA: Implementing Public Participation Approaches in Radioactive Wastes Disposal;
- MULTIBIODOSE: Multidisciplinary Biodosimetric Tools to Manage High Scale Radiological Casualties;
- ASGARD: Advanced Fuels for Generation IV Reactors: Reprocessing and Dissolution;
- RENEB: Realizing the European Network in Biodosimetry;
- NEWLANCER: New MS Linking for an Advanced Cohesion in Euratom Research.

The mission of the INCT is the implementation of nuclear energy for social development, health and environmental protection.

The Institute represents the Polish Government in the Euroatom Fuel Supply Agency, in Fuel Supply Working Group of Global Nuclear Energy Partnership and in Radioactive Waste Management Committee of the Nuclear Energy Agency (Organisation for Economic Co-operation and Development).

The Institute is listed in the cathegory I of scientific institutions based on the evaluation of the Ministry of Science and Higher Education.

The INCT Scientific Council has the rights to grant D.Sc. and Ph.D. degrees in the field of chemistry. The Institute carries out third level studies (doctorate) in the field of nuclear and radiation chemistry and in 2012 one Ph.D. thesis was defended.

In 2012, the INCT scientists published 82 papers in scientific journals registered in the Philadelphia list, among them 53 papers in journals with an impact factor (IF) higher than 1.0. Twenty one chapters in the books were written by the INCT research workers.

Annual awards of the INCT Director-General for the best publications and application achievements in 2012 were granted:

- first degree team award to Zbigniew Samczyński, Rajmund Dybczyński, Halina Polkowska-Motrenko, Ewelina Chajduk, Marta Pyszynska, Krzysztof Kulisa, Paweł Kalbarczyk for the application achievements – elaboration and implementation of the technology of obtaining two certified reference materials for inorganic trace analysis (Oriental Basma Tobacco Leaves – INCT-OBTL-5 and Polish Virginia Tobacco Leaves – INCT-PVTL-6);
- first degree team award to Ewa Gniazdowska, Leon Fuks, Przemysław Koźmiński for a series of seven papers on designing and synthesis of new pharmaceutical receptors – diagnostic and therapeutic;
- second degree team award to Andrzej Pawelec, Sylwia Witman for the application achievements – realization of the project "Studies on the removal of SO_2 and NO_x from the combustion gas formed in diesel shipping engines by means of an electron beam";
- second degree team award to Tomasz Stępkowski, Kamil Brzóska, Marcin Kruszewski for a series of four articles concerning the problems of mammal response to the action of stressful factors, oxidation stress being particularly considered;
- third degree team award to Grażyna Przybytniak, Ewa Kornacka, Andrzej Nowicki, Marta Walo, Leon Fuks for a series of four publications concerning studies on the properties of a selected group of polymers subjected to radiation-induced changes.

The research teams in the INCT were involved in the organization of 17 scientific meetings:

- 10th Meeting of the Ionizing Radiation and Polymers Symposium, IRaP'2012;
- International Symposium on "Free radicals in chemical biology";
- 1st European Nuclear Society-Young Generation Network Core Committee Meeting;
- X Conference on "For the city and environment – problems of waste disposal";
- two meetings concerning PlasTEP (Plasma technologies for environment protection) project;
- four meetings concerning IPPA FP7 EU project;
- three meetings concerning NEWLANCER FP7 EU project;
- Polish-French Meeting on Fuel Cycle;
- Regional Training Course "Validation and process control for electron beam radiation processing" in the frame of project RER 1/011 "Introducing and harmonizing standardized quality control procedures for radiation technologies";
- Scientific Seminar on "Analysis of the possibility of uranium supply from domestic resources";
- Seminar for the participants of postgraduate studies from the Kozminski University "Management of research projects and commercialization of research results. Postgraduate studies for scientists and subjects acting in favour of science".

The INCT also is editor of the scientific journal "Nukleonika" (www.nukleonika.pl) and the scientific-information journal "Postępy Techniki Jądrowej".

MANAGEMENT OF THE INSTITUTE

MANAGING STAFF OF THE INSTITUTE

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  Jacek Palige, Ph.D.
- Laboratory of Material Research
  Wojciech Starosta, Ph.D.
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- Laboratory for Detection of Irradiated Food
  Wacław Stachowicz, Ph.D.
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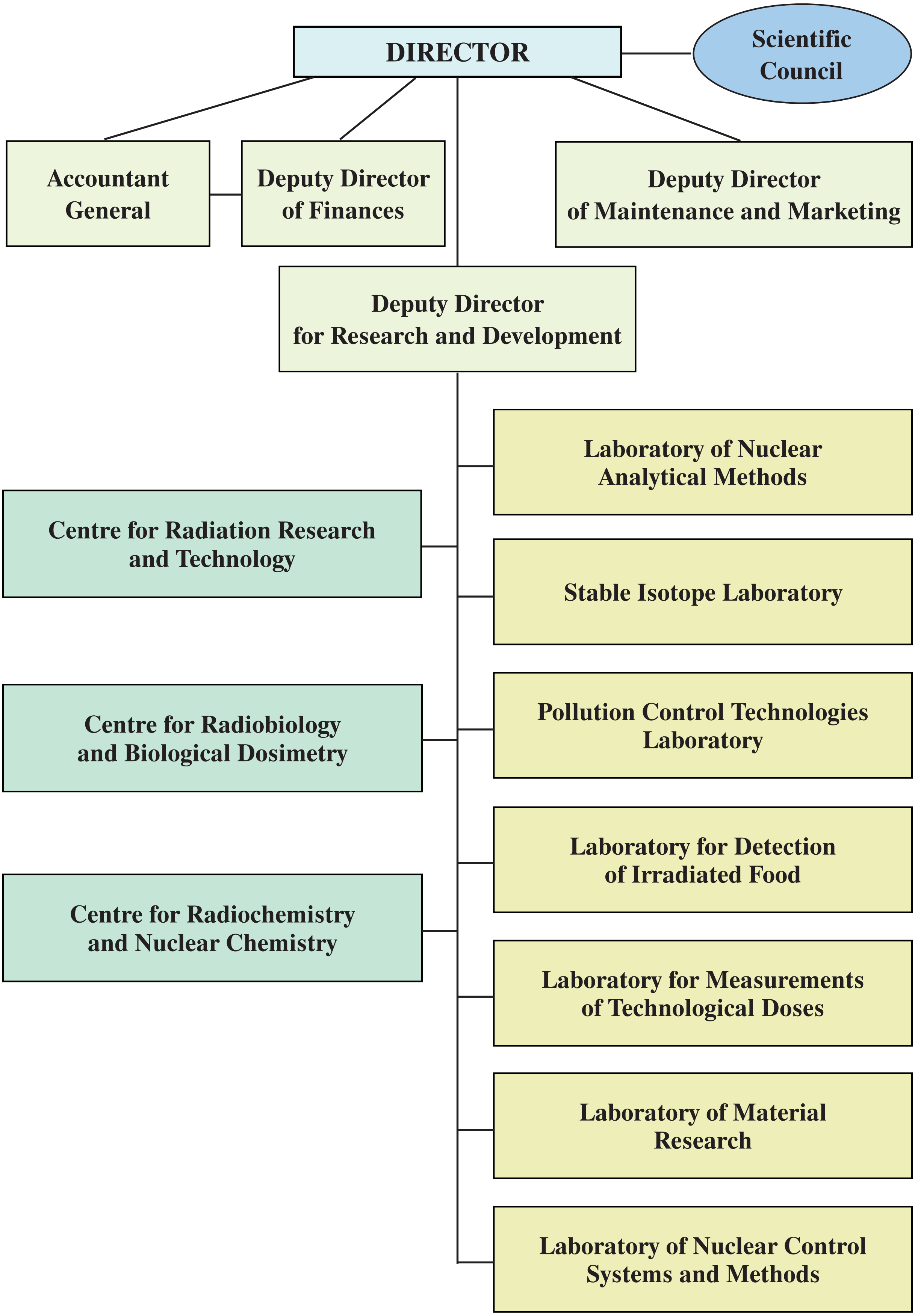

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CENTRE FOR RADIATION RESEARCH AND TECHNOLOGY

Electron beams (EB) offered by the Centre for Radiation Research and Technology located at the Institute of Nuclear Chemistry and Technology (INCT) are dedicated to basic research, R&D and radiation technology applications.

The Centre, in collaboration with the universities from Poland and abroad, apply EB technology for fundamental research on the electron beam-induced chemistry and transformation of materials. Research in the field of radiation chemistry includes studies on the mechanism and kinetics of radiation-induced processes in liquid and solid phases by the pulse radiolysis method. The pulse radiolysis experimental set-up allows direct time-resolved observation of short-lived intermediates (typically within the nanosecond to millisecond time domain), is complemented by steady-state radiolysis, stop-flow absorption spectrofluorimetry and product analysis using chromatographic methods. Studies on radiation-induced intermediates are dedicated to energy and charge transfer processes and radical reactions in model compounds of biological relevance aromatic thioethers, peptides and proteins, as well as observation of atoms, clusters, radicals by electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR), also focused on research problems in nanophase chemistry and radiation-induced cross-linking of selected and/or modified polymers and copolymers.

This research has a wide range of potential applications, including creating more environmentally friendly and sustainable packaging, improving product safety, and modifying material properties. Electron accelerators provide streams of electrons to initiate chemical reactions or break of chemical bonds more efficiently than the existing thermal and chemical approaches, helping to reduce energy consumption and decrease the cost of the process. The Centre may offer currently four electron accelerators for study of the effects of accelerated electrons on a wide range of chemical compounds with a focus on electron beam-induced polymerization, polymer modification and controlled degradation of macromolecules. EB technology has a great potential to promote innovation, including new ways to save energy and reduce the use of hazardous substances as well as to enable more eco-friendly manufacturing processes.

Advanced EB technology offered by the Centre provides a unique platform with the application for: sterilization medical devices, pharmaceutical materials, food products shelf-life extension, polymer advanced materials, air pollution removal technology and others. EB accelerators replace frequently thermal and chemical processes for cleaner, more efficient, lower-cost manufacturing. EB accelerators sterilize products and packaging, improve the performance of plastics and other materials, and eliminate pollution for industries such as pharmaceutical, medical devices, food, and plastics.

The Centre offers EB in the energy range from 0.5 to 10 MeV with an average beam power up to 20 kW and three laboratory-size gamma sources with Co-60. Research activity are supported by such unique laboratory equipment as:
- nanosecond pulse radiolysis and laser photolysis set-ups,
- stop-flow experimental set-up,
- EPR paramagnetic spectroscopy for solid material investigation,
- pilot installation for polymer modification,
- laboratory experimental stand for removal of pollutants from gas phase,
- laboratory of polymer and non-material characterization,
- microbiological laboratory,

- dosimetric laboratory,
- pilot facility for radiation sterilization and food product processing.

The unique technical basis makes it possible to organize a wide internal and international cooperation in the field of radiation chemistry and radiation processing including programmes supported by the European Union and the International Atomic Energy Agency (IAEA). It should be noticed that currently there is no other suitable European experimental basis for study radiation chemistry, physics and radiation processing in a full range of electron energy and beam power.

Since 2010, at the INCT on the basis of the Centre for Radiation Research and Technology, an IAEA Collaborating Centre for Radiation Processing and Industrial Dosimetry is functioning. That is the best example of capability and great potential of concentrated equipment, methods and staff working towards application of innovative radiation technology.

HALIDE RADICALS IN IONIC LIQUIDS. PULSE RADIOLYSIS STUDY

Jan Grodkowski, Rafał Kocia, Jacek Mirkowski, Małgorzata Nyga, Agnieszka Sulich, Tomasz Szreder

During the past decade, the number of study on ionic liquids (ILs) increases exponentially. The disparity between the classical aqueous solution and viscous ionic liquids underscores the importance of initiatives to track changes in the reaction rate and efficiency of radiation between those two systems. One of the ionic liquids applications is in the processing of spent nuclear fuel [1-4] where the unusual properties of ILs provide advantages over standard organic solvents. The low volatility and combustibility, wide liquids range, thermal stability, and enhanced safety against criticality conditions can make the IL-based nuclear fuel cycle reprocessing safer than that based on volatile organic compounds. Due to specific properties of ILs, it is possible to investigate reactions in ways that had not been possible previously. Consequently, there is a real need to understand processes such as ionization, charge transfer and redox reactions in ionic liquids for their successful use. The aim of the study is to understand radical-ion reactions for proper selection of ionic liquids for such application.

We examined the mechanism of formation and kinetic characteristics of iodide (which is a very unpleasant product in nuclear fission) derived radicals, mainly $I_2^{\bullet-}$, in methyltributylammonium N,N-bis(trifluoromethylosulphonyl)imide ($MeBu_3NNTf_2$) and triethylammonium N,N-bis(trifluoromethylosulphonyl)imide (Et_3NHNTf_2). The $I_2^{\bullet-}$ in those ionic liquids has a strong absorption band with a maximum of around 380 nm and a weaker band around 750 nm. We studied the kinetics and spectral characteristic of oxidizing radical anion $I_2^{\bullet-}$ in these solvents. The $I_2^{\bullet-}$ belongs to halide radicals "family" and is a known intermediate in radiation chemistry.

In our research we used ~10 ns pulses of ~10 MeV electrons from a LINAC linear electron with spectrophotometric detection. Energy from the incident electron beam radiation was absorbed in ionic liquids and generated a range of excited states (IL*) and ionizations that eject electrons from the ions of ionic liquid, leaving behind electron vacancies ("holes") [5]. The "holes" react with iodide anion and form radical $I^\bullet$:

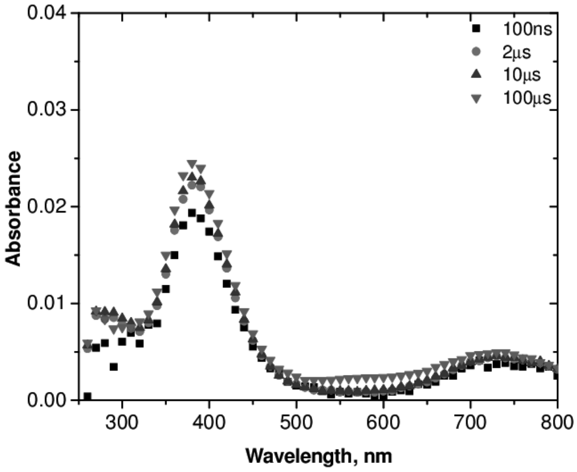

Fig.1. Pulse radiolysis of N_2O-saturated solution of tetrabutylammonium azide (0.06 M) in $MeBu_3NNTf_2$, intermediate absorption spectra: (■) 100 ns, (●) 2 μs, (▲) 10 μs, (▼) 100 μs after the pulse; 20 Gy.

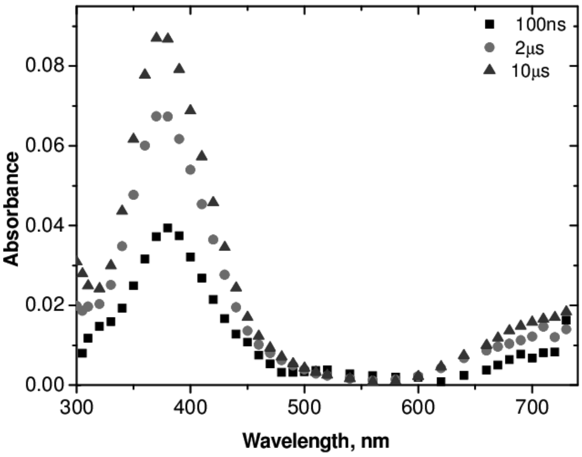

Fig.2. Pulse radiolysis of N_2O-saturated solution of tetrabutylammonium azide (0.06 M) in Et_3NHNTf_2, intermediate absorption spectra: (■) 100 ns, (●) 2 μs, (▲) 10 μs after the pulse; 28 Gy.

$$IL_{\text{"hole"}} + I^- \rightarrow I^\bullet + IL \qquad (1)$$

Then, this radical reacts *via* reaction (2). (The process is already known in I^- solutions in some classical solvents [6].)

$$I^\bullet + I^- \leftrightarrows I_2^{\bullet-} \qquad (2)$$

The calculation of equilibrium constants was based on equation:

$$\frac{1}{G} = \frac{1}{G_0} + \frac{1}{G_0\mathbf{K}} \times \frac{1}{[I^-]} \qquad (3)$$

where G – the radiolytic yield at given I^- concentrations, G_0 – the radiolytic yield at 380 nm extrapolated to infinitely high I^- concentrations, K = $[I_2^{\bullet-}]/[I^\bullet][I^-]$ – the equilibrium constant.

Pulse radiolysis of iodide anion solution in the ionic liquids $MeBu_3NNTf_2$ and Et_3NHNTf_2 leads to the formation of relatively long-lived dimer

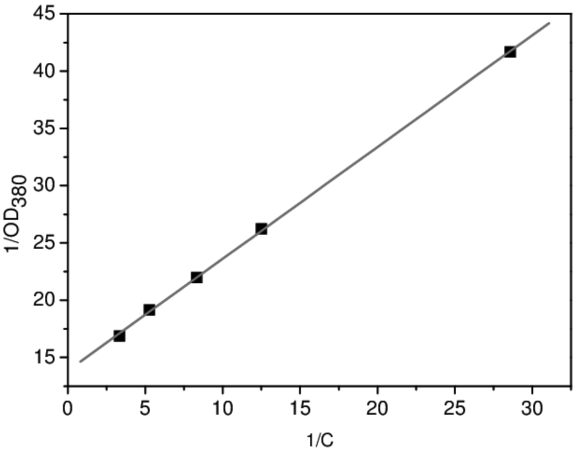

Fig.3. Plot of equilibrium optical densities at 380 nm according to Eq. (3).

radical anions characterized by intermediate absorptions presented in Figs.1 and 2.

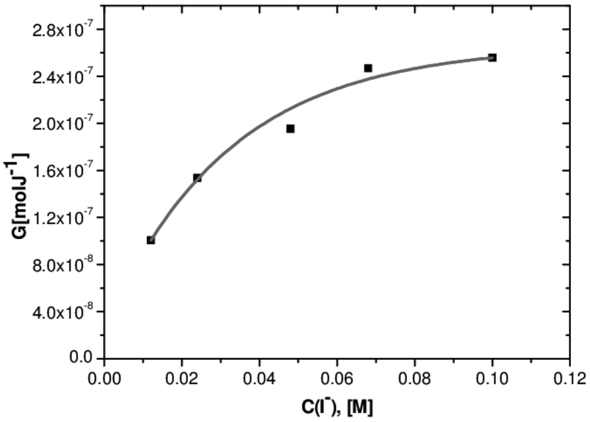

Fig.4. The dependence of $I_2^{\bullet -}$ yields as a function of the I^- concentration.

The intensity of absorption at 380 nm depends on iodide concentration, according to the mentioned Eq. (3). A plot of 1/G against $1/[I^-]$ is a straight line in the $MeBu_3NNTf_2$ solutions, what is consistent with the above analysis. From the slope, we can calculate the equilibrium constant K = 14 in this ionic liquid (Fig.3). Equilibrium constant K, equal to 1.1 x 10^5, was determined previously in water. In protic ionic liquids Et_3NHNTf_2 the situation is more complicated. We did observe the formation of $I_2^{\bullet -}$, but we could not calculate the equilibrium constant of reaction (2). In this protic ionic liquid electron solvated and probably dry reacts with Et_3NH^+ cation forming triethylammine and $H^\bullet$ atom. Both of these species are involved in further reactions making the mechanism of $I_2^{\bullet -}$ formation more complicated. The yield of $I_2^{\bullet -}$ for 0.1 M I^- solution in Et_3NHNTf_2 reaches almost plateau in the I^- concentration dependence with G ($I_2^{\bullet -}$) = 0.25 μmol J^{-1} (Fig.4).

Concluding, mechanisms involved with $I_2^{\bullet -}$ formation in protic ILs is more composed and needs further experiments.

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MECHANISM OF NICOTINE RADICAL REACTIONS

Katarzyna Kosno, Monika Celuch, Jacek Mirkowski, Ireneusz Janik, Dariusz Pogocki

Nicotine (3-(1-methyl-2-pyrrolidinyl)pyridine) is a natural alkaloid found in tobacco leaves. Despite its long-standing bad reputation as a major cause of tobacco-smoking addiction [1], nicotine has also medical application. Besides its common usage in nicotine replacement therapy, it has the potential to be widely used in a therapy of some major neurodegenerative disorders and diseases such as Alzheimer's and Parkinson's diseases, Tourette's syndrome or schizophrenia [2]. Neurodegenerative diseases are usually accompanied by an extensive oxidative stress, where nervous tissue is subjected to the presence of oxygen radicals beyond a threshold for proper antioxidant neutralization, therefore therapeutic usage of nicotine can be related to its free radical scavenging capacity.

Hydroxyl radical is a highly reactive oxidizing radical reacting rapidly with most of biomolecules. Since nicotine easily passes through the blood-brain barrier, it can react with endogenous radicals *(e.g.* $^\bullet$OH) in the cerebrospinal fluid forming neutral or less aggressive radical products [3]. However, application of nicotine to reduce oxidative stress was not experimentally confirmed so far. We need to get more data about radical reactions, involving nicotine and its metabolites, and about their influence on the organism. Finding out about the kinetics of these reactions is also important, because the rate of nicotine reaction with examined radicals should be high enough to exclude competitive reactions (Fig.1).

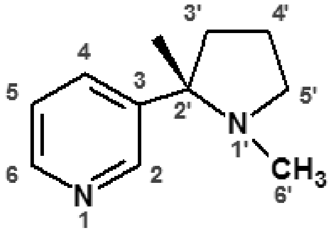

Fig.1. Structural formula of nicotine.

Nicotine molecule is made of two rings: aromatic pyridine and aliphatic pyrrolidine, so pyridine, pyrrolidine and N-methylpyrrolidine can be used as nicotine model compounds. Nicotine as a tertiary amine is a weak base with a pK_{a1} of 8.02 (pK_{a2} = 3.12) in aqueous solution at 25°C [4], so at pH 7.4 (physiological pH of blood) about 81 percent of nicotine is protonated at pyrrolidinyl nitrogen. It is worth noting that the state of protonation has the influence on nicotine radical reactions.

Mechanism of radical oxidation of nicotine and kinetics of its reaction with $^\bullet$OH radical were studied by pulse radiolysis technique applying UV/VIS time-resolved detection system. Experiments were performed with the LAE 10 [5] (Institute of Nuclear Chemistry and Technology) and Titan Beta Model TBS-8/16-1 [6] (Notre Dame Radiation Laboratory) linear accelerators. Reactions were studied in aqueous solutions saturated with N_2O, which eliminates hydrated electrons,

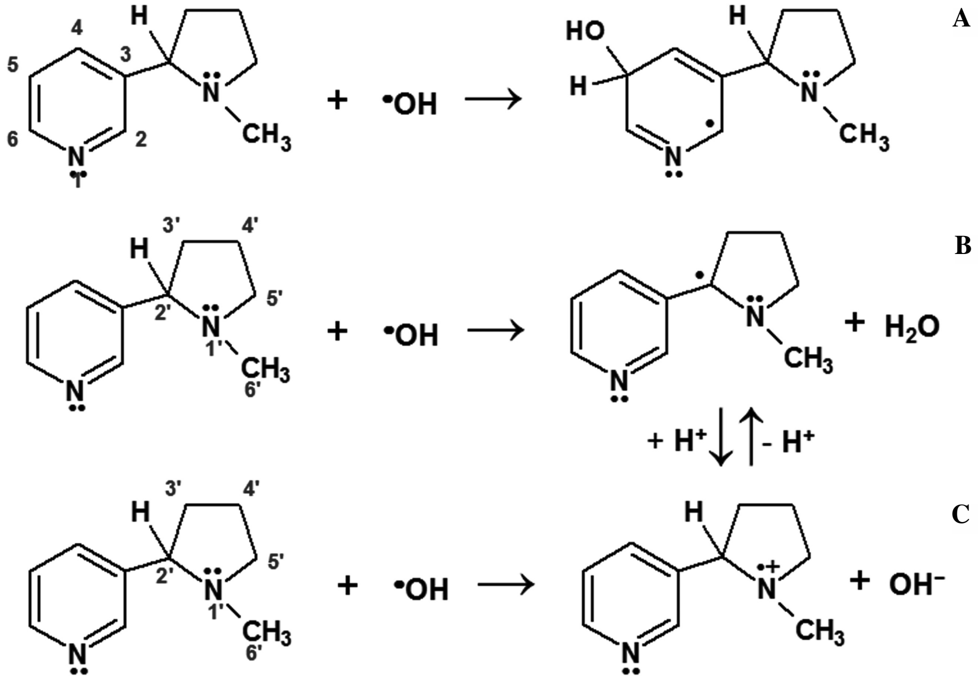

Fig.2. Three possible ways of nicotine reaction with •OH radical.

e_{aq}^-, from the system and nearly doubles the amount of •OH radicals available for the reactions with solute (Eq. (1); $k_1 = 9.1 \times 10^9\ M^{-1}s^{-1}$) [7]:

$$e_{aq}^- + N_2O \rightarrow O^{\bullet -} + N_2\,(+\,H_2O) \rightarrow {}^{\bullet}OH + {}^{-}OH + N_2 \qquad (1)$$

Nicotine radical reactions were studied for the first time with pulse radiolysis technique by Wang *et al.* in 2003 [3]. However, the conclusions presented in their work are by any means related to previous results obtained by Getoff's groups for the components of nicotine molecule, *i.e.* pyridine and pyrrolidine [8, 9]. For example, they postulated that •OH radicals react with nicotine by hydrogen abstraction and generated radicals absorb

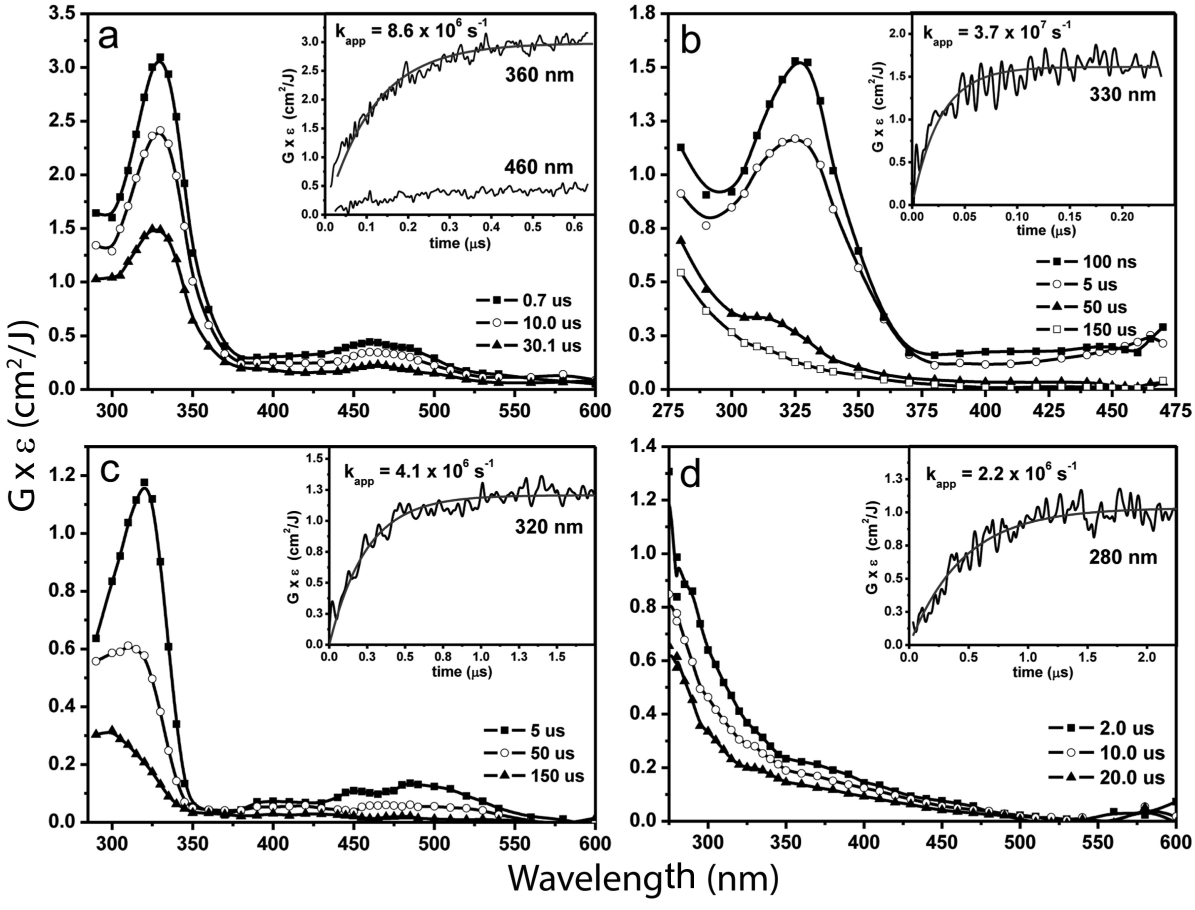

Fig.3. Transient absorption spectra recorded in N_2O-saturated aqueous solutions containing 1 mM of (a) nicotine at pH 10, (b) nicotine at pH 7.4, (c) pyridine at pH 10 and (d) N-methylpyrrolidine at pH 10.

with the maxima at 320 and 460 nm. Based on pulse radiolysis studies, Solar *et al.* [9] have determined that •OH radicals react with pyridinyl ring producing adducts. The transient absorption spectra of postulated •OH radicals adducts are almost identical with those observed lately by Wang *et al.* for nicotine derived transients [3]. Furthermore, radicals being the products of hydrogen abstraction from pyrrolidinyl ring have shown transient absorption with one maximum located close to 230 nm [8].

Based on the reaction mechanisms anticipated for nicotine and its model compounds, three pathways of its reaction with hydroxyl radical can be taken into account: formation of the •OH radical adduct to aromatic ring (Fig.2A), direct hydrogen abstraction from the aliphatic ring (Fig.2B) and formation of the cation radical at this ring (Fig.2C).

In the first reaction, substitution occurs mainly at the meta position, considering the electron density within the aromatic ring. Due to favourable energetic effect, the most probable product of the second reaction is a radical located at 2'-carbon atom.

Spectral and kinetic analysis was performed over a broad range of pH (1.0-13.6) providing results for protonated and deprotonated forms of nicotine. At all pH values, transient absorption spectrum exhibits a distinct absorption band with λ_{max} = 330 nm and a second, broad and much weaker absorption band with λ_{max} *ca.* 460 nm (Fig.3). Their kinetic behaviour suggests that both absorption bands belong to the same specie. There is also one absorption band coming from the shorter wavelengths beyond the measuring range (280-600 nm), partially overlapping absorption peak at 330 nm. Pulse radiolysis of pyridine in the same conditions gave a transient absorption spectrum with two maxima: one distinct at 320 nm and a second, broad at the visible spectral region. Repeating the experiment for pyrrolidine and N-methylpyrrolidine gave only a band coming from the shortwaves. Basing on collected data, absorption band at the shortwaves can be assigned to a radical at 2'-carbon and the maxima at 330 and 460 nm may come from the •OH radical adduct, however, it was not unambiguously confirmed so far.

The reaction rate constants of •OH radicals with nicotine were determined either by direct measurements of transient product absorptions or by monitoring the competitive reactions of •OH radicals among nicotine and SCN⁻ – reactions (2) and (3):

$$^{\bullet}OH + SCN^- \rightarrow OH^- + SCN^{\bullet} \quad (2)$$

$$^{\bullet}OH + \text{nicotine} \rightarrow \text{products} \quad (3)$$

Recognizing each protonation state of nicotine as distinct kind of species, one may assume that the rate $k_{(OH+Nicotine)}$ is the sum of rate constants for different forms of nicotine: deprotonated Nic, protonated NicH and doubly-protonated $NicH_2$, whose fraction depends on the pH value – Eq. (4):

$$k_{(OH+Nicotine)} = x_{NicH2} \times k_{(OH+NicH2)} + x_{NicH} \times k_{(OH+NicH)} + x_{Nic} \times k_{(OH\text{-}Nic)} \quad (4)$$

The second-order rate constants, $k_{(OH+Nicotine)}$, determined from kinetic traces at 330 nm collected in pseudo first-order conditions ([Nic] ≥ 1 mM) are collected in Table.

In order to check if nicotine reaction with hydroxyl radical can proceed with one-electron oxi-

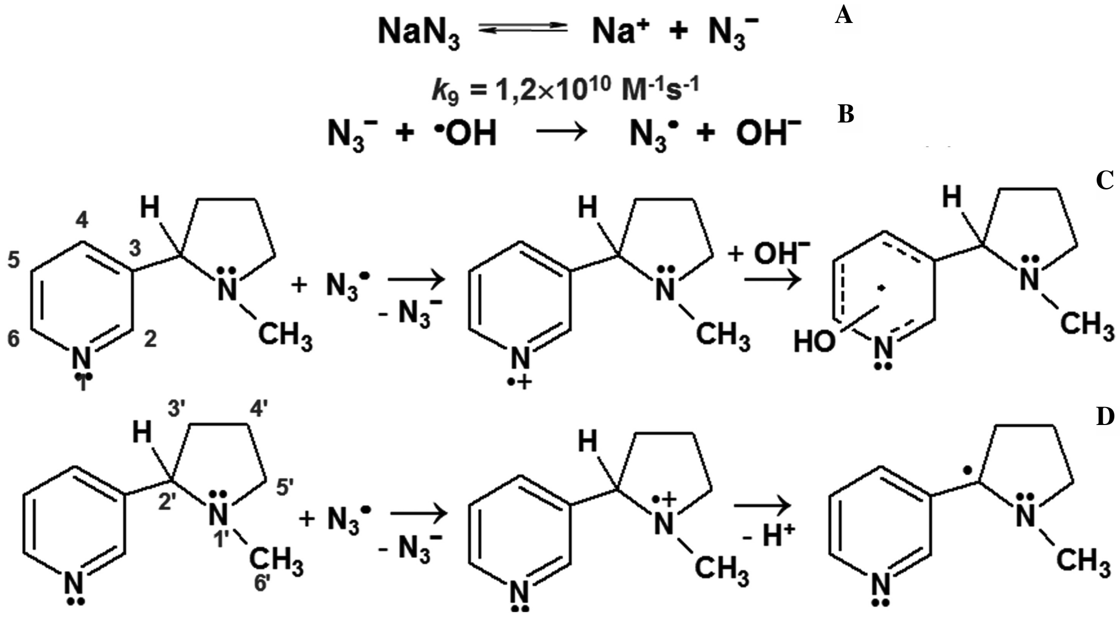

Fig.4. Reaction scheme for the oxidation of nicotine by azide radical.

Table. The rate constants k [$M^{-1}s^{-1}$] of nicotine reaction with •OH radical recorded at 330 nm, and derived from competitive kinetics (in parenthesis), at various pH, and the fraction of pH-dependent nicotine forms (x_{NicH2}, x_{NicH}, x_{Nic}).

pH	$k_{(OH+Nicotine)} \times 10^{-9}$	x_{NicH2}	x_{NicH}	x_{Nic}
1.0	0.32 ± 0 .06	0.99	0.01	0.0
3.0	(5.6 ± 0.2)	0.57	0.43	0.0
5.6	2.7 ± 0.1 (5.5 ± 0.1)	0.004	0.993	0.003
7.4	3.8 ± 0.2	0.0	0.81	0.19
10.0	6.2 ± 0.2 (12 ± 0.1)	0.0	0.09	0.91

dation of nitrogen, its reaction with $N_3^\bullet$ radicals was also studied (Fig.4A,B). Azide radical reacts mainly with the electron transfer. It is a weak oxidant – it does not abstract hydrogen atoms and does not form adducts. In its reaction with nicotine aromatic ring, nitrogen-centered cation radicals are generated, which are unstable and can react further with water forming $^\bullet$OH adducts to the pyridine ring (Fig.4C). In the reaction with aliphatic nitrogen, the cation radicals are generated, which can then undergo regrouping with proton abstraction (Fig.4D). Products generated in these reactions are the same as those obtained in the reaction with $^\bullet$OH radicals with this difference that in case of $N_3^\bullet$ radicals oxidation occurs with electrophilic attack on the nitrogen atoms. Transient products of $N_3^\bullet$ reaction with nicotine are characterized by a distinct maximum at 330 nm, and a broad absorption band at 470 nm (Fig.5). Spectra obtained for the reaction of nicotine with $N_3^\bullet$ and $^\bullet$OH are almost identical, what indicates that they could have a similar character.

Obtained results indicate that the $^\bullet$OH radicals can react with nicotine along at least two competitive pathways: the hydrogen atoms abstraction from the carbons of pyrrolidinyl ring, which can occur in accordance with the mechanism recently suggested by Wang *et al.* [3] and the formation of the $^\bullet$OH radical adduct to the aromatic pyridinyl ring according to the mechanism previously proposed for pyridine by Solar *et al.* [9]. Experiments with $N_3^\bullet$ radicals suggest that one-electron oxidation of nicotine is also possible. The second-order rate constants, $k_{(OH+Nicotine)}$, obtained at pH 7.4 is equal to 3.8×10^9 $M^{-1}s^{-1}$. Is worth noting that this value is one order of magnitude higher than that calculated for pH 7 by Wang *et al.* (4.5×10^8 $M^{-1}s^{-1}$) [3]. As regards the medical application, providing the adequate nicotine concentration, the obtained rate constant might be sufficient enough for secure and efficient scavenging of $^\bullet$OH radicals.

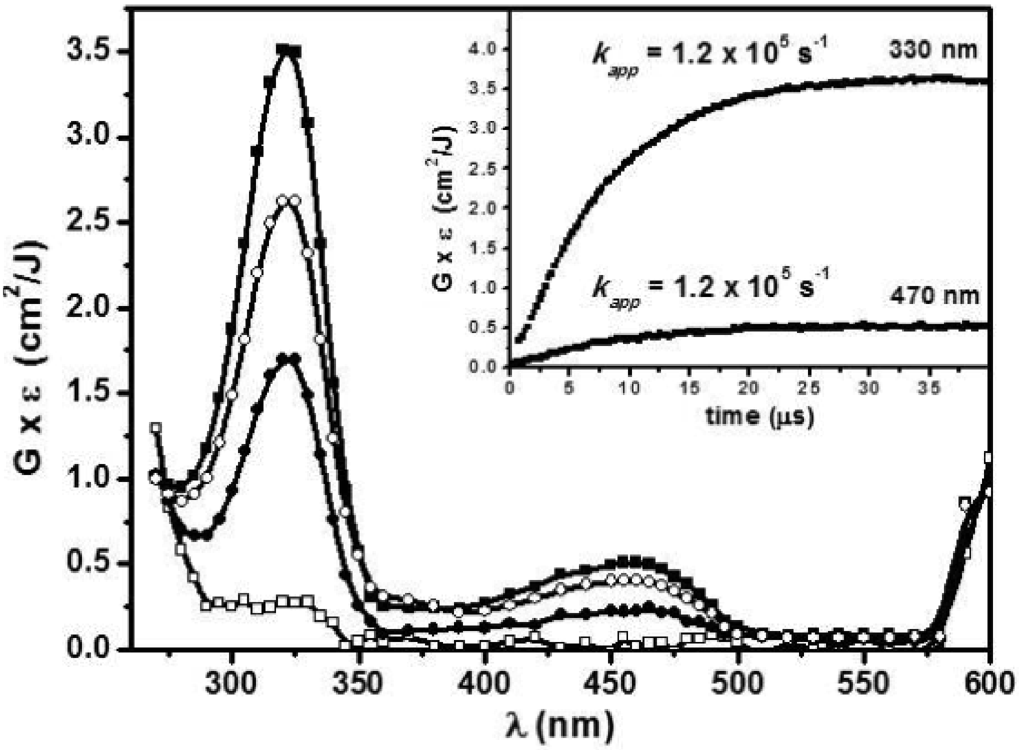

Fig.5. Transient absorption spectra obtained by $H_3^\bullet$-attack on nicotine recorded 100 ns (□), 5 μs (●) 50 μs (■) and 150 μs (○) after the pulse in the N_2O-saturated 1 mM nicotine solution containing 10 mM NaN_3, at pH 10. Inset: kinetic traces recorded at λ = 330 and 470 nm, respectively.

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EPR STUDY OF FINGERNAILS AS A BIOLOGICAL DOSIMETER

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The emergency dosimetry methods for fast monitoring of people during radiation accident are still of the interest of several research groups [1-3].

Ionizing radiation generates free radicals in biological materials (*i.e.* in fingernails, hairs) which are stable over long periods (days to weeks). They can be detected by using electron paramagnetic resonance (EPR) spectroscopy. EPR method is suitable for radiation dosimetry due to its accuracy, sensitivity and fast measuring procedures. When the relationship between EPR signal intensity of stable paramagnetic centre and the dose is of linear character, the material can be used as a dosimeter of absorbed radiation.

The most sensitive dosimeter based on the human tissues is tooth enamel and it was successfully used to evaluate the dose absorbed by workers taking part in nuclear or radiation accidents. Unfortunately, this material cannot be used for screening measurements of large population of potentially exposed people.

Here, we present the results of testing the possibility of using fingernail samples in natural form for an easy and fast dosimetry method of ionizing radiation.

Fingernails were collected from healthy adult male and female volunteers.

Samples about 30 mg were irradiated at dose of 2 to 35 Gy at room temperature in a Co-60 gamma source Mineyola in the Institute of Nuclear Chemistry and Technology (INCT).

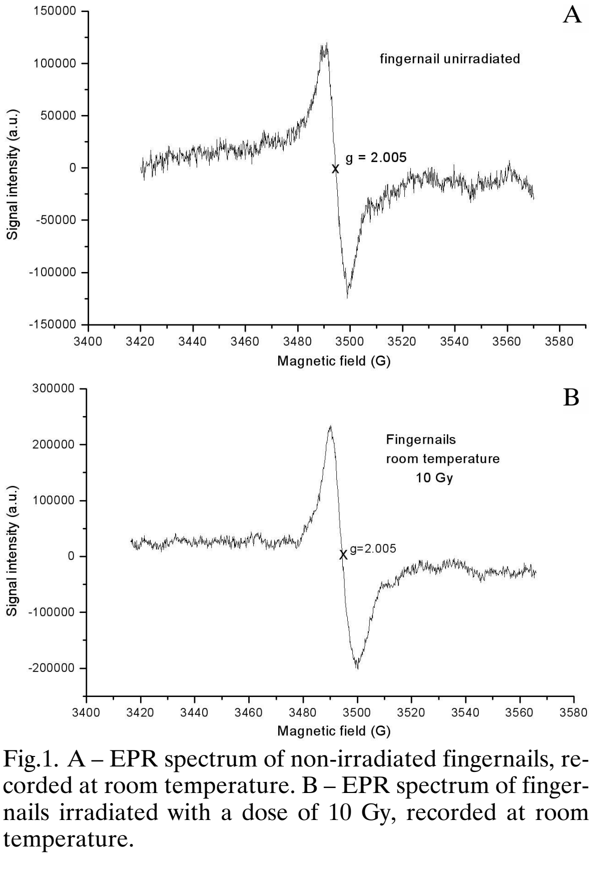

Fig.1. A – EPR spectrum of non-irradiated fingernails, recorded at room temperature. B – EPR spectrum of fingernails irradiated with a dose of 10 Gy, recorded at room temperature.

The EPR measurements at X-band (9.5 GHz) were carried out at room temperature just after the irradiation and after few days later using an ESP-300 Bruker spectrometer.

We have made the optimalization of EPR parameters for signal measurement: 5 mW – microwave power, 0.4 mT – modulation amplitude.

EPR signals recorded at room temperature in non-irradiated and irradiated samples are presented in Figs.1A and B, respectively. Unfortunately, in both cases signals have the same shape, character and spectroscopic parameters: a singlet with $g_{av} = 2.005$ and $\Delta H = 9.5$ G. However, its intensity increases with dose. Fingernails consist mainly of α-keratin, and it seems reasonable to assign the radiation-induced EPR signal to radicals generated in this protein.

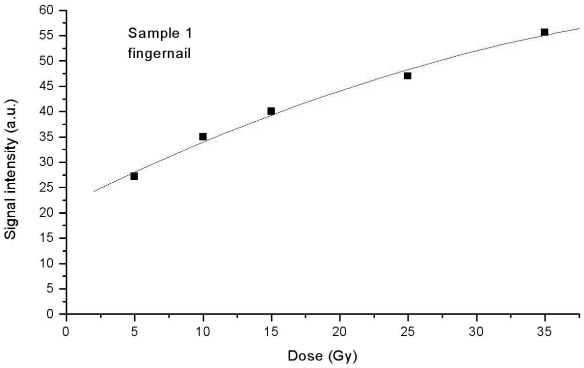

Fig.2. Dose-response curve for fingernails gamma-irradiated over a dose of 5-35 Gy.

The EPR signal intensity was measured as peak-to-peak height for the singlet and the relationship between signal intensity and dose has a linear character for a few different samples of fingernails (Fig.2).

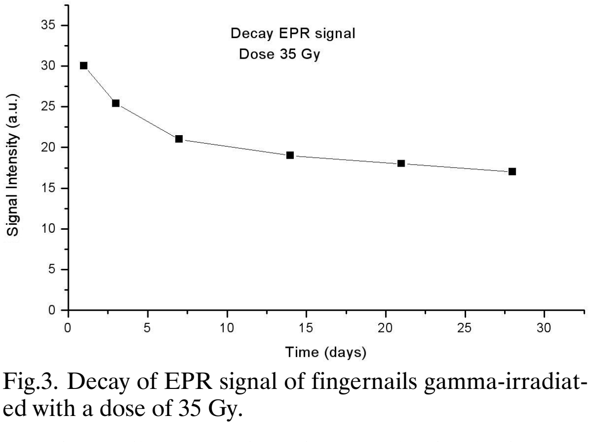

Fig.3. Decay of EPR signal of fingernails gamma-irradiated with a dose of 35 Gy.

The radiation-induced EPR singlet in human fingernails is not completely stable at room temperature. During the first 5 days, the signal decay is much faster than in the subsequent period. It makes the dose estimation more difficult, but it does not disqualify this material as biological dosimeter because even after 5 days the signal intensity is larger in irradiated than in non-irradiated samples. The decay of the EPR signal is presented in Fig.3.

Based on our results we conclude that the fingernails can be used as biological dosimeters only for radiation doses higher than 5 Gy, because of the intense EPR signal appearance in the non-irradiated sample. With this limitation, the fingernails show a high potential for rapid dosimetry in large-scale radiological or nuclear accidents.

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C-CENTERED PARAMAGNETIC SPECIES GENERATED RADIOLYTICALLY IN MOLECULAR SIEVES

Marcin Sterniczuk, Jarosław Sadło, Grażyna Strzelczak, Jacek Michalik

Free radicals are very often important intermediates in many processes of heterogeneous catalysis. However, in the real catalytic system they are very reactive and short-lived, thus difficult to study. One of the methods to stabilize these species is trapping them in zeolite matrices. Zeolites are crystalline microporous solids often used in the chemical industry. They have well-defined structures containing tetrahedral TO_4 building blocks connected to each other by sharing O atoms. T represents Si, Al or other tetrahedrally coordinated atoms. Their features like shape selective properties, well-defined microporous network and good thermal and mechanical stability make them attractive for heterogeneous catalysis [1-5].

Here, we present a study of paramagnetic carbon centres generated radiolytically in molecular sieves with adsorbed carbon oxide. The combinations of electron paramagnetic resonance (EPR) technique and quantum chemical computation have been applied in order to identify the radical centres and define their geometry and reactivity.

All samples after degassing and dehydration on a vacuum line were exposed to ^{13}CO and gamma-irradiated in a ^{60}Co source at 77 K with a dose of 5 kGy. The spin of C-13 is ½ which leads to the splitting of EPR lines when unpaired electron interacts with the C-13 nucleus. The EPR spectra were measured in the temperature range 100-370 K using a Bruker ESP 300 spectrometer. In all samples slightly anisotropic doublets with different ^{13}C hyperfine splittings were recorded just after irradiation. We assigned them to carbon centred radicals stabilized in different lattice sites. Bruker „Simfonia" program was used for spectra simulation. All theoretical calculations had been performed by using the Gaussian03W program on the DFT (density functional theory) level. For geometry optimalization strategy, an ONIOM model was employed [6].

Based on the EPR measurements and DFT calculations, we found that zeolite samples with a high silica alumina ratio as: ZSM-5/^{13}CO: Si/Al = 38÷200, FAU Y/^{13}CO: Si/Al = 30÷80 and MOR/^{13}CO: Si/Al = 8 stabilize three types of carbon centres. In the first one (centre A) $^{\bullet+}$CO radical cation interacts with oxygen located between Si and Al atoms $^{-}$[≡Si-O-Al≡]$^{\bullet+}$CO (Fig.1). In the second one (centre A`) $^{\bullet+}$CO is bounded to oxygen located between two Si atoms [≡Si-O-Si≡]$^{\bullet+}$CO. For last carbon centre we proposed the structure in which CO is attached to oxygen of terminal silanol group forming centre B: [≡Si-O]$^{\bullet}$CO. In zeolites with Si/Al < 5.1 as: LTA/^{13}CO or FAU/^{13}CO only centre A is stabilized. The values of ^{13}C hyperfine splitting for centre A in various zeolites differ from A_{iso} = 25.4 mT to A_{iso} = 27.8 mT (Fig.2). In zeolites with stronger acid sites the higher A(^{13}C) values were observed than in molecular sieves with weaker acid sites. We linked this dependence

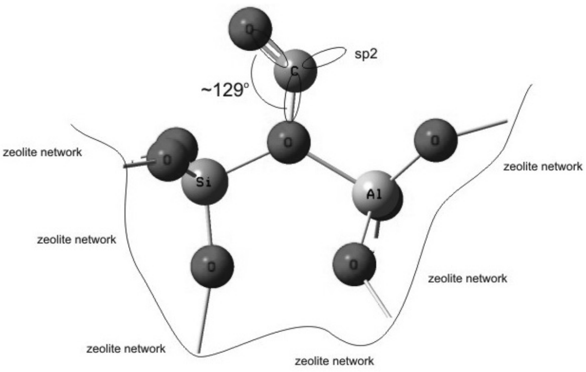

Fig.1. The model representing structure of A centre. The O-C-O angles for centre A are similar for all zeolites.

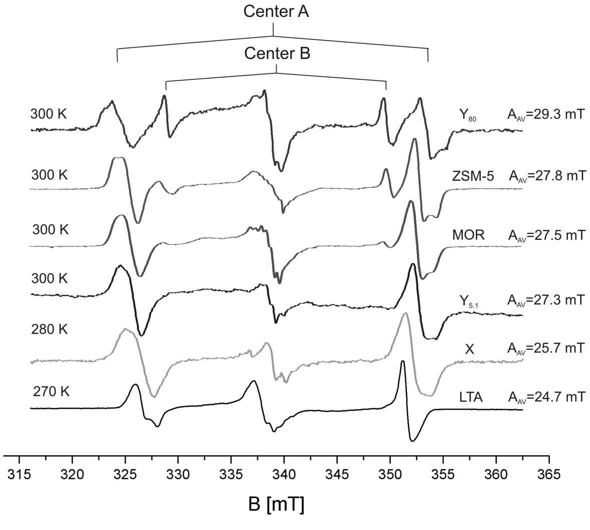

Fig.2. EPR spectra of gamma-irradiated zeolites exposed to ^{13}CO.

to the character of bonding between the carbon and lattice oxygen. According to DFT calculations, this bonding changes the character from covalent in zeolites with weak acid sites to ionic ones in lattices with stronger acid centres. Our results show that the hyperfine splittings of $^{+\bullet 13}$CO EPR doublet might be a useful tool for probing the active sites in zeolite catalysts.

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PREPARATION OF HOT-MELT ADHESIVE FOR THE INSULATION OF JOINTS IN PRE-INSULATION PIPES USED IN HEATING INSTALLATIONS

Andrzej Nowicki, Grażyna Przybytniak, Krzysztof Mirkowski

For joining pre-insulation pipes in hot water networks usually heat shrinkable elements (tapes, joints, tubes) are used that are manufactured applying radiation technology for their cross-linking. Both pipes and connecting elements are commonly made of polyethylene and a contact surface is sealed with an appropriate adhesive layer. In heating installations the hot-melt adhesives for the insulation of joints in pre-insulation pipes are widely used. Such thermoplastic materials are applied in the molten state and when cooled re-solidify forming a bond between surfaces.

The reported work was focused on the possibility of using polyamides for the preparation of hot-melt adhesives. Polyamide hot-melt adhesives are very versatile, and they are capable of bonding to many different materials, *e.g.* plastics, foils, papers, *etc*. They have better heat resistance than more common glue based on ethylene-vinyl acetate copolymer. However, due to the polar groups present in the polymer, adhesion to pipes, tapes or joints made of polyethylene is limited. Thus, it was assumed that polyamides require modification with polyolefines and other additives in order to increase compatibility between the adhesive and bonding surfaces. Our purpose was to develop the adhesive formulations customized to the particular requirements of heating industry.

In the first stage of the studies we (i) optimized the synthesis conditions and the applied substrates, (ii) examined how the properties of the final products depended on the chemical structures and ratio between the reactants and (iii) developed a procedure of polycondensation. The synthesizes of polyamides was conducted in the reactor equipped with a stirrer, a substrate feeder, a thermometer, and a descending condenser under vacuum. The polycondensation progress was controlled by FTIR spectroscopy analysing the decay of amine bands at 3320 cm^{-1} (Fig.1).

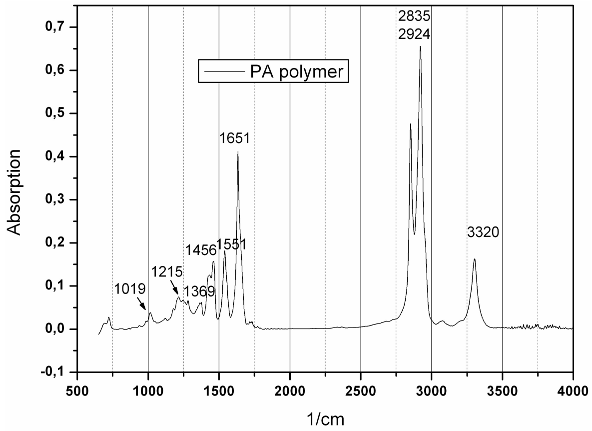

Fig.1. FTIR spectrum of PA presenting progress in polycondensation (3320 cm^{-1}).

In the next stage of experiments the polyamides were modified with various additives, *e.g.* radiation degraded polypropylene, oxidized polyethylene, resins, waxes, polyisobutylene, halloysite composite, *etc*. The most promising results were obtained when polyamide was synthesized from a dimmer of fatty acid Pripol®, adipic and stearic acids, ethylenediamine and hexamethylenediamine (PA) and subsequently modified with amorphous poly-alpha-olefins (APAO). The last component contained aliphatic and aromatic hydrocarbon resins, ethylene vinyl acetate copolymer, oxidized wax of polyethylene and 3% layered aluminosilicate.

In order to characterize the final adhesives the following tests were performed: apparent viscosity and surface free energy measurements, mechanical

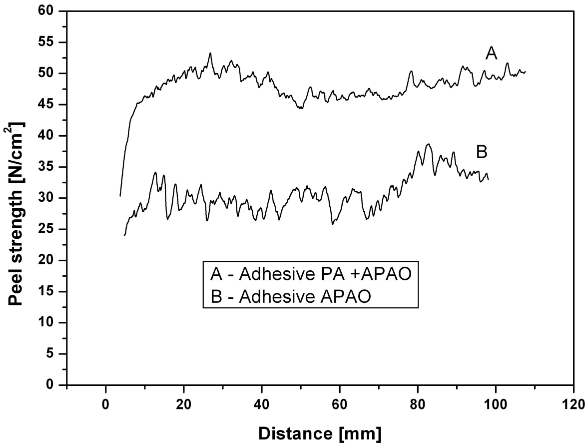

Fig.2. Peel strength for PA+APAO and APAO.

tests (tearing off and strip tests), thermal studies with application of DSC and TGA. As a screening test, the rheological measurements were conducted for each obtained material.

Figures 2 and 3 show the results of mechanical and rheological investigations for the optimal formulations of APAO and PA+APAO. As seen from Figs.2 and 3, APAO has a lower peel strength than PA+APAO composition, 31 and 50 N/cm, respectively, and relatively high application temperature situated in the range of 165-180°C which might result in the distortion of thermally shrinkable products during applying the glue on their surfaces. Therefore, the use of PA+APAO adhesive of advantageous properties is recommended for further R&D activity associated with the increase of production from the laboratory scale to pilot plant.

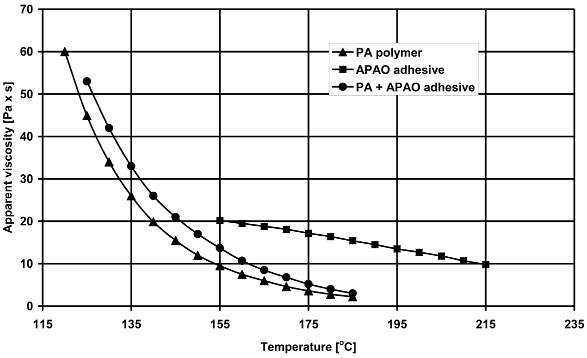

Fig.3. Apparent viscosity of PA, APAO and PA+APAO.

The final product, PA+APAO, has a long open time (several minutes) and might be applied in the moderate temperature range 145-155°C. The adhesive bond strength is higher than 50 N/cm and working temperature is located in the range from -20 till 120°C. It is made out of harmless ingredients and produced under environmentally friendly conditions (no organic solvents). Before application no mixing is required as the product is a single component.

The resulting adhesives PA-APAO and APAO were tested according to EN 489:2005 related to pre-insulated bonded pipe systems for directly buried hot water networks – joint assembly for steel service pipes, polyurethane thermal insulation and outer casing of polyethylene. The studies were performed using installation "box of sand" at the Research Laboratory OBRC SPEC SA (Warszawa, Poland) accredited by the Polish Accreditation Centre. Both investigated materials, PA+APAO and APAO, passed the tests. Figures 4 and 5 demonstrate photos documented the seal strength made of PA+APAO adhesive and its resistance on the water leakage investigated by a fluorescent dye used as an indicator.

Fig.4. The joint assembly before tests.

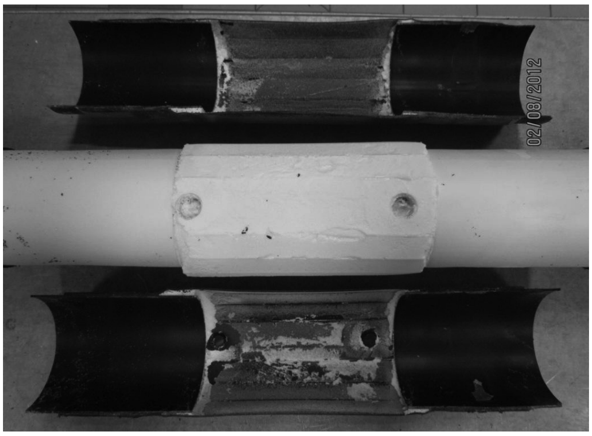

Fig.5. The joint assembly after tests. Penetration of water doped with fluorescent dye was not observed.

The procedures of PA+APAO and APAO production were formulated as an offer for the heating industry.

The work has been performed in the frame of research project No. R08 0014 06, 2009-2012 granted by the Ministry of Science and Higher Education (Poland).

AGING OF CABLES – ASSESSMENT AND COMPARISON OF DIAGNOSTIC METHODS

Jacek Boguski, Grażyna Przybytniak

Degradation of insulations and jackets of low voltage cables is a serious problem in nuclear power plants (NPPs) where degrading factors such as increased level of ionizing radiation, elevated temperature, oxidative atmosphere, humidity or mechanical stress occur during service lifetime estimated recently for 60 years. These factors induce the processes of oxidation, cross-linking or chain scission that lead to the deterioration of electrical and mechanical properties [1]. Cables and wires installed in many safety and control systems of NPPs usually cannot be exchanged during operational lifetime due to very high costs and technical problems. These are the main reasons for searching reliable and reproducible condition monitoring methods, especially that there are no convenient technical standards in this respect [2]. In this work two types of cables were studied. The first one consisted of outer jacket and three types of insulation (brown, blue, green), all made of ethylene-propylene rubber (EPR). The second one consisted of outer and inner jacket made of ethylene-vinyl acetate copolymer (EVA) and insulation made of cross-linked polyethylene (XLPE). Cables were accelerated aged by irradiation in gamma chambers with two dose rates: 0.6 kGy/h – Issledovatel (ISSL) and 7.0 kGy/h – Gamma Chamber 5000 (GC). A few diagnostic methods like: elongation at break (EaB), strength at break (SaB), oxidative induction temperature (OITp), gel fraction, degree of swelling and FTIR spectroscopy were used to compare and to verify their suitability as reliable condition monitoring methods. The replacement of the currently used EaB criterion (decrease of EaB to 50% of initial value) was analysed.

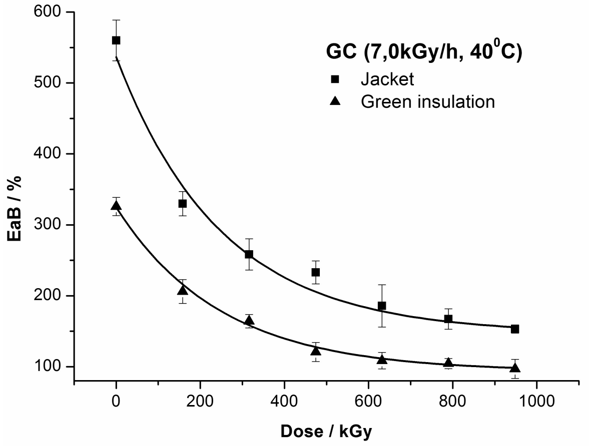

Fig.1. Elongation at break as a function of dose absorbed for EPR jacket and green insulation aged at 7.0 kGy/h dose rate.

Elongation at break values decrease with increasing dose absorbed for all the studied materials and for every type of aging. In the case of EPR cable, this dependence could be approximated by an exponential curve (Figs.1 and 2) whereas for EVA/XLPE cable there is no a distinct decrease in EaB values till 400 kGy except for XLPE insulation (Fig.3).

The oxidative induction temperature values decrease with dose absorbed for every type of material studied. In the case of EPR jacket and inner EVA jacket, the linear correlations between OITp and EaB were observed. This relationship reveals a very distinct influence of the dose rate on aging phenomena for EPR jacket (Fig.4). The 0.6 kGy/h dose rate applied makes the line steeper what could be interpreted as an enhanced contribution of oxidative degradation unlike in the case of ageing at 7.0 kGy/h when chain scission and/or cross-linking predominantly take place. The outer EVA jacket and XLPE insulation do not reveal such a correlation (Fig.5). In these cases the OITp values

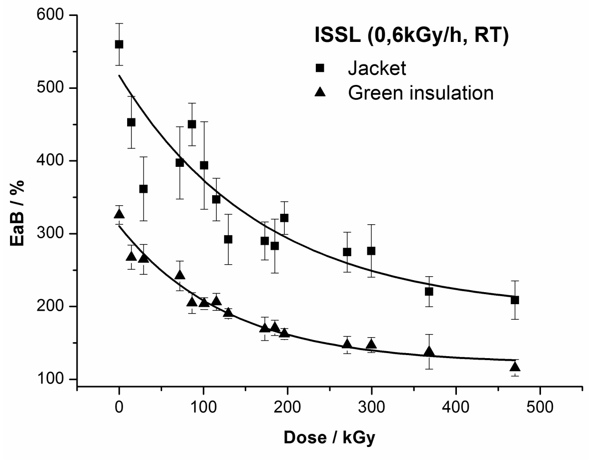

Fig.2. Elongation at break as a function of dose absorbed for EPR jacket and green insulation aged at 0.6 kGy/h dose rate.

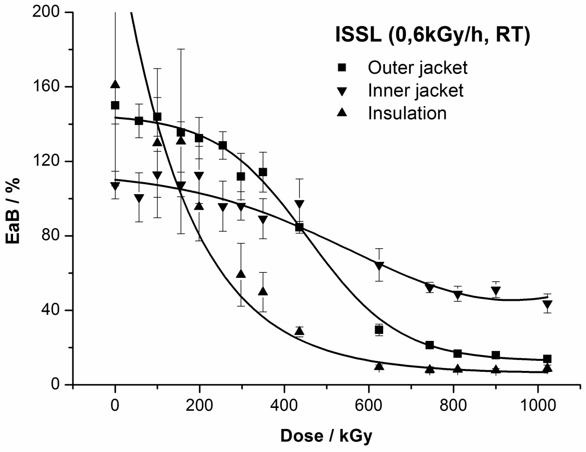

Fig.3. Elongation at break as a function of dose absorbed for EVA (outer and inner jacket)/XLPE (insulation) cable aged at 0.6 kGy/h dose rate.

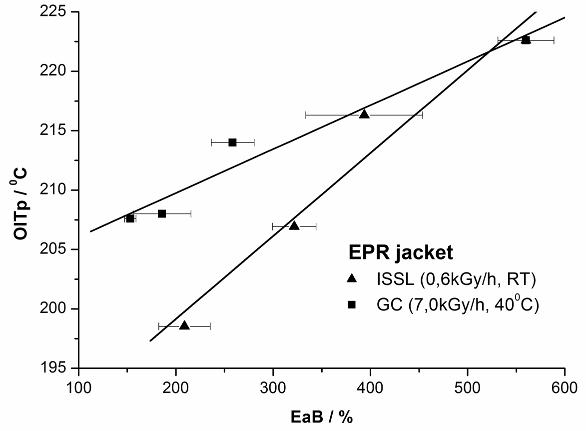

Fig.4. Correlation between oxidative induction temperature and elongation at break for EPR jacket.

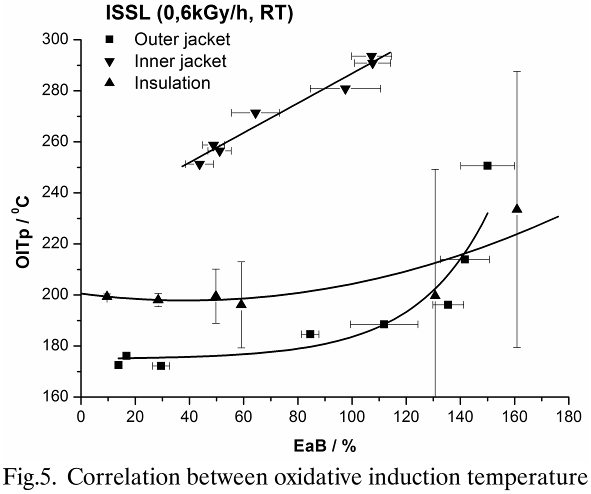

Fig.5. Correlation between oxidative induction temperature and elongation at break for EVA inner/outer jacket and XLPE insulation.

decreased rapidly and then remained at the same level till the end of the studied dose range. It seems that the applied for these materials antioxidant ran out at the beginning of aging influencing the OITp values what excludes using OITp as a quality factor replacing EaB. The high thermal stability of the inner EVA jacket was confirmed by the slow decrease of OITp as a function of EaB. The changes clearly revealed that nature and concentration of the additives applied for the same polymeric matrix can significantly influence its physical and chemical properties.

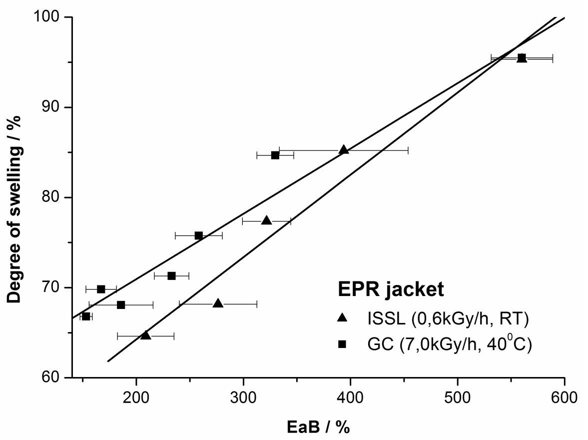

Fig.6. Correlation between relative mass growth (degree of swelling) and elongation at break for EPR jacket after 24 h of swelling in xylene.

The degree of swelling measurements were performed for EPR jacket aged at 0.6 and 7.0 kGy/h using a mixture of xylene isomers at 25°C for at least 24 h. The correlation between a relative mass growth expressed as a degree of swelling and EaB was found (Fig.6). The material studied saturated just after 6 h of swelling. Decrease in the degree of swelling with the dose absorbed was observed for all dose rates what was also revealed in the above-mentioned correlations. The saturation with xylene is lower for the samples aged at 0.6 kGy/h what probably results from the increasing polarity of polymer with the progress of oxidation and formation of oxygen containing functional groups. It all makes the degree of swelling a sensitive quality factor for EPR based cables.

Many other effects like the increase of gel fraction after annealing step (110°C, 24 h, air atmosphere) for aged XLPE insulation [3] or appearing C=C vibrational bond in the FTIR spectra confirming an α-β elimination mechanism for EVA outer jacket [4] were investigated. The observed dose rate effects, synergy between two degrading factors, *i.e.* elevated temperature and gamma irradiation, sequence of degrading factors applied and many others aging conditions could play a significant role in cable lifetime prediction. It is very important to consider all these facts in respect of replacing EaB criterion and developing new accelerated aging procedures.

The reported work was performed in the frame of FP7 Euratom "Aging diagnostics and prognostics of low voltage I&C cables" (ADVANCE) – grant agreement No. 269893.

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CENTRE FOR RADIOCHEMISTRY AND NUCLEAR CHEMISTRY

Chemical issues of nuclear power and radiopharmaceutical chemistry – the two top domains of contemporary applied radio- and nuclear chemistry over the world – remained the subject of the research activity of the Centre for Radiochemistry and Nuclear Chemistry in 2012. The main research projects of the Centre were financed from the European Commission (FP7 Euratom, Fission), from the Operational Programme Innovative Economy (PO IG). as well as from the National Science Centre (NCN) and the National Centre for Research and Development (NCBiR).

In line with the governmental plans to develop nuclear power programme in Poland, the main efforts of the Centre in 2012 were focused on the chemical issues of nuclear power. The research teams of three Centre laboratories (Radiochemical Separation Methods, Membrane Processes and Technologies, and Sol-Gel Technology) continued their studies on radioactive waste managing, and on special nuclear materials. In this respect, we have completed our participation in the European Collaborative Project ACSEPT, carrying out studies on solvent extractive separation of americium from highly radioactive nuclear waste by using new selective poly-N-heterocyclic ligands, accompanied by theoretical (quantum chemical) investigations on the potential origin of their selectivity for actinides over lanthanide fission products. Further work on new types of MOX nuclear fuels based on uranium oxides and carbides is the subject of a new European Collaborative Project ASGARD that started in 2012 with the participation of our Sol-Gel team. In 2012 we continued realization of two other European FP7 projects: (i) IPPA, aimed at the creation of an arena for the exchange of opinions and public acceptation of the problems of radioactive waste disposal, and (ii) NEWLANCER, aimed at the increase of participation of Polish teams in the coming research Euratom programmes.

The Centre also coordinated and realized two national projects related to: (i) the possibilities of supplying uranium from indigenous resources, financed from PO IG, and (ii) the workpackage on the management of spent nuclear fuel and radioactive wastes, a part of the NCBiR strategic project on the development of safe nuclear energy. Polish uranium resources have been evaluated and efficient methods have been adapted for extracting uranium from low-grade ores, secondary raw materials and industrial by-products. The works within the strategic project concern different aspects of management and storage of spent nuclear fuel and radioactive wastes formed in the course of exploitation of the nuclear power plants with a special emphasis on the Polish nuclear industry. Within other NCBiR projects, novel methods were studied for separation of metal ions, based on hybrid processes (combination of membrane filtration with sorption or complex formation), as the basis for further technologies of radioactive waste management. A method has been elaborated for the designing membrane plants for processing liquid radioactive waste of low and intermediate level, originating from research centres and other institutions that use radionuclides. Sol-gel methods were also developed for obtaining novel materials (silica glasses, SYNROC matrices) making it possible to encapsulate and immobilize nuclear waste.

Research on radiopharmaceutical chemistry (Laboratory of Radiopharmaceuticals Synthesis and Studies) were focused on obtaining novel potential radiopharmaceuticals, both diagnostic and therapeutic, by either labelling novel biomolecules (*e.g.* derivatives of tacrine and substance P) with the usual radionuclides (^{99m}Tc), or labelling peptide vectors (*e.g.* substance P) with novel radionuclides – therapeutic ^{223}Ra and ^{211}At (including labelling *via* nanoparticles of functionalized zeolite and titanium dioxide) or diagnostic (PET) – ^{43,44}Sc. Novel ^{211}At- and ^{99m}Tc-labelled bioconjugates were synthesized and tested as potential receptor radiopharmaceuticals. Microspheres of ^{90}Y-yttrium oxide were synthesized (Laboratory of Sol-Gel Technology) and tested as potential radiopharmaceuticals for anticancer therapy by radioembilization. Apart from the Institute statutory research, the studies in this field were funded from eight NCN and NCBiR projects, some of them under international cooperation. Two young researches continued their post-doc contracts at Duke University (NC, USA) and at the Institute of Transuranium Elements JRC (Karlsruhe, Germany). One member of the Centre staff defended his PhD thesis. The international and national scientific cooperation of the Centre in radiopharmaceutical chemistry was successfully continued and enhanced. The new bi- and multilateral research and development projects make the Centre team a desired partner not only on the national scale but also in the European research area.

Further medals or other prizes have been awarded to the staff of Sol-Gel Laboratory at four international trade shows and exhibitions for their three inventions of new materials.

A significant event for the Centre was the completion (in August 2012) of the PO IG project "Centre for Radiochemistry and Nuclear Chemistry – meeting the needs of nuclear power and nuclear medicine", directed towards modernization of the research infrastructure (laboratories and research equipment) of the Centre, financed from the structural funds of EU and of the Government of Poland. The Centre staff restarted their research activities in the up-to-dated chemical and radiochemical laboratories, with the use of modern research equipment. Among the most important items of this research equipment one may mention:

- coaxial HPGe detector (GX 1080) for gamma spectroscopy, with a multichannel analyser DSA-1000 (Canberra Packard) with Genie 2000 software (detection range – 10-5000 keV);
- automatic gamma counter Wizard 2480 (Perkin Elmer) with an NaI(Tl) detector (detection range – 15-2000 keV);
- alpha spectrometer Alpha Analyst (Canberra Packard) with a semiconductor detector PIPS of the 450 mm^2 active surface, resolution of *ca.* 18 keV, and low-background, equipped with an electrodepositon system;
- two HPLC chromatographs equipped with UV-VIS (VWR HITACHI) and radiometric (GabiStar – Raytest) detectors;
- Cyclone Plus – Storage Phosphor Imaging System (Perkin Elmer) for autoradiographic analysis of TLC strips/plates;
- dose calibrator ATOMLAB 500 (Biodex);
- laminar flow cabinet Mars Safety Class 2 (Scanlaf) for radiochemical syntheses of bioconjugates at microbiological safety;
- double "hot" cell of wall shielding thickness of 60 mm lead with ball tong manipulators (VF, Czech Republic) for safe operation with preparations of high gamma radioactivity, in particular for opening, processing and dispensing samples irradiated in nuclear reactors and/or cyclotrons;
- three glove boxes G(SAFE) – JACOMEX for safe processing α-emitting preparations;
- single crystal X-ray diffractometer (XRD) SuperNova E Dual Source (Agilent Technologies) equipped with a Cryostream 700 system (Oxford Cryosystems);
- mass spectrometer 6560 Accurate-Mass Q-TOF LC/MS (Agilent Technologies), with the electrospray ion source (ESI), the JetStream system, coupled with a liquid chromatograph, used for identification and relative quantification of chemical compounds, from simple organic, organometallic and metal complexes to peptides and proteins;
- spectrometer FTIR Equinox 55 (Bruker) for measuring liquid and solid samples in the range 4000-400 cm^{-1}, equipped with a single-reflection ATR accessory (PIKE Technologies);
- spectrophotometer UV-VIS Nicolet Evolution 600 (Termo Fisher Scientific) for spectral measurements in the range 190-900 nm, equipped with the thermostating Smart Peltier accessory for measurements in the range of 0-100°C;
- two vacuum rotary evaporators Rotavapor R-210 (Büchi);
- freeze dryer ALPHA 2-4 LSC (CHRIST) for lyophilization of various temperature-sensitive chemical and biochemical species to dry preparations;
- thermal analyser SDT Q600 coupled with a FTIR Nicolet iS10 spectrometer (Thermo Scientific) that enables the simultaneous analysis TGA-DTA and the TGA-DSC up to *ca.* 1500°C. The FTIR module enables identification of gases formed during thermogravimetric analysis in the range 7800-350 cm^{-1};
- ashing furnace L5/11/P330 (Nabertherm GmbH) (thermal processes – up to 1100°C);
- automatic high-temperature vacuum furnace VHT 08/18 GR (Nabertherm GmbH) (thermal processes in vacuum or in the atmosphere of a selected gas – up to 1800°C);
- analyser TOC multi N/C 3100 (Analytik Jena) for determination of bound carbon contents.

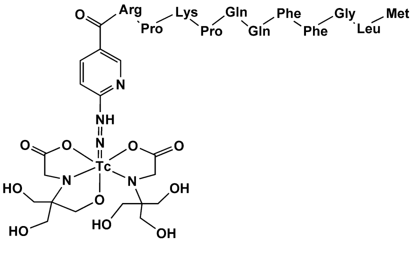
SUBSTANCE P(1-11) LABELLED WITH TECHNETIUM-99m USING ^{99m}Tc(III) AND/OR ^{99m}Tc(V) COMPLEXES

Ewa Gniazdowska, Przemysław Koźmiński, Leon Fuks

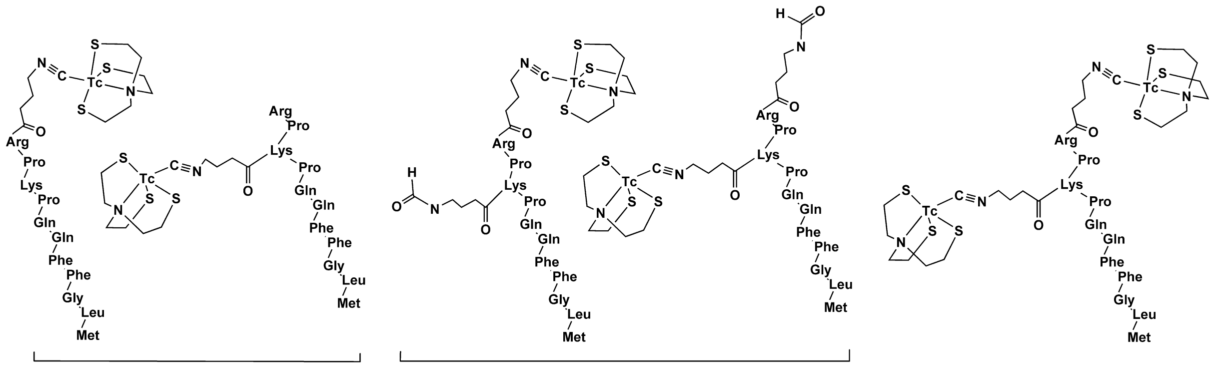
Substance P(1-11), SP, is an undecapeptide belonging to the family of neurokinins termed tachykinins (NKs). It is a mediator responsible for the neural-immune/hematopoietic cross-talk. SP is a preferential endogenous ligand for the neurokinin type 1 receptors (NK-1), which are overexpressed in malignant gliomas [1]. The sequence of the five amino acids Phe^7, Phe^8, Gly^9, Leu^{10} and Met^{11} located at the C-terminus of the SP peptide is responsible for its affinity towards the NK1 receptor (the N-terminal region of SP is not essential) [1]. SP has been already used in diagnostic/therapeutic receptor radiopharmaceuticals as a peptidic vector leading a diagnostic/therapeutic nuclide to the receptors located on the tumour cell surface [2, 3].

The aim of this work was to synthesize conjugates containing Substance P as a biologically active peptide and different mixed-ligand technetium-99m complexes (Fig.1), and to determine and compare their physicochemical properties, important from the radiopharmaceutical point of view.

Four conjugates – ^{99m}Tc-SP complexes – have been prepared on a n.c.a. (no-carrier-added) scale (Fig.1): compound **1** containing Hynic ligand bound to SP, *i.e.* Hynic-SP, and compounds **2a**/**b**, **3a**/**b** and **4** containing ^{99m}Tc-complexes (‘4+1’ type) with a tetradentate tripodal chelator tris(2-mercaptoethyl)-amine, NS$_3$, and a monodentate isocyanide ligand previously coupled with SP, CN-SP.



1. ^{99m}Tc(Hynic-SP)(tricine)$_2$:



2. ^{99m}Tc(NS$_3$)(CN-SP)

3. ^{99m}Tc(NS$_3$)(CN-SP-CHO)

4. (^{99m}Tc(NS$_3$)(CN))$_2$-SP

Fig.1. Conjugates studied in this work.

Substance P and Hynic ligand combined with Substance P, Hynic-SP, were purchased from GeneCust Europe, and tricine – from Sigma-Aldrich. All chemicals were used as obtained.

The tetradentate NS$_3$ ligand (tris(2-mercaptoethyl)-amine; 2,2’,2”-nitrilotriethanethiol) was prepared by the reaction of tris(2-chloroethyl) amine hydrochloride with potassium thioacetate, followed by reduction with LiAlH$_4$. The final product was precipitated as the oxalate salt and applied as such in forthcoming reactions. Details of the synthesis are given in [4].

The monodentate isocyanide ligand (isocyanobutyric succinimidyl ester) used as aliphatic linker CN-BFCA (bifunctional coupling agent) was synthesized according to the procedure described in [5].

CN-SP. Coupling reaction of the isocyanide linker CN-BFCA with Substance P was performed according to the procedure described in [6]. Crude product was purified by the semi-preparative HPLC (high performance liquid chromatography; system 1), then alkalized and lyophilized.

^{99m}Tc(Hynic-SP)(tricine)$_2$. To the solution containing 10 μg (6.7 x 10^{-3} μmol) of Hynic-SP, 20 mg (1.1 x 10^{-4} mol) of tricine and 5 mg of EDDA (2.8 x 10^{-5} mol) in 500 μL of the 0.1 M PBS buffer we simultaneously added 500 μL of a Na^{99m}TcO$_4$ solution (0.9% NaCl eluate from a ^{99}Mo/^{99m}Tc generator, 50-100 MBq) and 5 μL of SnCl$_2$ (5.3 x 10^{-3} M in 0.1 M HCl). The reaction mixture was incubated for 20 min at 90°C, and the reaction progress was checked by HPLC (system 2). The radiochemical yield of the ^{99m}Tc(Hynic-SP)(tricine)$_2$ conjugate was determined to be approximately 98%.

^{99m}Tc(NS$_3$)(CN-SP). In order to label various forms of Substance P with the ‘4+1’ ^{99m}Tc complex, two-step procedure was applied according to [6]. The reaction progress was checked by TLC (thin layer chromatography) and HPLC (system 3) methods. The overall radiochemical yields of ^{99m}Tc(NS$_3$)(CN-SP) were between 85 and 95%.

Conditions of HPLC systems are the following:

- System 1: Phenomenex Jupiter Proteo semi-preparative column (4 μm, 90 Å, 250 × 10 mm), UV/VIS detector (220 nm); elution conditions: solvent A – water with 0.1% TFA (v/v), solvent B – acetonitrile with 0.1% TFA (v/v), gradient – 0-20 min 20 to 80% solvent B, 20-35 min 80% solvent B; 2 ml/min.
- System 2: Supelcosil™ LC-18 HPLC analytical column (250 × 4.6 mm), gamma-radiation detector; elution conditions: solvent A – water with 0.1% TFA (v/v), solvent B – acetonitrile with 0.1% TFA (v/v), gradient – 0-20 min 5 to 70% solvent B, 20-25 min 70 to 95% solvent B; 1 ml/min.
- System 3: Phenomenex Jupiter Proteo analytical column (4 μm, 90 Å, 250 × 4.6 mm), gamma-radiation detector; elution conditions: solvent A – water with 0.1% TFA (v/v), solvent B – acetonitrile with 0.1% TFA (v/v), gradient – 0-20 min 20 to 80% solvent B, 20-35 min 80% solvent B; 1 ml/min.

Thin layer chromatography was performed using silica gel 60 F$_{254}$ TLC aluminum plates (Merck). All radioactive substances were placed on strips, developed with appropriate solutions and dried. Distribution of radioactivity on the strips was determined using an automatic TLC analyser SC-05 (home-made, INCT).

Lipophilicity of the compounds was characterized by determination of the logarithm of their partition coefficients, logD, in the *n*-octanol/PBS (pH 7.40) system, according to the procedure described elsewhere [7, 8].

Stability of the conjugates **1-4** in aqueous solutions containing a great extent of a strongly competing natural ligand (with the thione and/or nitrogen donor atoms, *e.g.* histidine or cysteine), usually present in the biological fluids in excess to the examined species, has been determined in challenge experiments described in [8].

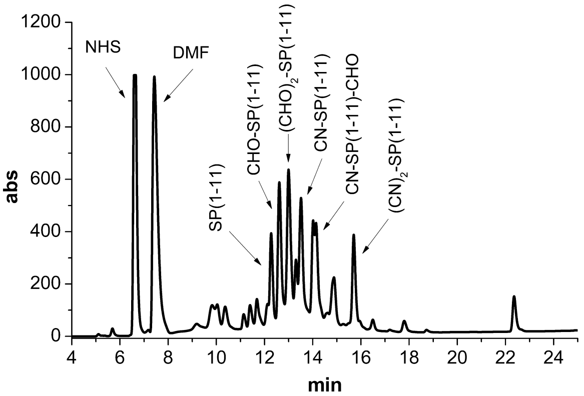


Fig.2. HPLC chromatogram of the reaction mixture resulting from coupling the isocyanide linker CN-BFCA with Substance P.

HPLC chromatogram of the mixture resulting from coupling of the isocyanide linker CN-BFCA with Substance P is shown in Fig.2.

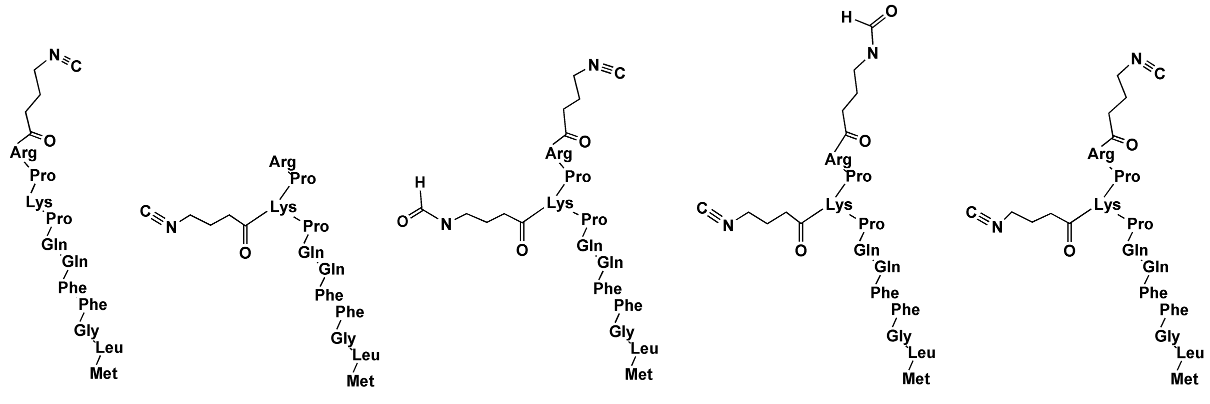
The reaction products (species corresponding to the peaks at R$_T$ of 12.3, 12.7, 13.1, 13.4, 13.6, 14.2 and 15.8 min) have been collected separately and characterized by MS (mass spectrometry) analyses. Basing on these results (Table 1), all species have been identified (Fig.3).

Due to the presence of two primary amine groups in the molecule of Substance P (α-amine group of Arg^1 and ε-amine group of Lys^3), the CN-BFCA linker may react either with one of them or with both amine groups simultaneously [9]. Because of higher reactivity of the α-amine group of Arg^1 than of the ε-amine group of Lys^3 [10, 11], the CN-SP.a product is formed with a higher yield (Fig.3, peak at R$_T$ = 13.6 min) than the product CN-SP.b (Fig.3, peak at R$_T$ = 13.4 min). Reaction mixture may also contain certain amounts of the CHO-BFCA compound, resulting from conversion of the isocyanide group CN- into the aldehyde group CHO- during reaction. As a result, the

Table 1. Results of the MS analyses of the products obtained in the course of coupling of the isocyanide linker CN-BFCA with Substance P.

Compound	RT [min]	MS analyses		Compound structure
		exact mass [g/mol]	found M+H$^+$ [g/mol]	
Substance P R-P-K-P-Q-Q-F-F-G-L-M	12.3	1346	1347.34	R-P-K-P-Q-Q-F-F-G-L-M unreacted peptide
CHO-SP	12.7	1459	1460.65	R(CHO)-P-K-P-Q-Q-F-F-G-L-M* or R-P-K(CHO)-P-Q-Q-F-F-G-L-M*
(CHO)$_2$-SP	13.1	1572	1573.56	R(CHO)-P-K(CHO)-P-Q-Q-F-F-G-L-M*
CN-SP	13.4	1441	1442.33	R-P-K(CN)-P-Q-Q-F-F-G-L-M or R(CN)-P-K-P-Q-Q-F-F-G-L-M
CN-SP	13.6	1441	1442.28	R(CN)-P-K-P-Q-Q-F-F-G-L-M or R-P-K(CN)-P-Q-Q-F-F-G-L-M
CN-SP-CHO	14.2	1554	1555.60	R(CN)-P-K(CHO)-P-Q-Q-F-F-G-L-M or R(CHO)-P-K(CN)-P-Q-Q-F-F-G-L-M
(CN)2-SP	15.8	1536	1537.59	R(CN)-P-K(CN)-P-Q-Q-F-F-G-L-M

* The species inactive in technetium-99m chelating reaction.



CN-SP.a **CN-SP.b** **CN-SP-CHO.a** **CN-SP-CHO.b** **$(CN)_2$-SP**

Fig.3. Different compounds CN-Substance P.

species CHO-SP, CN-SP-CHO and $(CHO)_2$-SP have been formed. However, the two aldehydes, namely CHO-SP (R_T = 12.7 min) and $(CHO)_2$-SP (R_T = 13.1 min), which do not contain the isocyanide group in the molecule, are inactive in respect to labelling with technetium-99m.

The compounds containing one or two isocyanides groups in the molecule, which are necessary for technetium-99m chelation, are shown in Fig.3.

Because the CN-SP.a and CN-SP.b species seem to be similar compounds (each of them contains only one isocyanide group), the difference in their HPLC retention time is only about 0.2 min. Both species make it possible to chelate technetium-99m, *i.e.* to synthesize the conjugate of technetium-99m complexes with the Substance P. Therefore, it is not important which amino group of Substance P (N-terminal α-amine group of Arg^1 or ε-amine group of Lys^3) couples with the CN-BFCA linker. Because both amino acids suitable for complex formation are located outside the biologically active fragment of the peptide, we did not try to solve the problem of peak assignment to the particular species (*i.e.* which of the peaks with the retention time of 13.4 and 13.6 min belongs to CN-SP.a and which to CN-SP.b). The peak at R_T = 14.2 min corresponds either to CN-SP-CHO.a or to CN-SP-CHO.b, *i.e.* to the species containing one isocyanide group and one inactive aldehyde group. The two latter forms, both being suitable for further reactions, are practically undistinguishable in HPLC analysis, although the peak at R_T = 14.2 min is a doublet (Fig.2). The compound $(CN)_2$-SP, corresponding to the peak at R_T = 15.8 min, contains two isocyanide groups (Table 1) and is also suitable for subsequent technetium-99m chelating.

Chromatogram of the reaction mixture, recorded after completing synthesis of the conjugate ^{99m}Tc(Hynic-SP)(tricine)$_2$, is shown in Fig.4. Lipophilicity (expressed in terms of the logD value) and stability of the isolated conjugate are presented in Table 2.

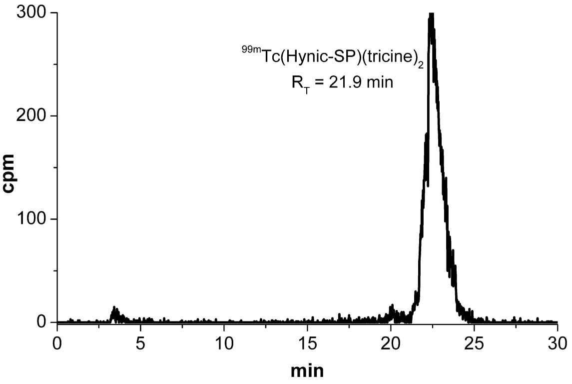


Fig.4. Chromatogram of the reaction mixture, recorded after formation of the ^{99m}Tc(Hynic-SP)(tricine)$_2$ conjugate had been completed.

For the syntheses of the conjugates of the '4+1' technetium-99m complex with the Substance P, the tetradentate tripodal chelator (tris(2-mercaptoethyl)-amine, NS_3) and the monodentate isocya-

Table 2. Lipophilicity and stability of the conjugates ^{99m}Tc(Hynic-SP)(tricine)$_2$, ^{99m}Tc(NS_3)(CN-SP), ^{99m}Tc(NS_3)(CN-SP-CHO) and (^{99m}Tc(NS_3)(CN))$_2$-SP.

Conjugate	RT [min]	logD oct/PBS (pH 7.40)	% of intact complexes after 20 h		
			PBS (pH 7.4)	cysteine 10^{-2} M	histidine 10^{-2} M
^{99m}Tc(Hynic-SP)(tricine)$_2$ (**1**)	21.9 (system 2)	-3.7 ± 0.3	~97	~99	~100
^{99m}Tc(NS_3)(CN-SP) (**2**)	12.7 (system 3)	-0.24 ± 0.02	~99	~99	~100
^{99m}Tc(NS_3)(CN-SP-CHO) (**3**)	12.9 (system 3)	-0.20 ± 0.01	~100	~100	~100
(^{99m}Tc(NS_3)(CN))$_2$-SP (**4**)	13.1 (system 3)	0.89 ± 0.02	~98	~98	~100

nide CN-BFCA ligand, previously coupled with the SP biomolecule, were used. The NS_3 molecule coordinates the ^{99m}Tc(III) cation and leaves the fifth coordination site available for one monodentate isocyanide ligand: CN-SP, N-SP-CHO or $(CN)_2$-SP. Chromatograms of the reaction mixtures, recorded after syntheses of the conjugates containing the ^{99m}Tc(III) cation, NS_3 species, and one isocyanide ligand, are presented in Fig.5. Lipophilicity and stability of the isolated conjugates are presented in Table 2.

The peaks recorded at R_T = 3.4 and 7.9 min (Fig.5) correspond to the intermediate complexes ^{99m}Tc(EDTA/mannitol) and ^{99m}Tc(NS_3), respectively.

The data presented in Table 2 show that the conjugate ^{99m}Tc(Hynic-SP)$(tricine)_2$ (**1**) is much more hydrophilic than the conjugates containing the ^{99m}Tc(NS_3) core (**2**-**4**). Among the last three conjugates, the logD value for compound **4** (which contains two technetium(III)-99m complexes in the molecule) is significantly higher than the corresponding values for **2** and **3**. Moreover, lipophilicity of ^{99m}Tc(NS_3)(CN-SP) (**2**), ^{99m}Tc(NS_3)(CN-SP-CHO) (**3**) and (^{99m}Tc(NS_3)(CN)$)_2$-SP (**4**) conjugates can easily be modified by introduction of either hydrophilic or hydrophobic group at the periphery of the NS_3 ligand [12].

Studies on stability of the isolated conjugates **1-4** show that despite comparatively high concentrations of interfering ligands (10 mM), the investigated technetium conjugates (present in solution in concentration of about 10^{-4} mM) do not undergo a detectable ligand exchange, neither by histidine nor by cysteine. After 16 h of incubation only trace amounts ($\leq$ 2%) of transchelation products were observed on the HPLC chromatograms.

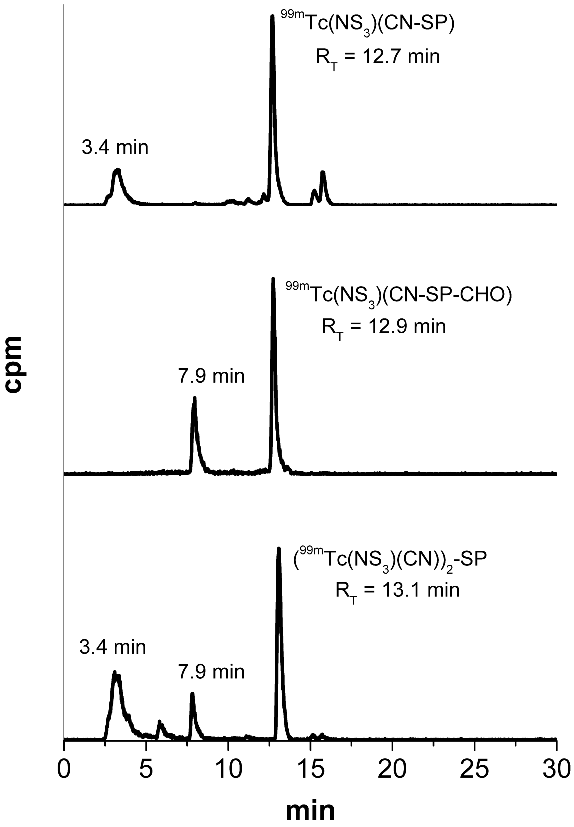


Fig.5. Chromatograms of reaction mixtures, recorded after syntheses of the conjugates ^{99m}Tc(NS_3)(CN-SP), ^{99m}Tc(NS_3)(CN-SP-CHO) and (^{99m}Tc(NS_3)(CN)$)_2$-SP.

All the synthesized conjugates of technetium-99m complexes with substance P are formed with high yields (> 85%) and are very stable in the presence of competitive cysteine/histidine ligands. Comparing the physicochemical properties of the conjugate containing ^{99m}Tc-Hynic complex and conjugates containing technetium-99m complexes of the ‘4+1’ type (tetradentate tripodal chelator tris(2-mercaptoethyl)-amine and monodentate isocyanide ligands) one can conclude that technetium-99m complexes of type ‘4+1’ are good radiopharmaceutical precursors. It also follows from this study that the new conjugates ^{99m}Tc(NS_3)(CN-SP), ^{99m}Tc(NS_3)(CN-SP-CHO) and (^{99m}Tc(NS_3)(CN)$)_2$-SP can be considered to be promising candidates for diagnostic radiopharmaceuticals. Moreover, the conjugate (^{99m}Tc(NS_3)(CN)$)_2$-SP containing two technetium-99m complexes in the molecule can be expected to be a very efficient receptor radiopharmaceutical.

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CYCLOTRON PRODUCTION OF ^{43}Sc ON NATURAL CALCIUM CARBONATE TARGET

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Personalized medicine requires theranostic approach which for nuclear medicine means the use of radioisotopes of the same element for diagnostics and therapy to maintain the same pharmacological properties of the injected radiopharmaceuticals. There are only a few elements that fulfil this requirement, and scandium is among them. Currently, increasing attention is focused on the production of its two radioisotopes: ^{47}Sc, which demonstrates therapeutic effect by emitting soft β^--particles, and ^{44}Sc – a prospective PET radioisotope. However, there is the third scandium radioisotope – ^{43}Sc, which may find application in diagnostics, because of its better nuclear properties than those of ^{44}Sc, like lower maximum energy of β^+-particles and lower energy of emitted γ-rays (Table 1). The first aim of our study was to choose the most convenient production method of ^{43}Sc.

Table 1. Comparison of nuclear properties of ^{44}Sc and ^{43}Sc.

Isotope	^{44}Sc	^{43}Sc
$T_{1/2}$	3.97 h	3.89 h
β^+-emission	95%	88%
$E_\beta$max	1.47 MeV	1.20 MeV
Main γ-ray [keV]	1157.0 (99%)	372.8 (23%)

There are several nuclear reactions that can be used to produce ^{43}Sc. One possibility is to use proton beam for bombardment of enriched calcium carbonate targets. The first option is the (p,n) reaction on enriched ^{43}CaCO$_3$, but the natural abundance of ^{43}Ca is less than 0.2%. The second one is the (p,2n) reaction on enriched ^{44}CaCO$_3$, but it requires proton energy higher than the energy available for common medical cyclotrons, and the reaction cross section is lower than that of the first one [1]. Nevertheless, these methods can give the highest activities of ^{43}Sc, because the accessible proton beam current in common cyclotrons is several times higher than those of other charged particles. On the contrary, the cost of highly enriched targets together with relatively low cross sections, compared to the ^{44}Ca(p,n)^{44}Sc reaction [1], result in low profitability and competitiveness of these methods.

Reduction of the production cost is possible when using natural potassium or calcium carbonate as the target material, however, the α-particle beam is necessary in these cases. Natural abundance of ^{41}K is higher than 6.5% and gives an opportunity to prepare cheap and thick targets. Also the cross section of the ^{41}K(α,2n)^{43}Sc reaction is sufficient, above 200 mb [1, 2]. However, the cross section of the ^{40}Ca(α,p)^{43}Sc reaction is much higher and lower energy α-particles are required (Table 2). The second aim of our study was to optimize irradiation conditions for ^{43}Sc production in the ^{nat}Ca(α,x)^{43}Sc reaction using thick targets.

Ultra-pure CaCO$_3$ (99.99%) was purchased from Merck (USA), and it was used as the target material. Irradiations were performed using the Scanditronix MC 40 cyclotron at the European Commission Joint Research Centre (Ispra, Italy). The samples were irradiated in aluminium capsules with an inner diameter of 10 mm. The capsule was inserted in a holder that allowed air cooling from front and water cooling from the rear side. The target material was prepared as pellets of 100 mg of CaCO$_3$, 10 mm in diameter and of 375 μm thickness, wrapped into an aluminium foil of 25 μm thickness.

Alpha-particles in the energy range of 14.8-35.0 MeV at a current of 0.5 or 1 μA were used for bombardment to define the yield of thick-target production yield of ^{43}Sc. The effective energies on the CaCO$_3$ targets, determined with the calculation code SRIM, ranged from 13.2 to 34.2 MeV. The radioactivity of ^{43}Sc and of other radionuclides obtained was measured by γ-ray spectrometry using a high-purity germanium (HPGe) detector. For quantification, the well resolved γ-ray peaks were chosen: at 372.81 keV for ^{43}Sc, at 1157.00 keV for ^{44}Sc, at 271.24 keV for ^{44m}Sc, and at 159.38 keV for ^{47}Sc.

There are two channels of the reaction of calcium with α-particles. The primary one is the di-

Table 2. Comparison of several methods for ^{43}Sc production.

Reaction	Target material	Energy [MeV]	Cross section [mb]
^{40}Ca(α,p)^{43}Sc	^{40}CaCO$_3$ (96.9%)	12.1 13.1	605 [1] 949 [3]
^{41}K(α,2n)^{43}Sc	^{41}K$_2$CO$_3$ (6.73%)	24.2 26.4	220 [1] 256 [2]
^{43}Ca(p,n)^{43}Sc	^{43}CaCO$_3$ (0.14%)	9.5	309 [1]
^{44}Ca(p,2n)^{43}Sc	^{44}CaCO$_3$ (2.09%)	22.2	170 [1]

rect $^{40}Ca(\alpha,p)^{43}Sc$ reaction and the secondary is an indirect route through ^{43}Ti which is produced in the $^{40}Ca(\alpha,n)^{43}Ti$ reaction and decays at once ($T_{1/2}$ = 0.51 s) to ^{43}Sc. It is difficult to experimentally distinguish, which route is the main one, however TALYS calculations show that the difference in the cross section for both reactions is approximately 1:45, and the calculated reaction yield is approximately 300 times higher for the first channel, so the contribution to the final activity from the second is not significant.

The analysis of the results obtained from the optimization studies showed that in the range of α-particle energy on the target material of 23.9-29.0 MeV, the production yield reached the plateau of about 100 MBq/μA·h (Table 3). Radionuclide purity of the obtained ^{43}Sc was higher than 99.8%. There were found some impurities of ^{44}Sc and ^{44m}Sc, which were below 0.1%, and of ^{47}Sc below 0.02%. These contaminating radionuclides were produced in the following nuclear reactions: $^{42}Ca(\alpha,pn)^{44}Sc$, $^{42}Ca(\alpha,pn)^{44m}Sc$ and $^{44}Ca(\alpha,p)^{47}Sc$.

The yield of thick target production is sufficient to obtain the activity of ^{43}Sc necessary for preparing several doses of ^{43}Sc-based radiopharmaceuticals. However, further investigation is required, especially on the thermal stability of the target material. The next step of this work is the development of a simple, fast and efficient separation method of ^{43}Sc from the target material used, and the confirmation of high labelling yield of one of the model DOTA-peptides.

Table 3. Yield of ^{43}Sc production in the nuclear reaction $^{40}Ca(\alpha,p)^{43}Sc$, as a function of the energy of α-particles on the target material. The optimum energies are marked in bold.

α-particle energy [MeV]	α-particle energy on target [MeV]	^{43}Sc [MBq/μAh]
14.8	13.2	16.9
20.0	18.7	48.7
25.0	**23.9**	**102.2**
27.5	**26.5**	**102.5**
30.0	29.0	98.8
35.0	34.2	51.6

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NEW TECHNOLOGY FOR PRODUCTION OF YTTRIUM OXIDE MICROSPHERES

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According to the global statistics relating to the diagnosed cases of liver malignant tumours, there are a million such cases a year. Primary liver tumours (hepatocellular carcinoma HCC and cholangiocarcinoma) belong to the most common tumours. In the event they are diagnosed, the survival factor among the patients is low. The methods used to fight tumours include surgical intervention, chemotherapy and radiotherapy. Unfortunately, both external radiotherapy and chemotherapy impact not only the tumour lesions but also destroy the sound neighbouring tissue in the human body.

The concept of intra-arteriol administration of radioactive microspheres is based on their preferable lodging in the vasculature of the tumour, after which the β^- radiation from ^{90}Y ($T_{1/2}$ = 2.67 d) damages and eliminates the tumour tissue. This idea was first explored by Blanchard *et al.* who injected glass microspheres labelled with yttrium-90 into the hepatic artery of tumour bearing rabbits. The results appeared promising – reduction of tumour size was found for all the ^{90}Y treated animals. The first clinical trials were carried out on selected patients, using the transcatheter radioembolization technique, in the mid-1980s [1-4]. This therapeutic method is currently applied in various nuclear medicine centres; but it is still scarce in Poland due to its very high costs. Microspheres of two types have been commercially manufactured: TheraSphere (ion-exchange resin loaded with radioyttrium; diameter 20-60 μm) and SIR-Spheres (glass with radioyttrium in matrix; 20-30 μm), which differ in their radioactivity per sphere and embolic effect.

Attempts were undertaken at this Centre, to develop a new type of yttrium microspheres by elaborating a less expensive sol-gel method for production of yttrium oxide beads, followed by their neutron irradiation in a nuclear reactor, which would result in the activation of natural yttrium in the nuclear reaction $^{89}Y(n,\gamma)^{90}Y$. This new technology for the production of spherical particles of yttrium oxide has been developed by the present authors [5] who used a combination of two methods: a variant of complex sol-gel process (CSGP) [6] with the ICHTJ (INCT) variant of sol-process [7].

The first step of the method consisted in the formation (from high purity products) of complex solution yttrium-nitrate-ascorbate sol by the addition of ascorbic acid – a very strong complexing agent – the salient feature of the CSGP process [6] – and then alkalization of the solution with

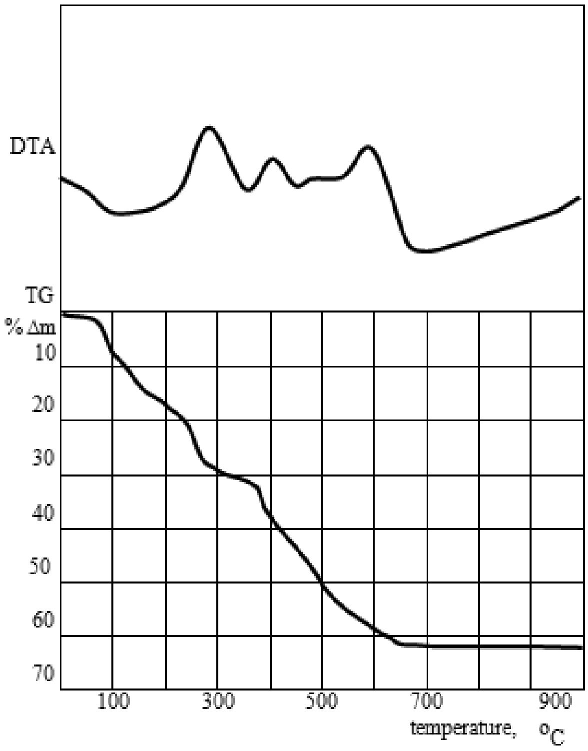

Fig.1. Thermal analysis (TG, DTA) of yttrium-nitrate-ascorbate gel.

aqueous ammonia to pH 7. In the second step, this sol was used as a substrate in the gelling procedure by variant ICHTJ process [7]), and finally the gel obtained underwent non-destructive thermal treatment. The beads of yttrium-nitrate-ascorbate gel were annealed, according to the temperature diagram obtained as a result of thermal analysis – TG, DTA (Fig.1). A special procedure for thermal treatment had to be followed to obtain homogeneous and non-destructed microspheres. Low heating rate of 2°C/min was applied for 4 h, until the temperature of 200°C had been reached, when ammonium nitrate decomposed, and water completely evaporated. The final thermal treatment step included heating the beads at 650°C with the same low rate for 2 h. Figure 2 shows the photographs of the obtained Y_2O_3 microspheres of the diameters below 50 μm, required for radioembolization. The SEM images show that the thermal treatment does not damage the crystallite structure of the beads.

A 7.7 mg sample of Y_2O_3 microspheres was irradiated in the research nuclear reactor MARIA in the thermal neutrons flux of 1.7×10^{14} n cm^{-2} s^{-1} for 10 h. The activity after 10 h cooling was equal to 1.3 GBq (4.53 mCi/g Y_2O_3). Radionuclide purity of the sample (^{90}Y) was 99.0% (no radioactive impurities were found).

The radioactive microspheres obtained will be subjected to leaching tests in aqueous solutions, including serum, and then – to preclinical trials.

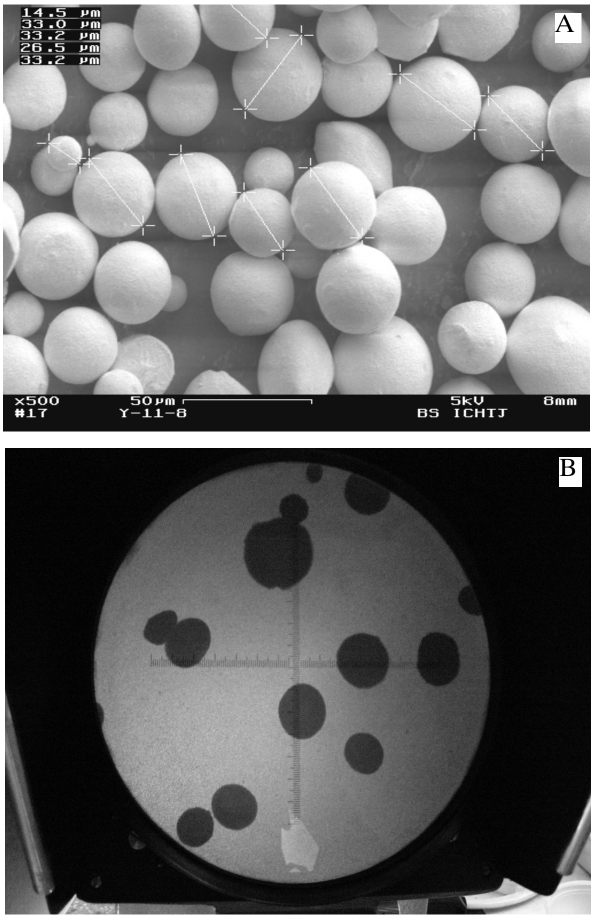

Fig.2. SEM of Y_2O_3 microspheres (A) and a photograph of Y_2O_3 microspheres (B).

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TRICARBONYLRHENIUM(I) COMPLEXES WITH N-METHYL-2-PYRIDINECARBOXYAMIDE – SYNTHESIS AND MOLECULAR STRUCTURE

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In the present studies originating from our interest in the chemistry of tricarbonyl compounds of rhenium(I) and technetium(I) with different coordination environments as potential precursors of radiopharmaceuticals [1, 2] we have examined N-methyl-2-pyridinecarboxyamide (LH) as a bidentate ligand in order to study the influence of the sixth monodentate ligand on the formation of resulting rhenium(I) complexes.

N-methyl-2-pyridinecarboxyamide is the amide derivative of picolinic acid. Its molecule contains three potential donor atoms: nitrogen atom of aromatic ring, oxygen atom of carbonyl group and nitrogen atom of amide part. In spite of that, the only possible is the bidentate way of complexation with metal ions.

Synthesis and structures of two tricarbonyl complexes of rhenium(I) with the bidentate ligand N-methyl-2-pyridinecarboxyamide and either iodide anion or monodentate 3,5-dimethylpyrazole (dmpz) molecule are presented in this work. The formation of two other similar complexes with N-methyl-2-pyridinecarboxyamide ligand and bromide anion or imidazole (im) molecule was described earlier [3, 4]. The structures of $[\mathrm{Re(CO)_3LH_{NO}I}]$ (**1**) and $[\mathrm{Re(CO)_3L_{NN}(dmpz)}]$ (**2**) compounds (Figs.1 and 2) were determined by single crystal X-ray diffraction on an Agilent Technologies SuperNova (dual) diffractometer equipped with an Eos CCD detector, using mirror-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) at a temperature of 100 K.

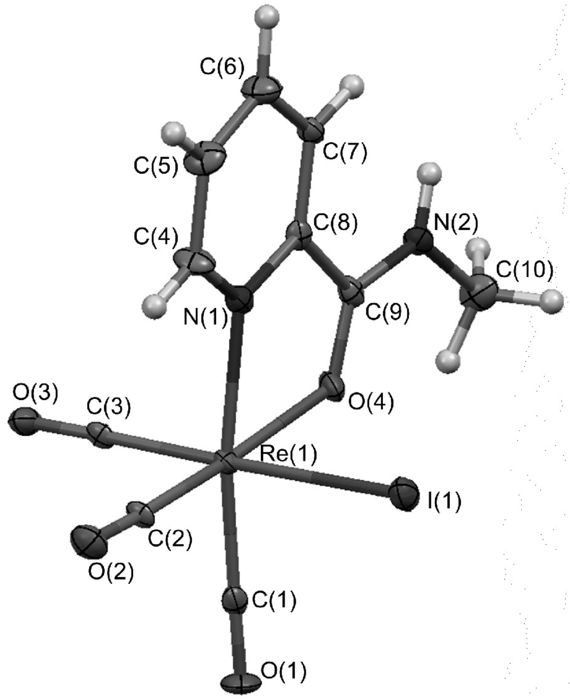

Fig.1. Molecular structure of $[\mathrm{Re(CO)_3LH_{NO}I}]$ (**1**). Selected bond lengths [Å] and angles [°]: Re(1)-C(1) 1.928(8), Re(1)-C(2) 1.895(7), Re(1)-C(3) 1.920(8), Re(1)-O(4) 2.163(5), Re(1)-N(1) 2.180(7), Re(1)-I(1) 2.7969(6), N(1)-Re(1)-O(4) 74.2(2), N(1)-Re(1)-I(1) 84.46(17), I(1)-Re(1)-O(4) 85.54(15), C(1)-Re(1)-C(2) 89.3(3), C(1)-Re(1)-C(3) 90.5(3), C(2)-Re(1)-C(3) 89.8(3).

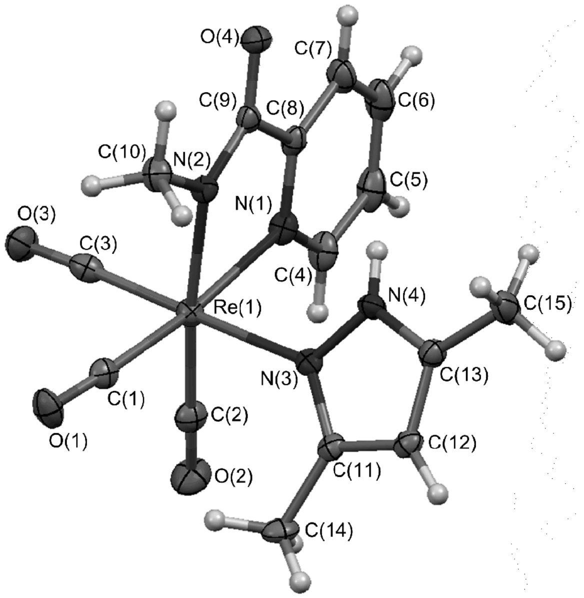

Fig.2. Molecular structure of $[\mathrm{Re(CO)_3L_{NN}(dmpz)}]$ (**2**). Selected bond lengths [Å] and angles [°]: Re(1)-C(1) 1.910(4), Re(1)-C(2) 1.924(4), Re(1)-C(3) 1.911(4), Re(1)-N(1) 2.171(3), Re(1)-N(2) 2,153(3), Re(1)-N(3) 2.213(3), N(1)-Re(1)-N(2) 74.76(12), N(1)-Re(1)-N(3) 88.00(11), N(2)-Re(1)-N(3) 85.36(11), C(1)-Re(1)-C(2) 89.77(16), C(1)-Re(1)-C(3) 86.03(15), C(2)-Re(1)-C(3) 87.93(15).

The first complex was synthesized by addition of KI to the refluxing water/methanol solution of $\mathrm{Re(CO)_5Br}$ with N-methyl-2-pyridinecarboxyamide, after previous precipitation of AgBr by means of $\mathrm{AgNO_3}$. Yellow crystals of $[\mathrm{Re(CO)_3LH_{NO}I}]$ were grown during storing the solution at room temperature within a few days. In the reaction of $[\mathrm{Re(CO)_3LH_{NO}Br}]$ synthesized earlier [3, 4] with 3,5-dimethylpyrazole in hot water/methanol solution, the first compound was transformed into $[\mathrm{Re(CO)_3L_{NN}(dmpz)}]$ complex which was obtained in the form of yellow crystals after about a year.

The structure of tricarbonylrhenium(I) complex with the bidentate LH ligand and a iodide anion is presented in Fig.1. The metal ion is surrounded by six donor atoms including three carbon atoms, one nitrogen, one oxygen and one iodine atom in a slightly distorted octahedral geometry. Three CO ligands are directed into the facial position of this octahedron. N-methyl-2-pyridinecarboxyamide behaves in **1** as a neutral ligand ($\mathrm{LH_{NO}}$) which chelates the rhenium(I) ion by means of nitrogen and oxygen atoms, forming a five-membered ring. The sixth coordination position of the metal ion is occupied by iodide anion what makes the molecule of [Re(CO)$_3$LH$_{NO}$I] complex neutral. Structures similar to **1** were reported earlier for similar complexes with chloride and bromide ions, [Re(CO)$_3$LH$_{NO}$Cl] [5] and [Re(CO)$_3$LH$_{NO}$Br] [3, 4], respectively.

In the structure of tricarbonylrhenium(I) complex with the same bidentate ligand and the monodentate 3,5-dimethylpyrazole (Fig.2) the metal ion is hexa-coordinated with three Re-C and three Re-N bonds. On the contrary to [Re(CO)$_3$LH$_{NO}$X] (X = Cl, Br, I) compounds, N-methyl-2-pyridinecarboxyamide in **2** and in [Re(CO)$_3$L$_{NN}$(im)] [3, 4] behaves as monoanionic ligand (L$_{NN}$) after loosing of the amide proton and forms a five-membered chelate ring upon attachment to the rhenium(I) ion through the N atom of aromatic ring and the N atom of amide group. The sixth coordination site around the metal centre is occupied by the N atom of 3,5-dimethylpyrazole molecule. Finally, the [Re(CO)$_3$L$_{NN}$(dmpz)] complex is neutral, similarly to [Re(CO)$_3$L$_{NN}$(im)].

The new structures of tricarbonylrhenium(I) complexes have the octahedral arrangements of donor atoms around the metal ion and the fac-[Re(CO)$_3$]$^+$ core. The three remaining sites are occupied by chelating ligand and monodentate ligand, what results in the so-called ‘2+1’ system. All the described and mentioned herein structures of complexes obtained result from the flexidentate behaviour of N-metylo-2-pyridinecarboxyamide ligand which coordinates either as a neutral *N*,*O*-donor in [Re(CO)$_3$LH$_{NO}$X] (X = Cl, Br, I) or as a monoanionic *N*,*N*-donor in [Re(CO)$_3$L$_{NN}$(dmpz)] and [Re(CO)$_3$L$_{NN}$(im)]. A similar behaviour in the formation of metal chelates was also observed for other amide ligands derived from picolinic acid, with the formula NC$_5$H$_4$-CO-NH-C$_6$H$_5$X (X = H, Cl, CH$_3$,) [6-9].

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SELECTIVITY OF BIS-TRIAZINYL BIPYRIDINE LIGANDS FOR AMERICIUM(III) IN Am/Eu SEPARATION BY SOLVENT EXTRACTION

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Selective separation of actinide elements from highly radioactive nuclear waste is a key issue for modern technologies of nuclear waste reprocessing. Partitioning of long-lived minor actinides, in particular americium, followed by their transmutation to short-lived radionuclides would lead to a significant reduction of long-term environmental hazard from this radiotoxic waste, and contribute to the development of safe nuclear power. Derivatives of 6,6’-bis([1,2,4]-triazin-3-yl)-2,2’-bipyridine (BTBP), tetra-N-dentate ligands that selectively extract trivalent actinides (An) over lanthanide fission products (Ln) from nitric acid solutions to organic solvents, have been considered the most promising species for hydrometallurgical recovering (partitioning) the minor actinides from high-level radioactive waste [1]. The problem of selectivity of moderately soft (HSAB concept) aromatic N-donor ligands for actinides over lanthanides was broadly studied with respect to various heterocyclic poly-N-dentate extractants, mainly BTBPs and their tridentate analogues – bis-triazinyl-pyridine derivatives (BTP) [1-3].

Quantum mechanical (QM) calculations on the BTP and BTBP complexes generally support the experimental conclusion on the somewhat higher covalency of the An–N than Ln–N bonds, albeit the question of participation in the bonding of certain metal orbitals remains controversial, and the origin of the actinide selectivity of aromatic N-donor ligands has not been clearly explained yet [3]. The aim of the present theoretical studies was to identify the major factors that influence the actinide selectivity of fairly soft BTBP ligands, and to shed more light on the origin of this selectivity.

Various complexes of An^{III} and Ln^{III} with BTBP ligands, of the 1:1 and 1:2 metal-to-ligand mole ratios. coexist in the organic phase of liquid-liquid extraction systems, and their relative amounts depend on the concentrations of metal, ligand and HNO$_3$, as well as on the diluent [4-6]. The present theoretical study, using the density functional theory method, was carried out on two kinds of the extractable americium(III) and europium(III) complexes with the 6,6’-bis-(5,6-diethyl-1,2,4-triazin-3-yl)-2,2’-bipyridine ligand (C2-BTBP or L;

Fig.1): heteroleptic neutral $[ML(NO_3)_3]$ and homoleptic cationic $[ML_2]^{3+}$, whose symmetric molecular structures were successfully optimized. The optimization process failed, however, for the $[ML_2(NO_3)]^{2+}$ complexes of very irregular, asymmetric structures, for which it was not possible to get convergence of the SCF wavefunction in a reasonable time.

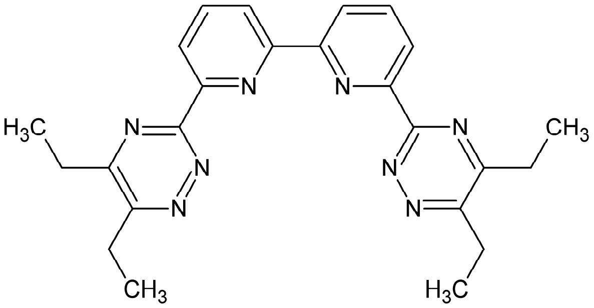

Fig.1. Structure of C2-BTBP ligand (conformation as in the complexes).

The structures were optimized at the B3LYP/6-31G(d) level, and total energies of the complexes in various media were estimated using single point calculations performed at the B3LYP/6-311G(d,p) level of the theory. The americium and europium ions were treated using pseudo-relativistic Stuttgard-Dresden effective core potentials and the accompanying basis sets. The computational details and preliminary results, also on metal-ligand bonding analysis, have already been reported [7, 8]. To check the correctness of the energy calculations at the B3LYP/6-311G(d,p) level of theory, we carried out additional calculations on the 1:1 complexes and hydrated metal ions at the correlated *ab initio* Moller-Plesset second order perturbation level of theory, using all electrons MP2/6-311G(d,p) level [9]. In this report we summarize the results obtained, and present the final conclusions.

The measure of selectivity in solvent extraction separation of two metal ions, Am^{III} and Eu^{III}, is the separation factor, $SF_{Am/Eu} = D_{Am}/D_{Eu}$, where D_M is the distribution ratio of the M ion:

$$-RT \ln SF_{Am/Eu} = \Delta G_{ex}(Am) - \Delta G_{ex}(Eu) = \Delta(\Delta G_{ex})_{Am/Eu}$$

where: ΔG_{ex} – the total change of Gibbs free energy in the extraction process, R – the gas constant, T – absolute temperature. For the sake of thermodynamic analysis, one may decompose the process of liquid-liquid extraction of metal ions into two main steps: (i) formation of the metal complex in the aqueous phase; and (ii) the transfer of the formed complex from the aqueous to the organic phase (partition step). The equilibrium constants of these two reactions are: (i) stability constant of the complex, β_i, and (ii) partition constant of the complex, P_i. In the systems where a few extractable species contribute to the D_M values, $SF_{Am/Eu}$ becomes a complex function of weighted contributions from their β_i and P_i values [9].

Table 1 presents the differences in the computed energies of complex formation, and of partition of these complexes in two systems water/organic solvent. The use of $\Delta(\Delta E)_{Am/Eu}$ values instead of $\Delta(\Delta G)_{Am/Eu}$ ones is justified only when the entropy changes in the reactions of formation of Am^{III}-BTBP complexes and of their liquid-liquid partition are equal to those of the corresponding Eu^{III} species; there are numerous indications that this is the case in the system studied [9]. Therefore, the $\Delta(\Delta E)_{Am/Eu}$ values calculated with the extended 6-311G(d,p) basis set (Table 1) were used to analyse the effects of the two major steps of extraction on the selectivity of Am/Eu separation.

Selectivity in solvent extraction separation of two metal ions is a cooperative function of contributions from all extractable metal complexes, depending on physicochemical properties of each individual complex and on its relative amount in the system. The negative $\Delta(\Delta E_{cf})_{Am/Eu}$ values for the two pairs of Am and Eu complexes in water (and probably the same for the $[M(C2\text{-}BTBP)_2(NO_3)]^{2+}$ pair [9]) mean that the Am complexes are more stable than their Eu counterparts. This difference, in line with a greater covalency of Am–L than Eu–L bonds (as concluded from bonding analysis, see below), is most likely the main reason of the observed selectivity of BTBP ligands for americium(III) in the separation processes.

The other potential reason of the selectivity, the differences in the lipophilic properties of the Am/Eu complexes, reveals at their liquid-liquid partition. The opposite signs of $\Delta(\Delta E_{part})_{Am/Eu}$ values for the two pairs of complexes, with the energies calculated for aqueous and organic media (PCM), show that the effect is more differentiated, therefore partition term influences the selectivity of

Table 1. Differences in the energies [kJ mol⁻¹] of complex formation (ΔE_{cf}) in the gas phase and in water (the $[M(OH_2)_9]^{3+}$ ions are the substrates), calculated using B3LYP/6-311G(d,p) and MP2/6-311G(d,p) methods, and in the energies of partition (ΔE_{part}) and extraction (ΔE_{ex}) from water to octanol and to trichloroethane (TCE), calculated using B3LYP/6-311G(d,p), for the two pairs of Am and Eu C2-BTBP complexes. The $\Delta(\Delta E_i)$ symbols denote the respective $\Delta(\Delta E_i)_{Am/Eu}$ values [9].

Phase	$\Delta(\Delta E_{cf})$		$\Delta(\Delta E_{part})$	$\Delta(\Delta E_{ex})$	$\Delta(\Delta E_{part})$	$\Delta(\Delta E_{ex})$
	B3LYP	MP2	water → octanol		water → TCE	
$[M(C2\text{-}BTBP)(NO_3)_3]$						
Gas	-10.2	-30.8	-	-	-	-
H_2O	-20.7	-43.1	-9.1	-29.8	-8.9	-29.6
$[M(C2\text{-}BTBP)_2]^{3+}$						
Gas	+11.2	-	-	-	-	-
H_2O	-11.2	-	+11.0	-0.2	+11.0	-0.2

Am/Eu separation, $\Delta(\Delta E_{ex})_{Am/Eu}$, to a lesser extent.

In order to understand the origin of the selectivity in separating Am^{III} from Eu^{III} ions with the use of BTBP ligands as the extractants, theoretical analysis of the metal-ligand bonding in the studied complexes was done, based on electronic structures of the species. It was addressed toward explaining the character of the metal-ligand bonds and defning the atomic orbitals (AO) of both metal ions, that mainly contribute to the covalency of these bonds. Three independent approaches were used in the bonding analysis: (1) quantum theory of atoms in molecules (QTAIM) [10], (2) canonical, molecular orbital (CMO) [11], and (3) natural bond orbital (NBO) [12] analyses. The details and preliminary results have been presented elsewhere [7, 8].

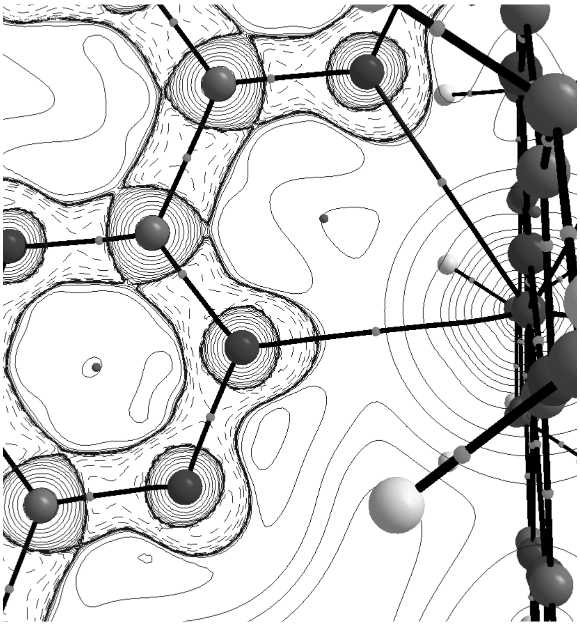

Fig.2. Contour plot of Laplacian ($\nabla^2\rho$) of electron density in the region between the central metal ion and nitrogen donor atoms in the $[Am(C2\text{-}BTBP)_2]^{3+}$ complex. Dashed lines represent negative $\nabla^2\rho$ values (charge concentration), while solid lines – positive $\nabla^2\rho$ values (charge depletion).

Figure 2 (QTAIM) presents the contour plot of the Laplacian ($\nabla^2\rho$) of electron density in the region between the central metal ion and nitrogen donor atoms in the $[Am(C2\text{-}BTBP)_2]^{3+}$ complex. Low electron densities at the bond critical points (dots on the bond paths) of the M–N bonds, less than 0.05 a.u., indicate mainly ionic character of the Am–N and Eu–N bonds, with a certain covalent contribution. This conclusion has been confirmed by the very small values of M–N bond orders (BO) in the $[M(C2\text{-}BTBP)_2]^{3+}$ complexes [8]. The bond orders related to single M–N$_{tr}$ and M–N$_{py}$ bonds in the $[M(C2\text{-}BTBP)_2]^{3+}$ molecules, calculated within the NBO methodology (NLMO approach), are equal to 0.30 and 0.28 for Am, and 0.26 and 0.24 for Eu, respectively, whereas the corresponding QTAIM values – delocalization indexes between M and N atoms, DI(M,N) are equal to 0.16 and 0.15, and 0.12 and 0.11, respectively. The calculated electron densities at the BCPs, ρ_b, of the M–N bonds [8] follow the same trend. The same relationships for the M–N bond orders and the BCP electron densities have been observed in the $[M(C2\text{-}BTBP)(NO_3)_3]$ complexes, though their numerical BO and ρ_b values are lower [7].

All these data point to the larger covalencies of: (i) M–N bonds in the Am than Eu BTBP complexes, and (ii) M–N$_{tr}$ than M–N$_{py}$ bonds in the complexes. This remains in agreement with the results of charge distribution analyses (NBO/NPA and QTAIM) [7, 8]. The positive charges on the central metal ions (Table 2), much smaller than the nominal values of +3, show a significant donation of the electron density from BTBP ligands to the metal ions. The charge on the central Am^{III} ion, lower than that on Eu^{III}, indicates that more electron density was donated from the ligands in the Am complex, which (with the more negatively charged nitrogen donor atoms in the Eu complex) makes the Am–N bonds more covalent than Eu–N ones.

Natural electronic configurations of Am and Eu ions in the $[M(C2\text{-}BTBP)_2]^{3+}$ (Table 2) and $[M(C2\text{-}BTBP)(NO_3)_3]$ [7] complexes (NBO analysis) give information on the atomic orbitals of the metal ions that considerably contribute to the covalency of the M–N bonds. Significant differences have been observed in the electron populations of particular valence and virtual (Rydberg type) AOs of Am^{III} and Eu^{III}. Further studies were carried out, within CMO and NBO, to examine this in details.

The results of Mulliken overlap population analysis of the $[M(C2\text{-}BTBP)_2]^{3+}$ complexes made it possible to select the bonding molecular orbitals (MO) with a significant overlap between the AOs of each M^{III} ion and AOs of the BTBP ligands. However, the overlap values are very small for both metals, and the MOs with a significant overlap have mostly a ligand character: 91÷98% in the Am complex and 94÷97% in the Eu one. This is another confirmation that the M–N bonds in both complexes are mainly of ionic character. The percentage contributions from AOs are estimated from the Mulliken analysis of the coefficients of AOs contribution, c_{ri}, to particular MOs. Ten MOs with $c_{ri} > 0.01$ have been found in the Am^{III} and six in Eu^{III} complexes. The overlap of the orbitals of the

Table 2. Natural charges and natural electronic configurations of Am and Eu ions in the $[M(C2\text{-}BTBP)_2]^{3+}$ complexes, calculated using NBO 5.0 methodology.

M	Natural charge	Number of electrons in core/valence/Rydberg spaces/total				Natural electron configuration
Am	1.64	85.98	7.02	0.36	93.36	[core] 7s(0.29) 5f(6.09) 6d(0.64) 6f(0.28) …
Eu	2.00	53.98	6.97	0.05	61.00	[core] 6s(0.06) 4f(6.10) 5d(0.81) …

central metal ion with those of the ligands is greater in the Am complex, in line with the previous conclusions on stronger Am–BTBP than Eu–BTBP bonds. The greater number of metal AOs significantly overlapping with the ligand lone-pair orbitals, and their higher AO coefficients, observed in the Am complex, also remain in agreement with these conclusions.

The energies of all bonding MOs in both complexes are in the range from -14 to -19 eV. Four distinct energy regions can be distinguished. The first region, of the highest energy (*ca.* -14 eV), represented in both complexes by one orbital (MO240), represents bonding between the M^{III} ion and triazine nitrogens. Three types of AOs contribute to this MO (*s*, *d* and *f*) but *s*-type orbitals of the M^{III} ion are dominant, moreover to a much larger extent in the Am than Eu complex. The second energy interval (from -15.7 to -16.3 eV), with five orbitals of Am and two of Eu, of apparently the highest overlap, represents donation from the pyridine nitrogen atoms to the M^{III} ions. The AO compositions of these orbitals are different: they mainly compose of *f*-type orbitals of Am, whereas of *p*-type orbitals of Eu. The AO compositions of MOs in the two other regions at lower energies (*ca.* -17.3 and *ca.* -18.8 eV) are similar for the Am and Eu complexes: *s*-type and *d*-type. This discussion can be illustrated by pictures of representative bonding MOs in the $[M(C2\text{-}BTBP)_2]^{3+}$ complexes. The overlapping of AOs of the central metal ion with ligand orbitals is illustrated with the crystal orbital overlap population (COOP) diagrams (Fig.3).

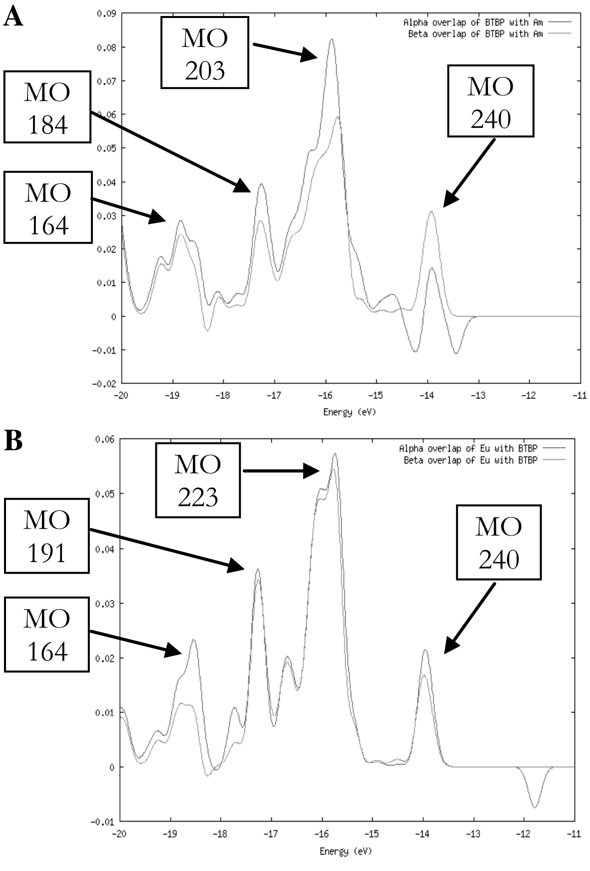

Fig.3. Selected fragments of the COOP diagrams for the americium (A) and europium (B) complexes. The two different lines denote the overlap of alpha or beta spins of metal and ligand orbitals. The most important MOs have been marked with their numbers. Note that the scales of the two figures are different.

The above analysis shows that the participation of *s*-type and *f*-type orbitals is larger in the Am complex, whereas *p*-type and *d*-type orbitals dominate in the Eu complex. These differences are in line with the results of natural electronic configurations analysis, in particular with: (i) the greater participation in the bonding of 7*s* shell of Am than 6*s* of Eu, (ii) the significant contribution from virtual Rydberg's 6*f* (not 5*f*!) orbitals of Am^{III} ion, and (iii) the dominant contribution from *d*-type orbitals of both metal ions (enhancement of electron densities by 0.64 and 0.81 a.u., respectively; Table 2). It must be remembered here that *p*-type orbitals are neglected in the NBO 5.0 methodology used. Moreover, the sum of overlap populations is significantly larger in the case of the Am complex, which supports the hypothesis on the more covalent Am–N than Eu–N bonds.

Also perturbative estimation of stabilization energies arising from electron donation from the lone pairs on the ligand nitrogen atoms to empty (or not fully occupied) orbitals of the central metal ions shows that the total stabilization is greater in the Am than Eu complex. The most stabilizing donor-acceptor interactions in both $[M(C2\text{-}BTBP)_2]^{3+}$ complexes stem from delocalization of the ligand lone pairs to the *d* orbitals of both metal ions, but a significant contribution in the Am complex is due to delocalization of the electron density to the *s* orbitals of Am, which has not been found in its Eu counterpart. The contribution of the *f* orbitals of both metal ions is rather small. This picture also remains in rough agreement with the results of natural electronic configurations analysis.

In the summary of the analysis of AO contributions to the bonding molecular orbitals in the BTBP complexes of americium and europium, we can conclude that the reason of stronger, more covalent Am–N than Eu–N bonds is due to a greater number of Am^{III} atomic orbitals which to a significant extent accept the electron density from the BTBP ligands, and also to their greater overlap with the lone pairs orbitals of the ligands than the overlap of Eu^{III} AOs. The origin of that is probably in the better match (energetic and spatial) of the lone pairs orbitals on the N donor atoms of BTBP ligands with a greater number of relativistically stabilized (or destabilized) atomic orbitals of the Am^{III} ion than of the Eu^{III} ion orbitals. The NBO 5.G calculations of orbital energies led to the values of -8.7 and -7.7 eV for the lone pairs orbitals of C2-BTBP, located on the N_{tr} and N_{py} donor atoms, respectively. In this energy region (from -5 to -12 eV) there are five AOs of Am^{III} ($6f_0$, $6d_{xy}$, $7p_{xy}$, 7*s* and 8*s*) whereas only two AOs of Eu^{III} ($5d_{xy}$ and 6*s*). The 8*s* (Am) and 6*s* (Eu) AOs are very diffuse, so they can hardly overlap with the lone pairs BTBP orbitals. The overlap of the remaining 6*f*, 6*d* and 7*s* orbitals of Am^{III} (the position of the $7p_{xy}$ is not clear) with the lone pairs BTBP orbitals results in the formation of more covalent Am–N bonds than Eu–N ones which are due to the overlap of only one 5*d* orbital of Eu^{III}. On the other hand, the energies of 5*f* (Am) and 4*f* (Eu) orbitals are so low (below -30 eV) that they hardly contribute to the formation of the M–N bonds. The latter conclusion is in agreement with rather small enhancement of electron density on these orbitals upon complex formation (0.09 and 0.10 a.u., respectively; Table 2).

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CALCIUM ALGINATE AND CHITOSAN AS POTENTIAL SORBENTS FOR STRONTIUM RADIONUCLIDES

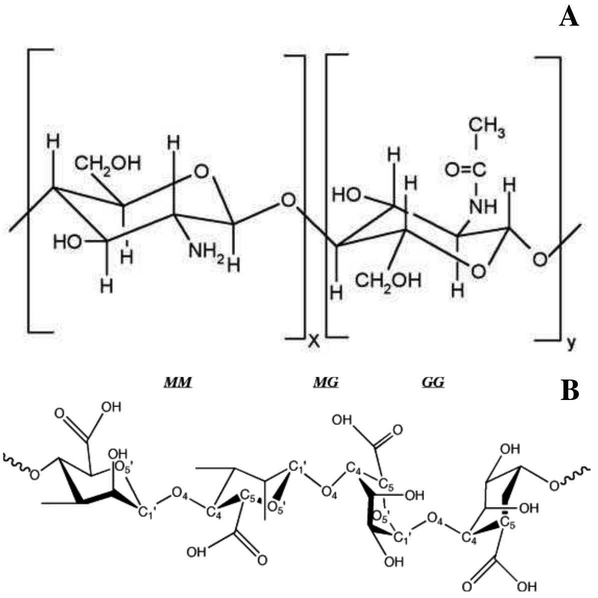
Leon Fuks, Agata Oszczak, Ewa Gniazdowska

In order to avoid contamination of ground water, it is highly needed to remove toxic/radioactive metal ions from aqueous waste solutions before their final release into the environment. For this purpose, numerous physicochemical techniques: ion-exchange, reverse osmosis, precipitation, electrochemical treatment, *etc.* have been used for a long time. However, their routine application is limited mainly by the high operational cost. Among main alternative methods, accumulation of different contaminants onto inexpensive solid materials of biological origin (called biosorbents) should be mentioned [1]. The major advantages of biosorption over the conventional treatment methods include: (i) low cost, (ii) high efficiency, (iii) minimization of chemical and/or biological sludge, (iv) no additional nutrient requirement, (v) easy regeneration of biosorbent, and (vi) possibility of metal recovery [1, 2]. Biosorption process involves a solid phase (sorbent or biosorbent; biological material) and a liquid phase (solvent, normally water) containing dissolved species to be sorbed (sorbate, metal ions).

Extracts from sea algae, bacteria and fungi or by-products from agriculture and common industries belong to the important biosorbents studied because of their effectiveness and their low price [3, 4]. Removal of heavy/radioactive metals from aqueous solutions by these materials is due to the presence of hydroxyl, carboxyl, phosphate or amine functional groups on the sorbent surface [1, 5, 6].

The objective of this study was to initiate an investigation of the removal of strontium radionuclides from aqueous solutions by calcium alginate (both commercially available from Sigma-Aldrich and a home-made material). The ability to bind Sr(II) by commercially available chitosan (Acros Organics) under the same conditions was also measured for comparison. Alginic acid is a naturally occurring hydrophilic, colloidal polysaccharide obtained from various kinds of brown seaweeds. This common name is given to the family of linear polysaccharide-like polymers containing three different functional groups: $-COO^-$ (carboxylate), -C-O-C- (ether) and -OH (alcohol). The acid consists of 1,4-linked β-D-mannuronic (M) and α-L-guluronic (G) acid residues arranged in non-regular blocks forming long chains. The most pronounced sequences are $-M(...)_{n1}M-$, $-G(...)_{n2}G-$ or $-MG(...)_{n3}GM-$. Chitosan is a linear polysaccharide composed of randomly distributed β-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit) and is obtained from shrimps or other crustacean shells. Main functional groups of chitosan are: -C-O-C- (ether) and $-NH_2/NHR$ (amine). Schematic representation of both biosorbent molecules is given in Scheme.

Batch sorption experiments were carried out by suspending accurately weighted samples (*ca.* 0.01 g) of solid sorbent (calcium alginate or chitosan) in a 10.0 ml of strontium solution of known initial concentration (in polyethylene vials). Initial pH of



Scheme. Polymers of chitosan (A) [7] and of the alginic acid (B) [8].

the solution (pH_{init}) was adjusted using dilute HNO_3 or NaOH solutions. The suspension was agitated in a thermostated shaker at different temperatures for a period between 1 min and 12 h to study time of reaching equilibrium. In the experiments on the effect of pH and on the sorption process the carrier-free ^{85}Sr radionuclide supplied from POLATOM Świerk was used.

The calculations by Hydra-Medusa software [9] show that the content of the Sr(II) species remains nearly constant in the pH region of 1-9 (Fig.1). $SrHCO_3^+$ and $SrCO_3$ (formed with carbon dioxide present in the air) appear starting from the pH of 6 and 7.5, respectively. The appearance of crystalline $SrCO_3$ in solutions of pH higher than 8 should also be taken into account in the sorption process. Also, the ionization state of functional groups was highly dependent on pH and should be studied.

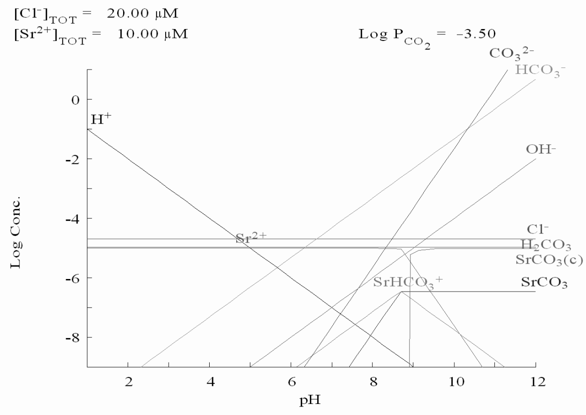
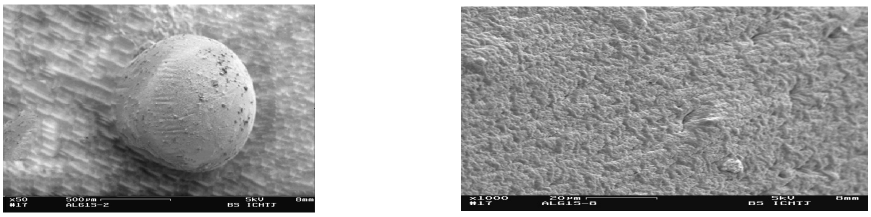


Fig.1. Speciation of strontium in aqueous $SrCl_2$ solutions, calculated by means of Hydra-Medusa software. Total strontium concentration – 10^{-6} mol L^{-1} [10].

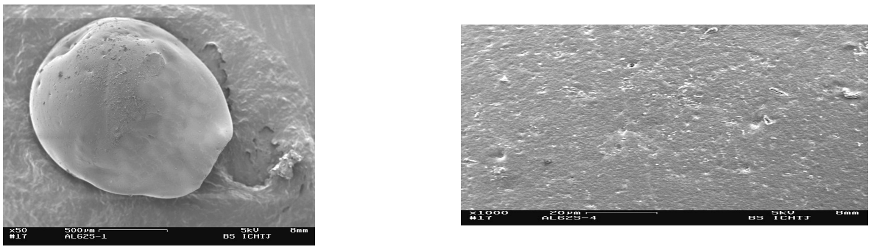
It is known from the literature that carboxyl groups present in the biomass play an important role in metal sequestration, being responsible for a major fraction of metal immobilization [4]. The pK_a value of the carboxylic group existing in biomass varies from about 2 to 4.7 [4], therefore at pH around 4.5, the extent of its dissociation should roughly approach 50%. Generally, at pH ≈ 1.5 the majority of other groups are protonated, inducing

A

Sodium alginate/0.5 M $CaCl_2$



Sodium alginate/0.05 M $CaCl_2$



B

Commercial calcium alginate (Sigma-Aldrich)

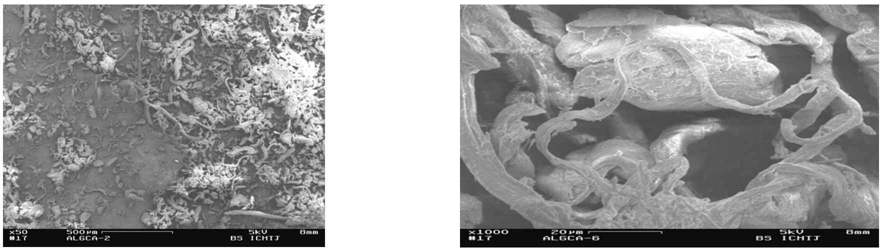
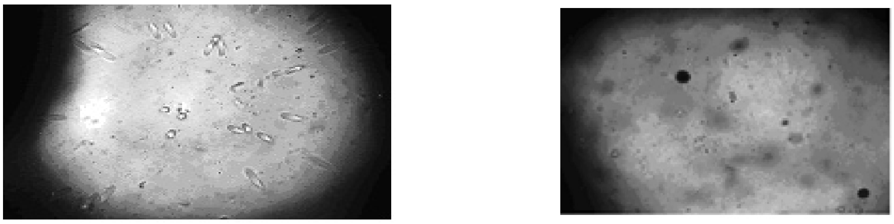
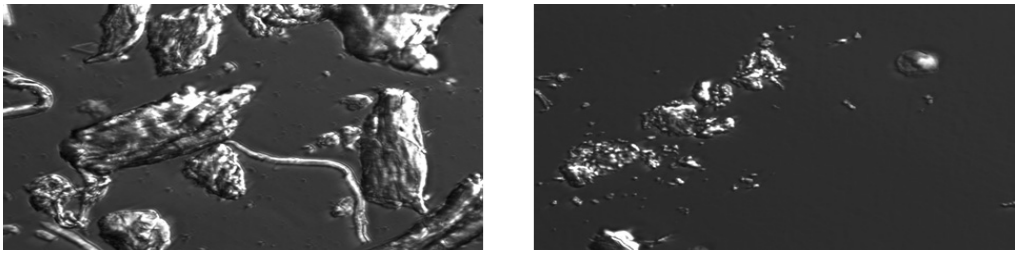


Fig.2. The results of SEM observations of calcium alginate: A – beads obtained in our Laboratory under different conditions, B – commercial product (Sigma-Aldrich). Magnification: x50 (left) and x1000 (right).



A Sodium alginate/0.5 M $CaCl_2$ Sodium alginate/0.05 M $CaCl_2$



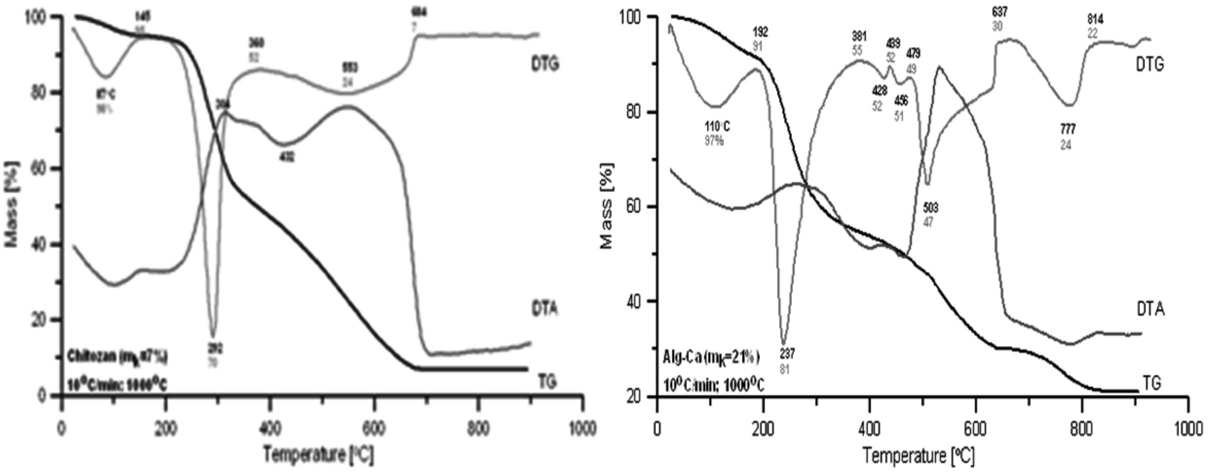
B Commercial calcium alginate (Sigma-Aldrich) Commercial chitosan (Acros Organics)

Fig.3. The results of OM observation of: A – calcium alginate beads obtained under different conditions, B – commercial products: calcium alginate (left) and chitosan (right).

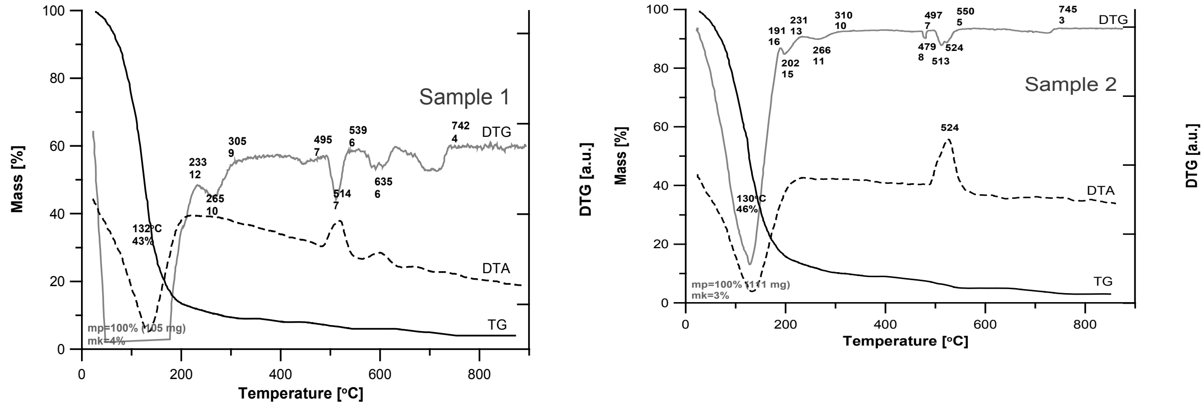
positive or neutral charge and hence, their interactions with positively charged strontium species are not favoured by electrostatic forces. With increasing pH, the negative charge density on the functional groups increases which favours their interaction with the positively charged Sr(II) species, thus their biosorption increases. The pH values strontium(II) sorption on alginic acid is in the range of 4.5-5, and is slightly higher for chitosan.

Decontamination factor – the ratio of specific activity prior to and after decontamination [11] has been found above 95% for ^{85}Sr on alginic acid (acidic polymer), while *ca.* 50% on polyamino polysaccharide-chitosan.

The biosorbents studied were examined by scanning electron microscopy (SEM) and stereoscopic optical microscopy (OM). Figure 2 presents the SEM images of different kinds of calcium alginates.



Commercial chitosan (Acros Organics) Commercial calcium alginate (Sigma-Aldrich)



Sodium alginate/0.5 M $CaCl_2$ Sodium alginate/0.05 M $CaCl_2$

Fig.4. Thermogravimetric (TG/DTA) analysis of the potential sorbents.

It is visible that both the shape and surface morphology strongly depend on the preparation method of calcium alginate. Texture of the surface of beads produced from the more concentrated aqueous $CaCl_2$ solution are more rough which allows us to expect more efficient binding the sorbate.

Figure 3 presents the OM comparison of the same sorbents. The OM images also show that calcium alginate beads obtained in our Laboratory under different conditions have a greater number of pores nearly perpendicular to the bead surface. Commercially obtained calcium alginate has the most scratchy texture with a well developed surface and chitosan is the most smooth material. So, the latter does not seem to be a proper material for adsorption.

Thermogravimetric (TG) and differential (DTG) curves of the materials studied were obtained in the temperature range from 0 to 1000°C (Fig.4). Commercially available products decompose at about 600°C (calcium alginate) and 700°C (chitosan) and the residue after ignition as mass is about 5-10% of the initial material. In contrast, the sorbents obtained in our Laboratory decompose at only *ca.* 200°C. This means that energy necessary to reduce the mass of the potential solid wastes formed from the latter calcium alginate may be considerably smaller than from the commercial sorbents.

Conclusions are the following:

- Laboratory obtained beads of calcium alginate seem to be a better sorbent than the materials commercially available.
- Calcium alginate is more effective than chitosan in binding strontium(II) potentially present in aqueous solutions.

This research has been financed from the National Centre for Research and Development (Poland) through the Strategic Programme "Technologies supporting development of safe nuclear power engineering", task 4 "Development of spent nuclear fuel and radioactive waste management techniques and technologies". We acknowledge Dr. B. Sartowska (INCT), Mr T. Stępkowski (INCT) and Dr. D. Sternik (Department of Chemistry, Maria Curie-Skłodowska University in Lublin) for their help in the SEM, OM and TG/DTG analyses.

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SOLVENT EXTRACTION OF URANIUM FROM POST-LEACHING SOLUTIONS

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The most perspective uranium mineralization in Poland occurs in the Lower and Middle Triassic rocks of the central part of Peribaltic Syneclise, where the maximum U content exceeds 1.5%. In black shales of the Podlasie Depression the average U concentrations of 75-250 ppm were found. These two deposits, although low-grade, were taken into consideration in the present studies on the possibility of obtaining uranium for nuclear energy from domestic resources in the future.

Acidic or alkaline leaching of uranium from the uranium-bearing ores as the first stage of uranium extraction was reported previously [1, 2]. The next important step in the technological scheme is uranium purification and concentration with the use of physical and chemical methods [3]. For this purpose, the following methods are being applied:

- liquid-liquid extraction;
- ion exchange;
- precipitation;
- integrated processes, such as ion exchange/liquid-liquid extraction.

The aim of the presently reported studies was the selection of extracting agents appropriate for the recovery of uranium from post-leaching solutions. The raw extracting agents, like tributylphosphate (TBP), di(2-ethylhexyl)phosphoric acid (D2EHPA), trioctylphosphine oxide (TOPO), triethylamine (TEA), tri-n-octylamine (TnOA), *etc.*, were tested. Uranium distribution ratios, D, were determined in model systems, in particular, the effects of extractants, sulphuric acid and uranium concentrations were investigated.

Various reagents were tested as strip solutions of uranium from the loaded phase. It is reported in the literature that uranium can be re-extracted by contacting the loaded organic solution with aqueous sodium carbonate or ammonium carbonate, or with hydrochloric, sulphuric or hydrofluoric acids [4, 5].

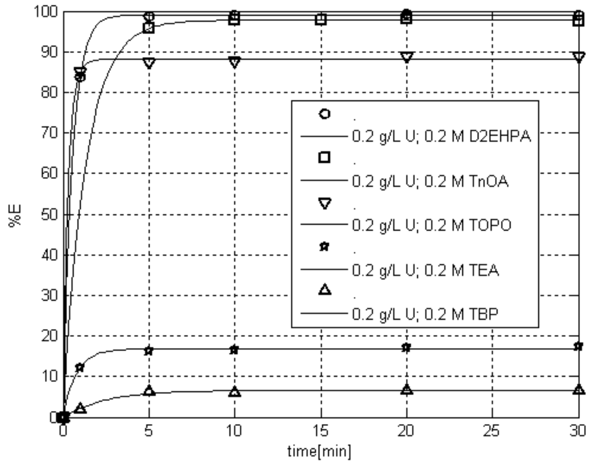

Fig.1. Time dependence of extraction efficiency of U for different extractants: 0.2 M (D2EHPA, TOPO, TEA, TBP, TnOA) in kerosene. The feed solution: 0.2 g U/L in 5% H_2SO_4.

Uranium solutions for the experiments were prepared by direct dissolution of a certain amount of uranyl nitrates in sulphuric acid to the uranium concentrations of 0.2 or 0.5 g/L. Liquid-liquid extraction experiments were performed by slow mechanical shaking of glass tubes with two liquid phases at ambient temperature for various time intervals (from 2 to 30 min). The volume ratio of the organic to the aqueous phase was fixed at 1:1. After centrifugation and the phase separation, suitable volumes of the aqueous phase were analysed for uranium content. The concentration of U(VI) ions was determined by ICP-MS (inductively coupled plasma-mass spectrometry) after diluting with H_2O and HNO_3 to the concentrations suitable for the ICP measurements.

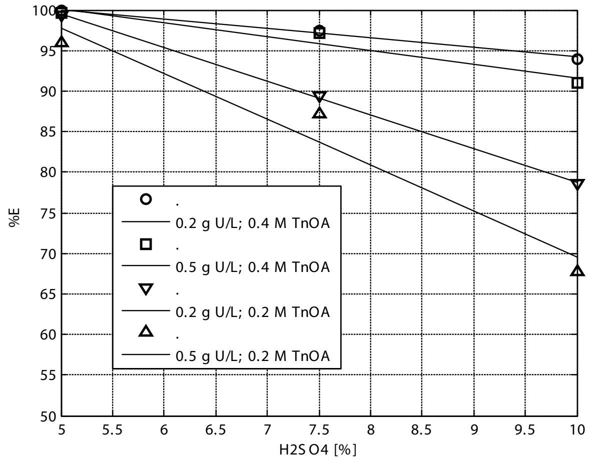

Fig.2. Effects of concentrations of extractant, uranium and sulphuric acid on the extraction of U(VI) by TnOA in kerosene from aqueous H_2SO_4 solutions.

In order to determine the extraction kinetics for different extractants, time dependence of the extraction efficiency of uranium was examined in the range of 2-30 min and the results are plotted in Fig.1. The extraction equilibrium was reached within 15 min for all the extractants tested.

Figure 2 presents the extraction efficiency of uranium at different concentrations of TnOA, sulphuric acid and uranium. The observed effects are consistent with those reported in the literature [6].

The increase in sulphuric acid concentration from 5% up to 10% had a significant effect on the extraction of uranium from aqueous solutions. H_2SO_4 concentration of 5% may be considered appropriate for uranium extraction. Tri-n-octylamine and di(2-ethylhexyl)phosphoric acid are the most effective uranium extractants, giving almost 100% recovery of uranium from 5% H_2SO_4 The efficiency of TOPO was found to be almost 90%.

The recovery of uranium from the organic phase was also examined. Preliminary results of stripping uranium from the loaded D2EHPA solution by sulphuric acid at high concentrations or with 1 M sodium carbonate and 1 M ammonium carbonate are shown in Table 1.

Table 1. Efficiency [%] of stripping of uranium from the loaded organic phase.

Extractant	[H_2SO_4]			1 M Na_2CO_3	1 M $(NH_4)_2CO_3$
	5 M	6 M	7 M		
D2EHPA	54	75	82	85	84

We also examined an alternative technique of extraction with the application of membrane contactors with continuous flows of two phases – aqueous and organic. Laboratory-scale installation (Fig.3) equipped with a membrane contactor (Liqui-Cel® Extra-Flow 2.5x8 produced by CELGARD Company) was used in the experiments on uranium extraction. The characteristics of the module are shown in Table 2. The mem-

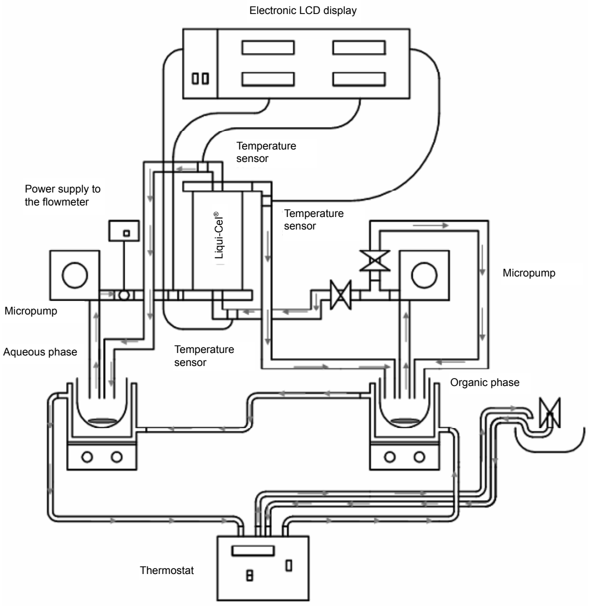

Fig.3. A scheme of the installation for membrane extraction of uranium.

brane contactor is connected to two circuits: with the aqueous and organic phases. The system was fitted with devices, which measure the parameters and control the process.

Table 2. Characteristics of Celgard X50-215 microporous hollow fiber membrane.

Material	Polypropylene X-50
Membrane geometry	capillary
Wall thickness (nominal)	40 μm
Internal diameter (nominal)	220 μm
Outer diameter (nominal)	300 μm
Effective pore size	0.04 μm
Porosity	40%
Burst strength	400 psi (15.5 kg/cm^2)

After preliminary tests of membrane resistivity and determination of extraction efficiency, D2EHPA was found to be the most favourable for the membrane extraction process. The experiments were carried out with model solutions of uranyl nitrate in 5% H_2SO_4, using 0.2 M D2EHPA in toluene as the extracting solution. The experimental results are summarized in Fig.4.

The results of the experiments show that the kinetics of membrane extraction using D2EHPA in toluene is similar for different concentrations of uranium. The fastest extraction was found for the solutions containing low concentrations of uranium, *e.g.* 0.1 g/L, when the efficiency reaches a constant value after less than one hour.

Membrane contactors allow a variety of applications like recovery and/or removal of heavy metals. In the present project they have been used to recover uranium from aqueous solutions at different stages of processing uranium ores and secondary raw materials. The resulting high efficiency of U extraction using D2EHPA and various advantages of the process enable to consider membrane extraction an alternative method for the extraction carried out in mixer-settlers.

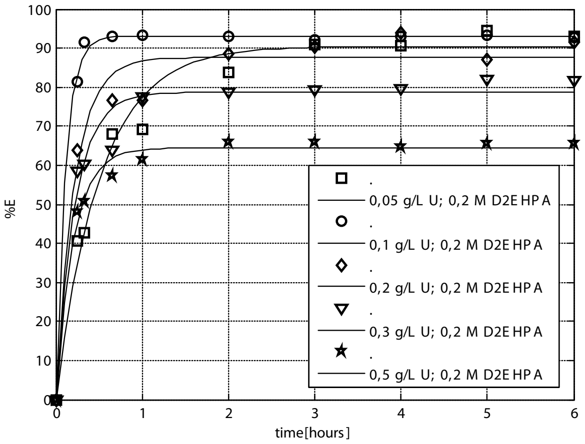

Fig.4. Membrane extraction using D2EHPA in toluene as the extractant. The aqueous phase flows inside the capillaries of the membrane contactor.

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THE STUDY ON THE SEPARATION OF URANIUM FROM ASSOCIATED METALS IN THE POST-LEACHING SOLUTION BY ION-EXCHANGE PROCESS

Grażyna Zakrzewska-Trznadel, Dorota Gajda, Rajmund Dybczyński, Zbigniew Samczyński, Irena Herdzik-Koniecko, Ewelina Chajduk, Bożena Danko

Interest in domestic uranium ores, which first appeared in the 1950s, at the beginning of the nuclear energy era in Poland, has been renewed at present, simultaneously with the development of the Program of Polish Nuclear Energy. Although mining of the Polish uranium deposits presently is not economically reasonable, the situation can change in the future together with the fluctuations in the global uranium market. Therefore, in parallel with studies on the prospects of recovery of this metal from secondary sources, the research on the methods of separating uranium from its ores, are currently in progress.

The main task within the project "Analysis of the possibility of uranium supply from domestic resources" is to devise the most suitable method for extraction of uranium from the ores. Leaching studies (both with acidic and alkaline solutions) performed in the Institute of Nuclear Chemistry and Technology (INCT) in order to develop suitable methods for the extraction of uranium from domestic ores: dictyonemic shale and sandstones have been described in paper [1]. The next stage of uranium production, after the solid-liquid extraction, proposed within the frames of the project, is the purification of uranium by ion-exchange process. The aim of the current stage of investigation are preliminary studies on uranium isolation from accompanying elements usually present in the post-leaching solution, using ion-exchange chromatography.

Dictyonemic shale collected from deposits in the Podlasie Depression (Rajsk and Hacki Deposits) was the material selected for laboratory studies. At the starting point of the investigation, a large volume (1000 mL) test sample (TS) was prepared by combination of 50 independent post-leaching solutions obtained in the experiments carried out in an autoclave. Autoclave leaching of the uranium ores was performed with the use of 10% H_2SO_4, at 80°C under pressure of 3, 5 and 7 bar for 2 h.

The chemical composition of TS was analysed. Two complementary analytical methods – inductively coupled plasma-mass spectrometry (ICP-MS) and neutron activation analysis (NAA) – were applied for determination of the total uranium content as well as of the accompanying metals. The concentration of sulphuric acid was estimated by ion chromatography (IC) to be 0.3 mol L^{-1} H_2SO_4. The results of elemental analysis by ICP-MS and NAA are shown in Table 1.

Table 1. The elemental characteristics of TS by ICP-MS and NAA.

No.	Element	ICP-MS		NAA		
		content [μg mL^{-1}]	uncertainty [μg mL^{-1}]	radionuclide*	content [μg mL^{-1}]	uncertainty [μg mL^{-1}]
1	Co	0.42	0.02	Co-60	0.364	
2	Ce			Ce-141	1.37	0.009
3	Cu	2.2	0.11			0.03
4	Eu			Eu-152	0.026	
5	Fe	478	24	Fe-59	440	0.002
6	La	0.51	0.03	La-140	0.644	8
7	Mn	24.1	1.2			0.01
8	Mo	4.02	0.2	Mo-99/Tc-99m	4.49	
9	Nd			Nd-147	0.825	0.06
10	Ni	4.88	0.24			0.119
11	Rb			Rb-86	0.935	
12	Sb	0.004	0.0002	Sb-122	0.011	0.088
13	Sc			Sc-46	0.114	0.001
14	Sm			Sm-153	0.132	0.001
15	Tb			Tb-160	0.011	0.004
16	Th	0.209	0.01	Pa-233	0.213	0.003
17	U	1.734	0.087	Np-239	1.68	0.005
18	Yb	0.021	0.001	Yb-169	0.023	0.03
19	V	18.2	0.9			0.005
20	Zn	96.7	4.8	Zn-65	89.5	

* Radionuclide formed during neutron irradiation of the analyte.

Commercially available anion exchange resin, Dowex 1 type (strongly basic) of different degree of cross-linking (X4, X8) and of different particle size (100-200 and 200-400 mesh) was used for the purification of uranium from accompanying elements in the test sample. Behaviour of U and some other elements, when TS (10 mL) was intro-

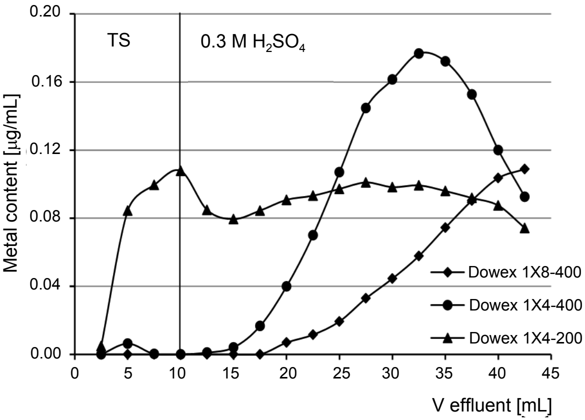

Fig.1. Elution of uranium from column: 0.301 cm^2 x 3.5 cm, with the use of 0.3 mol L^{-1} H_2SO_4 and different resin filling. Feed solution – TS (10 mL).

Table 2. Recovery of metals in 0.3 mol L^{-1} H_2SO_4.

Resin	Element [%]							
	U	Cu	Mn	Zn	La	V	Mo	Fe
Dowex 1X8 (200-400 mesh)	38	91	82	92	100	84	67	90
Dowex 1X4 (200-400 mesh)	87	100	100	100	100	100	100	100
Dowex 1X4 (100-200 mesh)	100	88	82	91	100	73	100	88

duced into the column, followed by the elution with 0.3 mol L^{-1} H_2SO_4 (35 mL) is shown in Fig.1, and the percentage of recovery of metals – in Table 2.

On the basis of these preliminary experiments most suitable resin, Dowex 1X8 (200-400 mesh), was chosen for further investigation. In this case, favourable conditions for elution of accompanying elements have been found.

In order to obtain the necessary information about the ion-exchange process aimed at selective separation of uranium from accompanying elements, the frontal analysis technique [2] was carried out in the series of model experiments with uranium, for different sulphuric acid concentrations (Fig.2). Spectrophotometry with arsenazo(III) (1,8-dihydroxynaphtalene-3,6-disulphonic acid-bis (azophenyl arsenic acid)), which is derived from chromotrophic acid and o-aminophenylarsonic acid, was employed for the determination of uranium(VI) [3, 4]. The method is based on the complex formation of uranium(VI) with arsenazo(III) at pH 2.0 ± 0.1, which shows maximum absorption at 651 nm.

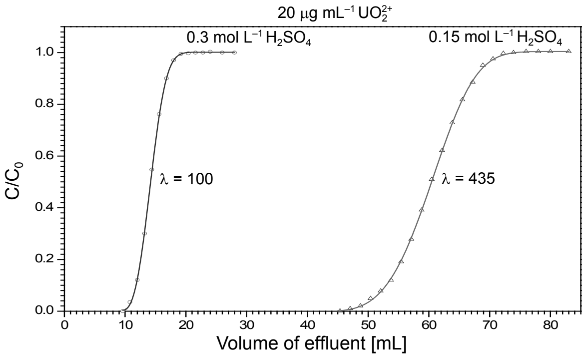

Fig.2. The effect of H_2SO_4 concentration on the break--through curve of uranyl ions. Dowex 1X8 (200-400 mesh), the column – 0.071 cm^2 x 5.0 cm, t = 20°C, u = 0.75 cm min^{-1}.

Break-through curves for uranium, as well as for accompanying elements, when the real test sample was introduced into the column under preferred experimental condition (0.15 mol L^{-1} H_2SO_4) are shown in Fig.3. The contents of uranium and other metals present in the examined sample were determined by ICP-MS This analytical technique enabled to measure directly the mass concentration of total elements in TS, without any chemical separation.

Strong affinity of the uranyl sulphate complex anion $[UO_2(SO_4)_3]^{4-}$ to the strongly basic anion exchange resin creates the possibility of effective separation of uranium from most of the accompanying elements present in the post-leaching solution. This method seems to be promising for uranium recovery, both on a laboratory and technical scale.

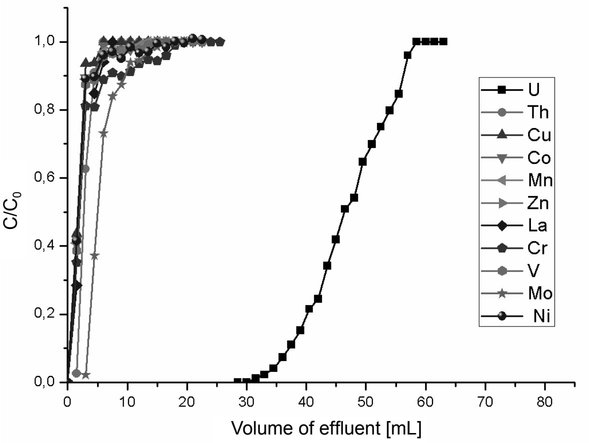

Fig.3. Break-through curves for uranium and other elements. Feed solution – test sample diluted (1:1) with water, 100 mL. Dowex 1X8 (200-400 mesh), the column – 0.071 cm^2 x 5.0 cm.

The studies were supported by POIG 01.01.02--094-090 research grant "Analysis of the possibility of uranium supply from domestic resources".

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CENTRE FOR RADIOBIOLOGY AND BIOLOGICAL DOSIMETRY

The Centre continued and completed the projects that were carried out in 2011. Studies carried out in 2012 concentrated on validation, adaptation and implementation of various biodosimetric methods, examination of regulatory elements in *PIR* gene and biological effects of nanoparticles.

The biodosimetric methods can be divided into two categories. The first category is for radiation dose estimation in a multiparametric triage test for nuclear and radiological mass-casualty incidents (supported by the European Union Structural Funds and Ministry of Regional Development (Poland) – project No. POIG.01.03.01-14-054/09). The second category of methods is that of cytogenetic methods and the work has been carried out in a close international cooperation in the frame of the European Union MULTIBIODOSE (241536 FP7-SECURITY SEC-2009-4.3-02) programme aimed at preparing multi-disciplinary biodosimetric tools to manage high scale radiological casualties. The participation involves cooperation with other European laboratories, exchange of samples and microscopic preparations in order to unify the procedures and training. Our contributions to the MULTIBIODOSE programme were presented at several international conferences. The Centre also is a member of RENEB, a coordination action project funded within the 7th EU framework EURATOM Fission Programme.

These programmes are targeted at testing large groups of potential victims. Hence, time is an important factor and the speed of analysis counts more than accuracy. We participate in an international effort to establish automated, high-throughput, cytogenetic biodosimetry methods to process a large number of samples for conducting the assays using peripheral blood from exposed individuals according to internationally accepted protocols (within days following radiation exposures). The Centre is being prepared to participate in triage tests with the use of various methodological approaches. Validation of the biodosimetric methods is presently carried out with the use of an automated metaphase finder and micronucleus finder.

Further, the Centre participates in the project "Technologies supporting development of safe nuclear power engineering" funded by the National Centre for Research and Development. Our contribution constitutes part of the plan of implementation of the highest standards and best methods for monitoring the effect of the nuclear power plant on the environment and human health.

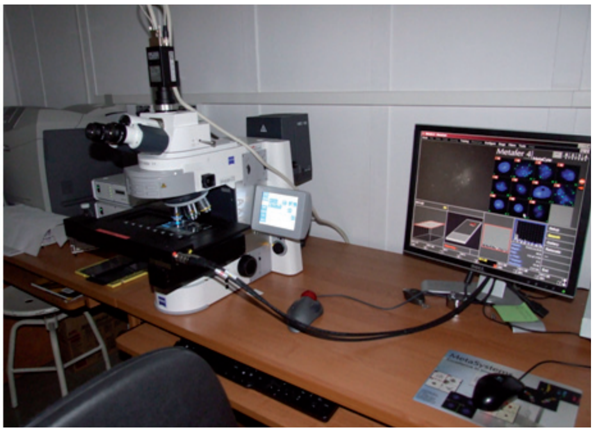

Image analysis system METAFER 4 (Metasystems) with a Zeiss fluorescent microscope at the Centre for Radiobiology and Biological Dosimetry.

The nanoparticle project has been carried out in the frame of the Polish-Norwegian Research Fund (PNRF-122-AI-1/07) in cooperation with several European laboratories. During 2012, we completed and prepared for publication among others, a study of the relation between oxidative stress, survival and various types of DNA damage induced by treatment with three types of nanoparticles in three human cell lines: hepatocellular liver carcinoma HepG2, colorectal adenocarcinoma HT29 and lung carcinoma A549.

In cooperation with the Jena University, in the frame of the Ministry of Science and Higher Education grant DPN/N23/NIEMCY/2009, we continued the study of the role of conjugated linoleic acids (CLA) in the cellular response to X-rays. We have previously found that the

X-irradiated colon cancer HT-29 cells become markedly radiosensitized in result of culture in a CLA complemented medium and this is accompanied by an impaired repair of DNA double strand breaks. These data were recently completed by a detailed analysis of lipid raft properties.

OXIDATIVE DNA DAMAGE DETERMINES LONG-TERM SURVIVAL OF HUMAN CELLS TREATED WITH Ag NANOPARTICLES

Marcin Kruszewski, Iwona Grądzka, Teresa Bartłomiejczyk, Maria Wojewódzka, Anna Lankoff, Teresa Iwaneńko, Sylwia Męczyńska-Wielgosz, Sylwester Sommer, Irena Szumiel

It is generally agreed that oxidative stress is the main cause of the silver nanoparticle (AgNP)-induced effects at the cellular level, such as genotoxicity and mutagenicity, disturbed mitochondrial respiration, impaired proliferation and apoptotic death. These effects may be the potential cause of toxicity of AgNPs and are sufficient to raise concern for the human health and the environment [1]. Although AgNPs belong to the nanoparticles most often studied ones, the mechanisms of their biological effects are still not fully understood. Moreover, there are numerous discrepancies in the reports on the type and extent of DNA damage induced by AgNPs in various mammalian cells in *in vitro* studies. Therefore, we examined the relation between DNA damage and clonogenic potential of three human cell lines, HepG2, HT29 and A549, treated with uncoated 20 or 200 nm AgNPs. Silver nanoparticles uptake corresponded to the formation of reactive oxygen species (ROS), shown in Fig.1. The endpoints examined were survival (cloning), DNA breakage (the comet assay), oxidative base damage recognized by formamido-pyrimidine glycosylase (FPG) (FPG+comet assay), frequencies of histone γH2AX foci and micronuclei. Each cell line studied had a different pattern of DNA breakage and base damage *vs.* NPs concentration and time of treatment. However, only the overall pattern of DNA breakage and base damage induction corresponded to the intracellular generation of ROS.

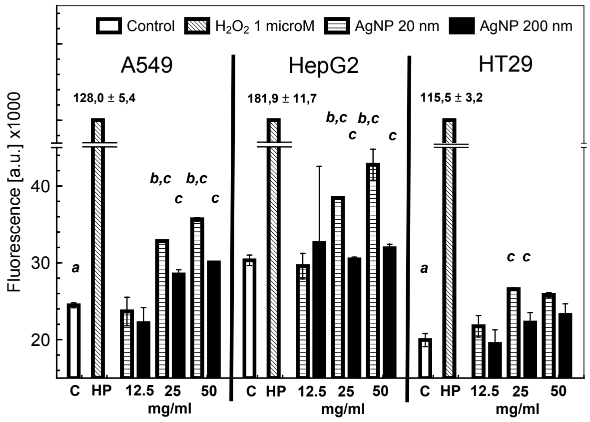

Fig.1. Generation of ROS in cells treated with 20 and 200 nm AgNPs. *a* denotes a significant difference between HepG2 control and other controls (Student's t-test, $p < 0.05$). *b* denotes significant difference between treated and control cells (Student's t-test, $p < 0.05$). *c* denotes significant difference between 20 and 200 nm AgNPs treated cells (Student's t-test, $p < 0.05$).

Formation of ROS upon the uptake of NPs, including AgNPs, is a well-documented phenomenon and has largely been reported to be implicated in AgNP-induced toxicity [2]. ROS are able to induce oxidative DNA damage and activate a wide variety of cellular events, such as cell cycle arrest, apoptosis and cellular signalling, that modify the cellular response to AgNPs. Also, the induction of oxidative DNA damage after 2 h treatment corresponded to the formation of ROS. The studied cell lines showed apparent differences in the ability to produce ROS upon treatment with AgNPs (Fig.1), likely due to the differences in nanoparticles uptake and efficiency of the antioxidant defence mechanisms. The lowest ROS level was in HT29 cells and this corresponded with the highest survival (Fig.2). Also, the high ROS level in HepG2 cells was accompanied with the lowest survival, whereas A549 cells exhibited a relatively high ROS production with an intermediate survival level, possibly related to the effective antioxidant defence of this cell line (Fig.2).

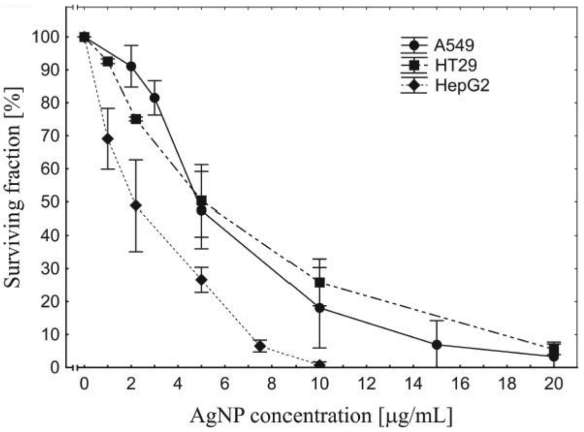

Fig.2. Colony forming ability of A549, HT29 and HepG2 cells treated for 24 h with 20 nm AgNPs.

There was no consistent relation between cell sensitivity estimated from the clonogenic ability and DNA damage levels. For example, in A549 cells that were most sensitive to 200 nm AgNPs in the clonogenicity test, the DNA was less damaged than in HepG2 and HT29 cells. In all three cell lines, single strand breaks (SSB) were not conversed into double strand breaks (DSB) as observed during DNA replication, *e.g.* [3], since no increases in histone γH2AX foci or in micronuclei frequency were evident. Thus, DSB are not the reason for the loss of the clonogenic ability in the tested cells. Lack of formation of γH2AX foci and a negligible role of DSB formation in AgNP-induced cytotoxicity was further confirmed by the lack of induction of micronuclei (MN). The reported experiments suggest that only oxidative DNA damage correlates with the loss of clonogenic ability of cells treated with AgNPs.

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IN SILICO ANALYSIS OF THE 5` UTR REGION IN THE *PIR* GENE IN SEARCH FOR THE REGULATORY MOTIFS ACTIVE AT THE RNA LEVEL

Kamil Brzóska, Tomasz Stępkowski, Marcin Kruszewski

The cellular response to increased level of reactive oxygen species (ROS) upon exposure to ionizing radiation, metallic nanoparticles or oxidants is orchestrated by transcription factors such as, among others, NRF2 and NF-κB. NRF2 is an oxidative stress-responsive transcription factor that binds to specific DNA sequences in the gene's regulatory regions called the antioxidant response elements (AREs) to induce the expression of a battery of detoxifying and antioxidant genes. NF-κB in turn regulates expression of numerous genes involved in stress response, inflammation and apoptosis. There are many links between NRF2 and NF-κB signalling pathways [1] and a new candidate for such link is the pirin protein. Pirin is a nuclear protein that was isolated and characterized as an interactor of the NFIX transcription factor [2]. Subsequently, it was revealed that pirin also forms complexes with Bcl3 and NF-κB1 (p50 subunit) and therefore, may be implicated in the regulation of the NF-κB-related transcription. Some studies have linked pirin orthologues with apoptosis and stress responses, whereas other have pointed out the deregulation of pirin expression in several human tumours.

PIR expression depends on the ARE regulatory sequence that constitute a DNA binding target for the hetero dimers of the transcription factor, NRF2 with other small basic leucin zipper proteins. Further, it can be expected that also the regulatory motifs that determine stability of mRNA are of key importance in regulation of *PIR* expression. Such motifs are located in the untranslated regions of mRNA (UTR), 5` and 3` UTR. Analysis of the *PIR* sequence accessed in the data bases ENSEMBL and NCBI indicated that the PIR protein is coded by two isoforms of mRNA differing in the 5` UTR sequence. There are no differences in the 3` UTR and protein coding sequences. The longer isoform of mRNA contains a 34 nucleotide insertion in the 5` UTR (bold font, underlined):
AGUUAAAAACAGAUUUCCCACAAGACCG
ACCGGAGCGCCGAUCAGAGCACCUGCCC
GGGCCACACAUUUCCUCCUGGAGCACAG
CAAGUGCCGCCUAAAUUACCCGAGUGAG
CAUCUCUUCCCGGCACGAGAGGCAGGGA
GGCCAAAGGGCCGCCAAGCUGGCCUGGG
AGAGGCGUAGGGCGGAGCGAGAGUGGA
GUGACAUUCCCGAGGGCGGAGCCCCAGG
GCCUCCGAGACCCGUAGACUCCCGCCUC
CCGCCUCCUCUAGGCCGCCGGCCGCGAA
GCGCUGAGUCACGGUGAGGCUACUGGA
CCCACACUCUCUUAACCUGCCCUCCCUG
CACUCGCUCCCGGCGGCUCUUCGCGUCA
CCCCCGCCGCUAAGGCUCCAGGUGCCGC
UACCGCAGC**GUGAGUACCUGGGGC**
UCCUGCAGGGGUCCACUAGCCCUCCAUC
CUCUACAGCUCAGCAUCAGAACACUCUC
UUUUUAGACUCCGAU

In order to obtain a model of the secondary RNA structure, both sequences were analysed with the use of the COTRAfold program (http://contra.stanford.edu/contrafold/). Comparison of both isoforms (Fig.) points to a considerable difference in the secondary structure of the respective mRNA isoforms due to the insertion present in the longer isoform.

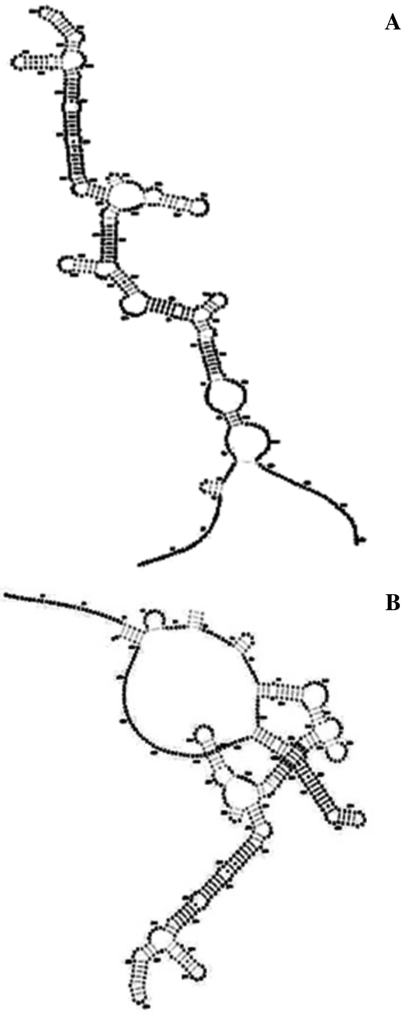

Fig. The secondary structures of the shorter (A) and longer (B) isoform of mRNA coding the pirin protein.

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COMPARISON OF METHODS OF MICROSCOPIC SLIDE PREPARATION AND SCORING FOR ESTIMATION OF MICRONUCLEI FREQUENCY

Sylwester Sommer, Iwona Buraczewska, Iwona Wasyk

Part of the programme aimed at preparing multi-disciplinary biodosimetric tools to manage high scale radiological casualties (MULTIBIODOSE) involved preparation for fully automated scoring of micronuclei (MN). This is a rapid and reliable method of establishing the dose of ionizing radiation. Nevertheless, as every method based on biological parameters, it has limitations. For example, it is of critical importance to understand the influence of age on the MN frequency level. Therefore, we compared both the technical aspects of slide preparations and the relation of MN frequency to donors' age. All donors were from the control group.

There were two groups of donors:

1. MB: 40 donors working at the Institute of Nuclear Chemistry and Technology (INCT); their blood was analysed in the frame of the MULTIBIODOSE project starting from 2011 on. MN were analysed in Giemsa stained slides, by visual (manual) or fully automated scoring, on 4'-6-diamidino-2-phenylindole (DAPI) stained slides, by visual or semi-automated scoring (MN positive cells visually corrected). In this group, visual and automated microscopy were used for scoring.
2. ICHTJ: 47 donors working at the INCT; their blood was analysed during last 15 years only in the Giemsa visual scoring mode. The transmitted light microscope was used for scoring.

The objectives of this study were:

- to compare the levels of control MN scored by automated, semi-automated and visual manner;
- to estimate the control (background) level of MN. This is important, because it defines the lower limit of the MN method. The level of the control MN is an inter-individual variable and therefore, using the MN method for biological dosimetry one can read the radiation dose only as low as 0.3 Gy;
- to find whether in the resulting data there is a correlation between the control level of MN and donors age that is comparable with that found in the literature.

Analysis of the results shows (Fig.1) that the control level of MN determined by fully-automated scoring is significantly higher (mean frequency 35 micronuclei in 1000 cells) than in the case of semi-automated or visual scoring (mean frequencies were 9 and 13, respectively). There is a slight difference in the control level for semi-automated scoring and visual scoring but it is not statistically significant. In contrast, other authors [1] observed that MN frequencies obtained with automated scoring were lower as compared to those detected by visual scoring. A strong positive correlation can be seen (Fig.2) between age and the control level of MN (correlation coefficient r = 0.55, p = 0.03). This result is in accordance with most of the data published by other authors [2].

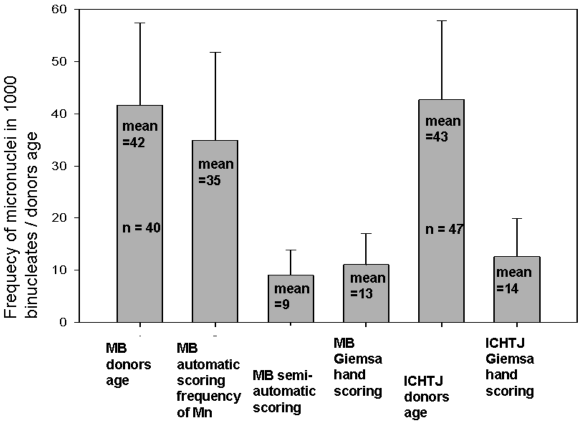

Fig.1. Comparison of the MN frequencies in two groups of donors, MB and ICHTJ (see text) that were obtained by various scoring modes.

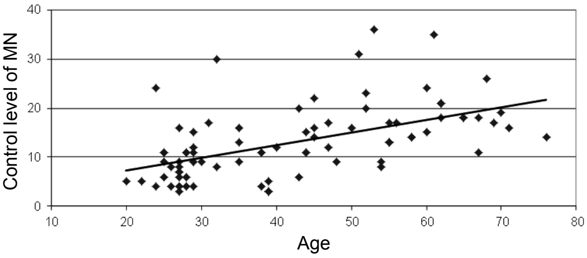

Fig.2. MN frequency-age relationship interpolated by linear regression (y = 0.2581x + 2.1761); $R^2 = 0.3019$.

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LABORATORY OF NUCLEAR ANALYTICAL METHODS

The Laboratory of Nuclear Analytical Methods was created in 2009 on the basis of the former Department of Analytical Chemistry. The research programme of the Laboratory has been focused on the development of nuclear and nuclear-related analytical methods for the application in a nuclear chemical engineering, radiobiological and environmental problems associated with the use of nuclear power (as well as other specific fields of high technology). New procedures of chemical analysis for various types of materials are also being developed. The main areas of activity of the Laboratory include inorganic trace analysis as well as analytical and radiochemical separation methods. The Laboratory cooperates with the centres and other laboratories of the INCT and provides analytical services for them as well as for outside institutions. The Laboratory has been also involved in the preparation and certification of new certified reference materials (CRMs) for inorganic trace analysis and is a provider of proficiency testing schemes on radionuclides and trace elements determination in food and environmental samples.

The main analytical techniques employed in the Laboratory comprise: neutron activation analysis with the use of a nuclear reactor (instrumental and radiochemical modes), inductively coupled plasma mass spectrometry (together with laser ablation and HPLC), atomic absorption spectrometry, HPLC including ion chromatography, as well as gamma-ray spectrometry and alpha- and beta-counting.

In 2012, the research projects carried out in the Laboratory were concerned with the chemical aspects of nuclear power, and nuclear and related analytical techniques for environment protection.

In 2012, the Laboratory participated, together with the Centre for Radiochemistry and Nuclear Chemistry, in Operational Programme Innovative Economy (PO IG) project “Analysis of the possibilities of uranium supply from indigeneous resources in Poland”. The Laboratory participated also in the strategic research project from the National Centre for Research and Development (NCBiR), Poland “New technologies supporting development of safe nuclear energy”.

In 2012, the Laboratory of Nuclear Analytical Methods conducted two proficiency tests (PT). The PT on the determination of Cs-137 and Sr-90 in water, food and environmental samples was conducted on the request of National Atomic Energy Agency, Poland for laboratories forming radiation monitoring network in Poland. Proficiency testing scheme PLANTS 12: Determination of As, Cd, Cr, Cu, Hg, Pb, Se and Zn in a dry edible mushroom powder was provided for laboratories analysing food and environmental samples. All proficiency tests are provided following requirements of ISO/IEC 17043:2010 and IUPAC International Harmonized Protocol (2006).

RADIOLYTIC DECOMPOSITION OF SELECTED PHARMACEUTICALS AND ENDOCRINE DISRUPTORS OCCURRING AS ENVIRONMENTAL POLLUTANTS

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The residues of pharmaceuticals and endocrine disruptors in recent years are commonly detected as anthropogenic pollutants in natural and treated waters [1]. This indicates the insufficient efficiency of their removal from industrial and municipal wastes with commonly employed routine technologies [2], hence numerous studies in recent years are focused on the development of efficient advanced oxidation processes (AOPs), based on radical reactions [3, 4]. As especially efficient AOP is considered the application of the ionizing radiation, where decomposition of organic pollutants in aqueous solutions occurs as a result of radical reactions with active products of radiolysis of water. The main advantage of such methodology is the possibility of simultaneously occurring oxidation reactions with $^{\bullet}$OH radicals and reduction reactions with solvated electrons e_{aq}^{-}. This creates a unique opportunity to decompose a large variety of different pollutants from the irradiated solutions.

In recent years an increasing number of papers is being published on radiolytic decomposition of pharmaceuticals occurring as residues in the environment, see *e.g.* [5-8], as well as some endocrine disruptors such as, *e.g.* bisphenol A [9, 10] or 17 β-estradiol [11]. In our recent studies the radiolytic decomposition was investigated on the pesticides carbendazim [12] and parathion [13], and also on pharmaceutical diclofenac (DCF) [14]. The radiolytic decomposition of diclofenac was also reported recently by other authors [15-17].

The studies reported here concerned further investigation of radiolytic decomposition of diclofenac, and other widely used anti-inflammatory drug ibuprofen ((RS)-2-(4-(2-methyl-propyl)phenyl)propanopic acid), and also a very commonly used antiepileptic drug carbamazepine (5*H*-dibenzo[b,f]azepine-5-carboxamide). All those considered drugs are widely detected in waters and also in municipal and some industrial wastes. Besides the above-mentioned works on radiolytic decomposition of diclofenac [14-17], very recently also first reports were published on radiolytic decomposition of ibuprofen [6] and carbamazepine [17]. Very preliminary experiments were also carried

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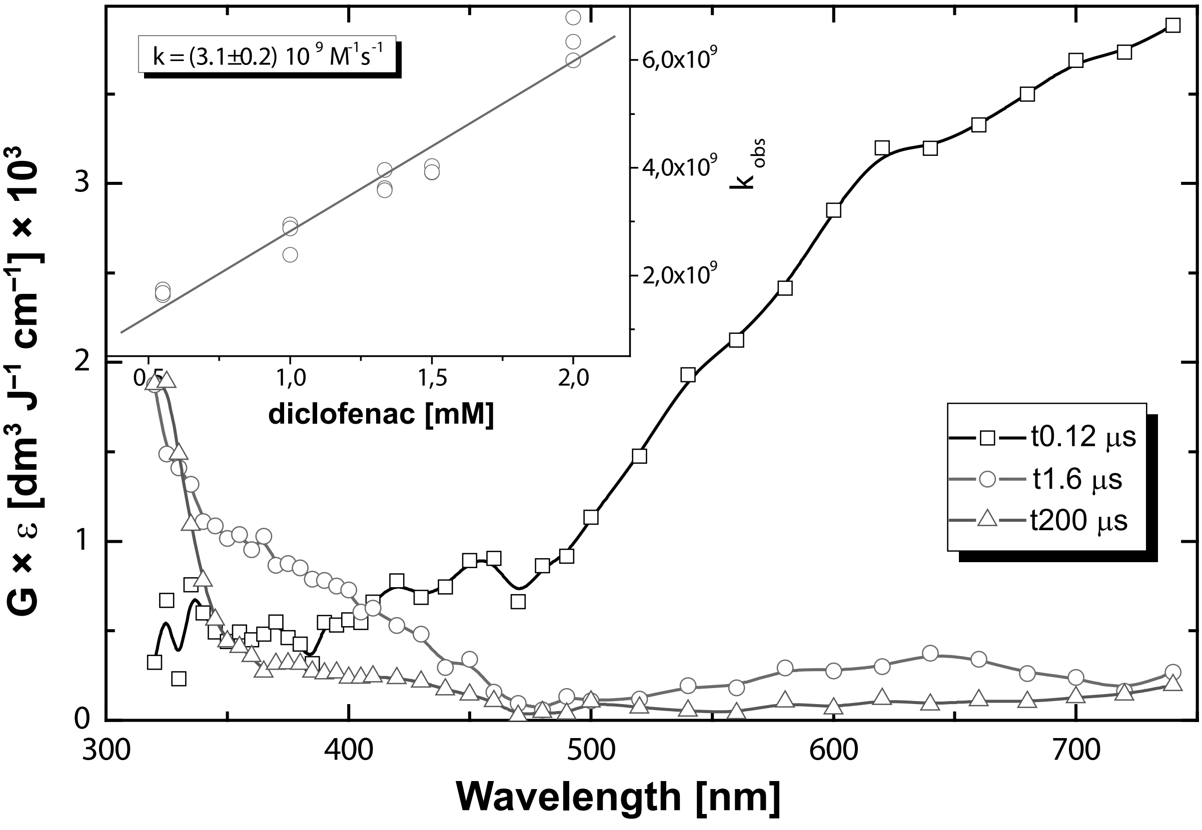

Fig.1. Transient absorption spectra recorded after pulse-irradiation in Ar-saturated aqueous solution containing diclofenac 0.1 mM and 0.5 M tert-BuOH. The spectra taken after following time delays after electron pulse: (□) 0.12 µs, (○) 1.6 µs, (△) 200 µs. Inset: Stern-Volmer plot of the absorption decay at λ = 700 nm.

Table. Tentative list of the products detected by LC-IT-TOF MS in 50 mg/L aqueous solution of diclofenac irradiated with a 3.6 kGy dose. (HPLC method: A: water 0.1% formic acid; B: acetonitrile, 0.1% formic acid. Flow-rate – 0.5 ml/min. Gradient: 0-3 min – 30% B, then 3-10 min – from 30% to 40%, then 10-40 min – from 40% to 65%, then 40-45 min – from 65% to 100%, then 45-46 min – 100%, then 46-47 min – from 100% to 30% (equilibration) and 47-55 min – 30% (initial mobile phase composition for equilibration). IT-TOF MS conditions: full-scan acquisition with polarity switching, mass range – m/z 150-1000, ion trap accumulation time – 50 ms.)

Compound	RT [min]	Experimental m/z ([M+H]$^+$)	Assigned elemental composition [M]	DBE	Error [ppm]	In-source CID fragments	Comments
Diclofenac	42.7	296.0234	$C_{14}H_{11}NO_2Cl_2$	9	1.9	278; 214	
DCF-TP1	44.50	250.0184	$C_{13}H_9NCl_2$	9	0.7	214/216 215/217	neutral loss of formic acid (more apolar TP)
DCF-TP2	44.0	248.0458	$C_{13}H_{10}NOCl$	9	6.0		
DCF-TP3	43.87	230.0333	$C_{13}H_8NOCl$	10	14.9		low intensity
DCF-TP4	41.58	214.0394	$C_{13}H_8NCl$	10	11.3		
DCF-TP5	41.43	278.0126	$C_{14}H_9NOCl_2$	10	2.8		
DCF-TP6	40.25	262.0577	$C_{14}H_9NOCl$	9	20		dechlorination
DCF-TP7	40.22	254.0086	$C_{12}H_9NOCl_2$	8	7.9		
DCF-TP8	37.11	244.0464	$C_{14}H_{11}NOCl$	10	24.5		-OH and -Cl
DCF-TP9	33.62	274.0237	$C_{14}H_8NO_3Cl$	11	10.4		+OH and -Cl
DCF-TP10	32.96	264.0414	$C_{13}H_{10}NO_3Cl$	9	3.0	246 (water loss)	
DCF-TP11	32.50	294.0053	$C_{14}H_9NO_2Cl_2$	10	10.3	245/247	
DCF-TP12	31.5	258.0309	$C_{14}H_8NO_2Cl$	11	2.8		
DCF-TP12	30.9	278.0573	$C_{14}H_{12}NO_3Cl$	9	2.0	230.02/232.03 260.0/262.03 197	-Cl + OH
DCF-TP13	30.7	266.0093	$C_{13}H_9NOCl_2$	9	15.4	248 (water loss)	
DCF-TP14	30.7	258.0309	$C_{14}H_8NO_2Cl$	11	2.8		
DCF-TP15	30.2	298.0050	$C_{13}H_9NO_3Cl_2$	9	6.0		
DCF-TP17	29.1	312.0156	$C_{14}H_{11}NO_3Cl_2$	9	10.3	position isomer of DCF-TP16 (check 246.030 coeluting frag)	DCF-OH
DCF-TP18	28.1	260.0452	$C_{14}H_{10}NO_2Cl$	10	8.0	frag 232.05/234.05 196/197/198	dechlorination
DCF-TP19	27.6	278.0546	$C_{14}H_{12}NO_3Cl$	9	11.7		
DCF-TP20	27.3	246.0295	$C_{13}H_8NO_2Cl$	10	8.7		-Cl-CH_2
DCF-TP21	27.1	264.0398	$C_{13}H_{10}NO_3Cl$	9	9.1		
DCF-TP22	27.0	278.0567	$C_{13}H_{10}NO_3Cl$	9	4.1	water loss (m/z 260) coeluting m/z 294.0037 need to check MS/MS	
DCF-TP23	26.4	260.0441	$C_{14}H_{10}NO_2Cl$	10	12.3		dechlorination
DCF-TP24	24.7	280.0237	$C_{14}H_{11}NOCl_2$	9	19.1	water loss	low intensity (check SPE vial)
DCF-TP25	23.8	244.0517	$C_{14}H_{10}NOCl$	10	2.8		low intensity
DCF-TP26	23.7	294.0500	$C_{14}H_{12}NO_4Cl$ $C_{15}H_{13}NOCl_2$ (2nd option)	9	9.4	water loss	to be confirmed elemental comp.

out on radiolytic decomposition of bisphenol A (4,4'-(propane-2,2-diyl) diphenol), which exhibits hormone like properties. It is a reagent commonly used in the production of polycarbonate polymers and it is detected in environmental samples, hence it raises concern due to its activity as endocrine disruptor.

In our earlier studies on radiolytic decomposition of diclofenac [14, 18] the effect of several experimental parameters on the yield of decomposi-

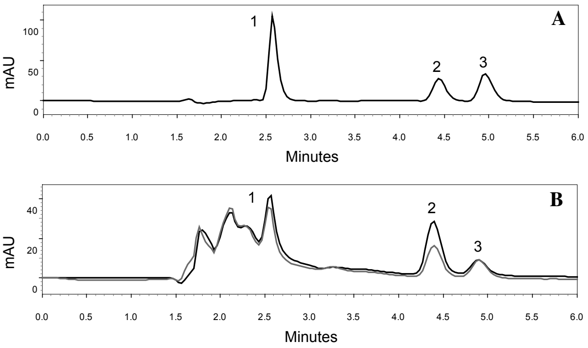

Fig.2. Chromatograms recorded in the HPLC system with UV detection at 220 nm for: (A) aqueous solution of carbamazepine (1), diclofenac (2) and ibuprofen (3) at 5 mg/L each; (B) the Vistula river water sample spiked with 17 μg/L carbamazepine, 55 μg/L diclofenac, and 15 μg/L ibuprofen, preconcentrated on Oasis sorbent without irradiation (upper curve), and irradiated with a 0.25 kGy dose (lower curve).

tion was investigated, including initial concentration of diclofenac, the magnitude of absorbed dose of gamma radiation, the presence of different scavengers of radicals, which may be present in natural waters, and the effect of the matrix of natural samples. Also, using the pulse radiolysis method, the rate constant for the reaction of diclofenac with •OH radical was evaluated as 1.24×10^{10} M^{-1} s^{-1}.

In this study the reaction of diclofenac with hydrated electron was examined in argon-saturated aqueous solutions containing *tert*-butanol, where •OH radicals are effectively scavenged. Based on the decay of hydrated electrons measured at λ = 700 nm, the reaction rate constant was measured as $k = (3.1 \pm 0.2) \times 10^9$ M^{-1} s^{-1}, proving a less efficient decomposition of diclofenac in the reduction process compared to the reaction with •OH radicals. Figure 1 shows the spectra recorded at different time delays after electron pulse and the Stern-Volmer plot (inset) which has enabled determination of the rate constant.

In our preliminary investigations on products of diclofenac radiolysis using GC/MS method, four main products were identified, only. These studies were continued using HPLC analysis with mass spectrometry detection in the system with an ion trap-time-of-flight analyser (LC-IT-TOF MS). The solutions of diclofenac were gamma-irradiated using a ^{60}Co source Gamma Chamber with a dose-rate of 8.0 kGy/h. For 95% decomposition of diclofenac (initial concentration – 50 mg/l) dose 3.6 kGy is needed, tens different products of diclofenac radiolysis can be detected. Their partial identification is given by the data listed in Table (together with conditions of chromatographic separation and MS detection). This is the most detailed attempt reported so far compared to other approaches [15-18], to identify products of diclofenac radiolysis, illustrating the complexicity of occurring processes.

Diclofenac may occur in surface waters even at a level up to 15 μg/L, while ibuprofen up to 1 μg/L [19]. Carbamazepine, besides pesticide atrazine and bisphenol A, is the most commonly occurring organic contaminant in waters in the USA [20], and in wastewater treatment effluents may reach a level up to 3 μg/L [21]. All those mentioned pharmaceuticals are only partly removed at conventional wastewater treatment plants [22]. Some preliminary attempt was made in this study to examine their decomposition in natural river water samples. The Vistula water sample was spiked with a 15-55 μg/L level of target pharmaceuticals and preconcentrated on a commercial Oasis HLB sorbent. The retained compounds were eluted with methanol and analysed using reversed-phase HPLC with UV detection at 220 nm. Figure 2 shows a comparison of the recorded chromatograms for spiked river waters non-irradiated and gamma-irradiated with a 0.25 kGy dose. One can see that these conditions of irradiation are not sufficient for the decomposition of carbamazepine and ibuprofen, while diclofenac is decomposed with a 60% yield. These results clearly show the need for further optimization of the irradiation process.

The preliminary studies were also carried out on radiolytic decomposition of bisfenol A (BPA), considered in overall score as the second of top ranking emerging organic contaminants in waters in the USA [20]. Recently, also decomposition of this pollutant was reported with gamma irradiation, where at 50 μM (11.4 mg/L) level the constant of BPA decomposition in the reaction with the •OH were evaluated as 0.45 μM/kGy [10]. In our work the effect of the absorbed dose of gamma irradiation was examined for irradiation of an aerated 6.87 mg/L solution of BPA. The results of HPLC analysis of irradiated solutions show that at a given initial concentration of BPA a complete decomposition of BPA occurs at the absorbed dose 0.7 kGy (Fig.3). Also in this case further experimental work is in progress in order to optimize the conditions of BPA decomposition for application in environmental samples, including examination of toxicity changes of irradiated solutions,

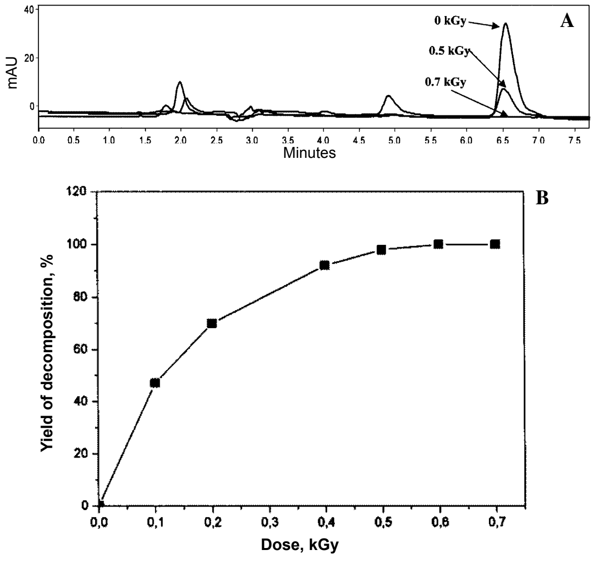

Fig.3. A – HPLC chromatograms with UV detection at 230 nm obtained for 6.87 mg/L aqueous aerated solutions of bisphenol A irradiated with different doses. B – Effect of the absorbed dose of gamma radiation on the yield of decomposition of bisphenol A at the initial concentration 6.87 mg/L.

as well as identification of products of radiolytic decomposition.

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RAPID METHOD FOR THE DETERMINATION OF URANIUM IN ORES BY SPECTROPHOTOMETRY UV/VIS

Zbigniew Samczyński

Several instrumental analytical techniques, namely inductively coupled plasma atomic emission spectrometry (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS), chromatography (IC), capillary zone electrophoresis (CZE), and flow injection analysis (FIA) are recently employed for the determination of uranium. Despite the favourable detection limits, they are time-consuming and involve the use of sophisticated and rather expensive apparatus. Spectrophotometry due to its satisfactory sensitivity, precision and accuracy can be successfully applied for uranium detection. Of great importance are also simplicity and rapidity of operation as well as a lower cost compared to other methods. The method can be used in routine analysis of great number of samples.

The uranyl ions UO_2^{2+} form with arsenazo III (Fig.1) a colour complex, which exhibits maximum absorption at 655 nm [1]. This reaction is the basis of the spectrophotometric method for the determination of uranium. The values of the molar absorptivity ε as well as the specific absorbance *a* ($6.1 \cdot 10^4$ L mol^{-1} cm^{-1} and 0.25 mL g^{-1} cm^{-1}, respectively) prove a high sensitivity of the method. The optimum pH range for complexation of uranium by arsenazo III is 1.3-3.0. However, it is not a selective reaction for uranium, because numerous elements also form colour species with arsenazo III in these conditions. Therefore, a simple determination of U, based only on a calibration curve is not possible. It is necessary to mask interfering ions in the form of stable complexes with other reagent, which simultaneously does not complex the analyte, *i.e.* uranium.

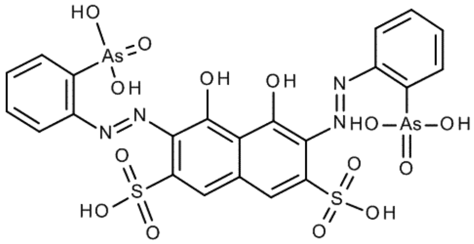

Fig.1. D structure of arsenazo III.

Diethylenetriaminepentaacetic acid (DTPA) and tartaric acid (TA) were selected as potentially useful masking agents (Fig.2). An influence of 38 elements (Mg, Ca, Sr, Ba, Al, Ga, In, Fe, Zn, Cd, Hg, Ni, Mn, Co, Cu, Sb, Bi, Sn, Ti, Hf, Cr, Mo, W, V, Ag, Au, Pd, Pt, Th, Sc, Y, La, Ce, Pr, Nd, Ho, Eu, Lu) on the reaction between U and arsenazo III was examined. Most of the above metals are effectively masked at pH around 2 and the concentration of a given ion up to 400 μg mL^{-1}. Masking was not complete in case of Ca, Cr, Th, La, Ce and Nd. In order to eliminate these interferences, the effect of pH, concentration of DTPA, concentration of TA and concentration of arsenazo III on the

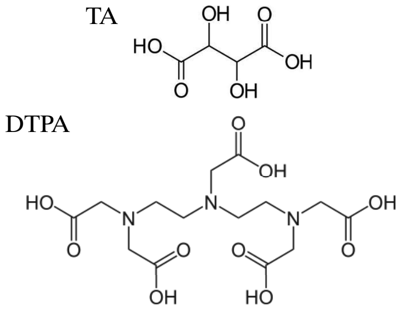

Fig.2. D structure of TA and DTPA.

determination of uranium was studied. As a result, the following parameters were finally established:

- pH in the range 3.25-3.45,
- concentration of DTPA not lower than 0.02 mol L^{-1},
- concentration of arsenazo III not lower than $4.8 \cdot 10^{-5}$ mol L^{-1},
- concentration of TA not lower than 0.02 mol L^{-1}.

In these conditions, the determination of U is feasible in the presence of most of the examined elements with the exception of Ca, La and Th, which interfere at the concentration exceeding 30 μg mL^{-1}. However, even in that situation the analyte can be determined employing the standard addition and successive dilution method [2]. It was confirmed by results obtained from the analysis of model samples, which showed good accuracy and precision.

The elaborated method can be applied to rapid analysis of geological samples. Selectivity of the method can be increased by introducing an additional stage aimed at the separation of uranium from interfering elements.

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LABORATORY OF MATERIAL RESEARCH

Activities of the Laboratory are concentrated on:

- studies of coordination polymers built of *s* block metals and azine carboxylate ligands,
- synthesis of nanoscale porous metal organic framework materials (nanoMOF) using particle track membranes as template,
- synthesis of functional materials – silver modified cotton and cellulose fibers using radiation beam techniques,
- modification of surface layer of engineering materials by implantation of lanthanide elements and nitrogen atoms using high intensity plasma pulses,
- characterization of art objects.

The design and construction of coordination polymers have been studied intensively in recent years, as evidenced by the very rapid growth of publications. Particularly, the porous coordination polymers or the so-called metal organic framework materials (MOF) are of great interest due to their potential applications for gas storage, gas separation, catalysis, sensors, *etc*. Despite many achievements in the field, new rational and effective methods for assembling coordination polymers with a specific or desired structure are still awaited. Our interests are focused on light *s* block metals coordination polymers with carboxylate ligands showing carboxylic group and/or hetero-ring nitrogen functionality. In the last year the crystal structures of seven new lithium coordination polymers with azine dicarboxylate ligands have been solved and published.

Authentication of the paintings and glass objects has been understood by means of the differentiation of the fakes as well as of the provenance and dating studies. The technological issue and historical comparative studies constitute an important approach to these investigations. Provenance studies will be the main goal of our research.

The main focus of the project connected with glass will be on medieval and post-medieval items, mainly tableware from archaeological context as well as from museums' collections. This problem has to be supported by careful technological interpretation of the chemical composition of glass and, if applicable, by written documentary sources like old manuscripts (glass recipes and so on) as well as the chemical characteristic of certain raw materials and their source deposits.

The investigations of trace elements content in lead white carried out by means of the NAA method so far concerned mostly samples of paintings created after 1500. Series of investigations to be carried out on Polish panel painting originating from the 15th century and representing the three historical regions of Poland – Małopolska, Silesian, Pomeranian and fifteenth century icons from South-Eastern Poland. All panel paintings belong to the collection of the oldest in Poland Diocesian Museum at Tarnów and National Museums in Warsaw and Gdańsk. Icons owned by the Castle Museum of Łańcut. This collection of Ortodox Church art, the largest in Poland, is stylistically of exceptional interest, as it was created in an area where the Byzantine and Latin influences met.

The working out of special analytical procedures constitutes important element of the project, too. It is also assumed that for the provenance studies of paintings and glass, hundreds of items have to be analysed by the use of the same procedures, reference materials and methods to set up reliable database. The main results are briefly summarized below:

- establishing the analytical procedures for the examination of historical glass artifacts and pigments,
- creation a database for trace elements in lead white from the Polish medieval panel paintings and for the different kinds of historical glass objects,
- dissemination and sharing the results and database for the community of historical glass and painting researchers.

STRUCTURAL STUDIES IN Li(I) ION COORDINATION CHEMISTRY

Wojciech Starosta, Janusz Leciejewicz

Diazine carboxylates provide variable bridging and chelating coordination modes due to the presence of functional groups represented by N,O chelating sites, carboxylate O atoms and separate hetero-ring N atoms, all connected with a rigid aromatic ring. This study shows the effect of bifunctional polydentate ligands as represented by diazine carboxylates on the structures and stability of Li(I) ion coordination modes. Moreover, it shows also how the structural topology is governed by ligand geometries and functionalities. The most important results are briefly summarized below:

- A characteristic feature of Li(I) complexes with monocarboxylate ligands is a tendency to adopt polymeric patterns. This effect has been observed in the structures of complexes with pyrazine-2-carboxylate [1], 3-aminopyrazine-2-carboxylate [2], 5-methylpyrazine-2-carboxylate [3] and pyrimidine-2-carboxylate ligands. The structure of a complex with pyrimidine-4-carboxylate ligand is built of tetrameric molecules [4], while only monomeric molecules constitute the structure of a complex with pyridazine-3-carboxylate ligand [5]. In all these structures water molecules complete the coordination environment of Li(I) ions.
- Centrosymmetrical dimeric moieties have been observed to form building units of a number of polymeric structures such as with: 3-aminopyrazine-2-carboxylate and water ligands [2], 5-methylpyrazine-2-carboxylate, nitrate and water ligands [3], pyridazine-4-carboxylate and water ligands [6] and pyrimidine-2-carboxylate, nitrate and water ligands [7].
- Structures of two Li(I) complexes with dicarboxylate ligands, built of monomeric molecules linked by short, centrosymmetrical hydrogen bonds show catenated molecular patterns [8, 9].
- Crystals of a complex with pyridazine-3,6-dicarboxylate and water ligands [8] was exposed to deprotonization which resulted in three novel structures. Hydrazine has been taken as the deprotonization agent. In the first experiment an addition of hydrazine to an aqueous solution of the complex [8] lead to crystals with a polymeric structure. Its building unit is a centrosymmetric tetrametric entity composed of two Li(I) ions, two ligand molecules and two doubly solvated Li(I) ions [10]. The tetramers bridged by carboxylate and water O atoms generate a two-dimensional layer molecular pattern. The structure of the subsequent compound is built of the same centrosymmetric tetramers, which linked only by Li attached aqua O atoms give rise to one-dimensional polyanions with singly protonated hydrazinium cations and solvation water molecules located between them [11]. As a final product, crystals with a structure composed of mono-protonated hydrazinium cations, centrosymmetric dimeric anions and neutral tetramers, the same as observed formerly, have been obtained [12]. Further addition of hydrazine resulted in a glassy product.
- A tendency to adopt penta-fold coordination mode is observed among 34 symmetry independent Li ions in 18 structures [1-18] which have been up to now determined in the course of the present project. Tetrahedral coordination geometry is shown by 12 Li ions and only in one structure a octahedral coordination is observed.
- Besides relevant diazine carboxylate ligands, bridging nitrate anions have been detected in the structures of complexes with pyrazine-2,3-dicarboxylate [13], and pyrimidine-2-carboxylate [7] ligands. The structures of both do not contain water molecules, despite the fact that they were synthesized and their single crystals grown in an aqueous solution. In the structure of the first complex nitrate anion is bridging Li ions in the μ_4 mode using one of its O atoms which acts as bidentate, the other two coordinate two different metal ions. A three-dimensional polymeric molecular pattern is formed. The nitrate anion in the structure of the second compound acts in μ_2 bridging mode: each of two its O atoms coordinate two different Li ions; a two-dimensional polymeric network is formed in this way. In the structure of a complex built of 5-methylpyrazine-2-carboxylate, water and nitrate ligands [3], the latter show a μ_3 bridging mode with one bidentate and one monodentate oxygen atom; the third O atom remains coordination inactive. Bridging action of nitrate anions leads to the formation of molecular columns which constitute the structure of this compound.

PART 12. Bis(hydrazin-1-ium) bis(μ_2-pyridazine-3,6-carboxylato)bis(aqualithiate) octaaquabis(μ_3-pyridazine-3,6-carboxylato)tetralithium

The structure is built of two singly protonated hydrazine cations, a centrosymmetric dimeric anion and a neutral centrosymmetric tetrameric molecule. The dimeric anion consists of pairs of symmetry related: Li1 ions, fully deprotonated ligand molecules and water O15 atom (Fig.1). The Li1 ion, coordinated by two *N,O* bonding groups donated by two ligands and the aqua O15 atom shows a transition from a distorted trigonal bipyramidal geometry with an equatorial plane composed of O13, N11^{ii} and O15 atoms with r.m.s. of 0.0059(1) Å, the Li1 ion is 0.0119(1) Å out of this plane, N12 and O11^{ii} atoms are at axial positions, to a square pyramidal geometry where the aqua O15 is at the apical position. The pyridazine ring is planar (r.m.s. of 0.0017(1) Å); carboxylate groups C17/O11/O12 and C18/O13/O14 make with it dihedral angles of 1.4(1)° and 1.7(1)°, respectively. An anionic dimer constitutes the core of the other complex molecule. The coordination of the Li2 ion can be described as a transition from trigonal bipyramidal arrangement (N22, O24^{i} and O25 atoms form the

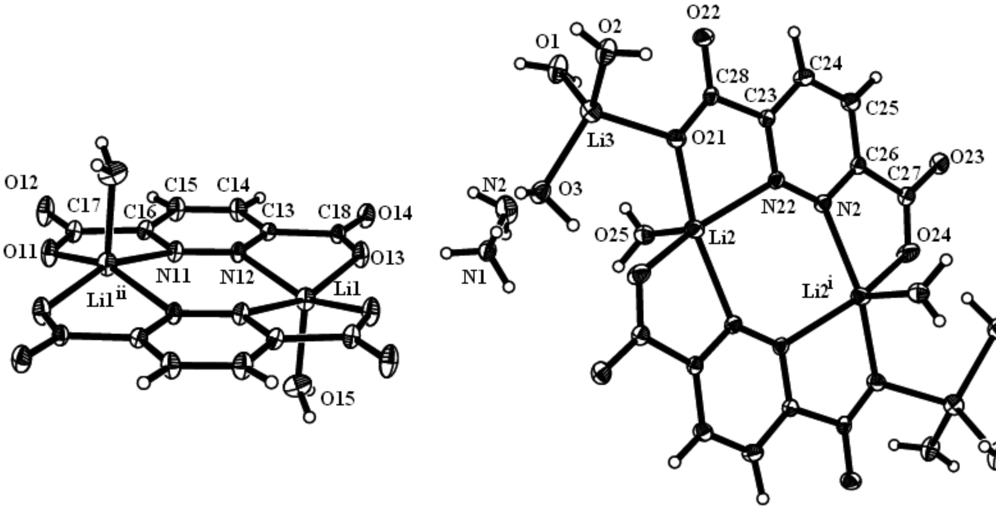

Fig.1 Structural units of the title compound with atom labelling scheme and 50% probability displacement ellipsoids. Symmetry code: (i) -x, -y+1, -z; (ii) -x, -y+2, -z+2.

equatorial plane, r.m.s. 0.0044(1) Å, the Li2 ion is 0.0088(1) Å out of the equatorial plane; O21 and N21^{i} are at the apices) to the square pyramidal with the water O25 at the apical position. The pyridazine ring is planar (r.m.s. 0.0009(1) Å); the carboxylate C27/O21/O22 and C28/O23/O24 groups make with it dihedral angles of 5.9(1)° and 0.7(1)°, respectively. In contrast to the anion complex, the carboxylate O21 atom in the neutral complex molecule acts as bidentate and bridges a $Li(H_2O)_3$ group, thus completing a tetranuclear molecule. The coordination environment of the Li3 ion formed by the O1, O2, O3 and O21 atoms is distorted tetrahedral. Pyridazine ring planes of the anion and the tetrameric molecule are inclined by an angle of 65.7(1)° each to the other (Fig.2). The ob-

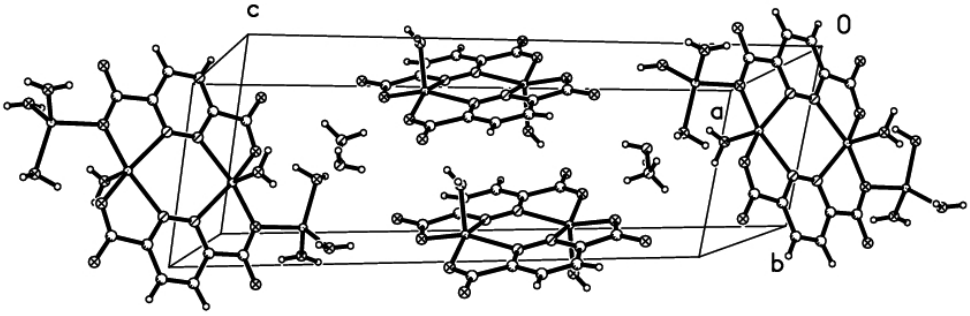

Fig.2. The packing diagram of the title structure.

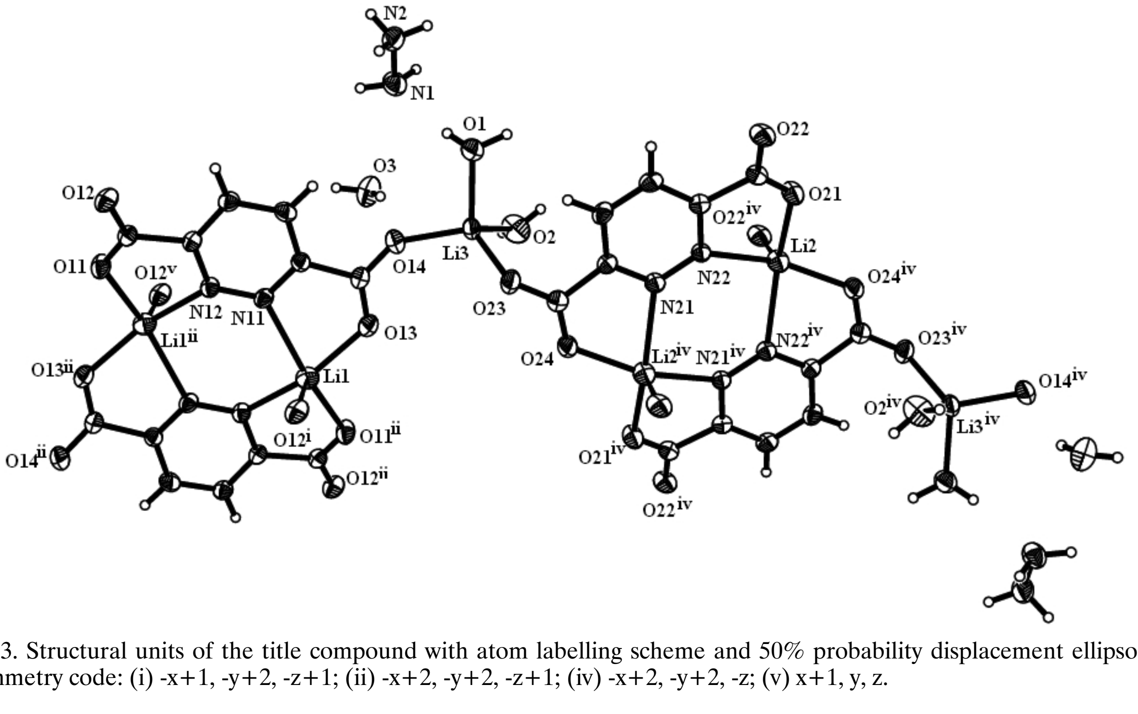

Fig.3. Structural units of the title compound with atom labelling scheme and 50% probability displacement ellipsoids. Symmetry code: (i) -x+1, -y+2, -z+1; (ii) -x+2, -y+2, -z+1; (iv) -x+2, -y+2, -z; (v) x+1, y, z.

served Li–O and Li–N bond distances are close to those reported in two other Li(I) complexes with the title ligand. Bond distances in the protonated hydrazine cations are almost the same as those reported in the structure of an hydrazine adduct of the pyridazine-3,6-dicarboxylic acid. An extended hydrogen bond system in which coordinated water molecules act as donors, carboxylate O atoms are as acceptors contributes to the stability of the structure.

Part 13. Poly[[hydrazin-1-ium(diaquabis((μ_4--pyridazine-3,6-dicarboxylato)trilithiate] monohydrate]

The unit cell of the title compound contains two symmetry independent dimers, each built of two Li(I) ions and two fully deprotonated pyridazine-3,6-dicarboxylate ligands (Fig.3). The dimers are bridged by a doubly solvated symmetry independent Li3 ion. In each dimer, ligand carboxylate groups act as bidentate. Apart from participation in *N,O* bonding groups chelating intra-dimer Li ions, they use the second O atoms to bridge the dimers to doubly solvated Li3 ions forming an ionic ribbon propagating in the unit cell *c* direction. A second bridging pathway with *a* direction normal to the ribbons links them into a polymeric two-dimensional framework (Fig.4). Two dimers and two doubly solvated Li3 ions carry a charge of (2-) which is compensated by two inversion symmetry related singly protonated hydrazinium cations positioned between adjacent dimers. There is also a solvation water molecule in the asymmetric unit cell. The coordination polyhedron around the Li1 ion, a distorted trigonal bipyramid, is composed of Li3 and is not coplanar with the dimer. O13, O12^{i} and N12^{ii} make an equatorial plane, the Li1 ion is 0.0863(2) Å out of it, N11 and O11^{ii} atoms are at apical positions. The strongly distorted trigonal bipyramidal coordination of the Li2 ion consists of N21, O22^{v} and O24^{iv} atoms which constitute its equatorial plane with the Li2 ion 0.0893(2) Å out of it; O21 and N22^{iv} atoms are at the apices. The penta coordination mode of Li1 and Li2 ions can be also visualized as a transition from distorted trigonal bipyramid to a deformed square pyramid, the latter with O12^{i} and O24^{iv} atoms at apical positions, respectively. The ligand 1 and 2 pyridazine rings are planar with r.m.s. of 0.0123(2) Å and 0.0077(1) Å, respectively. The carboxylate groups C17/O11/O12 and C18/O13/O14 make dihedral angles with the ligand ring 1 of 17.8(2)° and 13.3(2)°, respectively; the respective angles between C27/O21/O22 and C28/O23/O24 groups and the ligand 2 ring are 15.9(2)° and 8.4(2)°. The Li3 ion shows a distorted tetrahedral coordination geometry with a pair of bridging carboxylate O13 and O23 atoms and a pair of coordinated aqua O1 and O2 atoms in *trans* arrangement. Li3 ion is neither coplanar with dimer 1 nor dimer 2 as indicated by the O14-Li3-O23 angle of 110.6(3)°; its position in respect of adjacent dimers makes a half-open cavity which is occupied by the hydrazinium cation. The layers are held together by an extended system of hydrogen bonds in which the hydrazinium cation, coordinated and crystal water molecules act as donors to carboxylate O atoms.

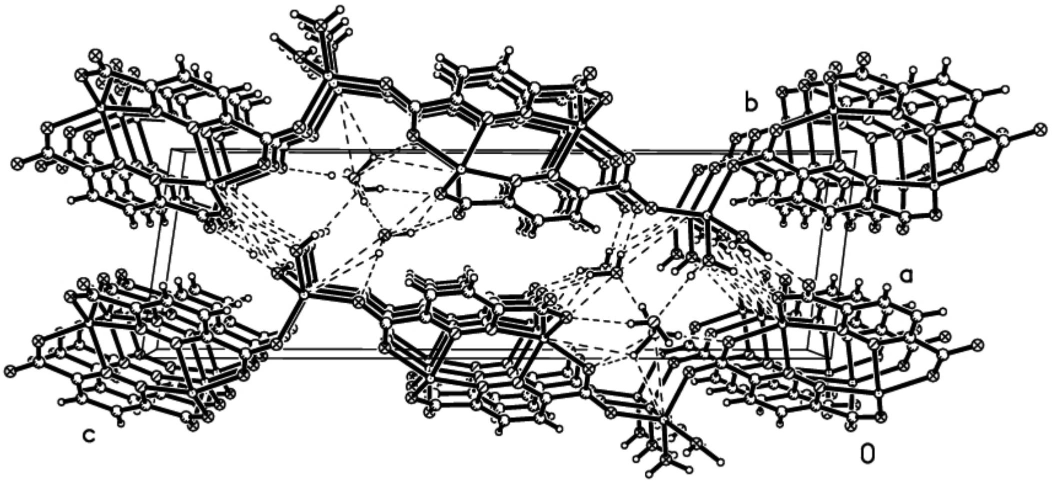

Fig.4. The packing diagram of the title structure.

Part 14. Poly[μ_2-aqua-μ_2-(pyrazine-2-carboxylato)lithium]

The structure of the title coordination polymer is composed of two Li(I) ions coordinated by ligand *N,O* bonding group with its O atom acting as bidentate and bridging two symmetry related Li1 and Li1^{i} ions, whereas the O2 atom remains chelating inactive. The metal ions are also bridged by coordinated aqua O atom forming a Li1–O1–Li^{i}–O3–Li1 connectivity with Li1-Li1^{i} distance of 3.052(4) Å (Fig.5). The observed bonding path-

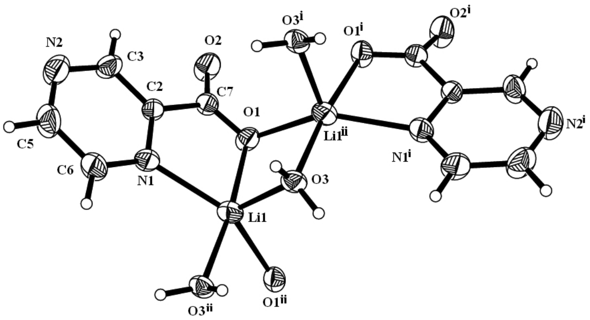

Fig.5. Structural units of the title compound with atom labelling scheme and 50% probability displacement ellipsoids. Symmetry code: (i) -x+1/2, y, z+1/2; (ii) -x+1/2, y, z+1/2.

ways –Li–O$_{\mathrm{carb.}}$ –Li– and –Li–O$_{\mathrm{aqua}}$–Li– give rise to a molecular ribbon which propagates in the unit cell *c* direction (Fig.6). The Li coordination polyhedron is distorted trigonal bipyramid with an equatorial plane composed of O1, N1^{i} and O3^{i}; the Li1 ion is 0.0405(2) Å out of the plane, O1 and O3 atoms are at the axial positions. The pyrazine ring is planar with r.m.s of 0.0019(1) Å; the dihedral angle between pyrazine ring and the carboxylate group C7/O1/O2 is 12.3(1)°. Hydrogen bonds operate between coordinating water and carboxylate O atoms.

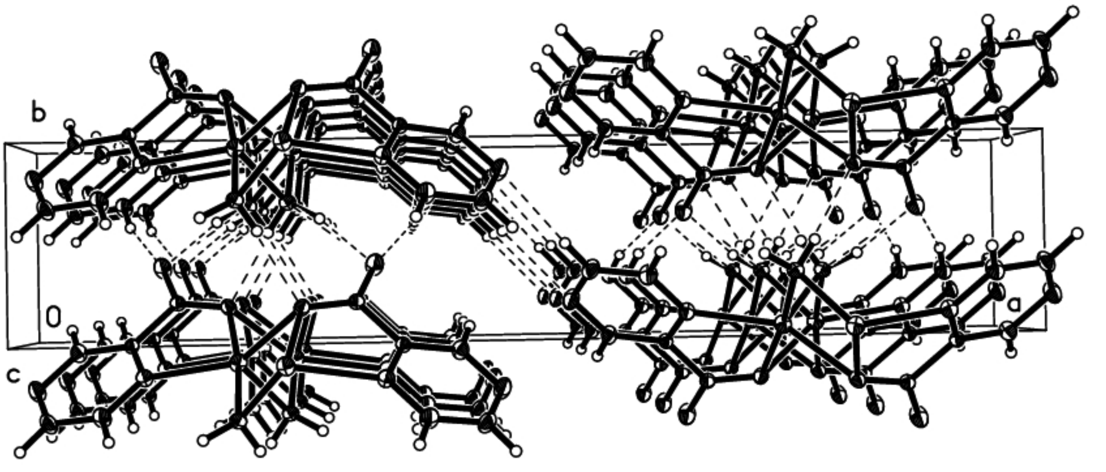

Fig.6. The packing diagram of the title structure.

Part 15. Bis(μ_3-pyrimidine-4-carboxylato)bis(μ_2-pyrimidine-4-carboxylato)tetrakis(aqualithium)

The structure of the title compound is built of tetrameric molecular clusters, each composed of two dinuclear units related by an inversion centre. A dinuclear unit consists of two symmetry independent Li1 ions, two symmetry independent ligand molecules and two symmetry independent coordinating water molecules (Fig.7). The ligand molecule PMC1 shows μ_2 bridging mode: its carboxylate O11 atom acts as bidentate bonded to Li1 and Li2 ions, leaving the O12 atom chelating inactive. Ligand PMC2 shows μ_3 bridging mode since both its carboxylate O atoms act as bridging: the O22 atom bridges the Li2 ion and the Li1 ion while the O21 atom links the Li2 ion and the Li1^{i}. The Li1–O11–Li2–O22–Li1 bridging pathway forms a core of a dinuclear unit with r.m.s. of 0.0133(2) Å, which through bridging O21 and O21^{i} atoms generates a centrosymmetric tetrameric molecular cluster with a core represented by a bonding loop Li1–O22–C27–O21–Li1^{i}–O22^{i}–C37^{i}–O21^{i}–Li1^{i} with r.m.s. of 0.1664(3) Å. Li1 ion, chelated by O1, O11, O22 and O21^{i} atoms shows a distorted tetrahedral coordination geometry. On the other hand, Li2 coordination polyhedron is a distorted trigonal bipyramid with an equatorial plane composed of O11, O2 and N23 atoms. The Li2 ion is 0.1809(2) Å out of this plane; N13 and O22 atoms are at axial positions. The observed Li–O and Li–N bond distances are typical. Both pyrimidine rings are planar with r.m.s. of 0.0080(2) Å and 0.0079(2) Å for ligand PMC1 and PMC2, respectively. The carboxylate groups C17/O11/O12 and C27/O21/O22 make dihedral angles of 4.3(1)° and 3.3(1)° with the respective rings. A hydrogen bond system in which water molecules are donors and carboxylate O atoms are acceptors is responsible for the cohesion of the structure (Fig.8).

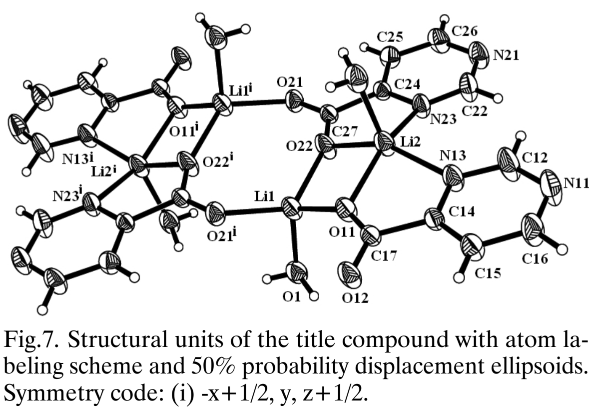

Fig.7. Structural units of the title compound with atom labeling scheme and 50% probability displacement ellipsoids. Symmetry code: (i) -x+1/2, y, z+1/2.

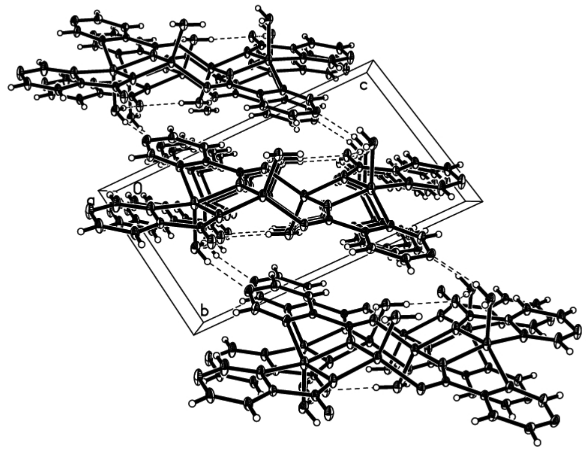

Fig.8. The packing diagram of the title structure.

Part 16. Poly[hexaaquabis(μ_4-pyrimidine-4,6-dicarboxylato)tetralithium]

The asymmetric unit of the title compound contains two symmetry independent Li(I) ions, one with a distorted trigonal bipyramidal, the other with distorted tetrahedral coordination geometry, a deprotonated ligand molecule acting in μ_4 bridging mode and two independent water molecules coordinated to metal ions. The structural unit is built of asymmetric units related by an inversion centre. The ligand *N1,O1* bonding group chelates the Li1 ion leaving the carboxylate O2 atom coordination inactive while its carboxylate O3 and O4 atoms bridge, related by an inversion centre, Li2 and Li2^{ii} ions. The latter are also coordinated by O4^{ii} and O3^{ii} atoms donated by the adjacent one related by the same inversion centre ligand forming a dimeric bonding loop which constitutes a core of a centrosymmetric structural unit composed of the Li1 ion, the ligand, the dimeric loop, the ligand^{ii} and the Li1^{ii} ion (Fig.9). The plane of the loop (r.m.s. 0.2647(5) Å) makes a dihedral angle of 24.0(2)° with the ligand ring plane. This unit, terminated on both sides by Li1 and Li1^{ii} ions linked to adjacent units *via N3*^{i}*,O3*^{i} and *N3*^{iii}*,O3*^{iii} bonding groups and *via N3,O3* and *N3*^{ii}*,O3*^{ii} bonding groups to Li1^{v} and Li^{iv} ions in adjacent units, generate a two-dimensional layer with Li1 ions as its nodes (Fig.9). The arrangement of the layers in the unit cell is shown in Fig.10. The coordination polyhedron of the Li1 ion, composed of the bridging *N1,O1* and *N3*^{i}*,O3*^{i} bonding groups and the aqua O5 atom is a distorted trigonal bipyramid. Its equatorial plane is formed by N1, N3^{i} and O5 atoms. The Li1 ion is 0.0908(2) Å out of this plane, O1 and O3^{i} atoms are at apical positions. The Li2 ion chelated by carboxylate O3,O4^{ii} atoms and aqua O6 with inversion related atoms shows a distorted tetrahedral coordination geometry. The pyrimidine ring is planar with r.m.s. of 0.0121(2) Å, C7/O1/O2 and C8/O3/O4 carboxylate groups make with it dihedral angles of 4.0(1)° and 24.0(2)°, respectively. Bond distances and bond angles are close to those observed in the structure. A network of hydrogen bonds in which coordinated water molecules act as donors and carboxylate O atoms are acceptors maintains the stability of the structure.

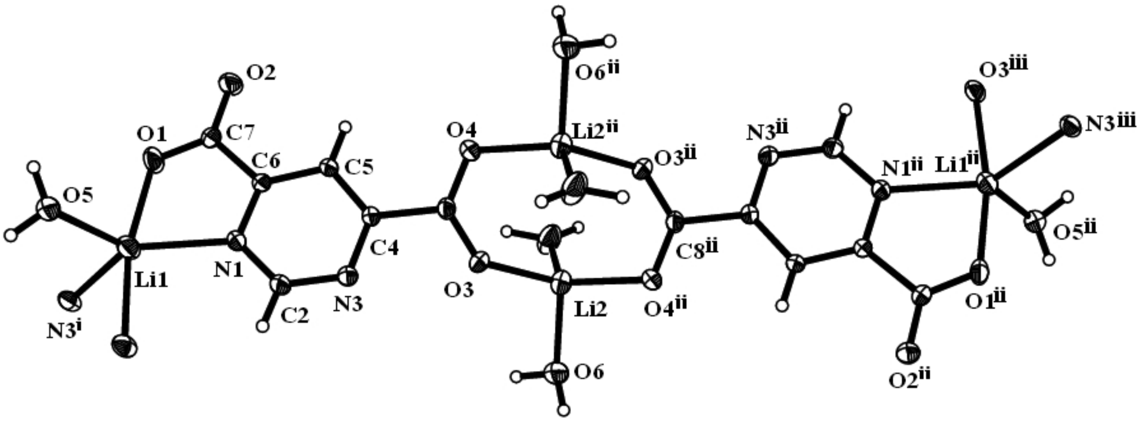

Fig.9. Structural unit of the title compound with atom labelling scheme and 50% probability displacement ellipsoids. Symmetry code: (i) -x+1/2, y+1/2, -z+1/2; (ii) -x+1, -y+1, -z+1; (iii) x+1/2, -y+1/2, z+1/2.

Part 17. *catena*-**Poly[[tetraaqua-μ-aqua-bis (μ_4-pyrimidine-2-carboxylato)tetralithium]dichloride]**

The asymmetric cell of the title compound contains two symmetry independent Li1 ions, one deprotonated pyrimidine-2-carboxylate ligand molecule, three symmetry independent water molecules which are coordinated to metal ions and one chloride anion. The latter maintains charge balance in the cell. Two symmetry related cells form a molecular moiety which can be visualized as a building unit of the structure (Fig.11). The ligand bridges Li ions in a μ_4 mode using both its carboxylate O atoms which act as bidentate. Ligand bonding groups *N1,O1* and *N3,O2* chelate Li1 and Li1^{ii} ions; the O1 and O2 atoms are also bonded to Li2 and Li2^{i} ions, respectively. Since the Li1 and Li1^{ii} ions are also coordinated by bonding groups from the adjacent symmetry related ligands, a

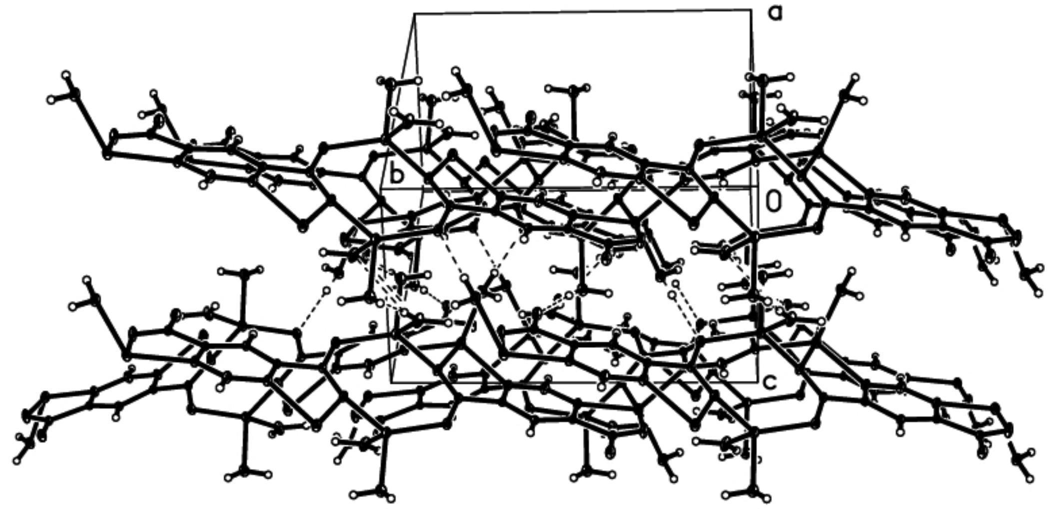

Fig.10. The packing diagram of the title structure.

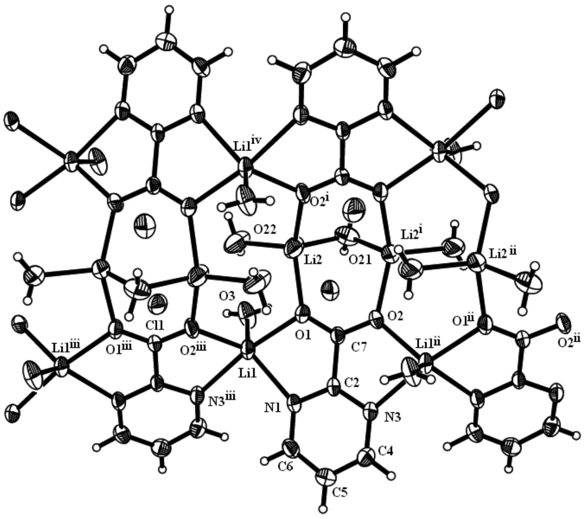

Fig.11. Structural unit of the title compound with atom labelling scheme and 50% probability displacement ellipsoids. Symmetry code: (i) -x, y, -z; (ii) x, -y+2, z-1/2; (iii) x, -y+2, z+1/2; (iv) -x, -y+2, z+1.

–Li1^{ii}–O2–O1–Li1–O2^{iii}–O1^{iii}–Li1^{iii}– bridging pathway is formed. Apart from two *N,O* bonding groups, Li1 coordination is completed by an aqua O3 atom. On the other hand, pairs of adjacent symmetry related Li2 and Li2^{i} ions are bridged by an aqua O21 atom while the other coordinated to them aqua O22 and O22^{i} atoms are not bridging. Adjacent moieties linked along the Li1 bridging pathway form a cationic ribbon propagating in the unit cell *b* direction (Fig.12). Chloride anions are located in the space between adjacent ribbons. Figure 11 shows, that a ribbon can be visualized as built of centrosymmetric molecular clusters in which Li ions form a tetrameric entities additionally connected by Li2–O21–Li2^{i} bridges. The Li1 ion exhibits a distorted trigonal bipyramidal coordination environment in which O1, O3 and N3^{iii} atoms form an equatorial plane with a Li1 ion 0.0619(2) Å out of it; N1 and O2^{iii} atoms are at apical positions. The coordination of the Li2 ion is strongly distorted tetrahedral. The Li–O and Li–N bond distances are close to those reported earlier in the structures of a Li complexes with the title and nitrate ligands. The pyrimidine ring is planar with r.m.s. of 0.0071(1) Å; the C7/O1/O2 makes with it a dihedral angle of 5.8(1)°. Weak hydrogen bonds in which water O atoms are as donors and chloride anions act as acceptors operate between adjacent ribbons.

Part 18. Poly[(μ_4-3-carboxypyrazine-2-carboxylato)(μ_4-nitrato)dilithium]

The asymmetric unit of the title compound contains two symmetry independent Li1 ions. Each shows a distorted trigonal bipyramidal coordination geometry. The Li1 ion is coordinated by ligand *N1,O1* bonding group, a carboxylato O3^{ii} atom from the adjacent ligand and O5 and O7^{i} atoms from two different nitrate ions. The O1, O5, O7^{i} atoms form a base, the Li1 ion is 0.1572(3) Å out of this plane; N1 and O3^{ii} atoms are at the axial positions. The same coordination geometry shows the Li2 ion which is situated 0.3616(3) Å out of the equatorial plane composed of N4, O1^{iii} and O6^{v} atoms, while the O3 and O5^{iv} atoms form the apices. The observed Li–O and Li–N bond distances are typical of Li(I) complexes with diazine carboxylate ligands. Ligand carboxylate O2 and O4 atoms remain coordination inactive. Fourier maps indicate clearly that the O2 atom is protonated acting as a donor in a low-barrier intramolecular hydrogen bond of 2.3955(19) Å to the O4 atom suggesting a partial proton transfer. The ligand is monovalent and with the nitrate anion maintains the charge balance in the structure. Pyrazine ring is planar with r.m.s. of 0.0051(2) Å; carboxylate groups C7/O1/O2 and C8/O3/O4 form with it dihedral angles of 8.4(1)° and 12.5(1)°, respectively. Ligand molecule bridges metal ions in μ_4 mode. Li1 and Li2 ions are chelated by both

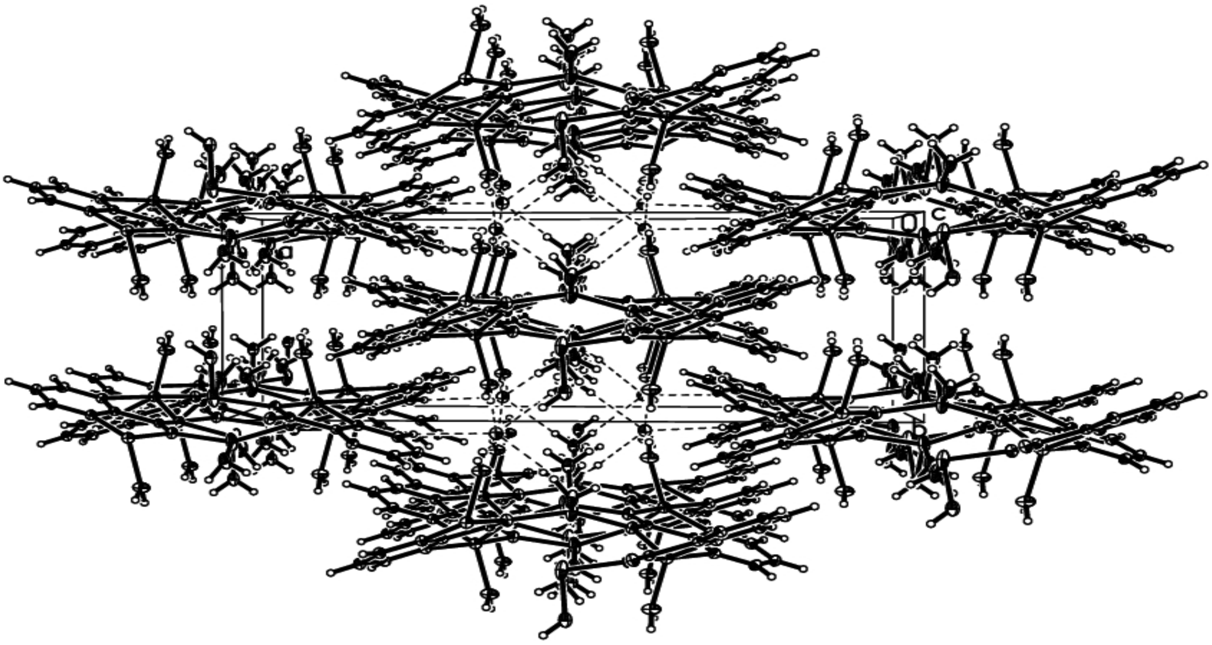

Fig.12. The packing diagram of the title structure.

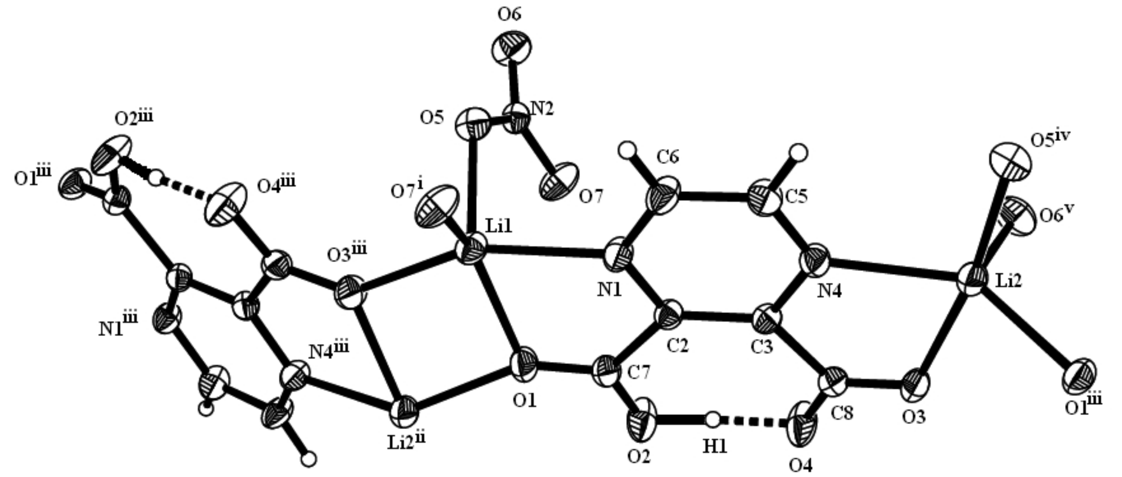

Fig.13. A fragment of the structure of the title compound with atom labelling scheme and 50% probability displacement ellipsoids. Symmetry code: (i) x+1, y, z; (ii) -x+1, y+1/2, -z+2; (iii) -x+1, y-1/2, -z+2; (iv) -x+1, y-1/2, -z+1; (v) -x, y-1/2, -z+1.

N,O groups of a ligand and bidentate O1^{ii} and O3^{ii} atoms (Fig.13). A dimeric moiety Li1/O1/L2^{ii}/O3^{iii} constitutes a link in a bridging pathway formed by ligand molecules, giving rise to molecular ribbons propagating in the [010] direction. A nitrate anion with r.m.s. of 0.0016(1) Å acts also in the μ_4 mode and forms the other bridging pathway: while the O6 atom coordinates the Li2^{v} and the O7 atom – the Li1^{iv} ion, the O5 atom acts as bidentate bridging to the Li1 and Li2^{iii} ions giving rise to a three-dimensional framework (Fig.14).

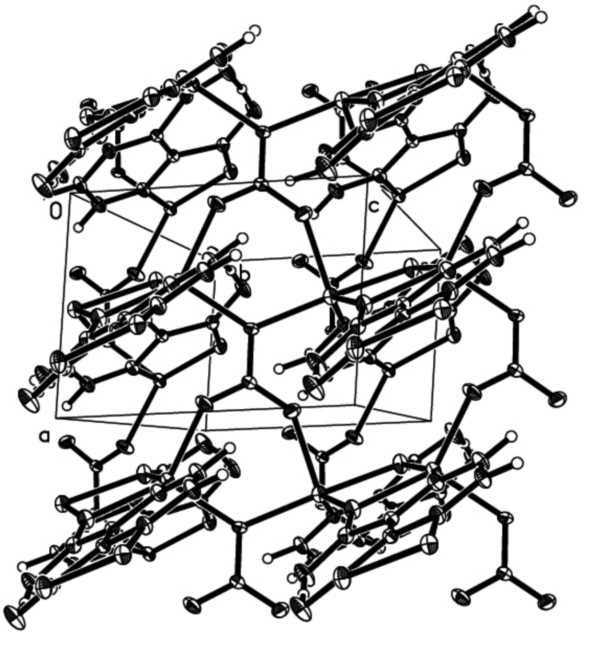

Fig.14. The packing diagram of the title structure.

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TRIBOLOGICAL PROPERTIES OF STAINLESS STEEL SURFACE LAYER ENRICHED WITH RARE EARTH ELEMENTS

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Due to their very good corrosion resistance austenitic stainless steels are used in numerous industrial applications, for example nuclear and petrochemical industries, pulp and paper chemical, food and chemical processing and biomedical industries. But poor tribological and mechanical properties of austenitic stainless steels limited their applications in engineering fields. Improvement of austenitic stainless steels is very important from engineers' and constructors' point of view. High oxygen affinity elements such as Y, Ce, La and other rare earth elements (REE) added to steels in small amounts can improve their resistance for wear [1], electrochemical corrosion [2] and high temperature oxidation [2, 3].

REE can be alloyed during the steel making process and then technical elements are produced from the obtained material, for example tubes, wires or machine details [4]. REE can be added to the surface region of materials using different surface modification techniques. REE incorporation to the surface layer of steels can be realized by: conventional ion implantation [2, 3, 5], pulsed plasma beams [6-8], plasma immersion ion implantation [6], metal organic chemical vapour deposition [9], sol-gel coating [5]. When high intensity, short duration ion or plasma pulses hit a solid, they can modify the structure of its near-surface region. Heating and cooling processes were of non-equilibrium type. Ion or plasma pulses can lead to variety of the processes such as: mixing of the predeposited films with substrate material, formation of new stable or/and metastable phases, grain refinement [7, 8].

In the present work we report results of investigations of stainless steel surface properties (morphology, REE concentration, presence of identified phases) after REE addition with or without melting.

Austenitic stainless steel AISI 316L with the main elements concentration: Cr – 16.3 wt.%, Ni – 11.5 wt.%, Mo – 2.0 wt.%, Mn – 1.3 wt.%, Fe – balance, hot rolled, was used as the substrate for investigations. As a REE source, the mishmetal with composition: Ce – 65.3 wt.%, La – 34.0 wt.% and balance of Fe, Mg, and Pr was used. As a source of the single element of REE, the targets made of Ce and La were used.

Two different methods were used for one surface of steel samples modification:

- REE ion implantation with parameters: 65 kV and nitrogen as the working gas up to REE doses in the range of 1 x 10^{15} to 5 x 10^{17} cm^{-2};
- high intensity pulsed plasma beams (HIPPB) in deposition by pulse erosion (DPE) mode with pulse energy density of 3.0 J/cm^2, duration in μs range and nitrogen as the working gas.

  The near surface layer with a thickness in μm range was melted and simultaneously doped with REE. Various parameters of the process

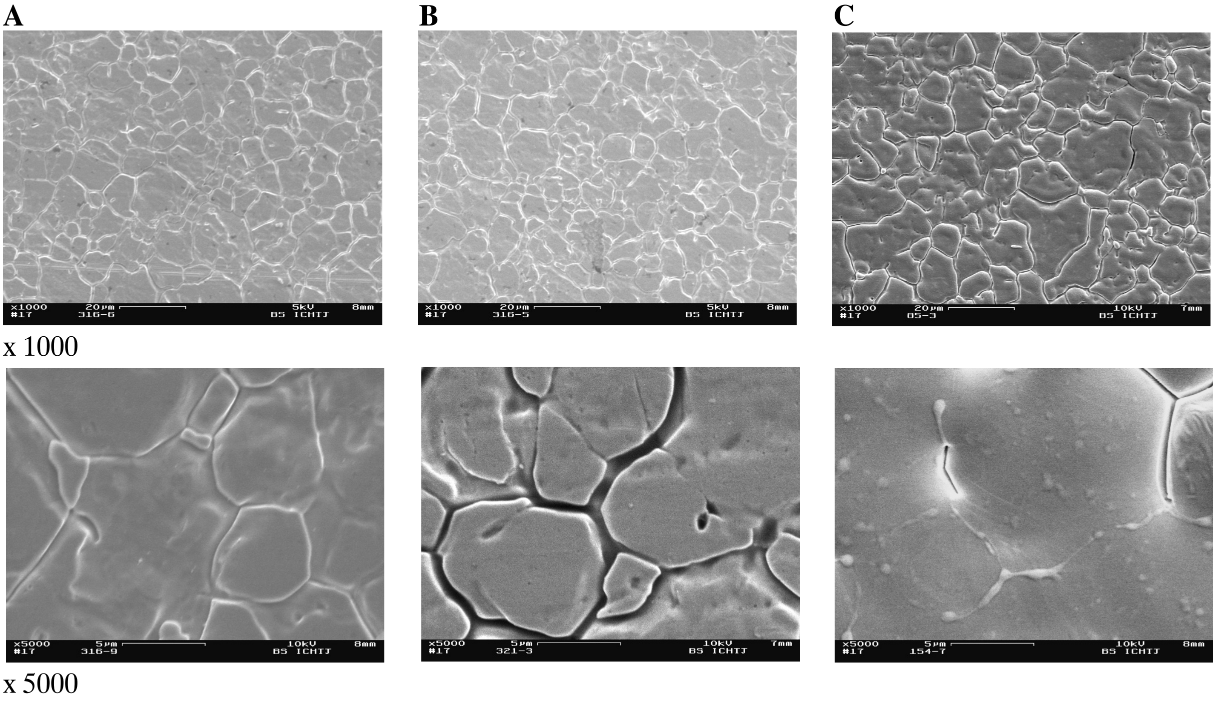

Fig.1. Details of surface morphologies of AISI 316L steel: A – initial, B – implanted up to REE concentration 0.9 wt.%, C – HIPPB treated and enriched with REE up to 1.0 wt.%.

were set up to get level of doping between 0.3-3.0 at.% REE. Deatils of the DPE mode are described in [4, 8]. In this mode of operation the plasma contains ions of the working gas and also ions/atoms eroded from the electrodes tips. In DPE process the transient melting of the near-surface occurs and the rapid solidification takes place.

Initial and modified samples were characterized by: scanning electron microscopy (SEM) with DSM 942 (Zeiss, Germany) for initial and modified surface morphology observations, energy dispersive X-ray spectrometry (EDX) with Quantax 400 (Bruker, Germany) for surface elemental concentrations determination, grazing angle X-ray diffraction (GXRD, ω = 5°) with CuK$_\alpha$ radiation using an X-ray diffractometer D8 Advance (Bruker, Germany) for phase identification in the surface layer of material, Amsler method of wear measurements (sliding friction distance – 3000 m, constant load – 5 daN, 41Cr4 steel counter-sample, single immerse lubrication) for tribological properties determination.

Samples surface morphologies are presented in Fig.1. At the surfaces of initial sample, the grains in different sizes are visible as a result of steel making process – steel was delivered after hot rolling as the finishing treatment (Fig.1A). After implantation the surface morphology was not changed – grain boundaries are still visible (Fig.1B). After HIPPB modifications, the initial grains disappeared and different morphological details and features of the mixed deposit-substrate material can be seen. Craters, cracks and other morphological features observed on the modified surfaces are typical of melted and rapidly solidified material (Fig.1C). These results show the first difference between the used modification methods.

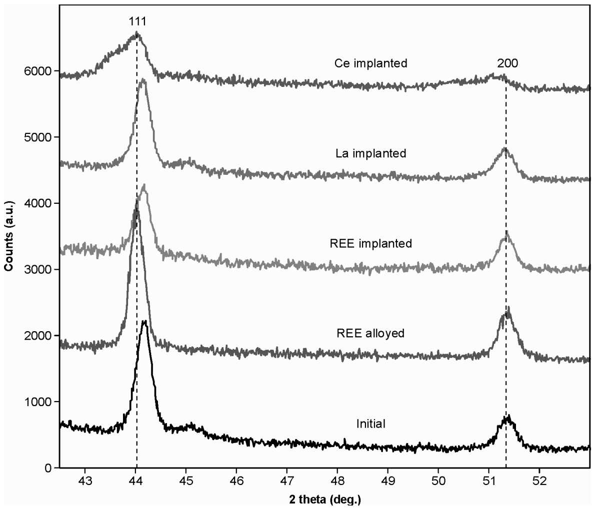

Fig.2. GXRD spectra of AISI 316L steel: initial, REE implanted and alloyed with REE.

Atomic concentrations of REE incorporated into specimens were in the range of 0.2-6.0 at.%. The ratio of Ce/La concentration was the same as in the used mishmetal.

Samples with a similar REE concentration (about 1.0 wt.%) were chosen to the phase identification. XRD spectra for initial and modified materials show the FCC phase (austenite) presence.

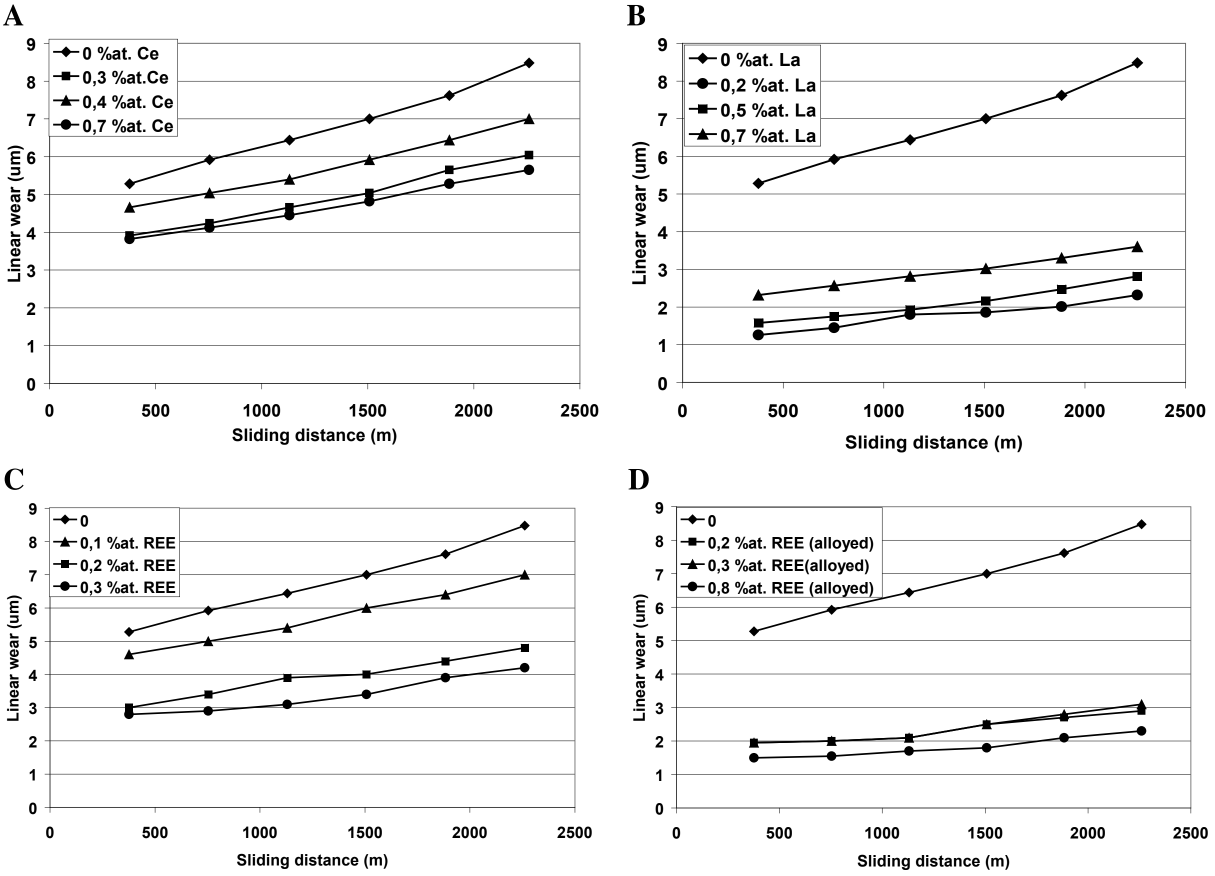

Fig.3. Wear measurements results: A – AISI 316L + Ce implanted, B – AISI 316L + La implanted, C – AISI 316L + REE (Ce + La) implanted, D – AISI 316L + REE (Ce + La) alloyed.

This is clear in the case of initial material – austenitic stainless steel. In the case of modified materials, the presence of peaks characteristic of FCC structure confirm that after enrichment the surface layer with REE austenitic phases still are present in the material. The first two peaks of GXRD spectra for initial and modified materials are presented in Fig.2. In the case of initial material, the peaks (111) and (200) were recorded and confirm the presence of austenitic structure of AISI 316L steel. In the case of investigations of the surface layer after ion implantation, the identified peak of austenite (111) were shifted towards the bigger angles what means that the lattice parameter of austenite was decreased. In the case of investigations of the surface layer modified with HIPPB, the surface layer was melted and the initial structure of steel was fully destroyed. During rapid solidification, the process of freezing of the austenite took place. Solidification took place when REE ions are present in the melts. So formed austenitic structures has a different lattice parameter than in the initial material. Identified peaks of austenite (111) and (200) were shifted towards the lower angles what means that the lattice parameter of austenite was increased. These results show the second difference between the used modification methods.

Dependence of the liner wear for the initial and modified with REE material is presented in Fig.3. The presented diagram shows a linear character of linear wear changes for all investigated samples. Modified AISI 316L steel reveals a smaller value of linear wear after each one part of wear measurements as compared with the initial material. Presented results show the bigger improvement of tribological properties for higher REE concentrations. Presented results – as results of carried out measurements up to 3 000 m of sliding distance – are very promising in respect of tribological properties improvement. The long distance trials are planned for investigations of the modified surface behaviour during simulated application conditions.

Using two different methods with ion application, the REE elements (here: Ce + La) were incorporated to the AISI 316L steel. The austenitic structures were present after modification processes, but in the case of ion implantation processes the initial austenitic structure of steel remains and in the case of HIPPB processes the austenitic structure was frozen as a result of rapid solidification. Enrichment steel surface later with REE leads to improvement of AISI 316L steel tribological properties.

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THE CHEMICAL COMPOSITION OF GLASS FROM THE HUNGARIAN GLASSHOUSES AND GLASS UTILIZED IN HUNGARY FROM THE 14TH CENTURY TO THE 17TH CENTURY

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The aim of the on-going project is to outline the development of Hungarian glass and glass utilized in Hungary from the 14th century to the 17th century. These preliminary results focus on chemical composition of material excavated in two glasshouses (Diósjenő, dated to the 14th-15th century and Visegrad, dated to the 15th-16th century) as well as in various places, including royal castles, of medieval and post-medieval Visegrad and Buda, dated to the 14th-17th century.

Scanning electron microscopy-energy dispersive spectrometry (SEM-EDS) has been applied to analyse 33 glass fragments. They represent colourless, coloured and opaque glass, vessel and window glass, including stained glass, as well as two bracelets in addition to the glass fragments, such as moils and slags gathered from the glasshouse sites. The measurements were carried out in the Wolfson Labs of the Institute of Archaeology (London, UK).

The simplified chemical compositions of the main chemical groups are shown in Table. Two main groups are woodash glass and soda plant ash glass (Fig.). Neither is homogeneous, suggesting diversity of glass production centres and/or raw materials used. Among soda plant ash glass, further

Table. The simplified chemical compositions of the main chemical groups identified (SEM-EDS [wt.%]); < – below DL.

Site	Type of glass	Period	Object	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3
Various sites in Visegrad and Buda	woodash glass	14th-17th century	vessel and window glass, av. (n = 17)	0.4	2.5	1.6	53.9	1.0	0.3	<	20.6	16.2	0.1	0.6	0.6
	soda plant ash glass		vessel glass, av. (n = 7)	12.4	3.5	0.8	67.5	0.2	0.3	0.8	2.2	10.8	0.1	0.7	0.5
Visegrad, Lower Castle		16th-17th century (Ottoman period)	green bracelet	14.5	1.7	2.2	66.9	0.3	0.1	0.9	4.0	7.2	0.1	0.4	1.0
			opaque blue bracelet	16.9	1.1	1.4	67.7	0.2	0.2	1.0	0.8	4.9	0.2	<	0.7
Visegrad, glasshouse site		15th-16th century	prunted beaker	12.8	3.4	0.9	67.3	0.3	0.3	0.7	2.2	11.1	<	0.6	0.4
			prunted beaker	12.3	3.4	0.5	67.7	0.3	0.4	0.8	1.9	12.1	<	0.4	0.4
	woodash or for woodash glass		glass from a pot	1.7	3.3	12.2	58.5	1.0	<	<	3.6	10.6	0.8	0.4	7.8
			fragment of vessel	0.2	2.0	1.0	55.4	1.1	0.3	<	27.2	11.7	<	0.6	0.5
Diósjenő, glasshouse site		14th-15th century	slag	0.3	1.4	5.4	68.6	0.5	0.3	<	15.1	7.2	0.3	0.2	0.9
			slag	0.4	2.7	4.4	57.9	1.4	0.1	<	14.9	16.2	0.4	0.2	1.5
			glass from a pot	0.6	0.2	6.5	79.7	<	<	<	11.5	0.6	0.6	0.0	0.3

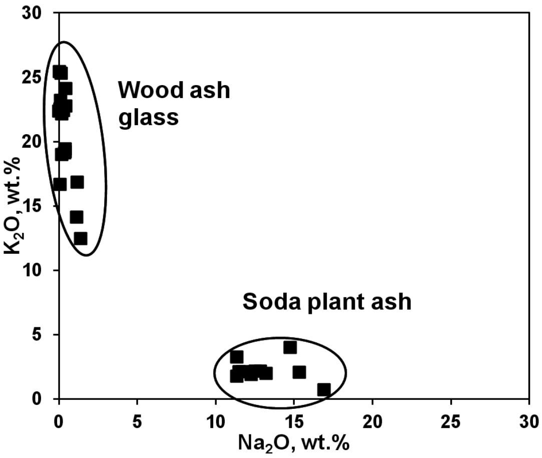

Fig. Two main chemical groups of Hungarian glass.

two main subgroups are: glass melted in a tradition of Italian glassmaking or in Italy and glass from Ottoman period (Turkish imports?). They were melted with the use of different plant ash as a source of alkalis. The composition of glass from the pots as well as of the slags found on the sites of two medieval Hungarian glasshouses suggests that woodash glass was melted in both glasshouses. However, the typical composition of soda ash glass of some prunted beakers found on the site of the glasshouse in Visegrad might support a hypothesis that soda plant ash glass was melted there, too.

The project shows a diversity of glass types used in late and post-medieval Hungary. The main glass trade and influence directions were, depending on a period, Italy and other Mediterranean areas (glass from Ottoman period) as well as central Europe, such as Germany and Bohemia.

The project identifies the use/or manufacturing of Ottoman glass in central Europe.

The majority of glasses, however, represent the typical wood ash technology, characteristic of both: domestic production and imports, mainly, from Germany and Bohemia.

Late and post-medieval glass in Hungary appears to be very diverse and influenced by various directions.

ANALYSIS OF GROUNDS FROM ICON PAINTING (KORYTNIKI ORTHODOX CHURCH, POLAND)

Ewa Pańczyk, Magdalena Pańczyk[1/], Elżbieta Gaździcka[1/], Jarosław Giemza[2/], Leszek Giro[1/], Justyna Olszewska-Świetlik[3/]

[1/] Polish Geological Institute-National Research Institute, Warszawa, Poland
[2/] Castle Museum in Łańcut, Poland
[3/] Nicolaus Copernicus University in Toruń, Poland

A physicochemical analysis of a painting is aimed at determining the exact nature of the various materials and the technical features of paint application stating their condition. An analysis of the pigments used in paintings is of the most importance in order to develop appropriate methods for their conservation as it provides a detailed characteristic of the materials and enables their origins to be determined. Individual features that typify a specific artist can also be extracted.

The main aim of this study was petrological, chemical and micropaleontological analysis of grounds from the icons of St. Demetrius Orthodox Church at Korytniki near Przemyśl (Poland), now collected at the Orthodox Art Department at the Castle Museum in Łańcut. The samples of grounds were taken from the 15th-17th centuries icon paintings representing the so-called South-Eastern Polish school. The following icons were selected for analysis: "Christ Baptism" (16th century), "St. Paraskeva" (15th century), "St. Onufry" (17th century), "St. John Evangelist" (16th century) and "Last Judgment" (16th century) [1-3].

Characterization of grounds was carried out by means of the following methods:

- optical microscopy – for description and identification of grounds, painting layers and potential source rocks;
- scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDX) – for morphology, distribution and chemistry of minerals as well as for identification of microfossils;
- instrumental neutron activation analysis (INAA) – for identification and concentration of elementary and trace elements;
- multi-parameter statistical analysis – for identifying the degree of similarity between the analysed objects and the sources of the mineral pigments.

The analyses of grounds carried out with SEM revealed a mass occurrence of coccoliths (*i.e.* calcite shields secreted by marine unicellular algae) in association with shells of planktonic foraminifers

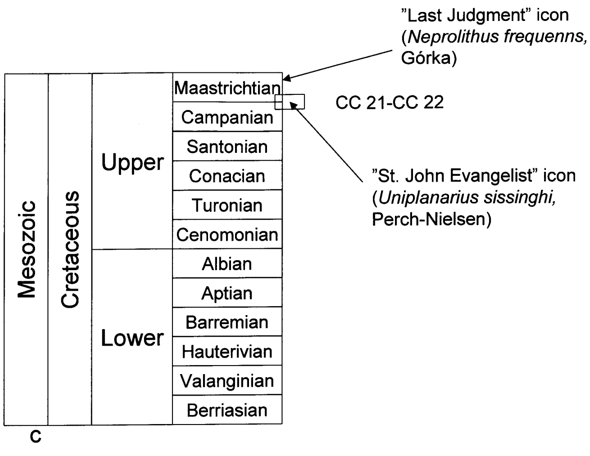

Fig.1. Stratigraphy table for Cretaceous.

(Figs.1 and 2). They are both of the Upper Cretaceous age, precisely the Upper Campanian and the Upper Maastrichtian. In the ground of the “Last Judgment” icon a reach and well preserved assemblage of coccoliths with *Arkhangelskiella cymbiformis* (Vekshina), *Cribrospaerella ehrenbergii* (Arkhangelsky), *Prediscosphaera cretacea* (Arkhangelsky) and *Nephrolithus frequens* (Górka) was found. The last species had a very short, in geological meaning, period of occurrence restricted

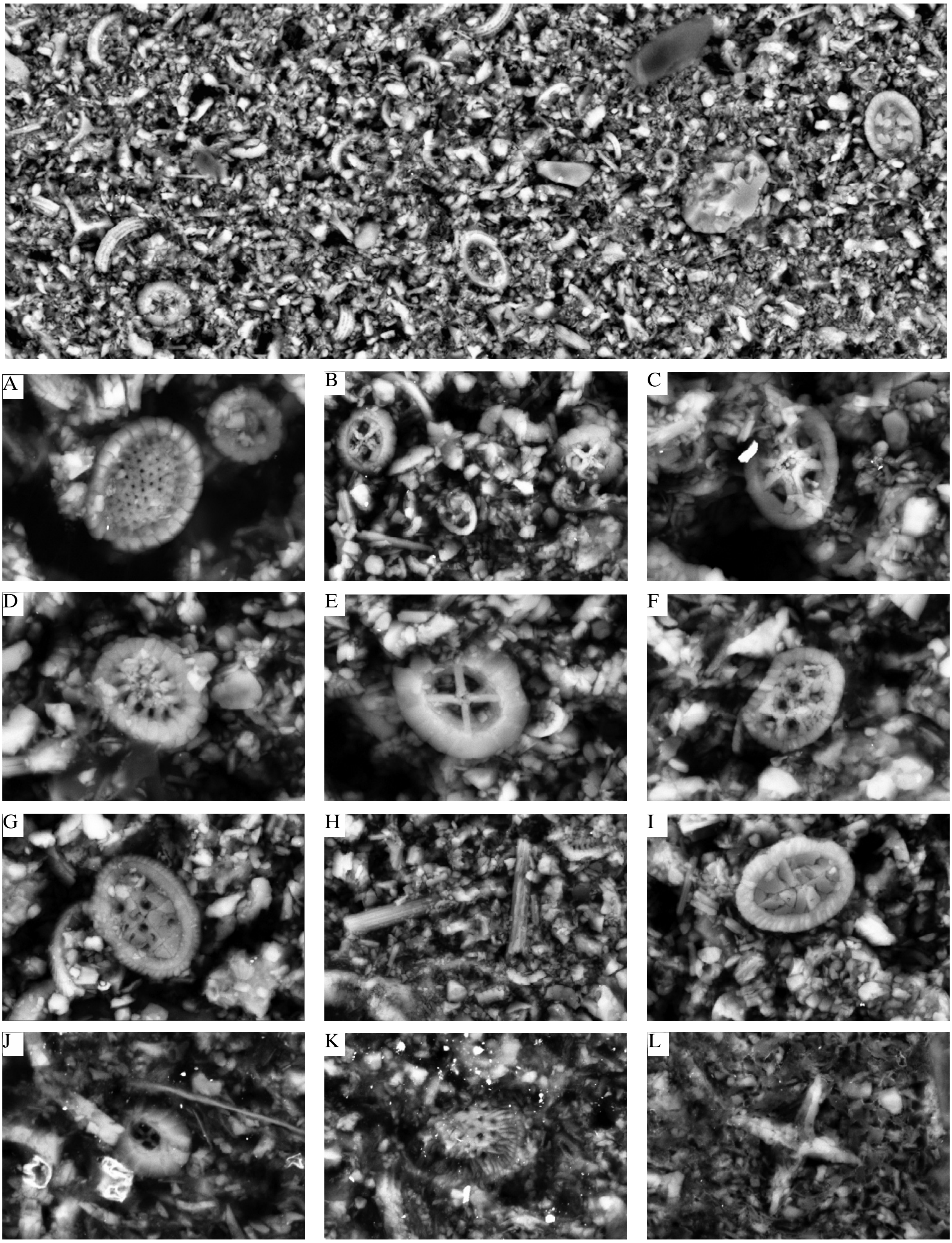

Fig.2. BSE image of grounds with coccoliths from the “Last Judgment” icon (A-I) and “St. John Evangelist” icon (J-L): (A) *Cribrosphaerella ehrenbergii* (Arkhangelsky), (B) *Prediscosphaera cretacea* (Arkhangelsky), (C) *Ahmuellerella octoradiata* (Górka), (D) *Retacapsa crenulata* (Bramlette *et* Martini); (E) *Prediscosphaera cretacea* (Arkhangelsky), (F) *Nephrolithus frequens* (Górka), (G) *Arkhangelskiella cymbiformis* (Vekshina), (H) *Microrhabdulus crenulatus* (Deflandre), (I) *Arkhangelskiella cymbiformis* (Vekshina), (J) *Prediscosphaera cretacea* (Perch-Nielsen), (K) *Camptnerius magnificus* (Deflandre), (L) *Uniplanarius sissinghii* (Perch-Nielsen).

to the Uppermost Maastrichtian [4]. Whereas in the ground of the "St. John Evangelist" icon *Uniplanarius sissinghii* (Perch-Nielsen), typical for the Upper Campanian, was found, what point out for the different source of rock material used by an icon painter. In all probability the strata of Maastrichtian and Campanian marls from the Skole Unit of Polish Outer Carpathian were the source rock for the studied calcitic grounds [5, 6].

The element characterization of studied grounds was carried out by INAA. The twenty eight elements were selected for multi-parameter statistical analysis aimed at identifying the degree of similarity of analysed samples. The STATISTICA 8 (StaSoft) program was carried out to identify the similarity degree of the analysed objects and principal components analysis. The statistical analysis of 17 icons was performed for standarized and logarithmic variables. Results of this analysis are presented in Fig.3. which clearly show division into groups closely related to origin of the tested samples.

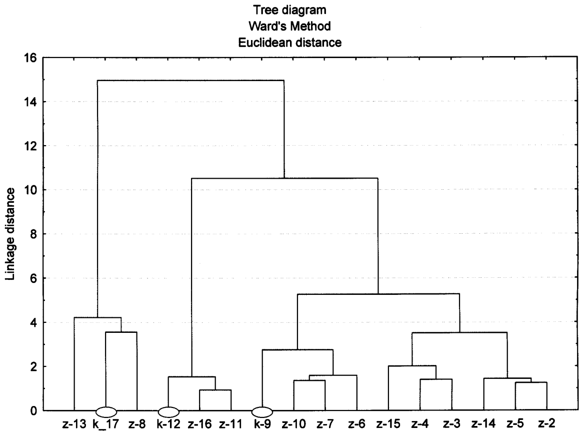

Fig.3. Cluster analysis of 17 icons paintings described by 20 elements.

The analysis results of Polish paintings from the so-called Małopolska and Silesian schools were evaluated to compare the type of grounds used in icon paintings in South-Eastern Poland [5, 6]. Figure 4 presents results of this analysis. The analysed icons constitute a separate group with the distribution of determined trace elements different than in the case of Małopolska and Silesian schools.

The aforementioned comparisons indicate that calcitic grounds used in the analysed icon paintings, constituting a unified, very typical group came from sources different than grounds used in Małopolska and Silesian paintings. Their "chemical finger prints" can distinctly identify samples and relationship between the matrix and the source of sample may be established.

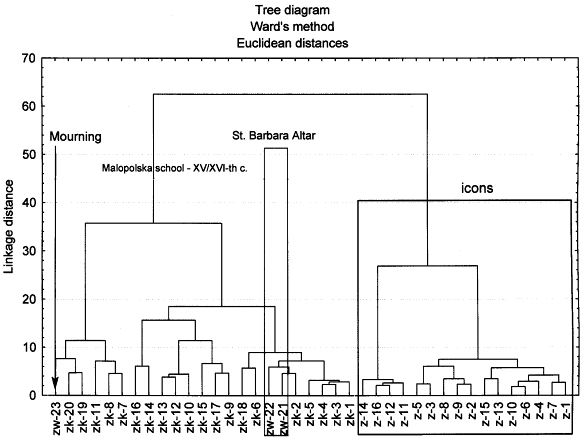

Fig.4. Cluster analysis of 49 paintings of Małopolska and Silesian schools, and icons described by 20 elements.

The results of technological and material research works are confronted with the knowledge on various artistic workshops, helped to attribute the paintings, to locate them in time and to reconstruct their history. The development of technological research together with more through studies of the achieves could explain the so far unknown stages of the history of the paintings and their restorations.

The research is supported by the Ministry of Sciences and Higher Education (Poland) – grant No. N N507 5847 38.

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POLLUTION CONTROL TECHNOLOGIES LABORATORY

Research activities of the Pollution Control Technologies Laboratory concern the concepts and application of methods of process engineering to the environmental area. In particular, we participate in research on the application of electron accelerators in such environmental technologies as flue gas and water treatment, wastewater purification, processing of different industrial waste, *etc*.

The main aims of activity of the Laboratory are:
- development of new processes and technologies of environmental engineering,
- development of environmental applications of radiation technologies,
- promotion of nuclear methods in the field of environmental applications.

The activities of our group are both basic and applicable research. Among them, the most important research fields are:
- development of electron beam flue gas treatment (EBFGT) technology,
- investigation of chemical reaction mechanisms and kinetics in gas phase irradiated by electron beam,
- study on the mechanism of removal of volatile organic compounds (VOCs) from flue gas by electron beam excitation,
- process modelling.

The Laboratory is equipped with such research tools as:
- an laboratory installation for electron beam flue gas treatment (flow rate up to 400 m^3/h),
- a gas chromatograph with a mass spectrometer,
- a portable gas analyser (NO_X, SO_2, CO, O_2, *etc*.).

In 2012, the research staff is involved in the following projects:
- "Dissemination and fostering of plasma-based technological innovation for environment protection in Baltic Sea Region – PlasTEP" (project co-financed by ERDF).
- "Electron beam flue gas treatment pilot tests".

The Laboratory is open to any form of cooperation. The most important partners of the Laboratory are:
- Faculty of Chemical and Process Engineering, Warsaw University of Technology (Poland);
- International Atomic Energy Agency;
- Saudi ARAMCO (Saudi Arabia);
- EB Tech Co., Ltd. (Republic of Korea);
- Technology Centre of Western Pomerania (Germany);
- Leibniz Institute for Plasma Science and Technology (Germany);
- Risø National Laboratory for Sustainble Energy, Technical University of Denmark (Denmark);
- Uppsala University, The Ångström Laboratory (Sweden);
- Kaunas University of Technology (Lithuania);
- Vilnius Gediminas Technical University (Lithuania);
- Robert Szewalski Institute of Fluid-Flow Machinery, Polish Academy of Sciences (Poland);
- West Pomeranian University of Technology (Poland);
- Ukrainian Engineering Pedagogic Academy (Ukraine).

TOLUENE DECOMPOSITION IN AIR IN THE PRESENCE OF CATALYST UNDER ELECTRON BEAM RADIATION

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

Volatile aromatic compounds contribute significantly to anthropogenic emissions of organic compounds and have a major impact on the photochemical production of ozone in troposphere. About 40% of ozone produced photochemically might contribute to emission of aromatics, mainly toluene [1]. Toluene destruction by using advanced electron beam (EB) [2-4] and electron beam combined with catalyst technology [5] has been studied extensively in recent years. In this work, toluene decompositions in air in the presence of catalyst under EB radiation were studied in batch system.

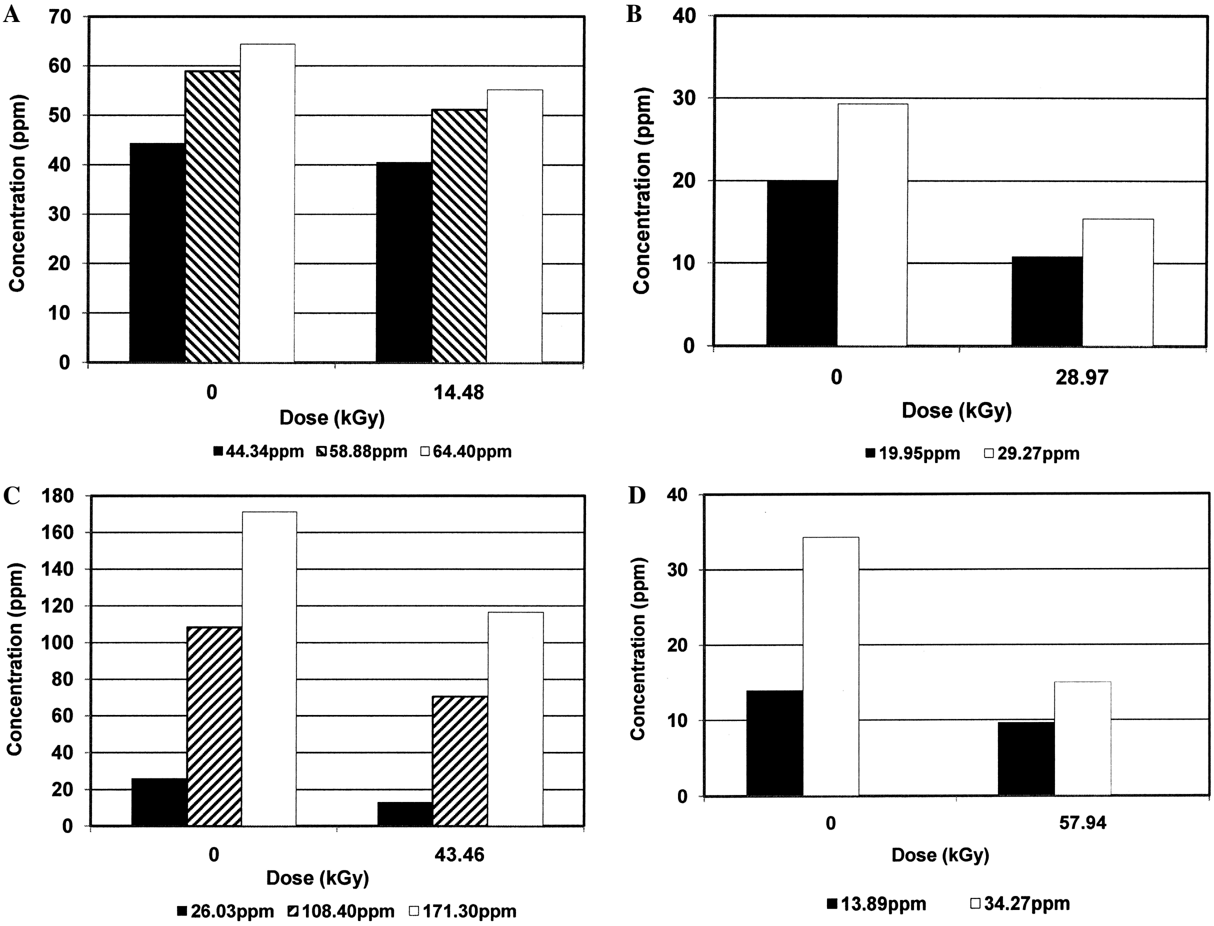

Fig.1. Concentration of toluene as a function of dose under EB radiation: A – 12.48 kGy, B – 28.97 kGy, C – 43.45 kGy, D – 57.94 kGy.

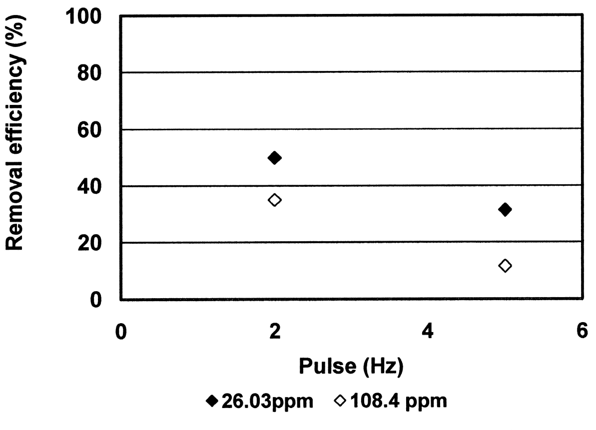

Fig.2. Pulse mode influence on toluene removal at the 43.45 kGy absorbed dose.

The $TiO_2/\gamma Al_2O_3$ catalyst (diameter < 1 mm, provided by KATALIZATOR Sp. z.o.o., Poland) was used. It was added inside the bottom of the glass reactors. Pure liquid toluene and synthesized air were used for the preparation of toluene/air mixture. A flowmeter was used to control initial concentration of toluene. ILU-6 pulse accelerator (2 MeV, 60 mA) was applied for irradiation. The results are given below:

- Different dose influencing toluene removal

Toluene removal in four different doses at 2 Hz pulse under EB radiation was investigated at different initial concentrations of toluene. The results were presented in Fig.1.

- Pulse mode influencing toluene removal

Two different pulse frequencies of 2 and 5 Hz were used to study toluene removal from air under EB radiation. The results were presented in Fig.2. Total irradiation dose was 43.45 kGy. For the initial concentration of 26.03 ppm toluene, 49.9% was removed at 2 Hz, while 31.27% toluene was removed at 5 Hz. For the initial concentration of 108.4 ppm toluene, 35.0% was removed at 2 Hz, while 11.48% toluene was removed at 5 Hz. The pulse mode with the lower frequency led to the higher removal efficiency of toluene.

This work was funded by the "Dissemination and fostering of plasma-based technological innovation for environment protection in Baltic Sea Region – PlasTEP" – project No. #033 of the Baltic Sea Region Programme 2007-2013, and this financial support is greatly appreciated.

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ELECTRON BEAM FLUE GAS TREATMENT PILOT TESTS

Andrzej G. Chmielewski, Andrzej Pawelec, Sylwia Witman-Zając, Janusz Licki[1/], Noushad Kunnummal[2/]

[1/] National Centre for Nuclear Research, Świerk, Poland

[2/] Saudi Arabian Oil Company Saudi ARAMCO, Dhahran, Saudi Arabia

The Saudi ARAMCO, a leading Saudi company is oriented at the continuous improvement of its operation plants in various fields as safety, production yield, economy and environmental protection. Therefore, the Saudi ARAMCO has initiated cooperation with the Institute of Nuclear Chemistry and Technology (INCT) for investigation of the feasibility of electron beam flue gas treatment (EBFGT) technology implementation in the refineries. On the request of Saudi ARAMCO, a pilot plant was constructed and operated in one of the refineries in Saudi Arabia.

The project was realized in the cooperation between several companies. The Institute of Nuclear Chemistry and Technology was the main contractor and coordinator of the project. It was responsible for all stages of the project, especially for design, experimental and reporting phase. As the INCT is the research and development body, some tasks were subcontracted to specialized companies. EB-Tech Co. (Republic of Korea) was responsible for supplying and operation of reaction unit, *i.e.* a mobile accelerator system with a reaction chamber. Also by-product collection unit (cyclone, bag filter and electrostatic precipitator) was supplied by this company. Nederman Co. (Poland) was responsible for manufacturing of plant body as well as assembling of the installation. Conditioning unit was manufactured by ChemTech Ltd. (Poland).

Flue gas to be treated was emitted from the oil fired boiler. The composition and parameters of the flue gas were assumed as typical for this type of boilers. Volumetric flow rate (wet basis) was assumed at 2000 Nm^3/h, while the temperature for 300°C. Oxygen content was 3.14% vol. and the humidity – 13.83% vol. Pollutants concentrations were as follows: SO_2 – 1503 ppmv and NO_x – 233 ppmv.

The facility was composed of such units as:

- inlet valve (flap),
- heat exchanger (cooler),
- flue gas conditioning (cooling and humidification),
- ammonia storage and dosing unit,
- reaction unit,
- by-product collection unit (bag filter, ESP),
- fan and gas outlet (stack).

A design scheme of the plant, including suggested measuring points, is presented in Fig.1.

The unique mobile electron accelerator developed by EB-Tech Co. was used as an electron beam source. The main accelerator parameters were as

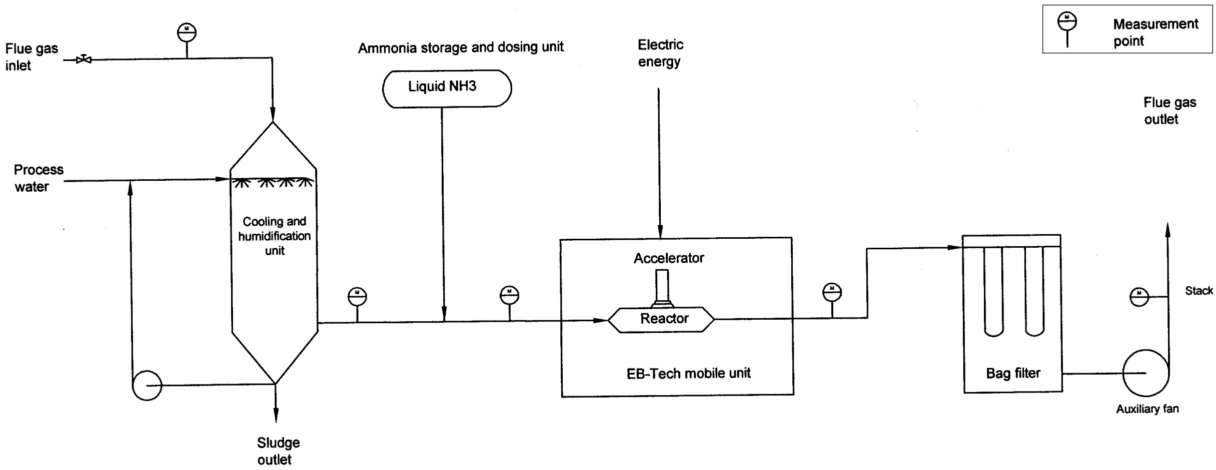


Fig.1. Design scheme of the facility.

follows: beam energy – 0.6 MeV and beam power – 20 kW. Two types of a by-product collection unit were tested – a cartridge bag filter and an electrostatic precipitator.

The obtained removal efficiencies reached 98.5% for SO_2 and 79.1% for NO_x at the optimal conditions (temperature in the process vessel inlet – 62°C, ammonia stoichiometry – 0.9, humidity – 10.3% vol.) as depicted in Fig.2. For the higher process temperature (90°C at process vessel inlet), NO_x removal efficiency reached 83.1%. The by-product obtained was a high quality fertilizer that may be used directly or as a substrate for NPK fertilizer blends. The by-product contained about 2% of water and up to 5% of insoluble impurities (up to 1.8% in case of the cartridge bag filter). The soluble part of by-product was almost pure ammonium sulphate (98-99%) with some amount of ammonium nitrate. The content of heavy metals in the by-product was very low and lower than the allowed standards in most cases by two orders of magnitude.

The most important operational drawbacks in the case of the tested pilot plant were connected with the by-product collection (filtration). The research confirmed that the bag filters are not appropriate for this technology, while electrostatic precipitators shall be carefully designed. However, most of the facility operation problems were previously solved during the works in the Pomorzany industrial EBFGT plant and these experiences shall be used in the case of further works.

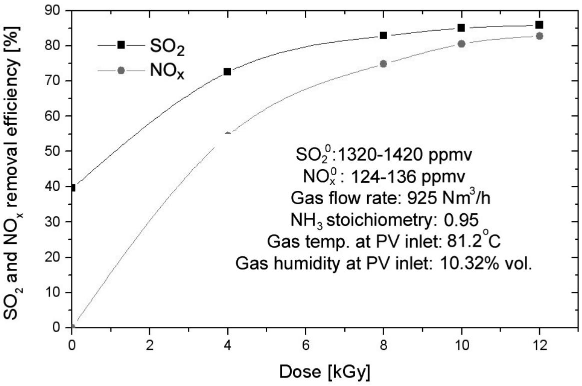


Fig.2. SO_2 and NO_x removal efficiency as a function of irradiation dose.

STABLE ISOTOPE LABORATORY

Basic activity of the Stable Isotope Laboratory concern the techniques and methods of stable isotope measurements by the use of an isotope ratio mass spectrometer – IRMS. Our activity area concerns also the application to the environmental area: stable isotope composition of hydrogeological, environmental, medical and food samples.

The main aims of activity of the Laboratory are:

- preparation and measurement of stable isotope composition of food and environmental samples;
- new area of application of stable isotope composition for food authenticity control, environmental protection and origin identification.

The Laboratory is equipped with the following instruments:

- mass spectrometer – DELTA^{plus} (FinniganMAT, Germany);
- elemental analyser Flash 1112NCS (ThermoFinnigan, Italy);
- GasBenchII (ThermoQuest, Germany);
- H/Device (ThermoQuest, Germany);
- gas chromatograph (Shimadzu, Japan);
- gas chromatograph with a mass spectrometer (Shimadzu, Japan);
- liquid scintillation counter (for ^{14}C and tritium environmental samples) 1414-003 Guardian (Wallac-Oy, Finland);
- portable gas analyser (N_2O, CO_2, CH_4, H_2S), (Nanosens, Poland).

Research staff of the Laboratory is involved in the following projects:

- "Formation of the data bank on original products for the juice sector, to supply requirements of the Polish market and producers, basing on the method of stable isotopes" (Ministry of Science and High Education grant PBZ-MEiN NR12-0043-10/2010);
- "Differentiation of organically and conventionally produced foodstuff by the stable isotope method";
- accreditation process (isotopic method for food authenticity control);
- interlaboratory proficiency test FIT-PTS (food analysis using isotopic techniques – proficiency testing scheme).

Specific activity: industrial emission control of greenhouse gases by the use of isotopic composition and food authenticity control and origin identification.

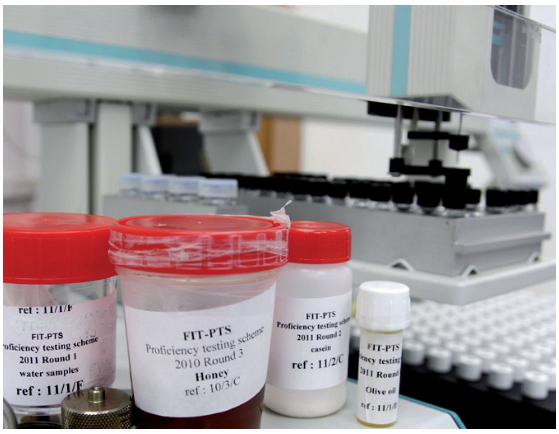
The Stable Isotope Laboratory is open for any form of cooperation. We are ready to undertake any research and development task within the scope of our activity. Especially, we offer our measurement experience, precision and proficiency in the field of stable isotope composition. Besides, we are open for any service in the area of food authenticity control by stable isotope methods supported by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) methods.

Our Laboratory cooperates with the following national partners:

- Inspekcja Jakości Handlowej Artykułów Rolno-Spożywczych,
- Krajowa Unia Producentów Soków,
- customs inspections,
- food export-import company,
- food control laboratories,
- private people – customers

and foreign partners:

- Eurofins Scientific Analytics (France),
- International Atomic Energy Agency (IAEA),
- Joint Research Centre (Ispra, Italy).



THE QUALITY ASSURANCE OF RESEARCH IN THE STABLE ISOTOPE LABORATORY BASING ON RESULTS OBTAINED IN PROFICIENCY TESTING PROGRAMME

Kazimiera Malec-Czechowska, Ryszard Wierzchnicki, Renata Adamska

Since many years the activity of Stable Isotope Laboratory of the Institute of Nuclear Chemistry and Technology (INCT) has been concentrated on the application of stable isotope mass spectrometry for environmental investigation and food authenticity control. The Laboratory is dedicated to the stable isotope analysis (^{13}C, ^{18}O, ^{15}N, ^{34}S and deuterium). Recently, the Laboratory implemented a management system appropriate to the scope of its activities and comply with PN-EN ISO/IEC 17025 standard [1].

According to point 5.9 of the PN-EN ISO/IEC 17025 standard, the Laboratory has at disposal quality control procedures for monitoring the validity of tests undertaken. The monitoring is planned and reviewed and includes the following points:

- regular use of certified reference materials and/or internal quality control using secondary reference materials;
- participation in interlaboratory comparison or proficiency testing programmes;
- replicate tests using the same or different methods;
- retesting of retained items;
- correlation of results for different characteristics of an item.

In 2010-2012, the Laboratory has taken a part in Food Analysis Using Isotopic Techniques – Proficiency Testing Scheme called FIT-PTS organized by Eurofins Scientific Analytics (Nantes, France) and Joint Research Centre – JRC (Ispra. Italy). FIT-PTS compiles with ISO/IUPAC/AOAC International Harmonized Protocol for proficiency testing of analytical laboratories.

Twenty three samples of different food products such as wine, fruit juice, honey, pure organic products and others were tested. All investigations are realized using the method of isotope ratio mass spectrometry (IRMS) according to international standards, the professional literature and own elaborated procedures [2-12].

The results supplied by the participants were statistically evaluated by organizations. For every measuring parameter, severally for every laboratory *z*-score was calculated. The value of *z*-scores can be interpreted as follows: $|z| \leq 2$ "satisfactory", $2 < |z| < 3$ "questionable", $|z| \geq 3$ "unsatisfactory". Values of *z*-score were used for the evaluation of the participating laboratory performance. Results obtained by our Laboratory are presented in Table and in Figs.1-3. Results obtained by our Laboratory within the framework of test are the basis for positive evaluation our technical competences in the accreditation process.

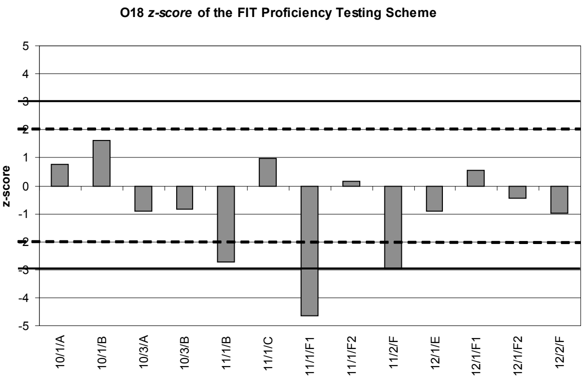


Fig.1. *z*-score of the FIT-PTS for oxygen ^{18}O/^{16}O in water calculated for the Stable Isotope Laboratory.

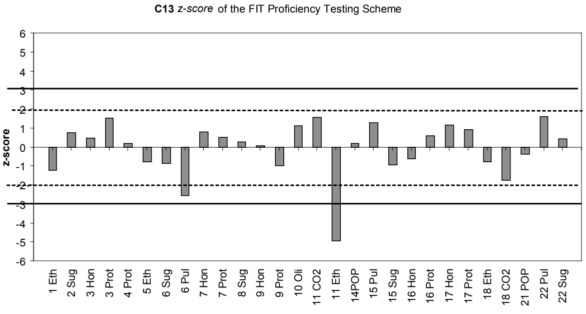


Fig.2. *z*-score of the FIT-PTS for carbon ^{13}C/^{12}C calculated for the Stable Isotope Laboratory.

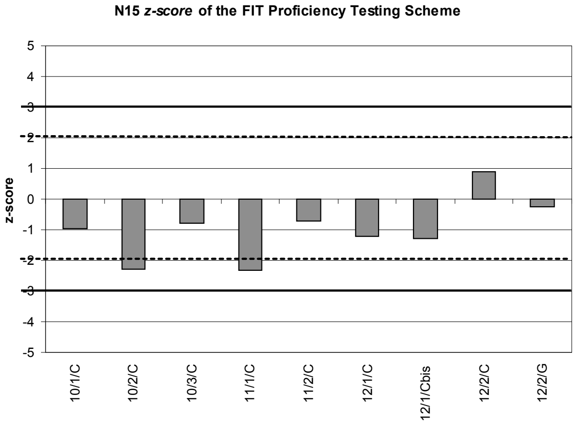


Fig.3. *z*-score of the FIT-PTS for nitrogen ^{15}N/^{14}N calculated for the Stable Isotope Laboratory.

In the next year we foresee to lodge an application to the Polish Centre of Accreditation for the impartment of accreditation.

Proposals of the scope of the accreditation in the first step is as follow:

- fruits and vegetable juices:
  - » determination of the stable carbon isotope ratio (^{13}C/^{12}C) of sugars from fruit juices [2, 10],
  - » determination of the stable oxygen isotope ratio (^{18}O/^{16}O) of water from fruit juices [3, 12],
  - » determination of the stable hydrogen isotope ratio (^{2}H/^{1}H) of water from fruit juices [4],
  - » determination of the stable carbon isotope ratio (^{13}C/^{12}C) in the pulp of fruit juices [5, 11];
- wine:

Table. Results obtained in years 2010-2012 by the Stable Isotope Laboratory within the framework FIT-PTS.

Year/Round	Sample number	Product/sample code	Parameters/*z*-scores				Comments
2010/Round 1	1	dry wine 10/1/A	ethanol C13 -27.64/-1.23	wine O18 2.98/0.78			all results satisfactory $z \leq 2$
	2	fruit juice 10/1/B	sugar C13 -24.54/0.76	juice O18 -6.37/1.62			
	3	honey 10/1/C	honey C13 -25.63/0.46	proteins C13 -25.23/1.53	proteins N15 4.04/-0.95		
2010/Round 2	4	proteins 10/2/C	proteins C13 -15.15/0.19	proteins N15 1.08/-**2.28**			one result questionable $2 < z \leq 3$
2010/Round 3	5	spirits 10/3/A	ethanol C13 -27.86/-0.77	water O18 -8.24/-0.90			one result questionable $2 < z \leq 3$
	6	fruit juice 10/3/B	sugar C13 -13.71/-0.87	pulp C13 -14.99/-**2.58**	juice O18 -4.69/-0.83		
	7	honey 10/3/C	honey C13 -23.65/0.78	proteins C13 24.89/0.49	proteins N15 2.38/-0.79		
2011/Round 1	8	grape juice spiked with SO_2 11/1/B	sugar C13 -24.91/0.25	juice O18 0.60/-**2.71**			two results questionable $2 < z \leq 3$ two results unsatisfactory $3 < z$
	9	honey 11/1/C	honey C13 -21.93/0.08	proteins C13 -26.31/-1.01	proteins N15 3.40/-**2.32**		
	10	olive oil 11/1/C	olive oil C13 -28.61/1.13				
	11	sparkling wine 11/1/C	wine O18 3.74/0.99	C13 CO_2 -22.87/1.55	ethanol C13 -27.37/-4.96		
	12, 13	set of 2 water samples 11/1/F	water 1 O18 12.65/-4.64	water 1 H2 28.10/-0.52	water 2 O18 -10.42/0.17	water 2 H2 -73.20/-0.38	
2011/Round 2	14	pure organic product Casein 11/2/C	C13 -25.16/0.19	N15 3.04/-0.70			one result questionable $2 < z \leq 3$
	15	orange juice 11/2/F	pulp C13 -24.58/1.28	sugars C13 -25.09/-0.96	juice O18 1.58/-**2.97**		

Table. contd.

2012/Round 1	16	honey 12/1/C	honey C13 -25.75/-0.62	proteins C13 -25.09/0.58	proteins N15 4.24/-1.22		all results satisfactory $z \leq 2$
	17	manuka honey 12/1/C bis	honey C13 -25.44/1.15	proteins C13 -26.18/0.92	C4 sugar addition 4.49%/0.41	proteins N15 1.50/-1.28	
	18	cider 12/1/E	CO_2 C13 -35.57/-1.74	ethanol C13 -28.56/-0.77	cider O18 -3.92/-0.92		
	19, 20	water samples 12/1/F	water 1 O18 -6.58/0.56	water 1 H2 -9.00/0.08	water 2 O18 -0.34/-0.43	water 2 H2 2.00/0.01	
2012/Round 2	21	pure organic product 12/2/C	C13 -16.75/-0.37	N15 -0.65/0.88			all results satisfactory $z \leq 2$
	22	orange juice 12/2/F	pulp C13 -25.48/1.61	sugars C13 -25.51/0.43	water O18 5.65/-0.99		
	23	grated hard cheese 12/2/G	C13 casein -19.22/*	N15 casein 5.85/-0.24			

* *z*-score was not calculated.

  - determination of the stable oxygen isotope ratio (^{18}O)/^{16}O) of water content in wines [6],
  - determination of the stable carbon isotope ratio (^{13}C/^{12}C) in wine ethanol or ethanol obtained by the fermentation of musts, concentrated musts or rectified concentrated musts [7];
- honey:
  - determination of the stable carbon isotope ratio (^{13}C/^{12}C) of honey and protein from honey [8, 9].

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STABLE CARBON ISOTOPE RATIO ANALYSIS OF APPLE JUICE COMPONENTS

Ryszard Wierzchnicki, Kazimiera Malec-Czechowska

Application of carbon stable isotope ratio δ^{13}C analysis to the juice authenticity control is not a new method [1-3]. In this work we were looking for the correlations between the δ^{13}C values for sugar components in apple juices from the Polish market. The subject of the study was the application of isotopic methods to juice authenticity by the use of internal isotopic references, that is, sugars, organic acids and vitamins. Ratios between the bulk sugars and individual acids (malic or citric) by IRMS (isotope ratio mass spectrometry) will be studied for control of sugars or acid addition. Pulp is the insoluble fraction of juice mainly consists of cellulose, pectin and proteins. A method for separation sugars and organic acids from fruit juices was elaborated for routine investigation (Fig.).

Apples were purchased from known origins: convenient stores and local markets. The fruits originate only from Poland. The concentrates were provided from the known producer.

For the separation of components, the whole fruit without core was taken. Typical composition (range of content) of sugars and acids for the apple juice is shown in Table 1. Apple fruits were squeezed in the Laboratory and 40 ml of the received juice was diluted to 100 ml by deionized water. After that, the solution was centrifuged at 4000 rpm (2320 x g) for 15 min. The supernatant was filtered through a 0.45-μm nylon membrane by vacuum filtration.

20 ml of the solution was passed through a glass column packed with BioRad hydroxide form AG 1-X8 resin (200-400 mesh). After flushed of the column with water, the pH of the eluate was adjusted to 8-9. This solution was passed down the column packed with BioRad hydrogen form AG 50W-X8 resin (100-200 mesh). The sugar was eluted from the column with water and after that was blended with acetonitrile (25:75). The prepared mixture was injected into an HPLC system. Indivi-

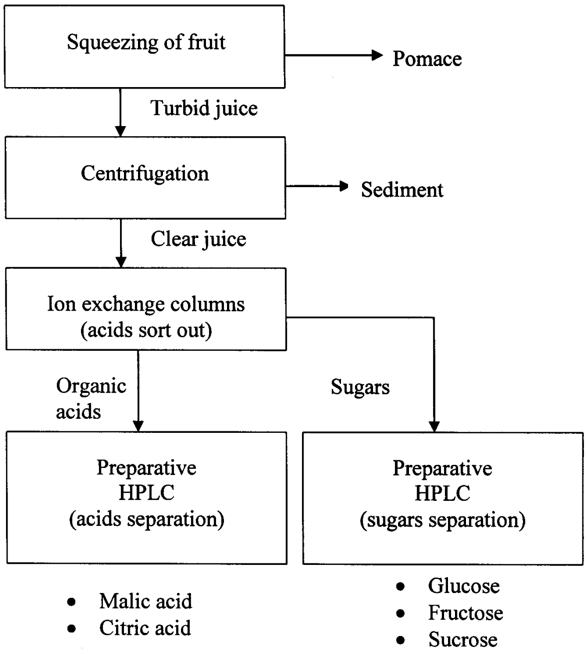

Fig. Scheme of separation of acids and sugars from fruit juices.

dual sugars were separated with a column Cosmosil Sugard-D (Nacalai Tesque) 250 x 10 with a guard column and RI (refractive index) detector RID-6A (Shimadzu), Table 2. For sucrose, glucose and fructose sample collection a fraction collector Gilson was used. After collection of the individual sugars, these samples were freeze dried to concentrate the extract. The dry matter was put in zinc containers and was introduced to the carousel of an autosampler of elemental analyser. The carbon isotope ratios were determined using a DELTA^{plus} (FinniganMAT) mass spectrometer associated with the elemental analyser Flash 1112NCS (ThermoFinnigan). All the measured stable carbon isotope ratios values are expressed by:

$$\delta^{13}C_{vsPDB} = \frac{\left[\frac{^{13}C}{^{12}C}\right]_{SAMPLE} - \left[\frac{^{13}C}{^{12}C}\right]_{STANDARD}}{\left[\frac{^{13}C}{^{12}C}\right]_{STANDARD}} * 1000\text{‰}$$

The standard deviation (SD) of measurements of carbon $\delta^{13}C$ is 0.1‰ for sugars and acids.

The combination of the two techniques: ion exchange processes and preparative HPLC forms a rapid and simple method for the separation of sugars and acids in apple juices. The literature studies [1-3] showed a good correlation between each of the sugars – sucrose, glucose and fructose. Minimal sample preparation and rapid separation support this procedure as method for the determination of isotope composition of sugars and acids in apple juice. The described methodology involves an optimized approach for the separation of sugars and organic acids from fruit juices. The correlation between the carbon isotope ratio of sugars and organic acids will be tested for other fruit juices from the Polish market. The carbon isotope ratio analysis will be involved in routine work in our Laboratory for detecting the addition of foreign sugars and organic acids to fruit juices.

Table 1. The content of sugars and organic acids in apple juice.

Components	Content [mg/100 g] (rough mean)
Sugars:	9 500-15 300
- fructose	3 840-8 001 (5 000)
- glucose	1 050-3 230 (1 700)
- sucrose	380-5 650 (3 500)
Organic acids:	
- ascorbic acids	(6)
- malic acid	193.3-1 993.7 (500)
- citric acid	0.8-49.1 (10)

Table 2. Equipment for HPLC separation of sugars and organic acids from apple juices.

Components	Column	Eluent	Detector	Flow rate [ml/min]
Sugars	for sugars	acetonitrile:water (75:25)	RI	1
Organic acids	C_{18}	water + H_3PO_4, pH 2.5	DAD UV 214 nm	0.4
Ascorbic acids	C_{18}	water + H_3PO_4, pH 2.5	DAD UV 254 nm	0.4

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LABORATORY FOR MEASUREMENTS OF TECHNOLOGICAL DOSES

The Laboratory for Measurements of Technological Doses (LMTD) was created in 1998 and accredited as testing laboratory in February 2004 (Polish Centre of Accreditation, accreditation number: AB 461).

The actual accreditation range is:

- gamma radiation dose measurement by means of a Fricke dosimeter (20-400 Gy),
- gamma radiation dose measurement by means of a CTA film dosimeter (10-80 kGy),
- electron radiation dose measurement by means of a CTA film dosimeter (15-40 kGy),
- electron radiation dose measurement by means of graphite and polystyrene calorimeters,
- irradiation of dosimeters or other small objects with Co-60 gamma radiation to strictly defined doses,
- irradiation of dosimeters or other small objects with 10 MeV electron beams to strictly defined doses.

The secondary standard of the dose rate using by the LMTD is a Co-60 gamma source “Issledovatel” and a Gamma Chamber 5000. The sources were calibrated in April 2009 and in March 2012, respectively, according to NPL (National Physical Laboratory, Teddington, UK) primary standard. The uncertainty of the dose rate was estimated to be 2.9 and 3.1% (U, k = 2).

VALIDATION OF METHODS FOR MEASUREMENTS OF ABSORBED DOSE OF ELECTRON RADIATION WITH THE USE RADIOCHROMIC FILM DOSIMETER B3

Anna Korzeniowska-Sobczuk, Aneta Sterniczuk, Magdalena Karlińska

Dosimetric measurements are an essential tool in the quality control of radiation treatment for medical devices, pharmaceutical products, transplants and implants. Performing routine dosimetric measurements, using the radiochromic film dosimeter B3 is an alternative to previously used in the sterilization stations of the Institute of Nuclear Chemistry and Technology (INCT) not standardized measurement methods based on PVC dosimetric response. The manufacturer must document that the entire process is continuously under control and in compliance with national and international standards for radiation sterilization. Most of the dosimetry with films is based on optical signal measurements [1]. All dosimetry systems commonly used in the irradiation industry are temperature sensitive. In a book, W. McLaughlin says that "Irradiation temperature is, in fact, the most important environmental factor contributing to errors in absorbed dose estimation, and in radiation processing it is sometimes poorly determined and difficult to correct for" [2].

The characteristics and dosimetric response of thin film dosimetry after irradiation in room temperature are exactly known. B3 is a film widely use in routine dosimetry and was introduced into practice a few years ago [1, 3].

Irradiation of low-temperature samples, must therefore take these dosimeter temperature effects into consideration. Validation of method is the process of determining the parameters characterizing the scope and limitations of the method and to check its suitability for a particular purpose.

Validation of the method includes:

- establishing which parameters characterizing the method should be determined (*e.g.* accuracy, scope, linearity),
- determining values of these parameters [4].

On this basis, one can determine whether or not the method meets our expectations in accordance with the established criteria for its application in low-temperature dosimetry.

Validation of the method and implementation issues related to the research on radiochromic film dosimeter B3 reflects the need to improve the quality of services provided by the Laboratory for Measurements of Technological Doses (LMTD), INCT, as well as the applicability of film dosimeter B3 for routine dosimetric measurements during sterilization of tissue grafts at the temperature of dry ice.

In experiments the film dosimeter B3 with an optical signal detection was used. The film dosimeter was irradiated with a 10-MeV electron beam from an industrial 10-kW linear accelerator. The mean electron energy, measured by the wedge method, was in the range 9.6-9.8 MeV. The approved dose range was 10-40 kGy, corresponding to the routine sterilization process. The interrelation between the electron beam flux and the speed of the conveyor delivering the dosimeter under the beam allowed keeping the dose at a specified level. The irradiated film dosimeter B3 was placed in polystyrene phantoms, containing ice and dry ice. The dose measurements were performed in a polystyrene or a graphite calorimetric dosimeters irradiated in the same experiment. The calorimetric dosimeters, film dosimeter B3 and phantoms were produced at the High Dose Radiation Laboratory – HDRL (Risø, Denmark).

The mean temperature of irradiation was calculated as the average of temperatures before and after the irradiation, which were measured with a calibrated thermocouple. The B3 film was heated (60°C, 5 min) immediately after irradiation to accelerate the chemical reactions initiated by ionizing radiation and playing a role in the growth of the dosimetric signals. The absorbance was measured by using a JASCO-V650 spectrophotometer UV/VIS (λ_{max} = 556 nm). The wavelength and absorbance scales were checked before each experiment by a calibrated reference standard.

In this study, we investigated the signal repeatability of the film dosimeter B3 irradiated at dif-

Table 1. The repeatability of the signal film dosimeter B3 after irradiation at different temperatures.

Dose [kGy]	Repeatability of dosimetry signal CV [%]		
	room temperature 20°C	ice temperature 0°C	dy ice temperature -78°C
40.33	1.77	4.74	3.66
34.16	3.42	0.67	4.53
29.46	1.42	1.20	0.45
24.86	0.82	4.68	0.76
19.84	1.73	5.47	2.96
14.69	3.47	2.01	0.93
9.64	0.75	3.44	2.90
4.5	3.52		

ferent temperatures. The results are shown in Table 1. The repeatability of the signal is not dependent on the dose and irradiation conditions, which reflects the random errors arising from the operating accelerator.

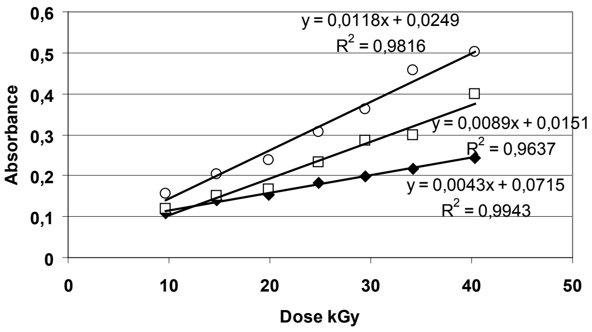

Fig.1. Calibration curves for the irradiated film dosimeter B3 with a 10 MeV electron beam from the accelerator at a temperature: (□) 0°C (ice – solid H_2O), (♦) -78°C (dry ice – solid CO_2), (○) 20°C (room temperature).

Calibration curves were constructed for the dosimeter B3 irradiated at room, ice and dry ice temperature (Fig.1). All of them are described in a linear equation and the coefficients of convergence exceeding 96%. The values obtained for the dry ice (convergence rate of 99%) are at the level of other accreditation methods in LMTD.

Comparative measurements were performed to determine the effect of the density of dry ice on the dosimetric signal attenuation of the irradiated film B3. Calibration curve response dosimetry of the film B3 for two different densities of dry ice are shown in Fig.2. It has been found that the influence of density is an important factor and should be taken into consideration during the process of irradiation at a temperature of dry ice.

Based on the results obtained for irradiated at dry ice temperature created the uncertainty balance implemented (Table 2). Criteria for validation of the methods for measuring doses of the film dosimeter B3 at dry ice temperature have been accepted.

Table 2. Balance of uncertainty for the measurement of the absorbed dose, using method film dosimeter B3 at different temperatures.

Sources of uncertainty	Room temperature 20°C	Dry ice temperature -78°C
Calibration of film dosimeter B3	2%	2%
Repeatability of dosimetry signal film B3	3.5%	4.5%
Errors of irradiation (work of accelerator)	1%	1%
Influence of the density of dry ice	-	5%
Standard uncertainty complex U	4.15%	7.1%

The obtained results allow to suggest the film dosimeter B3 for routine dosimetric measurements at the temperature of dry ice. However, this requires the cooperation with the tissue banks, so that the data obtained for the film B3, could be verified in the course of the process of sterilization of tissue grafts (number and position of dosimeters, graft placement, the expected layer of dry ice, *etc*.).

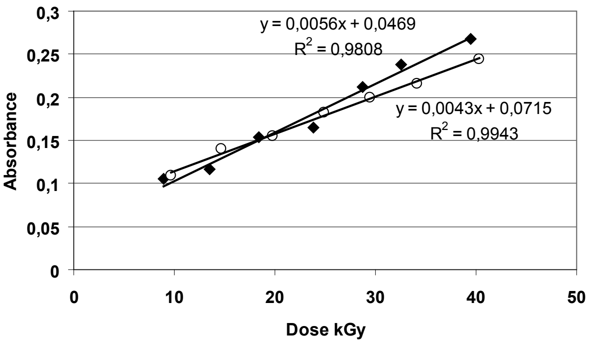

Fig.2. Differences in the response of the film dosimeter B3 in dependence on the density of dry ice: (♦) ~1.3 g/cm³, (○) ~1.45 g/cm³.

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LABORATORY FOR DETECTION OF IRRADIATED FOOD

The Laboratory for Detection of Irradiated Food was created in the Institute of Nuclear Chemistry and Technology in 1994 and, after adoption of the quality assurance system, received the accreditation certificate in 1999. From that time, the Laboratory has the status of accredited R&D laboratory. Professional staff is involved in the advanced work on the improvement and development of more sensitive and reliable methods for identification of irradiated food. The Laboratory offers professional analytical service to domestic and foreign customers comprising the detection of radiation treatment of food by adequate analytical methods. During the last 10 years of activity, the Laboratory successfully examined and classified nearly 2500 food samples. In 2010 the Laboratory received a new *Accreditation Certificate of Testing Laboratory Nr AB 262* issued by the Polish Centre of Accreditation with the validity until 24.10.2014. The *Scope of Accreditation*, the integral part of accreditation documentation, contains the list of detection methods which are authorized to be applied. These are:

- the method for the detection of irradiated food containing bone with electron paramagnetic resonance (EPR) spectroscopy based on an analytical procedure recommended by the CEN European standard EN-1786;
- the method for the detection of irradiated food containing cellulose with EPR spectroscopy based on an analytical procedure recommended by the CEN European standard EN-1787;
- the method for the detection of irradiated food containing crystalline sugars with EPR spectroscopy based on analytical procedures recommended by the CEN European standard EN-13708;
- the method for the detection of irradiated food from which silicate minerals can be isolated using thermoluminescence (TL) measurements based on analytical procedures recommended by the CEN European standard EN-1788;
- the method for the detection of irradiated food using photostimulated luminescence (PSL) based on analytical procedures recommended by the CEN European standard EN-13751.

The employment of five, searchingly tested and validated detection methods guarantees the reliability of positive or negative classification of food samples in the Laboratory, representing practically all food articles available on the market.

In addition, the Laboratory is engaged in the modification of analytical and measuring procedures adequate to each of detection methods making it possible the identification of radiation treatment in complex food articles, including diet supplements, herbal pharmaceuticals, food extracts. This products contain typically low concentration of irradiated ingredients and minerals detectable by luminescence methods. The attention was paid to testing of mineral yields and luminescence intensity depending on food type and place of its origin.

In 2012, in total 185 food samples for irradiation control delivered by domestic and foreign customers in Germany, Italy, Switzerland, the United Kingdom, Denmark, Spain, Hungary and Russia were examined. Food articles examined in the Laboratory for irradiation control were: spices, herbal pharmaceu-

Typical groups of products controlled in the Laboratory.

ticals, diet supplements, food extracts, mushrooms, rice, teas, mussels, dried fruits, bark and biomass. Eighteen samples (10%) of the total number of samples tested were found irradiated. Mainly TL, but also EPR and PSL methods were applied for the examination of foodstuffs in 2012.

The Laboratory was nominated by the Ministry of Health on 19th June 2012 the Reference Laboratory in the field of the detection of irradiated food in Poland.

The Laboratory was invited in 2012 to participate in the 4th Round of the "Intercomparative exercise for quality assurance on EPR, PSL and TL irradiated food detection methods" organized by the Food Technology Department of the Spanish Agency for Food Safety and Nutrition. The accredited, outstanding food analysis laboratories from European countries took part in this exercise.

ASSESSMENT OF THE RESPONSE OF TL, PSL AND EPR DETECTION METHODS IN THE IDENTIFICATION OF RADIATION TREATMENT OF FOOD

Wacław Stachowicz, Magdalena Sadowska, Grażyna Liśkiewicz, Grzegorz P. Guzik

Under the auspices of the Ministry of Health (Spain) and the Spanish Agency for Food Safety and Nutrition (AESAN), the National Centre for Food – CNA (Spain) has organized the 4th international exercise for testing the reliability of three most important analytical methods used for the detection of irradiated food. The study named ”Intercomparative exercise for quality assurance on TL, PSL and EPR irradiated food detection methods, 4th Round” assembled nineteen specialized laboratories from France, Germany, Poland, Romania and Spain. The organizing institution CNA possess accreditation for the detection of irradiated food and is experienced in thermoluminescence (TL), photostimulated luminescence (PSL) and electron paramagnetic resonance spectroscopy (EPR). It is also the case with most of the participating laboratories.

The participating laboratories are involved in the detection of irradiated food for customers and domestic food control institutions, while the exercise having qualification of laboratory proficiency testing plays an important role in the development of quality assurance programme in any of them. The exercise makes it possible to evaluate the reliability of detection methods addressed to specific food product and from the point of view of participants to evaluate by themselves the results obtained by using detection method based on the protocols adapted in each of the participating laboratories.

After collecting results delivered from the participating laboratories, the organizers analysed and evaluated the results which have been issued in the final protocol. The results referring to the participating laboratories were coded with numbers known to each of the laboratory involved.

It has to be noted that basic analytical procedures used by the participating laboratories were obligatory based on the CEN (European Committee for Standardization) standardized methods for the detection of irradiated food by EPR, TL and PSL methods [1-5]. However, this methods were validated with the use of simple model samples irradiated with the doses of ionizing radiation equal or close to technological doses recommended in normative documents [6]. Nowadays, mainly for economic reason, food producers and sellers accept the doses decreased as compared with the recommended ones to the lower level that still assures preservation effect and microbial safety. Such “optimal” doses from technological point of view whether are presently applied worldwide being much lower than those recommended in the Codex [6]. At present, the spectrum of food products found in the market is significantly extended and many of these products were not tested or validated whether their radiation treatment is detectable. This is a strong argument for the need of the organization of intercomparative studies as the present ones.

The present exercise is already the 4th intercomparative study organized in Spain with the participation of several European countries. Every of the earlier three exercises were dealing with samples of different composition. However, each exercise represent a logic complement to those previously conducted studies.

Organization of the exercise

The CNA Laboratory has prepared 12 test samples; part of the samples was irradiated while some remained non-irradiated. Sets of samples have been delivered to the participant by the post to be examined with the use of three detection methods based on TL, PSL and EPR spectroscopy. Each sample possessed a short description and code.

Each set of the samples comprised:

- two samples for TL standard method examination (each sample in duplicate);
- two samples for PSL standard method examination (each sample in duplicate);
- eight samples for the examination by three EPR standard methods suitable for the detection of irradiated food containing cellulose (two samples of spices and herbs), crystalline sugars (two samples of dried fruits) and hydroxyapatite (two samples of bone and two mollusc shells).

Irradiation of samples prior to examination in CNA

The CNA dose measurements were achieved with the use of ECB dosimeters calibrated at the High Dose Reference Laboratory of Risø National Laboratory (Denmark) traceable to the National Physical Laboratory (UK). The dose rate was 6.94 kGy/h.

Table 1. Product which were irradiated on 30.07.2012.

Sample	Irradiation dose [kGy]
Quail bone	1
Raisins	1
Curry	5
Cockle shell	1
Turmeric	1
Rosemary leaf	1

Dosimetric certificate, dated 30.07.2012 was provided for six samples treated with ionizing radiation as shown in Table 1.

Calibrated irradiation of samples in the INCT

The samples analysed by TL and PSL methods were exposed in the Institute of Nuclear Chemistry and Technology (INCT) to calibrated irradiation with a dose of 1 kGy using a ^{60}Co gamma source. The dose rate in the gamma source was controlled with a ferrous-ferric dosimeter (Fricke dosimeter) and was equal to 4.620 kGy/h (Gamma Chamber 5000).

Table 2. Samples prepared by the organizer to be analysed in the participating laboratories. Irradiation status is indicated.

Number	Sample	Irradiation dose
1	quail bone	1 kGy
2	pig bone	non-irradiated
3	raisins	1 kGy
4	raisins	non-irradiated
5	curry	5 kGy
6	cockle shell	1 kGy
7	mussel shell	non-irradiated
8	pistachio shell	non-irradiated
9	green tea	non-irradiated
10	turmeric	1 kGy
11	rosemary leaf	1 kGy
12	tarragon	non-irradiated

The following food products (Table 2) were selected to be tested in the study:

- TL examination: rosemary leaves, tarragon leaves;
- PSL examination: green tea leaves, turmeric powder;
- EPR spectroscopy examination: quail bone fragments, pig bone fragments, cockle shell , mussel shell, pistachio shell, carry powder, raisins dried fruits (two samples).

EPR examination in the INCT

The samples were examined following the procedures adapted in the Laboratory for Detection of Irradiated Food, INCT and based on recommended European standards:

- EN-1786 (quail bone, pig bone, cockle shell, mussel shell)[4],
- EN-1787 (curry, pistachio shell) [5],
- EN-13708 (raisins 1, raisins 2) [1].

The EPR measurements were done with the use of a Bruker ESP 300 spectrometer in X band. The samples (the column inside sample tube 4 mm in diameter, *ca.* 25 mm long) were placed in 5 mm Wilmad glass sample tubes 20 cm long. The EPR measuring conditions followed those recommended in the above-named standards.

PSL examination in the INCT

The samples were examined with a SURRC PPSL screening system installed in the Laboratory following the procedures recommended in the European standard EN-13751 [3]. The investigated samples (green tea and turmeric powdered) were placed in 5 cm diameter Petri-dishes. The PSL measuring conditions were adjusted as those recommended in the above-named standard document.

TL examination in the INCT

The mineral fraction was isolated from two investigated samples weighing *ca.* 20 g each. The separated mineral was placed in TL measuring cups and measured with a RISØ TL/OSL DA 20 TL Reader installed in the Laboratory. Measuring conditions: temperature range – 50-450°C; TL integration range – 150-250°C, temperature growth rate – 6°C/min.

The criteria adapted for the detection of radiation treatment of investigated samples were:

- EPR – identification of the EPR signal specific for irradiated samples;
- PSL – comparison of the lower and upper threshold values (T_1 = 700 cpm and T_2 = 5000 cpm) with those obtained during examination of the sample;
- TL – identification of glow maxima specific for irradiated stuff and evaluation of the glow ratio Glow 1/Glow 2 (TL integrated intensities) within the temperatures range 150-250°C. Glow ratio for irradiated sample was higher than 0.1.

Results of the intercomparison study obtained in the INCT

A. EPR examination (Table 3):

- all non-irradiated samples were classified correctly,
- all irradiated samples were classified correctly with the exception of curry which was classified non-irradiated.

B. PSL and TL examination (Table 4):

- all non-irradiated samples were classified correctly,
- all irradiated samples were classified correctly.

Conclusions

In general, the exercise delivered a new evidence for the reliability of standard detection methods

Table 3. Summarized results of EPR examination.

Sample weight [mg]	Sample	INCT results	CNA results
105.9	quail bone	positive	irradiated
109.5	pig bone	negative	non-irradiated
219.2	raisins	positive	irradiated
205.8	raisins	negative	non-irradiated
102.7	curry	negative	irradiated
207.2	cockle shell	positive	irradiated
207.4	mussel shell	negative	non-irradiated
119.9	pistachio shell	negative	non-irradiated

Table 4. TL and PSL examination of investigated sample.

Sample	Glow 1	Glow 2 – 1 kGy irradiation	INCT results	CNA results
Green tea	307	6 366	negative	non-irradiated
Turmeric	6 434	17 206	positive	irradiated
Rosemary leaf*	15 317 634	23 516 688	positive	irradiated
Tarragon**	173 786	5 890 023	negative	non-irradiated

* Rosemary leaf: Glow 1/Glow 2 = 0.65.
** Tarragon powder: Glow 1/Glow 2 = 0.02.

as related to the extended assortment of food products which have not been validated earlier. The samples examined by TL (rosemary leaves, tarragon) were unmistakably classified (glow ratios 0.65 and 0.02, respectively). Non-irradiated sample of green tea estimated by PSL delivered also univocal result. However, although the initial luminescence of irradiated turmeric sample exceeded the threshold value of 5000 cpm the excess luminescence was rather low (6434 cpm) proving low radiation-induced photoluminescence of the whole sample. Four samples (quail bone, pig bone, cockle shell, mussel shell) were examined by the EPR method based on the detection of specific asymmetric singlet ($g_1 = 2.002$, $g_2 = 1.998$) assigned to paramagnetic centres in hydroxyapatite [4]. Positive results of the analysis does not need any comment. The same can be said about the analysis of the results obtained with two samples of raisins. The appearance of a specific multicomponent signal in the irradiated sample and its lack by examination of non-irradiated sample [1] give evidence that there is no doubt as to the reliability of these results. There was found a real problem with the analysis of curry sample by the EPR method [5]. We did not found any traces of satellite lines expected in irradiated samples like this. In our opinion the reason lies in the low stability of this signal in time. The exercise samples were irradiated in July while were delivered and examined in November 2012. We know from our earlier study [7] that curry sample loosed its EPR signal after 5 months of storage. For that reason, it is not recommended, in our opinion, to examine this product by EPR but rather by the TL method.

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LUMINESCENCE OF SILICATE MINERALS AND SENSITIVITY OF THERMOLUMINESCENCE METHOD FOR DETECTION OF FOOD IRRADIATION

Magdalena Sadowska, Wacław Stachowicz

It has been proven experimentally that any food article of vegetal origin contains mineral impurity which can be isolated by applying a suitable analytical procedure. Mineral impurities are more or less strongly adhered to the outer surface of leaves, stems and roots of plants and are present in dried spices, herbs, teas, *etc*., including grounded products. This finding is supported by many years of observation and was the argument for adopting of thermoluminescence (TL) technique as a method suitable for the detection of radiation treatment in food [1]. Why? Since most of minerals exposed to the action of ionizing radiation are capable of collecting the excess energy in very stable energy traps placed in crystal lattice imperfection, at inclusion ions or in lattice or electron vacancies. The energy trapped in a mineral can survive stable for hundreds of years at ambient temperatures. However, under the action of high temperature or strong light illumination mineral traps undergo annealing while their energy is released in the form of light (thermo- or photoluminescence). Both effects have been utilized for the detection of irradiated food [2, 3].

It is certainly confirmed in practice that minerals can be found and isolated from the most of food articles. However, it has been observed by the examination of very different food samples of different origin that it is possible to meet a product whose TL response from mineral debris is negligible or remains not registered at all. In such a position the proper classification of a sample under examination by the TL method is simply not possible.

Quantity of mineral isolated from food sample

It has been evaluated that in order to obtain acceptable result of TL analysis the weight of mineral debris should exceed 0.1 mg. This figure is stated only by European standard EN-1788 [2]. The authors do not define, however, the lowest level of mineral weight which makes it possible to proceed TL analysis. It is because such a critical mass limit cannot be strictly defined as it will be demonstrated in the following discussion. There are two methods that in some cases can help in solving this problem.

The first method – by applying more effective means of mineral isolation from an organic pulp in the course of isolation procedure. We have shown in our earlier study [4] that in some cases it is possible to improve the isolation effect by adapting simplified separation procedures instead of that recommended in European standard EN-1788 [2].

The commonly used mineral isolation procedure is that recommended in European standard EN-1788 [2]. The method compiles several analytical steps including wet sieving, rinsing, application of ultrasounds, separation of vegetal pulp from minerals by following density separation method, *i.e.* applying a water solution of sodium polytungstate $Na_6[H_2W_{12}O_{40}]$ x H_2O as a medium of the density of 2 g per cc overlaying the pulp. The organic components of the density, typically lower than that of water (*ca.* 1 g per cc), are floating near to the surface of suspension, while the high density mineral fraction is collected behind in the lower polytungstate layer and sediment in the button of the beaker used. The organic fraction is removed by decantation while mineral deposit is washed with water and acetone. Acetone is dried off, leaving the mineral deposit adhering to the TL measuring cup [2]. The simplified methods are limited to the application of ultrasounds only or to simple washing the sample. It has to be pointed out, however, that the application of simplified method of isolation should be tested with each product in advance whether effective.

The second method is a simple but quite often effective and consist of a significant, at least two-fold increasing of the mass of a sample used in beginning to proceed isolation procedure. Typically, the mass of food sample does not exceed 50 g. So, if low volume of mineral is expected, the mass of sample should be increased to 100 g at least.

At present, more and more food samples ordered by customers for examination whether irradiated represent a complex system containing an irradiated component as an additive to the product dominated by non-irradiated components. For that reason, the difficulty in the detection of radiation treatment appears more frequently.

Composition of minerals isolated from food sample

Mineral contaminants which are found in food originate mainly from the soil that is the basis for the cultivation of plants giving rise to leaves, fruits, roots, *etc.,* which are used after dehydration worldwide as edible, aromatic additives to food (spices, herbs, teas) the products most frequently preserved by means of ionizing radiation. Stabilized energy traps in minerals giving rise to further thermo- and photoluminescence effects are formed under irradiation in silicate minerals only [1] in contrast to the other common soil components as loams, rigid clays, mica, *etc.,* which do not show luminescence at all. In particular, the mineral components giving rise to radiation-induced thermoluminescence are crystalline quartz and silicate minerals, mainly feldspar accompanying by wollastonite, albite and carbonates as proven by X-ray diffraction of minerals isolated from various food products [5]. The proportion or the presence or lack of some of these minerals influence the intensity of thermoluminescence of the mineral fraction despite of its volume.

Experimental

In the present study we compared the normalized yields of minerals isolated from several irradiated food products which are frequently delivered to the Laboratory from different countries to be examined whether irradiated. The aim of this study was to demonstrate how far the weights of isolated minerals as well as their luminescence are different from sample to sample and how much they influence the TL.

Fourteen samples of selected products have been taken for the analysis: powdered onion, grounded leek, grounded red paprika, two samples of dried mushrooms (champignons) from different sources,

Table 1. The weight of mineral fraction isolated by the same analytical procedure [2] from 14 commercial food products.

Product	Sample weight [g]	Isolated mineral fraction [mg]
Onion, powdered	20.0 ± 0.8 g	2.5
Leek, grounded		2.3
Paprika, grounded		2.3
Champignons, cut (1)		1.1
Champignons, cut (2)		1.0
Pepper black, grounded		1.0
Cinnamon powder		1.0
Propolis powder		1.0
Paprika green, cut		0.6
Onion, grounded		0.6
Birch bark, cut		0.6
Rice red, powdered		0.3
Artichoke, powdered		0.3
Garlic powder		0.1

Table 2. Thermoluminescence intensity normalized against the same mass of mineral equal to 1.5 mg.

Product	TL intensity of mineral	Relative TL intensity of mineral
Birch bark, cut	1576 x 10^5	525
Paprika, grounded	1428 x 10^5	476
Onion powder	1211 x 10^5	404
Champignons, cut	850 x 10^5	283
Artichoke powder	774 x 10^5	258
Champignons, cut	737 x 10^5	246
Leek	453 x 10^5	151
Cinnamon powder	250 x 10^5	83
Paprika green, cut	176 x 10^5	59
Garlic powder	160 x 10^5	53
Pepper black, grounded	90 x 10^5	30
Rice red fermented, powdered	42 x 10^5	14
Onion, grounded	10 x 10^5	3
Propolis powder	3 x 10^5	1

grounded black pepper, powdered cinnamon, powdered propolis used as died supplement, green paprika (cut), birch bark (cut) used after grinding as an ingredient to herbal pharmaceuticals and cosmetics, red rice powder, powdered artichoke and garlic. The weight of each sample taken for analysis was about 20 g. Some deviation, but not exceeding 0.8 g do appear with samples of mushroom, green paprika and birch bark.

As seen from Table 1, the mass of the isolated mineral fraction differs from sample to sample from 0.1 to 2.5 mg. It is the consequence of the different structure of food surface (porosity first of all) but the method and quality of initial cleaning (mechanical) of the product has to be also taken into consideration.

The intensity of thermoluminescence of each sample has been measured subsequently. In order to facilitate the comparison of the yields of luminescence coming from each of the samples the obtained results have been normalized to the same average mass of mineral equal to 1.5 mg. The results are comprehended in Table 2.

The relative TL intensities given in Table 2 are amazing, indeed. Some differences of the intensity of thermoluminescence between mineral samples were expected, of course. However, over 500-fold more intense luminescence from one sample as compared with the other was really not expected and it shows conclusively that the main factor influencing strongly thermoluminescence of isolated mineral is the composition of mineral or, in another words, the composition of soil on which the plant giving the product (spices, herbs, *etc.*) is cultivated.

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LABORATORY OF NUCLEAR CONTROL SYSTEMS AND METHODS

The main subject of the Laboratory activity in 2012 was the development of methods and apparatus, based generally on the application of ionizing radiation, and process engineering for measurements and diagnostic purposes. The research programme of the Laboratory was focused on the following topics:

- development, construction and manufacturing of measuring devices and systems for industry, medicine and protection of the environment;
- elaboration and implementation of wireless communication systems based on GPS or the Internet for data acquisition and transmission;
- construction and industrial testing of a gamma scanner for diagnostics of industrial installations;
- development of measuring equipments for other Institute laboratories and centres;
- development of a new leakage control method for testing of industrial installations during their operation;
- identification and optimization of industrial processes using tracers and radiotracer methods;
- application of membrane processes of biogas separation and their enrichment in methane;
- elaboration and implementation on an industrial scale of new methods and technology of biogas production by fermentation of agriculture substrates and by-products;
- hydrogen production from the synthesis gas using membrane separation.

In the field of elaboration and construction of new nuclear instrumentation the works were directed towards radioactive contamination detection, measurements of concentration of radon daughters and wireless data transmission.

A radiometric stand based on the application of large area thin scintillators for alpha-, beta- and gamma-radiation measurements, was constructed and tested for contamination detection in laboratory and industrial conditions.

The system for attached and unattached radon ^{222}Rn decay products in air or water was elaborated and tested in laboratory conditions. In the frame of realized R&D project, development of a new generation of mining radiometers was undertaken. The radiometer which be used in mines where methane gas can be present, must satisfy the explosion proof conditions.

All realized and constructed instruments are prepared in the version with wireless transmission of results and their storage in memory of data acquisition system. The Wi-Fi (Wireless Fidelity) and GSM (Global System for Mobile Communication) are used for data transmission depending on the distance between the detector and control unit. The same type of measuring equipment is used in a gamma scanner for diagnostics of large industrial installations.

TWO-STAGE BIOREACTOR FOR BIOMETHANE PRODUCTION

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The steady increase in demand for energy causes the search for sources of energy alternative to those based on the combustion of coal, oil and natural gas energy sources such as nuclear power and biotechnology. Energy production using biogas obtained in anaerobic digestion of selected agricultural products as well as agricultural and food wastes is important due to the large Polish agricultural potential. Most of the biogas reactors operate like flow reactors with a quasi-continuous supply of substrates.

The Institute of Nuclear Chemistry and Technology (INCT) is involved in the investigations and practical realization of biogas production process based on Polish patent [1]. Fermentation process is realized in a cascade of hydroliser and a fermentor introducing spatial separation of the hydrolysis of biomass from the basic methane fermentation process [1].

Researches of mesophilic anaerobic digestion of raw materials such as manure on colza straw, maize silage and grass silage were carried out at a pilot plant at Szewnia Dolna with a capacity of about 10 kW. The block diagram of installation is shown in Fig.1.

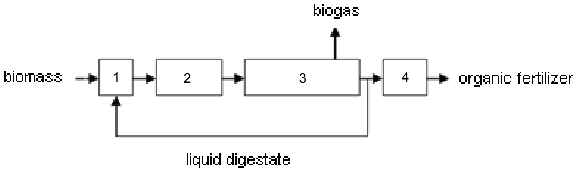

Fig.1. Block diagram of the system at Szewnia Dolna: 1 – biomass tank, 2 – hydrolyser, 3 – fermentor, 4 – tank for liquid digestate.

The raw materials charged to the hydrolyser was in the form of suspension with dry a matter content of approximately 8.5%. After about 25 days of process duration, the obtained methane concentration in the fermentor was in the range from 58 up to 69%. The biogas yield was on the level 0.35-0.40 m^3/kg dry mass.

Taking into account the literature data, results of the laboratory and pilot plant tests design guidelines were prepared for the construction of a biogas plant with a thermal capacity of about 400 kW for vegetable, agriculture and food waste treatment. A scheme of the proposed system is presented in Fig.2.

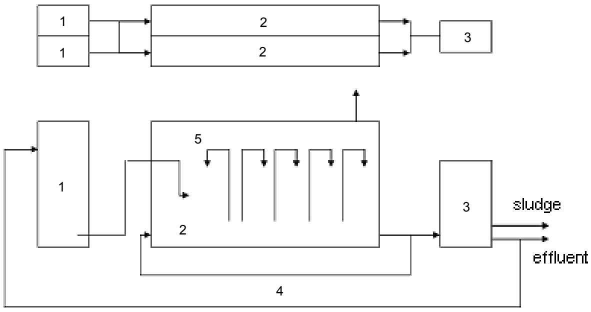

Fig.2. Scheme of the biogas plant: 1 – hydrolyser, 2 – fermentor, 3 – sludge separator, 4 – circulation of the slurry from the outlet to the inlet in the fermentor, 5 – internal circulation of the slurry from the bottom of the fermentor to the surface of the liquid phase.

The proposed bioreactor consists of two rectangular hydrolysers and two rectangular fermentors. Feeding of the installation is about 53 tons of biomass suspension per day. The assumed productivity is about 62 m^3/h of biogas with about 65% methane concentration.

The work was done in the framework of the research sub-step 2.1.B co-financed by the National Centre for Research and Development strategic programme "Advanced technologies of energy generation".

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ChemSession'12: IX Warszawskie Seminarium Doktorantów Chemików, Warszawa, Poland, 10.05.2012. Streszczenia, p. 112.

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Sorpcja izotopów promieniotwórczych Eu-152/154 i Am-242 na sorbencie alginianowym (Sorption of the radionuclides Eu-152/154 and Am-242 by the alginate sorbent).

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POSTĘPY TECHNIKI JĄDROWEJ

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INTERVIEWS IN 2012

1. Bilewicz A.

   Wolski A.: Atom ratuje ludzi (Atom saves people). Naukowy Wieczór z Jedynką. Program I Polskiego Radia, 29.08.2012.

2. Brykała M.

   Wolski A.: Atom ratuje ludzi (Atom saves people). Naukowy Wieczór z Jedynką. Program I Polskiego Radia, 29.08.2012.

3. Chmielewski A.G.

   Truszczak D.: Skutki środowiskowe i zdrowotne awarii w japońskiej elektrowni Fukushima w rok po tym wydarzeniu (Environmental and wholesome consequences of the accident in the Japanese nuclear power station Fukushima one year after). Naukowy Wieczór z Jedynką. Program I Polskiego Radia, 06.03.2012.

4. Chmielewski A.G.

   Wolski A.: Atom ratuje ludzi (Atom saves people). Naukowy Wieczór z Jedynką. Program I Polskiego Radia, 29.08.2012.

5. Smoliński T.

   Wolski A.: Atom ratuje ludzi (Atom saves people). Naukowy Wieczór z Jedynką. Program I Polskiego Radia, 29.08.2012.

THE INCT PATENTS AND PATENT APPLICATIONS IN 2012

PATENTS

1. Detektor do pomiaru stężenia produktów rozpadu radonu w powietrzu (Detector for measuring the concentration of radon decay products in air)

   B. Machaj, J. Bartak

   Polish Patent 212459
2. Dozymetr alaninowo-polimerowy o podwyższonej czułości (Alanine-polymer dosimeter with enhanced sensitivity)

   Z. Stuglik

   Polish Patent 212895
3. Sposób otrzymywania opatrunków hydrożelowych (Method for the preparation of hydrogel wound dressings)

   D. Chmielewska, W. Migdał, A.G. Chmielewski, U. Gryczka, P. Kik

   Ukrainian Patent (with KIKGEL, Poland)
4. Sposób otrzymywania opatrunków hydrożelowych (Method for the preparation of hydrogel wound dressings)

   D. Chmielewska, W. Migdał, A.G. Chmielewski, U. Gryczka, P. Kik

   Russian Patent (with KIKGEL, Poland)
5. Sposoby wbudowania elementów radioaktywnych w szkła krzemionkowe (The methods of disposal radioactive elements to silica glasses)

   A.G. Chmielewski, A. Deptuła, M. Miłkowska, W. Łada, T. Olczak

   Belarus Patent

PATENT APPLICATIONS

1. Sposób unieszkodliwiania odpadów radioaktywnych w „syntetycznej skale" (Method of immobilization of nuclear waste into "synthetic rock").

   T. Smoliński, A.G. Chmielewski, A. Deptuła, W. Łada, T. Olczak

   P- 400235
2. Klej termotopliwy do klejenia polietylenu i innych poli(alfa-olefin), zwłaszcza do izolacji złączy preizolowanych rur ciepłowniczych, oraz sposób jego wytwarzania (Hot-melt adhesive for gluing polyethylene and other polyolefins, used for the insulation of joints in pre-insulation of hot water pipes, and method for its production)

   G. Przybytniak, A. Nowicki, I. Legocka, K. Mirkowski

   P-401245
3. Sposób i sorbent do otrzymywania radionuklidu arsenu-72 oraz sposób wytwarzania tego sorbentu (Sorbent for receiving radionuclide arsenic-72, production of this sorbent and its use)

   E. Chajduk, H. Polkowska-Motrenko, A. Bilewicz, K. Doner

   European Patent Application
4. Sposób selektywnego wydzielania uranu i proaktynu z materiału zawierającego tor (A selective extraction of uranium and protactinium from material containing thorium)

   E. Chajduk, H. Polkowska-Motrenko, P. Kalbarczyk

   European Patent Application
5. Sposób i układ transportu i mieszania zawiesiny biomasy w hydrolizerze i fermentorze (Method and system of transferring and mixing of a biomass slurry in a hydrolyser and fermenter)

   A. Kryłowicz, K. Chrzanowski, J. Usidus, A.G. Chmielewski

   European Patent Application

6. Sposób pozyskiwania i separacji cennych pierwiastków metali, zwłaszcza z ubogich rud uranowych oraz ścieków radioaktywnych (Method for separation and obtaining of valuable metals particularly from low-grade uranium ores and radioactive effluents)

   G. Zakrzewska-Trznadel, A. Jaworska-Sobczak, A. Miśkiewicz, W. Łada, E. Dłuska, S. Wroński

   European Patent Application

7. Sposób i układ transportu i mieszania zawiesiny biomasy w hydrolizerze i fermentorze (Method and system of transferring and mixing of a biomass slurry in a hydrolyser and fermenter)

   A. Kryłowicz, K. Chrzanowski, J. Usidus, A.G. Chmielewski

   Ukrainian Patent Application

CONFERENCES ORGANIZED AND CO-ORGANIZED BY THE INCT IN 2012

1. FIRST NATIONAL MEETING ON NEWLANCER FP7 EU PROJECT, 3 FEBRUARY 2012, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Organizing Committee: Grażyna Zakrzewska-Trznadel, Ph.D., D.Sc., professor in INCT, Kinga Frąckiewicz, Ph.D., Agnieszka Jaworska, M.Sc.

2. 1st EUROPEAN NUCLEAR SOCIETY-YOUNG GENERATION NETWORK CORE COMMITTEE MEETING, 10-12 FEBRUARY 2012, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology, Polish Nuclear Society-Polish Young Generation Network

Organizing Committee: Marcin Brykała, M.Sc., Tomasz Smoliński, M.Sc., Kinga Frąckiewicz, Ph.D., Ewelina Miśta, M.Sc.

3. REFERENCE GROUP MEETING IN THE FRAME OF IPPA FP7 EU PROJECT, 9 MARCH 2012, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Organizing Committee: Grażyna Zakrzewska-Trznadel, Ph.D., D.Sc., professor in INCT, Barbara Zielińska, Ph.D.

4. PROGRESS MEETING No. 3 IN THE FRAME OF IPPA FP7 EU PROJECT, 23-25 APRIL 2012, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology, National Centre for Nuclear Research

Organizing Committee: Grażyna Zakrzewska-Trznadel, Ph.D., D.Sc., professor in INCT, Barbara Zielińska, Ph.D., Agnieszka Jaworska, M.Sc., Bogumiła Mysłek-Laurikainen, Ph.D., Ewelina Miśta, M.Sc.

5. PlasTEP (PLASMA TECHNOLOGIES FOR ENVIRONMENT PROTECTION) WORKSHOP, 14 MAY 2012, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Organizing Committee: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc., Andrzej Pawelec, Ph.D., Sylwia Witman-Zając, M.Sc.

6. PlasTEP (PLASMA TECHNOLOGIES FOR ENVIRONMENT PROTECTION) SEMI-ANNUAL MEETING, 15 MAY 2012, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Organizing Committee: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc., Andrzej Pawelec, Ph.D., Sylwia Witman-Zając, M.Sc.

7. REFERENCE GROUP MEETING IN THE FRAME OF IPPA FP7 EU PROJECT, 18 MAY 2012, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Organizing Committee: Grażyna Zakrzewska-Trznadel, Ph.D., D.Sc., professor in INCT, Barbara Zielińska, Ph.D., Agnieszka Jaworska, M.Sc., Agnieszka Miśkiewicz, M.Sc.

8. POLISH-FRENCH MEETING ON FUEL CYCLE, 21-23 MAY 2012, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Organizer: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.

9. SEMINARIUM DLA UCZESTNIKÓW STUDIÓW PODYPLOMOWYCH AKADEMII LEONA KOŹMIŃSKIEGO „ZARZĄDZANIE PROJEKTEM BADAWCZYM I KOMERCJALIZACJA WYNIKÓW BADAŃ. STUDIA PODYPLOMOWE DLA PRACOWNIKÓW NAUKOWYCH I PODMIOTÓW DZIAŁAJĄCYCH NA RZECZ NAUKI" (SEMINAR FOR THE PARTICIPANTS OF POSTGRADUATE STUDIES FROM THE KOZMINSKI UNIVERSITY "MANAGEMENT OF RESEARCH PROJECTS AND COMMERCIALIZATION OF RESEARCH RESULTS. POSTGRADUATE STUDIES FOR SCIENTISTS AND SUBJECTS ACTING IN FAVOUR OF SCIENCE"), 26-27 MAY 2012, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology, Kozminski University

Organizing Committee: Wojciech Maciąg, M.Sc., Justyna Wróbel, M.Sc., Ariadna Bednarz

10. TRAINING FOR STAKEHOLDERS "INTEGRATING PUBLIC PARTICIPATION INTO DECISION MAKING PROCESSES FOR SUSTAINABLE GOVERNANCE OF NUCLEAR ENERGY AND WASTE IN POLAND" IN THE FRAME OF IPPA FP7 EU PROJECT), 18-19 JUNE 2012, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Organizing Committee: Grażyna Zakrzewska-Trznadel, Ph.D., D.Sc., professor in INCT, Barbara Zielińska, Ph.D., Agnieszka Jaworska, M.Sc., Agnieszka Miśkiewicz, M.Sc.

11. SEMINARIUM NAUKOWE "ANALIZA MOŻLIWOŚCI POZYSKIWANIA URANU DLA ENERGETYKI JĄDROWEJ Z ZASOBÓW KRAJOWYCH" (SCIENTIFIC SEMINAR ON "ANALYSIS OF THE POSSIBILITY OF URANIUM SUPPLY FROM DOMESTIC RESOURCES), 21 JUNE 2012, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Organizing Committee: Grażyna Zakrzewska-Trznadel, Ph.D., D.Sc., professor in INCT, Kinga Frąckiewicz, Ph.D.

12. SECOND NATIONAL MEETING ON NEWLANCER FP7 EU PROJECT, 4 SEPTEMBER 2012, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Organizing Committee: Grażyna Zakrzewska-Trznadel, Ph.D., D.Sc., professor in INCT, Agnieszka Miśkiewicz, M.Sc., Agnieszka Jaworska, M.Sc.

13. INTERNATIONAL SYMPOSIUM ON "FREE RADICALS IN CHEMICAL BIOLOGY", 11 SEPTEMBER 2012, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Organizing Committee: Prof. Krzysztof Bobrowski, Ph.D., D.Sc., Prof. Marcin Kruszewski, Ph.D., D.Sc., Paweł Wiśniowski, Ph.D.

14. REGIONAL TRAINING COURSE "VALIDATION AND PROCESS CONTROL FOR ELECTRON BEAM RADIATION PROCESSING" IN THE FRAME OF PROJECT RER 1/011 "INTRODUCING AND HARMONIZING STANDARDIZED QUALITY CONTROL PROCEDURES FOR RADIATION TECHNOLOGIES", 24-28 SEPTEMBER 2012, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology, International Atomic Energy Agency

Organizer: Andrzej Rafalski, Ph.D.

15. 10TH MEETING OF THE IONIZING RADIATION AND POLYMERS SYMPOSIUM, IRaP'2012, 14-19 OCTOBER 2012, KRAKÓW, POLAND

Organized by the Radiation Research Foundation; Institute of Applied Radiation Chemistry, Technical University of Łódź; Institute of Nuclear Chemistry and Technology; International Atomic Energy Agency

Organizing Committee: Jacek Jurczakowski, M.Sc., Sławomir Kadłubowski, Ph.D., Wojciech Migdał, Ph.D., D.Sc., professor in INCT, Grażyna Przybytniak, Ph.D., D.Sc., professor in INCT, Bożena Rokita, Ph.D., Piotr Ulański, Ph.D., D.Sc., Radosław Wach, Ph.D., Zbigniew Zimek, Ph.D.

16. PILOT EXERCISE WORKSHOP WITHIN THE FRAMES OF NEWLANCER FP7 EU PROJECT, 6 NOVEMBER 2012, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Organizing Committee: Grażyna Zakrzewska-Trznadel, Ph.D., D.Sc., professor in INCT, Dorota Gajda, M.Sc.

17. X KONFERENCJA "DLA MIASTA I ŚRODOWISKA – PROBLEMY UNIESZKODLIWIANIA ODPADÓW" (X CONFERENCE ON "FOR THE CITY AND ENVIRONMENT – PROBLEMS OF WASTE DISPOSAL), 26 NOVEMBER 2012, WARSZAWA, POLAND

Organized by the Warsaw University of Technology, Institute of Nuclear Chemistry and Technology (PlasTEP project), Solid Communal Waste Utilization Plant (Warszawa), Gdańsk University of Technology

Organizing Committee: Robert Cherbański, Ph.D., Maria Obrębska, Ph.D., Michał Kalita, Ph.D., Agata Urbaniak, M.Sc., Sylwia Witman-Zając, M.Sc.

Ph.D. THESES IN 2012

1. Przemysław Andrzej Koźmiński, M.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
   Synteza i badanie właściwości fizykochemicznych koniugatów heteroleptycznych kompleksów technetu-99m z peptydem *n*-oktaacyl-[Ser^3]-greliną(1-6) jako potencjalnych radiofarmaceutyków diagnostycznych (Synthesis and physicochemical properties of conjugates technetium-99m complexes with *n*-octanoyl-[Ser^3]-ghrelin(1-6) peptide as potential diagnostic radiopharmaceuticals)
   supervisor: Prof. Jerzy Ostyk-Narbutt, Ph.D., D.Sc.
   Institute of Nuclear Chemistry and Technology, 27.09.2012

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 studies are:

- chemical aspects of nuclear energy,
- 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 will be employed at the Institute. The candidates can apply for a doctoral 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, University of Warsaw and the Polish Academy of Sciences. In the third year, the Ph.D. students are obliged to prepare a seminar related to the various aspects of nuclear energy. 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 Science and Higher Education, are:

- submission of a formal dissertation, summarizing original research contributions suitable for publication;
- final examination and public defence of the dissertation thesis.

In 2012, the following lecture series were organized:

- “Toxicology of heavy metals” – Dariusz Pogocki, Ph.D., D.Sc., professor in INCT (Institute of Nuclear Chemistry and Technology, Warszawa, Poland);
- “Basis of biochemistry and molecular biology” – Prof. Marcin Kruszewski, Ph.D., D.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland);
- “Radioactive wastes – characterization and management” – Grażyna Zakrzewska-Trznadel, Ph.D., D.Sc., professor in INCT (Institute of Nuclear Chemistry and Technology, Warszawa, Poland).

The qualification interview for the Ph.D. programme takes place in the mid of September. Detailed information can be obtained from:

- head: Prof. Aleksander Bilewicz, Ph.D., D.Sc.
  (phone: +48 22 504 13 57, e-mail: A.Bilewicz@ichtj.waw.pl);
- secretary: Dr. Ewa Gniazdowska
  (phone: +48 22 504 11 78, e-mail: E.Gniazdowska@ichtj.waw.pl).

TRAINING OF STUDENTS

Institution	Country	Number of participants	Period
International Atomic Energy Agency	Egypt	1	1 month
International Atomic Energy Agency	Syria	1	1 month
Lublin University of Technology Faculty of Mechanical Engineering	Poland	1	3 months

Institution	Country	Number of participants	Period
University of Rzeszów Faculty of Biology and Agriculture	Poland	3	2 weeks
		1	1 week
University of Warsaw Faculty of Chemistry	Poland	1	3 weeks
Warsaw University of Life Sciences Faculty of Food Sciences	Poland	44	one-day course
Warsaw University of Technology Faculty of Chemical and Process Engineering	Poland	1	1 year
		1	6 months
		8	one-day course
Warsaw University of Technology Faculty of Chemistry	Poland	1	3 months
		1	2 months
Warsaw University of Technology Faculty of Mathematics and Information Science	Poland	1	2 weeks
Warsaw University of Technology Faculty of Physics	Poland	14	one-day course
Warsaw University of Technology Faculty of Power and Aeronautical Engineering	Poland	1	3 months
		1	1.5 month
		1	1 month
WAT Military University of Technology Department of Chemistry and New Technologies	Poland	1	1 year
		1	2 months
The Jan Paweł II public grammar-school at Nowy Dwór Mazowiecki	Poland	20	one-day course

RESEARCH PROJECTS AND CONTRACTS

RESEARCH PROJECTS GRANTED BY THE NATIONAL SCIENCE CENTRE IN 2012

1. **Novel technetium and rhenium complexes with the N-heterocyclic aldehyde thiosemicarbazones – the potential radiopharmaceuticals.**
   supervisor: Leon Fuks, Ph.D.
2. **Provenance and chronology studies of selected silver coins minted in the Polish and Central Europe coinages by means of chemical composition, sources of raw materials and technology.**
   supervisor: Lech Waliś, Ph.D.
3. **Radiochemical separation of arsenic from selenium and its potential usage in the generator ^{72}Se/^{72}As construction.**
   supervisor: Ewelina Chajduk, Ph.D.
4. **Glass in Central Europe from the late-medieval times to the end of the pre-industrial era. Chemical composition.**
   supervisor: Jerzy Jakub Kunicki-Goldfinger, Ph.D.
5. **Participation of radiation chemistry in systems chemistry, especially in prebiotic chemistry.**
   supervisor: Prof. Zbigniew P. Zagórski, Ph.D., D.Sc.
6. **Functionalization of polyurethane surface by radiation-induced grafting (Preludium).**
   supervisor: Marta Walo, M.Sc.
7. **Nanozeolites as a carrier for radium in targeted therapy.**
   supervisor: Prof. Aleksander Bilewicz, Ph.D., D.Sc.
8. **Paramagnetic centres generated radiolytically in molecular sieves exposed to carbon oxides.**
   supervisor: Marcin Sterniczuk, M.Sc.
9. **Des-acyl ghrelin analog as a new carrier of radionuclides and a potential radiopharmaceutical.**
   supervisor: Grzegorz Wójciuk, M.Sc.

DEVELOPMENT PROJECTS GRANTED BY THE NATIONAL CENTRE FOR RESEARCH AND DEVELOPMENT IN 2012

1. **A new generation of mining radiometers for the measurement of radon decay products.**
   supervisor: Jakub Bartak, Eng.
2. **A plant for the liquid radioactive waste treatment in research institutes and organizations using radioactive substances.**
   supervisor: Grażyna Zakrzewska-Trznadel, Ph.D., D.Sc., professor in INCT
3. **Obtaining of carrier-free-scandium-47 – a radionuclide for therapeutic radiopharmaceuticals.**
   supervisor: Prof. Aleksander Bilewicz, Ph.D., D.Sc.
4. **Labelling of biomolecules with At-211 –- obtaining of therapeutic radiopharmaceuticals for nuclear medicine.**
   supervisor: Monika Łyczko, Ph.D.
5. **Preparation of a hot-melt adhesive for the insulation of joints in preinsulation pipes used in heating installations.**
   supervisor: Grażyna Przybytniak, Ph.D., D.Sc., professor in INCT
6. **Radiation sterilized substrata for plant cultivation inoculated with selected microorganisms.**
   supervisor: Wojciech Migdał, Ph.D., D.Sc., professor in INCT

7. **Formation of the data bank on original products for the juice sector, to supply requirements of the Polish market and producers, basing on the method of stable isotopes.**
   supervisor: Ryszard Wierzchnicki, Ph.D.
8. **Elaboration of the synthesis procedure of a receptor diagnostic radiopharmaceutical for breast cancer, of the type Her-2, imaging lapatinib labelled with technetium-99m.**
   supervisor: Ewa Gniazdowska, Ph.D.
9. **A mobile membrane installation for the enrichment of gas in methane (project INITECH).**
   supervisor: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.
10. **Technical project of high-performance installation for obtaining and management of biogas (project INITECH).**
    supervisor: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.
11. **Elaboration and certification of new reference materials needed for obtaining European accreditation by Polish laboratories involved in industrial analytics (project InnoTech, MODAS).**
    supervisor: Halina Polkowska-Motrenko, Ph.D., D.Sc., professor in INCT
12. **Optimization of two stages bioreactor for biogas with high methane contents production - elaboration of biostarters and biomarkers of methane fermentation. Task 2.1. Construction in laboratory scale of two stages bioreactors for biogas production with high methane concentration.**
    supervisor: Jacek Palige, Ph.D.
13. **Alternative methods for technetium-99m production. Task 8. Isolation of Tc-99m using zirconium modified TiO_2 nanotubes and by extraction method with HDEHP.**
    supervisor: Prof. Aleksander Bilewicz, Ph.D., D.Sc.
14. **Patent Plus – support for patented inventions.**
    supervisor: Wiesława Łada, Ph.D.

INTERNATIONAL PROJECTS CO-FUNDED BY THE MINISTRY OF SCIENCE AND HIGHER EDUCATION IN 2012

1. **Radiation supporting synthesis and curing of nanocomposites suitable for practical applications.**
   supervisor: Grażyna Przybytniak, Ph.D., D.Sc., professor in INCT
2. **Ageing diagnostic and prognostic of low voltage C and I cables (ADVANCE).**
   supervisor: Grażyna Przybytniak, Ph.D., D.Sc., professor in INCT
3. **Multi-disciplinary biodosimetric tools to manage high scale radiological casualties (MULTIBIODOSE).**
   supervisor: Sylwester Sommer, Ph.D.
4. **Implementing public participation approaches in radioactive waste disposal (IPPA).**
   supervisor: Grażyna Zakrzewska-Trznadel, Ph.D., D.Sc., professor in INCT
5. **PGAM5 protein as a signalling factor in the crosstalk between the oxidative stress protective pathway NRF2/KEAP1 and apoptosis and autophagy related to the activation of ASK1 kinase. The testing of the hypothesis and implications in Parkinson's disease (Iuventus Plus).**
   supervisor: Tomasz Stępkowski, M.Sc.
6. **Advanced fuels for generation IV reactors: reprocessing and dissolution (ASGARD).**
   supervisor: Andrzej Deptuła, Ph.D.
7. **Upgrading the capacities and capabilities in nuclear and radiation processing technology and applications by increasing the proficiency level in national nuclear institutions.**
   supervisor: Dagmara Chmielewska-Śmietanko, M.Sc.
8. **Formation, investigations and characterization of advanced nanoporous materials.**
   supervisor: Bożena Sartowska, Ph.D.
9. **Studies on solvent extraction of minor actinides and on their conversion to oxides.**
   supervisor: Prof. Jerzy Narbutt, Ph.D., D.Sc.

STRATEGIC PROJECT “NEW TECHNOLOGIES SUPPORTING DEVELOPMENT OF SAFE NUCLEAR ENERGY”

1. **Scientific problem no. 3: Principles to secure fuel needs for the Polish nuclear energy.**
   supervisor: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.
2. **Scientific problem no. 4: Development of techniques and technologies aiding the management of spent nuclear fuel and radioactive wastes.**
   supervisor: Leon Fuks, Ph.D.
3. **Scientific problem no. 5: Participation criteria of the Polish industry in the development of nuclear energy. Study of the case.**
   supervisor: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.
4. **Scientific problem no. 6: Development of methods securing nuclear safety and radiological protection for the current and future needs of nuclear energy.**
   supervisor: Prof. Marcin Kruszewski, Ph.D., D.Sc.
5. **Scientific problem no. 7: Analysis of hydrogen generation processes in nuclear reactor during normal exploitation and nuclear accidents in order to increase safety standards.**
   supervisor: Prof. Jacek Michalik, Ph.D., D.Sc.
6. **Scientific problem no. 8: Study of processes occurring under regular operation of water circulation systems in nuclear power plants with suggested actions aimed at upgrade of nuclear safety.**
   supervisor: Anna Bojanowska-Czajka, Ph.D.

STRATEGIC PROJECT “ADVANCED TECHNOLOGIES FOR GAINING ENERGY”

1. **Scientific problem no. 3: Elaboration of a technology of coal gasification for highly efficient production of fuel and electric energy** (coordinated by the Institute for Chemical Processing of Coal)
   - **Studies on the processes of membrane purification of synthesis gas**

   supervisor: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.
2. **Scientific problem no. 4: Elaboration of integrated technologies for production of fuels and energy from biomass, agriculture waste and others** (coordinated, in part, by the University of Warmia and Mazury in Olsztyn)
   - **Concentration of methane in biogas formed during fermentation and co-fermentation of lignocellulose** (4.2.1.C)

   supervisor: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.
   - **Studies on the degradation efficiency of lignocellulose materials under the influence of ionizing radiation** (4.4.A)

   supervisor: Wojciech Migdał, Ph.D., D.Sc., professor in INCT
   - **Design work on a biogas-plant** (2.1.B)

   supervisor: Jacek Palige, Ph.D.

IAEA RESEARCH CONTRACTS IN 2012

1. **Radiation supporting synthesis and curing of nanocomposites suitable for practical applications.**
   No. 16666
   principal investigator: Grażyna Przybytniak, Ph.D., D.Sc., professor in INCT
2. **Laboratory and feasibility study for industrial waste water effluent treatment by radiation.**
   No. 16454
   principal investigator: Zbigniew Zimek, Ph.D.

IAEA TECHNICAL AND REGIONAL CONTRACTS IN 2012

1. **Developing of an advanced industrial gamma scanning system with wireless data acquisition.**
   POL/0/010
2. **Regional Training on IAEA Validation and Process Control for Electron Beam Radiation Processing.**
   RER/1/011
3. **Supporting radiation synthesis and the characterization of nanomaterials for health care, environmental protection and clean energy applications.**
   RER/8/014
4. **Using nuclear techniques for the characterization and preservation of cultural heritage artefacts in the European Region.**
   RER/8/015
5. **Enhancing quality control methods and procedures for radiation technology.**
   RER/8/017

PROJECTS WITHIN THE FRAME OF EUROPEAN UNION FRAME PROGRAMMES IN 2012

1. **FP7 – EURATOM, Fission: Actinide recycling by separation and transmutation (ACSEPT).**
   principal investigator: Prof. Jerzy Narbutt, Ph.D., D.Sc.
2. **FP7 – EURATOM, Fission: Multi-disciplinary biodosimetric tools to manage high scale radiological casulaties (MULTIBIODOSE).**
   principal investigator: Sylwester Sommer, Ph.D.
3. **FP7 – EURATOM, Fission: Ageing diagnostic and prognostic of low voltage C and I cables (ADVANCE).**
   principal investigator: Grażyna Przybytniak, Ph.D., D.Sc., professor in INCT
4. **FP7 – EURATOM, Fission: Implementing public participation approaches in radioactive waste disposal (IPPA).**
   principal investigator: Grażyna Zakrzewska-Trznadel, Ph.D., D.Sc., professor in INCT
5. **FP7 – EURATOM, Fission: New MS linking for an advanced cohesion in Euratom research (NEWLANCER).**
   principal investigator: Grażyna Zakrzewska-Trznadel, Ph.D., D.Sc., professor in INCT
6. **FP7 – EURATOM, Fission: Advanced fuels for generation IV reactors: reprocessing and dissolution (ASGARD).**
   principal investigator: Andrzej Deptuła, Ph.D.
7. **FP7 – EURATOM, Fission: Realizing the European Network in Biodosimetry (RENEB)**
   principal investigator: Sylwester Sommer, Ph.D.
8. **FP7 – Transnational access to large infrastructure for a safe management of actinide (TALISMAN).**
   principal investigator: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.
9. **FP7 – Safety of actinide separation processes (SACSESS).**
   principal investigator: Prof. Jerzy Narbutt, Ph.D., D.Sc.

EUROPEAN REGIONAL DEVELOPMENT FUND: BALTIC SEA REGION PROGRAMME

1. **Dissemination and fostering of plasma based technological innovation environment protection in BSR PlasTEP.**
   supervisor: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.

INTERNATIONAL RESEARCH PROGRAMMES IN 2012

1. **European cooperation in the field of scientific and technical research. COST CM0703 Systems chemistry – Chemistry and molecular sciences and technologies. Participation of radiation chemistry in systems chemistry, especially in prebiotic chemistry.**
   supervisor: Prof. Zbigniew Zagórski, Ph.D., D.Sc.
2. **Formation, investigations and characterization of advanced nanoporous materials.**
   supervisor: Bożena Sartowska, Ph.D.

STRUCTURAL FUNDS:
OPERATIONAL PROGRAMME INNOVATIVE ECONOMY

1. **Centre of Radiochemistry and Nuclear Chemistry – meeting the needs for nuclear power and nuclear medicine.**
   supervisor: Roman Janusz, M.Sc.
2. **Analysis of the possibilities of uranium supply from indigenous resources in Poland.**
   supervisor: Grażyna Zakrzewska-Trznadel, Ph.D., D.Sc., professor in INCT
3. **New generation of electrical wires modified by radiation.**
   supervisor: Zbigniew Zimek, Ph.D.
4. **A multiparameter "Triage" test for assessment of radiation exposure to the general population.**
   supervisor: Prof. Marcin Kruszewski, Ph.D., D.Sc.
5. **A new generation of radiometric devices with wireless transmission of information.**
   supervisor: Adrian Jakowiuk, M.Sc.

LIST OF VISITORS TO THE INCT IN 2012

1. **Abad Lucille**, Philippine Nuclear Research Institute, Quezon City, Philippines, *22-23.10.2012*
2. **Al-Bachir Mahfouz**, Atomic Energy Commission of Syria, *25-30.03.2012*
3. **Amilkav Lopes Antonio**, Portugal, *13-16.11.2012*
4. **Bartesaghi Silviny**, Universidad de la República Uruguay, Montevideo, Uruguay, *09-13.09.2012*
5. **Bazil Fanny**, Integrated Nuclear Infrastructure Group, Division of Power, International Atomic Energy Agency, Vienna, Austria, *28.02.2012*
6. **Berejka Antoni**, Ionicorp$^+$, Huntington, New York, USA, *11-20.10.2012*
7. **Bernard Hervé**, Vice-chairman of the French Alternative Energies and Atomic Energy Commission (CEA), France, *22-23.05.2012*
8. **Bourg Stephane**, Radiochemistry and Processes Department, French Alternative Energies and Atomic Energy Commission (CEA), France, *22-23.05.2012*
9. **Buhler Pierre**, French Ambassador in Poland, *08.10.2012*
10. **Charbonnel Marie-Christine**, Radiochemistry and Processes Department, French Alternative Energies and Atomic Energy Commission (CEA), *22-23.05.2012*
11. **Covacic Nicolas**, Division of Nuclear Power, Department of Nuclear Engineering, International Atomic Energy Agency, Vienna, Austria, *28.02.2012*
12. **Daher Yaarob**, Atomic Energy Commission of Syria, *16.01.-15.02.2012*
13. **Driscoll Mark S.**, SUNY College of Environmental Science and Forestry, USA, *11-14.10.2012*
14. **Elnaguip Mohammed**, Egypt, *20.08.-19.09.2012*
15. **Grimaldi Natascia**, University of Palermo, Italy, *22-26.10.2012*
16. **Gudowski Wacław**, KTH Royal Institute of Technology, Stockholm, Sweden, *11.12.2012*
17. **Holcner Martin**, VF, a.s. Černá Hora, Czech Republic, *04.12.2012*
18. **Hoveé-Levin Chantal**, University of Paris-Sud 11, Orsay, France, *18-19.02.2012, 10-11.09.2012*
19. **Le Masne Dominique**, French Embassy, *22-23.05.2012*
20. **Moisy Philippe**, Radiochemistry and Processes Department, French Alternative Energies and Atomic Energy Commission (CEA), *22-23.05.2012, 06.12.2012*
21. **Nichipor Henrietta**, Joint Institute for Power and Nuclear Research "Sosny", National Academy of Sciences of Belarus, Belarus, *23.09.-06.10.2012*
22. **Orelovitch Oleg L.**, Joint Institute for Nuclear Research (JINR), Dubna, Russia, *01-10.08.2012, 10-29.09.2012*
23. **Paradis Luc**, Head of Waste Treatment and Conditioning Research Department, French Alternative Energies and Atomic Energy Commission (CEA), *22-23.05.12*
24. **Pierrard Philippe**, Counsellor on Nuclear Energy, French Embassy, *22-23.05.2012, 08.10.2012*
25. **Poinssot Christophe**, Head of Radiochemistry and Processes Department, French Alternative Energies and Atomic Energy Commission (CEA), *22-23.05.2012*
26. **Poumadere Claire Mays**, Regional Enviromental Centre (REC), France, *17-19.06.2012*
27. **Radi Rafaela**, Universidad de la República Uruguay, Montevideo, Uruguay, *09-13.09.2012*
28. **Tietze-Jaensch Holger**, Institute of Energy and Climate Research – IEK-6, Forschungszentrum Jülich GmbH, Germany, *29-31.08.2012*
29. **Tingas Kaidi**, Regional Enviromental Centre (REC), France, *17-20.06.2012*
30. **Torado Simony**, University of Palermo, Italy, *22-26.10.2012*
31. **Wang Jianglong**, Tsinghua University, China, *10-17.11.2012*
32. **Wishart James F.**, Brookhaven National Laboratory, USA, *10-12.09.2012*
33. **Yang Xiaoying**, Fudan University, China, *19-21.04.2012*
34. **Zheng Zheng**, Fudan University, China, *19-21.04.2012*

THE INCT SEMINARS IN 2012

1. **Anthony J. Berejka, Ph.D. (Ionicorp$^+$, Huntington, New York, USA)**
   Opportunities and challenges for industrial radiation processing
2. **Marcin Brykała, M.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**
   Synteza ziaren dwutlenku uranu dotowanych wybranymi pierwiastkami przy zastosowaniu kompleksowej metody zol-żel (CSGP) (Synthesis of uranium dioxide particles doped by selected elements by the complex sol-gel process (CSGP))
3. **Bartłomiej Ciesielski, Ph.D., D.Sc., professor MUG (Medical University of Gdańsk, Poland)**
   Efekty związane z LET-em promieniowania oraz ekspozycją na światło napromieniowanych detektorów alaninowych na ich sygnał EPR: przykłady zastosowań dozymetrii EPR w radioterapii (Effects connected with LET of radiation and light exposition of alanine detectors on EPR signal: examples of EPR dosimetry applications in radiotherapy)
4. **Prof. Wacław Gudowski (KTH Royal Institute of Technology, Stockholm, Sweden)**
   Transmutacja (zużytego) paliwa jądrowego – czy to naprawdę „być albo nie być" dla energetyki jądrowej (Transmutation of (spent) nuclear fuel – is it really "to be or not to be" for nuclear energetics)
5. **Grzegorz Guzik, M.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**
   Badanie trwałych efektów radiacyjnych w cukrach prostych pod kątem identyfikacji napromieniowania żywności (Studies of durable radiation effects in simple sugars for the identification of irradiated food)
6. **Bernd Hansel (Rafflenbeul Anlagenbau GmbH, Germany)**
   Molecular sieves and nonthermal plasma processes for minimizing waste air abatement costs
7. **Martin Holcner, Ing. (VF, a.s. Černá Hora, Czech Republic), Bożena Sartowska, Ph.D. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**
   Dosimetric systems in nuclear power plants (NPPs)
8. **Paweł Kalbarczyk, M.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**
   Badania nad oznaczaniem U w torze napromienianym neutronami dla zastosowania toru jako paliwa w jądrowym reaktorze energetycznym (Studies on uranium determination in neutron irradiated thorium for the application of thorium as a nuclear fuel)
9. **Agata Kasperek, M.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**
   Nanozeolity jako nośniki radioizotopów ^{223}Ra, ^{224}Ra i ^{225}Ra w celowanej terapii radionuklidowej (Nanozeolites as carriers for ^{223}Ra, ^{224}Ra and ^{225}Ra radioisotopes in targeted radionuclide therapy)
10. **Katarzyna Kosno, M.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**
    Badanie mechanizmów rodnikowych reakcji nikotyny i jej związków modelowych w celu ich późniejszego wykorzystania w medycynie (Studies on the mechanisms of radical reactions involving nicotine and its model compounds for later application in medicine)
11. **Agnieszka Miśkiewicz, M.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**
    Zastosowanie metody znaczników promieniotwórczych do badań procesów membranowych i aparatów do filtracji membranowej (Application of radiotracer methods for the investigation of membrane processes and membrane apparatus)
12. **Marcin Orzeszyna, M.Sc. (PGE Energia Jądrowa, Poland)**
    Proces wyboru potencjalnych lokalizacji na potrzeby budowy pierwszej polskiej elektrowni jądrowej (Process of choosing potential location for the construction of the first Polish nuclear power station)
13. **Prof. Janusz Rak, Ph.D., D.Sc. (Faculty of Chemistry, University of Gdańsk, Poland)**
    Bromonukleozydy – potencjalne foto- lub/i radiosensybilizatory (Bromonucleosides – potential photo- and/or radiosensibilizators)
14. **Alina Sionkowska, Ph.D., D.Sc., professor UMK (Nicolaus Copernicus University, Toruń, Poland)**
    Procesy fotochemiczne w biopolimerach (Photochemical processes in biopolymers)
15. **Agnieszka Sulich, M.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**
    Badanie wczesnych etapów radiolizy wybranych rozcieńczalników i ligandów do procesu SANEX w celu oceny i modyfikacji ich odporności radiacyjnej (Studies of the early stages of radiolysis of selected dilu-

ents and ligands applied in the SANEX process for the evaluation and modification of their radiation stability)

16. **Prof. Irena Szumiel, Ph.D., D.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**
    Mechanizmy komórkowe hormezy popromiennej (Cellular mechanism of radiation-induced hormesis)

LECTURES AND SEMINARS DELIVERED OUT OF THE INCT IN 2012

LECTURES

1. **Bilewicz A.**
   Ph.D. studies in INCT.
   Polish-French Meeting on Fuel Cycle, Warszawa, Poland, 21-23.05.2012.
2. **Bilewicz A., Kasperek A., Leszczuk E.**
   Nanoparticles as a platform for in vivo generators.
   "CYCLEUR" Cyclotron Research Workshop, Ispra, Italy, 29-30.11.2012.
3. **Bobrowski K.**
   •OH-induced oxidation of tyrosine in enkephalins.
   The COST CM1001 – Chemistry of non-enzymatic protein modification – modulation of protein structure and function: Working Group (WG1) Meeting, Paris, France, 12-16.04.2012.
4. **Bojanowska-Czajka A.**
   Coolant chemistry (light water).
   Polish-French Meeting on Fuel Cycle, Warszawa, Poland, 21-23.05.2012.
5. **Brykała M.**
   Fuel precursors for IV generation.
   Polish-French Meeting on Fuel Cycle, Warszawa, Poland, 21-23.05.2012.
6. **Brykała M.**
   Fuel precursors containing MA for IV generation. Immobilization of MA in inert matrix by CSGP.
   Seminar related to the visit of Dr. Holger Tietze-Jaensch from Forschungszentrum Jülich GmbH, Warszawa, Poland, 30.09.2012.
7. **Brykała M., Chmielewski A.G.**
   Zagadnienia chemiczne w wyborze technologii i eksploatacji reaktorów jądrowych (Chemical problems with the selection of technology and exploitation of nuclear reactors).
   Seminarium Edukacyjne „Zbudujemy bezpiecznie, bezpieczną elektrownię jądrową", Poznań, Poland, 25.01.2012.
8. **Brykała M., Deptuła A.**
   Synthesis of U-Nd oxides by complex sol-gel processes (CSGP).
   ACSEPT 4th Annual Meeting, Karlsruhe, Germany, 20-23.03.2012.
9. **Brykała M., Deptuła A., Rogowski M.**
   Synthesis of uranium carbides by complex sol-gel process (CSGP).
   ASGARD Project Meeting, Jáchymov, Czech Republic, 11-14.06.2012.
10. **Brykała M., Deptuła A., Rogowski M.**
    Synthesis of uranium dioxide doped with MA surrogates by complex sol-gel process (CSGP).
    ASGARD Project Meeting, Jáchymov, Czech Republic, 11-14.06.2012.
11. **Chajduk E., Polkowska-Motrenko H.**
    Uranium resources in Poland – the past and present.
    IAEA-CYTED-UNECE – Workshop "Recent developments in evaluation of uranium and thorium resources", Lisbon, Portugal, 15-18.10.2012.
12. **Chmielewski A.G.**
    Jak skutecznie uczestniczyć w projektach Euratom – polskie przykłady (How to effectively participate in the Euratom projects – Polish examples).
    Dzień Informacyjny: konkursy Euratom Fission 2012, Warszawa, Poland, 22.02.2012.

13. **Chmielewski A.G.**

    European dream – clean and cost free energy.

    Conference "EU energy security – seeking stronger Polish-German cooperation", Lublin, Poland, 02-04.03.2012.

14. **Chmielewski A.G.**

    Electron beam as a special tool for NO_x/SO_x reduction.

    PlasTEP International Workshop "Plasma technologies as a tool for environment protection", St. Petersburg, Russia, 21.03.2012.

15. **Chmielewski A.G.**

    The Polish nuclear strategy – insights into the fuel cycle.

    Polish-French Meeting on Fuel Cycle, Warszawa, Poland, 21-23.05.2012.

16. **Chmielewski A.G.**

    Działalność Instytutu Chemii i Techniki Jądrowej (Activity of the Institute of Nuclear Chemistry and Technology).

    Nuclear Career Seminar, Warszawa, Poland, 25.05.2012.

17. **Chmielewski A.G.**

    Implementation of nuclear techniques in mining and processing of fossil fuels – support and restrictions.

    Conference "Science for industry: necessity is the mother of invention – First networking event in the field of modern geochemical applications in geosystem exploration", Warszawa, Poland, 20-22.06.2012.

18. **Chmielewski A.G.**

    Industrial application of electron accelerators.

    National Seminar on Applications of Electron Accelerators in Science, Education, Health Care, Environment and Industry, Bratislava, Slovak Republic, 21.06.2012.

19. **Chmielewski A.G.**

    The Polish nuclear strategy – insights into the fuel cycle.

    Seminar related to the visit of Dr. Holger Tietze-Jaensch from Forschungszentrum Jülich GmbH, Warszawa, Poland, 30.09.2012.

20. **Chmielewski A.G.**

    Energetyka jądrowa w świecie (Nuclear energetics in the world).

    III Dni Techniki Pomorza Zachodniego 2012, Szczecin, Poland, 28-30.11.2012.

21. **Chmielewski A.G.**

    Wybrane surowcowe i ekologiczne aspekty rozwoju energetyki w kraju i na świecie (Selected raw materials and ecological aspects of the development of energetics in Poland and in the world).

    III Dni Techniki Pomorza Zachodniego 2012, Szczecin, Poland, 28-30.11.2012.

22. **Chmielewski A.G.**

    Recent developments in environmental applications of electron beam generated plasma.

    PlasTEP Final Conference "Perspectives of plasma technology for air and water cleaning", Berlin, Germany, 05-06.12.2012.

23. **Deptuła A., Brykała M.**

    Synthesis of uranium carbides by complex sol-gel process (CSGP).

    ASGARD Kick-Off Meeting, Uddevalla, Sweden, 11-13.01.2012.

24. **Deptuła A., Brykała M.**

    Synthesis of uranium dioxide doped with MA surrogates by complex sol-gel process (CSGP).

    ASGARD Kick-Off Meeting, Uddevalla, Sweden, 11-13.01.2012.

25. **Fuks L.**

    Fuel cycle and waste reprocessing.

    Polish-French Meeting on Fuel Cycle, Warszawa, Poland, 21-23.05.2012.

26. **Kasperek A., Bilewicz A.**

    Nanozeolites as a carrier for radium radionuclides.

    COST TD1004 Initial Meeting, Torino, Italy, 17-18.02.2012.

27. **Kasperek A., Bilewicz A.**

    Encapsulating of alpha and beta emitters in nanozeolites for radionuclide therapy.

    COST TD1004 Working Group 1 Meeting, Warszawa, Poland, 28-29.02.2012.

28. **Kosno K., Celuch M., Janik I., Kisała J., Mirkowski J., Pogocki D.**

Badania metodami radiolizy impulsowej i DFT nad utlenianiem nikotyny przez rodniki •OH w pH fizjologicznym (Pulse radiolysis and DFT studies on the oxidation of nicotine by •OH radicals at physiological pH).

Sesja Sprawozdawczo-Szkoleniowa KDM, Sterdyń, Poland, 19-22.04.2012.

29. **Krajewski S.**

^{44,43}Sc and ^{47}Sc as matched pair for theranostic approach to peptide receptor radionuclide therapy.

COST Action TD1004 Annual Meeting "Theranostics imaging and therapy: An action to develop novel nanosized systems for imaging-guided drug delivery", London, UK, 28-30.10.2012.

30. **Krajewski S., Bilewicz A., Cydzik I., Simonelli F., Holzwarth U., Bulgheroni A., Abbas K.**

Sc-43 and Sc-44 for PET imaging.

"CYCLEUR" Cyclotron Research Workshop, Ispra, Italy, 29-30.11.2012.

31. **Lankoff A.**

Zarządzanie projektami w Centrum Radiobiologii i Dozymetrii Biologicznej – dobre praktyki, sukcesy, problemy (Projects managements in the Centre for Radiobiology and Biological Dosimetry – best practices, successes, problems).

Seminarium dla uczestników studiów podyplomowych Akademii Leona Koźmińskiego „Zarządzanie projektem badawczym i komercjalizacja wyników badań. Studia podyplomowe dla pracowników naukowych i podmiotów działających na rzecz nauki", Warszawa, Poland, 26-27.05.2012.

32. **Leszczuk E.**

TiO_2 nanoparticles as vehicles of ^{212}Pb and ^{225}Ac for internal radiotherapy.

COST Action TD1004 Annual Meeting "Theranostics imaging and therapy: An action to develop novel nanosized systems for imaging-guided drug delivery", London, UK, 28-30.10.2012.

33. **Leszczuk E., Kasperek A., Bilewicz A.**

TiO_2 nanoparticles as vehicles of ^{212}Pb and ^{225}Ac radionuclides.

COST TD1004 Working Group 1 Meeting, Warszawa, Poland, 28-29.02.2012.

34. **Michalik J.**

Radiolytic and catalytic H_2 formation in reactor coolant water.

Polish-French Meeting on Fuel Cycle, Warszawa, Poland, 21-23.05.2012.

35. **Michalik J.**

Strategic nuclear energy project in INCT.

Seminar related to the visit of Dr. Holger Tietze-Jaensch from Forschungszentrum Jülich GmbH, Warszawa, Poland, 30.09.2012.

36. **Ostyk-Narbutt J.**

Minor actinides separation at fuel reprocessing process.

Polish-French Meeting on Fuel Cycle, Warszawa, Poland, 21-23.05.2012.

37. **Ostyk-Narbutt J.**

Recent INCT studies on separation of minor actinides from HLW originated from fuel reprocessing.

Seminar related to the visit of Dr. Holger Tietze-Jaensch from Forschungszentrum Jülich GmbH, Warszawa, Poland, 30.09.2012.

38. **Pawelec A.**

Large scale plasma-based NO_x/SO_x treatment through electron beam.

PlasTEP (Plasma technologies for environment protection) Workshop, Warszawa, Poland, 14.05.2012.

39. **Polkowska-Motrenko H.**

Activity of the Laboratory of Nuclear Analytical Methods for the purpose of the development of nuclear energy programme in Poland.

Seminar related to the visit of Dr. Holger Tietze-Jaensch from Forschungszentrum Jülich GmbH, Warszawa, Poland, 30.09.2012.

40. **Polkowska-Motrenko H., Chajduk E.**

Assignment of the concentration values in proficiency test materials for food analysis.

XXXVII Międzynarodowe Seminarium Naukowo-Techniczne "Chemistry for agriculture", Karpacz, Poland, 02-05.12.2012.

41. **Przybytniak G.**

Radiation effects on materials.

Polish-French Meeting on Fuel Cycle, Warszawa, Poland, 21-23.05.2012.

42. **Samczyński Z., Polkowska-Motrenko H., Dybczyński R.**
Similarities and differences in the certification campaigns for two varieties of tobacco leaves CRMs.
XXXVII Międzynarodowe Seminarium Naukowo-Techniczne "Chemistry for agriculture", Karpacz, Poland, 02-05.12.2012.

43. **Skłodowska A., Rewerski B., Chajduk E., Kalbarczyk P., Bartosiewicz I.**
Refractory sandstone ores and waste as alternative source of uranium.
IAEA Technical Meeting on Origin of Sandstone Uranium Deposits: A Global Perspectives, Vienna, Austria, 29.05.-01.06.2012.

44. **Smoliński T.**
Sol-gel vitrification of HLW.
Polish-French Meeting on Fuel Cycle, Warszawa, Poland, 21-23.05.2012.

45. **Smoliński T.**
Synthesis of SYNROC components by CSGP.
Seminar related to the visit of Dr. Holger Tietze-Jaensch from Forschungszentrum Jülich GmbH, Warszawa, Poland, 30.09.2012.

46. **Wojtowicz P.**
Vitrification of HLW by sol-gel method.
Seminar related to the visit of Dr. Holger Tietze-Jaensch from Forschungszentrum Jülich GmbH, Warszawa, Poland, 30.09.2012.

47. **Zakrzewska-Trznadel G.**
Analysis of the possibility of uranium production from low-grade indigenous resources.
Seminar related to the visit of Dr. Holger Tietze-Jaensch from Forschungszentrum Jülich GmbH, Warszawa, Poland, 30.09.2012.

48. **Zakrzewska-Trznadel G.**
Development of technologies for the treatment of liquid low- and medium-level radioactive wastes.
Seminar related to the visit of Dr. Holger Tietze-Jaensch from Forschungszentrum Jülich GmbH, Warszawa, Poland, 30.09.2012.

49. **Zakrzewska-Trznadel G., Polkowska-Motrenko H.**
Uranium enrichment from low grade resources.
Polish-French Meeting on Fuel Cycle, Warszawa, Poland, 21-23.05.2012.

50. **Zimek Z.**
Accelerator facilities for radiation processing based on X-ray application.
Workshop "The use of e-beam accelerator for the treatment and preservation of materials", Cairo, Egypt, 29.09.-05.10.2012.

51. **Zimek Z.**
Comparison between e-beam, X-ray and gamma radiation.
Workshop "The use of e-beam accelerator for the treatment and preservation of materials", Cairo, Egypt, 29.09.-05.10.2012.

52. **Zimek Z.**
Electron accelerators for radiation processing – criterions of selection and exploitation.
Workshop "The use of e-beam accelerator for the treatment and preservation of materials", Cairo, Egypt, 29.09.-05.10.2012.

53. **Zimek Z.**
Principles of e-beam accelerators of different design.
Workshop "The use of e-beam accelerator for the treatment and preservation of materials", Cairo, Egypt, 29.09.-05.10.2012.

SEMINARS

1. **Bilewicz Aleksander**
Projektowanie i badanie nowych radiofarmaceutyków w Instytucie Chemii i Techniki Jądrowej (Designing and studying novel radiopharmaceuticals at the Institute of Nuclear Chemistry and Technology).
National Centre for Nuclear Research, Otwock-Świerk, Poland, 25.10.2012.

2. **Bilewicz Aleksander**
   Radionuclides and radiopharmaceuticals at the Institute of Nuclear Chemistry and Technology (Warsaw).
   Laboratory of Radiochemistry and Environmental Chemistry, Paul Scherrer Institute, Villigen, Switzerland, 21.12.2012.
3. **Brykała Marcin**
   Zasoby i wydobycie uranu (Resources and production of uranium in Poland).
   Faculty of Chemical and Process Engineering, Warsaw University of Technology, Poland, 05.04.2012.
4. **Chajduk Ewelina**
   Blaski i cienie promieniotwórczości (Radioactivity – the pros and cons).
   I Liceum Ogólnokształcące im. Ks. A.J. Czartoryskiego, Puławy, Poland, 28.02.2012.
5. **Chmielewski Andrzej G.**
   Zastosowanie chemii radiacyjnej w ochronie środowiska (Application of radiation chemistry in environmental protection).
   Faculty of Chemistry, Gdańsk University of Technology, Poland, 31.05.2012.
6. **Jakowiuk Adrian**
   Wykorzystanie promieniowania gamma do diagnostyki obiektów przemysłowych (gamma skaning) (Use of gamma radiation for diagnosis of industrial facilities (gamma scanning)).
   Faculty of Mechatronics, Warsaw University of Technology, Poland, 24.01.2012.
7. **Jakowiuk Adrian**
   Wykorzystanie promieniowania gamma do diagnostyki obiektów przemysłowych (gamma skaning) (Use of gamma radiation for diagnosis of industrial facilities (gamma scanning)).
   Faculty of Mechatronics, Warsaw University of Technology, Poland, 08.05.2012.
8. **Kalbarczyk Paweł**
   Reaktory jądrowe (Nuclear reactors).
   Faculty of Biology, University of Warsaw, Poland, 16.01.2012.
9. **Kalbarczyk Paweł, Smoliński Tomasz**
   Energetyka jądrowa w Polsce – za czy przeciw? (Nuclear power in Poland – agree or disagree?).
   Maria Skłodowska-Curie Museum, Warszawa, Poland, 19.05.2012.
10. **Krajewski Seweryn**
    Selected INCT activities in the field of radiopharmaceutical chemistry.
    Department of Clinical Physiology and Nuclear Medicine, Herlev Hospital, University of Copenhagen, Denmark, 25.01.2012.
11. **Migdał Wojciech**
    Legal aspects and present status of food irradiation in Europe.
    Institute for Application of Atomic Energy, Chinese Academy of Agricultural Sciences, Beijing, China, 03.12.2012.
12. **Migdał Wojciech**
    Control and monitoring of irradiation process in INCT e-beam facility.
    Institute for Application of Atomic Energy, Chinese Academy of Agricultural Sciences, Beijing, China, 04.12.2012.
13. **Migdał Wojciech**
    Detection of irradiated food.
    Institute for Application of Atomic Energy, Chinese Academy of Agricultural Sciences, Beijing, China, 04.12.2012.
14. **Migdał Wojciech**
    INCT EB facilities.
    Institute for Application of Atomic Energy, Chinese Academy of Agricultural Sciences, Beijing, China, 04.12.2012.
15. **Migdał Wojciech**
    Mechanism and methods of irradiated food detection.
    Tianjin Institute of Technical Physics, China, 06.12.2012.
16. **Polkowska-Motrenko Halina**
    Procedury przygotowania materiału certyfikowanego (Procedures of preparation and certification of reference material).
    Faculty of Chemistry, University of Warsaw, Poland, 11.03.2012.

17. **Polkowska-Motrenko Halina**

    Korzyści z udziału w badaniach biegłości na przykładzie Sekcji POLLAB-CHEM (Advantages of participation in proficiency testing on example of POLLAB-CHEM division).

    XIV Międzynarodowe Targi Analityki i Technik Pomiarowych EuroLab 2012, Warszawa, Poland, 28.03.2012.

18. **Smoliński Tomasz**

    Energetyka jądrowa w Polsce – przeszłość, teraźniejszość, przyszłość (Nuclear energy in Poland – past, present, future).

    Maria Skłodowska-Curie Museum, Warszawa, Poland, 26.09.2012.

19. **Zimek Zbigniew**

    Electron accelerators for radiation processing.

    Nuclear and Technological Institute (ITN), Lisbon, Portugal, 30.03.2012.

AWARDS IN 2012

1. Method for the preparation of hydrogel wound dressings

   Gold Medal at the XV Moscow International Salon of Inventions and Innovation Technologies "Archimedes-2012", Moscow, Russia, 20-23.03.2012

   Institute of Nuclear Chemistry and Technology

2. Method of production yttrium oxide

   Silver prize at the Korea International Women's Invention Exposition 2012, Seoul, Korea, 03-06.05.2012

   Wiesława Łada, Danuta Wawszczak, Andrzej Deptuła, Edward Iller, Leszek Królicki, Jerzy Ostyk-Narbutt

3. Method of immobilization of nuclear waste into "synthetic rock"

   Silver Medal at the VI International Warsaw Invention Show IWIS 2012, Warszawa, Poland, 16-19.10.2012

   Tomasz Smoliński, Andrzej G. Chmielewski, Andrzej Deptuła, Wiesława Łada, Tadeusz Olczak

4. Method of immobilization of nuclear waste into "synthetic rock"

   Silver Medal at the Belgian and International Trade Fair for Technological Innovation "Brussels Eureka!", Brussels, Belgium, 15-17.11.2012

   Tomasz Smoliński, Andrzej G. Chmielewski, Andrzej Deptuła, Wiesława Łada, Tadeusz Olczak

5. New technology for production of yttrium oxide microspheres

   FIRI (the First Institute Inventors and Researchers in I.R.IRAN) award for the best invention at the Korea International Women's Invention Exposition 2012, Seoul, Korea, 03-06.05.2012

   Wiesława Łada, Danuta Wawszczak

6. Method of production yttrium oxide

   Special Award of the Asia Invention Association at the Seoul International Invention Fair 2012 – SIIF 2012, Seoul, Korea, 29.11-02.12.2012

   Wiesława Łada, Danuta Wawszczak, Andrzej Deptuła, Edward Iller, Leszek Królicki, Jerzy Ostyk-Narbutt

7. Method of production yttrium oxide

   Special Award of the Taiwan Invention Association at the Seoul International Invention Fair 2012 – SIIF 2012, Seoul, Korea, 29.11-02.12.2012

   Wiesława Łada, Danuta Wawszczak, Andrzej Deptuła, Edward Iller, Leszek Królicki, Jerzy Ostyk-Narbutt

8. Diploma of the Ministry of Science and Higher Education for the project "Method of production protective coatings made of titanium dioxide (TiO_2) or lithium titanate (Li_2TiO_2) on nickel cathodes"

   Andrzej Deptuła, Danuta Wawszczak, Wiesława Łada

9. Method for the preparation of hydrogel wound dressings

   Diploma of the All-Russian Society of Inventors and Rationalizers, Petersburg Branch, at the XV Moscow International Salon of Inventions and Innovation Technologies "Archimedes-2012", Moscow, Russia, 20-23.03.2012

   Institute of Nuclear Chemistry and Technology

10. Rozwiązania technologiczne instalacji do wytwarzania biogazu z surowców roślinnych (Technological solutions of the instalation for the production of biogas from plant raw materials)

    II place in the competition for the best poster at the IV All-Polish Scinetific Conference "Interdisciplinary problems in the engineering and environmental protection" EKO-DOK 2012, Szklarska Poręba, Poland, 15-18.04.2012

    Michał Krzysztof Zalewski

11. Recovery of metals from the uranium ores by combination of double stage leaching and ion-exchange chromatography

    Award for the best poster at the 7th International PhD Students and Young Scientists Confrerence – Young scientists towards the challenges of modern technology, Warszawa, Poland, 17-20.09.2012

    Dorota Gajda

12. Knight's Cross of Order of Polonia Restituta
    Lech Waliś
13. Gold Cross of Merit
    Aleksander Bilewicz
14. Gold Cross of Merit
    Krzysztof Bobrowski
15. Gold Cross of Merit
    Marcin Kruszewski
16. Gold Cross of Merit
    Wojciech Migdał
17. Gold Cross of Merit
    Halina Polkowska-Motrenko
18. Gold Cross of Merit
    Grażyna Przybytniak
19. Gold Cross of Merit
    Grażyna Zakrzewska-Trznadel
20. Silver Cross of Merit
    Ewa Gniazdowska
21. Silver Cross of Merit
    Iwona Kałuska
22. Silver Cross of Merit
    Witold Skwara
23. Bronze Cross of Merit
    Jakub Dudek
24. Bronze Cross of Merit
    Ewa Pańczyk
25. Gold Medal for Long Service
    Zyta Głębowicz
26. Gold Medal for Long Service
    Alicja Nowak
27. Gold Medal for Long Service
    Zofia Sikora
28. Gold Medal for Long Service
    Tadeusz Święcki
29. Gold Medal for Long Service
    Józef Tartas
30. First degree team award of Director of the Institute of Nuclear Chemistry and Technology for the application achievements – elaboration and implementation of the technology of obtaining two certified reference materials for inorganic trace analysis (Oriental Basma Tobacco Leaves – INCT-OBTL-5 and Polish Virginia Tobacco Leaves – INCT-PVTL-6)
    Zbigniew Samczyński, Rajmund Dybczyński, Halina Polkowska-Motrenko, Ewelina Chajduk, Marta Pyszynska, Krzysztof Kulisa, Paweł Kalbarczyk
31. First degree team award of Director of the Institute of Nuclear Chemistry and Technology for a series of seven papers on designing and synthesis of new pharmaceutical receptors – diagnostic and therapeutic
    Ewa Gniazdowska, Leon Fuks, Przemysław Koźmiński
32. Second degree team award of Director of the Institute of Nuclear Chemistry and Technology for the application achievements – realization of the project "Studies on the removal of SO_2 and NO_x from the combustion gas formed in diesel shipping engines by means of an electron beam"
    Andrzej Pawelec, Sylwia Witman

33. Second degree team award of Director of the Institute of Nuclear Chemistry and Technology for a series of four articles concerning the problems of mammal response to the action of stressful factors, oxidation stress being particularly considered

    Tomasz Stępkowski, Kamil Brzóska, Marcin Kruszewski

34. Third degree team award of Director of the Institute of Nuclear Chemistry and Technology for a series of four publications concerning studies on the properties of a selected group of polymers subjected to radiation-induced changes

    Grażyna Przybytniak, Ewa Kornacka, Andrzej Nowicki, Marta Walo, Leon Fuks

35. Distinction of the first degree of Director of the Institute of Nuclear Chemistry and Technology for the achieved progress in the preparation of thesis and professional activity, including published articles, participation in the actions organized and co-organized by the Institute and participation in the preparation and realization of research projects and contracts outside the Institute

    Edyta Leszczuk

36. Distinction of the second degree of Director of the Institute of Nuclear Chemistry and Technology for the achieved progress in the preparation of thesis and professional activity, including published articles, participation in the actions organized and co-organized by the Institute and participation in the preparation and realization of research projects and contracts outside the Institute

    Marta Walo

37. Distinction of the third degree of Director of the Institute of Nuclear Chemistry and Technology for the achieved progress in the preparation of thesis and professional activity, including published articles, participation in the actions organized and co-organized by the Institute and participation in the preparation and realization of research projects and contracts outside the Institute

    Tomasz Smoliński

38. Individual award of Director of the Institute of Nuclear Chemistry and Technology for the achievement of outstanding results, as from the opinion on scientists of the Institute in the years 2009-2011

    Leon Fuks

39. Individual award of Director of the Institute of Nuclear Chemistry and Technology for the achievement of outstanding results, as from the opinion on scientists of the Institute in the years 2009-2011

    Wojciech Starosta

40. Individual award of Director of the Institute of Nuclear Chemistry and Technology for the achievement of outstanding results, as from the opinion on scientists of the Institute in the years 2009-2011

    Zbigniew Zimek

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