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INSTITUTE
OF NUCLEAR CHEMISTRY
AND TECHNOLOGY

EDITORS

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GENERAL INFORMATION

In August 2015 the Institute of Nuclear Chemistry and Technology (INCT) together with the National Centre for Nuclear Research (NCBJ) and the Department of Nuclear Waste Utilization – the successors of the Institute of Nuclear Research (IBJ) will be celebrated the IBJ's 60th anniversary.

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 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 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 2014 one Ph.D. and three D.Sc. theses were defended.

The Institute won one of the ten projects granted in the action 2 of Erasmus+ programme. This project "Joint innovative training and teaching/learning program in enhancing development and transfer of application of ionizing radiation in materials processing" is intended to fill up the gap of education quality between different region of EU countries.

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

In 2013, the Evaluation Committee of Scientific Units in the Ministry of Science and Higher Education conferred the INCT cathegory A+.

The INCT has carried a project in the programme "Innovative Economy" PO IG, granted on the basis of high evaluation of the Institute's achievements:

- Development of a multi-parametric triage approach for an assessment of radiation exposure in a large-scale radiological emergency.

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:

- ASGARD: Advanced fuels for generation IV reactors: reprocessing and dissolution;
- RENEB: Realizing the European Network in Biodosimetry;
- ARCADIA: Assessment of regional capabilities for new reactors development through an integrated approach;
- EAGLE: Enhancing education, training and communication processes for informed behaviors and decision-making related to ionizing radiation risks;
- PLATENSO: Building a platform for enhanced societal research related to nuclear energy in Central and Eastern Europe;
- SACSESS: Safety of actinide separation processes;
- TALISMAN: Transnational access to large infrastructure for a safe management of actinide;
- UCARD-2 WP4: Applications of accelerators: The industrial and environemntal applications of electron beams.

In 2014, the INCT scientists published 67 papers in scientific journals registered in the Philadelphia list, among them 59 papers in journals with an impact factor (IF) higher than 1.0. Two scientific books and 3 chapters were written by the INCT research workers.

The following annual awards of the INCT Director-General for the best publications and application achievements in 2014 were granted:

- first degree team award to Marcin Kruszewski, Anna Lankoff, Maria Wojewódzka, Jadwiga Chwastowska, Teresa Bartłomiejczyk, Sylwia Męczyńska-Wielgosz, Iwona Grądzka, Sylwester Sommer, Ewelina Chajduk, Bożena Sartowska, Irena Szumiel for a series of eight publications concerning physicochemical properties of silver nanoparticles, titanium dioxide and silicon surface-modified and biological effects caused by the nanoparticles;
- second degree team award to Krzysztof Bobrowski, Gabriel Kciuk, Paweł Wiśniowski, Jacek Mirkowski for a series of three publications concerning the radical processes in peptide particles containing sulphur, induced by radioactivity and photochemistry;
- second degree team award to Halina Polkowska-Motrenko, Leon Fuks, Ewelina Chajduk, Jakub Dudek, Paweł Kalbarczyk, Agata Oszczak, Michał Zuba, Marta Pyszynska, Krzysztof Kulisa for the application achievements in 2012-2013 – elaboration of methodology of carrying out and implementing proficiency studies for analytical laboratories conducting research on the content of heavy metals and radionuclides in the environment and in food;
- second degree team award to Zbigniew Zimek, Andrzej Rafalski, Magdalena Rzepna, Sylwester Bułka, Iwona Kałuska for the application achievements in 2012-2013 – elaboration and implementation of the technology of radiation sterilization of new materials;
- third degree team award of Director of the Institute of Nuclear Chemistry and Technology to Agata Piotrowska, Edyta Leszczuk, Izabela Cydzik, Aleksander Bilewicz for two publications concerning the bonding of radium radionuclides in nanoparticles and their addition to biologically active particles and labelling of nanoparticles to toxicological studies.

In 2014, the research teams in the INCT were involved in the organization of 12 scientific meetings, among them:

- International Conference on Development and Applications of Nuclear Technologies NUTECH-2014 (21-24 September 2014, Warszawa, Poland),
- Workshop "The industrial and environmental applications of electron beams" (6-7 November 2014, Warszawa, Poland).

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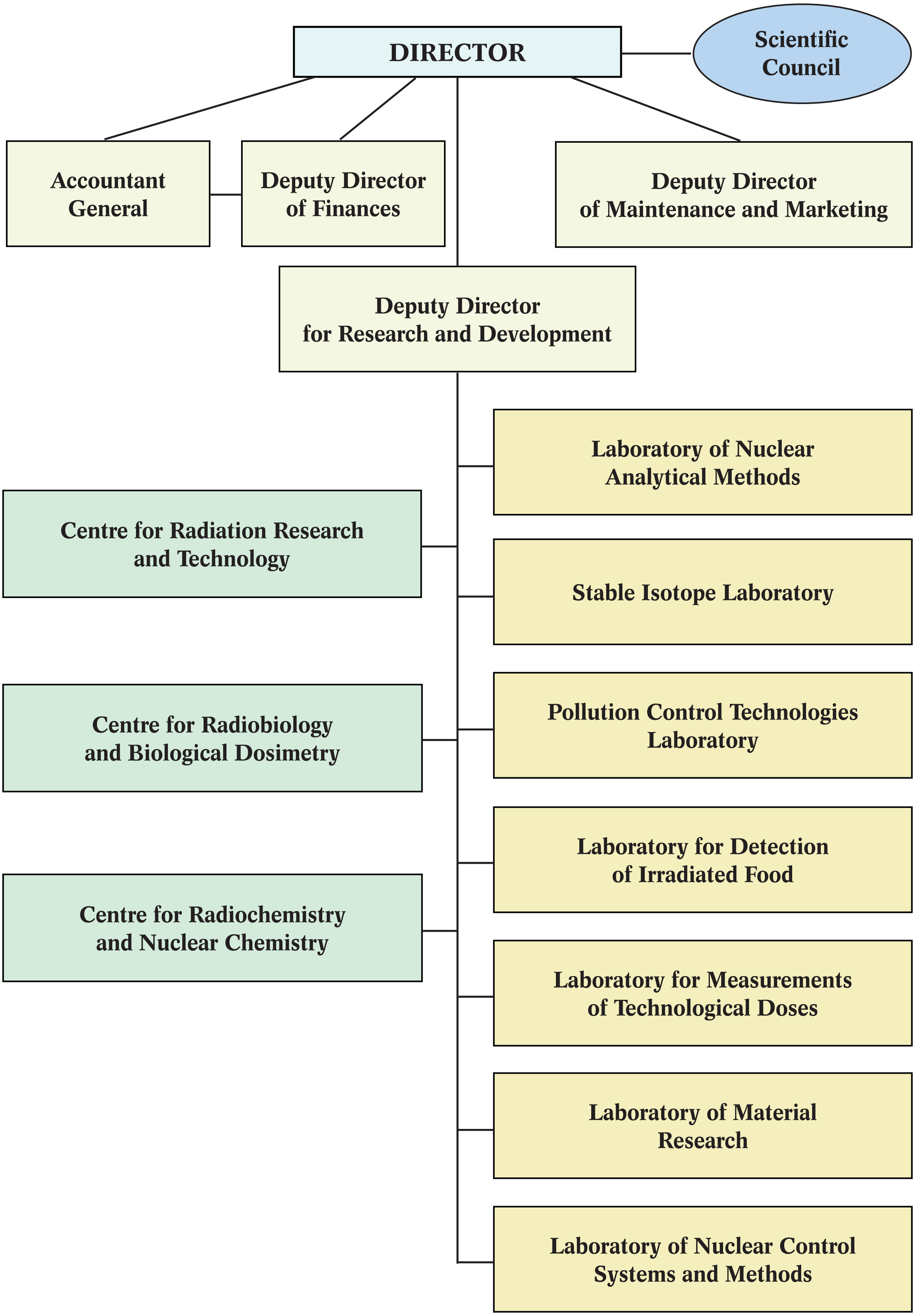

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CENTRE FOR RADIATION RESEARCH AND TECHNOLOGY

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, stopped-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 five 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,
- stopped-flow experimental set-up,
- EPR spectroscopy for solid material investigation,
- pilot installation for polymer modification,
- laboratory experimental stand for removal of pollutants from gas phase,
- laboratory of polymer characterization,
- pilot facility for radiation sterilization, polymer modification 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.

RADIATION-INDUCED OXIDATION OF 3-METHYLQUINOXALIN-2-ONE BY AZIDE RADICALS

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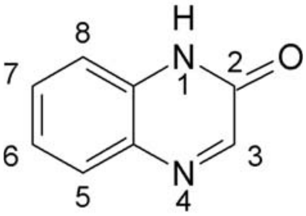
Quinoxalin-2-one derivatives have recently received much attention owing to their both biological properties and pharmaceutical applications [1,2] (Scheme 1). These derivatives are particularly interesting since some of them showed a variety of pharmacological properties, such as antimicrobial [3-6], antiviral [7], antifungal [5,8,9], anxiolytic [10], analgesic [9], antiinflammatory [6], antithrombotic [11,12], and antitumour [13-16] activities. For instance, as far as the antitumour activity is concerned, the recent studies have proved that quinoxalin-2-ones restrain activity of the platelet-derived growth factor receptors (PDGFR) [17], proteins responsible for a growth and division of cells. A cell cycle regulation, due to the inhibition of cyclin-dependent kinases (Cdk), is another example of anticancer activity of quinoxalinones [18]. Their receptors belong to tyrosine kinase family and are common targets in cancer treatment. The structure activity relationship (SAR) studies have revealed that quinoxalin-2-ones derivatives bound to proteins receptor (*e.g.* in Cdk) are generally located close to the adenosine triphosphate (ATP) binding pocket [13,17]. The fact that these compounds are bound in the very specific position in proteins may have serious consequences in their interactions with either amino acid residues or radicals derived from them. Certain amino acids residues – tyrosine (Tyr), tryptophan (Trp), and cysteine (Cys) are particularly vulnerable to oxidation. Therefore, the radical cations derived from quinoxalin-2-ones can modify these amino acids which are reasonably good electron donors and can be oxidized to tyrosyl (TyrO$^•$), tryptophyl (TrpN$^•$), and thiyl (CysS$^•$) radicals, respectively. On the other hand, these radicals are reasonably good electron acceptors and can potentially act as oxidants of quinoxalin-2-ones intercalated in a protein matrix.



Scheme 1. Structural formula of quinoxalin-2-one.

Some of drugs based on the quinoxalin-2-one structure are in medical use, *e.g.* caroverine-based Spasmium. Its activity is connected to calcium-channel blocking and it is used as antispasmodic agent. Studies indicate that caroverine is a potential antioxidant agent, which acts in concentration possible to achieve and to be safe in a human body [19]. In spite of that fact one cannot find many publications concerning transformations of quinoxalin-2-one based compounds in biological systems. It has been proven that 3-methylquinoxalin-2(1H)-one (3-MeQ) can be a potent hydroxyl radical scavenger [20].

Radical oxidation of 3-methylquinoxalin-2-one by azide radicals ($N_3^•$) and kinetics of its reactions were studied by pulse radiolysis technique coupled with the time-resolved UV/Vis spectrophotometric detection system. Reactions were studied in aqueous solutions containing NaN_3 (100 mM) saturated with N_2O.

Oxidation of 3-MeQ by $N_3^•$ radicals leads to the products characterized by an absorbance with λ_{max} = 350 nm. This absorbance is fully developed within 4 μs (Fig.1A, right inset), and then is decaying without the change of the shape (Fig.1A, curve b). Interestingly, the decay of the 350-nm absorption band showed biphasic kinetics (Fig. 1A, left inset). The first part of kinetic trace displayed a decay with a half-life of $t_{1/2}$ = 25 μs, followed by a very slow decay which reaches a plateau within 1.5 ms.

The rate constant for the reaction of $N_3^•$ radicals with 3-MeQ was determined from a linear dependence of the pseudo-first-order build-up of the absorbance at 350 nm on the 3-MeQ. The slope of this plot gives the bimolecular rate constant k ($^•N_3$ + 3-MeQ) = $(6.0 \pm 0.5) \times 10^9\ M^{-1}s^{-1}$ (Fig.1A, right inset). The high reactivity of $^•N_3$ radicals arises from the lower oxidation potential of 3-MeQ as compared with the oxidation potential of $^•N_3$ radicals (E^0 = 1.33 V *vs.* NHE). The short-lived absorption band with λ_{max} = 350 nm (Fig.1A, curve a) observed during reaction of 3-MeQ with $^•N_3$ radicals is tentatively assigned to the deprotonated form of the N-centred radical cation (Scheme 2). A major obstacle for performing a reliable comparison is due to depletion of 3-MeQ ground state, which absorbs at this spectral region as depicted in the inset of Fig.1B. In order to overcome this problem, experimental spectrum was corrected for bleaching in the spectral range 280-380 nm. Corrected spectrum is characterized by strong absorption maximum located at λ_{max} = 340 nm for transients resulting from $^•N_3$ reaction. Thus, one may suggest that the N-centred radicals (Scheme 2) are responsible for the short-lived and narrow absorption band with λ_{max} = 340 nm.

Results obtained indicate that quinoxalin-2-ones can be easily oxidized by $N_3^•$ radicals with the rate constants $k = (6.0 \pm 0.5) \times 10^9\ M^{-1}s^{-1}$. Oxidation takes place on the pyrazinone ring, leading to generation of the N-centred radicals (Scheme 2). Moreover, unidentified stable product(s) are generated which are indicated by formation of

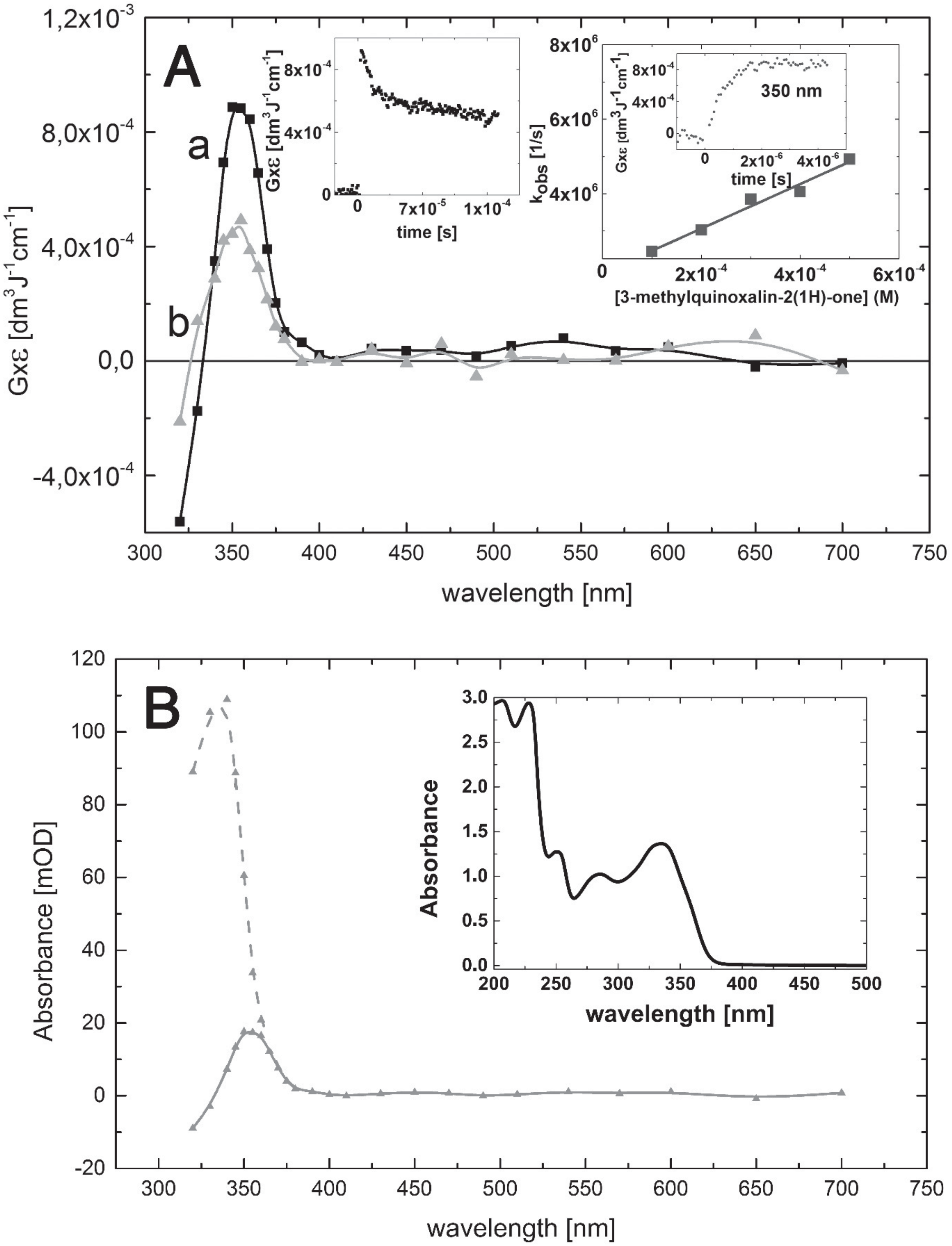
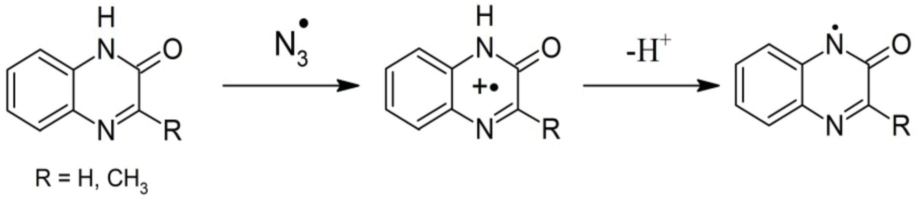


Fig.1. (A) Transient absorption spectra (uncorrected for the ground-state absorption) recorded in N_2O-saturated aqueous solution containing 0.1 mM 3-MeQ and 0.1 M NaN_3 at pH 7. Curve a – time delay 4 μs (■), curve b – time delay 1.5 ms (▲). Insets: (left) time profile representing decay at λ = 350 nm; (right) plot of the observed pseudo-first-order rate constants of the formation of the 350-nm absorption (k_{obs}) as a function of 3-MeQ concentration at pH 7. Inset of right inset: time profile representing growth at λ = 350 nm at 0.1 mM concentration of 3-MeQ. (B) Transient absorption spectra uncorrected (solid lines), and corrected for the ground-state absorption (dashed lines) recorded 4 μs after the electron pulse in N_2O-saturated aqueous solution at pH 7 and containing 0.1 mM of 3-MeQ with 0.1 M NaN_3 (▲). Inset: ground-state absorption spectrum of 3-MeQ in aqueous solutions at pH 7.

an absorption band with λ_{max} = 340 nm. Their identification needs further studies involving stationary radiolysis and chromatographic techniques.



Scheme 2. Oxidation of 3-MeQ by azide radical.

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THE ROLE OF SOFT AND HARD SEGMENTS IN RADIATION-INDUCED MODIFICATION OF POLY(ESTER-URETHANE)S

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Physical and chemical effects of ionizing radiation on polymeric systems are of interest in many researchers continuously for 60 years. It is commonly known that the final effect of radiation is affected by many factors, starting from the molecular structure, the presence of various additives such as stabilizers, plasticizers and antioxidants to the irradiation conditions. However, for newly synthesized materials such as composites, nanocomposites and for materials of the unique segmental structure, predicting the direction of these changes is very difficult. Therefore, it requires an insightful analysis of the effects of ionizing radiation on the diverse properties of such materials.

Among polymers, polyurethanes (PURs) are belonging to the most interesting materials. They are used in many applications, such as textiles, adhesives, modern materials for electronics and biomaterials [1]. Polyurethanes exhibit a broad range of physicochemical and mechanical properties, due to their structural diversity. PURs are known as phase-separated polymers but the extent of this separation depends on many factors, *e.g.* type and molecular weight of the oligodiol, the chemical structure and symmetry of diisocyanate, the hard segment (HS)/soft segment (SS) weight ratio, the synthesis method [2]. Formation of hydrogen bonding between urethane linkages also strongly influences PURs phase separation [3].

The physicochemical properties of aromatic polyurethanes have been studied extensively for a few last decades. In contrast, the influence of ionizing radiation on aliphatic PURs has been conducted relatively rarely. What is more, many researches examine radiation modified polyurethanes without paying attention to the impact of hard/soft segment contribution on the final effect of irradiation. It is well-known that polyurethanes are qualified as materials possessing excellent radiation stability (ISO:11137:2006). However, depending on the molecular architecture and segments composition, radiation resistance of polyurethanes differs significantly.

In the reported work we focused on the relationships between chemical composition and radiation sensitivity of poly(ester-urethane)s. To the best of our knowledge this is the first report describing the effect of soft and hard segment weight contribution on radiation stability of aliphatic PURs.

Experimental

Sample preparation

Isophorone diisocynate and 1,4-butanediol used for polyurethane synthesis were purchased from Sigma-Aldrich and were vacuum distilled. Oligo(ethylene-butylene adipate)diols (OAD) with molecular weight of 1000 and 2000 Da were purchased from Purinova (Poland) and were dried under vacuum for 2 h at 120°C before using. The polyurethanes were synthesized by a two-step polycondensation without any catalyst and solvents. The reaction progress was followed by measuring disappearance of isocyanate stretching band at 2260 cm^{-1} and its conversion into N-H group with a band at around 3350 cm^{-1}.

Polyurethanes denoted PUR1 40/60 contained 40 and 60 wt.% of hard and soft segments with MW = 1000 Da, respectively. Analogically, PUR1 60/40 was constructed from 60 and 40 wt.% of HS and SS. PUR2 40/60 and PUR2 60/40 had the same segmental composition like PUR1 except molecular weight which was MW = 2000 Da.

Irradiation

Polyurethane films were irradiated in the presence of air at ambient temperature with a 10 MeV electron beam generated in a linear electron accelerator Elektronika 10/10 to a dose of 112 kGy by the multipass exposure (28 kGy per one pass).

Attenuated total reflection Fourier transform infrared spectroscopy

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were recorded with a Bruker Equinox 55 FTIR spectrometer. The spectra were collected in the range of 4000-650 cm^{-1} at a resolution of 4 cm^{-1} by means of an accessory equipped with ZnSe crystal designed for a single reflection ATR technique. Curve-fitting simulations of the ATR-FTIR carbonyl region were performed using Origin 6.1 program. A flat baseline was chosen in the range of 1600 to 1850 cm^{-1}. The second derivatives of the spectra in C=O region were used to determine the number of Gaussian peaks.

Mechanical testing

Mechanical testing was made at ambient temperature and at a crosshead speed 100 mm/min using Instron 5565 apparatus. Five measurements were performed for each sample.

Dynamical mechanical thermal analysis

The dynamical mechanical thermal analysis (DMTA) was performed on a DMA Q-800 modulus (TA Instruments) in the temperature range from -100 to 150°C at 1 Hz.

Results and discussion

ATR-FTIR spectroscopy

ATR-FTIR spectroscopy was used to determine the microphase separation in polyurethanes by examining the relative contents of hydrogen bonds participating in the formation of separated segments. Hydrogen bonding in poly(ester-urethane)s involves N-H groups in urethane units as a proton donor, and ester and urethane carbonyl groups as proton acceptors [4]. For all PURs, it was found that almost all N-H groups (peaks located between 3200 and 3450 cm^{-1}) were involved in the hydrogen bonding system. Other bands located above 1700 cm^{-1} also reveal hydrogen bonding and are assigned to the urethane and ester carbonyl groups. In order to identify free and hydrogen bonded C=O groups in the polymer, spectrum deconvolution was employed [5]. As seen in Fig.1, the carbonyl absorption band is split distinctly into two peaks; the first is located at around 1700 cm^{-1} and the second one at 1730 cm^{-1}. The peak placed at lower wavenumbers corresponds to the hydrogen bonded C=O groups. The carbonyl groups uninvolved in hydrogen bonding have a peak shifted to 1730 cm^{-1}. On the basis of these results, the degree of phase separation (DPS) was calculated according to equation [6]:

$$DPS = A_{C=O\ bonded}/A_{C=O\ bonded} + A_{C=O\ free}$$

where: $A_{C=O\ bonded}$ – absorbance of bonded C=O groups, $A_{C=O\ free}$ – absorbance of free C=O groups.

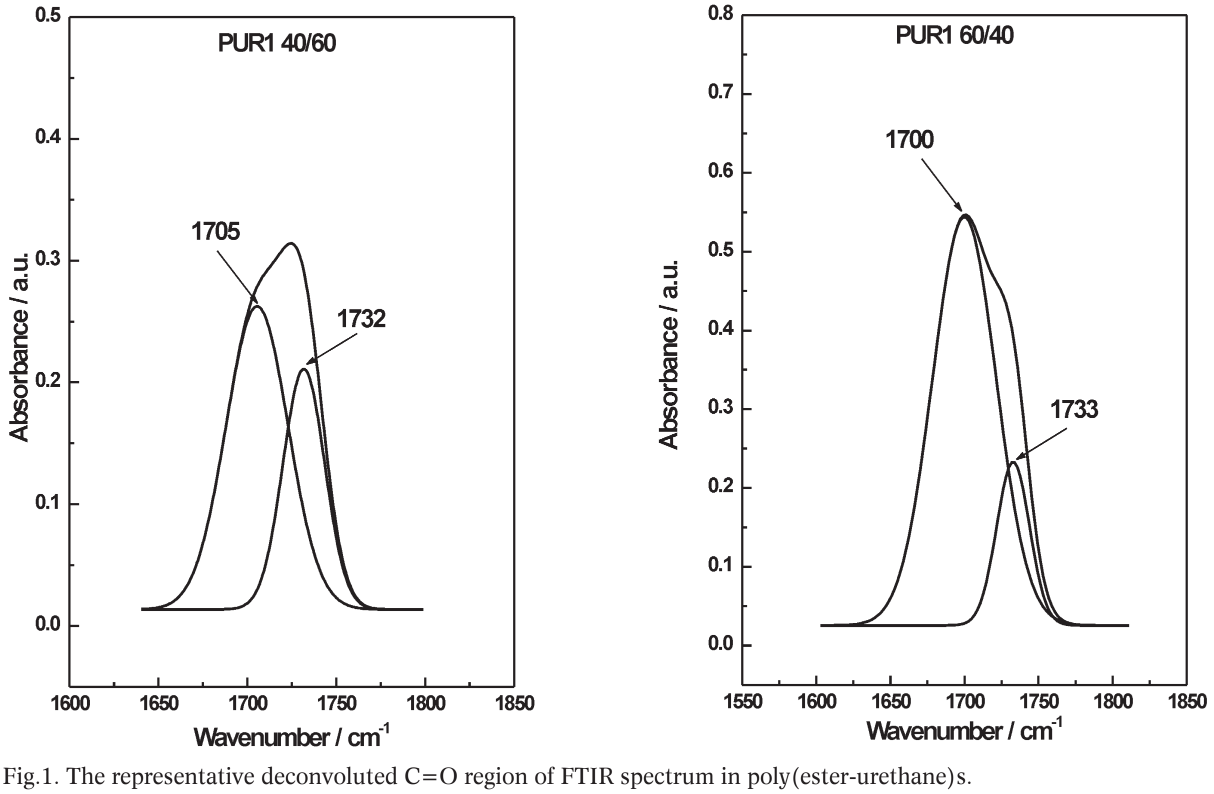

Fig.1. The representative deconvoluted C=O region of FTIR spectrum in poly(ester-urethane)s.

As was expected, the microphase separation is higher for PURs containing larger amount of hard segments. For PUR1 60/40, the DPS value reaches about 70% while for PUR1 40/60 is almost 15% smaller. Similar tendency was observed for PUR2 containing 60 and 40 wt.% HS. It was estimated that the degree of phase separation for these samples is about 64 and 54%, respectively.

Analysing the influence of the soft segment chain length on microphase separation it was found that molecular weight of the applied oligo(ethylene-butylene adipate)diol has a significant impact on DPS only if its participation is smaller than HS. We observed that for PUR2 60/40 constructed from OAD of MW = 2000 Da the degree of microphase separation is around 64%, *i.e.* noticeably lower as compare to DPS = 70% determined for PUR1 60/40 (OAD of MW = 1000 Da).

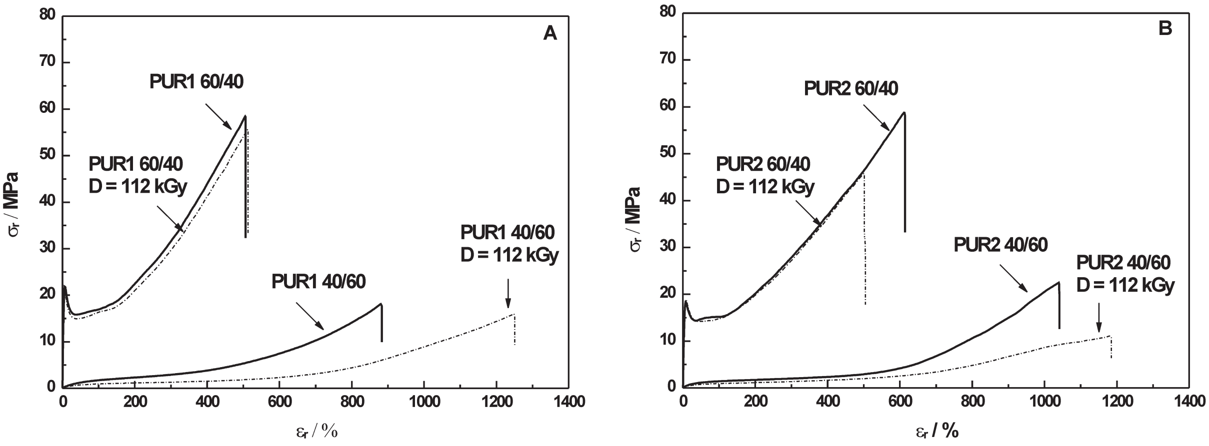

Fig.2. Stress-strain curves for poly(ester-urethane)s: (A) PUR1 and (B) PUR2.

These results confirmed that:

- The vast majority of N-H groups participate in the creation of hydrogen bonds as there is no peak situated at 3495 cm^{-1} related to the non-bonded (free) amino groups [7].
- Extent of the interurethane hydrogen bond network decreases with increasing content of SS as seen from diminishing microphase separation for PURs containing 60 and 40% soft segments.
- The phase separation decreases when the length of aliphatic chains increases, both for PURs 40/60 and for PURs 60/40.

Mechanical analysis

The tensile stress-strain properties of poly(ester-urethane)s are presented in Fig.2. It was observed that the hard/soft segment ratio has a significant influence on the mechanical properties of non-irradiated and irradiated samples. With increasing HS content the tensile strength increases while the ultimate elongation decreases considerably, demonstrating progress in the microphase separation. PURs 40/60 exhibit a high elasticity and a weak mechanical strength whereas PURs 60/40 demonstrate behaviour characteristic of semi-brittle materials.

There is a distinct difference in the mechanical properties of non-irradiated PURs constructed from SS of various molecular lengths as elongation at break is about 150% longer for PUR2 40/60 than for PUR1 40/60 and 100% longer for PUR2 60/40 than for PUR1 60/40. Additionally, exposure of the polyurethanes to an electron beam reveals further discrepancies concerning their radiation stability. It was found that upon irradiation the tensile strength of PUR1 40/60 decreased from 18 to 16 MPa whereas the ultimate elongation at break increased from around 880 up to 1250%. As given in Fig.2, the ultimate tensile strength of PUR2 40/60 decreased from around 20 to 10 MPa for irradiated sample, whereas the elongation at break increased by *ca.* 150%. PUR1 60/40 shows a significant radiation resistance contrary to PUR2 60/40 whose mechanical properties deteriorate upon irradiation.

Summarizing, the mechanical tests confirmed that:

- Contribution of particular segments in PUR determines its mechanical characteristic making the material either flexible or rigid and semi-brittle.
- Longer SS in PURs enhances the elongation at break preserving a similar level of tensile strength at break both for PURs 40/60 and PURs 60/40.
- Radiation-induced effects depend on the proportion between HS and SS. The poly(ester-urethane)s synthesized from short oligodiol (1000 Da) are more radiation resistant as, when irradiated to 112 kGy, either remain unchanged (PUR1 60/40) or gain additional flexibility (PUR1 40/60). PURs containing SS two times longer (2000 Da) are more susceptible to ionizing radiation since upon irradiation tensile stress distinctly decreases whereas the elongation at break for PUR2 60/40 declines and for PUR2 40/60 grows but far less than for PUR1 40/60.

Dynamic mechanical thermal analysis

The dynamic mechanical measurements of PURs containing various amounts of soft and hard segments and diverse lengths of soft segments are presented in Fig.3. In the temperature range from -100 to -25°C the poly(ester urethane)s are in the glassy state. Above -25°C, the loss modulus (E'') declines due to the glass transition of soft seg-

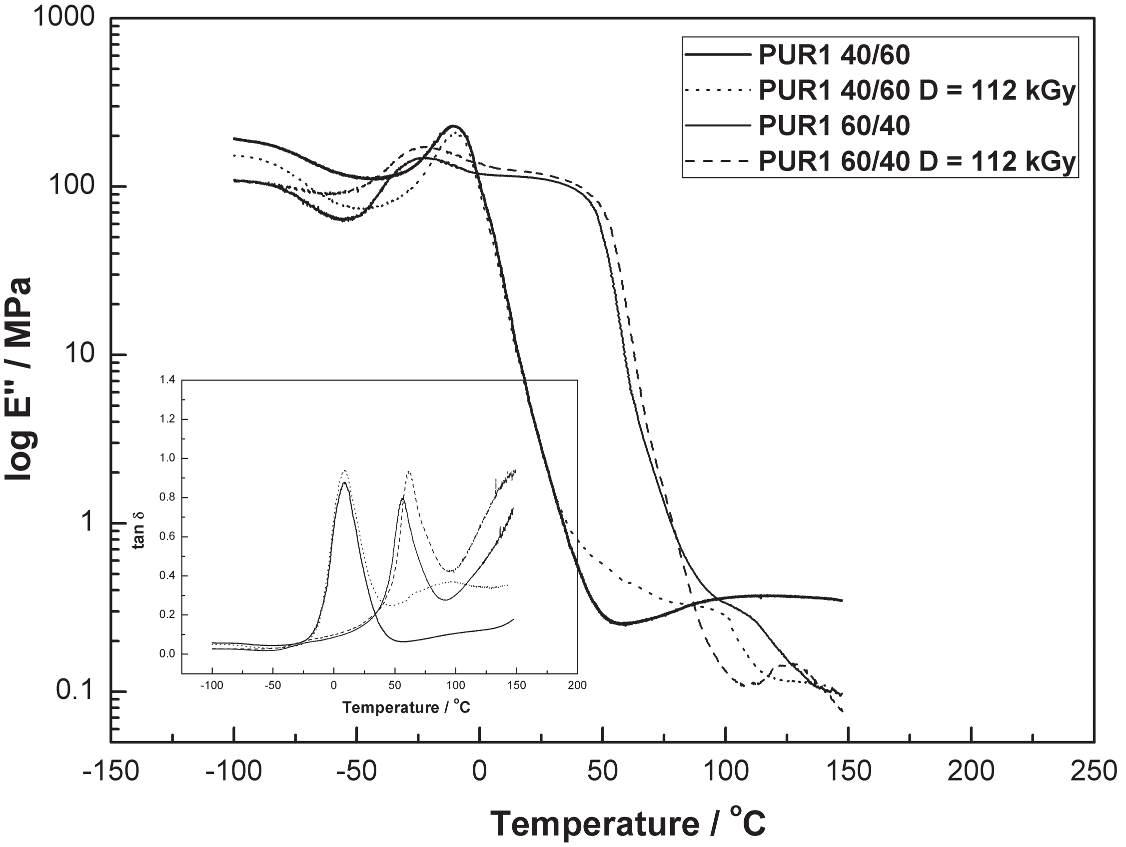

Fig.3. Representative DMTA profiles for PUR1.

ments (T_{gSS}). The new distinct rubbery state is reached only by PURs 40/60 as, contrary to this behaviour, the loss modulus of PURs 60/40 exhibits small broad variations at temperatures below 0°C and a very intensive decrease just at about 50°C assigned to the glass transition of hard segments (T_{gHS}). The changes in the region 50-55°C are attributed to the destruction of short-range order created during cooling and further annealing at room temperature. Minor changes in the log E'' curves in the region above 100°C are due to the dissociation of hard domains with long-range order (T_{HS}) [4]. A relationship loss tangent *vs.* temperature shows dominant transitions in the poly(ester urethane)s – low temperature peak of T_{gSS} characteristic of PURs 40/60 and high temperature peak of T_{gHS} distinctive for PURs 60/40. The interval between main transitions of PURs 40/60 and PURs 60/40 exceeds 50°C. At ambient temperature, the first group of materials is in the rubbery plateau region and as mechanical test showed, exhibits elastic, rubbery-like features. The character of PURs 60/40 is predominantly defined by the hard segment glass transition at about 50°C, therefore under stretching at room temperature they elongate continuously till fracture like a brittle solid.

In the reported work the glass transition temperatures were determined on the basis of E'' loss modulus changes. The obtained results are collected in Table 1.

The phase transition temperatures confirm the extensive segmental separation in PURs 60/40 as in these cases the distinct transitions assigned to the soft and hard regions were found. On the other hand, in the case of PURs 40/60 the HS phase transition effects are negligible revealing mixed, complex, undefined nature of the soft segments. The SS glass transition temperatures of PURs are almost the same before and after irradiation, while the temperatures associated with HS transitions are shifted towards higher temperatures upon radiation treatment.

Conclusion

Poly(ester-urethane)s morphology is complex and results from various contributions of two different types of phases of various order arising from hydrogen bond systems created between amino group of urethane unit and carbonyl group

Table 1. Glass transition temperature evaluated from E'' = f(T) curves.

Sample abbreviation	Dose [kGy]	T_{gSS} [°C]	T_{gHS} [°C]	T_{HS} [°C]
PUR1 40/60	0	-10.1	-	-
	112	-9.7	-	-
PUR1 60/40	0	-25.7	44.3	110.0
	112	-25.3	47.0	127.4
PUR2 40/60	0	-24.7	-	-
	112	-24.4	-	-
PUR2 60/40	0	-24.1	43.9	99.0
	112	-26.0	47.0	108.7

located either in urethane or in ester functional group. Increasing participation of SS in PURs facilitates generation of N-H---O=C (ester) linkages simultaneously reducing intraurethane bonding network which forms well-defined hard segment domains. Assuming that it SS has a dominant influence on PUR elasticity it seems that during irradiation the hydrogen bonds situated in this segment are ruptured as a consequence of radiation-induced effects in ester group regions what results in a distinct increase in the elongation at break observed for PURs 40/60. On the other hand, PURs 60/40 features are defined rather by hard segments. It is generally known that urethane groups of HS are relatively resistant to radiation effects [8] thus hydrogen bonding system of these domains is less affected by an electron beam treatment. Therefore, mechanical properties of PUR1 60/40 remain unchanged. When the chain lengths of SS increase, availability of ester groups grows due to an overall enhancement of flexibility what was confirmed by strain-stress measurements revealing that elongation at break of PUR2 60/40 is higher than PUR1 60/40. These structural changes result in the development of additional hydrogen bonds involving ester carbonyl groups, which, as was mentioned previously, are radiation susceptible. Thus, the observed for PUR2 60/40 radiation-induced deterioration of mechanical properties is related to the reduction of the degree of phase separation.

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MULTIFREQUENCY EPR STUDY ON RADIATION-INDUCED CENTRES IN CALCITE LABELLED WITH ^{13}C

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Calcium carbonates are commonly found in nature, especially in rocks in all parts of the world. The basic constituent unit in all carbonate minerals is the CO_3^{2-} ion [1]. This inorganic material occurs in three crystallographic forms: aragonite, calcite and vaterite, but the calcite with hexagonal symmetry is the only thermodynamically stable form. Naturally occurring calcite contains a variety of metal impurities in the carbonate lattice, which are usually substituted for Ca^{2+}. Several papers related to calcium carbonates mainly concern the study of paramagnetic Mn^{2+} ions present in these structures as the most popular impurity. In calcite exposed to ionizing radiation, different paramagnetic centres are formed. Some of them are very stable at room temperature and can be used for the measurement of absorbed radiation dose as well as for dating due to a very long lifetime (about 10^6 years) [1]. Several papers about EPR (electron paramagnetic resonance) measurements of calcium carbonates have recently been published, some dealing with carbonate radicals generated after γ-irradiation.

The purpose of the present work is to reconsider the problem by analysing the EPR spectra of calcite in a more detailed way and to compare the behaviour of carbonate radicals recorded in the temperature range 77-293 K using an X- and Q-band EPR technique. The use of samples enriched with ^{13}C allows to obtain additional information about assignment of carbon-centred radicals. Several types of carbonate and nitrate radicals, occurring in calcite, will be discussed based on the present work and literature data.

The calcite samples (with ^{12}C and ^{13}C) were synthesized at the Institute of Ceramics and Building Materials, Warszawa (ICiMB) [2]. Commercially available calcite powders from POCH and Johnson Mattey Chemicals (JMC) were used in the study as reference samples and compared with the ICiMB calcite powders.

The samples were placed into Suprasil quartz tubes and then irradiated at 77 K with a dose of 5 kGy in a Gamma Chamber 5000 (dose rate – 5 kGy/h) ^{60}Co source.

The EPR spectra of the two types of calcite, POCH and JMC, both irradiated at 77 K are similar and complex. At low temperature the most intense is the anisotropic orthorhombic signal assigned to CO_3^- radical anion located in the calcite crystalline lattice with g-factor values: $g_x = 2.0136$, $g_y = 2.0184$, $g_z = 2.0058$ (POCH). In the POCH sample, also less intense signals due to O_3^- and CO_3^- located on the surface of crystallites were recorded [3]. In comparison to POCH sample, in JMC calcite signals derived from O_3^- and CO_3^- localized on the surface are absent. Instead, there are a few overlapped signals not easy to interpret. Their most probable origin is the sulphur containing impurities, with analogous g-tensor components reported for similar systems [4].

The signals assigned to CO_3^- radicals anion were unstable and disappeared almost completely above 160 K. At 200 K, two other signals domi-

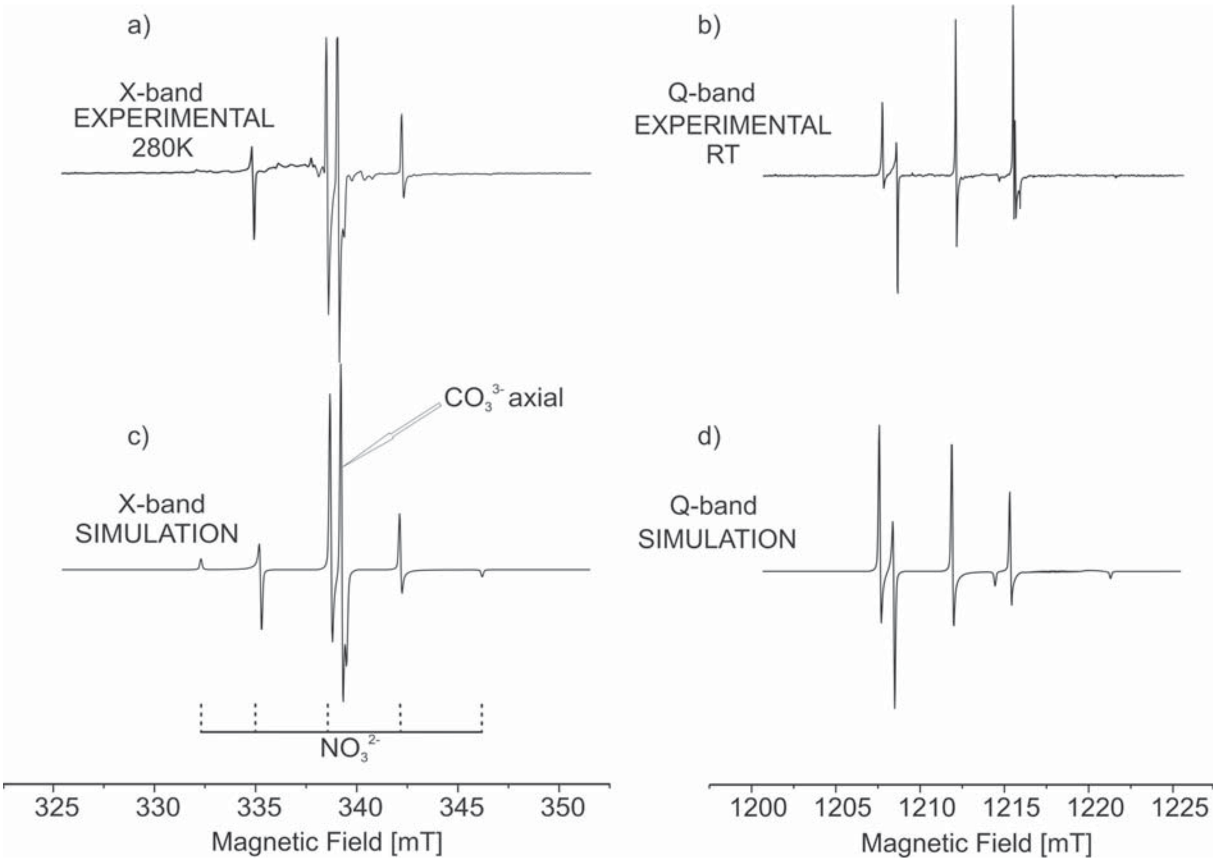

Fig.1. EPR spectra of γ-irradiated at 77 K calcite from POCH recorded at room temperature at X-band (a) and Q-band (b) together with theoretical spectra (c) and (d), respectively.

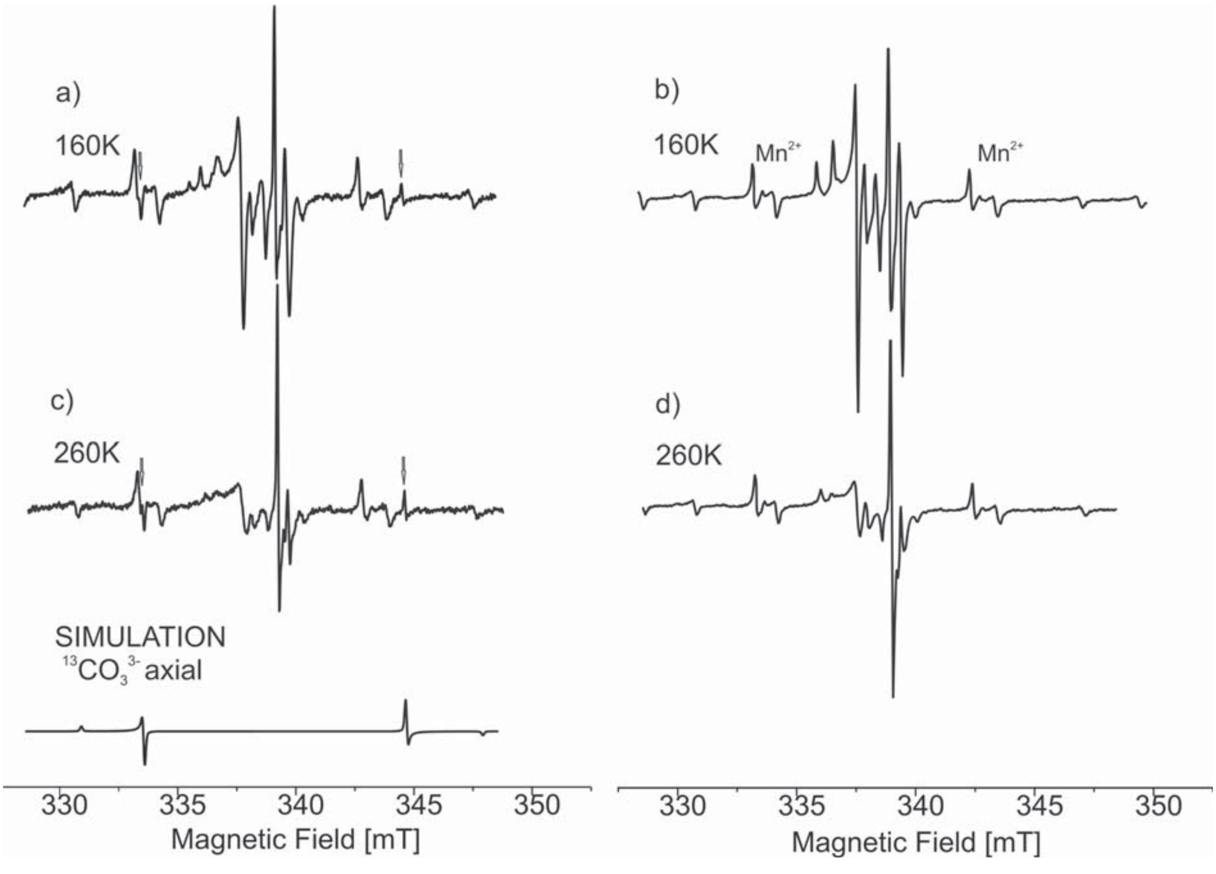

Fig.2. EPR spectra of γ-irradiated synthetic calcite recorded at 160 and 260 K, with natural content of carbon isotopes (b,d) and enriched with ^{13}C (a,c) together with the simulated spectrum for $^{13}CO_3^{3-}$ radical anion. The arrows indicate the lines of ^{13}C doublet.

nate in both calcites spectra. One of them is the narrow axial line corresponding to g-tensor components: $g_{\parallel} = 2.0013$, $g_{\perp} = 2.0028$. Analogous signal was reported previously in γ-irradiated calcite and hydroxyapatite and was assigned to CO_3^{3-} [1,3]. At 200 K, when CO_3^- disappears, CO_3^{3-} reaches its importance. The radical is stable even at room temperature for days. The second signal, present in spectra of both types of calcite, is a multiplet of narrow lines. For better resolution, Q-band EPR spectroscopy was used. A comparison of g-values and hyperfine splittings measured at two different frequencies shows that the spectrum is consistent with axial g- and A-tensors and the unpaired electron interacts with one nucleus with spin I = 1 (Fig.1). The best fit of the spectra at both frequencies was obtained for $g_{\parallel} = 2.0023$, $g_{\perp} = 2.0059$, $A_{\perp} = 3.44$ mT, $A_{\parallel} = 6.85$ mT. Almost the same parameters were reported earlier and assigned to NO_3^{2-} centre [1]. This radical is relatively stable at room temperature and is recordable by weeks and was observed by us even at 100 K.

Figure 2 shows the spectra of calcites synthesized in ICiMB. One of the sample~~s~~ was enriched with ^{13}C isotope. The spectra are complex and differ significantly in comparison to those for commercial samples from POCH and JMC. In both samples, with natural carbon isotopes and enriched with ^{13}C, the signals in the region close to g about 2 are similar and consist of several lines. The spectra of calcite sample with ^{13}C do not show any doublets at this region, that could come from CO_3^- radical anion. The doublet present in spectrum of sample enriched with ^{13}C and indicated by arrows, is assigned to CO_3^{3-} radical of axial symmetry reported earlier and characterized by parameters: $A_{\perp} = 11.13$ mT, $A_{\parallel} = 17.12$ mT, $g_{\perp} = 2.0031$ and $g_{\parallel} = 2.0025$ [1]. The spectrum due to CO_3^{3-} was visible from 100 K until room temperature.

It is worthy of notice, that the signals of CO_3^-, NO_3^{2-} and O_3^- were not seen in both synthetic samples, with natural and enriched ^{13}C content, indicating that nitrate impurities are absent. The carbonate impurities are represented by CO_3^{3-} but it is possible that CO_3^- radicals, detected in POCH and JMC samples, could be connected with structural defects in their crystalline lattice. This hypothesis is confirmed by the fact that carbonate CO_3^{3-} radicals are observed starting from low temperature when mobility of species is low and lattice rearrangement is not possible.

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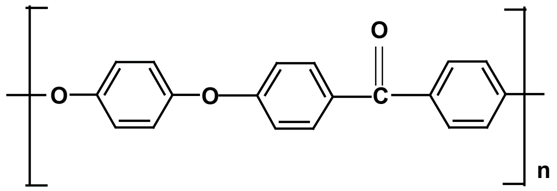
ELECTRON PARAMAGNETIC RESONANCE STUDIES OF THE RADIATION-INDUCED PROCESSES IN POLYETHER ETHER KETONE – PEEK

Ewa Maria Kornacka, Grażyna Przybytniak

Polyether ether ketone (PEEK) is a colourless, semicrystalline organic thermoplastic polymer in the polyaryletherketone (PAEK) family used in engineering applications. They are polymers of high chemical resistance and excellent mechanical and insulating properties that are retained at high temperatures. A characteristic structure of this kind of polymer is consisting of an aromatic backbone molecular chain, interconnected by ketone and ether functional groups [1]. The presence of aromatic groups in the polymer chains greatly reduces the sensitivity to radiation. In the study reported a commercial product, PEEK (trade name Victrex®) was used (Scheme 1). This polymer has, in addition to the already mentioned characteristics, poor solubility in organic solvents.

The aryl rings are interconnected *via* ketone and ether groups located at para positions of the ring. The structure of PEEK shows remarkable chemical resistance and radiation stability resulting from excitation of higher orbital electrons and conversion of energy absorbed into the heat. The reported high resistance of PEEK to ionizing radiation is associated with G-values of radical formation of about two orders of magnitude lower than for aliphatic polymers, such as polyethylene. The material may be effectively sterilized by gamma or electron beam irradiation in air which has a consequence in the use of PEEK to build new generation orthopaedic implants [2].



Scheme 1. The chemical structure of PEEK.

PEEK was obtained from Nortrade Company as a thin sheet specimen of a thickness 0.22 mm and was used as received. For the investigations conducted by the EPR (electron paramagnetic resonance) method under cryogenic conditions the PEEK samples were irradiated with a dose of 10 kGy in a Co-60 gamma chamber at a dose rate of 5.5 kGy. During exposure to ionizing radiation, the material was immersed in liquid nitrogen. EPR measurements were performed using an X-band Bruker ESP 300 spectrometer. In the series of experiments EPR spectra of the irradiated at 77 K specimens were recorded upon gradual heating of the samples to the selected temperatures.

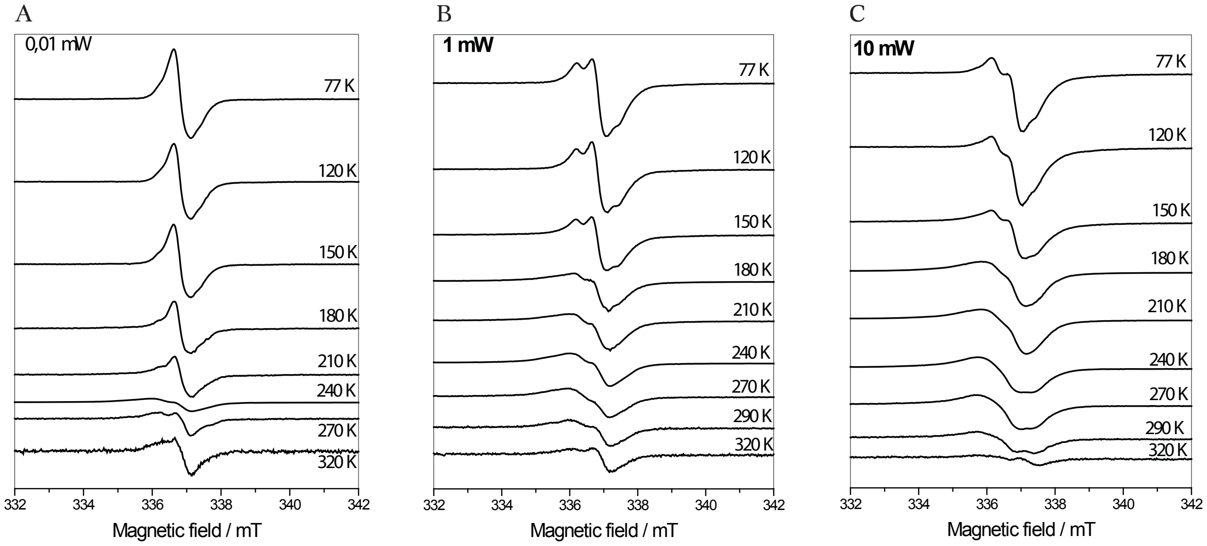


Fig.1. A series of EPR spectra recorded at different values of microwave power: (A) 0,01 mW, (B) 1 mW, (C) 10 mW after warming the irradiated samples to required temperatures.

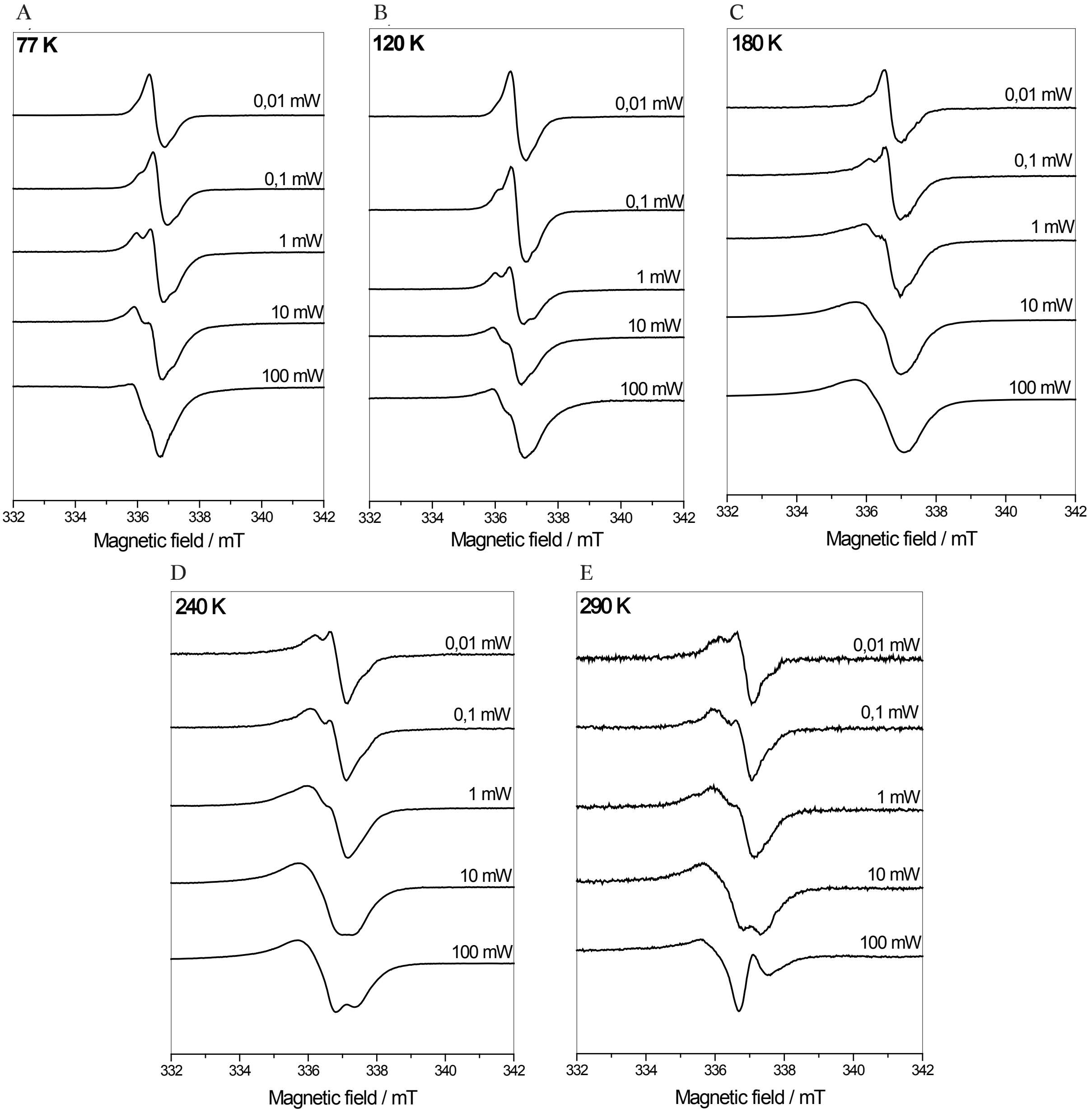


Fig.2. A series of EPR spectra of PEEK irradiated to a dose of 10 kGy at 77 K and annealed by warming to required temperatures: (A) 77 K, (B) 120 K, (C) 180 K, (D) 240 K, (E) 290 K recorded at different microwave powers.

The typical EPR parameters for spectra acquisition were as follows: sweep width – 20.0 mT, microwave power – 0.01-100 mW, modulation amplitude – 0.095 mT, time constant – 10 ms. Number of scans was adjusted to the experimental spectra intensity. The signals were analysed using Apollo software [3]. The relative contribution of radicals was determined by the comparison of spectral areas obtained by double integration of the signals recorded under cryogenic conditions, assuming that the concentration of radicals for the unheated sample corresponds to 100%.

EPR spectroscopy gives an insight into radical processes initiated, among others, by ionizing radiation. The studies under cryogenic conditions allow to find primary radicals and to follow their conversions triggered by the thermally induced relaxation of the system. The measurement was performed in a finger dewar adapted to low-temperature testing. After signal recording, the sample was defrosted gradually outside the dewar to the selected temperatures controlled by a thermocouple. Upon heating, the material was refrozen to 77 K. This procedure allows to eliminate differences in the EPR spectra resulting from various dynamics of macromolecules when temperature changes [4].

Figure 1 presents the three series of spectra for the samples annealed to the selected temperatures, recorded at microwave powers in the range of 0.01-10 mW. When microwave power increases, the character of spectra is changing from a singlet throughout an unresolved triplet to a strongly asymmetric singlet what proves that some signals are at least partly saturated.

Figure 2 shows a sequence of spectra for the sample heated gradually to the elevated temperatures, detected at the indicated microwave power. The gradual loss of the total population of radicals with increasing temperature is related to the transformation of the primary and secondary radicals to the diamagnetic products.

EPR spectra are presented as a first derivative of absorption, therefore double integration of the area under the signal recorded is proportional to the total amount of radicals. Primary radicals are relatively stable and the profiles of their decay depend on the microwave power applied since each relationship represents a different set of radicals (Fig.3). For 0.01 mW the radicals begin to convert into the non-paramagnetic species at temperatures above 120 K, and for 10 and 100 mW above 180 K; the differences are a consequence of gradual saturation of some peaks.

The first spectrum recorded after irradiation is a structureless singlet whose interpretation can base on the knowledge in the field of radiation chemistry of this group of aromatic components. Generally, it is believed that aromatic rings are able to scavenge electrons forming radical anion as a primary product. This phenomenon is supported by the enhanced ability of aromatic units to electron trapping. Heiland *et al.* reported that in PEEK irradiated at 77 K in vacuum about 84% of all paramagnetic species are radical anions [5,6].

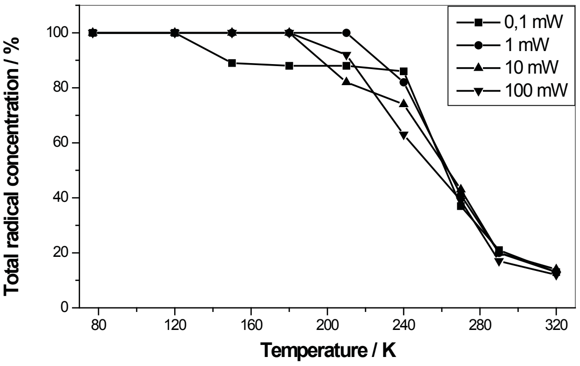


Fig.3. Relative concentrations of total PEEK radicals *vs.* annealing temperature.

Below 77 K such an intermediate demonstrates a single line vanishing either during thermal relaxation of the sample or its photo-annealing. In the case of our studies the spectrum of radical anion **R1** is a prevailing component of the low temperature signals. The most probable fate of the radical ion is a separation of unpaired spin and charge. Phenyl radical **R2** and a stable phenolate anion are proposed as the successors.

In phenyl radical the unpaired spin is localized on a σ orbital thus, its interaction with hydrogen atoms of aromatic rings is limited. Therefore, hyperfine splitting is small and for ortho position reaches only about 0.5 mT [7]. Such a splitting was found in the triplets detected above 120 K and was attributed to two ortho protons. The interaction of meta hydrogens falls within the width of the lines.

The radiation-induced ionic processes in PEEK are restricted due to the lack of functional groups providing mobile protons. The other possible pathway of radical processes is homolytic cleavage of C-O bond in ether groups what also results in the production of phenyl radical. Additionally, phenoxyl radical **R3** is formed. Such a type of radical might be relatively stable, particularly if electron donor groups are situated at para and ortho positions of the aromatic ring. It is well-known that when three additional butoxyl groups are present at these positions, then the radical reaches a high stability [8]. In the PEEK structure –Ph-O- might be considered as one of such a substituent. However, symmetrically located phenolic groups as well as the absence of other substituents hinder the effect. Phenoxyl radical shows a singlet of g-factor 2.0034, *i.e.* slightly larger than a value characteristic of free electron (2.0028) due to the influence of adjacent oxygen atom. The intermediate is formed during irradiation. It seems that phenoxyl radical spectrum dominates at high temperatures as (i) microwave power saturation of the singlet up to 10 mW is negligible, contrary to the carbon-centred radicals that are usually sensitive to saturation and (ii) resonance stabilizes the structure despite the absence of electron donor substituents. Additionally, a spectrum characteristic of peroxyl radical **R4** anisotropic features is revealed at elevated temperatures. Probably under cryogenic conditions the limited reactivity of radicals allows to reach vicinity of the radical centres by diffusing oxygen and subsequently to attack the molecule forming oxidation products.

Except unstable radical anion and phenoxyl radical which are unsusceptible to the reactions with oxygen, other radicals might be oxidized. Spectra of these products were found in the signals recorded at high microwave powers, when other lines attributed probably to carbon-centred radicals are almost saturated. At 180 K, an anisotropic singlet related predominantly to peroxyl species reveals $g_\perp = 2.0066$ and broad undefined $g_\parallel$ component (Fig.2C).

The other product of radiolysis found in some aromatic polymers [9] is cyclohexadienyl radical which demonstrates usually almost an isotropic spectrum covering about 5 mT due to interaction of the radical centre with hydrogen atoms of the methylene group. Such a signal was not found in the series of experimental spectra recorded upon warming the sample from 77 K to ambient temperature. It seems that either the yield of hydrogen abstraction is insignificant and, therefore, its attachment to aromatic ring is negligible or other mechanisms are much more efficient. It should be stressed that according to Heiland *et al.* the yield of gaseous products emitted was beyond detection even for doses as high as 1.5 MGy [6].

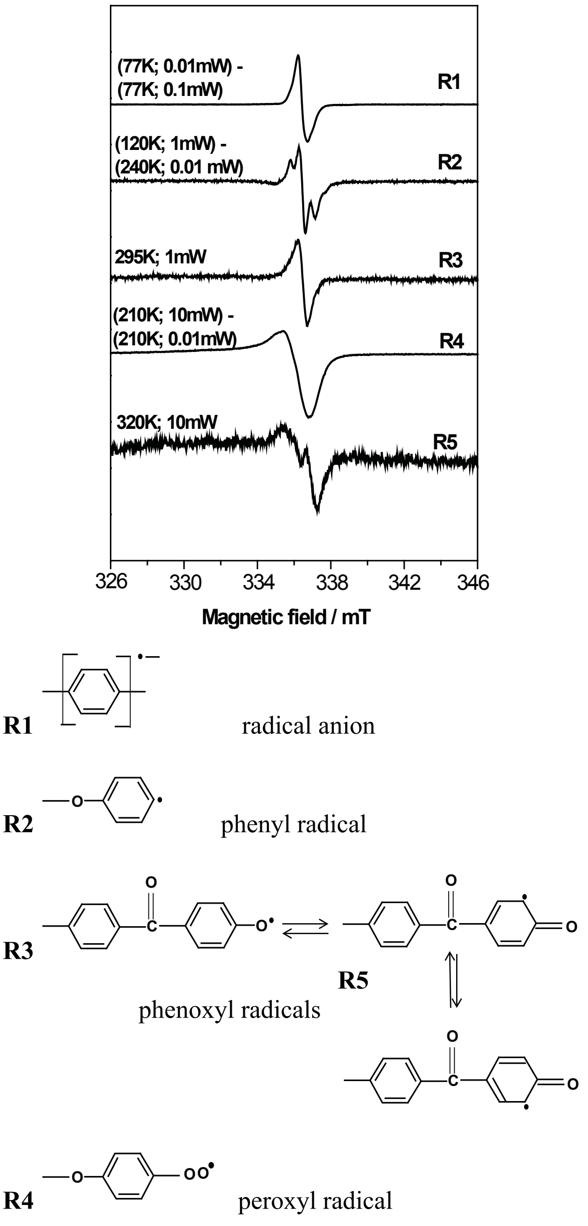


Fig.4. Signals of PEEK radicals isolated from experimental spectra and identified radicals of PEEK induced by γ-rays.

At 240-290 K, the pronounced high field line appears at 10 and 100 mW which turned out to be a component of the doublet emerging clearly when the irradiated under cryogenic conditions sample is warmed up to 320 K (Fig.4). Splitting between these two lines is 0.94 mT and g = 2.0032. The origin of this signal is obscure. However, if resonant structures of phenoxyl radical are at elevated temperature overpopulated, then the interaction of α proton with unpaired spin localized on carbon π orbital might be a source of the splitting observed.

Below 200 K, PEEK shows the low temperature relaxation (γ-relaxation) [10] related to the local conformational movements of aromatic rings in glassy state. Upon irradiation under oxidative conditions, the intensity of γ-relaxation decreases significantly at a dose as high as 8 MGy. Thus, we can assume that the thermal transitions of irradiated to 10 kGy and untreated PEEKs are comparable. The EPR studies reveal that a significant decay of all radicals starts in the range of 180-200 K what is consistent with the thermally induced molecular rearrangements.

Interestingly, it has been reported that PEEK, when irradiated to high doses, undergoes crosslinking. No intermediates participating in the process were observed. The radicals found in our studies could combine by the fusion of reactive centres situated at the end groups of macromolecules. However, such a process does not contribute to intramolecular crosslinking. The only radical that is able to initiate formation of 3D network is the ketyl radical which, due to sterical obstacles (bulky rings), is an implausible candidate. The other agent that can initiate the reaction is cyclohexadienyl radical which theoretically might be generated also in PEEK and was confirmed by Ravasio *et al.* in PET [11]. Nevertheless, the product of hyperfine splittings: $a(H\alpha) = 0.73$ mT, $2a(H\beta) = 4.5$ mT and $a(H\gamma) = 1.22$ mT was undetected. The discussed intermediate cannot be formed *via* proton transfer to radical anion at elevated temperatures as there are not efficient proton donors in the studied system. The other mechanism involves attachment by aromatic rings hydrogen atoms released in the earlier stages of PEEK radiolysis. The resulting cyclohexadienyl radical reacting with other radicals might form H type or T type (a result of end-linking) crosslinks. If under cryogenic conditions both stages of the processes are fast enough, the paramagnetic species involved might avoid detection by EPR spectroscopy. It should be taken into account that the optimal dose for PEEK crosslinking is even 20 MGy [12].

The relative stability of the excited electronic states of aromatic units towards dissociation involves a high probability for transformation of energy absorbed into the heat and de-excitation [13]. That is the reason for low yield of radical formation and hydrogen abstraction in the irradiated PEEK. The carbon- and oxygen-centred radicals are postulated, namely radical anion, σ phenyl radical, phenoxyl radical and peroxyl radical. The end group radicals can combine in the subsequent reactions, but the processes do not cause material crosslinking. Two intermediates, ketyl and cyclohexadienyl radicals, were not identified although just they might be responsible for the formation of the intermolecular bonding network. One of the option under consideration is fast reactions of the radicals, even under cryogenic conditions, which excludes detection by EPR spectroscopy. On the other hand, chain scission mechanism might proceed *via* two various pathways – ionic and non-ionic.

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CENTRE FOR RADIOCHEMISTRY AND NUCLEAR CHEMISTRY

Chemical issues of nuclear power and radiopharmaceutical chemistry – the two top domains of applied radio- and nuclear chemistry in the world – remained the main subject of the research activity of the Centre for Radiochemistry and Nuclear Chemistry in 2014. The research projects of the Centre were financed in the form of grants from the National Centre for Research and Development (NCBR) and the National Science Centre (NCN), as well as in the form of funding the Institute's statutory research and international collaboration from the Ministry of Science and Higher Education. International resources included the European Commission (FP7 Euratom, Fission) and other (IAEA, COST).

The teams of three Centre laboratories (Radiochemical Separation Methods, Membrane Processes and Technologies, and Sol-Gel Technology) continued their studies on radioactive waste management, and on special nuclear materials. In this respect, the Sol-Gel team continued the execution of the European Collaborative Project ASGARD, contributing to the development of new types of MOX nuclear fuels based on uranium oxides and carbides. The work was accompanied by research on the synthesis of another potential nuclear fuel, mixed thorium-uranium dioxide in the form of microspheres. The Separation team continued their research on actinide/lanthanide separation by solvent extraction, in the frame of the European Collaborative Project SACSESS (Safety of actinide separation processes). Cooperation with CEA Marcoule, on actinide complexes with hydrophilic, polyheterocyclic-N-dentate ligands used for actinide stripping from the organic phase, was formalized in a bilateral research agreement.

The research in the NCBR strategic project on the development of safe nuclear energy in Poland has been completed. Various aspects were studied, related to the management and storage of spent nuclear fuel and radioactive wastes formed in the course of exploitation of nuclear power plants, with a special emphasis on the Polish nuclear industry. One of the outputs was the result of advanced quantum chemical calculations, which allowed to explain the reason of actinide selectivity of some ligands used for solvent extraction separation of actinides from lanthanide fission products. This knowledge may allow us to design and synthesize novel, more selective ligands for such separations.

Within another NCBR project and statutory research, novel methods were examined for the separation of radionuclides and heavy-metal ions, based on hybrid processes (membrane filtration combined with sorption or complex formation, and micellar-enhanced ultrafiltration), as the basis for further technological advancement for radioactive waste management. The application of advanced membrane systems in nuclear desalination was tested within the frame of IAEA CRP. Basic research on the phenomena occuring during the operation of membrane units was continued in the scope of an NCN research project on the development of sensitive methods for studying concentration polarization and membrane fouling.

The Centre actively participated in European initiatives of the development of new nuclear reactors including those of Generation IV – ALFRED and ALLEGRO. Evaluation of the potential of European institutions to participate in such initiatives was performed in the scope of PLATENSO and ARCADIA Euratom projects.

Special attention was paid to social and societal implications of nuclear energy and applications of ionizing radiation. These aspects were studied with international consortia in the frames of Euratom projects PLATENSO and EAGLE. Social and socio-economic effects of implementation of Polish Nuclear Power Programme with the development of macroeconomical tools for assessment were studied within IAEA CRP in cooperation with the Ministry of Economy.

Research on radiopharmaceutical chemistry (Laboratory of Radiopharmaceuticals Synthesis and Studies) were focused on obtaining and studying novel potential radiopharmaceuticals, both diagnostic and therapeutic. Novel biomolecules, derivatives of tacrine, substance P, and lapatinib, as well as antibiotics used in medical treatment of bacterial infections, were labelled with ^{99m}Tc or ^{68}Ga, resulting in potential diagnostic tools for Alzheimer's disease, glioma brain tumours, breast cancer and diabetic foot, respectively. A part of the research was carried out in cooperation with the Department of Pharmaceutical Chemistry and Drug Analyses, Medical University of Łódź. The ^{99m}Tc-labelled antibiotics were used in medical experiments in the Department of Nuclear Medicine, Medical University of Warsaw.

New methods for cyclotron productions of diagnostic radionuclides, both SPECT (^{99m}Tc) and PET (^{43}Sc, ^{44}Sc, ^{72}As) were developed in cooperation with the Heavy Ion Laboratory of the University of Warsaw, and the National Centre for Nuclear Research – POLATOM, within two projects awarded by NCBR. Also potential therapeutic radiopharmaceuticals were obtained and studied. Peptides and proteins were labelled with alpha emitters (^{211}At, ^{225}Ac and ^{223}Ra) *via* functionalized soft-metal chelates (metal bridge), and by the use of functionalized nanoparticles such as nanozeolites and gold nanoclusters. The synthesized bioconjugates exhibit high receptor affinity and high radiotoxicity. Nanobodies labelled with either beta or alpha emitters were studied in cooperation with Vrije Universiteit, Brussels. Studies on the use of alpha emitters to destroy very resistant cancer stem cells, initiated in 2014 in cooperation with the JRC Institute of Transuranium Elements, Karlsruhe, will be continued, supported from the Foundation for Polish Science.

The interest in energy related issues and our expertise in separation methods allowed to build the industrial consortium capable to develop a research project devoted to elaboration of the technology for treatment of fluids after hydraulic fracturing of shale with water reuse and recovery of valuable metals. The project awarded by NCBR in the course of the Blue Gas competition will enable to expand the expertise of the Centre to new areas of competence.

The year 2014 was marked with a number of events concerning the staff of the Centre. A team of four researchers experienced in spectroscopy and molecular modelling, guided by Prof. Jan Cz. Dobrowolski, joined our staff. Also Prof. Janusz Lipkowski, a well-known specialist in physical chemistry, was employed part-time at the Centre. One of the Centre staff members was nominated as a full professor, and another one got his DSc degree (habilitation). In the spring, friends and fellow colleagues of Prof. Jerzy Ostyk-Narbutt, the Centre Head, organized a scientific session devoted to the 50th anniversary of his employment by the Institute. At the end of the year, Prof. J. Narbutt handed over his post and responsibilities to the Deputy Head, Prof. Grażyna Zakrzewska-Kołtuniewicz. A few members of the Centre staff were awarded gold medals during an international inventions exhibition.

The international and national scientific cooperation of the Centre was successfully continued and enhanced, making the Centre teams desired partners not only on the national scale, but also over the European research area.

MODELLING OF MIGRATION OF RADIONUCLIDES IN THE SURROUNDINGS OF RADIOACTIVE WASTE REPOSITORIES

Grażyna Zakrzewska-Kołtuniewicz, Wioleta Olszewska, Agnieszka Miśkiewicz

The migration of radionuclides in the surroundings of radioactive waste repository is an important issue in every stage of repository existence: from siting up to final closing with the phase of long-term post-closure monitoring [1].

There are many protective barriers around the repository, which avoid migration of radioactive pollutants. They include natural (geological) barriers and artificial (engineered) barriers. This system is a very good protection against release of radioactive substances from a repository and their further movement in the environment [2].

To verify the correct operation of multi-barrier system one can use computational codes which should allow examining the migration of radionuclides to the environment. Migration of radionuclides to surrounding water can be the result of natural evolution of the environment and slow degradation of barriers. Eventual danger of the above examples depends on the type and activity of radionuclides contained in the storage and its release rate.

To increase safety around the radioactive waste disposal facility and predict the behaviour of the waste in the closed repository, the computer simulations are performed and appropriate models of the transport of radionuclides are elaborated. To validate the models it is important to prepare relevant data necessary to formulate the initial and boundary conditions and to determine values of the model coefficients. Based on the information of the medium geometry, physicochemical characteristics of fluid, it is possible to estimate the values of some coefficients. However, sufficiently precise definition of all these factors can be difficult. In such situations, it is necessary to conduct research in order to obtain results adequate to reality. The correct definition and evaluation of mechanisms affecting the migration of radionuclides is essential to carry out accurate calculations and estimates determining long-term safety of the planned repositories.

Multi-barrier system and mathematical codes should be considered as a whole for assessing the safety of the repository. These two factors are the protection against the various black scenarios such as gaping tanks, destruction of subsequent barriers and the release of radionuclides to the environment.

Vertical migration of radionuclides depends on the processes of transformation of chemical forms and the free-moisture content in the soils. The mathematical model of migration of radionuclides includes moisture-transfer equations and transfer equations for radionuclides with account for the kinetics of sorption, diffusion, and radioactive decay [3].

The mathematical simulation is a set of operations consisting of the development of computational models based on physicochemical processes, their verification using available experimental setups and analysis of variants associated with prediction of the development of the processes and optimization of possible consequences. Numerical modelling approaches in the literature generally use regular grids and the partially implemented dispersion tensor [4]. In the context of mathematical modelling it is necessary to properly define the mechanisms, which influence the migration of radionuclide. The wording of the flow model, which consists of the equation of continuity, resistance to motion with the initial and boundary conditions is a next step of this approach, mass and energy balance – Eq.(1). The last element indicates that the rate of change of mass within the observed volume, over a given period of time, is the summation of two components: the net mass flux through the boundary surface and the mass generated within the volume.

$$\frac{d}{dt}\int_{V_n}^{'} M^K dV_n = \int_{\Gamma_n}^{'} F^K \cdot n d\Gamma_n + \int_{V_n}^{'} q^K dV_n \quad (1)$$

where: V_n – volume in question, Γ_n – boundary surface, M – mass or energy per volume, K – the mass components and an extra heat “component” if the analysis is non-isothermal, F – mass or heat flux, q – sinks and sources, n – a normal vector on surface element $d\Gamma_n$, pointing inward to V_n [5].

The other basic flow, Eqs. (2) and (3), is described by Darcy’s law, which is often used to estimate fluid flow through a porous medium. It assumes a linear relationship between the fluid velocity and the friction forces experienced by the fluid.

$$u = -\frac{k}{\mu}(\nabla p - \rho g) \quad (2)$$

where: u – the seepage velocity vector, k – total permeability, μ – viscosity, p – pressure, ρ – density, g – gravity vector.

For multiphase flow, Darcy’s law is modified to introduce the concept of relative permeability:

$$u_\beta = -k\frac{k_{r\beta}}{\mu_\beta}(\nabla p_\beta - \rho_\beta g) \quad (3)$$

where: β – the phase, $k_{r\beta}$ – relative permeability for phase, p_β – the fluid pressure in the phase, which is the sum of the pressure in a reference phase and the capillary pressure.

The Tough2 is one of the most popular codes used in such cases. This is a numerical simulator for non-isothermal flows of multicomponent, multiphase fluids in one-, two-, and three-dimensional porous and fractured media. This software is based on the finite difference method [6].

The Tough2 can be used for modelling the spread of radionuclides in radioactive waste repository. Below, there is a sample model of repository, where radionuclide leaked into the environment (Fig.1).

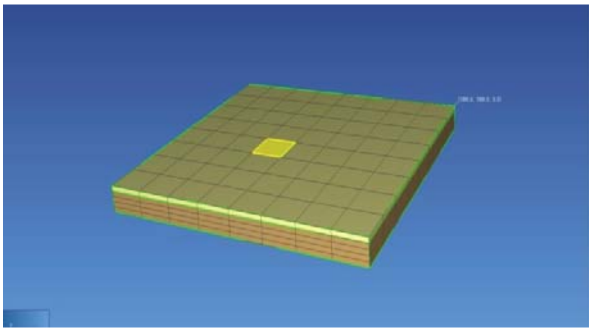

Fig.1. Repository model, in which is located a source of Cs-137 in the first storage layer.

Table 1. The parameters of sand and clay.

Parameter	Sand	Clay
Density [kg/m^3]	2000	2210
Porosity	0.4	0.3
Permeability [m^2]	$5.4 \cdot 10^{-12}$	$4.9 \cdot 10^{-14}$
Wet heat conductivity [W/m °C]	0.4	0.85
Specific heat [J/kg °C]	840	840

The model, which has been made, is consisting of two layers with higher and lower permeability. In the first layer a source of Cs-137 (Rn1) has been placed (Fig.1). During the decay of this source, the isotope Ba-137 was created. The initial conditions which were assumed are atmospheric pressure and temperature of 20°C. The other parameters assumed in calculations were the rate 3.17E-11 kg/s and the enthalpy 83798 J/kg of the placed source of Cs-137. The parameters [7] of materials are presented in Table 1.

In order to simulate the migration of radionuclides in the environment the EOS7R is used. This is an enhanced version of the EOS7 module in which two additional mass components have been added. The module enables selection of radionuclides with user-specified half-life that are of the user's interest. There are two types of radionuclides in this model. The radionuclide 1 (Rnl) is the "parent" and radionuclide 2 (Rn2) the "daughter" [8].

The mass fractions of parent/daughter radionuclides were simulated. Below it is shown how these parameters change after 1, 10 and 100 years.

The following pictures show the simulation of radionuclide propagation (Figs.2 and 3).

Mass fraction of radionuclide 1 (Cs-137) changes over time. After the first year, a mass fraction of this isotope is 2.49E-12, after 10 years – 2.20E-11 while after 100 years is already 9.60E-11.

The spread of isotope of Ba-137 occurs faster than in case of the "parent" radionuclide. After first year, the maximum of mass fraction is 3.73E-14,

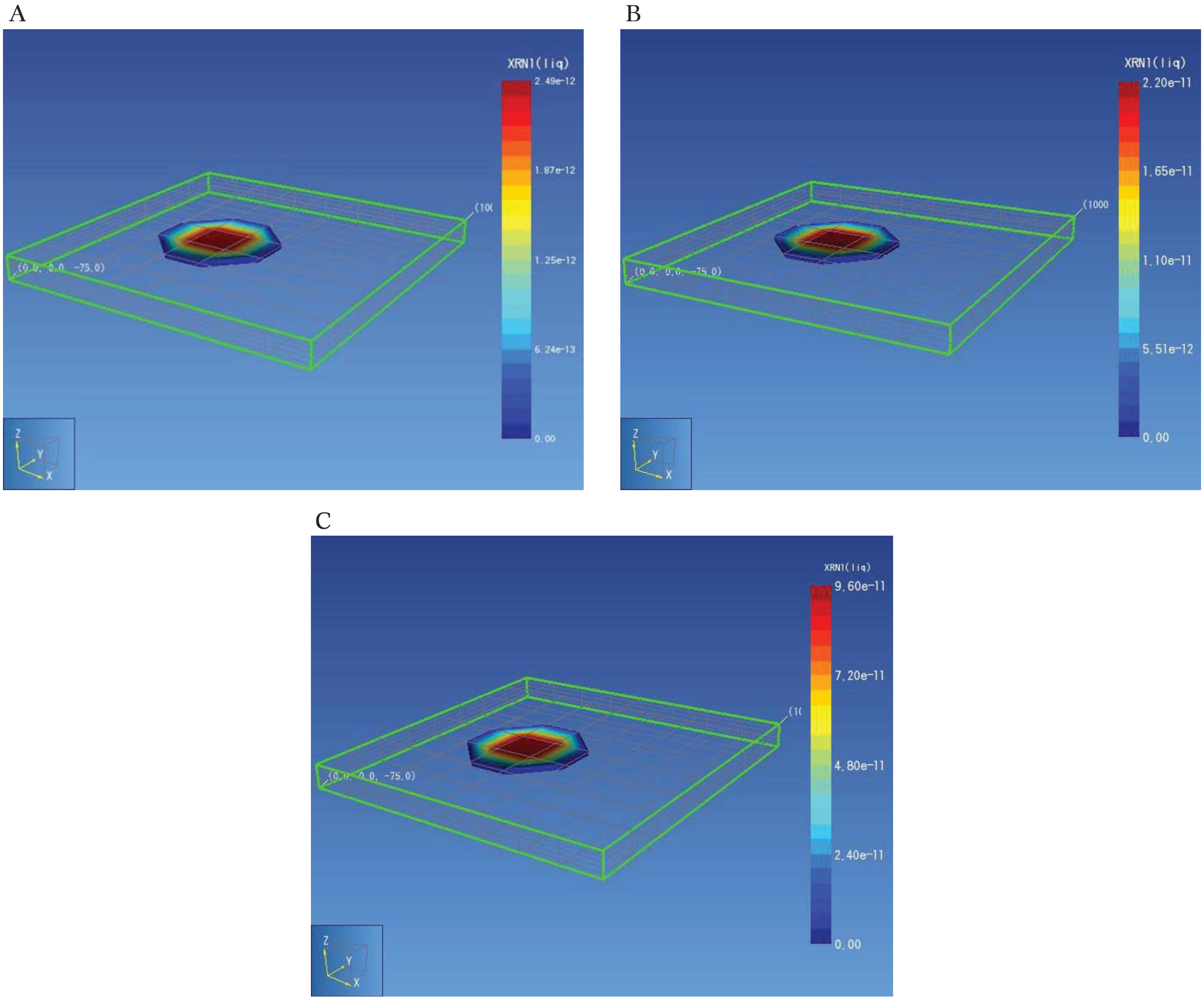

Fig.2. Contours of mass fraction of radionuclide 1 (Cs-137) in liquid, after: A) 1 year, B) 10 years, C) 100 years.

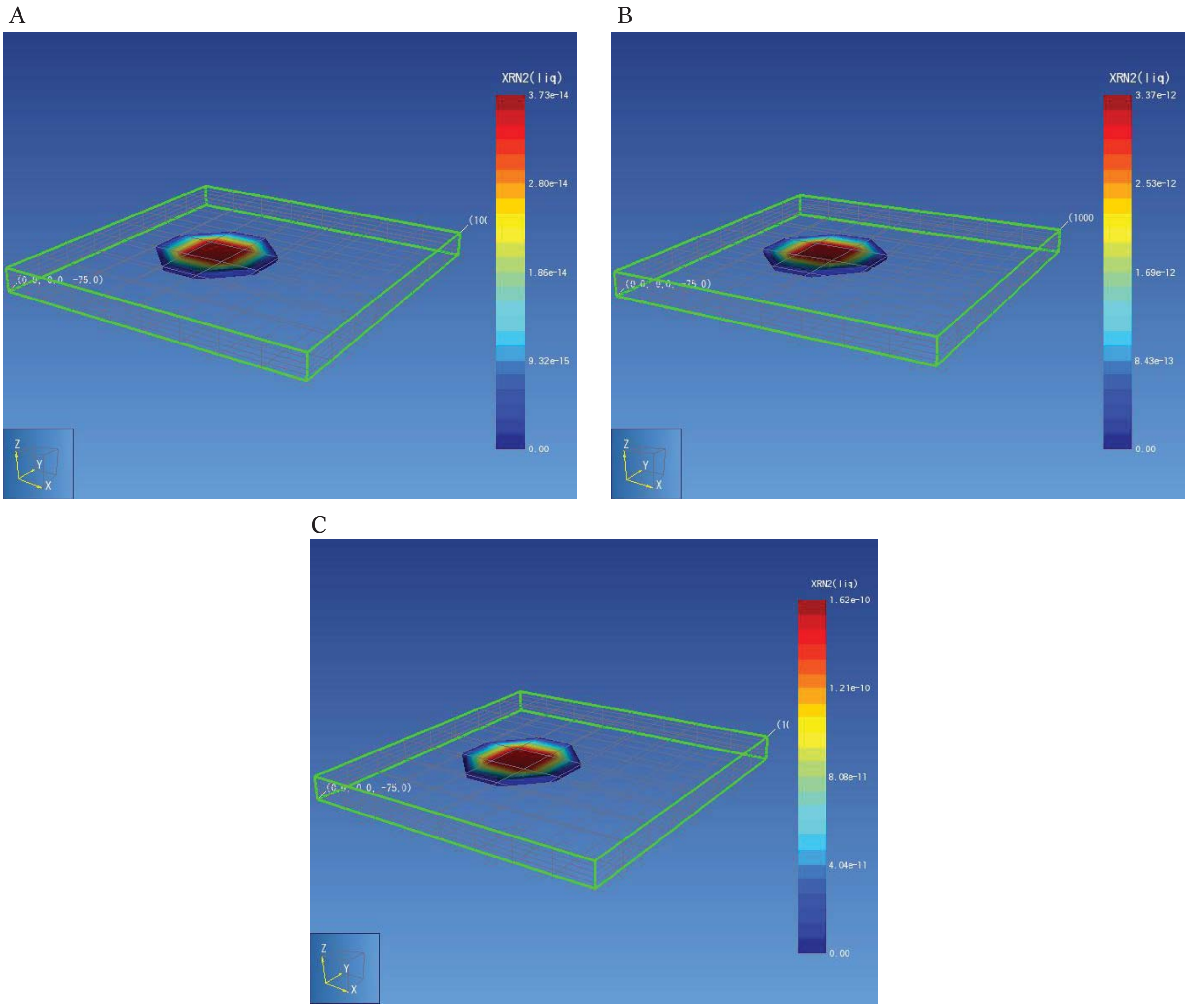

Fig.3. Contours of mass fraction of radionuclide 2 (Ba-137) in liquid, after: A) 1 year, B) 10 years, C) 100 years.

after 10 years – 3.37E-12, however, after 100 years is already 1.62E-10.

Simulated model shows what is happening in and around the source. On the basis of such examples, the used barriers can be verified, and the new ones can be created to prevent the spread of radionuclides into the environment [9]. Multi-barrier system and mathematical codes should be considered as a whole for assessing the safety of the repository. These two factors are the protection against the various black scenarios such as gaping tanks or the release of radionuclides to the environment.

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A STUDY OF PRECIPTITATION OF YELLOW CAKE FROM URANIUM LIQUORS FOR PRODUCTION OF NUCLEAR FUEL

Katarzyna Kiegiel, Anna Abramowska, Dorota Gajda, Grażyna Zakrzewska-Kołtuniewicz

Uranium plays an important role in generation of nuclear power. The selective isolation of uranium is of particular interest in the context of both energy resources and treatment of nuclear waste. In January 2014, the Polish Government adopted the Polish Nuclear Power Programme [1]. One of the objectives of this programme is to identify new uranium sources to meet future needs for this metal.

According to OECD-NEA Red Book (2014) [2] identified conventional uranium resources in Poland count 7270 t; historical research led to the determination of 20 000 t of speculative resources. The basic steps of processing uranium ores are crushing and grinding, leaching [3,4], solid-liquid separation, ion exchange [5], solvent extraction, and precipitation fallowed by calcination to obtain final product: yellow cake U_3O_8 (Fig.1) [6].

The production of yellow cake is the most crucial step in the preparation of uranium for fabrication of fuel for the use in nuclear power plants. In general, uranium present in acidic solutions obtained from the ion-exchange or solvent-extraction processing or uranium in carbonated ore leach solutions, is typically precipitated as polyuranate. From acidic solutions, uranium is precipitated by the addition of neutralizers such as sodium hydroxide, magnesium oxide or aqueous ammonia. The precipitation with hydrogen peroxide is also very effective. From alkaline solutions, uranium is most often precipitated by the addition of sodium hydroxide producing an insoluble sodium diuranate. It can also be precipitated by acidification and then, neutralization of alkaline solution. In all cases, the final product is the yellow uranium salt, commonly known as yellow cake.

In the present work, the precipitation of three different forms of yellow cakes: $(NH_4)_2U_2O_7$, $Na_2U_2O_7$ and $UO_4{\cdot}2H_2O$ was carried out from a model uranium solution (Fig.1). The influence of temperature and concentration of uranyl ions in the solution was examined.

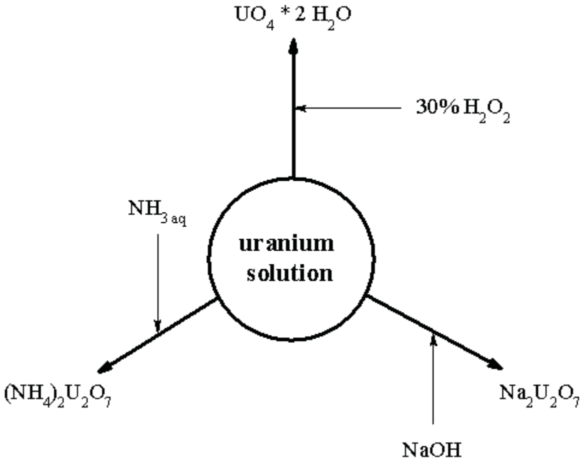

Fig.1. Precipitation of yellow cake.

The addition of sodium hydroxide to solution of $UO_2(NO_3)_2$ in sulphuric acid results in precipitation of sodium diuranate – Eq. (1). The precipitation was conducted at 40°C and pH 7-8. The obtained product was impure by co-precipitation of other sodium salt. The process was not optimized.

$$2UO_2^{2+} + 6Na^+ + 6OH^- \rightarrow Na_2U_2O_7 + 4Na^+ + 3H_2O \qquad (1)$$

In alternative process the alkaline solution of uranium was mixed with acid and carbon dioxide was removed. The resulting solution was neutralized with ammonia, whereupon uranium precipitated as ammonium diuranate – Eq. (2).

$$2UO_2^{2+} + 6HN_{3aq} \rightarrow (NH_4)_2U_2O_7 + 4NH_4^+ + 3H_2O \qquad (2)$$

The influence of temperature and concentration of uranyl ions in the solution was examined.

Table 1. The precipitation of $(NH_4)_2U_2O_7$ from solution of $UO_2(NO_3)_2$ in 0.5 M $(NH_4)_2CO_3$.

[U] [mg/mL]	Temperature [°C]/time [h]	pH	Yield [%]
0.9	40°C/4 h	10	26
0.9	90°C/4 h	10	47
2.4	40°C/4 h	10	84
2.4	60°C/4 h	8	74
2.4	90°C/4 h	10	95
4.7	60°C/4 h	8	94
4.7	60°C/4 h	10	96

The representative results are presented in Table 1. The precipitation of ammonium diuranate from solution of uranium in 2 M H_2SO_4 was also examined (Table 2). It is significant that ammonium diuranate precipitated from solutions containing low concentration of uranium (0.3-0.5 mg/mL).

Table 2. The precipitation of $(NH_4)_2U_2O_7$ from solution of $UO_2(NO_3)_2$ in 2 M H_2SO_4, pH 10.

[U] [mg/mL]	Temperature [°C]/time [h]	Yield [%]
0.3	40°C/4 h	84
0.3	60°C/4 h	85
0.3	90°C/4 h	83
0.5	40°C/4 h	96
0.5	60°C/4 h	97
0.7	60°C/4 h	98
0.9	40°C/4h	95
0.9	60°C/4 h	98
2.4	40°C/7 h	94
2.4	60°C/7 h	95

The precipitation was followed by a calcination step at a temperature of 750°C, at which U_3O_8 is formed.

Uranium peroxide hydrates can be synthesized by adding excess of hydrogen peroxide (H_2O_2) to acidic solution of uranyl ions, as is shown by Eq. (3). Uranium peroxides can be selectively precipitated from eluted solution [7]. Gupta *et al.* used the solution with concentration of uranium 3.8 g/L. In the presented study, the precipitation was carried out from the solutions with a concentration of uranium 0.5-0.9 g/L and obtained results are very promising (Table 3).

Table 3. The precipitation of $UO_4{\cdot}2H_2O$ from solution of $UO_2(NO_3)_2$ in 2 M H_2SO_4, pH 10.

[U] [mg/mL]	Temperature [°C]/time [h]	Yield [%]
0.5	60°C/4 h	17
0.5	90°C/4 h	93
0.9	60°C/4 h	63
0.9	90°C/4 h	99

$$UO_2^{2+} + H_2O_2 + 4H_2O \rightarrow UO_4 \cdot 2H_2O + 2H_3O^+ \quad (3)$$

The results of the presented studies have shown that the uranium could be recovered from dilute uranium solutions (< 1 mg/mL) with high efficiencies. The optimal conditions of precipitation of ammonium diuranate are as follows: temperature 60°C and pH 10. It is worthy of noticing that the precipitation occurred with a high yield from dilute uranium solution (0.3 mg/mL, 84%). From alkaline solution, uranium was precipitated by the addition of neutralizers such as aqueous ammonia followed by precipitation. The higher efficiencies of precipitation of uranium peroxides was observed in the process that was carried out at a temperature of 90°C and pH 10.

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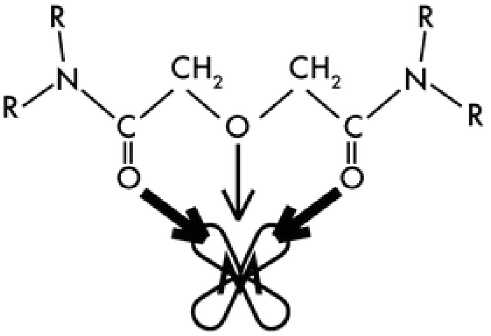
MODERATE CHEMICAL SOFTNESS OF CERTAIN OXYGEN-BEARING LIGANDS USED IN PROCESSES OF SOLVENT EXTRACTION OF TRIVALENT ACTINIDES AND LANTHANIDES

Jerzy Narbutt

The Pearson HSAB concept [1], related to organic ligands considered either "hard" or "soft" Lewis bases, is a useful tool for *a priori* selecting efficient extractants able to separate actinides(III) from chemically similar lanthanide fission products [2]. The actinide cations, slightly softer than lanthanides, eagerly form complexes with soft bases such as sulphur- and nitrogen-bearing ligands. Such complexes appear somewhat more covalent, *i.e.* stronger than their lanthanide counterparts. In the case of sufficiently lipophilic ligands, the difference in the covalency makes possible efficient solvent extraction separation of these metals. On the other hand, hard ligands bearing donor oxygen atoms favour complexation of somewhat harder lanthanides.

Large polydentate ligands, particularly those containing different donor atoms of different reactivities toward the metal ions, cannot be explicitly classified in terms of global hardness or softness. The reactivity in such systems is better described with the use of indices related to the particular sites of interaction – the local softness and hardness [3]. Careful analysis is required, however, when attributing these descriptors to given donor atoms in the ligands. Unfortunately, such caution is sometimes overlooked. In particular, it is customary to consider all donor oxygen atoms as hard, irrespective of their atomic environment in the molecule. Such an approach often makes problems with interpretation of the results of investigations. For example, the conclusion from quantum mechanical (QM) calculations, on more covalent Am–O than Eu–O bonds in 2,9-dicarboxyl-1,10-phenantroline complexes, has been interpreted that "the presence of softer nitrogen atoms in the Phen moiety … has a profound influence in changing the soft nature of the actinide ion, which in turn binds with the hard oxygen atoms in a stronger way" [4]. In my opinion, such interpretation is over-sophisticated and unjustified, moreover, no acceptable explanation of the more covalent Am–O than Eu–O bonds can be done assuming the donor oxygen atoms to be hard.

Our recent QM study aimed at a better understanding the origin of selectivity of complex formation and solvent extraction of actinides with some polydentate N- and O-donor ligands [5] has shed some light on the problem. One of the ligands we studied was a neutral tri-O-dentate *N,N,N',N'*-tetraethyl-diglycolamide (TEDGA). It is a homologue of TODGA, the promising extractant in actinide partitioning, where $[M(TODGA)_3]^{3+}$ complexes are extracted to the organic phase with no pronounced An/Ln selectivity [6]. Our analysis of charge distribution over the TEDGA molecules, both free and coordinated in the $[M(TEDGA)_3]^{3+}$ complexes, has shown a significant shift of electron density from the ligand to the central metal ions (M = Am^{III} and Eu^{III}). The shift was greater on the Am^{III} than Eu^{III} ion, and the difference appeared mainly in the greater occupation of the 6*d*(Am) than 5*d*(Eu) orbitals, which was interpreted in terms of a greater space extension of the former [5]. The role of the *s* and *f* orbitals of both Am^{III} and Eu^{III} cations as electron acceptors was much less. The electron density was shifted on the metal ions mainly from the two lateral alkylamide fragments, $(C_2H_5)_2N(C{=}O_{amid})$-, of the TEDGA molecule and to a less extent from the central ethereal fragment, -CH_2-O_{eth}-CH_2-, [5] (Scheme 1).



Scheme 1. Shift of electron density from the fragments of TEDGA ligand to M^{3+} cations.

All the computational methods used in the bond analysis confirmed the greater covalency of the M–O_{amid} than M–O_{eth} bonds in the complexes. Also the calculated lenghts of the former bonds (*ca.* 2.4 Å) were significantly shorter than those of the latter (*ca.* 2.6 Å). Unexpectedly, the total shifts from the TEDGA ligand were only slightly smaller than those from the BTBP ligand, although the former ligand was considered hard while the latter – a soft base. Though the character of the ligand-to-metal bonds in all the complexes studied is mainly ionic, the covalent contributions in the TEDGA complexes of both metals are only slightly less than those in their BTBP counterparts. Therefore, in contrast to the common opinion, we have concluded that the diglycolamide ligands are not hard but rather moderately soft bases. This conclusion has been corroborated by computation of ionization potentials (IP) and electron affinities (EA) of both ligand molecules, which resulted in a small difference between the values of their global hardness, $\eta = ½(IP – EA)$, equal to 4.4 and 3.4 eV, respectively [5]. The softening of the TEDGA ligand is undoubtedly due to the presence of the alkylamide groups in the molecule, while the ethereal group, donating less electron density, makes the molecule harder. Using the terminology of "local softness and hardness" we can state that the amide oxygen atoms are relatively soft, but the ethereal oxygen atoms are hard.

Our hypothesis on the moderate softness of polydentate ligands with donor carbonyl groups (of amide but also of carboxylic moieties) may be helpful for proper interpretation of numerous experimental and theoretical results. Apart from providing a simple interpretation of the greater covalency of Am–O than Eu–O bonds in 2,9-dicarboxyl-1,10-phenantroline complexes, computed by Manna and Ghanty [4], it also explains the good ability to coordinate Am^{3+} and Eu^{3+} ions by amide oxygen atoms in the 2,9-diamide-1,10-phenantroline ligand, greater than that by ketone oxygen atoms in 2,9-diketone-1,10-phenantroline, reported by Mariani *et al.* [7], because this order correlates with the greater softness of amides than ketones [5]. Also the more negative formation energies of Am(III)/Eu(III) complexes with pyridine-bis(alkyl-aryl)amide ligands than with pyridine-bis(dialkyl)amide ligands, computed by Ustynyuk *et al.* [8], can perhaps be explained by our hypothesis. This may be due to a greater shift of electron density to the metal ions from the arylamide moieties, *i.e.* to somewhat greater softness of arylamide ligands. On the other hand, because both An^{3+} and Ln^{3+} ions are rather hard acids, still softer di- and triamides become less efficient ligands than the moderately soft TODGA in both complex formation and solvent extraction, as observed by Sasaki *et al.* [9]. The work in this field is still in progress.

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REMOVAL OF Sr(II) AND Am(III) RADIOACTIVE METALS FROM AQUEOUS SOLUTIONS BY SORPTION ON MATERIALS OF BIOLOGICAL ORIGIN: ROOTS OF THE DANDELION MEDICAL (*Taraxacum officinale*)

Leon Fuks, Agata Oszczak, Wanda Dalecka

Low-level radioactive wastes (LLW) are generated from medical, industrial and research establishments. They comprise paper, rags, tools, clothing, filters, *etc.* contaminated with small amounts of mostly short-lived radionuclides. They do not require shielding during handling and transport and are suitable for shallow land burial. To reduce their volume, they are often compacted or incinerated before disposal. They comprise some 90% of the volume, but only 1% of the radioactivity of all radioactive waste. Medium-level wastes (MLW) are more radioacte and some of them require shielding. They typically comprise ion-exchange resins, chemical sludges and metal fuel cladding as well as contaminated materials from decommissioning of nuclear reactors. Smaller items and any solids may be solidified in concrete or bitumen for disposal. Such a solididified material makes up some 7% of the volume and 4% of the radioactivity of all radwaste.

Despite the extensive literature available on biosorption of metal ions, little information is available on the applications of biosorption in nuclear waste management. For a long time, this method was considered the most appropriate technology for radionuclide removal from environmental water [1,2]. Biosorption as a biomass-based system is particularly a cost effective and flexible method in detoxification of very dilute effluents [3].

The major advantages of biosorption over conventional methods include low cost, high efficiency, minimization of chemical and biological sludge, and regeneration of biosorbent and possibility of pollutant recovery [4].

Some biosorbents have been reported to be effective and eco-friendly having low cost material options. These biosorbents include algae, fungi, yeast, bacteria, and some waste materials of plant origin. There are reports regarding the use of both living and dead microbial cells which are able to uptake radionuclides and offer potential inexpensive alternative to conventional adsorbents. However, living cells are subject to toxic effect of radionuclides, resulting in cell death. Moreover, living cells often require the addition of nutrients and increase the biological and chemical oxygen demands (BOD and COD, respectively) in the effluent. For these reasons, the use of non-living biomass or dead cells has gained importance as metal binding compounds because toxic ions do not affect them. Moreover, non-living materials require less care and maintenance, and are cheaper. Dead biomass could be easily regenerated and reused.

Roots of the popular and cheap perennial weed, dandelion (*Taraxacum officinale*), contain inulin [5], starch like substance that may help balance blood sugar and stimulates digestion, with the addition of alkali and alkaline earth levulinates. Herbalists use also the dandelion root to detoxify the liver and gallbladder. It is supposed also, that dandelion root may have anticancer properties. Since a long time they have been used in traditional herbal medicine. Till now, however, there have not been any systematic scientific studies on dandelion. The content of the main metal complexing substance, polysaccharide inulin, in dandelion roots range from 2% in spring to 40% in autumn [6]. It is an oligosaccharide composed of 2 to 60 fructose units connected by β(2-1) links and terminated by a glucose unit. Ratio of glucose to fructose is rarely lower than 80:20. Structure of inulin is presented in Fig.1.

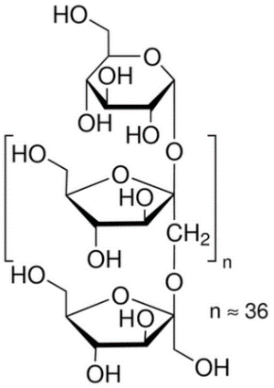
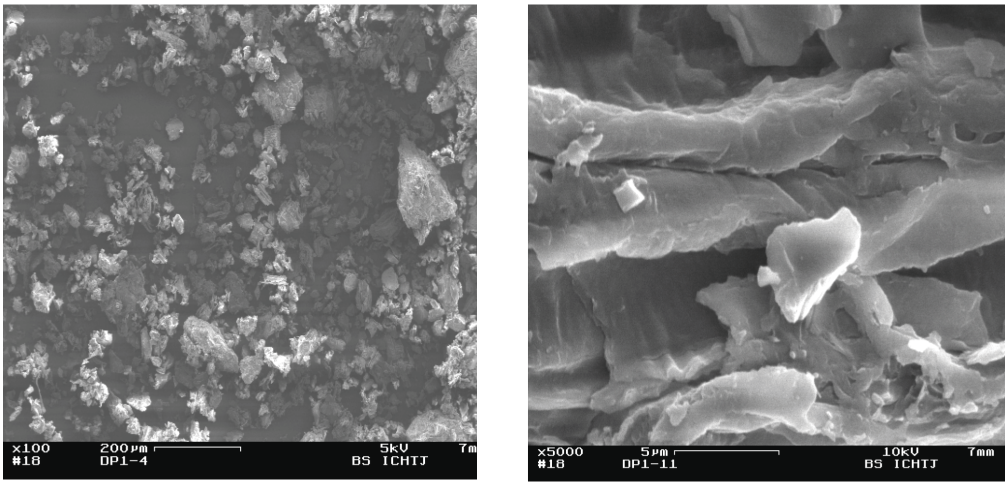


Fig.1. General structure of fructan inulin from *Taraxacum* [7].

Detailed literature inspection has shown, however, that either inulin or the whole dandelion roots till now have not been tested as potential sorbents of radioactive metals from the waste water. Detailed literature inspection on the heavy and/or radioactive metal environmental pollutant indication by the dandelion medicinal shows for a very limited number of published papers and conference announcements of the problem. As a result of the work performed within the strategic project "Technologies supporting development of safe nuclear power engineering", task 4 "Development of spent nuclear fuel and radioactive waste management techniques and technologies", we have for the first time checked the possibility of application of the powdered dandelion root as a cost-less, renewable and reusable sorbent for both environmentally important radionuclide cations from aqueous solutions and liquid radioactive wastes. Taking into account complex composition of the DRB, it might be expected that it should strongly bind heavy/radioactive metals.

Dandelion root (DRB, Kawon Herbalist's Work, Gostyń, Poland) was obtained from a public phar-

Initial material



Europium sorbed

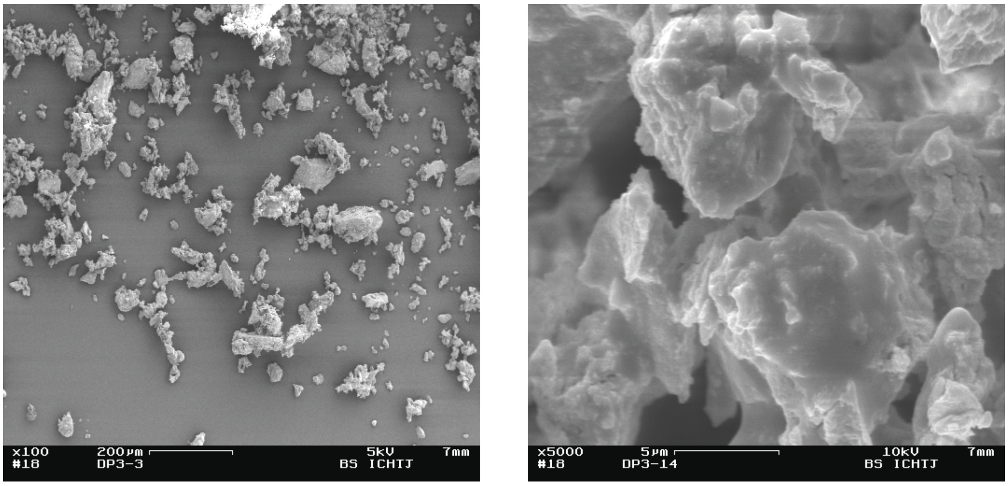


Fig.2. The results of SEM observation of the dandelion root biosorbent. Magnification: 100x (left) and 5000x (right).

maceutical shop and ground in a bead mill for 2 h. Its price may be estimated as about US$ 10 per one kilogram. After homogenization of the powdered solid material, it was sieved and the fraction of 0.5-1 mm was collected. For the sorption studies, it was used as obtained above. Five 0.1 g lots were equilibrated with the same volume of the initial solution of both studied radionuclides under optimized conditions of pH, temperature and contact time. Values of the metal removal efficiency ($Y_M = (C_0 - C_{eq})/C_0 \times 100\%$) by the DRB for all samples did not differ from each other. This shows that biomaterial was homogeneous and the biomass might be used for the entire study (Fig.2).

Batch adsorption experiments of Sr(II) and Am(III) ions by the DRB were carried out with initial strontium addition of either 100 mg/L (*ca.* 1.14 mmol/L), added as $SrCl_2$, or alternatively in the n.c.a. of ^{85}Sr(II) concentration. For the sorption studies of ^{241}Am(III) in the presence of the weight amount of the salt, 100 mg/L (*ca.* 1.14 mmol/L) of $EuCl_3$ has been applied. It is well-known that Eu(III) is the Am(III) congener and their chemistry is similar each other.

Figure 3 shows the time dependence of the amount of sorbed ^{85}Sr(II). As can be seen, in the time interval from 90 min to 4 h, removal efficiency is independent of the contact time of the equilibrated phases. In details, removal efficiency of ^{85}Sr(II) at pH *ca.* 5.6 and temperature 25°C reaches the value 81.0 ± 1.9%. However, even mixing for only 30 min permits removal of more than 75% of ^{85}Sr(II). Furthermore, it was found that the pseudo-second-order model provides the best fit for the ^{85}Sr(II) removal giving value for the pseudo-second-order rate constant $K_2 = 1.33 \cdot 10^5$.

The effect of pH on ^{241}Am(III) and ^{85}Sr(II) sorption onto DRB was studied in the pH range

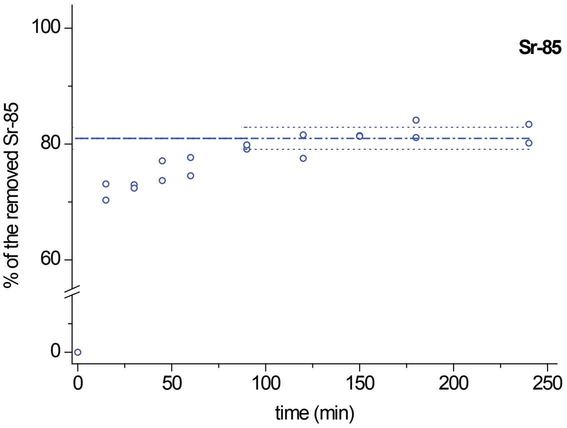


Fig.3. Time depending removal efficiency of Sr(II) by the dandelion root biomass (25°C, initial pH 5.6).

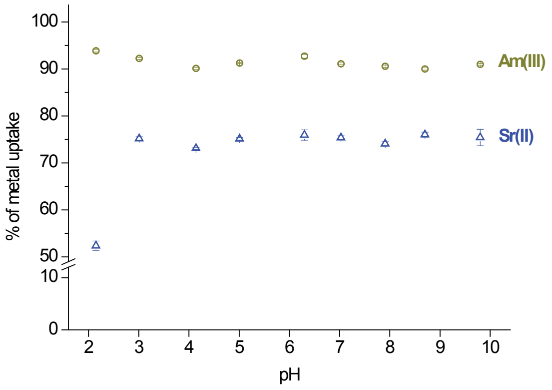


Fig.4. Effect of acidity on the removal efficiency of both cations by the dandelion root biomass (25°C, t = 2 h).

2-10 and the results are presented in Fig.4. It can be seen that uptake of both metals by the DRB in the pH range of 3-10 oscillates slightly around the plateau of 91.4 ± 1.3% for Am(III) and 76.0 ± 1.0% for Sr(II).

Two of the most popular models, those of Langmuir and Freundlich, were used to analyse the adsorption data. It was found that the Freundlich equation fits better the data than the Langmuir one. So, we may assume that the sorbent has a surface with a non-uniform distribution of sorption centres. In addition, multilayer chemisorption may be proposed as dominant process of the metal sorption by the DRB.

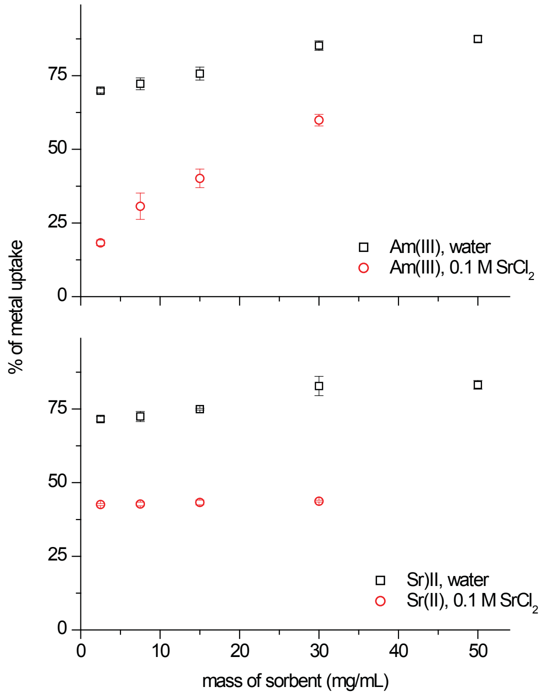


Fig.5. Effect of mass of the DRB on the removal efficiency of both cations by the dandelion root biomass (25°C, t = 2 h).

The dependence of ^{241}Am(III) and ^{85}Sr(II) sorption on the ratio of the adsorbent mass : decontaminated solution volume was studied by varying the amount of the sorbent from 2.5 to 50 mg/mL, keeping other parameters (pH and contact time) constant. Figure 5 shows the results obtained. It can be seen, as expected, that the sorption capacity improves with increasing sorbent dose in the full range up to 30 mg/mL. About 90% of Am(III) and 80% of Sr(II) were removed when 30 mg of the sorbent was put in 1 mL of the solution. After

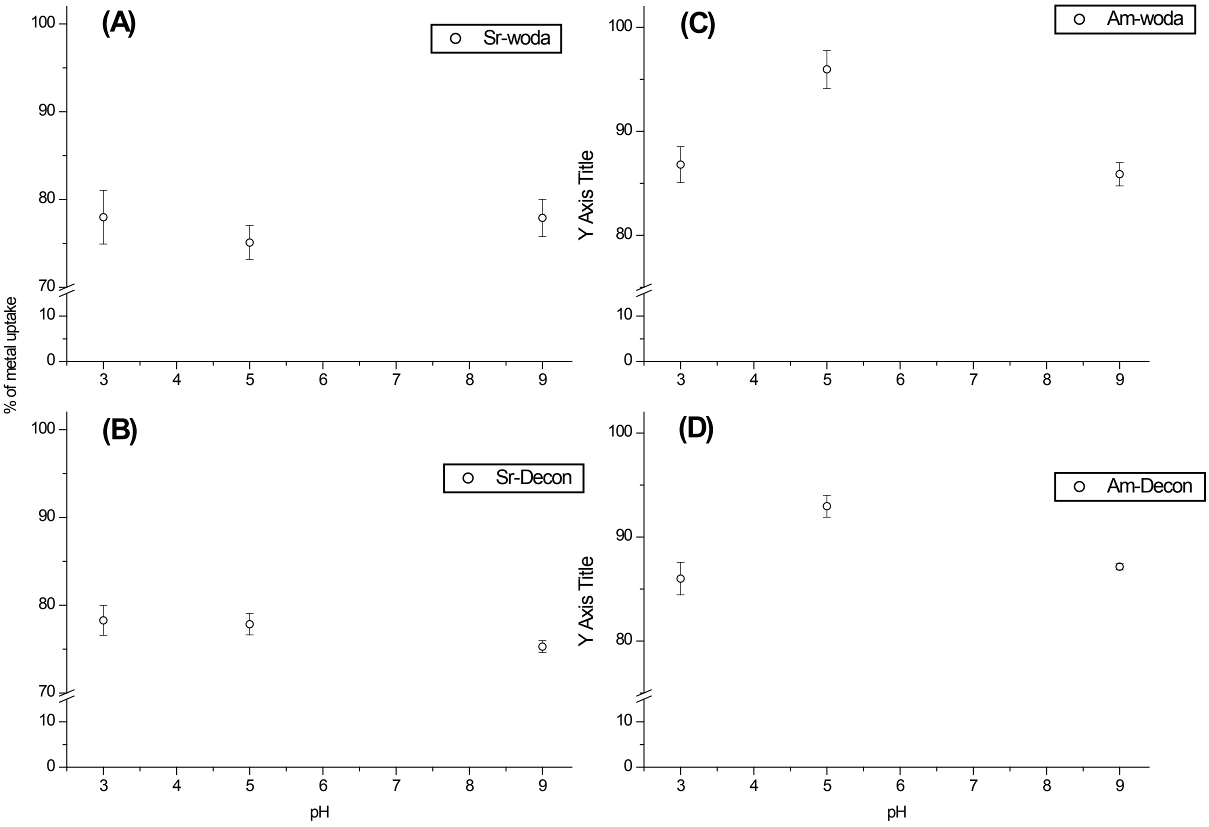


Fig.6. Sorption of Sr(II) and Am(III) by DRB from drinking water (A and C, respectively) as compared with the decontamination solutions (B and D, respectively).

reaching this dose, sorption percent values do not change considerably even with further addition of the sorbent.

Treatment of liquid radioactive wastes quite often demands the use of special decontamination solutions. Among the most popular, the CANDEREM (Canadian decontamination and remediation process) solution and the CANDECON (Canadian decontamination process) may be mentioned. Approximate composition of the solution is: 0.3 g/L oxalic acid, 0.2 g/L citric acid and 0.5 g/L EDTA (*i.e.* about $2 \cdot 10^{-3}$ M, each) [8]. It has been found that the complexation of Sr(II) and Am(III) by a mixture of strong chelating agents, *i.e.* citrate, oxalate and EDTA, does not diminish significantly sorption efficiency of the sorbent. In details, percentage of sorption from the solutions of the initial pH 3, 5 or 9, respectively, are in the range of 90 and 75% for Am(II) and Sr(II), respectively. It implies that designing of the process of water processing should not include any additional step. Figure 6 shows the obtained results.

The recycling of the biomass was investigated in the consecutive desorption experiments. It has been found that in four consecutive washings the recovery ratios appeared to be 0.331 ± 0.004 and 0.821 ± 0.020% for Sr(II) and Am(III), respectively. Such small values indicate that if fixed by the DRB, both radionuclides may be safely stored as solid phase matter in the radioactive waste repository.

In conclusion, it may be said that biomaterial of the dandelion root is a perspective material for treating of low-level radioactive liquid wastes.

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MODIFICATIONS OF SOL-GEL METHOD TO THE SYNTHESIS OF MICROSPHERES OF URANIUM DIOXIDE

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The main application for UO_2 microspheres is as a fuel in high-temperature gas-cooled reactors (HTGRs), such as a generation IV reactor [1-4]. The HTGRs created in the early 1960s required a special procedure for production of fuels. It came to be known as the Oak Ridge National Laboratory (ORNL) sol-gel process [5]. Considerable progress in the production of these nuclear fuels has been reported at international conferences over the years [6-9]. Other sol-gel processes for nuclear technology have also been reported [6-9]. In the sphere-pac process, for example, gel-derived spheres of nuclear materials, preferably of three different sizes with diameter ratios of approximately 40:10:1, are loaded directly into rods and packed by low-energy vibration to achieve a smear density of 88% of theoretical. Pelletization of sol-gel–produced microspheres can also produce suitable fuels [6-9].

Three main families of sol-gel processes for production of UO_2 microspheres have been described in the literature [5-10]:

- water extraction from a U(IV) sol, and recently, by internal gelation, as developed at ORNL [10];
- external gelation by neutralization of UO_2^{2+} solution with ammonia, as developed at SNAM (Italy), KEMA (the Netherlands), and NUKEM (Germany) [5];
- internal gelation process by neutralization of UO_2^{2+} solution with ammonia generated by decomposition of hexamethylenetetramine at elevated temperature, as developed at KEMA (the Netherlands) and KFA (Germany) [5].

Microspheres ≤ 150 μm were prepared by mechanical stirring of sols in a solvent. For higher-diameter sols, two-fluid nozzles were used. The diameter of the drops was regulated by relation of streams feeding sol to drive the fluid. When our programme was started at the Institute of Nuclear Chemistry and Technology (INCT), the ORNL water extraction process was followed. Among the options, this process appeared to be a true sol-gel process, in contrast to the other, where uranyl ion precipitated ammonium polyuranates had been used during kernel formation. The use of the ORNL process was expected to make use of the advantages of a sol-gel process, such as lower sintering temperature.

It is well-known that U^{4+} ions only form colloidal solutions. Consequently, as reported previously [6-9], we employed reduction of 0.5 M uranyl nitrate in 4.5 M HNO_3/0.4 M HCOOH. The flow chart of the procedure is shown in Fig.1. During the washing step, the total concentration of remaining anions was estimated on the basis of conductivity measurements, and it was fixed at a level sufficient for self-peptization of hydroxide.

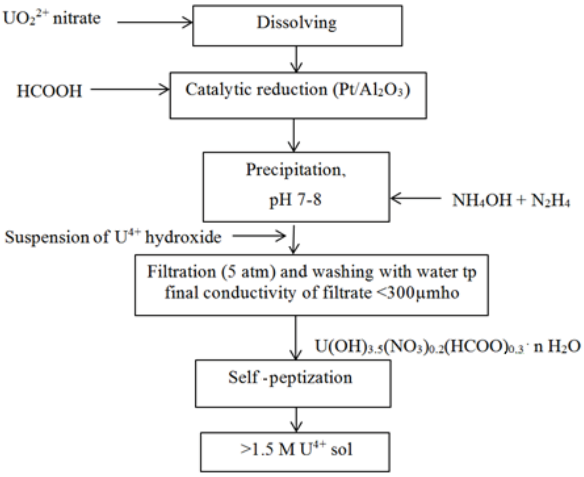

Fig.1. Preparation of U^{4+} sol by a peptization process (all operations carried out in N_2).

The self-peptization step required approximately 15 days at room temperature, but at a temperature of 70°C it required only 2 h. This process proved, however, to be laborious. Per information from ORNL [11,12], we applied a process named concentrated uranium sol production (CUSP), in which nitrates are extracted with Amberlit LA2 from U(IV) solutions containing only nitrates and formic acid. Urea and hydrazine are eliminated because the formation of ammonia from those components at elevated temperature (at which the aqueous phase aged between successive extraction stages), caused thickening of the sol. We applied Primene JMT diluted 1:1 with petroleum, as used in our other processes for production of spherical powders of inorganic compounds [5,13]. We also used a highly active Pt/γ-Al_2O_3 catalyst home prepared [14]. The course of the reduction of 1 M $UO_2(NO_3)_2$-0.5 M HCOOH with hydrogen was controlled both analytically and by measuring the U(VI)/U(IV) redox potential. It was imperative to finish the process immediately after complete reduction of U(VI) to U(IV), as indicated by an inflection point. Further action of hydrogen (in the absence of UO_2^{2+}) induced reduction of NO_3^- to ammonia, which would be deleterious in extraction. We routinely obtained sols with molar ratios $NH_4^+/\Sigma U < 0.04$, when carrying out extraction in the apparatus shown in Fig.2.

All glassware was heated with a transparent layer, allowing visual control of process steps, such as decreasing the Primene JMT stream when traces of precipitate were noted. In the first step, at 40°C, a sol with the molar ratio $NO_3^-/\Sigma U \approx 0.8$ was obtained. The aqueous phase was then heated at 60°C for 5 min. In the next extraction step, also at 60°C, 1.05-1.1 M uranium sols of the molar ratio $NO_3^-/\Sigma U \approx 0.3$ were obtained. These sols were gelled to microspheres by the aforementioned ORNL water extraction process which used 2-ethylhexanol-1 containing the surfactant SPAN-80. We produced (1) medium-size spheres ≤ 150 µm in diameter in equipment, as described in detail in [12], and (2) kernels 0.2-1.5 mm in diameter in a standard ORNL tapered column. In the first process, we improved formation of the emulsion by the application of vibratory capillary feeding the sols. In both processes, we radically decreased the dewatering temperature (by *ca.* 100°C) by the use of vacuum.

The primary goal of this work was to synthesize UO_2 by the complex sol-gel process (CSGP) in which ascorbic acid (ASC) is used as a strong complexing agent [15]. This procedure was then successfully applied to the synthesis of new gen-

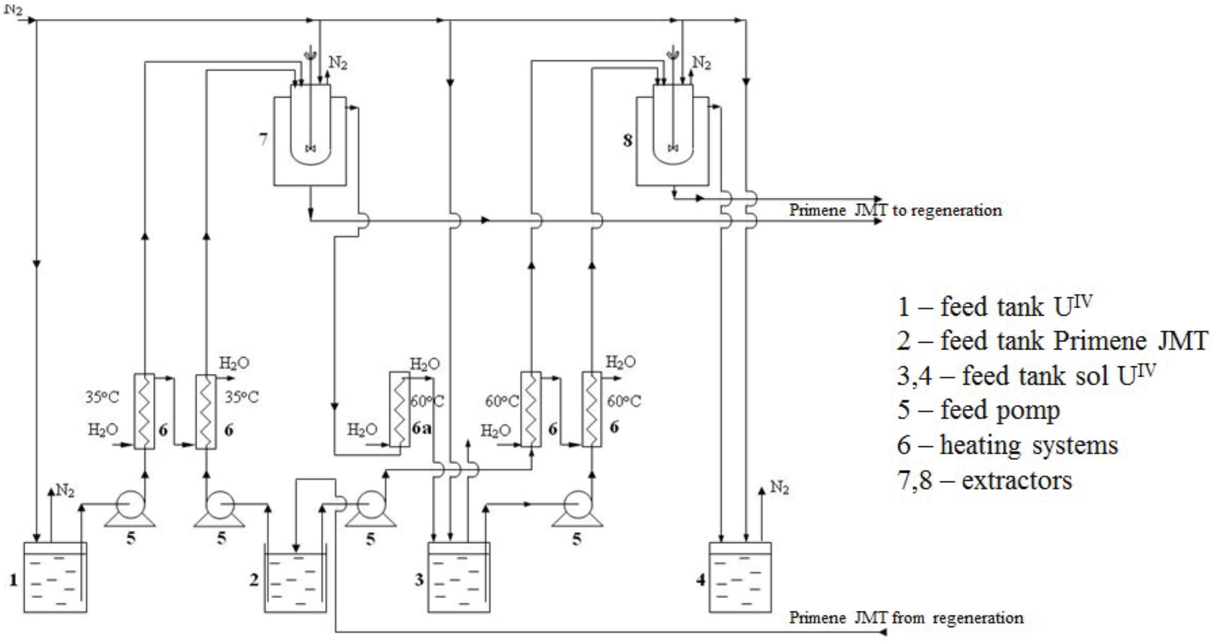

Fig.2. Equipment for producing concentrated (> 1 M) urania sol by nitrate extraction.

erations of advanced ceramics, including high-temperature superconductors, hydroxyapatite, Li-containing spinels, layered oxides for cathodes in Li-ion batteries, and TiO_2 and other titanates such as Li_2TiO_3 for breeding blankets in fusion reactors [15,16]. The application of the CSGP allowed us to obtain concentrated (*ca.* 1 M) uranium-ascorbate sols directly from U(VI) compounds without the laborious step of reduction of UO_2^{2+} to U^{4+}. Solid uranium trioxide and a solution of uranyl nitrate were used as precursors. The flowchart for the production of microspheres is presented in Fig.3. Aqueous ammonia was added to facilitate formation of an emulsion in 2EH. The time of gelation was much longer (0.5 h) than that for classic sols.

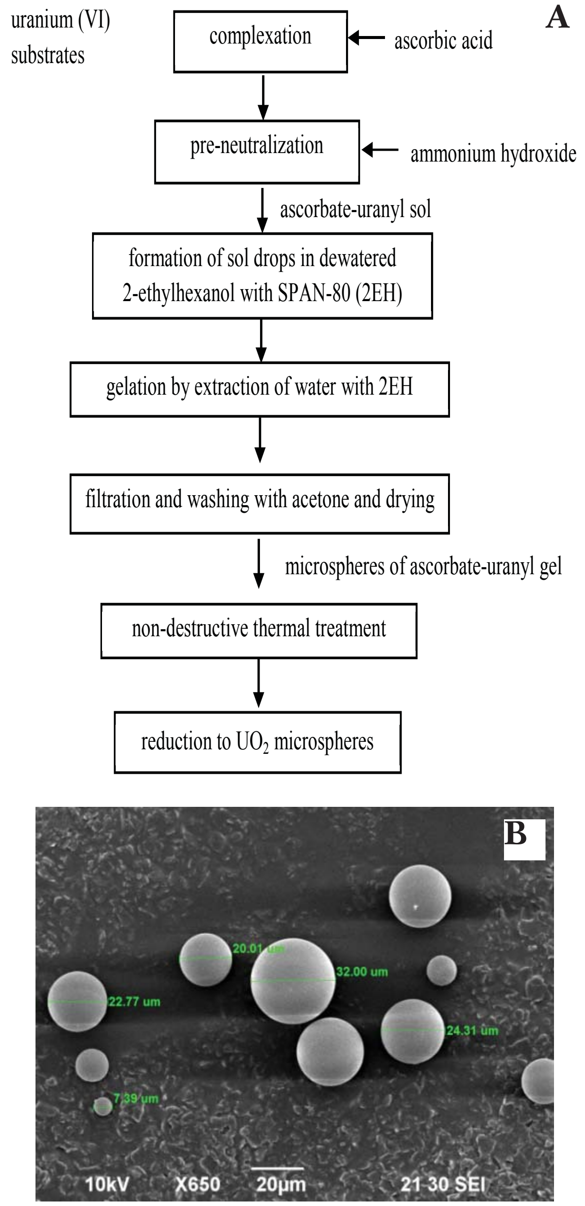

Fig.3. Flowchart (A) of preparation of uranium dioxide by CSGP in the form of microspheres (B) of diameter < 120 μm.

The thermal treatment of gels was based on differential thermal analysis (DTA) and thermogravimetric analysis (TG). The first weight loss at 100-350°C for all the gels was connected with evaporation of bonded as molecular water and hydroxide groups. For gels prepared from uranyl nitrate, it also reflected violent decomposition of the U-ASC-NO_3-NH_4OH complex, with strong exothermic effect at *ca.* 250°C. The next weight loss, with a broad exothermic effect at 350-550°C, was connected with the combustion of ASC and the products of its decomposition. This step was generally similar to that observed for the gels derived from UO_3. However, the temperature of final weight stabilization to U_3O_8 was increased by *ca.* 100°C (Fig.4).

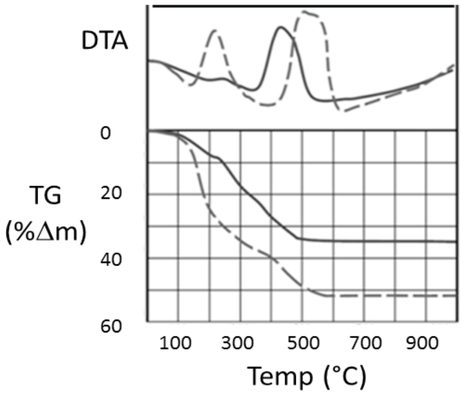

Fig.4. DTA and TG of ascorbate-uranyl gels obtained from uranium trioxide (solid line) and uranyl nitrate (dashed line).

Thermal analyses of gels produced from uranyl nitrate revealed the thermal decomposition to be a complex process that required special procedures to avoid strong exothermic reactions.

Figure 5A shows the three-step process of calcination of nitrate-derived gels, which eliminated violent exothermic effects and preserved the spherical shape of the grains. When uranium trioxide was used, this three-step process could be avoided, and a simple calcination process with 5°C/min heating rate up to 650°C could be applied. Final reduction of the material to UO_2 required the special conditions shown in Fig.5B. XRD analyses indicated after the calcination step only one phase was observed – U_3O_8 (Fig.5A) – and only one phase after reduction – UO_2 (Fig.5B).

We also demonstrated that doping of surrogates of minor actinides (*e.g.* Nd as the surrogate of Am) into UO_2 powders could be easily realized by CSGP. $Nd(NO_3)_3$ was added to the sol in the concentrations of 10-40 at.% of Nd to U. The resulting ascorbate-uranyl-neodymium sols were gelled to microspheres in a process similar to that used for pure uranium gels. XRD patterns of final products indicated that only the UO_2 phase was present. Therefore, the Nd was distributed uniformly.

UO_2 microspheres were produced in diameters ≤ 150 μm and 200-1500 μm. First, a modification of the ORNL variant for water extraction from U(IV) nitrate sol was developed. To eliminate the necessary reduction of U(VI) to U(IV), a novel sol-gel process (a variant of the CSGP) was developed [16]. Perfect microspheres of UO_2 were produced on a laboratory scale.

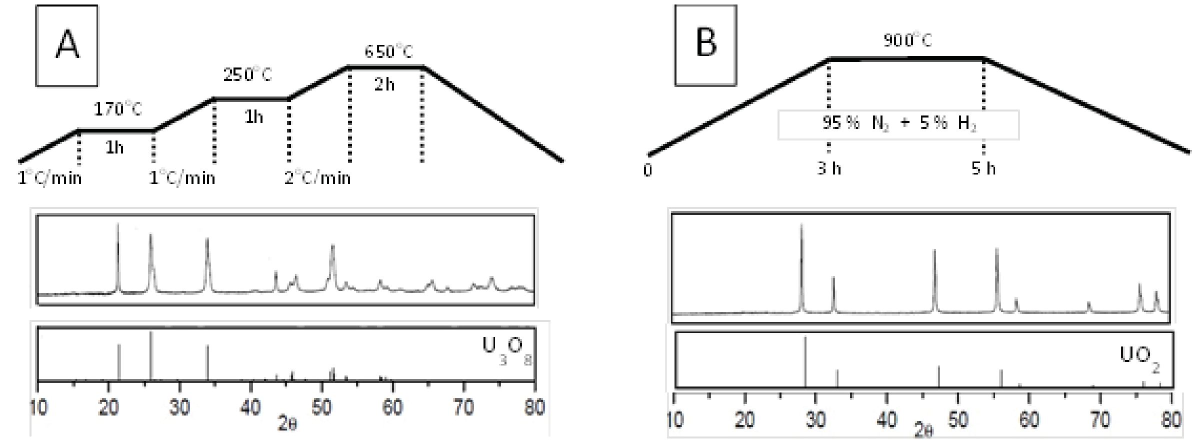

Fig.5. Flowcharts of calcination and reduction steps with XRD analysis of products obtained.

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LABELLED ANTIBIOTICS AS POTENTIAL RADIOPHARMACEUTICALS FOR INFECTION IMAGING

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Scintigraphic imaging of infection and inflammation is a powerful diagnostic tool in the management of patients with infectious or inflammatory diseases. Radiolabelled leukocytes are still considered the gold standard to detect infectious and inflammatory lesions in patients. However, their preparation is time-consuming, laborious and has risk associated with handling of potentially contaminated blood. There is still a great interest in the development of new radiopharmaceuticals for infection imaging.

Technetium-99m is the most widely used diagnostic radionuclide due to its nearly ideal nuclear properties (low radiation dose to the patient, optimum gamma-energy profile, short physical and biological half-lives), rich coordination chemistry [1,2] and easy commercial availability *via* generators.

Ciprofloxacin (CF), a fluoroquinolone antibiotic (Fig.1A), is incorporated by bacteria and binds to and inhibits DNA gyrase [3-5]. The other antibiotic, ceftriaxone (CFTX, Fig.1B), belongs to the third generation cephalosporins and is used against the majority of aerobic and anaerobic gram-positive and gram-negative pathogenic bacteria that cause infections in lower respiratory tract or skin and bone infections [6-8].

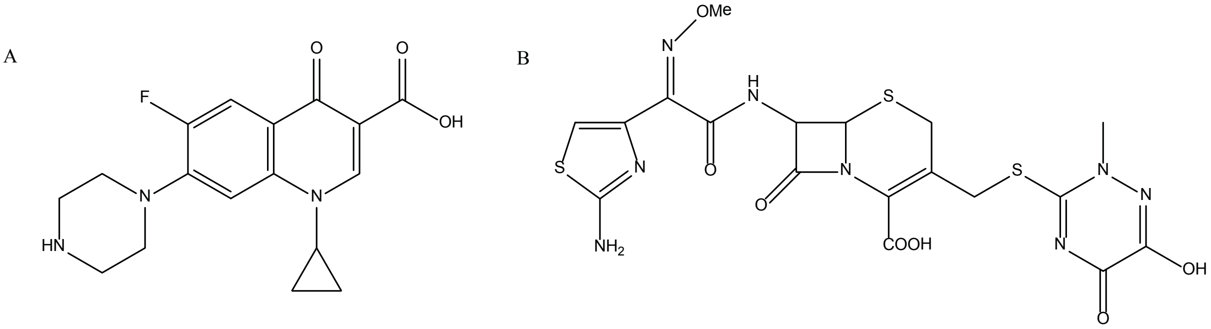

Fig.1. Chemical structure of ciprofloxacin (A) and ceftriaxone molecule (B).

The aim of this work was to label ciprofloxacin and ceftriaxone with technetium-99m, to determine the best condition for labelling, to test the stability of labelled products, and to obtain a ready-to-use single-vial kit of antibiotic.

Each vial contained 0.5-2 mg lyophilized ciprofloxacin and 50-100 μg of stannous chloride as a reducing agent. The labelling was done by adding 1 mL of freshly eluted $^{99m}TcO_4^-$, then the vial was shaken virgorously and heated at 90°C for 15 min. In the case of ceftriaxone, a lyophilized vial kit contained 10-30 mg of sodium salt of ceftriaxone and 50-100 μg of stannous chloride. Ceftriaxone was labelled with ^{99m}Tc as described above but instead of heating the mixture was left standing at room temperature for 30 min.

Radiochemical purity was determined by TLC (thin layer chromatography) technique using silica gel-coated fiber glass sheets. All radioactive substances were spotted on the strip. To determine reduced/hydrolysed $^{99m}TcO_2$ (colloid) and free $^{99m}TcO_4^-$, two mobile phases were used: (1) acetone and (2) a solvent mixture of ethanol : water : ammonium hydroxide (2:5:1). In the system (1) free $^{99m}TcO_4^-$ migrated with the front of the mobile phase, $R_f \approx 1.0$, while a colloid and ^{99m}Tc-CF or ^{99m}Tc-CFTX were found at the origin, $R_f \approx 0.0$ (Fig.2A). The second strip was developed in the system (2) where the colloid remained at the origin, while the labelled product and free $^{99m}TcO_4^-$ moved with the solvent, $R_f \approx 1.0$ (Fig.2B). The distribution of radioactivity on the strip was determined using home-made automatic TLC analyser SC-05 (INCT) or Cyclone® Plus storage phosphor system (PerkinElmer). The radiochemical yield of the labelled antibiotics was higher than 92%.

In this study ciprofloxacin and ceftriaxone were labelled with ^{99m}Tc with high radiochemical yield and high purity. The optimum labelling yield was achieved when 1 mg of CF (or 20 mg of CFTX) and 80 μg of $SnCl_2$ were used. Both labelled compounds were stable up to 24 h in 10 mM histidine or cysteine solution and in human serum, with a very slow release of free $^{99m}TcO_4^-$, up to 5%.

In conclusion, the formulated kits are handy to use. The determined physicochemical properties of ^{99m}Tc-ciprofloxacin and ^{99m}Tc-ceftriaxone can be an important basis for futher consideration of the labelled antibiotics as a useful tool in the early detection and treatment of a wide variety of deep-seated bacterial infections.

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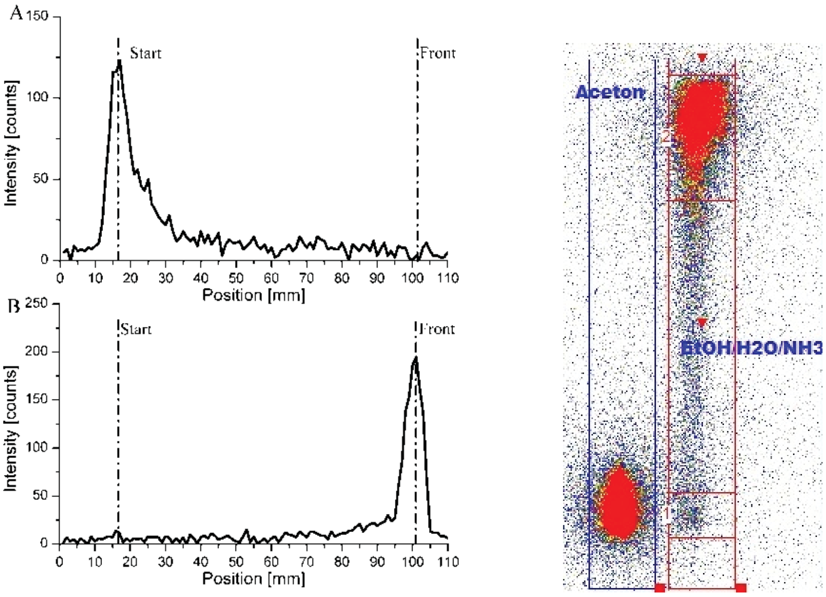

Fig.2. TLC analysis of ^{99m}Tc-CF (left) in (A) acetone and (B) ethanol:water:ammonium hydroxide (2:5:1) mobile phases and ^{99m}Tc-CFTX (right).

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LAPATINIB LABELLED WITH ^{68}Ga FOR PET DIAGNOSIS

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At present, intensive development of nuclear medicine in the field of cancer diagnosis and therapy takes place. The most important diagnostic and therapeutic radiopharmaceuticals which selectively distribute within given tissues or organs are formed by coordination compounds with diagnostic or therapeutic radiometal firmly attached to selected biologically active molecule (BM).

Breast cancer is the second leading cause of deaths in women and is the most common cancer among them. One third of women affected by breast cancer die due to this ailment [1]. Studies show that approximately more than 30% of breast cancer patients have tumours that are human epidermal growth factor receptor 2 (Her-2) positive [2]. Her-2 overexpression is associated with increased tumour growth, increased rate of metastasis and decreased overall survival rate of the patient. Overexpression of Her-2 can be a prognostic biomarker for breast [3], ovarian [4,5], bladder [6] and lung [7] carcinomas. In breast cancer it can be also a predictive biomarker for stratification of patients for Her-2-targeted therapies with anticancer drugs Herceptin or Tykerb [2]. Herceptin is a Her-2-specific drug (containing the humanized IgG1 monoclonal antibody, trastuzumab, mAb) approved for use by the U.S. Food and Drug Administration (FDA) in September 1998. Tykerb (in Europe named also Tyverb) which contains lapatinib di-*p*-toluenesulphonate, is a second Her-2-specific drug approved for use by the FDA in 2007. Lapatinib molecule (Fig.1A) enters into the cell interior (the part of lapatinib molecule, responsible for its interaction with Her-2 receptor, is 4-anilinequinazoline fragment [8]), binds with intracellular parts of Her-2 and Her-1 receptors and inhibits receptors ability to accelerate cell transformation, cell growth and division [9].

The aim of this work was to synthesize a conjugate containing an inert Ga-68 complex as a label, and lapatinib as the biologically active molecule (Fig.1B), and then to determine physicochemical properties of the conjugate, important from the radiopharmaceutical point of view. It was expected that lapatinib labelled with Ga-68 may serve as a diagnostic receptor radiopharmaceutical, used in PET (positron emission tomography) method for determination of Her-2 overexpression in patients suffering from breast cancer of the Her-2-positive type. Lapatinib labelled with Ga-68 may become an imaging agent superior to both [^{11}C]Lapatinib [10] and [^{18}F]Lapatinib [11] compounds, because of easier availability of gallium-68 radionuclide (from the portable ^{68}Ge-^{68}Ga generator) than that of positron-emitting radionuclides C-11 and F-18, as well as easier synthesis routes of potential lapatinib-based radiopharmaceuticals containing these radionuclides [10,11].

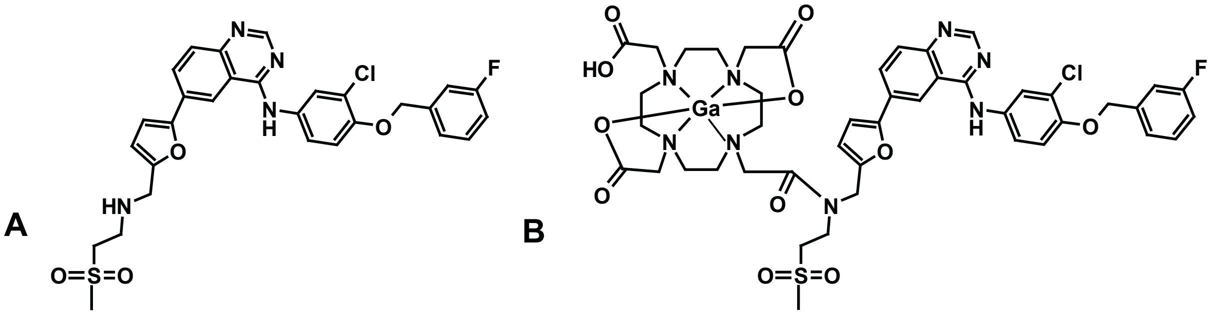
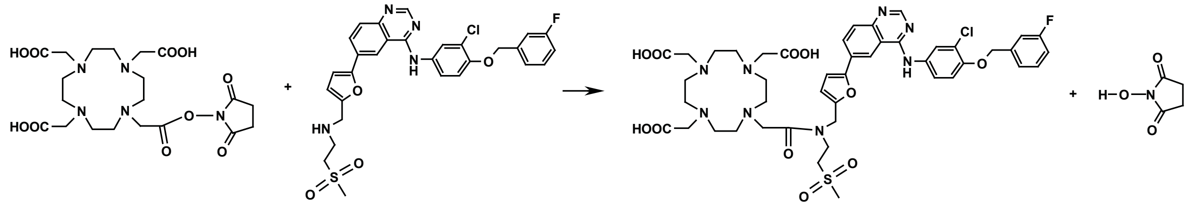


Fig.1. Lapatinib molecule (A) and conjugate ^{68}Ga-DOTA-lapatinib (B).

The coupling reaction of 2.57 mg (3.41 μmol) of DOTA-NHS (1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid mono-N-hydroxysuccinimidyl ester) with 1.32 mg (2.27 μmol) of lapatinib was performed in DMF solution in the presence of 1.27 μl (9.08 μmol) of Et_3N (Scheme 1) at 50°C. Crude product DOTA-lapatinib was purified on a semi-preparative HPLC column (system 1), then alkalized and lyophilized, with the yield of *ca.* 45%.

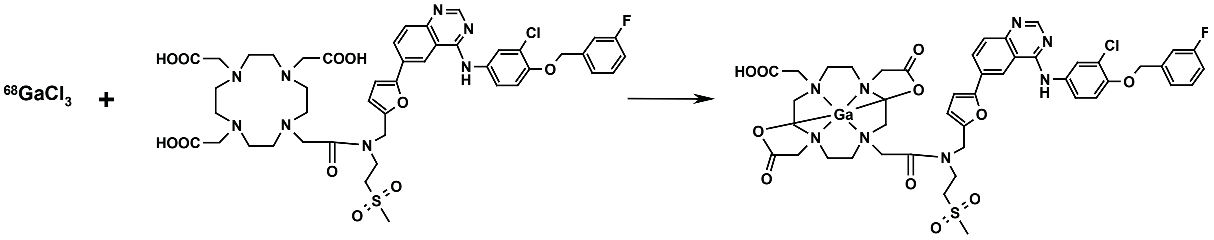
MS: m/z: calcd. – 967.40, found – 967.41 [M+H$^+$].

The ^{68}Ga-DOTA-lapatinib conjugate was synthesized according to Scheme 2. To the vial containing about 50 μg of lyophilized DOTA-lapat-



Scheme 1. Coupling reaction of DOTA with lapatinib molecule.

inib, 300 µL of acetate buffer (pH = 5.89) and 50÷100 µL of $^{68}GaCl_3$ eluate from the ^{68}Ge-^{68}Ga generator (70÷100 MBq) were added. The eluate was previously concentrated using a cation exchange column. The reaction mixture was heated for 30 min at 95°C. The reaction progress was checked by TLC (thin layer chromatography) and HPLC (system 2) methods. The radiochemical yield of the synthesized conjugate was higher than 98%.



Scheme 2. Synthesis of ^{68}Ga-DOTA-lapatinib conjugate in n.c.a. scale.

In order to verify the identity of the ^{68}Ga-DOTA-lapatinib conjugate synthesized in n.c.a. scale with the non-radioactive reference compound, the Ga-DOTA-lapatinib conjugate was prepared in milligram scale, isolated by HPLC method and characterized by MS (mass spectrometry) analysis.

TLC analyses were performed using Merck 60 F_{254} aluminum sheets. All radioactive substances were placed on the strip, developed with appropriate solutions and dried. Distribution of radioactivity on the strip was determined using home-made automatic TLC analyser SC-05 (INCT). The lipophilicity of ^{68}Ga-DOTA-lapatinib conjugate isolated from the reaction mixture (HPLC, system 3) was characterized by determination of the logarithm of its partition coefficient, log P, in the *n*-octanol/PBS (pH 7.40) system. Stability of the isolated conjugate was investigated (HPLC, system 3) both as a function of time and in challenge experiments (in the presence of excess of histidine or cysteine), as well as in human serum.

Conditions of the HPLC systems were the following:

System 1: Phenomenex Jupiter Proteo semi-preparative column (4 µm, 90 Å, 250 x 10 mm), UV/Vis detector (220 nm); elution conditions: solvent A – water with 0.1% TFA (v/v), solvent B – acetoni-

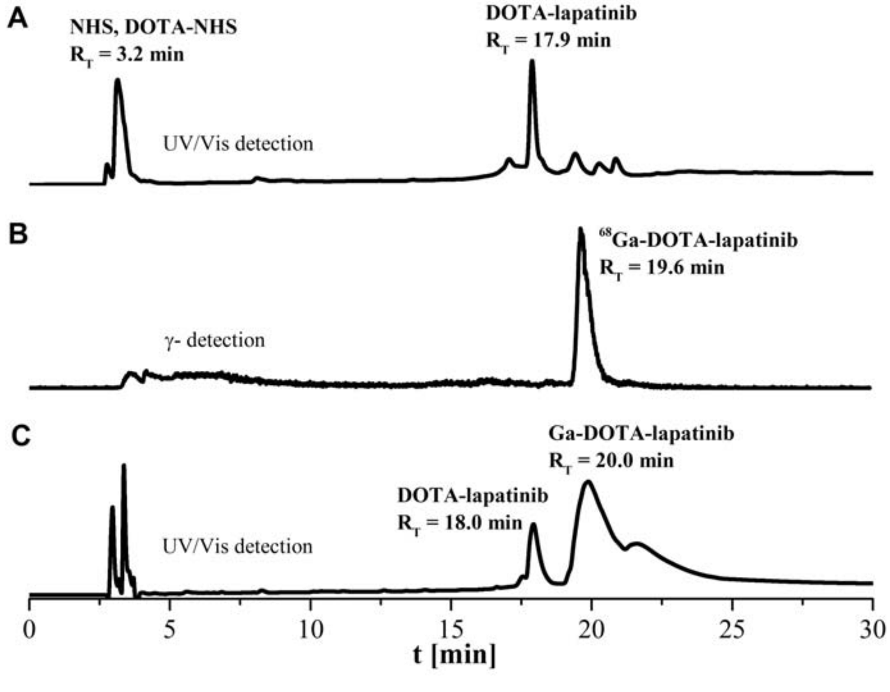


Fig.2. The HPLC analyses (performed in system 3) of the reaction mixtures after synthesis of DOTA-lapatinib (A), ^{68}Ga-DOTA-lapatinib (B) and Ga-DOTA-lapatinib (C) conjugates prepared in this study.

trile 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: Phenomenex Jupiter Proteo analytical column (4 μm, 90 Å, 250 x 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.

System 3: Supelcosil^{TM}-LC-18 analytical column (5 μm, 120 Å, 250 x 4.6 mm), UV/Vis detector (220 nm) or 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.

The HPLC chromatograms of the compounds DOTA-lapatinib (system 3, UV/Vis detection, R_T = 17.9 min), ^{68}Ga-DOTA-lapatinib (system 3, gamma detection, R_T = 19.6 min) and Ga-DOTA-lapatinib (system 3, UV/Vis detection, R_T = 20.0 min), synthesized in this study, are shown in Fig.1. The conjugate ^{68}Ga-DOTA-lapatinib (Fig.1B) is formed with high yield and high purity. The non-radioactive reference conjugate Ga-DOTA-lapatinib (Fig. 1C) isolated from the reaction mixture was characterized by MS. Almost the same R_T values of ^{68}Ga-DOTA-lapatinib and Ga-DOTA-lapatinib conjugates confirmed the existence of the ^{68}Ga-DOTA--lapatinib conjugate in the reaction mixture in n.c.a. scale.

MS (Ga-DOTA-lapatinib): m/z: calcd. – 1035.10, found – 1035.14 [$M+H^+$].

The studied ^{68}Ga-DOTA-lapatinib conjugate exhibited high stability. After 5 h of incubation in 10 mM histidine or cysteine solution and in human serum the obtained HPLC chromatograms have shown mainly the existence of only one radioactive species in the solution, with the retention time characteristic for the studied conjugate. Thus, we can consider that the conjugate does not undergo any ligand exchange reaction with amino acids or other strongly competing natural ligands containing SH or NH groups. Stability studies of the ^{68}Ga-DOTA-lapatinib conjugate in human serum confirmed that the conjugate containing the non-peptidic synthetic compound lapatinib does not undergo the enzymatic biodegradation. The measurements of radioactivity of both the supernatant and precipitate (protein) fractions indicated that the percentage of ^{68}Ga-DOTA-lapatinib conjugate which has been bound by the serum components was in the range of 7-12%, while about 88% of the studied conjugate remained in the serum in the unchanged form.

The lipophilicity value of the ^{68}Ga-DOTA-lapatinib conjugate, appropriate for distribution in the body, was found to be 0.60 ± 0.14.

In conclusion, one can say that the physicochemical properties of the ^{68}Ga-DOTA-lapatinib conjugate can be an important basis for further consideration of the conjugate as a potential diagnostic radiopharmaceutical. Taking into account that the coupling of the radionuclide complex with lapatinib molecule (*via* amine group located near methylsulphonyl group) does not change its biological properties [12], one can conclude that the ^{68}Ga-DOTA-lapatinib conjugate may be considered a promising diagnostic radiopharmaceutical for patients suffering from breast cancer of Her-2 type. From the view-point of application in nuclear medicine, it is important to note that the ^{68}Ga-DOTA-lapatinib conjugate can easily be synthesized in hospital laboratories using portable ^{68}Ge-^{68}Ga generators and the previously prepared lyophilized kit formulations. It can be thus a useful tool for stratification of patients for the so-called personalized therapy.

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CATIONIC TRICARBONYLRHENIUM(I) COMPLEXES WITH *N*-METHYL-2-PYRIDINECARBOXYAMIDE – SYNTHESIS, STRUCTURE AND SPECTROSCOPIC CHARACTERIZATION

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Tricarbonylrhenium(I) complexes with one bidentate and one monodentate ligand (so-called '2+1' system) still remain an interesting field to explore. Besides their possible applications in medicine [1,2], the rhenium(I) tricarbonyl complexes in a '2+1' layout are widely studied because of their excellent photophysical and photochemical properties [3-6]. For the synthesis of tricarbonylrhenium(I) complexes, commercially available pentacarbonylrhenium(I) compounds, $\mathrm{Re(CO)_5X}$ (X = Cl, Br), are increasingly used.

In the present study we have chosen the bidentate ligand *N*-methyl-2-pyridinecarboxyamide ($\mathrm{NC_5H_4}$-CO-NH-$\mathrm{CH_3}$, LH*(Me)*), the amide derivative of picolinic acid. This compound contains three potential donor atoms: the nitrogen atom from the aromatic ring, the oxygen atom from the carbonyl group and the nitrogen atom from the amide part. In spite of the three donor atoms, only the bidentate mode of complexation to metal ions is possible. However, amide ligands derived from picolinic acid are known to bind metal ions either in the amide form (as a neutral *N*,*O*-donor) or in the amidate manner (as an anionic *N*,*N*-donor) after releasing the amide proton [7,8]. Both types of coordination of the *N*-methyl-2-pyridinecarboxyamide ligand can be found for the $[\mathrm{Re(CO)_3(LH}(Me)_{\mathrm{NO}})\mathrm{X}]$ (X = Cl, Br and I) and $[\mathrm{Re(CO)_3(L}(Me)_{\mathrm{NN}})\mathrm{Y}]$ (Y = imidazole (Him) and 3,5-dimethylpyrazole (Hdmpz)) complexes reported previously [9-11]. The synthesis and the structures of two new cationic tricarbonyl complexes of rhenium(I) with the bidentate ligand *N*-methyl-2-pyridinecarboxyamide and one of monodentate heterocyclic molecules like imidazole and 3,5-dimethylpyrazole are presented in this work.

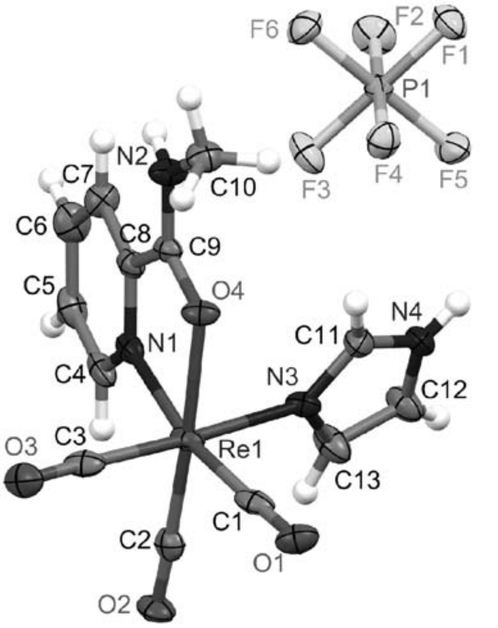

Fig.1. Molecular structure of $[\mathrm{Re(CO)_3(LH}(Me)_{\mathrm{NO}})\mathrm{(Him)]PF_6}$ compound (**1**) with the atom numbering scheme, plotted with 50% probability displacement ellipsoids.

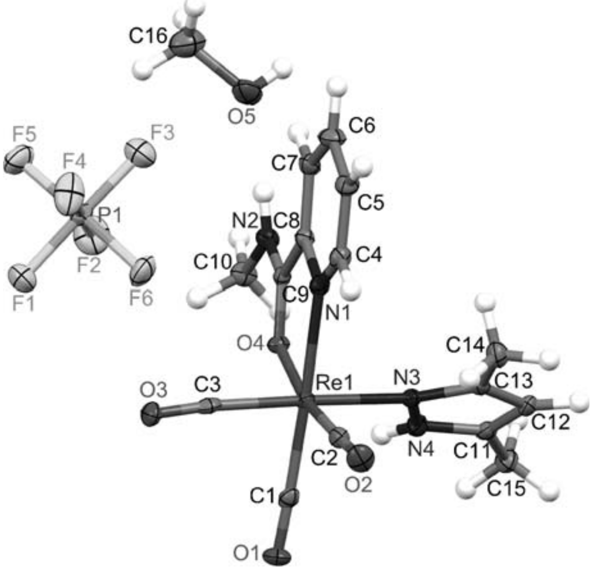

Fig.2. Molecular structure of $[\mathrm{Re(CO)_3(LH}(Me)_{\mathrm{NO}})\mathrm{(Hdmpz)]PF_6 \cdot CH_3OH}$ compound (**2**) with the atom numbering scheme, plotted with 50% probability displacement ellipsoids.

The structures of $[\mathrm{Re(CO)_3(LH}(Me)_{\mathrm{NO}})\mathrm{(Him)]PF_6}$ (**1**) and $[\mathrm{Re(CO)_3(LH}(Me)_{\mathrm{NO}})\mathrm{(Hdmpz)]PF_6 \cdot CH_3OH}$ (**2**) compounds (Figs.1 and 2) were determined at a temperature of 100 K by single crystal X-ray diffraction on an Agilent Technologies SuperNova (dual source) diffractometer equipped with an Eos CCD detector, using microfocus Mo Kα radiation ($\lambda = 0.7107$ Å). Crystallographic parameters and refinement details for the new complexes are presented in Table 1.

The complex **1** was synthesized by refluxing a methanol solution of $\mathrm{Re(CO)_5Cl}$ with *N*-methyl-2-pyridinecarboxyamide and imidazole after previous precipitation of AgCl by means of $\mathrm{AgPF_6}$. The volume of this solution was decreased in a desiccator under reduced pressure. A yellow crystalline material was obtained when storing the solution for a few weeks in a refrigerator. Similar synthetic route was applied for the complex **2** for which 3,5-dimethylpyrazole was used instead of imidazole. Both syntheses were carried out in a PFA flask to avoid possible contamination with $\mathrm{SiF_6^{2-}}$ anions caused by dissolution of a glass material *via* the presence of $\mathrm{PF_6^-}$ ions [12].

In contrast to the tricarbonylrhenium(I) complexes with the bidentate *N*-methyl-2-pyridine-

Table 1. Crystallographic data and structure refinement parameters for the studied complexes **1** and **2**.

	Complex **1**	Complex **2**
Formula	$C_{13}H_{12}F_6N_4O_4PRe$	$C_{16}H_{20}F_6N_4O_5PRe$
Formula weight	619.44	679.5
T [K]	100(2)	100(2)
λ (Mo Kα) [Å]	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P\ 2_1/c$	$C\ 2/c$
a [Å]	6.8616(2)	24.0660(4)
b [Å]	9.5107(2)	12.27781(14)
c [Å]	29.0090(7)	15.5955(2)
β [°]	92.906(3)	104.2013(14)
V [Å]	1890.65(9)	4467.31(11)
Z	4	8
D_{calc} [g·cm^{-3}]	2.176	2.021
μ [mm^{-1}]	6.598	5.597
F (000)	1176	2624
Reflections collected	12257	8136
Independent reflections	3312	3924
R_{int}	0.0250	0.0235
Data/restraints/ parameters	3312/0/271	3924/0/314
Final R indices [I > 2σ(I)]	R_1 = 0.0302 wR_2 = 0.0586	R_1 = 0.0211 wR_2 = 0.0508
GOF	1.281	1.071
Largest differences in peak/hole [e·Å^{-3}]	1.335/-0.997	1.262/-0.507

carboxyamide ligand, presented earlier [9-11], the compounds **1** and **2** form cationic metal complexes (Figs.1 and 2) neutralized by hexafluorophosphate ion. In addition, the presented $[Re(CO)_3(LH(Me)_{NO})(Hdmpz)]PF_6$ compound crystallizes with one solvent molecule (methanol). The metal ion in these complexes is surrounded by six donor atoms including three carbon atoms, one oxygen and two nitrogens in a slightly distorted octahedral geometry. The three CO ligands occupy the facial position of this octahedron. Contrary to the compounds of the $[Re(CO)_3(L(Me)_{NN})Y]$ (Y = Him and Hdmpz) type, but similarly to the $[Re(CO)_3(LH(Me)_{NO})X]$ (X = Cl, Br and I) species, *N*-methyl-2-pyridinecarboxyamide in **1** and **2** behaves as a neutral ligand which chelates the rhenium(I) ion by means of nitrogen and oxygen atoms, forming a five-membered ring. The sixth coordination site at the metal centre is occupied by the N atom of heterocyclic molecule (Him or Hdmpz). The charge of both complexes is equal to +1.

The geometric parameters (Table 2) for the presented tricarbonylrhenium(I) complexes, originating from the crystal structure determinations, are in agreement with quantum mechanical calculations performed at the DFT level of theory with the use of B3LYP functional and basis sets: 6-31G(d,p) for H, C, N and O atoms and LANL2DZ for Re atom by means of Gaussian program [13]. In the case of the studied compounds, the molecular structures of $[Re(CO)_3(LH(Me)_{NO})(Hdmpz)]^+$ and $[Re(CO)_3(LH(Me)_{NO})(Him)]^+$ ions were included in the optimization. In most cases the differences between the experimental and theoretical bond lengths are no larger than 0.05 Å, with a clear tendency for a bit slightly shorter experimental distances.

Table 2. Selected bond lengths [Å] and angles [°] for complexes **1** and **2**, obtained from experiments and DFT calculations.

	Complex **1**		Complex **2**	
	exp.	calcd.	exp.	calcd.
Re1-C1	1.925(6)	1.937	1.926(4)	1.937
Re1-C2	1.893(5)	1.909	1.892(4)	1.910
Re1-C3	1.926(6)	1.937	1.928(4)	1.936
Re1-N1	2.197(5)	2.227	2.183(3)	2.228
Re1-O4	2.151(3)	2.208	2.150(2)	2.216
Re1-N3	2.168(4)	2.234	2.191(3)	2.238
C9-O4	1.264(6)	1.258	1.252(4)	1.260
C9-N2	1.319(7)	1.335	1.303(4)	1.334
C10-N2	1.449(7)	1.464	1.472(4)	1.464
N1-Re1-O4	74.32(14)	73.11	74.14(9)	73.13
N1-Re1-N3	81.27(16)	86.56	87.69(10)	87.64
O4-Re1-N3	84.54(14)	83.40	79.59(9)	80.98
N3-Re1-C1	90.8(2)	90.55	91.42(11)	89.94
N3-Re1-C2	95.18(19)	92.62	93.59(12)	95.89
O1-C1-Re1	177.8(5)	177.84	177.3(3)	178.03
O2-C2-Re1	177.9(5)	175.86	177.6(3)	177.10
O3-C3-Re1	178.3(5)	179.20	175.3(3)	178.95

The molecular packing in **1** is stabilized by the presence of intermolecular hydrogen bonds of 2.935(6) Å (N2−H···F6), 2.970(6) and 3.031(6) Å (N4−H···F5). Moreover, the PF_6^- ions form characteristic two-dimensional grids with two short distances of 2.794(4) Å (F6···F6), 2.880(4) Å (F4···F4), and one longer distance of 3.369(5) Å (F5···F5) between neighbouring anions. The crystal structure of **2** is stabilized by the formation of hydrogen bonds of 2.796(4) Å (N2−H···O8), 2.841(4) Å (O8−H···F4), 3.147(6) Å (O8−H···F1) and 3.142(4) Å (N4−H···F2), caused by the presence of methanol molecules and hexafluorophosphate anions in the crystal lattice.

The presence of a few very strong bands in the infrared absorption spectra in the range 1850-2050 cm^{-1} for the studied complexes, originating from the coordinated CO ligands, is characteristic for the formation of a tricarbonyl core around the rhenium atom. Moreover, the C=O stretching vibration, observed at around 1674 cm^{-1} in the uncoordinated ligand, is found to be shifted to 1647 and 1645 cm^{-1} for **1** and **2**, respectively. The main bands belonging to the hexafluorophosphate ion are located at 851 and 559 cm^{-1} in **1**, and at 845 and 559 cm^{-1} in **2**, just as for other compounds containing these anions [14]. The characteristic three carbons of the facial carbonyl groups appear in the downfield region around 197-193 ppm in the ^{13}C NMR spectra of the complexes. The signal of the carbon belonging to the C=O group of the *N*-methyl-2-pyridinecarboxyamide ligand, observed at 167.3 ppm for free compound, is shifted to 174.5 and 174.4 ppm in the complexes, which shows its coordination to the tricarbonylrhenium(I) core. In general, the electronic absorption spectra of the studied complexes show intense absorptions below 300 nm. In addition, for both compounds a band with lower intensity can also be observed in the 300-350 nm region. For comparison, a maximum of absorption at 265 nm can be observed for the pure *N*-methyl-2-pyridinecarboxyamide ligand. Time-dependent DFT/CAM-B3LYP calculations for the absorption spectra of the studied complexes in simulated solvent (methanol) by applying the polarizable continuum model (IEFPCM) are in reasonable agreement with the experimental data. The results presented in Table 3 correspond to the lowest energy singlet excitations. In the case of compounds **1** and **2**, only the HOMO has a mixed Re/monodentate ligand/CO character, while the HOMO-1 does not possess any component from the Hdmpz or Him molecule. The LUMO of both complexes is predominantly the π* orbital of the bidentate ligand. According to the TD-DFT calculations, the lowest energy transitions in the case of complexes **1** and **2** involve the promotion of an electron, mainly from the HOMO and HOMO-1 to the LUMO (Table 3). On the basis of calculated orbital contours (Fig.3) it can be concluded that the lowest-lying electronic transitions of complexes **1** and **2** have a mixed metal-to-ligand (Re → bidentate ligand; MLCT) and ligand-to-ligand (monodentate ligand → bidentate ligand; LLCT) charge transfer character.

Table 3. The highest wavelength absorption data from calculations (TD-DFT) and experiments for the studied complexes.

Complex	Calcd.			Exp.
	λ [nm]	oscillator strength	main components [%]	λ [nm]
1	315.3	0.0688	H→L (79), H-1→L (13)	335
	309.0	0.0490	H-1→L (73), H→L (12)	
2	321.7	0.0906	H→L (90)	347
	307.8	0.0160	H-1→L (80)	

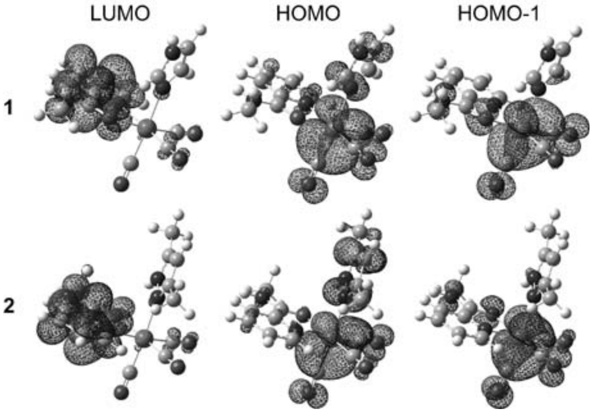

Fig.3. Orbital contours of the lowest energy transitions for the studied tricarbonylrhenium(I) complexes.

The presented structures of the tricarbonylrhenium(I) complexes are characterized by the octahedral arrangement of donor atoms around the metal ion and by the formation of the *fac*-[Re(CO)$_3$]$^+$ core. The three remaining positions in the core are occupied by the chelating ligand and by the monodentate ligand, which results in formation of the so-called ‘2+1’ system. The use of the heterocyclic monodentate ligand in the reaction mixture together with the bidentate ligand (*N*-methyl-2-pyridinecarboxyamide) in the presence of hexafluorophosphate anions leads to the formation of cationic tricarbonylrhenium(I) complexes: [Re(CO)$_3$(LH(*Me*)$_{NO}$)Y]$^+$ (Y = Him, Hdmpz) in the form of PF_6^- salt. The *N,O*-coordination mode of the *N*-methyl-2-pyridinecarboxyamide ligand can be found in the studied compounds.

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SIMPLE CHARACTERISTICS OF CHIRALITY, π-ELECTRON DELOCALIZATION, AND VIBRATIONAL ACTIVITY OF BUILDING BLOCKS FOR CONDUCTING POLYMERS

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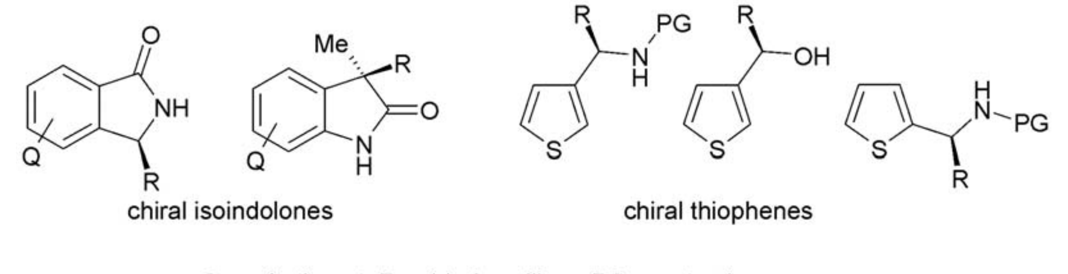
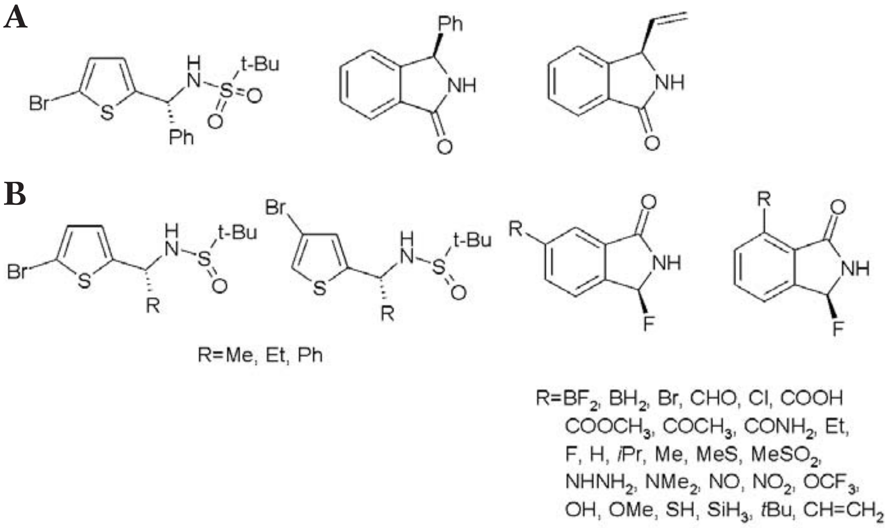
The significance of chiral compounds in modern chemistry, medical chemistry and material engineering cannot be overestimated. In 2001, the world market of enantiopure drugs was estimated to be worth USD 147 billion and (depending on the particular medical discipline) it has increased from 5 to 20% per year [1]. A lot of the cores of chiral drugs ("the actual drug in the drug" [2-5]) can play the role of the chiral monomers of chiral conductive polymers [6,7]. The importance of chiral polymers, such as enantioselective sensors [8], adsorbents, membranes, and phases [9], catalysts of asymmetric synthesis [10], or chiral electro-optic materials [11,12], is steadily increasing as well. A lot has already been written about conducting polymers [6-12]. However, so far chiral conductive polymers were reviewed only twice [6,13]. Thus, there is much room for research on the propagation of the properties of individual monomers into the properties of oligomers and various other structural types of polymers. One of the great potentials of chiral conducting polymers results from the possibile fluent control of their structure, for example by tuning using their electro-optic properties. In the second quarter of 2014, we started conducting experimental and computational studies within the National Science Centre (NSC) grant entitled "Chiral cores/monomers of drugs and conducting polymers: From calculations to experimental characteristics". The grant project was formulated in June 2013, *i.e.*, much before the Spectroscopy and Molecular Modelling Group was transferred to the Institute of Nuclear Chemistry and Technology (INCT). Thus, the grant goals are not directly connected to the Institute's mainstream activity. Possible connections to the INCT's prevailing activity are mentioned in the section "Conclusions".

The main idea of the grant is to predict, synthesize, and characterize chiral molecules (Scheme 1) that can either be the centres of new bioactive molecules of interest for medicinal chemistry, the monomers of new chiral conductive polymers, or play both roles simultaneously. The research team working in the INCT, the chemistry faculties of the University of Warsaw, Warsaw University of Technology, Siedlce University of Natural Sciences and Humanities, Jagiellonian University, National Medicines Institute and Mossakowski Medical Research Centre PAS, was focused in the first year of its activity on the computational prediction of the properties and asymmetric syntheses of the selected chiral compounds (Scheme 2).

In 2014, several substances were synthesized (Scheme 2A) and calculated (Scheme 2B). For the calculated systems, numerous physicochemical characteristics (such as vibrational circular dichroism spectra, chirality measures, HOMA (harmonic oscillator model of aromaticity) indices, sEDA and pEDA substituent effect descriptors) were determined. However, in this report we cover only the topic of our research that is related to the development of new tools for the characterization of both the chirality of the molecules and the electron delocalization in conducting polymers. The chirality characterization tools are based on chiral graph theory founded within the project [14] and the π-electron delocalization tools are based on the definition formula of the HOMA index [15,16] adapted to non-aromatic and acyclic systems [17,18]. Based on the chiral graph theory, we programmed the CHIGRA computer program that calculates the topological indices of chiral compounds based on the hypervertex approach [19]. To develop a simple tool for characterizing the electron delocalization in conducting poly-



Scheme 1. Types of compounds to be synthesized with the project.



Scheme 2. Compounds synthesized (A) and calculated (B) within the first stage of the project.

mers, both aromatic [17,20] and extended linear systems [17,18] were analysed.

The chiral graph theory and the CHIGRA program

The chirality of compounds can be evaluated using chirality measures [21] based on either the distance to an achiral reference [22], the distance to the second enantiomer [23], or on a topological index adapted to the chiral compounds [24]. The number assigned to the chirality measure is positive for a chiral structure and is null for an achiral structure. To distinguish enantiomers, we often use pseudomeasures that ascribe a sign to the measure. Recently, we introduced a consistent chiral graph theory [14]. It introduces the modified graphs containing information on chirality elements as defined by IUPAC [25]: chirality vertices, axes, planes, and additionally, the topological chirality of the molecule. The chiral graphs are defined using two equivalent approaches: hypervertex and hyperedge. Among other uses, graph theory in chemistry is used to produce topological indices: the numbers specific for a given substance. The chiral graph theory allows us to construct chiral matrices and chiral topological indices that are assignable to chiral graphs. The chiral matrices are derived from the chiral incidence matrix in which entries corresponding to chirality elements are represented by 5-tuple hypercomplex numbers. Standard operations on the chiral incidence matrix, formulated either in the hypervertex or hyperedge representation, allow obtaining chiral adjacency, valency, distance, Laplacian, Zagreb, and Randić matrices – all of which contain information on chiral elements present in the chiral graph. The definition of the algebra for hypercomplex numbers allows for distinguishing among the types of chirality elements present in the chiral topological indices unless the molecule is a *meso* form and the index becomes real.

The constructed chiral graph theory serves as a backdrop for the use of chiral topological indices in QSAR studies of chiral molecules. However, the formulas obtained within the theory are complicated, and for molecules that are of interest in medicinal chemistry, they need to be calculated

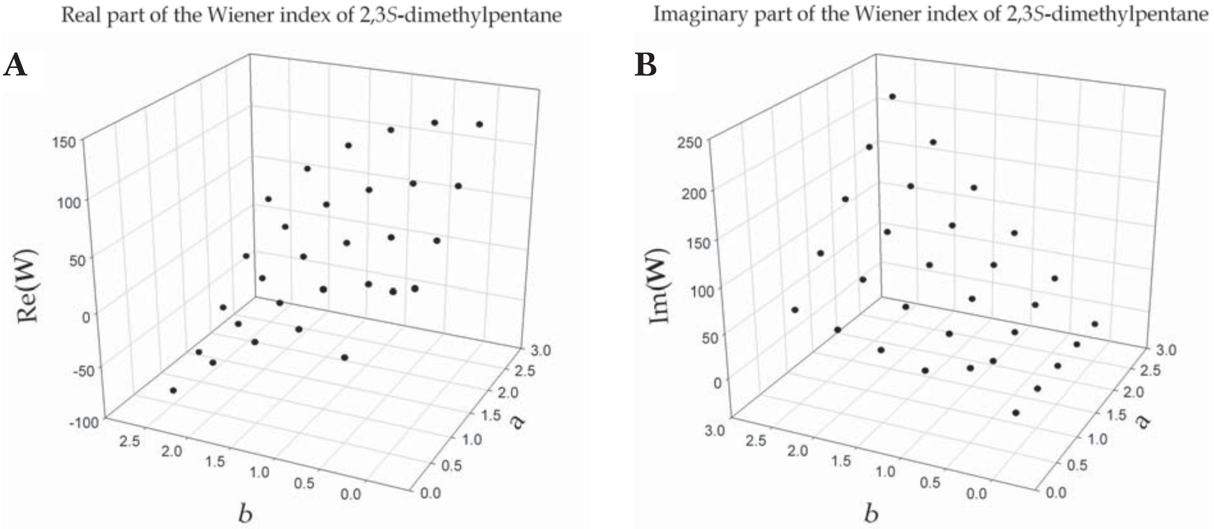


Fig.1. Variation of the real (A) and imaginary (B) parts of the Wiener index of the chiral graph of the 2,3*S*-dimethylpentane molecule with the change of real (a) and imaginary (b) parts of the (a+*i*b) entry assigned to the chiral 3*S* vertex in the chiral matrices [14].

using the appropriate software. This is why the CHIGRA computer program was developed [19]. The molecules are introduced into the program in the form of protein database (.pdb) files widely used in computational and structural chemistry. The chiral incidence matrix, adjacency, distance, Zagreb, and Randić matrices are then generated and the appropriate chiral topological Wiener, Zagreb 1, Zagreb 2, and Randić indices are calculated. The example of the results obtained for the Wiener index of the 2,3*S*-dimethylpentane molecule is presented in Fig.1. In the next stage of the grant, the chiral indices will be evaluated for their relevance in describing different properties of the chiral compounds considered in the study.

HOMA characteristics of the π-electron delocalization in linear systems

An aromaticity index assigns a number to the cyclic structures and evaluates the degree of π-electron delocalization in the analysed ring. The HOMA index [15,16] is one of the most elementary as well as most successful of aromaticity indices. The HOMA index estimates the geometric aspect of aromaticity using the following expression:

$$\mathrm{HOMA(R)} = 1 - \frac{a}{n} \cdot \sum_{i=1}^{n} (R_I - R_{opt})^2$$

where: R_i and R_{opt} – the distances of the i-th ring bond in the analysed structure and the reference optimal bond in benzene (1.388 Å), n – the number of CC bonds in the ring, $\alpha = 257.7$ Å^{-2} – a normalization factor guaranteeing that the unitless HOMA index of an aromatic compound approaches 1 and of that of its Kekulé non-aromatic structure approaches 0.

Looking for the characteristics of π-electron delocalization in conducting polymers, we realized that interlinking the HOMA index with aromaticity is caused by the minimization condition of the bond variance and the use of the benzene CC bond distance as a reference [17]. Also, we have shown that using the HOMA expression one can define a function in which the bond distance R is replaced by a p parameter such as, for example, the characteristics in the bond critical point (BCP) revealing another aspect of the bond. In this way a large variety of HOMA(p) indices can be generated [17].

Presenting HOMA(Rho) as a function of the HOMA(R) index (where: Rho – electron density in BCP, R – bond distance, α_{Rho} – set to 250) for a series of n-membered carbocyclic structures (n = 4-7), both aromatic and not, saturated, singly or doubly unsaturated, demonstrated an excellent quadratic correlation [17]. Thus, we came to the conclusion that this correlation reveals that the group of HOMA indices are not only the aromaticity indices, but they also reflect the much more general feature combining information on cyclicity, the degree of unsaturation, and the way rings condense in polycyclic systems. We proposed to call the generalization of the aromaticity the "savoricity" [17]. We also demonstrated that the index can probably be used for the characterization of linear systems.

First, we illustrated that several points deviate from the quadratic correlation found for the majority of carbocyclic systems [18]. This is the case for cyclic alkynes, cyclic polyynes, cyclic polyallenes, poly-spiro-cyclopropanes, as well as bicyclic systems cumulated with a cyclic alkyne ring. This suggests that the divergences are due to substantial ring strains. However, acyclic allenes and polyynes deviate from the main correlation as well. Thus, the cause of the deviation is more complex than a shear ring strain.

In the next step, we studied the changes of the HOMA(R) index for acyclic systems such as alkanes, polyenes (both all-*trans* and all-*cis*), poly-

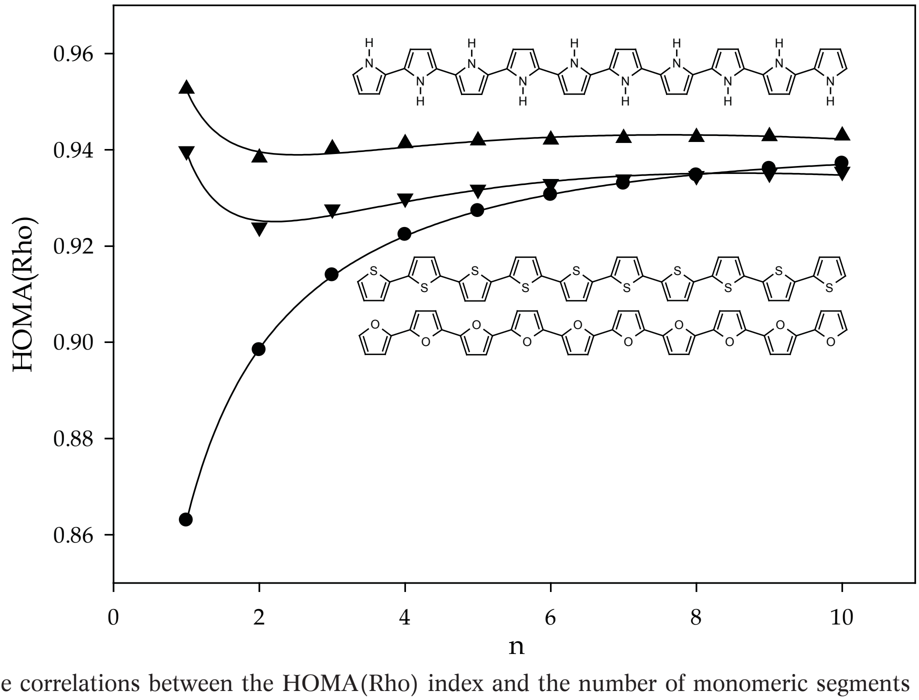


Fig.2. Example correlations between the HOMA(Rho) index and the number of monomeric segments of model polymers: polypirrole, polyfuran, and polythiophene [18].

ynes and similar systems. Interestingly, we found the asymptoting convergence to be at a maximum or a minimum when the number of monomeric segments increases [18]. However, the HOMA(R) index calculated, for instance, for allenes and polyynes reveals a different pattern: they converge asymptotically to almost the same negative value close to -3, but for allenes the function is monotonically decreasing while for polyynes it is increasing. The negative limit of the HOMA(R) index of polyallenes and polyynes indicates the very different electric/conductive properties of these systems more so than those of all-*trans* polyenes, which have HOMA(R) converging to the value of *ca.* 0.6. This exceeds the HOMA(R) index of most 6-membered rings in n-acene molecules (n > 2) [26].

Finally, we showed that the asymptotic value of the HOMA(R) index of the cyclopentadiene polymers is only slightly negative whereas if the cyclopentadiene's CH_2 moiety is replaced by the O, S, and Se heteroatoms or the NH heteroatomic group in polyfuran, polythiophene, polyselenophene, and polypyrrole conducting polymers, respectively, the limit HOMA(R) value may exceed 0.8 and HOMA(Rho) exceeds 0.92 [18] (Fig.2). For six-membered aromatic rings in polyaromatic hydrocarbons such as naphthalene or perylene, HOMA ~ 0.8 indicates the presence of significant π-electron delocalization in the system. Thus, the simple HOMA(R) index, which can easily be estimated for large systems of interest, calculated at the adequate level of theory, can be the first-order approximation of the conducting properties for the designed new conducting polymers.

Conclusions

The aim of our studies in 2014 was to develop simple tools for the characterization of molecular chirality and electron delocalization. This has been connected to the performance of the grant research focused on chiral molecules that can both be the cores of bioactive agents as well as the monomers of chiral conducting polymers. We developed the chiral graph theory with which a variety of chiral topological indices distinguishing enantiomers can be derived. We then wrote the CHIGRA computer program that calculates the Wiener, Zagreb, Laplacian, and Randić indices of chiral graphs, composed of as much as 120 vertices. In our other line of research, we attempted adapting the well-known HOMA geometrical aromaticity index to describe π-electron delocalization in linear systems that may find applications as conducting polymers. We successfully showed that the HOMA index exhibits an interesting convergence as the number of monomers in the olygomer increases and that it can be used beyond the limits established by the theory of aromaticity.

The problem of chirality is ubiquitous in all chemical disciplines and thus can have serious implications on nuclear- and radiochemistry. Indeed, changing the chirality of radiopharmaceuticals may moderate its bioavailability, which may be crucial for the efficacy of imaging diseased tissue as well as the effectiveness of radiotherapy. Chirality may also be exploited in the characterization and separation of actinide and lanthanide complexes. Also, the organic conducting materials can possibly be used as sophisticated detectors in several processes taking place in the presence of radionuclides and high-energy radiations. These aspects will be carefully considered when performing the next stages of the grant.

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CENTRE FOR RADIOBIOLOGY AND BIOLOGICAL DOSIMETRY

Studies carried out in 2014 concentrated on the validation, adaptation and implementation of various biodosimetric methods in the frame of the strategic research project "Technologies supporting development of safe nuclear power engineering" from the National Centre for Research and Development (SP/J/6/143 339/11), as well as in the "Development of multiparameter »triage« test to assess population exposure to ionising radiation" funded in the frame of the Operational Programme Innovative Economy (POIG 01.03.01-14-054/09). The latter is supported by the European Union Structural Funds and the Ministry of Regional Development (Poland). A package of procedures is being developed and a strategy is prepared of proceeding in the case of a large-scale radiation event. Quick estimation of radiation dose and allotment of casualties into groups of risk will allow an effective and efficient rescue operation. The set of documents and manuals will be transferred to subjects connected with the nuclear industry, and in particular, to the responsible authorities for the nuclear safety and the protection, the national defence, the administration and internal matters and environmental protections.

The Centre also participates in the Coordination Action project RENEB founded within the 7th EU Framework Programme EURATOM – Fission. The project is aimed at establishing a sustainable European network in biological dosimetry involving 23 organizations from 16 EU countries. Their competence has been identified by a survey carried out in 2009 and proofed by the interlaboratory comparison in 2011. The project will significantly improve the response capabilities in the case of a large-scale radiological emergency. An operational network has been created, based on coordination of the existing reliable and proven methods in biological dosimetry. This will guarantee the highest efficiency in processing and scoring of biological samples for fast, reliable results implemented in the EU emergency management. We take part in WP1, WP3 and WP4 of the RENEB project. Besides dicentric assay, micronuclei assay and histone γ-H2AX assay, which are implemented and calibrated in the Centre, other two methods of biological dosimetry are being introduced in the frame of RENEB: PCC and FISH-translocation assay. The Institute of Nuclear Chemistry and Technology (INCT) is the leader organization of Task 4.1 of WP4 "Infrastructure, transport, linking to first responders, disaster management units" and is the only Polish partner of the project. The results obtained in the frame of the RENEB project were described in several publications and presented at international conferences.

An important research topic for the last few years has been the oxidative stress, its molecular and cellular mechanisms in mammalian cells exposed to ionizing radiation and/or nanomaterials. In particular, differentiation of Lund human mesencephalon (LUHMES) cells to a dopaminergic neuron-like phenotype was examined and found that it leads to a decrease in expression of the mitochondrial PGAM5 phosphatase. Further experiments indicated that an increased expression of this enzyme was accompanied by a pronounced enhancement of apoptosis. Studies of the cellular response to ionizing radiation with a special emphasis on the molecular mechanisms of the oxidative stress have been continued: the role of pirin protein and the signalling pathway NRF2/KEAP1 in relation to apoptosis (grant IUVENTUS PLUS funded by the Ministry of Science and Higher Education, Poland, No. IP2011052071).

ADAPTATION OF HepG2 CELLS TO SILVER NANOPARTICLES-INDUCED STRESS IS BASED ON THE PRO-PROLIFERATIVE AND ANTI-APOPTOTIC CHANGES IN GENE EXPRESSION

Kamil Brzóska, Sylwia Męczyńska-Wielgosz, Tomasz M. Stępkowski, Marcin Kruszewski

Silver nanoparticles (AgNPs) are one of the most widely used nanomaterials due to their antibacterial properties. Owing to the recent boost in the usage of AgNPs-containing products, human exposure to AgNPs is increasing, highlighting the need for careful evaluation of AgNPs toxicity in humans. AgNPs effects include oxidative stress, DNA damage and viability decrease [1,2]. We used two cellular models, hepatic HepG2 and epithelial A549 cell lines to study the mechanism of AgNPs-induced toxicity at the cellular level. These two cell lines differ significantly in their response to AgNPs treatment [3].

AgNPs of nominal size 20 and 200 nm were purchased from Plasmachem GmbH, Germany. Asynchronous cell cultures in the exponential phase of growth were used in all experiments. As viability test we applied the neutral red assay. Appropriate numbers of cells were seeded on 6 cm Petri dishes and left to settle down without nanoparticles for 24 h to obtain optimal cell attachment to the surface. Subsequently, the fresh AgNPs stock suspension (or carrier mix for control plates) was added directly to the cell cultures to obtain the final concentration of 100 μg/ml. After treatment, the plates were washed and cells were trypsinized and harvested for alkaline comet assay or RNA isolation. RNA isolation, reverse transcription, and real-time PCR were carried out. The Human Signal Transduction PathwayFinder PCR Array (SABiosciences cat. no. PAHS-014) was used to analyse the expression of 84 genes representative of 18 different signal transduction pathways including pathways important for developmental, immunological, metabolic, and stress-activated processes. to determine the expression of genes.

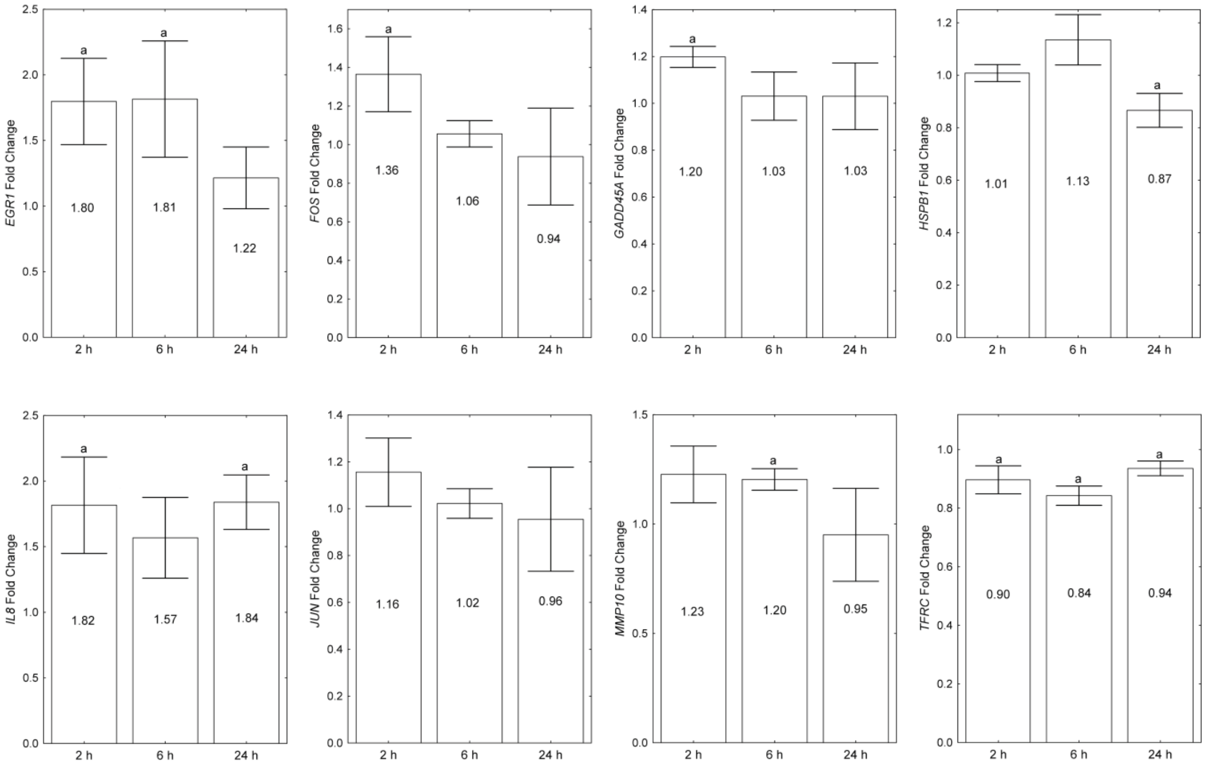

Fig.1. Changes in the expression of *EGR1*, *FOS*, *GADD45A*, *HSPB1*, *IL8*, *JUN*, *MMP10* and *TFRC* in A549 cells after treatment with 100 μg/ml of 20 nm AgNPs for 2, 6 and 24 h. The data are expressed as mean fold change and 0.95 confidence intervals from three independent experiments. "a" denotes a statistically significant difference in gene expression *vs.* corresponding control group (Mann-Whitney U test, $p < 0.05$). The exact mean fold change values are depicted on the respective columns.

In the case of A549 cells, a minor decrease in viability and increase in the extent of DNA breakage were observed; also, no significant changes in gene expression have been found (Fig.1). In contrast, after 20 nm AgNPs treatment, in short term, a marked increase in DNA breakage was observed suggesting that the basal activity of antioxidant defense in these cells was not sufficient to efficiently protect them from the nanoparticle-induced stress. Interestingly, after prolonged exposure the extent of DNA breakage decreased to the

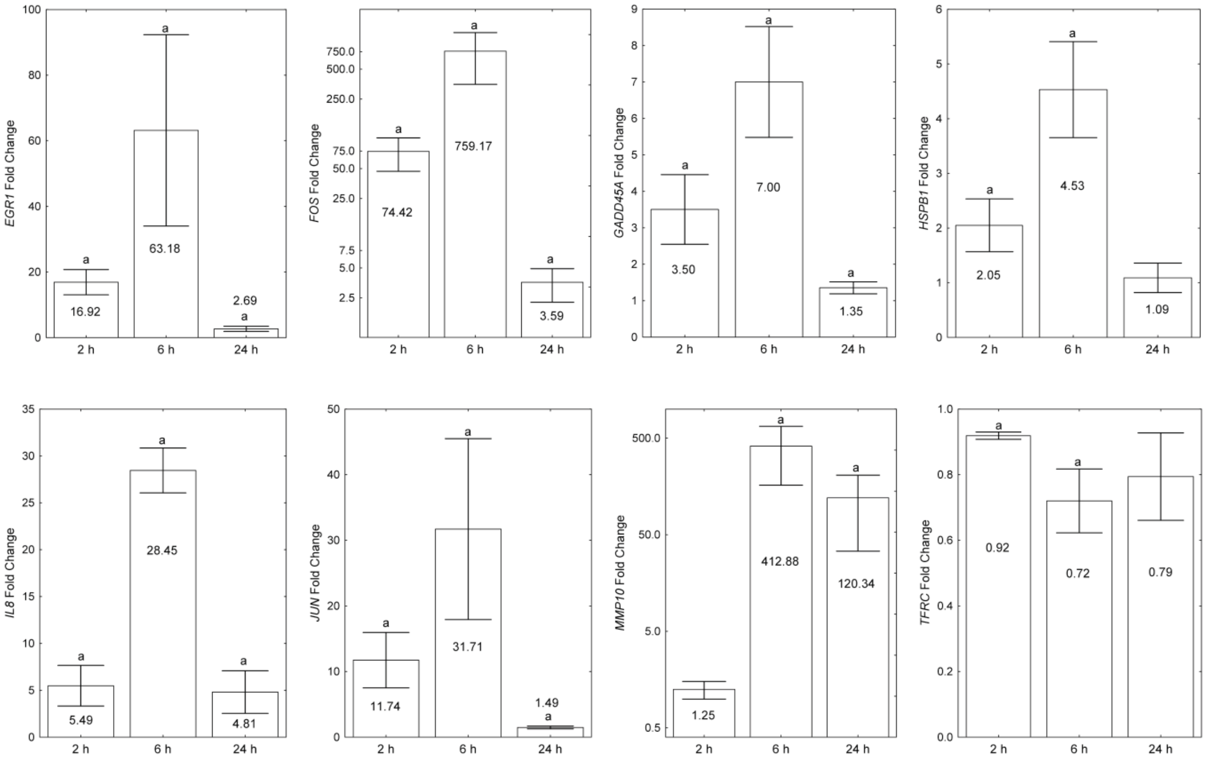

Fig.2. Changes in the expression of *EGR1*, *FOS*, *GADD45A*, *HSPB1*, *IL8*, *JUN*, *MMP10* and *TFRC* in HepG2 cells after treatment with 100 μg/ml of 20 nm AgNPs for 2, 6 and 24 h. The data are expressed as mean fold change and 0.95 confidence intervals from three independent experiments. "a" denotes a statistically significant difference in gene expression *vs.* corresponding control group (Mann-Whitney U test, $p < 0.05$). For *FOS* and *MMP10* values are presented on a logarithmic scale. The exact mean fold change values are depicted on the respective columns.

level observed in the control cells proving that a successful adaptation to the new conditions has taken place.

A significant increase in HepG2 cells was observed in the expression of genes related to mitogenesis, proliferation and migration (*EGR1*, *FOS*, *JUN*, *HK2*, *IL4*, *MMP10*, *VEGFA*, *WISP1*), stress and DNA damage response (*HSPB1*, *GADD45A*), immune and inflammatory response (*CEBPB*, *IL8*, *SELPLG*), as well as genes coding anti-apoptotic proteins (*BCL2A1*, *CCL2*). At the same time, a significant decrease in expression was observed for *CDKN1B* (gene encoding a cyclin-dependent kinase inhibitor controlling the cell cycle progression at G1), *GREB1* (early response gene in the estrogen receptor-regulated pathway), and *TFRC* (gene related to iron metabolism). 200 nm AgNPs had slighter impact on gene expression in HepG2 cells. Only up-regulation of *MMP10* and down-regulation of *FOXA2* and *GREB1* were observed (Fig.2). This observation allows to conclude that HepG2 cells can adapt to the AgNPs-induced stress through activation of the pro-proliferative and anti-apoptotic transcriptional programme. The presence of highly resistant population of cells should be taken into account in the case of medical applications of nanoparticles since the sustained proliferative signalling and resistance to cell death are hallmarks of cancer, acquired by the cells in the process of carcinogenesis.

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SYNTHETIC PARTHENOLIDE DERIVATIVES AFFECT THE CELL CYCLE DISTRIBUTION OF HepG2 CELLS

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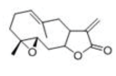
Parthenolide, a sesquiterpene lactone (AJ-1), isolated from feverfew (*Tanacetum parthenium*) has been extensively studied in relation to its anticancer properties. PTL and its derivatives were shown to inhibit proliferation and induce apoptosis in various human cancer cells *in vitro* [1-3]. They are known as potent NF-κB inhibitors that can specifically suppress NF-κB-mediated inflammation [2]. Additionally, these compounds are considered as potential radiosensitising drugs, that could be applied in combined modality therapy of cancer [4-7]. One of the proposed mechanisms is the suppression of NF-κB activity that leads to the diminishment of the cell's pro-survival signals and the induction of apoptotic pathways [5,6]. In addition, the response to ionizing radiation depends on the cell cycle phase and it was shown that parthenolide and its derivatives may affect the cell cycle distribution [3,8].

The parthenolide derivatives were synthesized at the Technical University of Łódź. Their cytotoxic effects in two breast cancer cell lines were analysed previously [3]. Here, we present the cytometry analysis of the cell cycle distribution and apoptosis in human hepatocarcinoma HepG2 cells treated with parthenolide and its two derivatives (the structures given below). The metabolic activity assay (MTT) allowed for ranking the compounds according to their cytotoxicity: AJ-14 > AJ-1 > AJ-6. For investigation of the effects on the cell cycle distribution and apoptosis, HepG2 cells were incubated for 24 h with AJ compounds at their IC_{50} concentrations (the concentrations at which 50% growth inhibition was observed). Then, all the cells were harvested and washed with PBS. One part of each sample was directly stained with the use of FITC Annexin V apoptosis Detection Kit II (BD Pharmingen) for detection of apoptotic and necrotic cells. The other part was prepared for the cell cycle analysis, based on DNA content in individual cells; this procedure included fixation in 70% ethanol, treatment with RNase A and finally staining of DNA with propidium iodide (PI). The measurements were performed in LSR Fortessa 5L cytometer (Becton Dickinson) and the analysis of the cell cycle distribution was made with the use of ModFit LT software (Verity Software House).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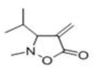
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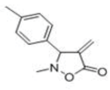
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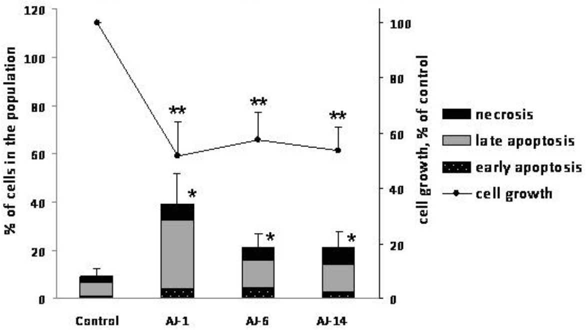

Fig.1. Cell growth (right axis, assessed by direct counting) and percentages of the cells in different stages of cell death (left axis, cytometric measurements) after 24 h incubation with AJ-1, AJ-6 and AJ-14. Asterisks show statistical significance of the differences: * $P < 0.05$; ** $P < 0.01$, by Student's t-test.

Among the three compounds tested, AJ-1 showed the greatest ability to induce apoptosis in HepG2 cells. At the 24th hour of incubation, the late apoptosis was predominating stage of the cell death for all the AJ compounds (Fig.1). The influence of parthenolide and its derivatives on the progression through the cell cycle is presented in Fig.2. In all cases, after 24 h of the incubation the percentage of cells in G1 phase has significantly diminished. Parthenolide (AJ-1) caused the accumulation of the cells in S phase, whereas AJ-6 led to arrest in both S and G2/M and AJ-14 – in G2/M phase of the cell cycle. The presented results have shown that parthenolide and its derivatives AJ-6 and AJ-14 substantially differ in their potency, ability to induce apoptosis and the influence on the cell cycle distribution in HepG2 cells. This in turn, suggests differences in the mechanism of action of these compounds. The desirable extension of this study would be the test the compounds for the ability of sensitization to ionizing radiation.

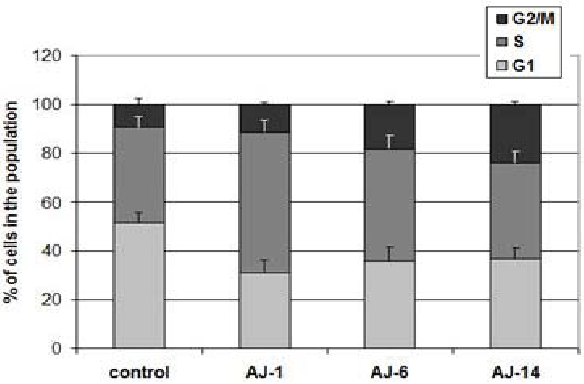

Fig.2. The effect of 24 h incubation with AJ-1, AJ-6 and AJ-14 compounds on the cell cycle distribution in HepG2 population, measured by flow cytometry. Shown are means of three independent experiments ±SD.

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THE RAPID INTERPHASE CHROMOSOME ASSAY (RICA): COMPARISON OF TWO BIODOSIMETRY METHODS

Sylwester Sommer, Iwona Buraczewska, Katarzyna Sikorska, Teresa Bartłomiejczyk, Irena Szumiel, Grzegorz Wójciuk, Marcin Kruszewski

Biodosimetry methods that enable estimation of the absorbed dose of ionizing radiation are based on examination of morphological changes in the chromosomes of peripheral blood lymphocytes. The standards in biodosimetry are the tests of dicentric chromosomes and micronuclei frequency. The analysed cells must pass mitosis. In some cases this may be difficult to achieve: after high doses of radiation, the heavily damaged cells can remain in the G2/M block for a long time, so that they will not be included in the pool of cells analysed. This may lead to an underestimation of the radiation dose or, in extreme cases, makes the analysis impossible. The method of premature chromosome condensation (PCC) is used in biological dosimetry for estimation of high doses of radiation, where the classic dosimetric tests cannot be used. The method can be applied in interphase cells. In the case of chemically induced PCC, the entry of G_0 lymphocytes in the cell cycle and reaching the G2/M phase is necessary. In the alternative approach, fusion with the mitotic CHO cells, lymphocyte entry into the cell cycle is not necessary.

A new variant of the PCC method, the rapid interphase chromosome assay (RICA) Prasanna *et al.* [1,2] involves a partial condensation of chromatin of the unstimulated human lymphocytes. This effect is obtained by treatment with the inhibitors of serine/threonine protein phosphatases (PP1 and PP2A), calyculin A or okadaic acid, in the presence of ATP and the CDK1 (cyclin-dependent kinase 1)-cyclin B kinase complex, an essential component of the mitosis-promoting complex. To count ionizing radiation-induced aberrations in a chosen chromosome, chromosome painting is applied using a whole-chromosome probe and *in situ* hybridization method (FISH).

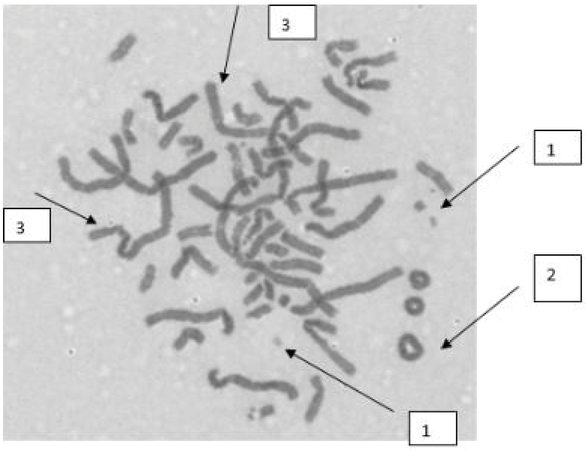

Fig.1. Human lymphocyte chromosomes, γ-irradiated (5 Gy); PCC induced chemically (okadaic acid): 1 – additional PCC fragments, 2 – three rings, 3 – long chromosomes resulting from fusion of several chromosomes.

We have recently implemented the RICA method for the current biodosimetry work carried out at the Biological Dosimetry Laboratory of the Centre for Radiobiology and Biological Dosimetry, INCT. We adapted the RICA method to the analytical tools available in the Laboratory and compared the results with those of two other PCC methods. The chemically induced PCC method (Fig.1) was used according to [3,4], the fusion-induced PCC method (Fig.2) – according to private communications and papers [5,6].

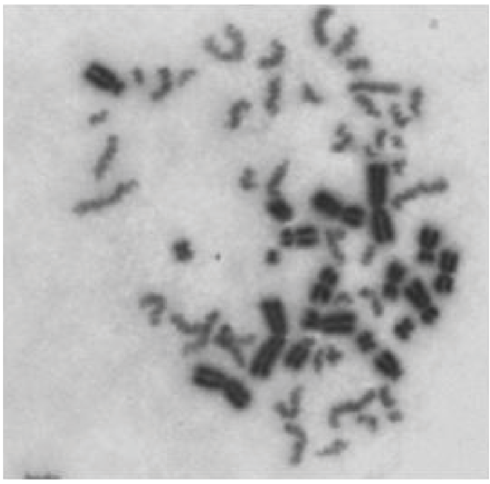

Fig.2. Fusion of a mitotic CHO cell (large, dark stained chromosomes with visible double chromatids) with an interphase human lymphocyte (smaller, less brightly stained chromosomes).

The dose-effect curves were obtained for the RICA method for cytospin or hand application of lymphocytes exposed to X- or Co^{60} γ-rays. The following parameters were fitted for the dose (D) range 0-3 Gy:

- $Y = 0.0461 (\pm 0.0070) + 0.0253 (\pm 0.0078) * D$, X-rays, hand application;
- $Y = 0.0061 (\pm 0.0041) + 0.0504 (\pm 0.0065) * D$, X-rays, cytospin application;
- $Y = 0.0029 (\pm 0.0023) + 0.0365 (\pm 0.0052) * D$, Co^{60} γ-rays, cytospin application.

For PCC induced by fusion with CHO cells the calibration curve was obtained for 1 h after exposure in the dose range of 0-6 Gy of Co^{60} γ-rays (fitted for linear dependence):

$Y = 0.0000 (\pm 0.0000) + 3.4540 (\pm 0.1863) * D$; Co^{60} γ-rays

similar to those obtained in Athens and Leiden laboratories, where the α parameter equals 4.1 ($Y = 0.0 + 4.1 * D$) [7].

For the chemically induced PCC test we used calyculin A added to lymphocyte cultures 48 h after treatment with phytohaemagglutinin. The following parameters were established for the dose-effect curves for X-ray irradiation (fitted for linear dependence):

- ring frequency: $Y = -0.0286 (\pm 0.0016) + 0.0309 * D (\pm 0.0014)$, goodness of fit = 0.6730, dose interval – 1-20 Gy;
- frequency of long chromosomes: $Y = -0.0235 (\pm 0.0027) + 0.0235 * D (\pm 0.0027)$, goodness of fit = 0.5001, dose interval – 1-20 Gy;
- frequency of PCC fragments: $Y = -0.1743 (\pm 0.0312) + 0.3552 * D (\pm 0.0269)$, dose interval – 0-20 Gy.

The data presented here allowed to draw several conclusions concerning RICA application in biodosimetry. In our hands okadaic acid was better suited for RICA than calyculin; with the RICA method a linear dose-effect relation for X- or γ-rays was obtained only for the 0-3 Gy dose range; at higher doses the relation was not linear; the method should be validated; since its use is not time-consuming, it is ideally suited for triage tests; there is a possibility to use the automatic microscope to retrieve the cell images and to apply the automatic image analysis.

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TRANSIENT OVEREXPRESSION OF THE MITOCHONDRIAL PROTEIN PGAM5 IN HUMAN LUNG CARCINOMA A549 CELLS LEADS TO A CELL CYCLE ARREST IN G1 PHASE

Tomasz M. Stępkowski, Iwona Grądzka, Iwona Wasyk, Marcin Kruszewski

The mitochondrial protein PGAM5 is a novel regulator of mitophagy. Following mitochondria depolarization with the depolarizing agent, carbonyl cyanide m-chlorophenyl hydrazine, CCCP, the PARL protease, that in normal conditions initiates degradation of PINK1 (a mitophagy activating protein) starts instead to cleave PGAM5. Hence, PINK1 is no longer cleaved and its full form associates with the outer mitochondrial membrane, thus providing a "mark" for mitophagy [1]. The PGAM5-mediated mitophagy apparently plays a pro-survival role, since mice deficient in PGAM5 display defects in mitophagy leading to a PD (Parkinson`s disease)-like phenotype [2]. Here, we aimed at testing whether overexpression of PGAM5 affects the cell cycle distribution of human lung cancer cells, A549. Another question examined was whether there is a link between the PGAM5 role in mitophagy activation and cell cycle arrest.

Two isoforms of the PGAM5 protein were overexpressed in A549 cells treated with CCCP to ana-

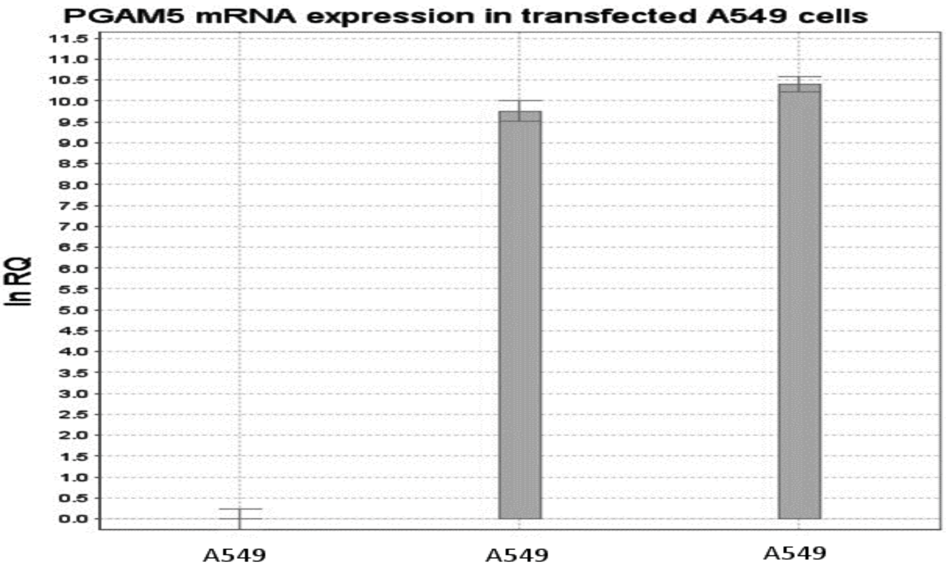

Fig.1. The natural logarithm of relative quantification of the mRNA levels in samples from A549 cells transiently transfected with plasmids pCMV6 bearing PGAM5-L and PGAM5-S isoforms cDNA coding sequence. Bars represents natural logarithm of the expression fold change in comparison to control – cells transfected with a mock plasmid without PGAM5 sequence. Error bars represent 95% confidence interval.

lyse their effect on the CCCP mediated cell cycle alterations. The cells were chemotransfected with plasmids bearing PGAM5-L or PGAM5-S coding sequences and incubated for 27 h before harvesting. For the last 3 h CCCP (10 μM) was added. The PGAM5-L and PGAM5-S overexpression was confirmed by real-time PCR (Fig.1) and Western blotting (not shown). The cell cycle analysis was based on DNA content in individual cells by means of flow cytometry (LSR Fortessa 5L cytometer, Becton Dickinson) and the cell cycle distribution was analysed with the use of ModFit LT software (Verity Software House).

PGAM5-L and PGAM5-S overexpression resulted in a significant cell growth decrease (Fig.2). Overexpression of PGAM5-L led to a cell cycle arrest in G1 phase. CCCP alone had no effect on the cell cycle in mock transfected cells but strengthened the effect of the G1 arrest caused by PGAM5-L overexpression. The growth retardation observed in these experimental conditions was not a result of intensified cell death processes, as the levels of dead cells between the control and the treated samples (including treatment with CCCP alone) were not significantly different (not shown). Rather, overexpression of PGAM5 led to cell growth arrest, clearly seen as the G1 block in PGAM5-L transfected cells. In this context, it seems important that the FBXO7 protein not only interacts both with PINK1 and Parkin in the mitophagy pathway but has also another function: in a short time window during G1 phase, it also is a regulator of the cell cycle, participating as an assembly scaffold for the formation of cyclin D/Cdk6 complexes (review in [3]).

In conclusion, the PGAM5 overexpression-mediated cell cycle arrest may be related to the role of PGAM5 in the mitophagy control because the cell cycle arrest is necessary for a proper mitochondria "recycling" as a part of a larger pro-survival process. Such conclusion, however, needs further testing along with a more detailed examination of the role of PGAM5-L as a convergent point of multiple cellular functions.

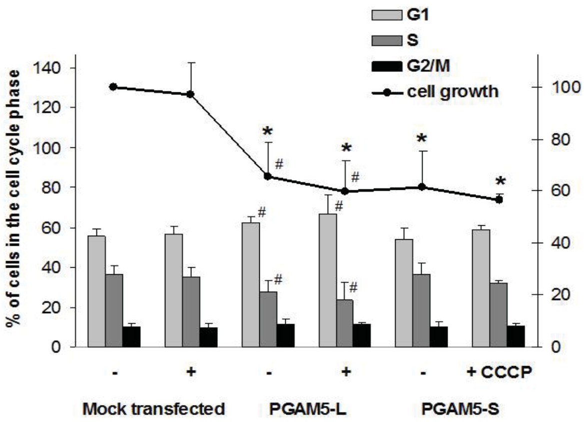

Fig.2. The influence of transient PGAM5-L or PGAM5-S overexpression on the cell growth (right axis) and cell cycle distribution (left axis) after 3 h incubation with (or without) 10 μM CCCP. Shown are means ±SD of three independent experiments. Asterisks indicate statistically significant differences compared to control (mock transfected -CCCP), $P < 0.01$ by unpaired Student's t-test. Additionally, # symbols mark statistically significant fold changes (values not shown): a decrease in the cell growth in PGAM5-L after CCCP addition, with simultaneous increase in the percentage of G1 phase at the expense of the S phase (both in relation to the control and PGAM5-L -CCCP), $P < 0.05$, by paired Student's t-test.

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THE EFFECT OF ISOQUINOLINE ALKALOIDS, BERBERINE, PALMATINE AND CORALYNE ON THE FREQUENCY OF X-RAY–INDUCED MICRONUCLEI IN HeLa CELLS

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Isoquinoline alkaloids, berberine, palmatine and coralyne of the protoberberine group occur in various plant species. They have been applied in the traditional medicine in many countries because of their antibacterial and antimalarial activity. At present these compounds are considered as potential anticancer drugs with a significantly low toxicity [1].

Several research groups using various biophysical techniques aimed at elucidation of the mode and mechanism of action of these alkaloids (reviewed in [2]). Their anticancer properties are supposedly based on their interaction with the polymorphic nucleic acid structures (B-form, A-form, Z-form, H(L)-form, triple helical form, quadruplex form) and their topoisomerase inhibitory activity [2,3] Additionally, alkaloids of the isoquinoline group have been found to bind polyadenylic acid, poly(A) with remarkably high affinity [4]. This property may be related to the biological effects of these alkaloids: the poly(A) tail of mRNA has been recently established as a potential drug target due to its significant role in the initiation of translation, maturation and stability of mRNA as well as in the production of alternative proteins (isoforms) in eukaryotic cells.

The DNA binding of the planar coralyne is found to be stronger and thermodynamically more favoured compared to the buckled structure of berberine and palmatine and correlate well with the intercalative mechanism of coralyne and the partial intercalation by berberine and palmatine [3]. Nucleic acid binding properties are also interpreted in relation to their anticancer activity. The structure of the 3 compounds used in this report are shown in Fig.1. Nevertheless, the mechanism of action of the examined alkaloids remains unclear. Berberine induced a G1-phase cell cycle arrest and caspase-3-dependent apoptosis *in vitro* (human prostate carcinoma cells) [5]. Cell growth arrest, apoptosis, induction of expression of the pro-apoptotic proteins NAG-1, and ATF3 were noted in the berberine-treated human colorectal cancer cells [6]. The protein product of the nonsteroidal anti-inflammatory drug (NSAID) activated gene (*NAG-1*) was identified as a pro-apoptotic and anti-tumourigenic protein with homology to members of the TGF-β superfamily. ATF3 is a transcriptional factor and also has a pro-apoptotic activity. *In vivo* (in mice) anticlastogenic effects of berberine were reported [7], whereas Ali and Dixit [8] observed an antioxidative effect of palmatine.

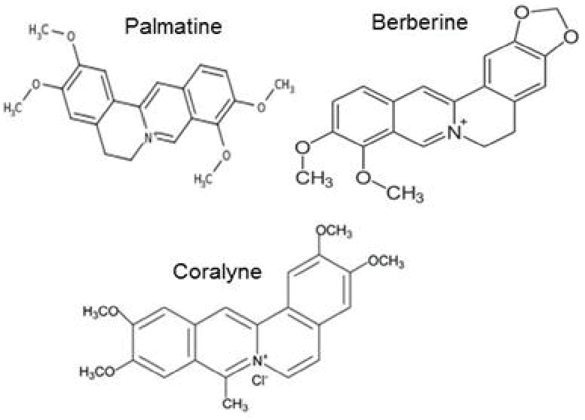

Fig.1. Structure of the examined isoquinoline group alkaloids.

Table 1. Micronuclei frequency in HeLa cells upon single agent or combined treatment (alkaloid: palmatine, berberine or coralyne; 2 Gy X-rays). Mean results from 3 independent experiments, standard deviation indicated). Data for coralyne ± X-rays are from a separate series of experiments.

Cell treatment	Mean ± SD
Control	16.0 ± 2.5
2 Gy	235.0 ± 19.3
Palmatine 5 μM	176.0 ± 28.0
Palmatine 5 μM + 2 Gy	351.0 ± 30.0
Berberine 5 μM	102.0 ± 19.1
Berberine 5 μM + 2 Gy	250.0 ± 41.0
Control	7 ± 0
2 Gy	224 ± 0
Coralyne 5 μM	154.3 ± 51.8
Coralyne 5 μM + 2 Gy	321.0 ± 14.7

To our best knowledge, the interaction of the isoquinoline alkaloids with ionizing radiation at the cellular level has not been examined, so far. We used HeLa cells as the cell model and the micronucleus test according to Fenech [9]. X-irradiation was at a single dose, 2 Gy. The results are summarized in Table 1. All three alkaloids show a high clastogenic affect at the concentration applied. This could be expected on the basis of the data concerning their ability to bind DNA, a feature that most probably corresponds with their anticancer properties, as mentioned above, but is in an apparent contradiction with the reported anticlastogenic activity [7]. A more than additive effect of combined (alkaloid + X-rays) treatment would indicate a radiosensitizing property of the alkaloids. However, the effect of combined treatment is less than additive for all 3 compounds examined, indicating that the X-ray–induced DNA lesions probably overlap with those resulting from adduct formation by the alkaloids.

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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 laboratories of the INCT and provides analytical services for them as well as for the outside institutions. The Laboratory is a producer of certified reference materials (CRMs) for the purpose of inorganic trace analysis and 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-ray counting.

In 2014, the research projects carried out in the Laboratory were concerned with chemical aspects of nuclear power, and nuclear and related analytical techniques for environment protection.

In 2014, the Laboratory participated in the strategic research project from the National Centre for Research and Development (NCBR), Poland "New technologies supporting development of safe nuclear energy". The Laboratory participated also in MODAS project from NCBR being a member of the consortium of 8 leading Polish universities and scientific institutes. Within the scope of the MODAS project, the laboratory was involved in the preparation and certification of four new environmental CRMs certified for the contents of a possibly great number of trace elements. The materials in question have been: Bottom Sediment, Herring Tissue, Cormorant Tissue and Cod Tissue.

In 2014, the Laboratory of Nuclear Analytical Methods conducted a proficiency test (PT) on the determination of Cs-137 and Sr-90 in water, food and environmental samples. PT was provided on the request of the National Atomic Energy Agency (PAA), Poland. Thirteen laboratories took part in the PT, 8 laboratories forming radiation monitoring network in Poland (on the request of the PAA) and 5 other laboratories. The proficiency test was provided following requirements of ISO/IEC 17043:2010 and IUPAC International Harmonized Protocol (2006).

APPLICATION OF IONIZING RADIATION FOR DECOMPOSITION OF PERFLUORINATED SURFACTANTS

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From the point of view of environmental protection, a very important group of anthropogenic pollutants are perfluorinated anionic surfactants, in which in long alkyl chains all hydrogen atoms are replaced by fluorine atoms. These compounds are widely used on industrial scale in fire extinguishers and for impregnation of numerous materials, in cosmetics and household products [1-3]. Their environmental threat results first of all from a very large chemical stability in the environment, comparable to common persistent organic pollutants such as chloroorganic pesticides, polycyclic aromatic hydrocarbons or polychlorinated biphenyls. Since the beginning of 1990s, it is known that they occur practically all over the globe, as they were detected in surface waters in the most remote regions on the Earth [4] and in organisms of wild animals in all continents, in tissues of fishes and birds [5]. They are commonly detected in human organisms [6], being a serious health threat because, *e.g.* of destruction of lipid balance and possibility of their incorporation into a bilayer lipid cell membranes. The most commonly detected compounds in the environment are perfluoroctanoic acid (PFOA) and perfluorooctanesulphonic acid (PFOS).

The environmental proliferation of perfluorinated compounds (PFCs) on a global scale, their presence in organisms of animals and humans even in very remote locations, and including them into persistent organic pollutants [7], are the main reasons stimulating an intensive development of analytical methods for their determination. Determination of PFCs in different matrices is a very tough challenge for analytical chemists [8]. In spite of a great progress in the development of new methods and application of increasingly sophisticated instrumentation, still numerous problems and challenges remain to solve. Most commonly employed methods are predominated by chromatographic methods, mostly with a mass spectrometry detection, but HPLC can be also employed with conductivity or fluorimetric detection, while gas chromatography with flame ionization or electron capture detections. An increasing attention is focused in recent years on the determination of branched isomers of perfluoroalkyl compounds. Another difficulty is a limited number of available standards, and especially of the certified reference materials. From one side, it is necessary to develop new methods and improve instruments, *e.g.* for the separation of isomers of PFCs, but on the other hand there is the need for much simpler methods and instruments, enabling wide routine monitoring of those pollutants in the environment. Their large variety in analysed samples, makes those determinations very difficult and time-consuming, hence it seems that for common monitoring a very helpful alternative can be evaluation of such total indices as extractable organic fluorine, or total organic fluorine [9]. The trend observed in last years is also increasing interest in the determination of PFCs in foods for tracking the pathways of human exposure.

The common occurrence of perfluorinated surfactants in the environment is the reason of increasing interest in the development of methods of their removal from waters and wastes [10]. The classical methods of their removal from waters include reverse osmosis, sorption on activated carbon, but also sonochemical pyrolysis or incineration. The decomposition of perfluorinated compounds with release of total fluorine can be carried out with various combustion methods [11], or by the use of very strong reducing agents such as, *e.g.* metallic magnesium in supercritical carbon dioxide, sodium in dry ammonia or sodium biphenyl. These methods, because of high cost of instrumentation and reagents, are employed mostly on a microscale, for instance, for analytical purposes. For technological purposes, including environmental protection, the studies on biodegradation [12], and the use of advanced oxidation/reduction processes with application of radical reactions are carried out [13,14]. As especially effective, however, the sonolytic conversion of PFOA and PFOS into inorganic products was reported [15]. Recently also reductive defluorination, *e.g.* of perfluorooctane sulphonate with Ti(III)-citrate and vitamin B_{12} as catalyst was reported [16]. The obtained results suggest the microbial transformation of some PFOS isomers might be possible in anaerobic environments. As generally, the fate of PFOS and PFOA in, *e.g.* drinking water treatment processes is recognized [17], still numerous approaches for their removal from waters and wastes are investigated.

The application of ionizing radiation (γ from ^{60}Co or ^{137}Cs sources, and accelerated electron beam) is quite intensively investigated in recent decades as one of the most efficient advanced oxidation/reduction processes (AO/RP) for the removal of organic pollutants from waters and wastes. Recent papers published on their applications concerned, *e.g.* removal of pharmaceutical residues [18-22], environmental pesticide residues [19-23], and environmental pollutants of industrial origin [24,25]. There are also undertaken studies on operation of an industrial scale electron beam wastewater treatment plant [26], and decontamination of pesticide residues in vegetable and fruits [27].

Until now, studies on the radiolytic decomposition of perfluorinated alkyl compounds are un-

Table 1. Reaction rate constants for perfluorinated surfactants with $^{\bullet}$OH radical and hydrated electron.

Compound to be decomposed	Reactive reagent	Reaction rate constant [M^{-1} s^{-1}]	Reference
PFOA	$^{\bullet}$OH	≤ 1 x 10^5 3 x 10^7	[10] [28]
PFOA	e_{aq}^-	1.3-5.1 x 10^7 1.7 x 10^7	[28] [29]
PFOS*	e_{aq}^-	7.3 x 10^7	[28]

* Triethanolamine salt.

dertaken sporadically, mostly in order to determine the rate constants for their reactions with active products of water radiolysis. Their values listed in Table 1 show quite a large discrepancy of their values, and also indicate that they are about 2 to 3 orders of magnitude smaller, than the rate constants for reactions of other classes of organic environmental pollutants. This is also evidence of their particular chemical resistance.

The described above attempts on the decomposition of PFCs in oxidative conditions [10,30,31], the reported rate constant for PFOA reaction with $^{\bullet}$OH radical [28], and also reported earlier application for this purpose of persulphate [13,32], implied our first attempts on PFOA decomposition in oxidative conditions [33]. Because of the use of capillary electrophoresis for the monitoring of decomposition yield, the studies were carried out at a relatively high initial concentration of PFOA 5 mM. In most favourable conditions, in the presence of 27 mM sodium persulphate, at absorbed dose as large as 192 kGy with electron beam irradiation, 24% of PFOA was decomposed, only [33].

During this study, the examined aqueous solutions of PFOA and PFOS were irradiated in different conditions discussed below using a gamma ^{60}Co source Gamma Chamber model GC-5000 (BRIT/BARC, Mumbai, India) with a dose rate of 4.8 kGy/h, and electron beam accelerator 10 MeV with a mean beam power of 10 kW.

The analytical determination of perfluorinated analytes and fluoride ion released during the irradiation were carried out using an ion chromatograph Dionex model 2000i/SP, equipped with an electrochemical anion self-regenerating suppressor model Dionex ASRS 300, and a conductivity detector model Dionex CDM-II. Determinations of PFOA and PFOS were carried out using Kromasil C_{18} reversed phase column with a mixture of 20 mM boric acid and 4.0 mM NaOH adjusted to pH 8.0 with 38% acetonitrile as eluent, while determinations of fluoride were carried out using a Dionex Ion Pac AS9HC analytical column and an Ion Pac AG9HC guard column, and using 9.0 mM solution of Na_2CO_3 as eluent.

The decomposition of PFOA and PFOS was also monitored using LC/MS system consisting of an Agilent 1200 series HPLC system, and an Agilent Q-TOF mass analyser model Acurate Mass 6530 with electrospray ionization. Measurements were carried out using an XTerra C18 column (2.1 mm x 10 mm x 3.5 μm) with 5 mM ammonium acetate/methanol eluent of pH 6.0.

Pulse radiolysis was carried out in a nanosecond pulse radiolysis facility based on the electron accelerator model LAE 10. It allows carrying out pulse radiolysis experiments with a pulse duration of 4-10 and 100 ns, electron energy 10 MeV, and beam power 0.2 kW.

The application, in the studies reported herewith, a chromatographic monitoring of radiolytic decomposition of PFOA using suppressed ion chromatography with conductivity detection and

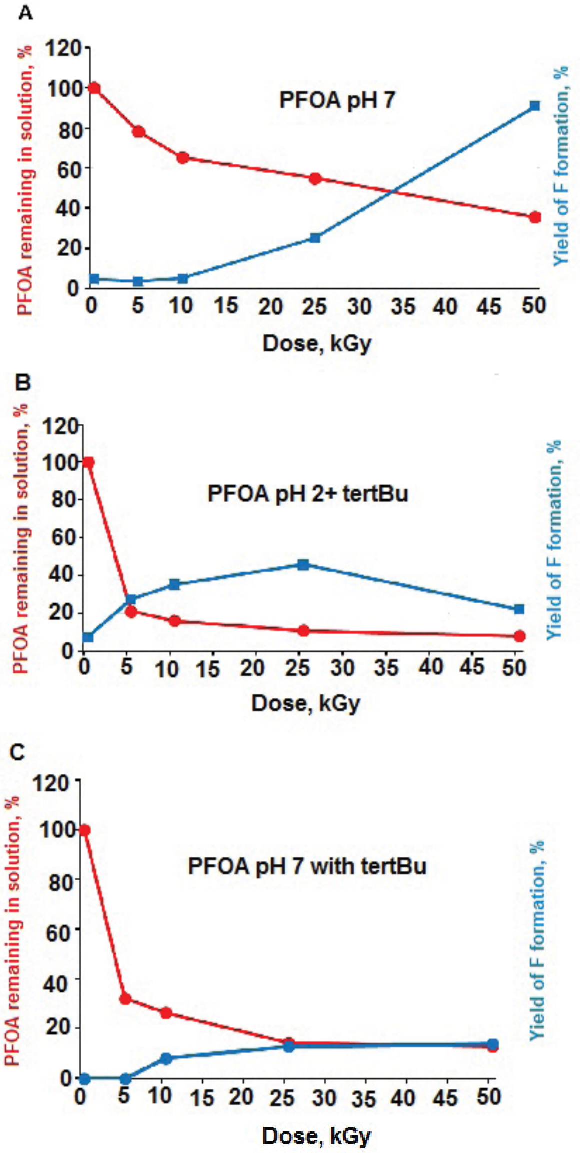

Fig.1. The effect of the absorbed dose of gamma radiation on the yield of decomposition of PFOA and release of fluoride ion both determined by ion chromatography in aqueous solutions of initial concentration 1 mg/L (2.4 μM) in: A – aerated solution of pH 7.0, B – argon-saturated solution of pH 2.0 containing 20 mg/L of *t*-butanol, and C – argon-saturated solution of pH 7.0 containing 20 mg/L of *t*-butanol. Dose rate – 4.8 kGy/h.

liquid chromatography/mass spectrometry allowed the tracing out the decomposition processes taking place at a much lower level of initial concentration, namely 1 mg/L (which corresponds to 2.4 μM). The investigation of the yield or decomposition in function of absorbed dose of gamma radiation was carried out in the range up to 50 kGy, comparing the irradiation in aerated aqueous solution, pH 7.0, with irradiation in reductive conditions, where hydrated electron predominated (pH 7.0 with the addition of 20 mg/L *t*-butanol) or hydrogen radical $^{\bullet}$H (pH 2.0 with 20 mg/L *t*-butanol). In Fig.1, changes of PFOA concentration measured by ion chromatography is shown together with the increase of concentration of released fluorine as fluoride ion. The most effective decomposition of PFOA was observed in conditions where a hydrogen radical predominates, and at a 5 kGy absorbed dose an 80% yield of decomposition is observed. The application of ten times larger radiation dose increases this yield only up to 90% (Fig.1A). The obtained results of the released fluoride ion concentration in function of absorbed dose are difficult to interpret. While in an aerated solution of pH 7.0 a monotonous increase of this concentration was observed, in reductive conditions an increase was observed only up to a 25 kGy absorbed dose, and then even slight decrease was noted, which can be partly connected with protonation of fluoride in the applied conditions (Fig.1B).

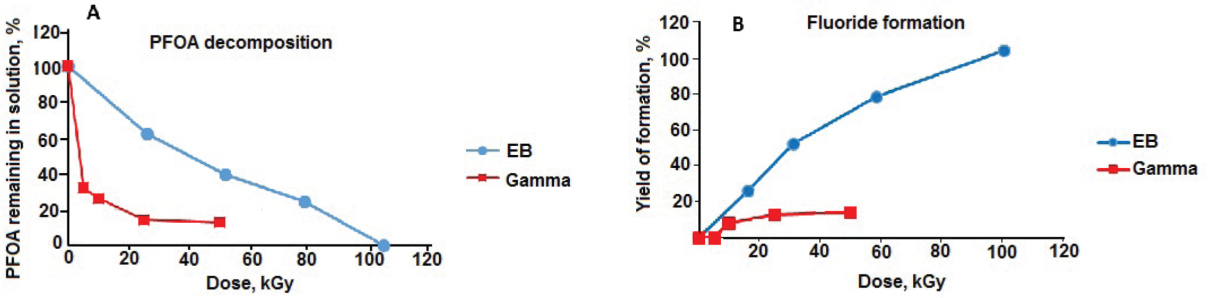

Fig.2. The effect of the absorbed dose of gamma irradiation (■) and accelerated electrons using electron beam irradiation (●) on the yield of PFOA decomposition (A) and fluoride ion release (B). Irradiations carried out in 1 mg/L aqueous solutions of PFOA of pH 7.0 saturated with argon and with added 20 mg/L of *t*-butanol. Dose rate – 4.8 kGy/h.

In pulse radiolysis measurements of the rate constant for the pseudo-first-order reaction between PFOA and hydrogen radical was determined. Measurements were carried out at 270 nm, where the formation of reaction product was detected. They were conducted in 1.0 mM PFOA aqueous PFOA solution of pH 1.0 saturated with argon, and with the addition of 0.1 M *t*-butanol. For 20 Gy of the absorbed dose, the value of rate constant was evaluated as 9.0 x 10^4 s^{-1}.

In case of the necessity of applying larger doses of radiation (> 10 kGy), and especially in technological applications, it is advantageous to employ rather electron beam irradiation instead of gamma radiation from cobalt or caesium sources. This can be associated, however, with a certain dose-rate effect, which was reported, *e.g.* for radiolytic decomposition of perchloroethylene [34], benzene, toluene, phenol and chloroform [35], and also antineoplastic drug cyterabine [36]. A high dose rate may increase the interradical reactions, hence, as it was observed for, *e.g.* cyterabine, gamma radiation was more efficient at elevated dose rates [36]. In case of perchloroethylene, however, it was demonstrated that gamma irradiation (low dose rate) was more efficient than electron beam irradiation (high dose rate). A similar comparison was conducted in this work for PFOA decomposition in reductive conditions. Figure 2 shows such a comparison for conditions, where during irradiation the hydrated electron predominates, while in Fig.3 when the hydrogen radical predominates. Generally, with employed sources of irradiation, the same absorbed doses are obtained in case of accelerated electrons (about two orders of magnitude), however an 80-90% yield of radiolytic decomposition is obtained at much smaller absorbed doses of gamma than electron beam. The application of electron beam is however much more efficient in the case of complete release of fluorine from organic compounds with the for-

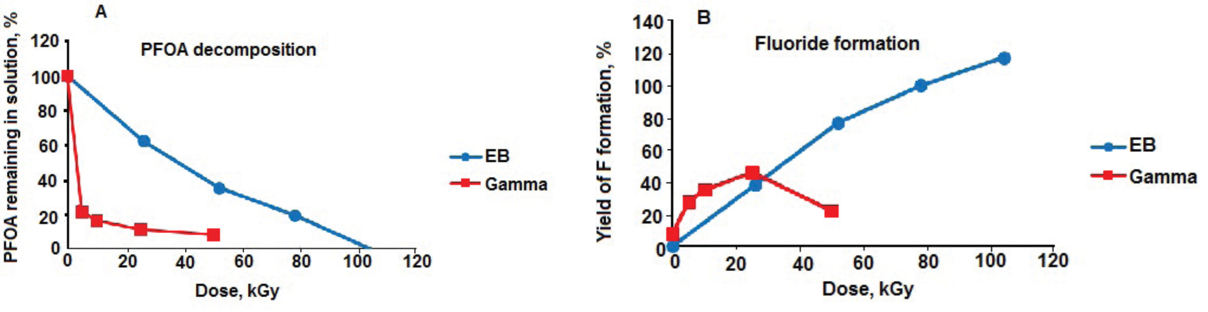

Fig.3. The effect of the absorbed dose of gamma irradiation (■) and accelerated electrons using electron beam irradiation (●) on the yield of PFOA decomposition (A) and fluoride ion release (B). Irradiations carried out in 1 mg/L aqueous solutions of PFOA of pH 2.0 saturated with argon and with added 20 mg/L of *t*-butanol. Dose rate – 4.8 kGy/h.

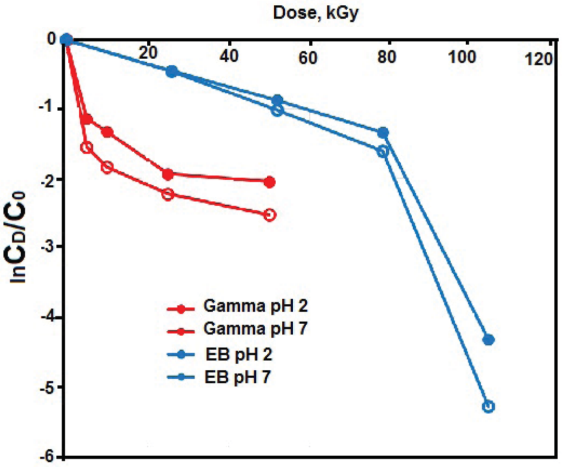

Fig.4. The dose rate effect in radiolytic decomposition of PFOA examined by comparison of yield of irradiation in the processes with gamma irradiation (●,○) and electron beam irradiation (■,□) of 1 mg/L aqueous solution of PFOA. Irradiations carried out in aerated solutions of pH 2.0 with 20 mg/L of *t*-butanol (□,○), and argon-saturated solutions of pH 7.0 with 20 mg/L of *t*-butanol (■,●). The yield of decomposition is expressed by the values of ln C_D/C_O, where: C_D – the concentration of PFOA after irradiation, C_O – the concentration of initial PFOA solution prior to the irradiation.

mation of fluoride ions, where a monotonous increase of concentration with absorbed dose was found.

A comparison of courses of radiolytic PFOA decomposition is also shown on the plot, which was used for the determination of initial values of radiation yield G_o and dose constant (Fig.4), according to commonly used procedures [37]. With the lack of linear dependence of $\ln(C_D/C_O)$ values on the magnitude of absorbed dose, the dose constant was determined from the initial experimental values for the smallest applied dose. The obtained values were compared in Table 2 with those obtained in our earlier studies for other anthropogenic organic pollutants of the environment, which demonstrates a particular resistance of PFOA against radicals formed during irradiation of aqueous solutions. This confirms also exceptional chemical stability of PFOA widely reported in the literature.

Further studies within this project should include the determination of products of PFOA decomposition, and evaluation of the yield of decomposition at a concentration level of their presence in real samples in the presence of natural matrices of environmental samples.

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Table 2. Figures of merit for processes of decomposition of selected environmental pollutants with gamma irradiation.

Compound	Examined concentration [mg/L]	Reaction rate constant [M^{-1} s^{-1}] (with $^\bullet$OH radicals)	Radiation yield G_o [μM J^{-1}] (at dose [kGy])	Dose constant [kGy^{-1}]	$D_{0.9}$ [kGy] (dose required for 90% decomposition)
Parathion	15	4.2-9.7 x 10^9	1.31 (0.2)	1.76	1.31
Bisphenol A	6.9	6.9 x 10^9	1.36 (0.1)	7.19	0.32
Aflatoxin B1	10	not found	4.89 (0.02)	9.33	0.25
Diclofenac	10	12 x 10^9	1.42 (0.2)	6.02	0.38
Ibuprofen	10	6.7-10 x 10^9	1.58 (0.2)	7.02	0.33
Carbamazepine	10	2.0-9.7 x 10^9	1.05 (0.2)	4.37	0.53
PFOA *	1.0	9.0 x 10^7 *** (with hydrogen radicals)	0.0032 (10)	0.31	7.43
PFOA **	1.0	1.3-5.1 x 10^7 (with hydrated electrons)	0.0033 (10)	0.228	10.1

* Irradiation carried out in solution of pH 2.0 with added 20 mg/L of *t*-butanol (predominated $^\bullet$H radical).
** Irradiated solution of pH 7.0 saturated with argon, and containing 20 mg/L of *t*-butanol (predominated hydrated electron).
*** Determined in this work.

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STUDY ON INTERFERENCES IN FLOW-INJECTION DETERMINATION OF ^{90}Sr WITH ICP-MS DETECTION

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There are numerous methods developed for the determination of strontium-90 in environmental samples (waters, soil), but also in foods and other samples connected to human activity, where strontium-90 content may play a crucial role [1-11]. An example of such a field is a nuclear power plant technology, where the main source of ^{90}Sr is reactor fuel reprocessing. Strontium-90 is produced by fission of uranium, but it also occurs by decay of plutonium nuclei. Reactor fuel fission process occurs in fuel rods, where zirconium claddings filled with a nuclear fuel are located. In order to slow down the neutrons, as well as to overtake the heat from the process, the fuel rods are placed in a pool with a coolant. This design of a reactor system is employed in most operating reactors, however, due to the nature of the process, it requires continuous monitoring of fuel claddings. Under the prevailing conditions of the process, they can be damaged and lead to a failure of the reactor. It should be noted that this kind of an accident is always preceded by cladding leakiness and fission product release to the reactor coolant.

There are some components of nuclear fission products, such as ^{90}Sr, which can be applied as an indicator of an accident threat. An implementation of flow analytical techniques to continuous monitoring of ^{90}Sr in the reactor coolant is a promising idea. It is expected that during normal working operation of the reactor, the radionuclide is not present in the coolant and its presence will be a warning signal of an installation failure. Flow techniques very often requires, however, a complex sample preparation and processing of the radioactive sample. It may consist of a preconcentration of the analyte as well as its separation from other sample components, which may interfere in the detection. In case of ^{90}Sr determined by inductively coupled plasma mass spectrometry (ICP-MS) it can be any kind of isobaric or polyatomic ions with mass 90, while, when using radiochemical detection (*e.g.* liquid scintillation counter), one should pay attention to other β-emitters present in the sample.

Flow analysis requires to build a manifold with dedicated units for a simultaneous preconcentration and separation of radionuclides. The most common methods for chemical isolation of ^{90}Sr include liquid extraction [10], solid-phase extraction employing molecular recognition [12,13], ion exchange [4,5,8,14], extraction chromatography [1,11,12,15,16], and a combination thereof [3,6,7,17-19]. New specialized analytical systems are equipped with columns packed with ion exchange resins [4,5], and commercially available extraction chromatography resins such as Sr-resin® *etc*. [1,3,11,12,15]. Thus, it can be generalized that the ^{90}Sr isolation processes conducted in flow analysers can be grouped in two leading categories, based on ion exchange chromatography [20,21] and extraction chromatography [11]. The preconcentration of radionuclides can also take place on-line in the flow system as well. For this purpose, for example, the Dowex 50WX8 solid sorbent can be applied for the preconcentration of cations such as strontium [17]. This enables complete processing of a sample in a closed flow system in an automated way controlled by a computer.

In the literature, a few of examples of the flow analysis applications in measurements of ^{90}Sr have been already reported. They are mainly based on the use of extraction resin for matrix component separations, and different detection methods employed allow obtaining different limits of detection. So far, however, neither of the developed flow systems was dedicated for measuring ^{90}Sr in a reactor coolant. The main objective of this study was to optimize the flow-injection procedure for the determination of strontium-90 with a particular consideration of interferences in the determination of ^{90}Sr with ICP-MS detection.

The measuring setup employed in this study is based on a multisyringe flow injection analysis (MSFIA) – a lab-on-valve (LOV) concept, which allows performing a series of operations including analyte preconcentration and separation of matrix components. The applied MSFIA-LOV system consists of a multisyringe burette (BU4S, Crison Instruments, Spain) equipped with four 10 mL glass syringes (Hamilton, Switzerland), however, only one of them was used in this study. The LOV (Sciware, Spain) was fabricated from methacrylate and it incorporated 8 microchannels (1.5 mm I.D./16 mm length) dedicated for operating with the reagents. One of them was a sorbent minicolumn (3.2 mm I.D./16 mm long) for preconcentration and separation processes. The microcolumn was automatically filled with renewable beads of 40 mg of Sr-resin, which were contained in a 1 mL plastic syringe mounted on one of microchannels of the LOV. A glass fibre prefilter (Millipore) was used at the end of the column to prevent sorbent leaking. The unit was connected with a syringe burette with a PTFE holding coil (1.5 mm I.D./7 m long). The rest of flow network was constructed with 0.8 mm I.D. PTFE tubes connected to the microchannels of LOV, and they were used for direct aspiration of eluents from their reservoirs. The flow procedure was programmed and operated by the software AutoAnalysis 5.0 (Sciware, Spain). The employed ICP-MS instrument was Elan DRC II provided by Perkin-Elmer (USA), equipped with a crossflow nebulizer, a Scott double-pass spray chamber, and nickel cones.

The multi-step procedure developed in this study is based on the separation of sample components, involving the methodology of extraction chromatography by the use of a commercial crown ether-based Sr-resin. The automated procedure consists of preparing the column by filling it with the sorbent and then conditioning it to introduce the sample. The interferences presented in the sample are removed by the use of a strongly acidic eluent. Finally, strontium retained on the column was eluted with water. The processed samples are collected by the autosampler and then off-line ICP-MS detection was carried out. Details of the developed procedure are presented below:

- Sr-resin is loaded into a microcolumn: 1 mL of Sr-resin suspension (40 mg in 8.0 M HNO_3) is aspirated at a flow rate of 1 mL min^{-1} firstly to the holding coil and then to the microcolumn built in LOV.
- Conditioning of Sr-resin: The sorbent bed is conditioned with 3 mL of 8.0 M HNO_3 aspirated by port 3 in LOV to the holding coil and then to the microcolumn at a flow rate of 2 mL min^{-1}.
- Sample loading: The 250 μg L^{-1} sample solution of Sr, prepared from strontium standard solution in different volumes of 8.0 M HNO_3, is taken by port 4 in LOV to the holding coil at a flow rate of 5 mL min^{-1}, and then injected to a Sr-resin bed packed in the microcolumn at a flow rate of 0.6 mL min^{-1}.
- Removing of interferences: The potential interferences are removed by the use of 1 mL of 8.0 M HNO_3 taken from port 3 at a flow rate of 5 mL min^{-1} to the holding coil and then aspirated through the microcolumn at a flow rate of 2 mL min^{-1}.
- Elution of strontium: The strontium retained on the resin is eluted with 10 mL of water at a flow rate of 2 mL min^{-1}.
- ICP-MS detection: The solutions of strontium eluted from the column are collected and diluted twenty times with 2% HNO_3 containing 5 μg L^{-1} indium as an internal standard prior to the measurement.

The determination of ^{90}Sr requires a multi-step procedure, which involves first of all the process of removing interferences that may disturb the employed detection. Therefore, an important task is to define all possible interferences, considering those which may occur due to the sample matrix, and affecting particular detection. For instance, in the analysis of a reactor coolant sample by radiometric detection other interferences can be expected (*e.g.* Cs), than for ICP-MS detection. In the latter detection a special attention should be paid to the potential spectral interferences – isobaric, as well as polyatomic. The main isobaric interferences in ^{90}Sr determination are yttrium-90 and zirconium-90, which are daughters resulting from the radioactive decay of ^{90}Sr. Po-tential polyatomic interferences include $^{58}Ni^{16}O_2^+$, $^{74}Ge^{16}O^+$, $^{52}Cr^{38}Ar^+$ and $^{54}Fe^{36}Ar^+$. Besides this, the matrix of reactor coolant itself also carries the difficulty of determinations by ICP-MS due to the high concentration of boric acid, which is one of the principal components of the reactor coolant. Its concentration overreaches even 12 g L^{-1}, as a high concentration of boron is required for an effective slowing down the neutrons in the reactor. From the analytical point of view, such a high concentration of boric acid interferes in ICP-MS detection, and hence it is necessary to separate strontium from a large excess of boric acid. In the process of interference removal, included in the developed procedure, a Sr-resin was applied, which allowed effective separation of the analyte from other sample components. In such a

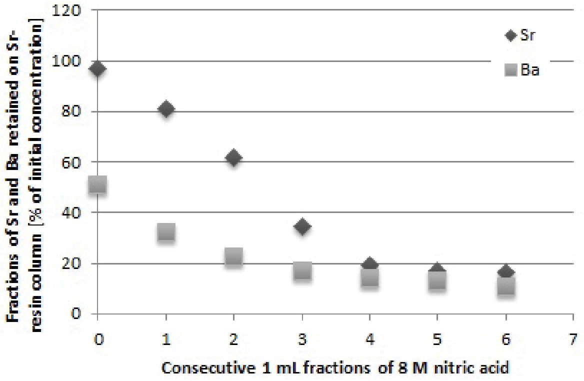

Fig.1. Optimization of the volume of 8.0 M nitric acid solution, which was employed for the elution of barium retained on the Sr-resin column in the process of separation of barium from strontium. Loaded 1 mL solution 250 µg L^{-1} Sr and Ba; 16 mm/3.2 mm I.D. column packed with 40 mg Sr-resin.

case also alkaline earth metals should be taken into account due to similar chemical properties that have high affinity to Sr-resin and thus are difficult to separate from strontium. As a representative of this group, for the present study barium was selected, as the degree of its affinity to the Sr-resin is similar to that of strontium. Moreover, bearing in mind the investigation of the reactor water, the presence of barium radionuclides can be expected as a result of fission of nuclear fuel. Concluding, the interferences considered in the developed procedure of ICP-MS ^{90}Sr determination included alkaline earth metals, ICP-MS spectral interferences, and a large concentration of boric acid.

In sample processing using the Sr-resin microcolumn it was observed, that in optimized conditions, when the sample of strontium solution containing barium passes the microcolumn, at the employed concentration level about 50% of barium is not retained. Then, the retained barium can be removed by using 8.0 nitric acid solution, however, the volume of employed eluent has to be optimized. The use of an eluent volume greater than 2 mL allows for nearly 95% elution of barium (Fig.1), but the elution of barium by 8.0 M nitric acid is also accompanied by a partial elution of strontium retained on the column. It was found that the most appropriate volume of acidic eluent is 1 mL and this was employed in further studies.

For examination of isobaric ICP-MS interferences, yttrium-90 and zirconium-90 were introduced into the strontium solution and determined in basic steps of the flow procedure. The obtained results demonstrate that those interferences have no significant affinity to Sr-resin so they are easily removed in the first two stages of analysis and will not appear in the analyte solution prepared for ICP-MS detection (Fig.2). Concerning the polyatomic interferences, the elements capable of forming a charged polyions with mass 90 were examined. This investigation also involved elements, which can be present in reactor water such as Co, Mn, and Li. The obtained results indicate a low influence of potential polyatomic interferences on

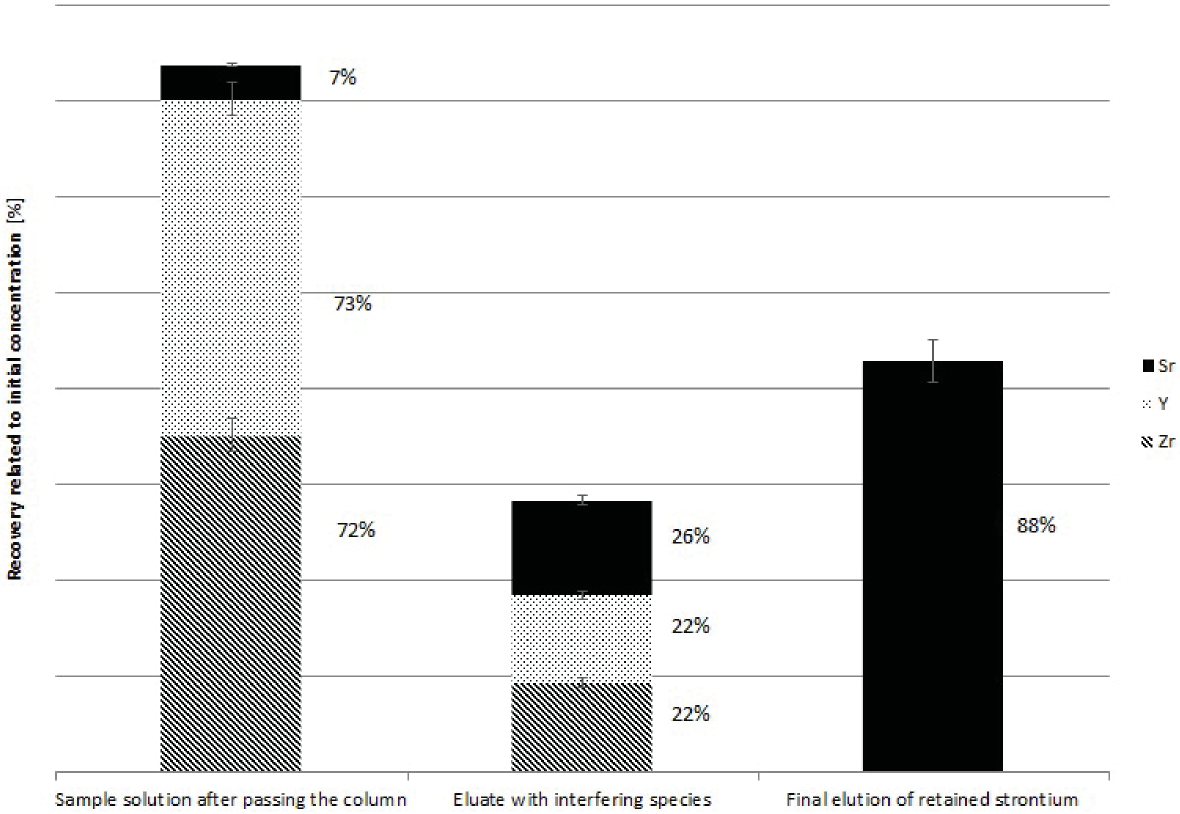

Fig.2. Efficiency of separation strontium from mixtures with yttrium and zirconium expressed by the recovery of each component in sample solution after passing the Sr-resin column, in 1 mL of 8 M HNO$_3$ solution employed for elution of interferences, and in 10 mL of water used for final elution of strontium retained on the Sr-resin. Initial concentration of each component – 250 µg L^{-1}; initial sample volume – 1 mL; 16 mm/3.2 mm I.D. column packed with 40 mg of Sr-resin.

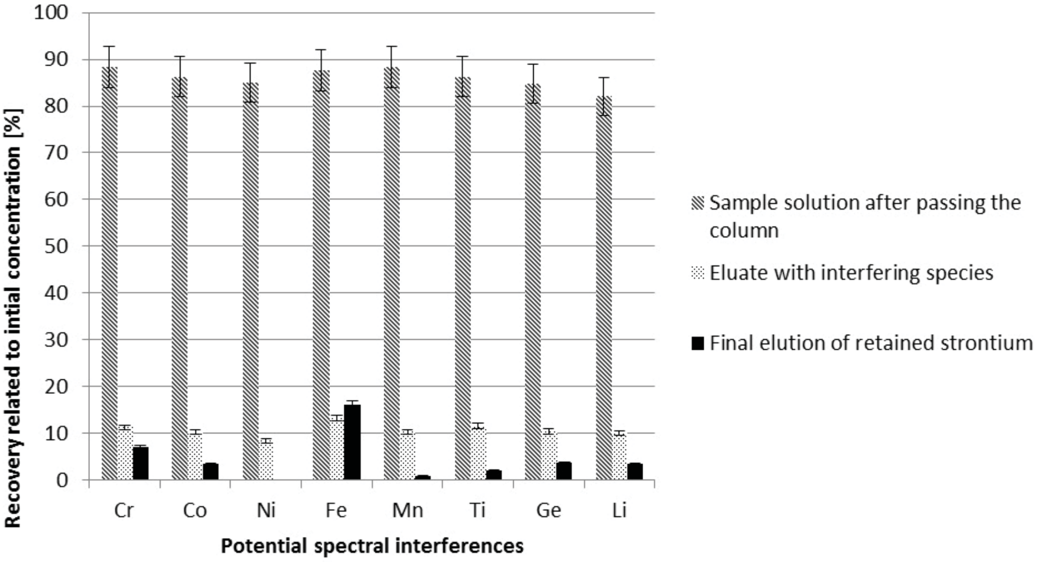

Fig.3. Efficiency of removal of potential spectral interferences in ICP-MS determination of strontium using 16 mm/3.2 mm I.D. column packed with 40 mg of Sr-resin, expressed by the recovery of each interferrig element in the sample flown through the Sr-resin column, in 1 mL of 8 M HNO_3 solution used for elution of interferring elements, and in 10 mL of water used for the elution of retained strontium. In each case was processed 1 mL of Sr solution containing 250 μg L^{-1} of interferring elements.

^{90}Sr determination by the use ICP-MS detection, because they are isolated with 90-95% yield in the first two stages of analysis (Fig.3).

High concentration of boric acid present in a reactor coolant makes a direct ICP-MS measurement impossible, hence in the conducted experiments with the developed SPE procedure strontium solutions were analysed in the presence of increasing concentration of boric acid from 4 to 12 g L^{-1}. As it could be expected, boric acid has no affinity to Sr-resin so it is not retained on the column. In the whole range of the examined boric acid concentration the determination of ^{90}Sr was not affected (Fig.4).

Further studies in this project will include the modification of the reported above flow procedure by adding an initial step of solid-phase preconcentration of strontium on an ion exchange column, and evaluation of the detection limit of the whole optimized procedure. A final step will be the determination of ^{90}Sr in real samples of nuclear reactor coolant, spiked and non-spiked with ^{90}Sr, and also comparison of the obtained result with a conventional manual method using a liquid scintillation counter.

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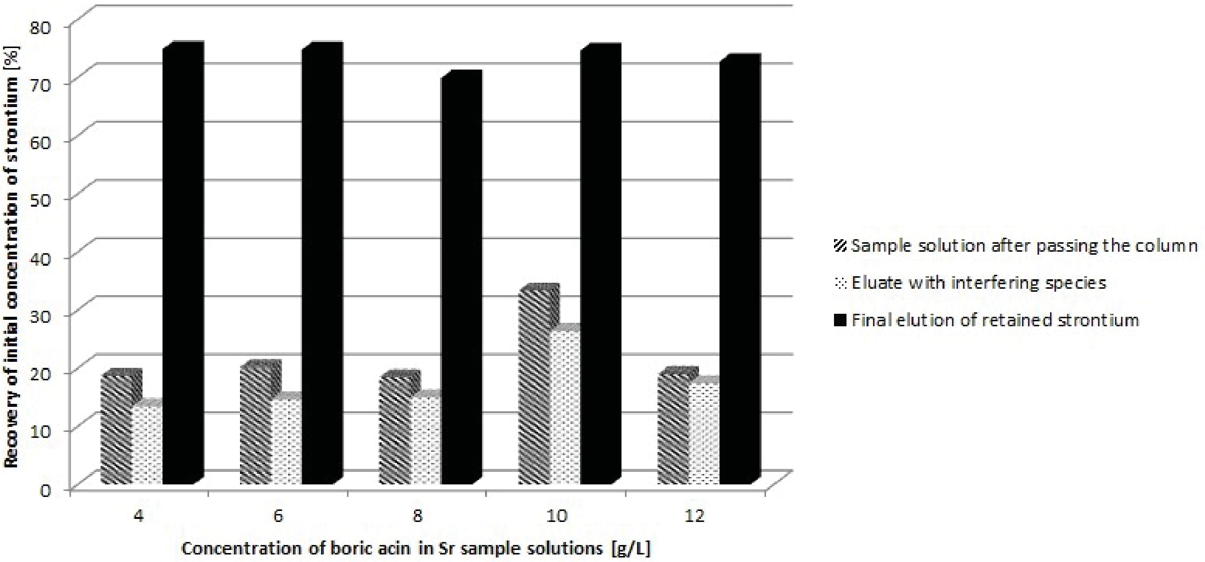

Fig.4. Effect of different concentration of boric acid on strontium retention and elution with the use of 16 mm/3.2 mm I.D. column packed with 40 mg of Sr-resin, expressed by the concentration of Sr measured in the sample solution flown through the column, in 1 mL of 8 M HNO_3 solution used as potential eluate for interferences, and in 10 mL of water used for final elution of Sr. Initial sample volume – 2 mL; initial Sr concentration – 200 μg L^{-1}.

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SELECTIVE AND QUANTITATIVE SEPARATION OF CHROMIUM FROM BIOLOGICAL MATERIALS

Iga Kużelewska, Halina Polkowska-Motrenko, Bożena Danko

Chromium occurs commonly in the earth crust [1-3]. It can exist in several oxidation states. The most important are +3 and +6. Toxicity of chromium compounds strongly depends on its oxidation state [4]. Trivalent chromium – Cr(III) is recognized as an essential trace element which is a component of the enzymes affecting the metabolism of glucose [5,6]. Its deficiency can lead to diabetes and cardiovascular diseases. Hexavalent chromium – Cr(VI) the most prominent example of toxic chromium – is a strong oxidizing agent. It can penetrate biological membranes of plant or animal tissue and has mutagenic properties modifying DNA transcription process [7,8]. Excessive exposure to Cr(VI) increases the chances of lung, kidney or liver cancer. That is why the content of chromium in the environmental materials and food should be monitored and very reliable methods of its determination are needed. The analytical methods most frequently used for chromium determination are atomic absorption spectrometry (ASA), inductively coupled plasma optical emission spectrometry (ICP-OES), spectrophotometry, chemiluminescence [9,10]. In this study a new procedure for the determination of chromium in biological materials by the radiochemical neutron activation analysis (RNAA) was developed. Advantages of RNAA and its significance in metrology are well-known [11-14]. The most important are a low limit of detection for a large group of elements and lack of blank. The developed method is based on the selective and quantitative post-irradiation separation of ^{51}Cr from all accompanying radionuclides, followed by a γ-ray spectrometric measurement.

Experimental

MnO_2 Resin, 75-150 μm (Eichrom Technology, USA) were loaded into the columns and equilibrated with appropriate solutions before use.

Hydrochloric and nitric acid p.a. (POCH) were used.

All other reagents used in the procedure were of analytical reagent grade.

18 MΩ cm – grade water from Mili.Q RG Ultra Pure Water System Millipore Co was used throughout.

Cr standard solution (10 mg g^{-1}) was prepared from metallic Cr (Spectra-pure, K-L, Koch Light) by dissolving it in HCl. The concentration of stock solution was determined by weighing. Standards for NAA (50 μg) were prepared by dropping the aliquots of the stock solution onto the filter paper circles, ø = 7.7 mm (Schleicher & Schull), placed in HDPE snap-cap capsules, weighed on an analytical balance (Sartorius) and dried.

The following radioactive tracers were used in elaboration and optimization of the separation scheme: ^{134}Cs ($T_{1/2}$ = 2.06 y), ^{60}Co ($T_{1/2}$ = 5.27 y), ^{51}Cr ($T_{1/2}$ = 27.7 d), ^{46}Sc ($T_{1/2}$ = 83.8 d), ^{65}Zn ($T_{1/2}$ = 244 d). All tracers were prepared by neutron irradiation of spectrally pure oxides or salts (mostly nitrates) in the Polish reactor MARIA.

Analytical procedure

Biological samples, chromium standards in PE capsules were irradiated at thermal neutron flux of 10^{14} cm^{-2} s^{-1} for 50 min. After one week cooling time, samples were quantitatively transferred to digestion vials. Then, the mineralization process was carried out in a high pressure microwave system, using a mixture of 6 mL of concentrated

Table 1. Distribution coefficients for chromium and other radioactive tracers in HCl, HNO_3, H_2SO_4 on MnO_2 Resin.

Acid	C [mol/L]	Cr-51	Cs-134	Sc-46	Zn-65	Co-60
HCl	0.01	43 147	252	329	13	2 246
HNO_3		7 003	175	172	5	965
H_2SO_4		79 299	293	93	5.64	1 292
HCl	0.1	3 668	147	25	12	949
HNO_3		2 241	67	16	5	407
H_2SO_4		259	190	0.92	4.89	240
HCl	0.5	1 252	76	3	29	181
HNO_3		436	101	4	12	46
H_2SO_4		52	136	0.68	3.65	24
HCl	1	1 803	90	13	84	103
HNO_3		197	72	4	12	17
H_2SO_4		35	108	0.52	6.92	14
HCl	2	1 043	58	9	313	55
HNO_3		50	50	4	10	10
H_2SO_4		22	63	0.23	4.97	6
HCl	8	6.9	3	4	67	38
HNO_3		6.2	5	3	11	4
H_2SO_4		0.31	10	0.20	2.73	1.64

HNO_3 and 2 mL of H_2O_2. The resulting solutions were evaporated to wet salts and dissolved in 0.01 M H_2SO_4 (three times). Finally, the sample was introduced onto the top of a column filled with a MnO_2 Resin (h = 10 cm, ϕ = 0.25 cm). The column was washed with 15 mL of 0.1 M HNO_3 (impurities elution: antimony, rubidium, zinc and cobalt) then, the column was washed with 4 M HCl (elution of caesium and the rest of rubidium). Chromium retained on the column was quantitatively eluted with 8 M H_2SO_4. The content of chromium was determined by γ-ray spectrometry *via* the 320 keV line.

Results and discussion

The MnO_2 Resin was devised for Ra separation from natural water samples over a wide range of pH. It was also used to isolate radium from the liquid wastes from the uranium industry and sorption of radionuclides release to sea waters from a nuclear reactor. The resin was used for the separation of chromium from human blood [15-17]. As an inorganic resin, it is resistant to high temperature and ionizing radiation, and shows a high selectivity to polyvalent metal [18]. In order to find the best conditions for separation of chromium from other elements, the distribution coefficients of Cr, Zn, Co, Sc and Cs on MnO_2 Resin in HCl, HNO_3 and H_2SO_4 acids were determined. The obtained results are shown in Table 1.

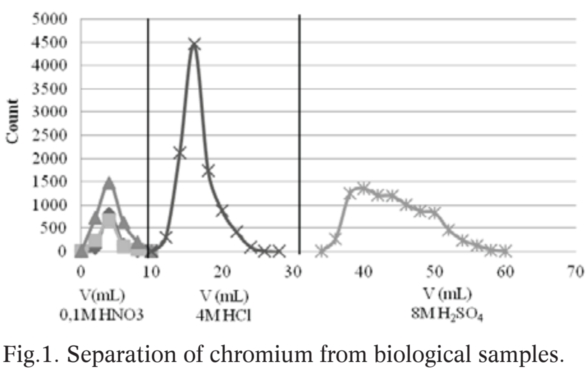

Fig.1. Separation of chromium from biological samples.

As can be seen from Table 1, the absorption of Cr takes place in the dilute solutions of hydrochloric, nitric and sulphuric acid and decrease with increasing concentration of the acids. The distribution coefficient values of chromium in 0.01 M acids are sufficiently high to ensure its quantitative retaining on the sorbents. The above conclusions were verified by the series of column experiments. In Fig.1, the results of separation of chromium on MnO_2 Resin are shown.

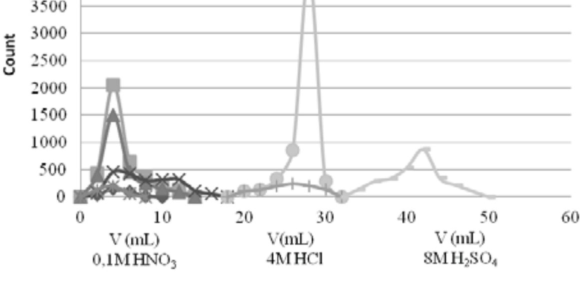

Fig.2. Separation of chromium from other elements in Tea Leaves INCT-TL-1.

The devised separation procedure was validated by the analysis of two certified reference materials (CRMs): Tea Leaves INCT-TL-1 and IAEA-452 Scallop Tissue. Figure 2 shows the re-

Table 2. Results of the determination of chromium in CRMs: Tea Leaves INCT-TL-1 and IAEA-452 Scallop Tissue.

Certified reference materials	Certified value and confidence limits [μg/g]	Value obtained by the developed method X ± U (k = 2) [μg/g]
Tea Leaves INCT-TL-1	1.91 ± 0.22	2.04 ± 0.09
Scallop Tissue IAEA-452	5.2 ± 0.7	5.45 ± 0.13

sults obtained for the separation of Cr from Tea Leaves INCT-TL-1.

A comparison of the results of chromium determination obtained by the developed method with the certified values is shown in Table 2.

As can be seen from Table 2, the results for Cr determination in biological materials, obtained by the newly elaborated RNAA method, agree very well with the certified values. The described procedure gives accurate results with low uncertainties.

The presented method can be used to the determination of total chromium content in the biological samples.

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DETERMINATION OF RADIUM-266 IN VARIOUS ENVIRONMENTAL SAMPLES BY ICP-MS METHOD

Michał Zuba, Ewelina Chajduk, Zbigniew Samczyński, Halina Polkowska-Motrenko

Radium-226 is one of NORM (naturally occurring radioactive material). It is considered one of the most toxic radionuclides. In the Polish legislation, Ra-226 belongs to the first, the highest class of radiotoxicity. This is due to the fact, that radium as an alkali earth metal is the chemical analogue of calcium, one of the major macroelements in human body. Radium follows the same routes as calcium in human organism, and finally, is built in the bones. Studies have shown that 15-20% of radium from food is transferred to the blood, and 25% radium from blood is built in the bones. Once it is built-in, it stays in human body with half-life of 45 years, and deposits the activity from both: decay of radium and decay of its daughters, short-lived radionuclides with a high specific activity [1-8].

Main source of radium in the environment is mining of uranium and other metalliferous and non-metallic ores as well as heavy sands, fossil fuels (coal, oil, natural gas). Another source of radium is the production of phosphate fertilizers. Lot of radium can be found in scrapyards and old military objects, as a result of using it in radioluminescent paints [2]. In addition, radium has quite a high mobility in the environment. At present, radium is still used on a low scale for medical purposes. It is also used in geological and oceanographic studies as an important tracer and in laboratories for preparation of radon standard solution and Ra-Be neutron sources [1].

Environmental concentration of radium in water rarely exceeds values that allow radium to form any compound that could precipitate (*e.g.* sulphate) and accumulate. It usually co-precipitates as $Ba(Pb)SO_4$, and that way it accumulates in the water reservoirs and forms the deposits [2-8].

For the determination of radium in environmental samples, usually radiochemical procedures are used, however these procedures are time-consuming. Ra-226 emits mostly alpha radiation (E = 4.78 MeV), and gamma radiation (E = 186 keV) with a low abundance what limits the use of gamma-ray spectrometry without processing of the sample.

Alpha spectrometry is the method most commonly used for the determination of radium in various environmental samples. Preparation of a radium containing sample for alpha spectrometry is a multistage process consisting of Ra separation and obtaining a thin layer precipitate by co-precipitation. Because of complexity, it takes a long time and could result in losses of the analyte [5,9-12]. Radiochemical methods for the determination of radium could be too time-consuming in the case of emergency when there is the need of quick and accurate Ra determination (*e.g.* when there is a risk for human health).

In our study we have used the inductively coupled plasma mass spectrometry (ICP-MS) method for the determination of Ra-226 after its separation from environmental samples. For a few past years, the ICP-MS method has become popular in the measurement of long-lived radionuclides [3,7,8,13-15]. The ICP-MS method has a lot of advantages, among them low limits of detection for many elements and a very short measurement time. Also sample preparation could be shortened. Main disadvantage of ICP-MS is the possibility of isobaric and spectral interferences. Ra-226 is measured at m/z = 226, and mostly polyatomic interference could have an influence on radium signal, because there is no stable, single charged isotopes at this mass/charge ratio. According to the literature it is possible to form the following interferences for m/z = 226: $^{88}Sr^{138}Ba^+$, $^{87}Sr^{139}La^+$, $^{86}Sr^{140}Ce^+$, $^{89}Y^{137}Ba^+$, $^{92}Mo^{134}Xe^+$, $^{94}Mo^{132}Xe^+$, $^{95}Mo^{131}Xe^+$, $^{96}Mo^{130}Xe^+$, $^{97}Mo^{129}Xe^+$, $^{98}Mo^{128}Xe^+$, $^{100}Mo^{126}Xe^+$, $^{86}Kr^{140}Ce^+$, $^{78}Kr^{148}Nd^+$, $^{80}Kr^{146}Nd^+$, $^{82}Kr^{144}Nd^+$, $^{83}Kr^{143}Nd^+$, $^{40}Ar^{40}Ar^{146}Nd^+$, $^{40}Ar^{186}W^+$, $^{18}O^{208}Pb^+$ and $^{1}H^{16}O^{209}Bi^+$ [3]. Our study has shown that only tungsten above 25 ppm can interfere with the signal of radium by forming $^{40}Ar^{186}W^+$. However, radium should be separated and concentrated before ICP-MS measurement because of a very low content in environmental samples. Based on the literature, the strong cation exchange resin Dowex 50WX8 was chosen for the separation of radium [1,8,12,14,16-19]. The distribution coefficient of radium in the system: Dowex 50WX8 – HCl and HNO_3 has been determined (Fig.1).

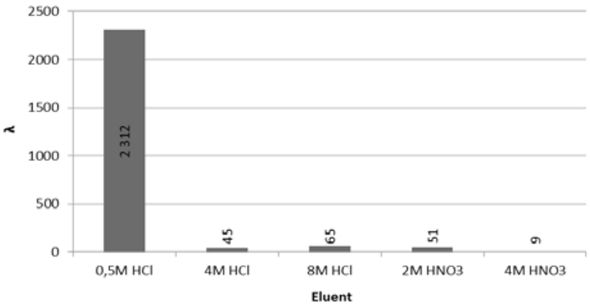

Fig.1. Distribution coefficients of radium in the system: cation exchange resin Dowex 50WX8 – HCl and HNO_3.

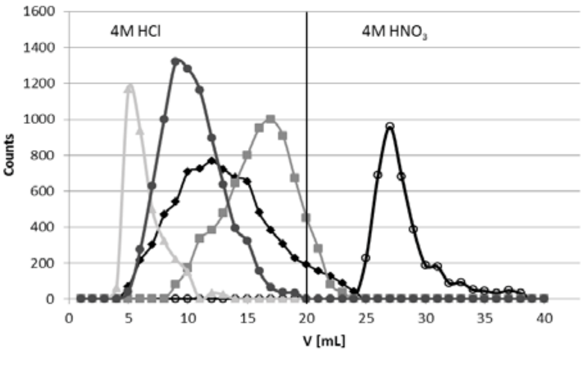

Fig.2. Separation of Ra from Cr, Cs, Co and Zn on Dowex 50WX8 – 4 M HCl and 4 M HNO_3.

As can be seen, the lowest value of the distribution coefficient is in 4 M HNO_3. Thus, the following procedure for the separation of radium from other metals was proposed: solution (0.5 L) consisting of a mixture of metal ions and Ra was loaded onto a column with Dowex 50WX8, then most of the ions were eluted with 4 M HCl, and finally radium was eluted with 4 M HNO_3. The obtained results are shown in Fig.2.

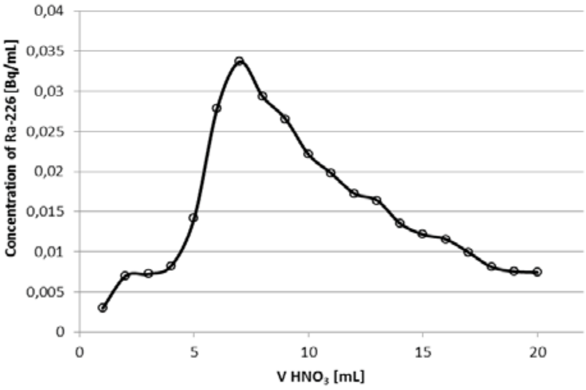

Fig.3. Elution of Ra-226 from column packed with Dowex 50WX8 (sample 500 mL, C_{Ra} = 1.1 Bq/L).

Recovery of radium and other elements was 99.8%. Radium was determined in the effluent by the ICP-MS method. The developed procedure was used to determine radium in drinking water spiked with a known amount of Ra-226 (1 and 10 Bq/L, respectively). Drinking water (0.5 L) was acidified to 0.5 M HCl and processed as described above. Results of the determination of Ra by ICP-MS are shown in Figs.3 and 4.

In both these experiments radium was successfully separated from the sample and measured by the ICP-MS method. Calculated limit of the detection (LOD) for radium by the applied ICP-MS

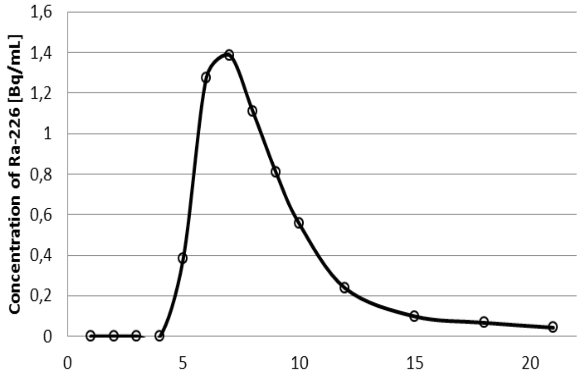

Fig.4. Elution of Ra-226 from column packed with Dowex 50WX8 (sample 500 mL, C_{Ra} = 10 Bq/L).

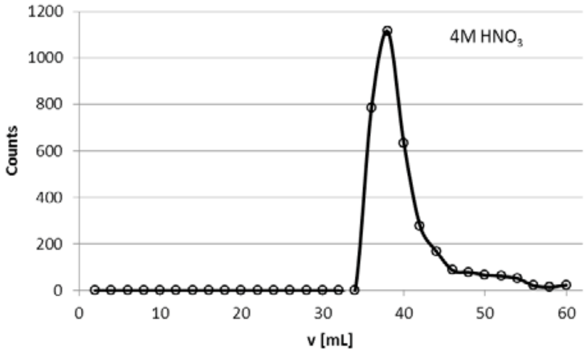

Fig.5. Seawater sample: elution curve of Ra-226 from Dowex 50WX8 column; eluents: 2 M HCl and 4 M HNO_3. Determination of Ra-226 by the ICP-MS method.

apparatus ELAN 6000 DRC II (PerkinElmer) with an ultrasonic nebulizer U6000AT+ (CETAC) was 0.003 Bq/mL (0.08 pg Ra/mL). Taking into account the whole procedure, the limit of detection for Ra in water is equal to 0.12 Bq/L.

The developed separation procedure was used to analyse more complex matrices like seawater and ore/soil/sediment samples. In the case of seawater samples, the procedure was as follows: 0.5 L of water sample was acidified to 0.5 M HCl, spiked with radium-226 and loaded on the column Dowex 50WX8. Then the elution was carried out using 2 M HCl and next 4 M HNO_3. Results of Ra-226 determination by the ICP-MS method are shown in Fig.5.

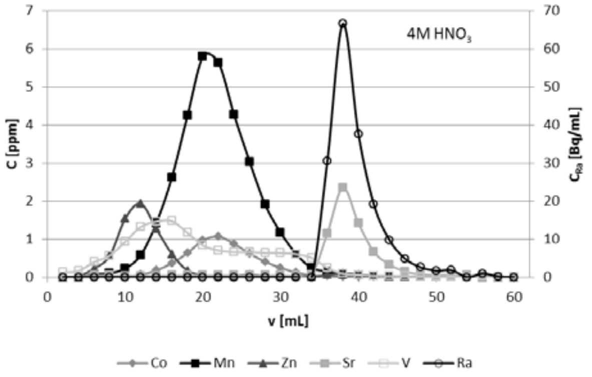

Fig.6. Uranium ore sample. Elution of ions from Dowex 50WX8 column; eluents: 2 M HCl and 4 M HNO_3. Determination of Ra-226 by the ICP-MS method.

Sample of ore/soil/sediment spiked with radium was mineralized in a mixture of HF, HNO_3 and H_3BO_3 acids (2:6:13) in a high-pressure microwave digestion system Anton Paar Multiwave 3000. Then, the obtained solution was evaporated 3 times near to dryness and the obtained precipitate was dissolved in 0.5 M HCl. After that the solution was loaded on the Dowex 50WX8 column and elution was carried out with 2 M HCl and next with 4 M HNO_3. Ra-226 was quantitatively eluted with 4 M HNO_3 (Fig.6).

The developed procedures allows for a quantitave separation of Ra-226 from various environmental samples, liquid and solid and its determination by the ICP-MS method. The procedure is relatively rapid. It can be used for both – routine analysis and emergency situations, when a fast answer about radium concentration is needed.

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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 pulsed plasma beams (HIPPB),
- 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 three novel lithium complexes – two with pyrazine-2,3,5,6-tetracarboxylate ligand and one with pyrimidine-2-carboxylate ligand have been solved and published.

High intensity pulsed plasma beams with duration of pulse in the microsecond range and energy density up to 20 J/cm^2 may lead to the melting and solidification of the surface layer of material with simultaneous introduction of ions from electrodes or discharge gas. The results of studies on tribological properties improvement of AISI 316L steel surface layer by implantation with rare earth elements (REE) using high intensity pulsed plasma beams are reported.

Track-etched membranes possess unique structural properties as their pore size, shape and density can be varied in a controllable manner. The advances in polymeric track-etched membranes preparation with channels of different geometrical form and their possible applications are reviewed.

For the examination, characterization and analysis of cultural heritage artefacts or art objects and their component materials, a conservation scientist needs a palette of non-destructive and non-invasive techniques, in order to improve our knowledge concerning their elaboration, their evolution and degradation during time, and to give a basis for their restoration and conservation. Among various methods used for the examination of art objects, nuclear techniques are crucial due to their high sensitivity and reproducibility. Medieval Central Europe coins: the Saxon coins, so-called the Otto and Adelheid denarii as well as the Polish ones, the Władysław Herman and Bolesław Śmiały coins, were examined to determine their provenance and dating. Totally, about two hundred coins were studied excavated from 19 archaeological stations and the so-called hoards. The ores from selected deposits such as Upper Silesia, Świętokrzyskie Mountains and Rammelsberg were also analysed to determine the provenance of metals used for coins manufacturing.

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 (glassrecipes and so on) as well as the chemical characteristic of certain raw materials and their source of deposits. Recently, two Stangengläser from the collection of the Museum of Decorative Arts in Prague were studied to reveal their decorative techniques and chemical composition.

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. In the course of our systematic studies in Li(I) coordination modes with a small heterocyclic nitrogen containing carboxylate ligands 22 novel crystal structures have been already reported. This study presents the crystal and molecular structure of three novel lithium complexes – two with pyrazine-2,3,5,6-tetracarboxylate ligand [1,2] an one with pyrimidine-2-carboxylate ligand [3].

PART 23. (μ-Dihydrogen pyrazine-2,3,5,6-tetracarboxylato-$\kappa^6 O^2,N^1,O^6;O^3,N^4,O^5$)bis-(diaqualithium) monohydrate

The structure of the title compound reveals a dimeric unit of 2/m crystallographic symmetry in which two symmetry related doubly aqua-coordinated Li(I) ions are bridged by a ligand molecule *via* its both N,*O*,*O* bonding sites (Fig.1). The Li(I) cation is in distorted trigonal-bipyramidal coordination. Its equatorial plane is formed by N1, O3, O3$^{(i)}$ and the Li1 atoms; the O1 and O1$^{(i)}$ atoms are at the apices. The O1–Li–O1$^{(i)}$ angle is 151.7 (3)°. The pyrazine ring is planar. Two carboxylate groups remain protonated to maintain charge balance. Bond distances and bond angles within the hetero-ring do not differ from those reported in the structure of the parent acid. Short, symmetric hydrogen bond is formed in which the carboxylate O2 atom is as a donor and the O1$^{(ii)}$ is as an acceptor. A dihedral angle formed with the pyrazine ring by the carboxylic group C1/O1/O2 is 4.7 (1)°. Fourier maps show a clear disorder in hydrogen positions at the solvation and coordinated water molecules with position occupancy of 0.5. The title molecules are held together by a network of hydrogen bonds in which coordinated water molecules act as donors and carboxylate O atoms as acceptors forming molecular layers propagating in the crystal *a* direction A view of a single layer is displayed in Fig.2. The layers are linked by weak hydrogen bonds in which solvation water molecules are involved.

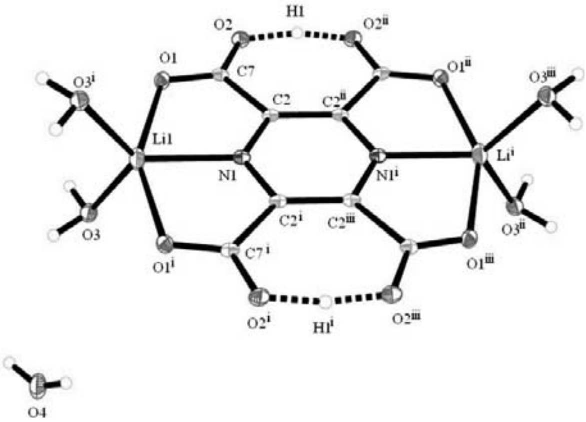

Fig.1. The molecule of the title compound with atom labelling scheme and 50% probability displacement ellipsoids. Symmetry code: (i) -*x*, -*y*, *z*; (ii) *x*, *y*, -*z*; (iii) -*x*, -*y*, -*z*.

PART 24. catena-Poly[[lithium-μ_2-(dihydrogen pyrazine-2,3,5,6-tetracarboxylato)-$\kappa^6 O^2,N^1,O^6;O^3,N^4,O^5$-lithium-di-$\mu$-aqua-$\kappa^4$O:O] 2,5-hydrate]

The structure of the title compound is composed of molecular ribbons propagating in the crystal [001] direction. The structural unit of a ribbon is built of a centro-symmetric ligand molecule which bridges two Li ions using its both *N,O,O* bonding sites. Two water molecules chelated simultaneously to Li ions belonging to adjacent structural units, bridge them into a molecular ribbon (Fig.3). The coordination environment of a Li ion is distorted trigonal-bipyramidal. Its equatorial plane is composed of coplanar Li1, N1, O3, O4 atoms; O1 and O1$^{(i)}$ are at the apices. The

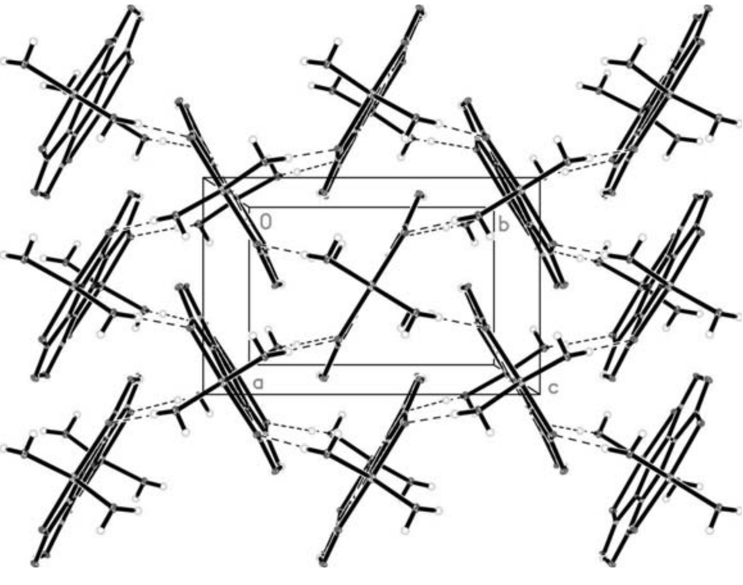

Fig.2. A single molecular layer composed of the dimers linked by a hydrogen bond network as viewed along the crystal *c* direction.

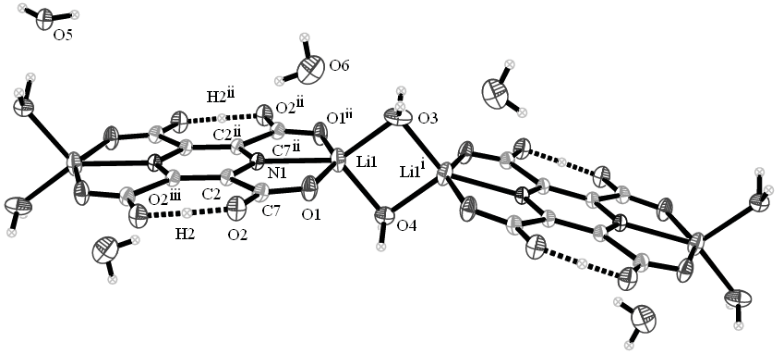

Fig.3. A fragment of a [001] chain in the title compound with 50% probability displacement ellipsoids. Symmetry code: (i) $x, y, -z+1$; (ii) $-x+1, y, z$; (iii) $x, -y, -z+1$.

Li–O and Li–N bond distances are usual. Within a ligand two carboxylate groups remain protonated to maintain charge balance and form short, intramolecular symmetric hydrogen bonds of 2.409 (1) Å. The ligand ring is almost planar (r.m.s. is 0.0003 (1) Å); the carboxylate C17/O1/O12 group makes with it a dihedral angle of 2.6 (1)°. The Fourier map shows two solvation water molecules (O5 and O6), both at special positions. The refinement reveals a disorder of the O6 aqua molecule with 0.25 positional occupancy, *i.e.* two molecules at random in a unit cell. This molecule locates coplanarly with the N1, O3, O4 and Li1 atoms at a distance of 2.538 (2) Å from the latter. The ribbons are held together by a system of hydrogen bonds in which coordinated and solvation water molecules act as donors and carboxylate O atoms as acceptors giving rise to a three-dimensional framework (Fig.4). The structures of two other Li complexes with the title ligand have been recently reported. The structural unit of the title polymer is closely related to that one observed in the structure of the first compound which consists of discrete dimeric molecules built of two aqua-coordinated Li ions bridged by the ligand molecule *via* both its N,*O*,*O* bonding sites [1]. The structure of the second complex is built of anions each consisting of an aqua coordinated Li ion chelated to a doubly deprotonated ligand molecule and of aqua coordinated Li cations [4].

PART 25. Crystal structure of catena-poly[[[aqualithium(I)]-μ-pyrimidine-2-carboxylato-κ^4*N*^{1},*O*^{2}:*N*^{3},*O*^{2}] hemihydrate]

A molecular assembly consisting of an aqua-coordinated Li(I) cation and a bonded pyrimidine-2-carboxylate ($C_5H_3N_2O_2$) ligand constitutes the structural unit of the title polymeric compound, $\{[Li(C_5H_3N_2O_2)(H_2O)]\times 0.5H_2O\}n$. There are four such assemblies in the asymmetric unit. Linked into pairs, they form molecular ribbons in which the ($C_5H_3N_2O_2$) ligand bridges adjacent Li(I) cations using both its N,O bonding sites

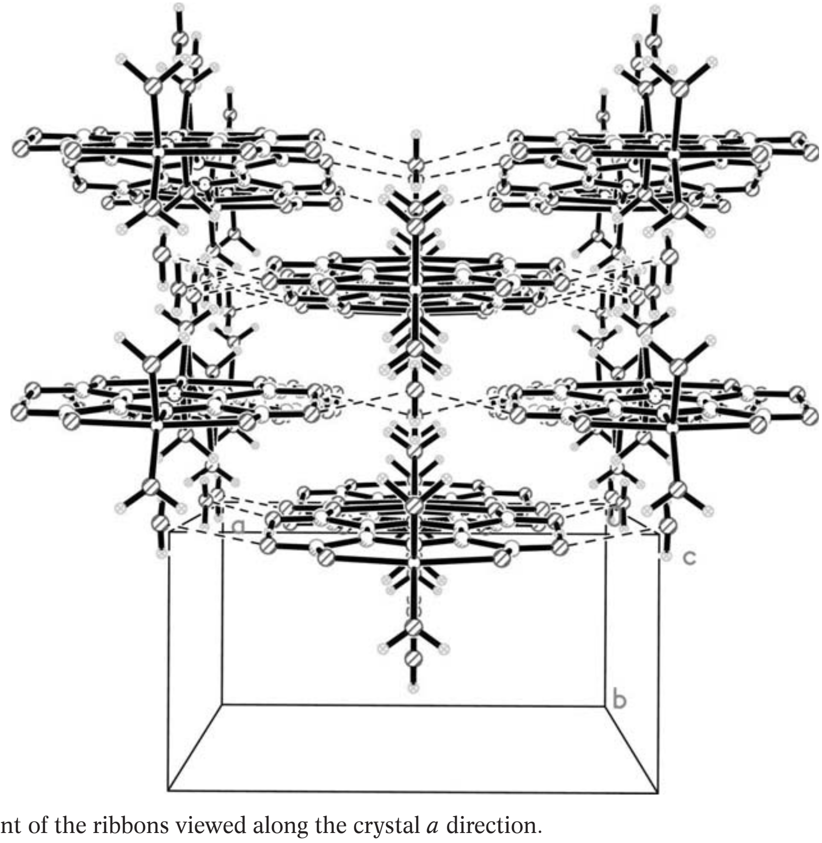

Fig.4. The alignment of the ribbons viewed along the crystal *a* direction.

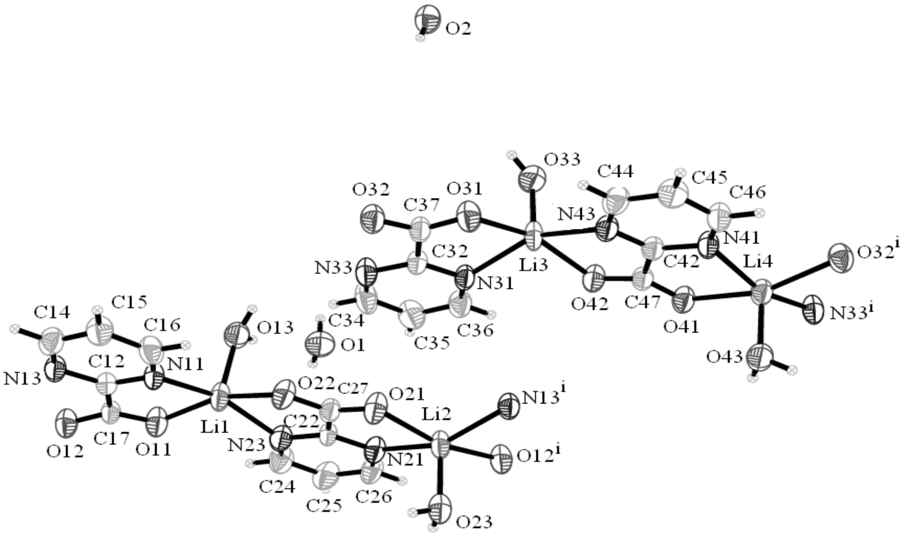

Fig.5. Fragments of two molecular ribbons in the structure of the title compound, showing the atom labels and 50% probability displacement ellipsoids for the non-H atoms. Symmetry codes: (i) *x*, *y*, *z+1*; (ii) *x*, *y*, *z–1*.

(μ_2-bridging mode), (Fig.5). The ribbons propagate in the *c* axis direction (Fig.6). All four Li(I) cations show a penta-coordination mode which can be described by two alternative geometries: either trigonal-bipyramidal or square-pyramidal, both slightly deformed. For example, in the case of the Li1 cation, the equatorial plane of a trigonal bipyramid consists of atoms O13, N11 and N23 with Li1 0.0712 (5) Å out of this plane; atoms O11 and O22 are at the apices. On the other hand, the base of the square pyramid is formed by the O11, O22, N11 and N23 atoms (r.m.s. 0.0069 (1) Å), O13 is at the apex; the Li1 cation is 0.3989 (8) Å out of the base. A similar description can be made for the remaining three independent LiO_3N_2 groups. The pyrimidine rings of all four ligand molecules are almost planar, with r.m.s. deviations ranging from 0.0024 (1) Å (ligand 4) to 0.0094 (1) Å (ligand 1). The carboxylate groups make dihedral angles with hetero-rings in the range from 2.8 (1)° (ligand 2) to 7.6 (1)° (ligand 1).

The ribbons interact *via* a network of hydrogen bonds. Water molecules of solvation act as donors, while the carboxylate O atoms from adjacent ribbons act as acceptors. Hydrogen bonds between coordinating water molecules as donors and carboxylate O atoms belonging to adjacent ribbons as acceptors are also observed.

The title compound is the third Li complex with the pyrimidine-2-carboxylate ligand reported so far. In one of these complexes [5], molecular ribbons composed of Li cations bridged by the bidentate carboxylate groups and bridged by bidentate nitrate anions form molecular layers. An

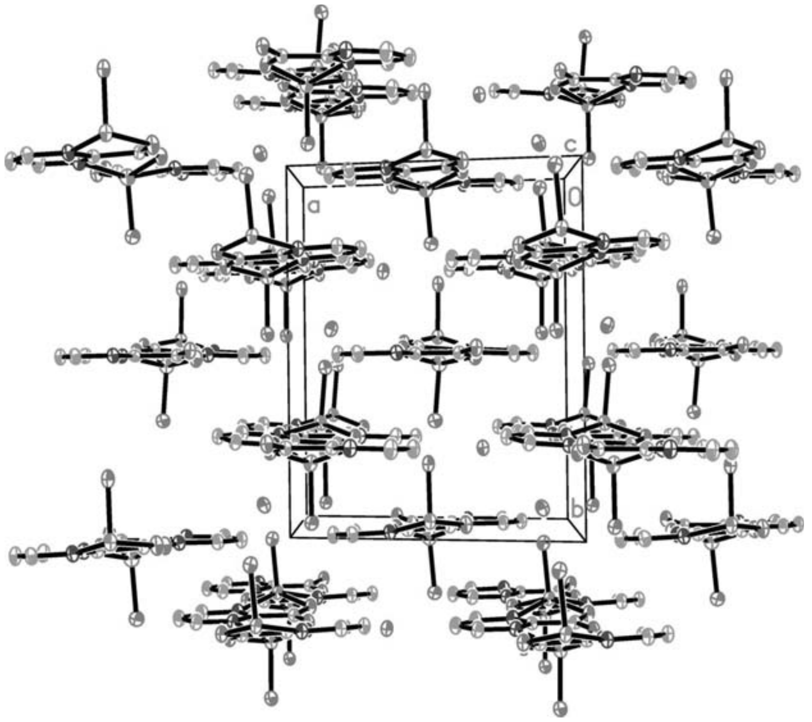

Fig.6. The packing of molecular ribbons in the structure of the title compound as viewed down the ribbon direction (the crystallographic *c* axis). For clarity, H atoms are not shown.

interesting feature is the absence of any N,O chelating bonding to the metal ion. The structural motif in the remaining complex [6] consists of a molecular chain similar to that in the title compound. In this structure, the chains are bridged by pairs of aqua-coordinated Li ions interconnected by an aqua O atom. The tetrahedral coordination of each of these Li cations is completed by two carboxylate O atoms acting in a bidentate mode and donated by the ligands belonging to adjacent chains. The charge of the resulting cationic ribbon is compensated by the interspersed chloride anions.

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POLYMERIC TRACK-ETCHED MEMBRANES AND THEIR POSSIBLE APPLICATIONS

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The energetic ions create changes in a material along their trajectory when they travel through the material. Ions deposit energy in material and create radiation damage. During chemical etching the damaged zone of a latent track is removed and transformed into a hollow channel [1]. Pore geometry is based on two parameters: the bulk etch rate, V_B, and the track etch rate, V_T. Track-etched membranes consist of a thin polymer foil with channels – pores – from surface to surface. The production process of membranes is well-known and described in the literature [2,3]. The increasing interest in polymer track-etched membranes with nanochannels is connected with the development and creation of nanoporous materials with advanced properties, for example: the development of materials with highly asymmetrical nanopores for molecular sensors [3,4], study of propagation of X-rays and acoustic waves through track-etched membranes as a model of porous medium [5], development of nanocapillary bodies for modelling the transport of molecules and ions in constrained volumes [4]. One of the polymer used for track-etched membrane production is polyethylene terephthalate (PET) with molecular formula $(C_{10}H_8O_4)_n$. A PET film 12-μm thick (Hostaphan RNK, Mitsubishi Polyester Films) was irradiated with accelerated heavy ions: 170-MeV Xe-ion beam with the ion fluency in the range of 5 x 10^4 to 1 x 10^8 cm^{-2} from an IC-100 accelerator at the Flerov Laboratory of Nuclear Reactions (Dubna, Russia). Symmetrical membranes with cylindrical pores were obtained using a standard etching procedure (NaOH solution as the etchant, 60°C, different process time). For obtaining the asymmetrical membranes, one surface of the irradiated foil was exposed to ultraviolet radiation. Then, the samples were etched (different times, 60°C, NaOH solutions with the surfactant 0.05% (w/w) Dowfax 2A1 (Dow Chemicals)). Membranes were examined using a scanning electron microscopy (SEM) technique with DSM 942 (Zeiss, Germany) and an LEO 1530 (Zeiss, Germany) field-emission scanning electron microscope (FESEM).

As a result of the standard etching process, the symmetrical membranes with cylindrical pores perpendicular to the surfaces with diameters of 0.2, 0.4, 1.2 and 2.3 μm were obtained (Fig.1A). As a result of the advanced etching process, the membranes with pores with different shape were obtained. FESEM images of asymmetric pores are presented in Fig.1B,C.

Filtration

Investigations of micro impurities in environmental water samples – from rain and snow have been carried out using track-etched membranes.

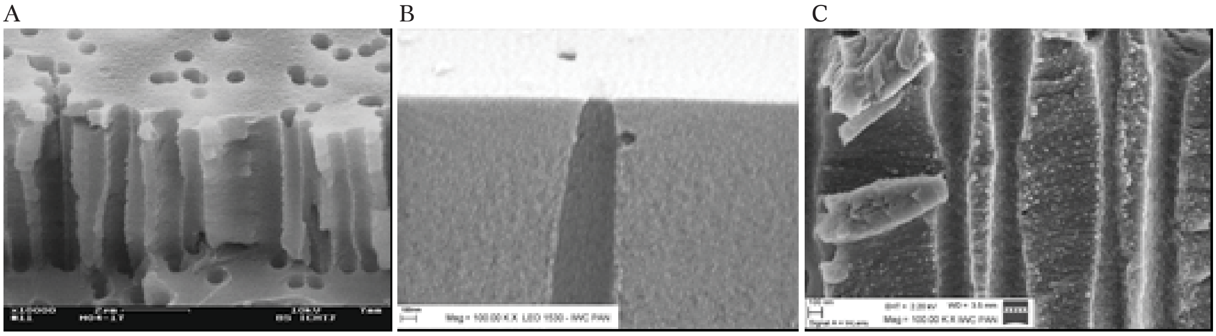

Fig.1. Fractures of symmetrical and asymmetrical polymeric (PET) track-etched membranes with pores in the shape of: (A) cylindrical, (B) bullet-like, (C) hourglass-like.

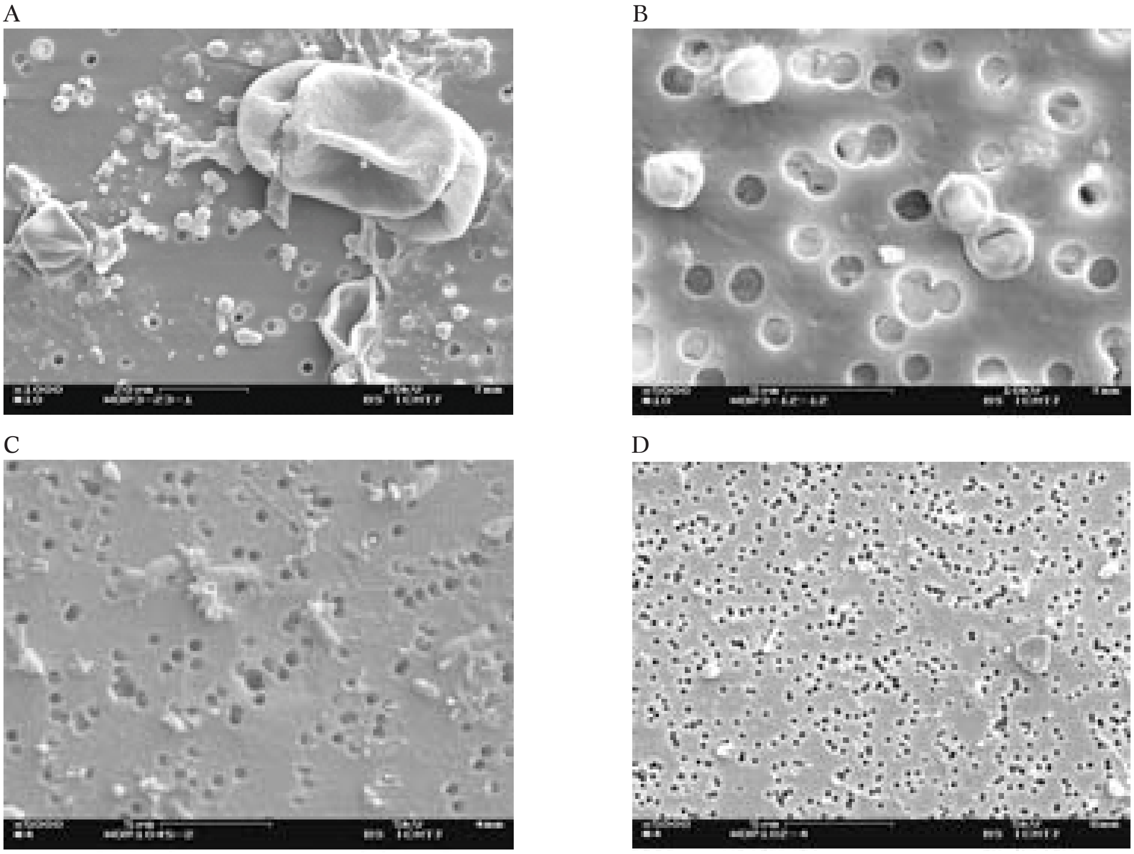

Fig.2. Results of cascade filtration of environmental samples through the track-etched membranes with pores with a diameter of: (A) 2.5 μm, (B) 1.2 μm, (C) 0.4 μm, (D) 0.2 μm.

Microfiltration processes through membranes with a pore diameter of 2.5, 1.2, 0.4 and 0.2 μm has been used for the cascade filtration. Sediments were observed with a scanning electron microscopy (Fig.2). Biological objects as well as inorganic particles can be clearly seen and identified on the surface. Elemental compositions of sediments remaining on each membrane were investigated with total reflection X-ray fluorescence (TXRF) analysis (PicoTAX I.U.T GmbH). Sediments consist mainly of Ca, K and S elements. Cascade filtration can be used with success for investigation of impurities in liquid samples, for example, in environment investigations and health protection.

Template synthesis

Deposition of materials inside well-defined pore membranes offers unique possibilities for the formation of objects: one-dimensional, high aspect ratio, with dimensions in nano-range. These objects can be made from any solid materials like metals and alloys, semiconductors, carbon, metal oxides, polymers and can have the form of rods, wires, tubules, multiwall tubules and multilayer rods [6,7]. Different deposition methods for filling the pores can be applied, for example: electrochemical deposition, layer-by-layer self-assembly, sol-gel deposition, polymerization inside pores. Polypyrrole (PPy) is a conductive polymer very stable in typical environmental conditions. Such polymer can be used as switching device, catalytic support and carrier of active media. Examples of PPy nanotubes grown inside pores in track-etched membranes are presented in Fig.3A. Separated nanotubes geometrical parameters correspond to the

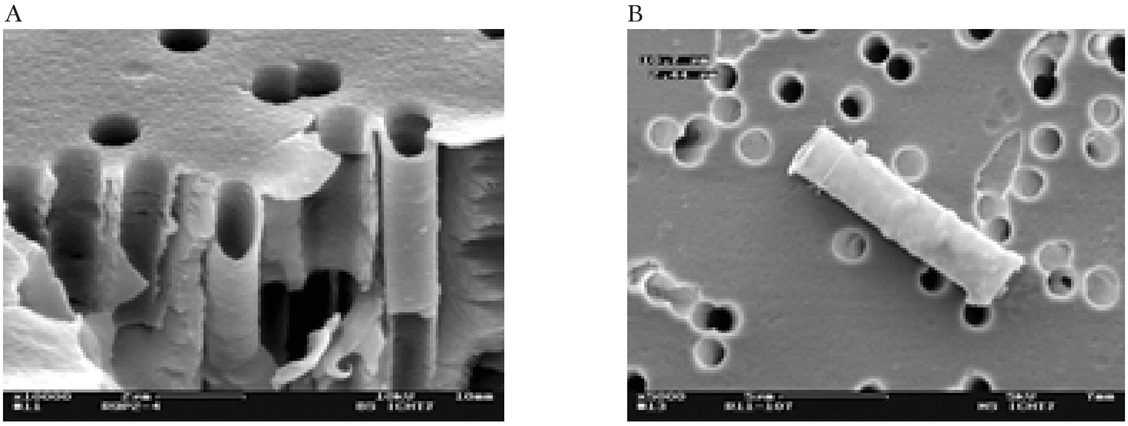

Fig.3. PPy nanotubes: (A) obtained after 15 min of polymerization process inside the pores of 1.2 μm, (B) single nanotube.

geometrical parameters of template, here: membrane with a thickness of 10 μm and pore diameter 2.5 μm (Fig.3B) [8].

Rectification

The asymmetric pores with a highly tapered tip exhibit nonlinear current-voltage characteristics in electrolyte solution. The tip of asymmetric pores diameter of about 30 nm with a shape of bullet like is presented in Fig.4A. The state with high conductance is observed when positive voltage was applied to narrow end of the pore (Fig.4B). The behaviour of the rectification ratio dependence on electrolyte concentration is shown in Fig.4C, where the data of samples with gradually increasing tip diameters are presented. Samples 1, 2, 3 and 4 were obtained using an etching time of 2.5, 3.5, 5 and 6 min, respectively. It can be seen that the rectification radio peaks at KCl concentration of 0.05-0.1 M.

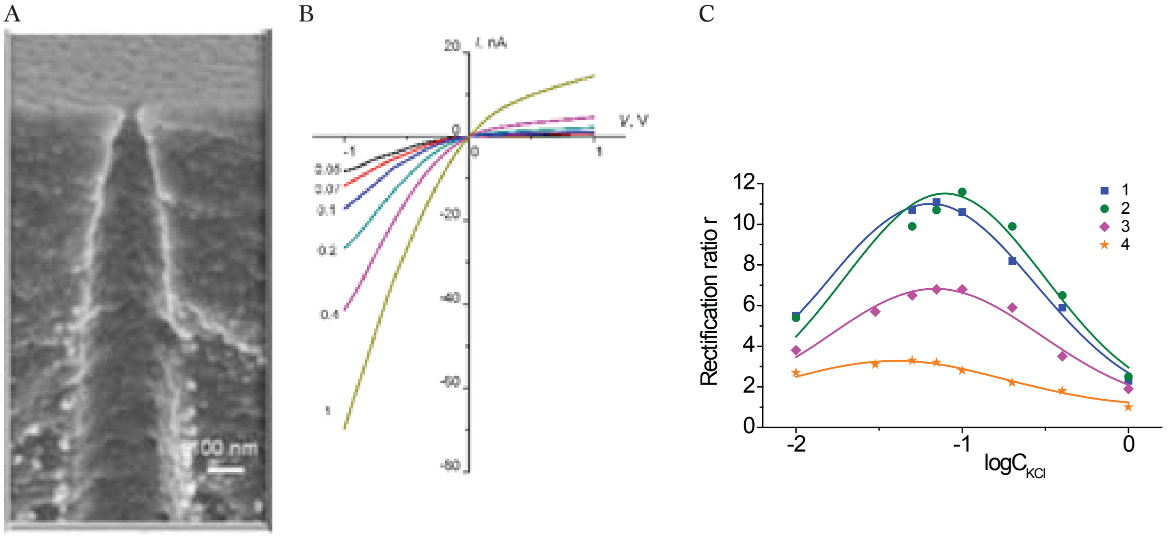

Fig.4. Asymmetrical polymeric track-etched membrane characterization: (A) bullet like tip, (B) current-voltage characteristic of a membrane with highly tapered pore tips, (C) rectification ratio *vs.* concentration of KCl for asymmetric membranes.

The conclusions are as follows:

- Polymeric track-etched membranes were obtained by PET foil irradiation with accelerated 170 MeV Xe-ions and chemical etching: standard procedure for symmetrical (cylindrical) pores and advanced chemical etching for asymmetrical pores in the shape of cone, cigar-like, bullet-like and hourglass-like.
- Possible applications of the obtained porous materials are, for example: micro- and ultrafiltration, matrix for template synthesis and molecular sensing.

Research was supported by the cooperation programme between the Polish scientific institutes with the Joint Institute for Nuclear Research, Dubna, Russia (04-5-1076-2009/2014) and by the Polish Ministry of Science and Higher Education (2804/ZIBJ Dubna/2014).

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TRIBOLOGICAL PROPERTIES OF AISI 316L STEEL SURFACE LAYER IMPLANTED WITH RARE EARTH ELEMENTS (REE)

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Austenitic stainless steels with a very good corrosion resistance are used in industrial applications, for example: in nuclear and petrochemical industries, pulp and paper chemical, food and chemical processing. Improvement of the wear resistance of austenitic stainless steels can be achieved using enrichment of the surface layer with reactive elements. It is known that high oxygen affinity elements such as Y, Ce, La, Er and other rare earth elements (REE) added to steels in small amounts can improve their useful properties, including the wear resistance [1,2]. The amount of REE addition have to be precisely controlled. There is no positive effects if the REE addition is too small and the negative effects are observed if the REE addition is too high. REE can be incorporated to the surface area of materials using different methods of surface modifications, as, for example: ion implantation [3-5], sol-gel coating [5,6], metal organic chemical vapour deposition [7,8], plasma beams application [9,10].

Austenitic stainless steel AISI 316L (Cr – 16.3 wt.%, Ni – 11.5 wt.%, Mo – 2.03 wt.%, Mn – 1.3 wt.%) was used as the substrate. The mishmetal (MM) with composition: Ce – 65.3 wt.%, La – 34.0 wt.% was used as a REE source. REE were incorporated into the one surface of steel samples using a MEVVA type implanter with parameters: implantation energy – 65 kV, applied ion doses – 1 x 10^{15}, 5 x 10^{15} and 5 x 10^{16} ion/cm^2. Samples were characterized by: Quantax 400 EDS system (Bruker, Germany) for the determination of elemental concentrations, a D8 Advanced (Bruker, Germany) diffractometer ($\omega = 10^o$, Cu K_α) for the determination of material structure and Rutherford backscattered spectroscopy – RBS (energy – (1.77/ch + 44) keV, and a detector resolution – 19.5 keV) for elemental composition and thickness for the determination of modified surface layer. Wear resistance measurements were carried out using the Amsler method with an A135 Amsler machine (constant load – 5 daN, 41Cr4 steel counter-sample).

The RBS spectra of the initial and REE (Ce+La) implanted samples with applied doses are shown in Fig.1. The upper part of the figure shows the spectra of initial AISI 316L steel with appropriately marked positions of main steel components. The lower part of the figure shows the experimental spectra of the REE samples implanted with marked threshold positions of the implanted elements. The RBS spectra were analysed using a SIMNRA code assuming that the ratio of Ce and La elements concentration was 2:1. The thickness of the layer with implanted elements, calculated for Fe substrate, was about 75 nm for all applied doses.

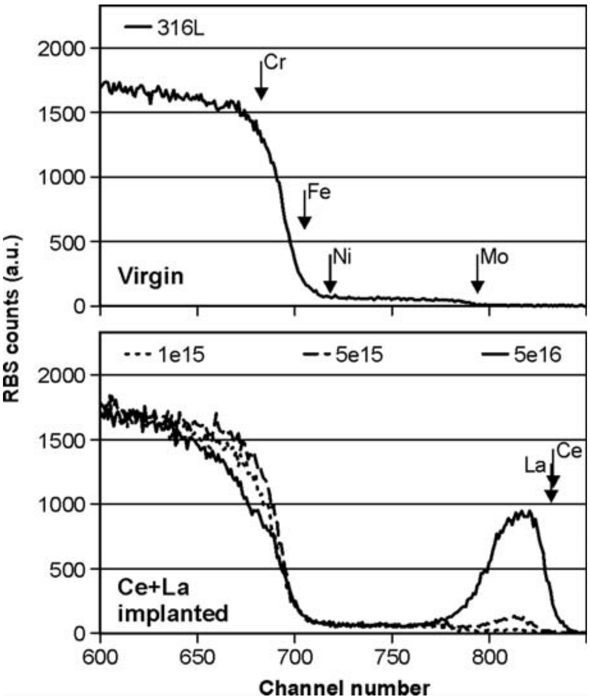

Fig.1. RBS spectra for initial and modified steel.

GXRD (grazing angle X-ray diffraction) spectra analysis confirmed the presence of FCC phase – austenitic structures – with a space symmetry group Fm-3m in the initial and modified materials. An increasing of the austenite lattice parameter was observed in the order to applied doses (Table 1). The present authors assumed that the changes in the crystalities size as well as the presence of internal stress in the modified surface layer is the reason of increasing austenite lattice parameter. In the fixed angle of measurements the beam penetrated the investigated layer to a depth of 74 nm.

Table 1. Austenite lattice parameter and its changes due to the dose of REE ion implantation.

Dose [ion/cm^2]	REE implanted		
	lattice parameter [Å]	change [Å]	change [%]
Initial	3.5830		
1.0 x 10^{15}	3.5980	0.0150	0.42
5.0 x 10^{15}	3.6018	**0.0188**	**0.53**
5.0 x 10^{16}	3.6020	0.0180	0.53

Changes of the linear wear observed for all the investigated samples show the linear character (Fig.2). It can be seen that there was no effect in wear resistance value in the case of used dose of 1 x 10^{15} ion/cm^2 (1.06 wt.% of REE incorporation). In the case of REE implanted with doses of 5 x 10^{15} and 5 x 10^{16} ion/cm^2 with 1.26 and 1.92 wt.% REE incorporation, respectively, the smaller value of linear wear means a higher wear resistance as compared with the initial material. Obtained results are in agreement with the fact of the necessity of precisely controlled REE amount. The dose 1 x 10^{15} ion/cm^2 was probably too small to evoke positive results. It is assumed that the improvement of tribological properties is caused by the increase of hardness what is connected with the presence of internal stress in the modified surface layer.

The conclusions are as follows:

- Implantation REE (Ce+La) into AISI 316L stainless steel with doses: 1x10^{15}, 5x10^{15} and

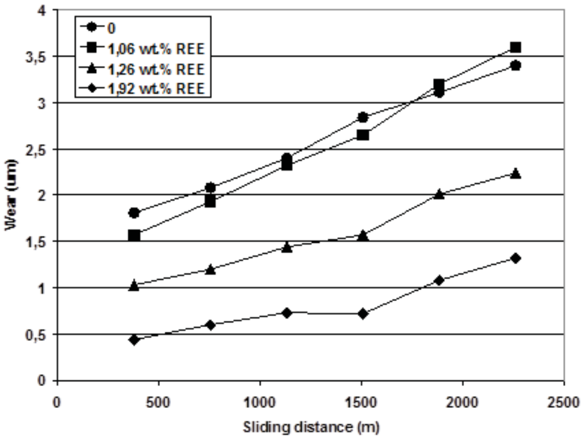

Fig.2. Linear wear of AISI 316L steel implanted with REE.

5×10^{16} ion/cm^2 lead to the formation of the enriched with dopants near surface layer with a thickness below 1 μm.
- Austenitic phases (FCC) were identified in the modified layer with increased lattice parameters in the order to used implantation doses as compared with the initial material.
- Obtained modified surface layers enriched with REE (Ce+La) with the dose of 5×10^{15} and 5×10^{16} ion/cm^2 showed a significant improvement of the wear resistance of 35 and 60%, respectively, as compared with the initial material.

The work was partially supported by the project "Support of public and industrial research using ion beam technology (SPIRIT)" under EC contract 227012 and by the Polish Ministry of Science and Higher Education (Decision 2871/SPIRIT/2013/0).

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PIXE ANALYSIS OF MEDIEVAL SILVER COINS

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An overall aim of the present study is to determine the provenance and dating of a few groups of the early medieval Central Europe silver coins. An attribution and chronology of them often constitute a serious problem for historians and numismatists. Material research of historical artifacts constitutes an important additional factor that helps us to choose the proper conservation methods. Denarii which were struck approximately from X-th century till XI-th century in Central Europe were found in a great number of hoards excavated in Poland. Individual characteristic of these coins is cross picture and legend on obverse and reverse sides. Iconography of denarii has not included information about mints [1-4]. Basing on the iconography criterion it is possible the differentiation of eight main types of denarii. For comparison, Otto and Adelheid denarii (991-995 A.D.) [5], dirhams (XI-th century), Hungarian and Czech denarus as well as the Polish ones, the Bolesław Chrobry, Bolesław Śmiały and Kazimierz Wielki coins were examined, too. Totally, 48 coins were selected which are important specially for debasement analysis.

As the Saxon denarii are particularly rare and, therefore of high value, it was intended to perform the analysis without sampling or with very small interference. Particle induced X-ray emission spectroscopy (PIXE) is a non-destructive elemental analytical technique. It is very similar to the well-known X-ray fluorescence (XRF) method, but in PIXE, instead of X-rays or gamma rays, the sample to be studied is bombarded by an energetic particle beam instead of (2-4 MeV proton beams in most cases) produced by a particle accelerator. The energetic protons also ionize the inner electron shells of the atoms in the bombarded volume and in the electron rearrangement process characteristic X-rays are emitted. The energies of these X-rays are strictly related to the atomic number of the emitting element, while the intensities of the X-rays are related to its concentration. Because of the intensive slowing down of the bombarding protons in matter and the absorption of the outgoing X-rays PIXE is inherently sensitive for the surface layers of thicknesses up to some tens of micrometers. In principle, elements from Al to U can simultaneously be detected using conventional energy dispersive X-ray detector, incidental and elemental sensitivities down to ppm levels can be achieved in favourable conditions. In the so-called external-beam version of PIXE the protons are extracted to air through a properly thin exit foil allowing non-destructive qualitative and quantitative elemental analysis of samples of practically any sizes. This method is especially useful for the

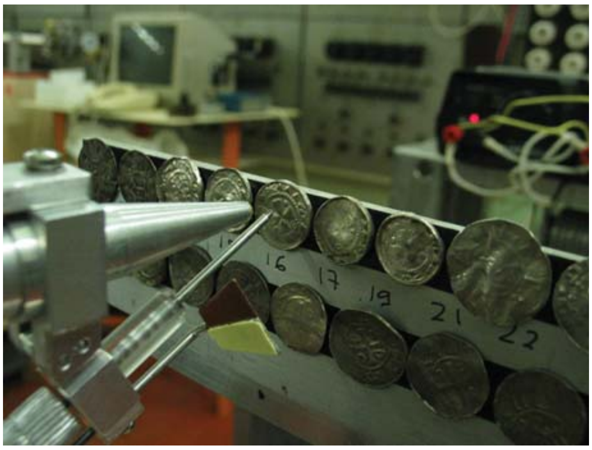

Fig.1. A positioned of a microbeam external facility at the Wigner RCP.

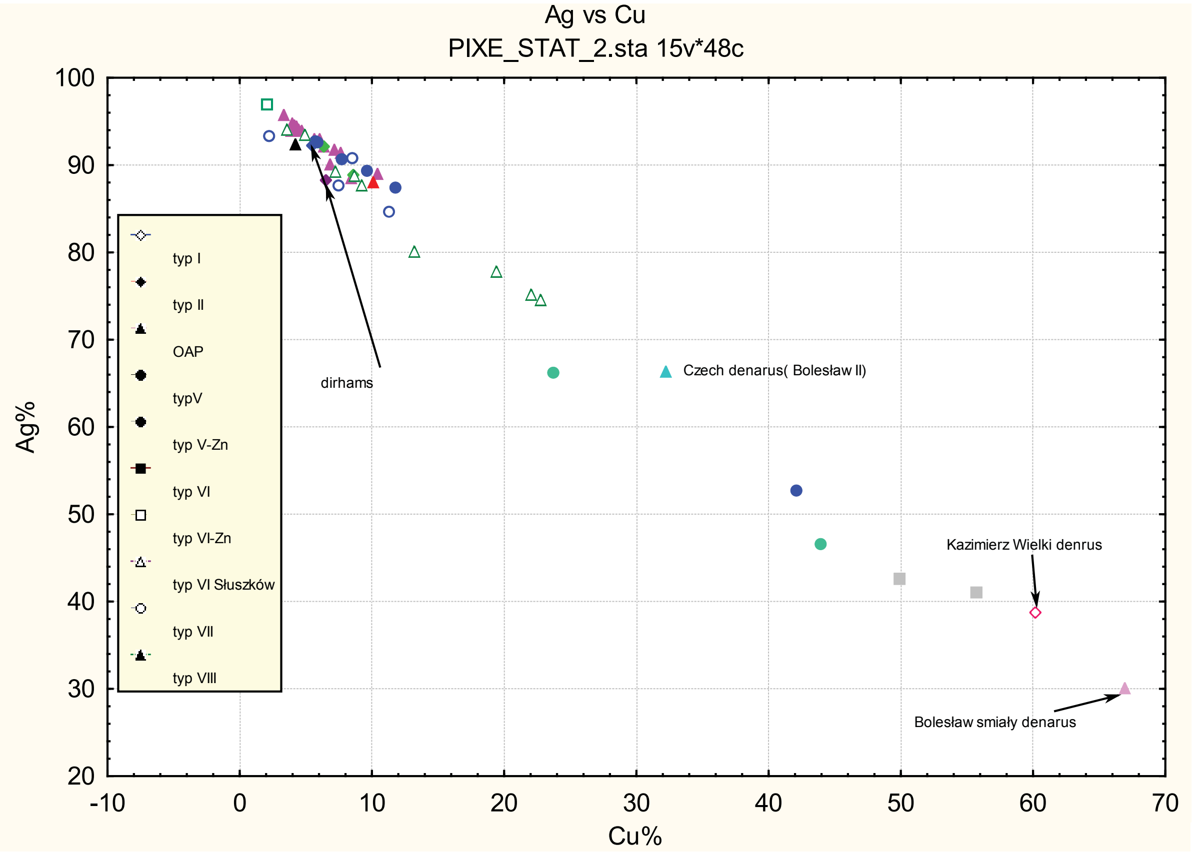

Fig.2. Ag *vs.* Cu (XRF method). The Saxon coins type I, II, V, VI, VII and VIII, Otto and Adelheid denarii, dirhams, Bolesław Śmiały and Kazimierz Wielki denarii, Czech and Hungary denarii – 48 coins.

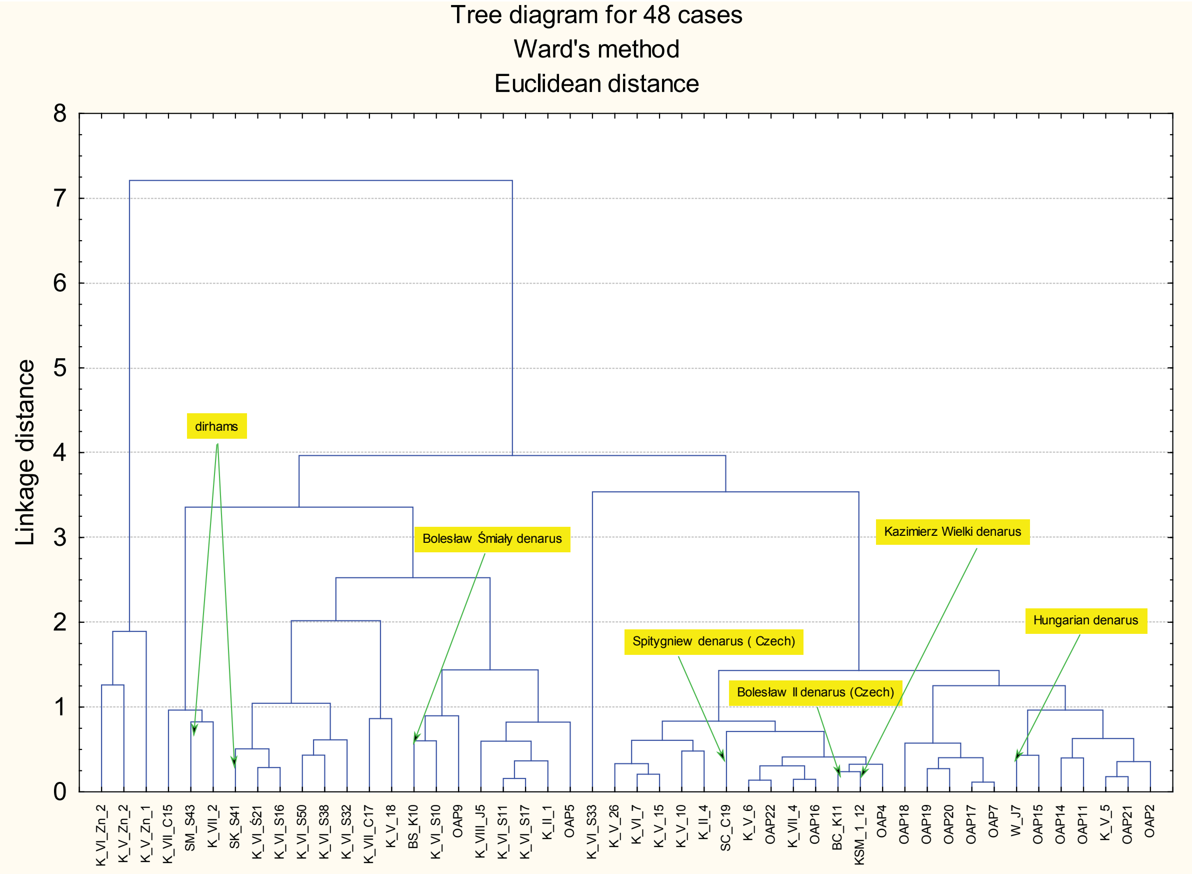

Fig.3. Cluster analysis of the studied Saxon coins type I, II, V, VI, VII and VIII, Otto and Adelheid denarii, dirhams, Bolesław Śmiały and Kazimierz Wielki denarii, Czech and Hungary denarii – 48 coins. Analysis was carried out for trace elements (Mn, Fe, As, Se, Sn, Zn, Au, Hg, Pb, Bi) determined by the PIXE method. Features number = determined elements number.

non-destructive study of unique and valuable cultural heritage objects (*e.g.* archaeological findings and artworks objects) [6,7].

The PIXE measurements were performed at the 5 MV Van de Graaff accelerator of the Institute for Particle and Nuclear Physics, Wigner Research Centre for Physics (Wigner RCP), Hungarian Academy of Sciences (Budapest, Hungary). Proton beam of 2.5 MeV energy was extracted from the evacuated beam pipe to air through a 7.5 μm thick Kapton foil. Target-window distance of 10 mm was chosen at which distance the beam diameter was found to be about 1 mm. Silver coins to be analysed were put on pure carbon sticker ribbon and fixed to a micromanipulator, enabling accurate three-dimensional positioning. External beam currents in the range of 1-5 nA were used. Characteristic X-ray spectra were taken by an AMPTEK X-123 X-ray spectrometer. The energy resolution of the 25 mm^2 x 500 μm SDD detector was 125 eV for the Mn Kα line. The detector was positioned at 135° with respect to the beam direction. To reduce the low energy X-ray counts an Al absorber of 100 μm thickness was applied in front of the detector. The net X-ray peak intensities and the concentration calculations were made by the off-line GUPIX program package [8]. PIXE set-up at the Wigner RCP with analysed denarii is presented in Fig.1.

Twelve elements were determined in each silver coin (Cu, Ag, Mn, Fe, Zn, As, Se, Sn, Au, Hg, Pb and Bi). The content of silver in the investigated coins was found between 30 to 98% and that of copper was found to be from 2 to 60%. The correlation Ag and Cu is presented in Fig.2.

The percentage of Cu and Ag (about 90%) is found to be almost of the same order in Otto and Adelheid denarii, dirhams, Czech denarus (Spitygniew) as well as in the denarii type I and II. The twelve 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 analysed coins. The statistical analysis was performed for standardized and logarithmic variables. Results of this analysis are presented in Fig.3, which clearly shows the division into groups closely related to the type of tested coins.

In spite of the surface analysis, important information was obtained about the major and trace elements in early medieval silver coins minted in Central Europe. The results of these investigations are significant for our knowledge of the history of Central European coinage, especially of Polish coinage. An interpretation of the results of the statistical methods allowed us to differentiate the artefacts in relation to the various production centres (mints), various recipes as well as various raw materials and methods of their purification.

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MATERIAL ANALYSIS AND DECORATIVE TECHNIQUES OF TWO STANGENGLÄSER FROM COLLECTION OF THE MUSEUM OF DECORATIVE ARTS IN PRAGUE

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Two tall vessels, called Stangengläser, one with allegory of *caritas* and Zierotin coat of arms, made of grayish glass (inv. no. 39654) and the second one with dancing couples, made of greenish glass (inv. no. 10041) from the collection of the Museum of Decorative Arts in Prague (Czech Republic) were studied to reveal their decorative techniques and chemical composition. Both vessels were diamond-point engraved, gilded and cold painted. They originate from the beginning of the 17th century. It was suggested that they could have been made in the glassworks at Wilhelmberg (present-day Staré Hutě near Hojná Voda) in south Bohemia.

Binding media were identified using an FTIR microscope (Perkin-Elmer 2000 AutoIMAGE, range 4000-700 cm^{-1}, using resolution 4 cm^{-1} and 16 scans). Samples were analysed in transmission on BaF_2 and AgCl plates. This method permitted the analysis of selected parts of the sample. Several spectra were obtained from each sample, their quality varied with the thickness of the section. Selected representative spectra were compared with a specially developed database of pure substances and standard reference materials, both young and deteriorated. From the Stangenglas with allegory of *caritas*, the samples originating from beige incarnate and the red skirt of the figure were analysed. The samples had a following stratigraphy: the under layer of varnish, the middle layer of paint and the upper layer of varnish. The varnish of both layers proved to be the same, consisting of terpenoid resin. The obtained spectra were found to have very good agreement with gummi olibanum. In the middle layer polysaccharide originating from a plant gum was identified as a binder. The samples of red and beige paint were found to contain madder (*Rubia tinctorum* L.) and lead white as a pigment. From the Stangenglas with dancing couples a sample of white paint originating from the inscription background was analysed. Only protein without additives was found, the binding media were identified as egg white.

The glass samples were embedded in epoxy resin, ground flat with silicone carbide, polished with diamond pastes down to 0.25 μm and finally coated with a thin layer of carbon. They were analysed using SEM-EDS (CamScan Maxim 2040 scanning electron microscope equipped with an Oxford Instruments ISIS energy dispersive X-ray spectrometer). For elemental analysis, the electron beam was rastered at a magnification of 500x over an area of fresh glass for 100 s, at 20 kV accelerating voltage. Count-rate on metallic cobalt was around 4000 cps. Standards were pure oxides and minerals and quantification was carried out using the ZAF method. Oxide weight percent was calculated stochiometrically. Analytical totals have been normalized to 100% for comparative purposes. The glass Corning D was used as a secondary reference material and good agreement between recommended and analysed results was obtained. The simplified results are shown in Table 1. The two Stangengläser were found to have similar composition, representing the same technological type characteristic rather of Bohemian than German production. This can be seen, among others, at an elevated concentration of SiO_2 and lower contents of CaO, P_2O_5 and MgO. We cannot tell what batch composition was used for their production. However, two possibilities are very probable. The first is a mixture of sand, wood ash and potash; the second is a mixture of sand, potash and lime (in both cases, possibly with an addition of manganese compounds). According to written sources, lime as a separate raw material was already used in Bohemian glasshouses at the beginning of the 17th century.

Table 1. Chemical composition of the glass samples (SEM-EDS).

Inv. No.	Na_2O [wt.%]	MgO [wt.%]	Al_2O_3 [wt.%]	SiO_2 [wt.%]	P_2O_5 [wt.%]	SO_3 [wt.%]	Cl [wt.%]	K_2O [wt.%]	CaO [wt.%]	TiO_2 [wt.%]	MnO [wt.%]	Fe_2O_3 [wt.%]
39654	1.5	2.5	1.8	62.4	1.2	0.3	0.3	11.0	17.8	<	0.7	0.5
10041	1.5	1.7	2.0	64.6	1.1	0.4	0.4	10.9	15.8	0.3	0.7	0.6

The analyses offered insight into the early 17th century glassmaking and decorating techniques in Bohemia. Close glass compositions of the two Stangengläser indicate that they could have been blown in the same glasshouse. However, the question of the Stangengläser provenance could, as yet, not be answered satisfactorily. Further comparative analyses of glasses excavated in Wilhelmberg and elsewhere would be needed to confirm this glassworks as a place where the two Stangengläser could have been produced.

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,
- support of industrial implementation of EBFGT process,
- 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:

- laboratory installation for electron beam flue gas treatment;
- UV pulsed fluorescent SO_2 analysers Model 40 and chemiluminescent NO/NO_x analysers with a molybdenum converter Model 10 A/R, manufactured by Thermo Electron Corporation (USA);
- gas chromatograph GC-17A with a mass spectrometer GCMS-QP5050, manufactured by Shimadzu Corporation (Japan);
- portable gas analyser type Lancom II, manufactured by Land Combustion (UK) (NO_x, SO_2, CO, O_2, *etc*.).

The Laboratory is open for any form of cooperation. Especially we offer such activities as:

- laboratory research on environmental application of electron accelerators,
- theoretical modelling of chemical processes under electron beam irradiation,
- concept design of electron beam technology implementation,
- process equipment design with use of CFD methods.

In recent years the Laboratory cooperated with such institutions as:

- 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).

KINETIC MODELLING OF NO HETEROGENEOUS RADIATION-CATALYTIC OXIDATION ON THE TiO_2 SURFACE IN HUMID AIR UNDER ELECTRON BEAM IRRADIATION

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Electron beam flue gas treatment (EBFGT) technology has been applied on an industrial scale in the EPS Pomorzany. The high removal efficiency of SO_2 (> 90%) was obtained at an 8 kGy absorbed dose, while about 70% NO_x was removed at the same absorbed dose. NO_x removal needs much more energy consumption than the SO_2 removal. There is a need to decrease energy consumption for NO_x removal by using EBFGT. However, electron accelerators with high power and high energy are very expensive, the price of an accelerator is proportional to its power and energy. It is also very costly to study this process of EBFGT experimentally, especially on an industrial scale. Theoretical study of the process of EB treatment of flue gas are being looked for.

In this work, theoretical study of NO_x removal from humid air by using a hybrid system (catalyst combined with electron beam) was carried out at the aim of studying the possibility of decreasing energy consumption for NO_x removal by using the EBFGT technology.

When the gas reactants are in contact with a catalyst under EB irradiation, they are adsorbed onto the active sites over its surface. The process can be described by the reactions (1-7) [1]:

$$TiO_2 + \text{electron beam} \rightarrow e^- + \text{hole}^+ \qquad (1)$$

$$h^+ + TiO_2\text{-}H_2O \rightarrow OH\bullet + H^+ \qquad (2)$$

$$e^- + TiO_2\text{-}O_2 \rightarrow O_2^- \qquad (3)$$

$$TiO_2 + NO \rightarrow TiO_2\text{-}NO \qquad (4)$$

$$TiO_2\text{-}NO + OH\bullet \rightarrow TiO_2\text{-}HNO_2 \qquad (5)$$

$$TiO_2\text{-}HNO_2 + OH\bullet \rightarrow TiO_2\text{-}NO_2 + H_2O \qquad (6)$$

$$TiO_2\text{-}NO_2 + OH\bullet \rightarrow HNO_{3(aq)} \qquad (7)$$

Thus, NO is removed from the gas phase.

The concentration of NO and NO_2 along the reaction vessel is solved numerically using program Scilab 5.3.0.

The calculations was made for the ILU-6 accelerator with the following parameters: electron energy – 900 keV, pulse current – 250 mA, pick power – 225 kW, pulse duration – 400 μs, pulse repetition rate – 50 Hz.

Parameters of the reaction vessels are: cylinder shape configuration with a diameter 2.0 dm and

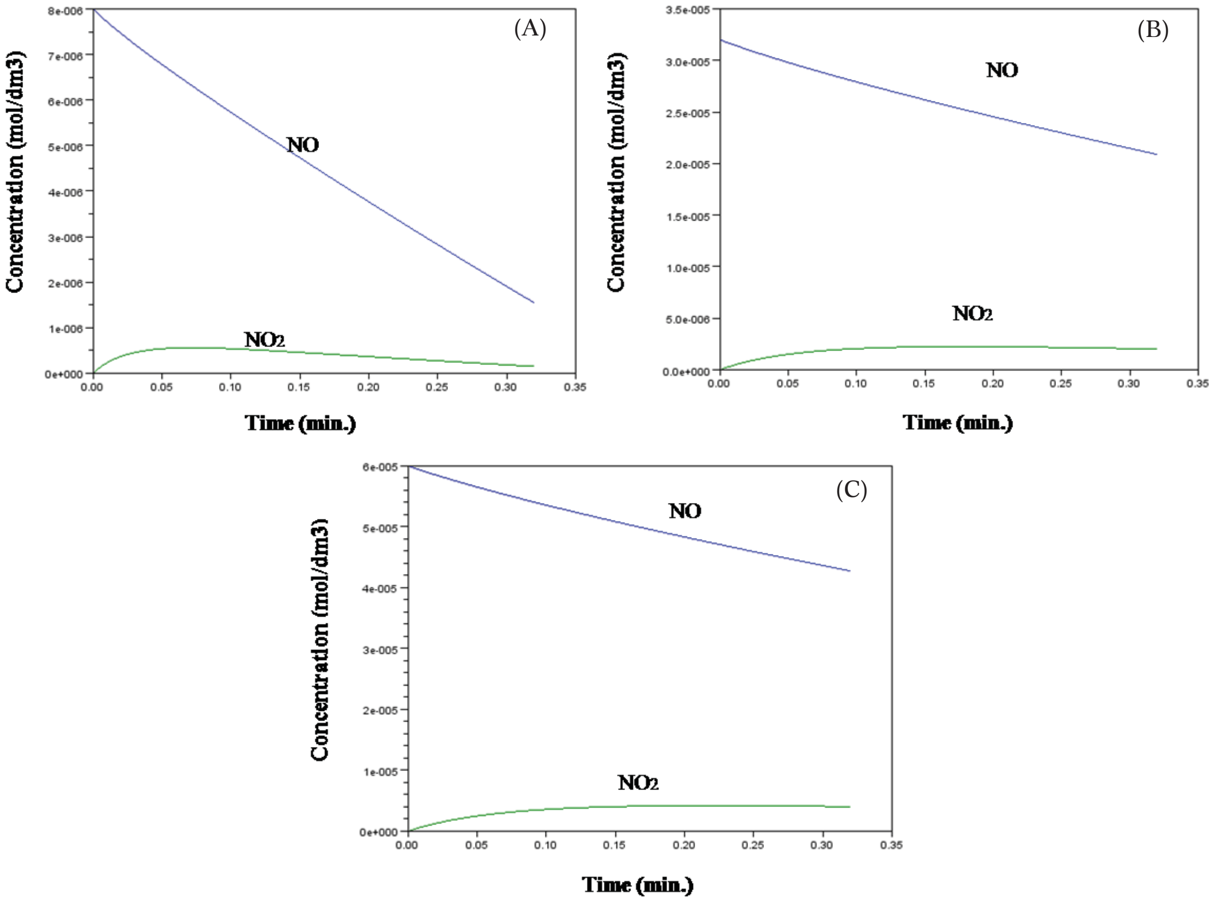

Fig.1. NO and NO_2 concentrations *vs.* retention time of gas mixture inside the catalytic reaction vessel under EB irradiation (pulse repetition rate – 50 Hz) at a different inlet concentration of NO (1 ppm = 4 x 10^{-8} mol dm^{-3}): (A) 200 ppm, (B) 800 ppm, (C) 1500 ppm.

a length 8.5 dm, irradiation window – 3.5 dm (length) x 1.2 dm (width). The gas flow rate is 5000 $dm^3 h^{-1}$ and the gas mixture is: air + 8.62%vol. H_2O + NO (200, 800 or 1500 ppm, respectively).
Catalyst: $TiO_2/\gamma Al_2O_3$, Ø2-3 mm, specific surface area is 60-70 $m^2 g^{-1}$ TiO_2.
Catalyst content D_{tio_2} is 0.5 g g^{-1}. Temperature is 25°C.
The calculation results of NO and NO_2 concentration *vs.* residence time of the gas mixture inside the catalytic reaction vessel under EB irradiation are presented in Fig.1 for the inlet concentration of NO 200, 800 and 1500 ppm. The maximum residence time of the gas mixture inside the reaction vessel is 0.32 min.

It is seen from Fig.1 that the concentration of NO is deceased with increasing the residence time of the gas mixture inside the catalytic reaction vessel under EB irradiation. The NO_2 formation from NO oxidation is below 6% due to the desorption and mass transportation of NO_2 from the surface of the TiO_2 catalyst to air [1]. The final product of the radiation-chemical oxidation of NO is HNO_3.

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MODELLING STUDY OF THE ABATEMENT OF SO_2 AND NO_x FROM THE ACCELERATED ELECTRON BEAM BY USING MATLAB

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Air pollutants like sulphur dioxide (SO_2) and nitrogen oxides (NO_x) can be released into the atmosphere during many different industrial processes. The composition of the flue gases (*i.e.* the concentrations of pollutants) emitted vary depending on the type of fuel and type of process (fossil fuel burning, chemical industry, metallurgical industry, *etc*.). Despite the fact that in recent years, the level of pollution from land sources gradually decreased, the noxious emission levels from marine sources are still increasing. Moreover, within the next few years, stricter laws and regulations will be in force, as stated by the International Maritime Organization in reference to the lower limits of sulphur emission in the Sulphur Emission Control Areas (SECAs), which include the Baltic and North Sea.

Currently, there is a wide variety of methods employed for the removal of pollutants from flue gases (selective catalytic reduction – SCR), wet scrubbing, methods based on adsorption, *etc*.). There have also been developed methods based on irradiation, such as the electron beam flue gas treatment (EBFGT), the corona, dielectric barrier or radio-frequency discharge methods. EBFGT is one of the most promising and still under continuous development, which gives the hope for achieving cost effective, waste-free method for the future use. In this study we created a mathematical model for theoretical calculations of EBFGT process.

The gas phase model, which was created and solved in MATLAB (MathWorks®, Natik, MA, USA) programming environment, contains 903 reactions involving 110 species. All of the reactions and constant rates are taken from the literature [1-3]. The variations in the concentrations of the active species, which were generated by irradiation, are given by the Eq. (1):

$$\frac{dC_i}{dt} = G_{value} \cdot D \cdot X_i \cdot \rho \qquad (1)$$

where: C_i – the concentration of species i, which has mole fraction X_i in flue gas; D – a dose rate; ρ – an average density [unit of 100 eV/cm^3s]. The G_{values} are yield rates [unit of molecules/100 eV] and are listed in the Eqs. (2-5):

$$4.14\ N_2 \rightarrow 0.885\ N^2D + 0.295\ N^2P + 1.87\ N^4P + 2.27\ N_2^+ + 0.69\ N^+ + 2.96\ e^- \qquad (2)$$

$$5.3\ O_2 \rightarrow 2.98\ O + 2.25\ O^1D + 2.07\ O_2^+ + 1.23\ O^+ + 3.3\ e^- \qquad (3)$$

$$6.7\ H_2O \rightarrow 0.51\ H_2 + 4.25\ OH + 4.15\ H + 0.46\ O^3P + 1.99\ H_2O^+ + 1.99\ e^- \qquad (4)$$

$$7.54\ CO_2 \rightarrow 4.72\ CO + 5.16\ O + 2.24\ CO_2^+ + 0.51\ CO^+ + 0.07\ O^+ + 2.82\ e^- \qquad (5)$$

For the concentrations of all species, which take part in the reactions considered, we have employed the system of first-order differential equations, represented by the Eq. (6):

$$\frac{dC_i}{dt} = [G_{value} \cdot D \cdot X_i \cdot \rho] + \text{rate of formation} - \text{rate of disapperance} \qquad (6)$$

Calculations were provided for the following gas composition: NO – 250 ppm, H_2O – 10%, O_2 – 5%, CO_2 – 10%, NH_3 – 650 ppm, N_2 – 75%, SO_2 – 200 ppm, the temperature being 100°C and absorbed dose – 10 kGy.

Based on the calculation results, we learnt that with time of irradiation the concentrations of both pollutants (NO and SO_2) decrease. Removal efficiencies increase with time of irradiation and after 10 s achieve 87, 71 and 63% for NO, NO_x and SO_2, respectively.

We also studied the influence of absorbed dose on the concentration of NO and SO_2 (Figs.1 and 2). We changed the base dose (10 kGy) by adding or subtracting 20, 10, 5 and 2% of the output

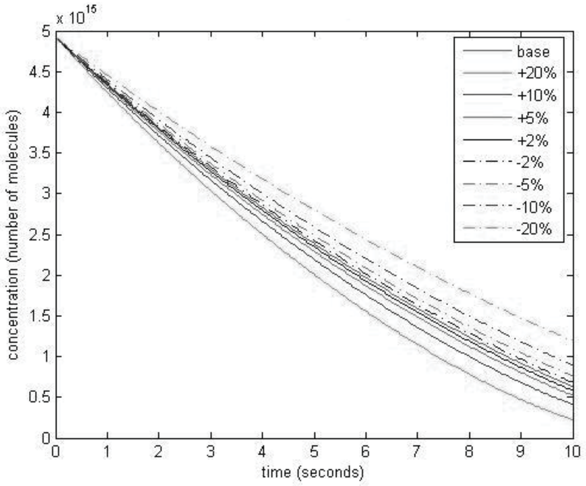

Fig.1. Dose influence on the concentration of NO within the time of irradiation.

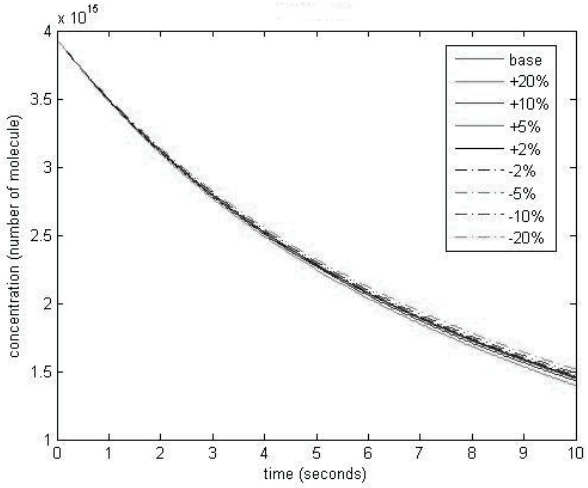

Fig.2. Dose influence on the concentration of SO_2 within the time of irradiation.

value. The increase of absorbed dose results in the decrease of concentrations of both pollutants.

Conclusions are drawn as follows:

- Removal efficiencies of both pollutants increase with irradiation time.
- Changes in the absorbed dose have an influence on the concentrations of NO and SO_2. With the increase of absorbed dose the concentration of both pollutants decrease.
- Changes in the absorbed dose influence more strongly the removal of NO than SO_2.

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ANALYSIS OF MULTISTAGE IRRADIATION IMPACT ON NO_x REMOVAL EFFICIENCY

Andrzej Pawelec, Andrzej Dobrowolski, Sylwia Witman-Zając

Most of the energy in the electron beam flue gas treatment process is spent on the NO_x removal. During previous research, it was found that the proper construction of a reactor may increase energy efficiency of the process. Both interstage mixing application and installation of two double-sided vanes in the reactor increases NO_x removal efficiency and reduces energy demand of the process.

The research was continued by examination of the impact of a number of irradiation stages, in combination with interstage mixing, on the remov-

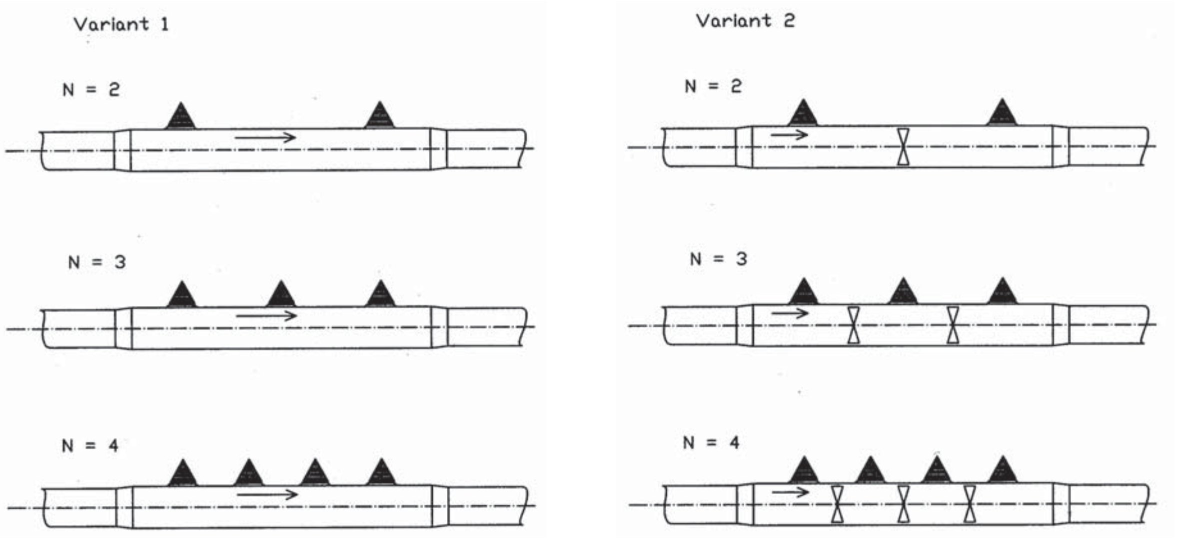

Fig.1. A scheme of the considered reactor constructions: variant 1 – without interstage mixing, variant 2 – with interstage mixing, N – number of irradiation stages.

al of NO_x. Two variants of reactor construction were examined – without interstage mixing (variant 1) and with interstage mixing (variant 2). For the purpose of this work, ideal mixing between irradiation stages for variant 2 was assumed. For each reactor construction variant, three cases of gas irradiation (for 2, 3 and 4 irradiation stages) were examined. A scheme of considered reactor construction variants for 2, 3, 4 irradiation stages is shown in Fig.1.

In order to determine the impact of a number of irradiation stages and mixing conditions in the reactor, calculations of NO_x removal efficiency in dependence on dose were performed for a moderate (248 ppm) and high (400 ppm) NO_x inlet concentration. For the purpose of this work, equal dose delivery ratio at each irradiation stage was assumed. The results of calculation are shown in Table 1 and Fig.2.

For both the considered reactor construction variants, typical NO_x removal efficiency dependence on dose and NO_x inlet concentration is observed. However, the NO_x removal efficiency increases with increasing number of irradiation stages and interstage mixing application. The impact of increase of irradiation stages is stronger for a lower number of irradiation stages, *i.e.* the NO_x increase of removal efficiency between 2 to 3 irradiation stages is greater than between 3 and 4 irradiation stages. On the other hand, the impact of interstage mixing is greater for a higher number of irradiation stages (3 and 4) than in the case of double irradiation. Moreover, the impact of interstage mixing is greater than the impact of increase of irradiation stages. Higher NO_x removal efficiency values were obtained for a 2 irradiation stage reactor with interstage mixing in comparison to a 3 and 4 irradiation stage reactor without mixing. This phenomenon was observed especially for the higher doses applied (7÷16 kGy for a 248 ppm NO_x inlet concentration and 10÷16 kGy for a 400 ppm NO_x inlet concentration).

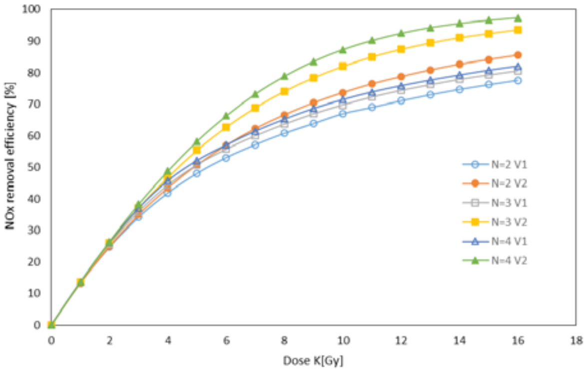

Fig.2. Dependence of NO_x removal efficiency on the dose for 2, 3 and 4 irradiation stages and two reactor construction variants: without interstage mixing (V1) and with interstage mixing (V2).

The above described increase of NO_x removal efficiency corresponds with the increase of energy efficiency of the process. According to the calculations performed for the dose distribution and 248 ppm inlet the NO_x concentration, NO_x removal efficiency for 2 irradiation stage without mixing and 10 kGy dose is 67% (Table 1). Analogical calculations for 4 irradiation stage with interstage mixing gives an 87.3% efficiency (30% increase

Table 1. Dependence of NO_x removal efficiency on dose for variant 1 (V1) and variant 2 (V2) of reaction construction and N = 2, 3, 4 irradiation stages.

Dose [kGy]	NO_x removal efficiency [%]											
	$[NO_x]_0$ = 248 ppm						$[NO_x]_0$ = 400 ppm					
	N = 2		N = 3		N = 4		N = 2		N = 3		N = 4	
	V1	V2	V1	V2	V1	V2	V1	V2	V1	V2	V1	V2
0	0	0	0	0	0	0	0	0	0	0	0	0
1	13.3	13.3	13.6	13.6	13.7	13.7	8.4	8.4	8.6	8.6	8.6	8.6
2	24.7	24.9	25.7	26.0	26.3	26.5	16.2	16.3	16.6	16.7	16.9	16.9
3	34.2	35.0	36.0	37.1	37.1	38.3	23.2	23.4	24.1	24.3	24.6	24.8
4	41.9	43.5	44.4	46.8	45.8	48.8	29.5	29.9	30.9	31.5	31.7	32.3
5	48.1	50.8	50.8	55.4	52.2	58.2	35.0	35.9	36.9	38.1	38.1	39.4
6	53.1	57.0	55.8	62.7	57.1	66.3	39.9	41.3	42.2	44.2	43.6	46.0
7	57.2	62.3	60.0	68.9	61.5	73.2	44.2	46.2	46.7	49.9	48.2	52.1
8	60.8	66.7	63.7	74.1	65.3	78.9	47.9	50.6	50.6	55.0	52.0	57.8
9	63.9	70.5	67.0	78.4	68.7	83.6	51.1	54.5	53.8	59.8	55.1	63.0
10	67.0	73.7	69.8	82.0	71.5	87.3	54.0	58.1	56.7	64.0	58.0	67.8
11	69.0	76.5	72.3	85.0	73.9	90.2	56.5	61.4	59.3	67.9	60.7	72.0
12	71.1	78.8	74.4	87.4	75.9	92.5	58.9	64.3	61.7	71.3	63.2	75.9
13	73.0	80.9	76.2	89.4	77.7	94.3	61.0	67.0	63.9	74.4	65.5	79.2
14	74.7	82.7	77.9	91.1	79.3	95.6	62.9	69.3	66.0	77.1	67.6	82.2
15	76.2	84.2	79.3	92.4	80.8	96.6	64.7	71.5	67.9	79.6	69.6	84.8
16	77.6	85.6	80.6	93.6	82.1	97.4	66.3	73.5	69.6	81.8	71.3	87.1

in relation to previous result). However, for this case a 67% NO_x removal efficiency was obtained for a 6.1 kGy dose that means a 39% energy consumption decrease.

The results of the work indicate that the combination of increase of irradiation stages with interstage mixing is a very effective way to increase process efficiency, however the interstage mixing effect is much stronger than the increase of irradiation stages. These conclusions may be used as a background for further design of reactors for electron beam flue gas treatment.

STABLE ISOTOPE LABORATORY

Basic activity of the Stable Isotope Laboratory concern the techniques and methods of stable isotope measurements (H, C, N, O, S) 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$^{\text{plus}}$ (FinniganMAT, Germany);
- elemental analyser Flash 1112NC (ThermoFinnigan, Italy);
- GasBench II (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);
- freeze dryer Alpha 1-2 LD plus (Christ, Germany).

Research staff of the Laboratory is involved in the following projects:
- “The study of the influence of the environmental factors on the isotopic compositions of dairy products”,
- accreditation process (isotopic method for food authenticity control),
- interlaboratory proficiency test FIT-PTS (food analysis using isotopic techniques – proficiency testing scheme).

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:
- Agricultural and Food Quality Inspection,
- Polish Association of Juice Producers,
- customs inspections,
- food export-import company,
- food control laboratories,
- private customers

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

STUDY OF ISOTOPIC COMPOSITION AND TRACE ELEMENTS CONCENTRATION OF MILK

Ryszard Wierzchnicki, Kazimiera Malec-Czechowska, Zbigniew Samczyński

The food products are a mixture of basic elements: carbon, hydrogen, oxygen, nitrogen and sulphur. The measurements of stable isotope composition of the bioelements provide a very sensitive method for control of origin and authenticity; the method being applied to analyse wine, juice, and honey [1,2]. The aim of the study is to explore the relationship between isotope composition and trace elements concentration of milk and its geographical origin and seasonal variation of those parameters. The stable isotope composition of food is strictly related to environmental condition like climate, geographical region and included pollutions. The isotopic effects accompanying many physical, chemical and biological processes are responsible for different isotopic composition of food. The different composition of cow fodder (grass, maize and hay) and different composition of drink water are the reason of seasonal and regional variation of isotopic composition of fresh milk and finally of dairy products like UHT milk, cheeses.

Natural products such as wine, spirits, fruit juices, oils, honey and other organic materials are the prime targets for fraudulent adulteration because of their high prices. Traditional analytical methods like HPLC, GC and GC-MS make it possible the identification and quantification of all the major molecules present, but more sophisticated analytical methods are required to detect whether natural ingredients have been mixed with similar materials from cheaper (synthetic) sources. Stable isotope composition is an important tool for food authenticity and control of the origin. It allows detecting the origin from the geographic point of view or from the point of view of the production processes. The measurement of various isotopic ratios (D/H, $^{18}O/^{16}O$, $^{13}C/^{12}C$, $^{15}N/^{14}N$ and $^{34}S/^{32}S$) in different fractions of a product often enables characterization of the origin of starting materials.

The aim of this study was to demonstrate the differences in regional and seasonal variations of isotopic composition of milk. Carbon isotope ratios are expected to reflect diets of the milk-producing animals. Nitrogen isotope ratios of milk protein will be useful for the characterization of some samples from mountains regions due to their specific environmental conditions. Sulphur isotope ratios for the same substances will be connected to the geological differences of the regions investigated (Fig.1). Dealing with the fact that there is a well-known pattern of D/H and $^{18}O/^{16}O$ in meteoric water as well as in ground water, every material including plants and animals gets a significant marker in the tissue water depending on their region. If the water has been changed or lost by drying, the organically bound forms of oxygen and hydrogen serve as indicators as well. The pattern of D/H and $^{18}O/^{16}O$ in the meteoric water depends mainly on the temperature, landscape altitude and the distance from sea.

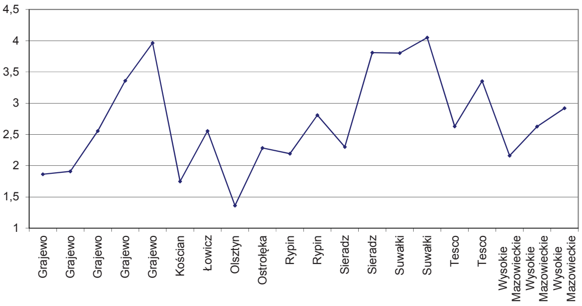

Fig.1. Isotopic composition of sulphur in UHT milk.

Soils show different isotope ratios of $^{15}N/^{14}N$ and $^{34}S/^{32}S$ depending firstly on the natural geological composition and secondly on the cultivation. Finally, there is an existing link in the food chain from the fodder to cattle and to milk as well. The $^{13}C/^{12}C$ isotope ratio depends on the type of metabolism and of a local climatic influence as water stress under heat. Drawing the conclusion, plants as maize (C4-plants) show different $^{13}C/^{12}C$ ratios in wheat (C3-plants). Therefore, it is possible to determinate the nutrition composition in cattle's tissue and in milk products.

The mass spectrometry technique is the main method for measurement of the stable isotopes content in food and beverages. This technique connected with an H/Device instrument gives the possibility to determine hydrogen isotope ratio. Oxygen isotope ratio can be determined in water samples on a GasBench instrument connected with a mass spectrometer (Fig.2). For the determination of C, N, and S in solid materials elemental analyser coupled with a mass spectrometer is used.

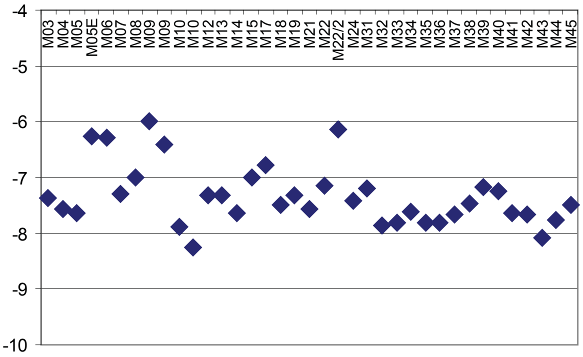

Fig.2. Isotopic composition of oxygen $\delta^{18}O$ in (water) UHT milk.

The isotope ratio is expressed as the difference relative to a standard in the "delta" (δ) notation (parts per million [‰]) according to the equation:

$$\delta = \frac{R_{sample} - R_{standard}}{R_{standard}} \text{ x } 1000$$

For extending the research possibility, an additional parameter was employed – the content of

Table 1. Concentration of trace elements in milk from different regions of Poland.

Name of product	Place of origin	Region	Th	Cu	Mn	Zn	Sr	V	Mo	Ni	Fe	Pb
Mu!	Sieradz	łódzkie	0	0.603717	0.454481	32.39333	84.72377	0.104651	0.295971	0.573388	25.75134	0.357073
Sudowia	Suwałki	podlaskie	0	0.002746	0	29.3358	48.3642	0.05022	0.224785	0.363951	22.09918	0
Uchate	Raciąż	mazowieckie	0	0	0.046056	28.08214	61.58883	0.127938	0.178649	0.397367	21.55281	0
Zambrowskie	Grajewo	podlaskie	0	0.096512	0.014081	28.19485	48.07825	0.10909	0.168641	0.510894	21.84648	0.143265
Mlekovita	Wysokie Mazowieckie	mazowieckie	0	0.140689	0.692141	36.7468	63.58662	0.113006	0.065108	0.463706	25.56908	0.160302
1	Rypin	kujawsko-pomorskie	0,014781	1.469157	0.790517	32.38922	81.36207	0.09296	0.27123	1.295544	32.82866	0.252423
Łaciate	Grajewo	podlaskie	0	5.012084	0	28.87077	44.32759	0.078788	0.170764	0.278549	30.36868	0
Zambrowskie	Grajewo	podlaskie	0	0	0	29.2025	55.87299	0.135235	0.056893	0.404306	30.12432	0
Mu!	Sieradz	łodzkie	0	0.000895	0	30.8431	71.78461	0.148539	0.137763	0.425934	31.63006	0
Carrefour	Rypin	kujawsko-pomorskie	0	0.003646	0.017819	31.94333	73.60146	0.15656	0.169722	0.41229	28.67113	0
mój Kubek	Wysokie Mazowieckie	mazowieckie	0,043901	0.860665	0.106459	30.27871	60.24094	0.118937	0.238103	0.479521	44.34332	0
Białe	Grajewo	podlaskie	0	0	0.000809	26.17495	46.2025	0.106264	0.063986	0.268761	25.21574	0

trace elements (Table 1) as a criterion for identification of the origin of a sample. The measurements were executed for a limited group of ecological and industrial products. On this stage of project the research had a survey character only.

Application of the multielement (isotopic composition and trace element concentrations) method for origin control of dairy products requires additional research on a larger population of dairy product samples, from organic and commercial farms. After identification of precision, repeatability of the method, it can be used as standard method for origin control of dairy products. As an additional result of the study, the isotopic method for control of organic dairy products on the basis of their isotopic composition in controlled samples will be elaborated.

This work was partially supported by the Polish Ministry of Science and Higher Education under grant W196/FAO/IEAE/2013.

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ISOTOPIC COMPOSITION OF STRAWBERRY FOR AUTHENTICITY CONTROL OF FRUIT PRODUCTS

Ryszard Wierzchnicki, Kazimiera Malec-Czechowska

Strawberries, as the most popular fruit in the world, are consumed in various ways such as fresh and frozen fruits, juices, jams and many other products. They contain above 80% water, 6-9% carbohydrates, 0.6-0.7% elements important to health (K, P, Ca, Mg, Fe, Zn, Mn), vitamins, pectin and cellulose. In the production of strawberries Poland occupies the tenth place in the world and the fourth in Europe (FAOSTAT Database 2012). In Poland, similarly as in other countries, strawberries are cultivated using conventional and organic methods of production.

Strawberries are one of the most important commodities produced in Poland, which are exported (above 10% production). During the last two decades, there has been increasing interest of consumers in organic products, because they are considered to be more safer and healthy, due to the absence of pesticide residues and more environmentally compatible method of production. Results presented by M. Rochalska for Polish strawberry variety Elkat, indicate that the content of ascorbic acid is significantly higher for fruits from organic farming than from conventional farming. Also, the iron content was significantly higher in fruits from organic farming [1].

The EU protected food name scheme highlights regional and traditional foods whose authenticity and origin can be guaranteed. The product is awarded one of three marks: protected designation of origin (PDO), protected geographical indication (PGI) and traditional speciality guaranteed (TGS).

Under this system, the named food or drink registered at the European level will be given legal protection against imitation throughout the EU. The first Polish fruit to enjoy protection under European Union law is the Kashubian strawberry (truskawka kaszubska). Its name was registered in November 2009 as a protected geographical indication.

The isotope ratio mass spectrometry (IRMS) methods play a very important role in food authenticity and origin control. Stable isotope analysis for the control of declared origin is already routinely applied in the EU for wine, fruit juice and honey. For other foodstuffs, published studies already exist and demonstrate the potential for verification of origin and authenticity for milk and milk products, olive oil, asparagus and meat (pork, beef, and lamb).

The Stable Isotope Laboratory of the Institute of Nuclear Chemistry and Technology (INCT) since many years is carrying out studies of isotope composition of food by IRMS method implementation and is creating database for some food from the Polish market [2]. In this work the δ^{13}C, δ^{15}N values for dehydrated strawberry fruits are presented. The δ^{13}C for sugars and δ^{18}O for water extracted with different variety fruits of strawberry produced in Poland.

Samples (above 1 kg) of fresh strawberries of different variety such as: Honeyone, Marmolada, *etc.* were bought in the market or received from experimental tillage or home garden. The ecological fruits were market "organic logo".

Fresh fruit (5-7 g) from each sample were sliced into thin pieces packed into a special glass tube and freeze-dried for 24 h using vacuum installation of our own construction (Fig.1). The dehydrated materials were milled and transferred into plastic containers and stored at room temperature until measurements. The water was collected into glass containers and stored at 4-6°C temperature until oxygen measurements [3].

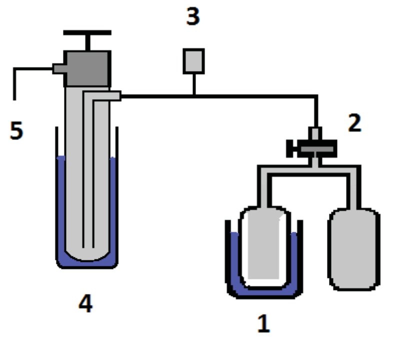

Fig.1. Scheme of vacuum line for water separation from fruit samples: 1 – sample, 2 – cut-off valve, 3 – vacuum meter, 4 – "cold finger", 5 – to vacuum pump.

Table 1. Isotope ratio $\delta^{13}C$, $\delta^{15}N$ and $\delta^{18}O$ strawberries and their chemical components (water, sugars).

Strawberry variety	Origin of samples	$\delta^{13}C$	$\delta^{15}N$	Water $\delta^{18}O$	Sugars $\delta^{13}C$
Honeoye	experimental	-25.32	1.19	-5.51	-25.78
Honeoye	market	-26.41	-1.93	-2.07	-26.27
Honeoye	market	-26.57	-0.82		-26.15
Honeoye	market	-24.29	2.75	-1.95	-23.52
Honeoye	market	-26.19	-0.50	-4.89	-24.75
Honeoye	market	-25.12	-0.47		-25.15
Honeoye	home garden	-24.52	0.33	-3.41	-24.87
Honeoye	home garden	-24.79	0.79		-24.50
Honeoye	home garden	-26.76	2.70	-2.46	-26.13
Honeoye	home garden	-26.84	2.49		-26.30
Honeoye	organic	-26.29	2.65	-2.44	-24.78
Honeoye	organic	-26.18	3.51		
Honeoye	organic	-26.19	4.00	-2.43	-26.11
Honeoye	organic	-25.57	3.01		-26.04
Marmolada	market	-25.35	1.71	-4.79	-25.78
Marmolada	market	-25.95	3.24	-5.12	-25.34
Marmolada	market	-25.82	4.81		-25.13
Marmolada	market	-25.61	-0.63	-3.49	-25.53
Marmolada	market	-25.94	-0.47		-25.70
Elsanta	experimental	-26.86	3.23	-2.21	-26.62
Elsanta	experimental	-26.43	4.15	-4.90	-26.64
Senga Sengana	market	-26.10	0.32	-5.21	-25.76

Preparation of sugars with strawberry juices was carried out according to PN-ENV 12140:2004 [4].

Multielement isotope ratios ($\delta^{13}C$, $\delta^{15}N$ and $\delta^{18}O$) were performed on an isotope ratio mass spectrometer DELTA^{plus} (FinniganMAT, Bremen,

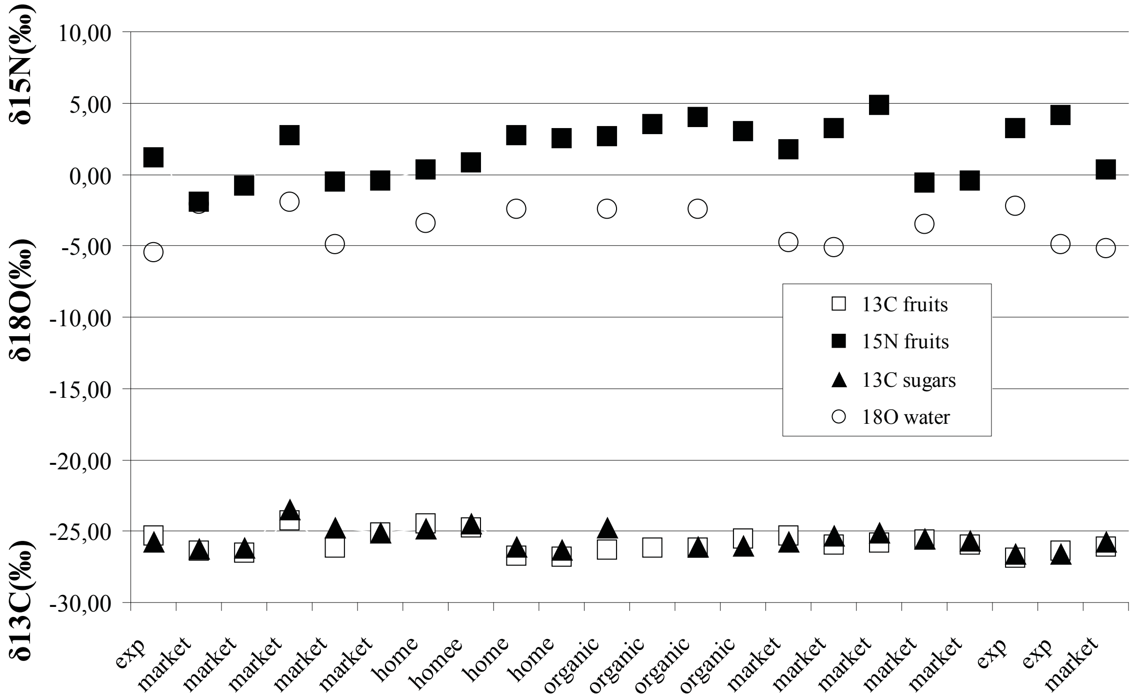

Fig.2. Isotopic composition $\delta^{13}C$, $\delta^{15}N$ and $\delta^{18}O$ (water) in Polish strawberries originated from different production systems.

Germany), interfaced to an elemental analyser Flash 1112 NC (ThermoFinnigan, Italy) and Gas-Bench II (for oxygen in water). The values of the isotopic ratios are expressed in δ [‰] and correspond to international standards (Vienna Pee Dee Belemnite for δ^{13}C, Air for δ^{15}N and Vienna – standard mean ocean water for δ^{18}O) according to the following general formula:

$$\delta\ [‰] = (R_{sample}/R_{standard} - 1) \times 1000$$

where R represents the ratio between the less abundant and more abundant stable isotopes.

Experimental data are presented in Table 1 and in Fig.2. The δ^{13}C values for dehydrated fruits range from -26.86 to -24.29‰ and are similar to δ^{13}C in sugars (-26.64 to -23.52‰). The δ^{18}O values for water extracted with fruits are in the range -5.51 to -1.95‰. Presented data show differences in the δ^{15}N values between fruits from different production systems. The δ^{15}N average values are: 2.86 ± 1.51‰ for experimental tillage, 1.58 ± 1.19‰ for home garden, 3.29 ± 0.59‰ for organic fruits and 0.72 ± 2.11‰ for fruits from the market. The use of stable isotopes as tracers for food authentication has been well established [5-7]. However, only limited research has been conducted using stable isotopes to distinguish fruits produced by the two cultivation practices. The studies focused on experimental studies under laboratory conditions [8-10]. Paolo Rapisarda presented the nitrogen metabolism components as a tool to discriminate between organic and conventional citrus fruits. The results obtained in that work indicated that total nitrogen and synephrine content was significantly higher in conventional fruits, whereas the δ^{15}N ‰ values were higher in the organic ones [9]. Initial δ^{15}N results for Polish strawberries show also the possibility of use of this parameter to the discrimination between the fruits from the production conventional and organic.

The measurement of stable isotope composition of nitrogen δ^{15}N and carbon δ^{13}C might be useful for the determination method of production (organic or conventional) of strawberries. The study is based on the preliminary data from limited sample size and sampling period. On the other hand, the gathered data δ^{15}N, δ^{13}C and δ^{18}O for strawberry are a continuation to create the database of isotopic characteristic of Polish food by the Stable Isotope Laboratory.

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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).

RECALIBRATION OF DOSIMETER FILMS PVC

Anna Korzeniowska-Sobczuk, Magdalena Karlińska

The response of most films used in routine dosimetry are usually influenced by environmental conditions such as temperature during irradiation, dose rate and post-irradiation storage [1]. Many problems may be encountered in the routine dosimetry applied for radiation processing, because the conditions in irradiation facilities may differ considerably from the conditions in which dosimeter films were calibrated.

Meeting the requirements of PN 13845 standard and GMP, forces full control over the dosimetric systems used. Ensuring traceability, exercise recalibration and ongoing calibration of dosimetry systems is essential to meet the quality requirements arising from the management system. Currently, Radiation Sterilization Station of the INCT is located approximately 15 reels of a PVC film dosimeter purchased in the 70s of the last century in the company STAUFEN. This is the amount that allows for approximately 10 years, to use PVC dosimeter for measuring radiation energy, electron beam and determining a minimum and maximum dose and dose distribution in the product.

Implementation issues related to studies of PVC film dosimeter, results from the need to monitor continually the quality of performed services [2]. In the Laboratory for Measurements of Technological Doses (LMTD) there is the accreditation

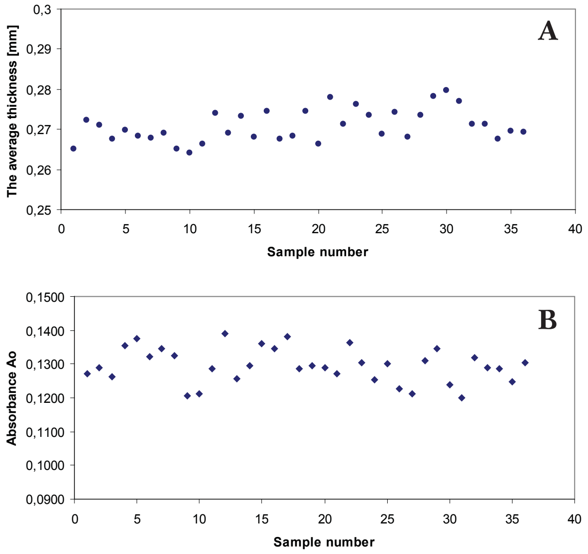

Fig.1. The physicochemical parameters of the dosimeter films PVC.

Table 1. Reproducibility of dosimetric signal PCV film.

	Dose [kGy]			
	10	20	30	40
Dosimetric signal $A - A_o$	0.1881	0.3124	0.5902	0.8902
	0.1901	0.3101	0.5743	0.8792
	0.1868	0.3118	0.5942	0.8467
	0.1859	0.3112	0.5852	0.8770
	0.1841	0.3045	0.5770	0.8770
	0.1852	0.3072	0.5886	0.9014
	0.1835	0.3178	0.5869	0.8674
	0.1872	0.3089	0.5998	0.8663
	0.1870	0.3060	0.6056	0.8935
	0.1905	0.3121	0.6033	0.8879
	0.1916	0.3198	0.6143	0.8674
	0.1848	0.3080	0.6021	0.8792
	0.1830	0.3107	0.6062	0.8580
	0.1819	0.3110	0.6108	0.8674
	0.1870	0.3115	0.6027	0.8846
	0.1939	0.3151	0.5936	0.8498
	0.1979	0.3151	0.6155	0.8528
	0.1914	0.3265	0.6203	0.8457
	0.1894	0.3166	0.6132	0.8447
	0.1828	0.3115	0.6038	-
Arithmetic average	0.1876	0.3124	0.5994	0.8703
Standard deviation	0.0041	0.0051	0.0128	0.0173
CV [%]	0.82	1.02	2.56	3.46

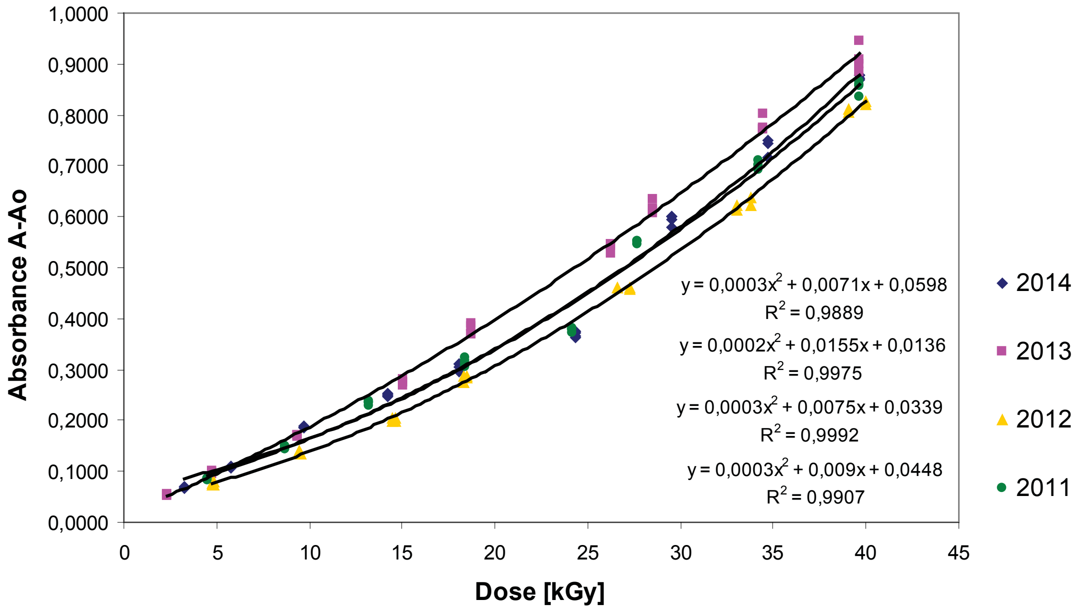

Fig.2. Summary of the calibration curves for PVC films made in different years from the date of purchase of the film.

method for irradiation of dosimeters with 10 MeV electron beams to strictly defined doses and for measuring the sensitivity of film dosimeter. The LMTD having the accreditation of the Polish Centre for Accreditation, in accordance with the requirements of PN-EN ISO/IAC 17025:2005 [3] imposed on the implementation of improved activities, preventive as well as quality control tests. The implementation of this subject allows for comprehensive requirements according to previous experimental data and after irradiation of the PVC film dosimeter, it will allow to trace the changes in the long term.

The film dosimeters PVC were irradiated with 10 MeV electron beams from an industrial 10 kW linear accelerator radiation (Elektronika 10/10) and with control of doses by the calorimetric method, traceable to a primary standard maintained by the National Physical Laboratory (NPL). The mean electron energy measured by the wedge method was in the range 9.6-9.8 MeV. Approved dose ranges were 10-40 kGy, which corresponded to the routine sterilization process.

In the experiments film dosimeters PVC were used, with optical signal detection. Immediately after irradiation, the sample PVC was kept for 30 min at 70°C and the spectrophotometric measurement was carried out after subsequent 30 min. The absorbance was measured by using a JASCO-V650 spectrophotometer UV/Vis (λ_{max} = 396 nm). The wavelength and absorbance scales were checked before each experiment by a calibrated reference standard.

In 2014, the first stage of the study was to verify physicochemical parameters of unexposed film and a comparison with the data contained on the score sheet dosimeter (after recalibration in 2005). Comparison of the absorbance A_0 and an average thickness of 36 samples no radiation PVC film is shown in Fig.1.

Dosimetric signal reproducibility was checked at doses of 10, 20, 30 and 40 kGy. Details are presented in Table 1. Results of the compilation of all annual calibrations (30 min after irradiation) and aging of the PVC film are shown in Fig.2. Adapting the measuring points to the calibration curve, in many cases R2 > 0.98.

The most important achievements (scientific and practical applications) are as follows:

- Dispersion of the initial absorbance value of less than 4% and a thickness not exceeding 1.5% corresponds to parameters contained in the imprint of the PVC film dosimeter. Differences in thickness within one series (spool) of the PVC film are negligible.
- Repeatability of the signal of irradiated PVC film is within the entire measuring range and is less than 4.2%.
- Respons of the dosimetry of the PVC studied was presented as the second degree polynomial coefficient R2 = 0.9883 convergence.
- The uncertainty of irradiation in the accelerator Electronika 10/10 was 6%.

The results confirm that the PVC film dosimeter can still be used for routine dosimetric measurements carried out in Radiation Sterilization Station. The slight decrease in the dosimetric repeatability signal in the PVC foil over the period 2011-2014 is not due to the changes occurring during aging of PVC, but is characteristic of the individual spools and their random use during routine measurements. It may be desirable prior to the start of new spool, not only to perform calibration measurements but also measurements of the thickness and the initial absorbance.

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LABORATORY FOR DETECTION OF IRRADIATED FOOD

The Laboratory for Detection of Irradiated Food was created at the Institute of Nuclear Chemistry and Technology in 1994. The adoption of the quality assurance system resulted in the accreditation of this unit in 1999. Laboratory received its first accreditation certificate from the Polish Centre of Accreditation. From that time, the Laboratory for Detection of Irradiated Food possess constantly the status of accredited R&D unit and is authorized to proceed the examination of food samples and to classify them whether irradiated or not irradiated. Every four years, the Laboratory accreditation certificate has to be renewed after passing positively the PCA expert audit. The current, already the 5th accreditation certificate, was received on 30th September 2014 and is valid until 24th October 2018.

Professional and well-experienced staff is engaged in the improvement of irradiation detection methods adapted in the Laboratory to make them more sensitive and reliable for the identification of radiation treatment in the extended group of food articles. The Laboratory offers analytical service in this field to domestic and foreign customers an extended assortment of food articles with the use of five appropriate and normalized analytical methods. The *Scope of Accreditation* – an integral part of accreditation certificate, offers to the customers five methods suitable for the detection of radiation treatment in almost all food assortments available in the open market. During the last 15 years of analytical activity, nearly 3000 food samples were successfully examined and classified.

Nowadays, a lot of many component food assortments like herbal pharmaceuticals, diet supplement, food extracts are delivered from our domestic and foreign customers for examination whether irradiated.

The Laboratory implemented and validated the following detection methods:

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

The application of the above five standardized detection methods addressed to specified groups of foods and validated in the Laboratory guarantees accurate analysis and reliable classification of food samples delivered to the Laboratory for testing.

The Laboratory is currently active in effective implementation of improved analytical and measur-

Typical groups of products controlled in the Laboratory.

ing procedures suitable for the detection of irradiation in complex food articles containing low or very low concentration of irradiated ingredients. These are typically aromatic herbs and spices admixed to the product.

It has been proven experimentally that modification of mineral isolation procedure, the determination of mineral content isolated and the effectiveness of mineral thermoluminescence are the important factors which influence the detection ability of analytical method in use.

In 2014, the samples for irradiation control were delivered from domestic and foreign firms. The latter from Germany, Italy, Denmark, Switzerland, Great Britain, Russia, China, Latvia. The assortment of samples comprised spices, fermented rice, mushrooms, teas, herbal pharmaceuticals, diet supplements, food extracts. In total, 181 samples were examined. 180 samples (99.5%) were examined by the TL method, while PSL based analytical procedures was applied only once (0.5%).

From 19th June 2012, the Laboratory has the status of the reference laboratory in the field of the detection of irradiated food in Poland under the nomination of the Ministry of Health. As such, the Laboratory is responsible for the organization of the control and monitoring of irradiated food around the country.

THE INFLUENCE OF SAMPLE MOISTURE ON THE RELIABILITY OF THE EPR DETECTION OF IRRADIATED FOOD

Grzegorz P. Guzik, Wacław Stachowicz

High X-band absorption of microwave power in water limits significantly the measuring ability of food samples containing water by the EPR (electron paramagnetic resonance) spectrometry. The problem is of great importance if samples of fresh food have to be examined. The EPR technique is widely used for the detection of irradiated food [1-3] and for that reason the negative influence of moisture in food undergoing irradiation control has to be always taken into consideration. The aim of the present study is to throw a bit more light on this problem by controlling the EPR signal intensity evoked by the action of ionizing radiation on some representative food samples of different water content. These are dried raisins imported from South Africa, powdered red paprika from Spain and fresh tomato of domestic origin, all purchased in the market. The only effective way to proceed the EPR measurements on fresh tomato which contains 94.5% of water is to examine the peel taken off this fruit and subsequently dried in open air. All three products were irradiated in a ^{60}Co gamma source (Gammacell 5000) with a dose of 4 kGy. The samples of each product were placed in glass ampoules 4 mm in diameter and EPR was measured with a Bruker ESP 300 spectrometer. The recorded EPR signals of fresh samples of raisins, powdered paprika and tomato peel are shown in Figs.1, 2 and 3, respectively.

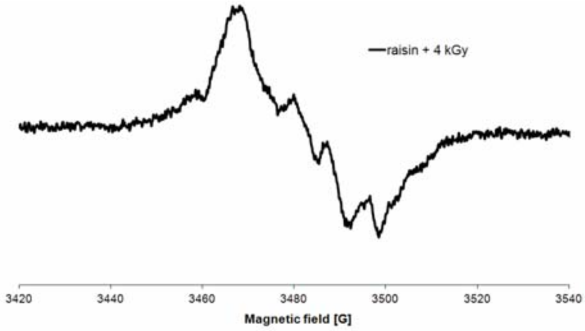

Fig.1. EPR signal of dried raisins irradiated with 4 kGy of ^{60}Co gamma radiation. The multiline broad signal is typical of radiation treated food products containing crystalline sugar.

The EPR signal recorded with irradiated raisins is a broad (5.8 mT), multiline spectrum derived from stable radicals trapped in crystalline sugars. This kind of stable EPR signals are recorded with most of the commercially available dried fruits [3,4]. The EPR signal of irradiated powdered paprika is a triplet with a strong central line. The distance between two weak satellite lines is about 6 mT with g = 2.004 and it is the evidence that cellulose radicals are involved [2,5]. The EPR signal recorded with irradiated tomato peel represents an unidentified multiline signal 7.4 mT broad.

Dried samples were obtained from fresh samples dried for 48 h at 40°C with the access of air. The samples of increased moisture content, in turn, were obtained by adding of several drops of redistilled water to glass ampoules with the sample which were tightly closed and kept overnight. The moistness level of the samples was controlled by weighing the samples after the treatment. Typically, the increase of weight by 0.6% up to 1.1% was obtained. The increase of the weight of the moistened samples higher than 2% resulted in the inability of tuning the EPR spectrometer making not possible to proceed the EPR measurement and recording the spectra. The EPR measurements on fresh, dried and moistened samples were done 1 day after the irradiation to avoid the interference of short-lived radicals produced be radiation. Then, the samples we measured 30 and 90 days after the irradiation to prove the stability of the EPR signals involved. The results of the experiment are comprehended in Table 1.

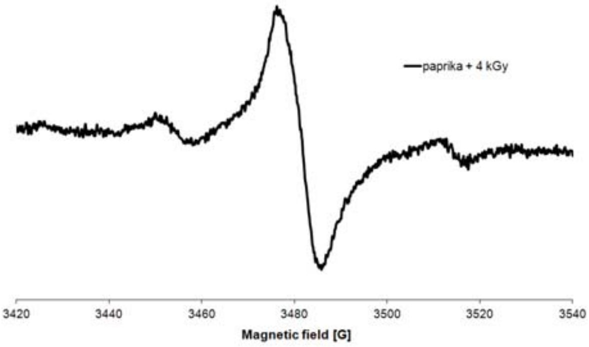

Fig.2. EPR signal of powdered red paprika irradiated with 4 kGy of ^{60}Co gamma radiation. Two weak satellite lines on both sided of central line prove that cellulose radiation evoked radicals are involved.

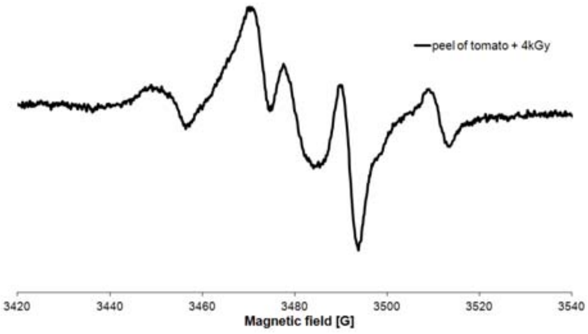

Fig.3. EPR signal of fresh tomato peel. Multiline, broad signal recorded is not identified until now. The whole fruit was irradiated with 4 kGy of ^{60}Co gamma radiation.

The intensity of the EPR signals recorded with fresh raisins and tomato exposed to radiation are markedly higher than those registered with the dried ones. This is in contrast to powdered paprika showing the highest EPR signal intensity with the dried sample. The explanation lies prob-

Table 1. The integrated EPR signal intensity of dried raisins, powdered paprika and tomato peel exposed to the action of ionizing radiation.

No.	Storage time [days]	Integrated EPR signal intensity [a.u.]								
		dried raisins			powdered paprika			tomato peel		
		fresh*	dried	moistened	fresh*	dried	moistened	fresh*	dried	moistened
1	1	24 877	16 237	11 741	14 562	28 978	7 339	22 125	5 330	5 953
2	30	9 032	5 836	4 729	3 986	9 736	2 849	6 958	1 715	2 097
3	90	8 443	3 654	2 554	3 003	5 781	2 710	4 388	1 485	1 986

* Market product.

ably with the different initial state of the samples. The powdered products are much more hydrophilic than the solid ones and for that reason commercial powdered paprika is moistened in advance.

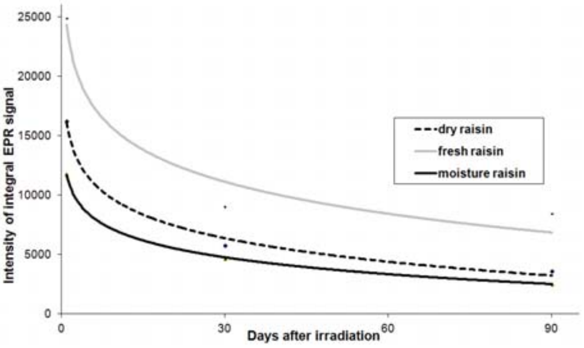

Fig.4. Stability of the integrated EPR signal intensity of dried raisins with different water content.

The decrease of the EPR signal intensity *vs.* time (Fig.4) proceeds with all samples roughly exponentially. It is relatively fast during 30 days and much slower between the 30th and 90th day of storage. The stabilities of the EPR signals recorded with dried, fresh and moistened samples is comparable.

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THE INFLUENCE OF IRRADIATION DOSE ON THE DETECTION OF IRRADIATED DIET SUPLEMENTS

Grażyna Liśkiewicz, Magdalena Sadowska, Wacław Stachowicz

The diet supplements are currently the articles of common use and for that reason as an article of food are controlled whether irradiated. The majority of diet supplements contain herbal and spicy ingredients. Both dried herbs and spices, in turn, belong to this group of food articles which are relatively often treated with ionizing radiation to eliminate a harmful microbial contamination.

In view of the 1999/2/EC Directive of the European Parliament and the Council [1] the blended food articles with an admixture of irradiated ingredients should be obligatorily labelled in the same way as radiation treated food. It is required, therefore, to label diet supplements if they contain irradiated herbal or spicy components. Any unit wrapping or container which contains diet supplement with an irradiated admixture requires information in written "treated with ionizing radiation" or "was irradiated". It is obvious that the producers are not enthusiastic to follow this requirement. For that reason diet supplements, food extracts, herbal pharmaceuticals are controlled more frequently, *i.e.* examined in specialized analytical laboratories whether irradiated. The method suitable for the control of radiation treatment of these kind of products is thermoluminescence (TL) [2]. In our earlier INCT Annual Reports the influence the mineral separation procedure [3] and the quality and quantity of mineral isolated from the product [4,5] were discussed on the sensitivity of TL analysis. Taking advantage of these studies, the methodology of TL analysis has been modified resulting in the increased detection and sensitivity of the irradiation control done with complex food articles. The dose of ionizing radiation applied to food supplements to assure their microbial safety depends, in principle, on the initial pest contamination of herbs and spices added. Nowadays, in view of the credible information, irradiation dose applied to complex food products including diet supplements is very often surprisingly low (1-3 kGy) as compared with that recommended and applied earlier (7-10 kGy). It becomes reasonable, therefore, to proceed the study in what a degree the decrease of irradiation dose influences the sensitivity and reliability of TL detection of diet supplements.

Two coded diet supplements commercially available and apricot powder which is one of consistuents were taken to proceed the experiment. The samples were irradiated with 0.2, 0.5, 1, 3, 7 and 10 kGy, respectively. According to EN-1788 European standard [2], the basic criterion indicating radiation treatment of a sample is the ratio Glow1/Glow2 of the integrated the TL intensities over the 150-250°C temperature interval. Glow1 is TL intensity of mineral isolated from a sample while Glow2 the TL intensity of the same mineral after subsequent irradiation with 1 kGy of gamma rays for the purpose of calibration. If the glow ratio is greater than 0.1 the sample is irradiated. Glow ratios of not irradiated samples (0 kGy) are always lower than 0.1. The results of the experiments are comprehended in Table 1.

Table 1. The influence of dose of gamma irradiation on the integrated TL intensity and on Glow1/Glow2 ratios obtained with an apricot powder and two coded diet supplements.

Product	Irradiation dose [kGy]	Sample weight [g]	TL Intensity Glow1 (150-250°C) [counts]	TL intensity Glow2 (150-250°C) [counts]	Glow1/Glow2 (150-250°C)	TL max. Glow1 [°C]	TL max. Glow2 [°C]
Apricot powder	0	55.49	86 x 10^3	90 909 x 10^3	0.001	273	182
	1	56.00	174 709 x 10^3	208 596 x 10^3	0.866	193	193
	3	53.12	197 681 x 10^3	127 233 x 10^3	1.5537	204	200
	7	50.46	222 355 x 10^3 210 694 x 10^3	168 922 x 10^3 143.365 x 10^3	1.3163 1.4696	195	197
	10	54.87	162 702 x 10^3	109 032 x 10^3	1.4922	200	189
Diet supplement no. 1	0	47.23	25 x 10^3 27 x 10^3	113 628 x 10^3 94 153 x 10^3	0.0002 0.0003	335 348	195 195
	1	47.00	147 948 x 10^3 115 820 x 10^3	145 273 x 10^3 118 316 x 10^3	1.0184 0.9789	187 191	189 191
	3	46.27	166 150 x 10^3	81 679 x 10^3	2.0342	184	184
	7	46.34	136 307 x 10^3	7 191 x 10^3	1.8372	210	199
	10	46.47	82 933 x 10^3 148 203 x 10^3	35 083 x 10^3 68 097 x 10^3	2.3639 2.1764	203 193	184 177
Diet supplement no. 2	0	40.13	64 x 10^3 73 x 10^3	67 146 x 10^3 94 650 x 10^3	0.0010 0.0008	282 290	199 200
	0.2	40.23	30 656 x 10^3 23 647 x 10^3	142 794 x 10^3 95 514 x 10^3	0.2147 0.2476	204 206	195 195
	0.5	40.04	35 258 x 10^3 33 010 x 10^3	75 420 x 10^3 74 616 x 10^3	0.4675 0.4424	193 204	191 202
	1	40.15	51 885 x 10^3 65 799 x 10^3	54 609 x 10^3 67 264 x 10^3	0.9501 0.9782	193 197	200 193

The results obtained with an apricot powder and diet supplement no. 1 both irradiated with the doses from 1 to 10 kGy were found not very different. The glow ratios of samples irradiated with 3, 7 and 10 kGy were all found markedly higher than 1.0 (from 1.31 to 2.36), whereas those irradiated with 1 kGy were only slightly lower (0.866 and 1.018). With such results exceeding significantly 0.1 all these samples are classified no doubt irradiated. This is a very important observation from practical point of view. It is clear that samples of diet supplements which contain the irradiated admixture treated with relatively low doses of ionizing radiation (1 and 3 kGy) are easily detected by the TL method. Surprisingly, a similar result has been obtained with diet supplement no. 2 irradiated with even lower doses 0.2 and 0.5 kGys. In fact, the glow ratios of these samples were slightly lower in this than in the latter case (from 0.214 to 0.467). Nevertheless, they exceed still markedly the critical 0.1 level and prove unmistakably radiation treatment. This unexpected observation is beneficial and perspective in view of the present trend to suppress the irradiation dose to the lowest critical level. The effect can be explained in terms of high trapping abilities of ionizing energy in silicate minerals isolated from diet supplement and originated probably from spices or herbs.

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LABORATORY OF NUCLEAR CONTROL SYSTEMS AND METHODS

The main subject of the Laboratory activity in 2014 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;
- elaboration of biotechnology for uranium recovery from former uranium mines waste materials.

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.

The new radiometric stand based on the application of large area thin scintillators for alpha-, beta- and gamma-radiation measurements, were 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.

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. The new apparatus for tomography of industrial installations, based on the gamma scanning principle, was elaborated.

METHOD OF LOCATION OF PLACES WHERE DEFECTS OF INSTALLATION BLANKET OCCUR

Adrian Jakowiuk, Łukasz Modzelewski, Jacek Palige

Method of the location of places where defects of installation blanket occur was developed on the basis of the fast cooling column investigations. The installation is made of a steel blanket with a thickness of approximately 12 mm. There is also a chemoresistant covering made of two layers of graphite and acidproof bricks on the inner side, and the warm-protective isolation on the outer side. During the work of installation, as a result of leakage, the hydrogen chloride can get through the layer of bricks to the blanket. Then, the corrosion pits which reduce the thickness of the wall are made. Previously established maximum value of the loss is about 6 mm, which is a half of the thickness of the blanket.

The purpose of this study was to develop a method that helps to locate places of defects in the blanket, without the need to stop the work of the installation or remove the external components. The acquaintance of places of the defects' appearance allows to take appropriate actions and prevent the occurrence of leaks.

To the location of defects in the installation blanket a gamma scanning technique [1,2] was used. The diagram (Fig.1) presents the "ideal" situation in which on the surface of the installation there are not any obstacles. In fact, the technological holes and nozzles are located on the installation. Additionally, one should take into account the location of the landings.

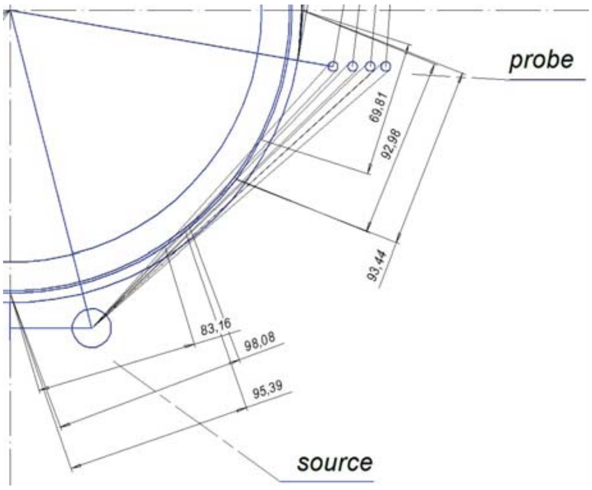

Fig.2. The tested part of the installation – measuring runs.

As part of the verification of the method, a number of measurements were made on the tested installation. Four test runs were performed with a length of 1 m (Fig.2) [3]. The first scan ran partly through the steel blanket and the inner fill (brick chimney) and was performed three times. The second scan involving a large part of the steel blanket and a small part of external heating was performed three times. The third scan ran mostly by the heating, and, to a small extent, by the blanket. The fourth scan ran through the heating and

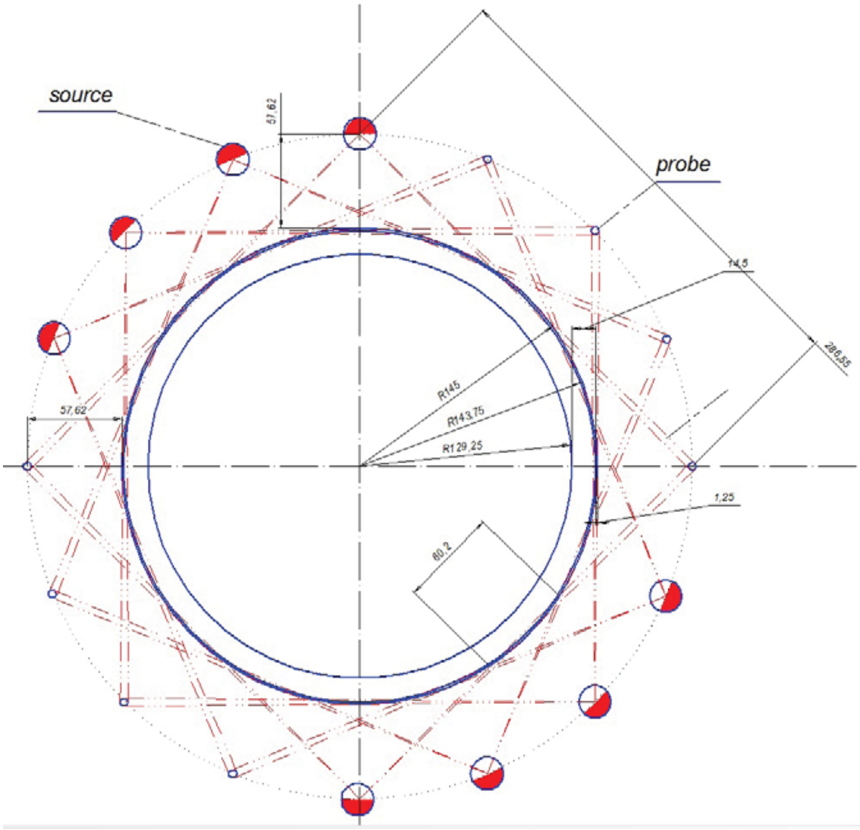

Fig.1. The proposed measurement scheme.

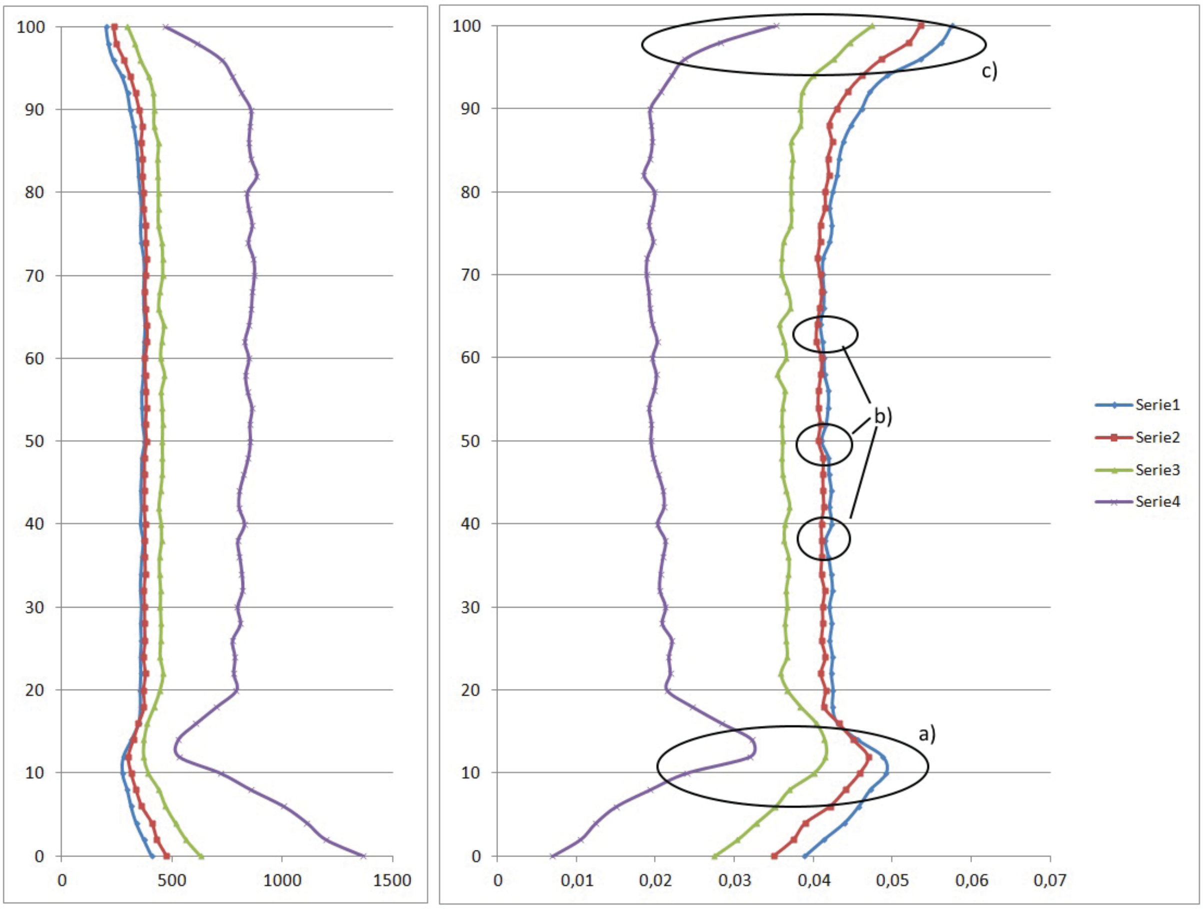

Fig.3. The results of the scan. Left graph – x: imp/s, y: height; right graph – x: density, y: height. Series 1, 2, 3 and 4, respectively measurement runs. a) A flange C1; b) on the series 1 graph places of the join of chimney bricks are shown; c) the nozzle collar becomes visible, it is not shown in the installation diagram.

extended beyond the installation. The results of the scans are shown in Fig.3.

In the scanned area there are no signs of loss of the steel blanket in the tested installation. If the loss had occurred, it should have been visible on the second scan graph and partially on the first scan graph.

On the basis of the performed tests we can confirm the usefulness of the method used for testing the degree of degradation of the inner surface of the steel blanket in a fast cooling column. However, on account of the way of fitting the column with the outside infrastructure the making of scans of the entire surface of the column is not possible. It is estimated that the scanning of 50-70% of the surface of the column will be possible. The examination will apply to areas of the column about the width of 40-60 cm and the height dependent on the possibility of fastening device to gamma scanning. Each measurement will consist of the measurements in the system (Fig.2): one setting of the source and 3-4 different settings of the probe.

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    Resistive switching behavior of Pt/Zn/O/pyrographite devices for memory applications.

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Oddziaływanie promieniowania jonizującego na materię (The effects of ionizing radiation on matter).

Sympozjum „Techniki radiacyjne w przetwórstwie tworzyw sztucznych", Warszawa, Poland, 16-17.06.2014, p. 12.

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Radiacyjna konserwacja dzieł sztuki (Radiation conservation of works of art).

Sympozjum „Techniki radiacyjne w przetwórstwie tworzyw sztucznych", Warszawa, Poland, 16-17.06.2014, p. 37.

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Radiacyjna odporność papieru (Radiation resistance of paper)

Sympozjum „Techniki radiacyjne w przetwórstwie tworzyw sztucznych", Warszawa, Poland, 16-17.06.2014, p. 24.

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Wykorzystanie technologii radiacyjnych do eliminowania patogenów roślin w podłożach (Use of radiation technology for the elimination of plant pathogenes in substrates).
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Zastosowanie promieniowania jonizującego w diagnostyce dużych instalacji przemysłowych (The use of ionizing radiation in the diagnosis of large industrial installations).
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Determination of ^{90}Sr using MSFIA-LOV system with ICP-MS detection.

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XI Warszawskie Seminarium Doktorantów Chemików, ChemSession'14, Warszawa, Poland, 16.05.2014. Streszczenia, p. 106.

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Wykorzystanie procesów radiacyjnych w polimerach stosowanych w medycynie (Use of radiation processes in polymers applied in medicine).

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Radiacyjna funkcjonalizacja powierzchni poliamidu 6,10 monomerami NVP i AAm jako metoda otrzymywania nowych materiałów (Radiation functionality of the surface of polyamide 6.10 by monomers NVP and AAm).

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    41. Annual Meeting of the European Radiation Research Society, ERR2014, Rhodes, Greece, 14-19.09.2014. Abstract book, pp. 49-50.

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157. **Zimek Z., Przybytniak G., Nowicki A., Bułka S., Roman K., Mirkowski K.**

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XXIII Poznańskie Konwersatorium Analityczne: Nowoczesne metody przygotowania próbek i oznaczania śladowych ilości pierwiastków, Poznań, Poland, 8-9.05.2014, p. 122.

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5. **Chmielewski A.G., Urbaniak A., Wawryniuk K.**

   Membrane enrichment of biogas from two-stage pilot plant using agricultural waste as a substrate.

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6. **De la Fuente J.R., Aliaga C., Canete A., Kciuk G., Szreder T., Bobrowski K.**

   Photoreduction of azaoxoisoaporphines by amines: laser flash and steady-state photolysis and pulse radiolysis studies.

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7. **Guzik G.P., Stachowicz W.**

   Study on organic radicals giving rise to multicomponent EMR spectra in dried fruits to ionizing radiation II. D-Glucose.

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8. **Licki J., Chmielewski A.G., Pawelec A., Zimek Z., Bigos A.**

   Electron beam technology for multi-pollutant emissions control at a coal-fired boiler, current issues.

   Journal of Power Technologies, 93, 5, 330-338 (2013).

9. **Smoliński T., Deptuła A., Łada W., Wawszczak D., Brykała M., Olczak T., Zaza F.**

   Synthesis of perovskite doped Sr, Co, Cs and Nd by complex sol gel process.

   XVII International Sol-Gel Conference, Madrid, Spain, 25-30.08.2013, [1] p.

10. **Smoliński T., Deptuła A., Łada W., Wawszczak D., Olczak T., Brykała M., Rogowski M., Zaza F.**

    Metoda syntezy perowskitu dotowanego Cs, Sr, Co, Nd (The method of the synthesis of perovskite dopped by Cs, Sr, Co, Nd).

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6. Radiation methods in decision support system for food safety
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7. Silver nanoparticle accumulation by aquatic organisms – neutron activation as a tool for the environmental fate of nanoparticles tracing
   M. Asztemborska, M. Jakubiak, M. Książyk, R. Stęborowski, H. Polkowska-Motrenko, G. Bystrzejewska-Piotrowska
8. In memoriam – Professor Heino Nitsche (1949-2014)

Information

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2. Pasywne urządzenia do usuwania wodoru z obudowy bezpieczeństwa reaktora jądrowego (Passive recombiners for the removal of hydrogen from the containment of nuclear reactor)
   Z. Zimek
3. Raport z eksploatacji reaktora badawczego MARIA w 2013 roku (Report on the operation of the research reactor MARIA in 2013)
   A. Gołąb
4. Odpady promieniotwórcze – kilka informacji o składowaniu odpadów i zamykaniu składowisk (Radioactive waste – some information about waste storing and closing of storages)
   P. Sampławska
5. Wpływ energetyki jądrowej i odnawialnych źródeł energii na koszty w systemie energetycznym Polski (Influence of nuclear energy and renewal energy sources on the costs in the Polish energy system)
   A. Strupczewski
6. Wolno rosnące klony komórek białaczki L5178Y i zagadka wewnątrzklonalnej odnowy popromiennej (Slow clones of the L5178Y murine lymphoma and the riddle of the postirradiation intraclonal recovery)
   I. Szumiel

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1. Wywiad z Januszem Włodarskim, Prezesem Państwowej Agencji Atomistyki (Interview with Mr. Janusz Włodarski, President of the Polish National Atomic Energy Agency)
   S. Latek
2. Trudne nowe zadania przed instytucjami odpowiedzialnymi za zapewnienie bezpieczeństwa jadrowego i ochrony radiologicznej w Polsce (New difficult duties of the institutions responsible for ensuring the nuclear safety and radiological protection in Poland)
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3. Dekontaminacja chemiczna systemów pierwotnego obiegu chłodzącego w elektrowniach jądrowych (Chemical decontamination of the NPP primary circuit cooling systems)
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4. Reaktory jądrowe przyszłości i likwidacja problemu wysokoaktywnych odpadów promieniotwórczych (Future nuclear reactors and liquidation of the high-level radioactive waste problem)
   T. Denkiewicz
5. Technologia radiacyjna w ochronie roślin (Radiation technology for the plants protection)
   U. Gryczka, W. Migdał, M. Ptaszek, L.B. Orlikowski
6. Postęp w technikach radiacyjnych (Progress in radiation techniques)
   W. Głuszewski
7. Słowackie elektrownie jądrowe (Slovak nuclear power plants)
   J. Klepáč

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   W. Kiełbasa
2. Systemy detekcji skażeń promieniotwórczych opracowane w Instytucie Chemii i Techniki Jąrowej (Systems for radioactive contamination detection elaborated in the Institute of Nuclear Chemistry and Technology)
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   J.L. Parus, R. Mikołajczak
4. Radioliza papieru (Radiolysis of paper)
   W. Głuszewski
5. Przegląd metod obliczania dawek dla organizmów żywych innych niż człowiek (Review of the methods of the doses estimation for the living organisms other than human being)
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3. Dyrektywa Rady Unii 2013/59/EURATOM (Directive of EU Council No. 2013/59/EURATOM)
   T. Musiałowicz
4. Działalność WANO – Światowego Stowarzyszenia Operatorów Elektrowni Jądrowych (Activity of WANO – World Association of Nuclear Operators)
   D.W. Kulczyński
5. Polak we władzach Instytutu Lauego Langevina (A Pole – member of the Laue Langevin Institute authorities)
   M. Nowina-Konopka
6. Maria Skłodowska-Curie – znane i mało znane fakty z życia Uczonej (Maria Skłodowska-Curie – known and little known facts from the life of that Scientist)
   B. Gwiazdowska, W. Bulski, M. Sobieszczak-Marciniak
7. Projekt CTA – Cherenkov Telescope Array – czyli Sieć Teleskopów Czerenkowa (CTA Project – Cherenkov Telescope Array)
   M. Nowina-Konopka
8. Chemia jądrowa w praktyce (Nuclear chemistry in practice)
   W. Łada, D. Wawszczak, A.G. Chmielewski

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INTERVIEWS IN 2014

1. Chmielewski A.G.

   Tycner A.: Energetyka odnawialna długo jeszcze nie zastąpi w Polsce tradycyjnej (Renewable energy still for a long time will not place traditional energy in Poland). http://www.polskieradio.pl/42/3167/Artykul/1336756 (28.12.2014).

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THE INCT PATENTS AND PATENT APPLICATIONS IN 2014

PATENTS

1. Sposób unieszkodliwiania odpadów promieniotwórczych w szkłach krzemionkowych (Method for the disposal of radioactive wastes in structures of silica glasses)
   A.G. Chmielewski, A. Deptuła, M. Miłkowska, W. Łada, T. Olczak
   Polish Patent No. 217122
2. Sposób otrzymywania opatrunków hydrożelowych zawierających kompleks radiacyjnie degradowanego polisacharydu i srebra (Method for the preparation of hydrogel wound dressings containing complex of radiation-degraded polysccharide with silver)
   D. Chmielewska, W. Migdał, A.G. Chmielewski, U. Gryczka, P. Kik
   Polish Patent No. 217447 (with KIKGEL, Poland)
3. Sposób rozpuszczania tlenku toru (Method of dissolution of thorium oxide)
   K. Łyczko, M. Łyczko, I. Herdzik, B. Zielińska
   Polish Patent No. 217150
4. Sposób otrzymywania terapeutycznych ilości radionuklidu ^{47}Sc (Method for obtaining therapeutic amounts of the ^{47}Sc radionuclide)
   A. Bilewicz, B. Batroś, E. Chajduk
   Polish Patent No. 217857
5. Radiofarmaceutyk terapeutyczny znakowany radionuklidami radu oraz sposób jego wytwarzania (Therapeutic radiopharmaceutical labelled with radionuclides of radium and method for its obtaining)
   A. Kasperek, A. Bilewicz, T. Olczak
   Polish Patent No. 217466
6. Sposób wytwarzania nanokompozytu wolframowo-cyrkonowego (Method of production of a tungsten-zirconium nanocomposite)
   E. Iller, D. Wawszczak, A. Deptuła, W. Łada, T. Olczak
   Polish Patent
7. Sposób otrzymywania dwutlenku uranu o ziarnach sferycznych i nieregularnych (Process for the preparation of uranium dioxide with spherical and irregular grains)
   A.G. Chmielewski, A. Deptuła, M. Brykała, W. Łada, D. Wawszczak, T. Olczak
   Polish Patent
8. Sonda detekcyjna skażenia promieniotwórczego ze scyntylatorem plastikowym (Detector of radioactive contamination with plastic scintillator)
   B. Machaj, E. Kowalska, J. Mirowicz, J. Pieńkos
   Polish Patent
9. Sposób otrzymywania nowych krzemionkowych sorbentów metali i biocydów (Method for obtaining new silica sorbents of metals and biocides)
   A. Łukasiewicz, D. Chmielewska-Śmietanko
   Polish Patent
10. Sposób otrzymywania sferycznych ziaren trójtlenku itru (Method for obtaining spherical grains of yttrium trioxide)
    W. Łada, A. Deptuła, T. Olczak, D. Wawszczak
    Polish Patent
11. Sposób unieszkodliwiania odpadów promieniotwórczych w szkłach krzemionkowych (Method for the disposal of radioactive wastes in structures of silica glasses)
    A.G. Chmielewski, A. Deptuła, M. Miłkowska, W. Łada, T. Olczak
    Ukrainian Patent
12. Sposób otrzymywania dwutlenku uranu o ziarnach sferycznych i nieregularnych (Process for the preparation of uranium dioxide with spherical and irregular grains)

A.G. Chmielewski, A. Deptuła, M. Brykała, W. Łada, D. Wawszczak, T. Olczak

Ukrainian Patent

13. Sposób i sorbent do otrzymywania radionuklidu arsenu-72 oraz sposób wytwarzania tego sorbentu (Sorbent for reciving radionuclide arsenic-72, production of this sorbent)

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

    European Patent No. 2618335

PATENT APPLICATIONS

1. Sposób wydzielania uranu z roztworów po kwaśnym ługowaniu rud uranowych (Uranium extracting after acidic leaching of uranium ores on Dowex 1 X 10)

   Z. Samczyński, R. Dybczyński, G. Zakrzewska-Kołtuniewicz, B. Danko, I. Herdzik, D. Gajda, E. Chajduk, W. Łada

   Polish Patent Application P-407936

2. Sposób otrzymywania oksywęglika uranu metodą zol-żel (Method of synthesis of uranium oxycarbide by the sol-gel process)

   M. Brykała, M. Rogowski, W. Łada

   Polish Patent Application P-408672

3. Jonit do selektywnego wydzielania jonów cezu(I) z roztworów wodnych oraz sposób jego wytwarzania (Ion-exchanger for the selective separation of caesium ions (I) from aqueous solution and its manufacturing method)

   K. Borowik

   Polish Patent Application P-408673

4. Sposób otrzymywania tlenkowych prekursorów paliw mieszanych typu MOX, w postaci proszków o ziarnach sferycznych (Method of synthesis of mixed oxide fuel precursors of the MOX-type in the form of spherical particle powders)

   M. Brykała, M. Rogowski, W. Łada, A. Deptuła

   Polish Patent Application P-410288

CONFERENCES ORGANIZED AND CO-ORGANIZED BY THE INCT IN 2014

1. PROJECT MEETING NO 2 WITHIN THE PLATENSO PROJECT – BUILDING A PLATFORM FOR ENHANCED SOCIETAL RESEARCH RELATED TO NUCLEAR ENERGY IN CENTRAL AND EASTERN EUROPE, 12-13 MAY 2014, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Organizing Committee: Grażyna Zakrzewska-Kołtuniewicz, Ph.D., D.Sc., professor in INCT, Agnieszka Miśkiewicz, Ph.D., Katarzyna Kiegiel, Ph.D., Dorota Gajda, M.Sc.

2. XI WARSZAWSKIE SEMINARIUM DOKTORANTÓW CHEMIKÓW ChemSession'14 (XI WARSAW SEMINAR OF PhD STUDENTS OF CHEMISTRY AND YOUNG CHEMISTS ChemSession'14), 16 MAY 2014, WARSZAWA, POLAND

Organized by the Polish Chemical Society – Warsaw Branch, Institute of Nuclear Chemistry and Technology

Organizing Committee: Anna Bitner, M.Sc., Karolina Czerwińska, M.Sc., Leon Fuks, Ph.D., Dorota Gajda, M.Sc., Agnieszka Górska, M.Sc., Anna Kundys, M.Sc., Klaudyna Leniarska, M.Sc., Izabela Madura, Ph.D., Sławomir Ostrowski, Ph.D., Alicja Pawełko, M.Sc., Renata Rybakiewicz, M.Sc.

3. SEMINARIUM „60 LAT RADIOCHEMII W IChTJ" ORAZ JUBILEUSZ 50-LECIA PRACY NAUKOWEJ PROF. DR. HAB. JERZEGO OSTYK-NARBUTTA (SEMINAR ON 60 YEARS OF RADIOCHEMISTRY IN THE INCT AND A JUBILEE OF 50 YEARS OF THE SCIENTIFIC WORK OF PROF. JERZY OSTYK-NARBUTT), 23 MAY 2014, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology – Centre for Radiochemistry and Nuclear Chemistry

4. SPOTKANIE „MASS MEDIA I KOMUNIKACJA: BUDOWANIE NARODOWEGO DIALOGU. DIALOG W POLSCE" W RAMACH PROJEKTU EAGLE (MEETING "MASS MEDIA AND COMMUNICATION: BUILDING A NATIONAL DIALOGUE. DIALOGUE IN POLAND" WITHIN THE EAGLE PROJECT – ENHANCING EDUCATION, TRAINING AND COMMUNICATION PROCESSES FOR INFORMED BEHAVIORS AND DECISION-MAKING RELATED TO IONIZING RADIATION RISKS), 29 MAY 2014, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Organizing Committee: Grażyna Zakrzewska-Kołtuniewicz, Ph.D., D.Sc., professor in INCT, Paulina Nieścior-Browińska, M.Sc., Wioleta Olszewska, M.Sc., Agnieszka Miśkiewicz, Ph.D., Katarzyna Kiegiel, Ph.D., Dorota Gajda, M.Sc.

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Organized by the Institute of Nuclear Chemistry and Technology

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6. SYMPOZJUM „TECHNIKI RADIACYJNE W PRZETWÓRSTWIE TWORZYW SZTUCZNYCH" (SYMPOSIUM "RADIATION TECHNIQUES IN PLASTICS PROCESSING), 16-17 JUNE 2014, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Organizing Committee: Ewa M. Kornacka, Ph.D., Wojciech Głuszewski, Ph.D., Andrzej Nowicki, Ph.D., Marta Walo, Ph.D.

7. SEMINARIUM DOTYCZĄCE ZADANIA BADAWCZEGO nr 8 „ANALIZA PROCESÓW ZACHODZĄCYCH PRZY NORMALNEJ EKSPLOATACJI OBIEGÓW WODNYCH W ELEKTROWNIACH JĄDROWYCH Z PROPOZYCJAMI DZIAŁAŃ NA RZECZ PODNIESIENIA POZIOMU BEZPIECZEŃSTWA JĄDROWEGO" STRATEGICZNEGO PROJEKTU BADAWCZEGO „TECHNOLOGIE WSPOMAGAJĄCE ROZWÓJ BEZPIECZNEJ ENERGETYKI JĄDROWEJ" (SCIENTIFIC MEETING CONCERNING RESEARCH TASK 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" IN THE FRAMEWORK OF THE STRATEGIC RESEARCH PROJECT "TECHNOLOGIES SUPPORTING DEVELOPMENT OF SAFE NUCLEAR POWER ENGINEERING"), 27 JUNE 2014, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Organizer: Anna Bojanowska-Czajka, Ph.D.

8. SEMINARIUM DOTYCZĄCE ZADANIA BADAWCZEGO nr 7 „ANALIZA PROCESÓW GENERACJI WODORU W REAKTORZE JĄDROWYM W TRAKCIE NORMALNEJ EKSPLOATACJI I W SYTUACJACH AWARYJNYCH Z PROPOZYCJAMI DZIAŁAŃ NA RZECZ PODNIESIENIA POZIOMU BEZPIECZEŃSTWA JĄDROWEGO" STRATEGICZNEGO PROJEKTU BADAWCZEGO „TECHNOLOGIE WSPOMAGAJĄCE ROZWÓJ BEZPIECZNEJ ENERGETYKI JĄDROWEJ" (SCIENTIFIC MEETING CONCERNING RESEARCH TASK No. 7 "STUDY OF HYDROGEN GENERATION PROCESSES IN NUCLEAR REACTORS UNDER REGULAR OPERATION CONDITIONS AND IN EMERGENCY CASES, WITH SUGGESTED ACTIONS AIMED AT UPGRADE OF NUCLEAR SAFETY" IN THE FRAMEWORK OF THE STRATEGIC RESEARCH PROJECT "TECHNOLOGIES SUPPORTING DEVELOPMENT OF SAFE NUCLEAR POWER ENGINEERING"), 30 JUNE 2014, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Organizer: Prof. Jacek Michalik, Ph.D., D.Sc.

9. INTERNATIONAL CONFERENCE ON DEVELOPMENT AND APPLICATIONS OF NUCLEAR TECHNOLOGIES NUTECH-2014, 21-24 SEPTEMBER 2014, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology, AGH University of Science and Technology, Polish Nuclear Society

Organizing Committee: Grażyna Zakrzewska, Ph.D., D.Sc., professor in INCT, Wojciech Migdał, Ph.D., D.Sc., professor in INCT, Zbigniew Zimek, Ph.D., Wojciech Głuszewski, Ph.D., Urszula Gryczka, M.Sc., Agnieszka Miśkiewicz, Ph.D., Wioleta Olszewska, M.Sc., Dorota Gajda, M.Sc., Zdzisław Stęgowski, Ph.D., D.Sc., professor in AGH

10. WORKSHOP "THE INDUSTRIAL AND ENVIRONMENTAL APPLICATIONS OF ELECTRON BEAMS", 6-7 NOVEMBER 2014, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Organizing Committee: Magdalena Rzepna, M.Sc., Dagmara Chmielewska-Śmietanko, M.Sc.

11. REGIONAL TRAINING COURSE "SAFE OPERATION OF IRRADIATION FACILITIES" IN THE FRAME OF THE IAEA TECHNICAL COOPERATION REGIONAL PROJECT RER/1/014 "INTRODUCING AND HARMONIZING STANDARDIZED QUALITY CONTROL PROCEDURES FOR RADIATION TECHNOLOGIES", 1-5 DECEMBER 2014, WARSZAWA, POLAND

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

Organizing Committee: Andrzej Rafalski, Ph.D., Magdalena Rzepna, M.Sc., Wojciech Głuszewski, Ph.D.

12. TL-IRMP "JOINT INNOVATIVE TRAINING AND TEACHING/LEARNING PROGRAM IN ENHANCING DEVELOPMENT AND TRANSFER KNOWLEDGE OF APPLICATION OF IONIZING RADIATION IN MATERIALS PROCESSING" – KICKOFF TRANSNATIONAL MANAGEMENT MEETING, 8-9 DECEMBER 2014, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Organizer: Yongxia Sun, Ph.D., D.Sc. professor in INCT

Ph.D./D.Sc. THESES IN 2014

Ph.D. THESES

1. Macin Jarosław Konior, M.Sc. (National Centre for Nuclear Research, Otwock-Świerk, Poland)
   Nowa technologia wytrwarzania generatorów radionuklidowych ^{188}W/^{188}Re (New technology of producing generators ^{188}W/^{188}Re)
   supervisor: Edward Iller, Ph.D., D.Sc., professor in NCBJ
   Institute of Nuclear Chemistry and Technology, 27.02.2014

D.Sc. THESES

1. Yongxia Sun, Ph.D. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
   Degradation of air pollutants in non-thermal plasma generated by electron beam. Experimental and theoretical study
   Institute of Nuclear Chemistry and Technology, 28.03.2014
2. Janina Kopyra, Ph.D. (Siedlce University of Natural Sciences and Humanities, Faculty of Sciences, Siedlce, Poland)
   Oddziaływanie niskoenergetycznych elektronów z cząsteczkami o biologicznym znaczeniu (Interaction of low energy electrons with biologically relevant molecules)
   Institute of Nuclear Chemistry and Technology, 13.06.2014
3. Michał H. Jamróż, Ph.D. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
   Analiza PED teoretycznych widm oscylacyjnych za pomocą programu VEDA (PED analysis of theoretical oscillation spectra by the VEDA program)
   Institute of Nuclear Chemistry and Technology, 12.12.2014

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 2014, the following lecture series were organized:

- “Basis of molecular spectroscopy: optical spectroscopy” – Prof. Jan Cz. Dobrowolski, Ph.D., D.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland);
- “Basis of nuclear magnetic resonance spectroscopy” – Marta Jamróz, Ph.D. (Medical University of Warsaw, Faculty of Pharmacy, Warszawa, Poland);
- “Radiation chemistry and technology of polymers” – Prof. Olgen Guven (Hacettepe University, Chemistry Department, Ankara, Turkey);
- “Structural supramolecular chemistry” – Prof. Janusz Lipkowski, Ph.D., D.Sc. (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
Cardinal Stefan Wyszyński University in Warsaw, Faculty of Mathematics and Natural Sciences	Poland	1	1 month
Gimnazjum nr 95 w Warszawie	Poland	23	one-day course
Gimnazjum nr 123 w Warszawie	Poland	17	one-day course

Institution	Country	Number of participants	Period
Technical University of Łódź, Faculty of Chemistry, Institute of Applied Radiation Chemistry	Poland	13	one-day course
University of Warsaw, Faculty of Chemistry	Poland	9	3 weeks
		1	1 month
		1	1 year
University of Warsaw, Faculty of Physics	Poland	1	1 year
		1	1.5 year
University of Rzeszów, Faculty of Biology and Agriculture	Poland	1	2 weeks
Warsaw University of Life Sciences – SGGW, Faculty of Agriculture and Biology	Poland	1	1.5 year
Warsaw University of Life Sciences – SGGW, Faculty of Food Sciences	Poland	30	one-day course
Warsaw University of Technology, Faculty of Chemical and Process Engineering	Poland	1	1 month
		2	3 months
		1	7 months
Warsaw University of Technology, Faculty of Chemistry	Poland	1	1.5 week
		1	3 weeks
		1	1 month
Warsaw University of Technology, Faculty of Physics	Poland	1	3 months
		24	one-day course
XXXIV Liceum Ogólnokształcące w Warszawie	Poland	25	one-day course
		26	one-day course

MASTER'S AND BACHELOR'S DISSERTATIONS

1. Justyna Moskal

   Master's dissertation: Badania analityczne perfluorowanych związków organicznych pod wpływem promieniowania gamma (Analytical investigation of decomposition of perfluorinated organic compounds under the influence of ionizing radiation)

   supervisor: Prof. Marek Trojanowicz, Ph.D., D.Sc.

   supervisor in INCT: Anna Bojanowska-Czajka, Ph.D.

   University of Warsaw, Faculty of Chemistry

2. Paweł Łęcki

   Bachelor's dissertation: Trikarbonylkowe kompleksy renu(I) w układzie „2+1" z 2,2'-bipirydylem i wybranymi chlorowcami (Tricarbonylrhenium(I) complexes in '2+1' system with 2,2'-bipyridyl and selected halogens)

   supervisor: Prof. Krzysztof Woźniak, Ph.D., D.Sc.

   supervisor in INCT: Krzysztof Łyczko, Ph.D.

   University of Warsaw, Faculty of Chemistry

3. Barbara Panas

   Master's dissertation: Znakowanie lapatinibu radionuklidem ^{68}Ga dla diagnostyki PET (Lapatinib labelled with ^{68}Ga for PET diagnosis)

   supervisors: Rafał Kuś, Ph.D., Ewa Gniazdowska, Ph.D.

   University of Warsaw, Faculty of Physics

4. Monika Małgorzata Szołucha

   Master's dissertation: Biołgowanie uranu z rud ubogich (Bioleaching of low-grade uranium ores)

   supervisors: Prof. Eugeniusz Molga, Ph.D., D.Sc., Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.

   Warsaw University of Technology, Faculty of Chemical and Process Engineering

5. Przemysław Walczak

   Bachelor's dissertation: Badanie sorpcji Co-58, radioaktywnego produktu korozji elementów konstrukcyjnych reaktorów jądrowych, na nanorurkach tlenku tytanu(IV) (The study of sorption of radioactive Co-58, a corrosion product of construction elements in nuclear reactors, on the titanium dioxide nanotubes)

   supervisor: Maciej Chotkowski, Ph.D.

   supervisor in INCT: Monika Łyczko, Ph.D.

   University of Warsaw, Faculty of Chemistry

RESEARCH PROJECTS AND CONTRACTS

RESEARCH PROJECTS GRANTED BY THE NATIONAL SCIENCE CENTRE IN 2014

1. **Radiochemical separation of arsenic from selenium and its potential usage in the generator ^{72}Se/^{72}As construction.**
   supervisor: Ewelina Chajduk, Ph.D.
2. **Functionalization of polyurethane surface by radiation-induced grafting (Preludium).**
   supervisor: Marta Walo, Ph.D.
3. **Nanozeolites as a carrier for radium in targeted therapy.**
   supervisor: Prof. Aleksander Bilewicz, Ph.D., D.Sc.
4. **Des-acyl ghrelin analog as a new carrier of radionuclides and a potential radiopharmaceutical.**
   supervisor: Grzegorz Wójciuk, Ph.D.
5. **Physicochemical and biochemical studies of selected biological conveyers of nitrogen oxide. Relation between the molecular structure and distribution of electric charge and the biological activity of nitrosyl complexes of iron.**
   supervisor: Hanna Lewandowska-Siwkiewicz, Ph.D.
6. **Chiral cores/monomers of drugs and conducting polymers: from calculations to experimental characteristics.**
   supervisor: Prof. Jan Cz. Dobrowolski, Ph.D., D.Sc.
7. **Nanobodies labelled with alpha emitters as potential radiopharmaceuticals in targeted radioimmunotheraphy.**
   supervisor: Marek Pruszyński, Ph.D.
8. **Nanoparticles of gold, gold-gold sulphide and titanium dioxide modified with tellurium as carriers for At-211 for targeted alpha theraphy.**
   supervisor: Prof. Aleksander Bilewicz, Ph.D., D.Sc.
9. **Studies on the phenomena occurring in the membrane boundary layer during the filtration of aqueous solutions and suspensions proceeding in membrane apparatuses with different configurations.**
   supervisor: Agnieszka Miśkiewicz, Ph.D.
10. **The influence of nanoparticles on beta-amyloid removal by microglia cells.**
    supervisor: Katarzyna Sikorska, M.Sc.

INNOTECH PROJECTS GRANTED BY THE NATIONAL CENTRE FOR RESEARCH AND DEVELOPMENT IN 2014

1. **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
2. **Conspan BlueGas – technology for treatment of flowback fluids from gas-bearing shales hydraulic fracturing with water recycling and reclamation of valuable metals.**
   Konsorcjum naukowe: Pyrocat Catalyse World (lider), Institute of Nuclear Chemistry and Technology, Polish Geological Institute – National Research Institute

APPLIED RESEARCH PROGRAMME OF THE NATIONAL CENTRE FOR RESEARCH AND DEVELOPMENT IN 2014

1. **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.
2. **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.

INTERNATIONAL PROJECTS CO-FUNDED BY THE MINISTRY OF SCIENCE AND HIGHER EDUCATION IN 2014

1. **Radiation supporting synthesis and curing of nanocomposites suitable for practical applications.**
   supervisor: Grażyna Przybytniak, Ph.D., D.Sc., professor in INCT
2. **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.
3. **Advanced fuels for generation IV reactors: reprocessing and dissolution (ASGARD).**
   supervisor: Andrzej Deptuła, Ph.D.
4. **The industrial and environmental applications of electron beams.**
   supervisor: Dagmara Chmielewska-Śmietanko, M.Sc.
5. **Formation, investigations and characterization of advanced nanoporous materials.**
   supervisor: Bożena Sartowska, Ph.D.
6. **Safety of actinide separation processes (SACSESS).**
   supervisor: Prof. Jerzy Narbutt, Ph.D., D.Sc.
7. **Transnational access to large infrastructure for a safe management of actinide (TALISMAN).**
   supervisor: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.
8. **Advanced nanostructured porous materials formation and characterization (NONAMAPOR).**
   supervisor: Bożena Sartowska, Ph.D.
9. **Based on starch-PVA system and cellulose reinforced active packaging materials for food prepared using of radiation modification (PackRad).**
   supervisor: Krystyna Cieśla, Ph.D., D.Sc., professor in INCT
10. **Studies on influence of synthesis condition on morphology and sorption properties of hydrothermally synthesized nanotitanate sorbents (NaTiSorb).**
    supervisor: Wojciech Starosta, Ph.D.
11. **Attracting investments in plasma-based air and water cleaning technologies (PlasTEP+).**
    supervisor: Andrzej Pawelec, Ph.D.
12. **Application of advanced membrane systems in nuclear desalination (NUCDESAL).**
    supervisor: Grażyna Zakrzewska-Kołtuniewicz, Ph.D., D.Sc., professor in INCT
13. **Coordination of actinides with hydrophilic ligands.**
    supervisor: Prof. Jerzy Narbutt, Ph.D., D.Sc.
14. **Development of dosimetry methods and safety of radiation and nuclear facilities.**
    supervisor: Roman Janusz, M.Sc.
15. **Studying the social and socio-economic effects of the implementation of the Polish nuclear programme using new methodology.**
    supervisor: Agnieszka Miśkiewicz, Ph.D.

STRATEGIC PROJECT "TECHNOLOGIES SUPPORTING DEVELOPMENT OF SAFE NUCLEAR POWER ENGINEERING"

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 spent nuclear fuel and radioactive waste management techniques and technologies.**
   supervisor: Leon Fuks, Ph.D.
3. **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.
4. **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.
5. **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.

IAEA RESEARCH CONTRACTS IN 2014

1. **Radiation supporting synthesis and curing of nanocomposites suitable for practical applications (NANO-RAD).**
   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.
3. **Application of hybrid nuclear techniques in the multiphases flows investigations in wastewater treatment and biogases production plants.**
   No. 17366
   principal investigator: Jacek Palige, Ph.D.
4. **Based on starch-PVA system and cellulose reinforced active packaging materials for food prepared using of radiation modification (PackRad).**
   No. 17493
   principal investigator: Krystyna Cieśla, Ph.D., D.Sc., professor in INCT.
5. **The study of the influence of the environmental factors on the isotopic compositions of dairy products.**
   No. 18056
   principal investigator: Ryszard Wierzchnicki, Ph.D.
6. **Application of advanced membrane systems in nuclear desalination.**
   No. 18539/RO
   principal investigator: Grażyna Zakrzewska-Kołtuniewicz, Ph.D., D.Sc., professor in INCT
7. **Studying the social and socio-economic effects of the iomplementation of the Polish nuclear programme using new methodology.**
   No. 18541/RO
   principal investigator: Agnieszka Miśkiewicz, Ph.D.
8. **Interlaboratory comparison in the range of high technological doses in the frame of project IAEA RAS1015.**
   principal investigator: Andrzej Rafalski, Ph.D.

IAEA TECHNICAL AND REGIONAL CONTRACTS IN 2014

1. **Regional Training on IAEA Validation and Process Control for Electron Beam Radiation Processing.**
   RER/1/011
2. **Supporting radiation synthesis and the characterization of nanomaterials for health care, environmental protection and clean energy applications.**
   RER/8/014
3. **Using nuclear techniques for the characterization and preservation of cultural heritage artefacts in the European Region.**
   RER/8/015
4. **Enhancing quality control methods and procedures for radiation technology.**
   RER/8/017

PROJECTS WITHIN THE FRAME OF EUROPEAN UNION FRAME PROGRAMMES IN 2014

1. **FP7 – EURATOM, Fission: Advanced fuels for generation IV reactors: reprocessing and dissolution (ASGARD).**
   principal investigator: Andrzej Deptuła, Ph.D.
2. **FP7 – EURATOM, Fission: Realizing the European Network in Biodosimetry (RENEB)**
   principal investigator: Sylwester Sommer, Ph.D.
3. **FP7 – Transnational access to large infrastructure for a safe management of actinide (TALISMAN).**
   principal investigator: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.
4. **FP7 – Safety of actinide separation processes (SACSESS).**
   principal investigator: Prof. Jerzy Narbutt, Ph.D., D.Sc.
5. **FP7 – Assessment of regional capabilities for new reactors development through an integrated approach (ARCADIA).**
   principal investigator: Grażyna Zakrzewska-Kołtuniewicz, Ph.D., D.Sc., professor in INCT
6. **FP7 – Enhancing education, training and communication processes for informed behaviors and decision-making related to ionizing radiation risks (EAGLE).**
   principal investigator: Grażyna Zakrzewska-Kołtuniewicz, Ph.D., D.Sc., professor in INCT
7. **FP7 – Building a platform for enhanced societal research related to nuclear energy in Central and Eastern Europe (PLATENSO).**
   principal investigator: Grażyna Zakrzewska-Kołtuniewicz, Ph.D., D.Sc., professor in INCT
8. **FP7 – EUCARD-2 WP4 – Applications of accelerators: The industrial and environemntal applications of electron beams.**
   principal investigator: Dagmara Chmielewska-Śmietanko, M.Sc.

EUROPEAN REGIONAL DEVELOPMENT FUND: BALTIC SEA REGION PROGRAMME

1. **Attracting investments in plasma-based air and water cleaning technologies (PlasTEP+).**
   supervisor: Andrzej Pawelec, Ph.D.

OTHER INTERNATIONAL RESEARCH PROGRAMMES IN 2014

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. **Advanced nanostructured porous materials: formation and characterization** (with Joint Institute for Nuclear Research, Dubna, Russia).
   supervisor: Bożena Sartowska, Ph.D.
3. **Neutron small angle scattering studies of titanates** (with Joint Institute for Nuclear Research, Dubna, Russia).
   No 04-4-1069-2009/2014
   supervisor: Wojciech Starosta, Ph.D.
4. **Coordination of actinides with hydrophilic ligands** (with the French Alternative Energies and Atomic Energy Commission – CEA).
   supervisor: Prof. Jerzy Narbutt, Ph.D., D.Sc.

STRUCTURAL FUNDS: OPERATIONAL PROGRAMME INNOVATIVE ECONOMY

1. **Development of a multi-parametric triage approach for an assessment of radiation exposure in a large-scale radiological emergency.**
   supervisor: Prof. Marcin Kruszewski, Ph.D., D.Sc.
   POIG.01.03.01-14-054/09

PROJECTS GRANTED BY THE FOUNDATION FOR POLISH SCIENCE IN 2014

1. **New radiopharmaceuticals based on alpha emitters against glioblastoma stem cells.**
   supervisor: Agnieszka Majkowska-Pilip, Ph.D.

THE NCBR STRATEGIC RESEARCH PROJECT “TECHNOLOGIES SUPPORTING DEVELOPMENT OF SAFE NUCLEAR POWER ENGINEERING”

Task 4

Development of spent nuclear fuel and radioactive waste management techniques and technologies

Leon Fuks, person in charge of the Task 4
Agata Oszczak, secretary of the Task 4

The Institute of Nuclear Chemistry and Technology (INCT) participated since September 2011 until the end of 2014 in the strategic research project “Technologies supporting development of safe nuclear power engineering” financed by the National Centre for Research and Development (NCBR). This project is a response to the need of increasing energy safety under the conditions of implementation of nuclear energy in Poland. The project arised from the implementation of “Energy policy of Poland until 2030”, a document approved by the National Government Cabinet and from the acceptance of the Climate and Energy Package by the European Union. The results of the project were directly addressed to fill up knowledge needed for the Polish Nuclear Power Programme (PPEJ) and related to the interest of the investor of a nuclear plant. Within the research project, the Institute of Nuclear Chemistry and Technology has been the main executive of Task 4 “Development of spent nuclear fuel and radioactive waste management techniques and technologies”. The main goal of Task 4 were the scientific studies and development works for storage and processing of spent nuclear fuel and radioactive waste generated during operation of Poland’s future nuclear plants as well as the industry and nuclear medicine.

Detailed goals of the task looked as follows:

- methods of plutonium and long-lived actinides separation and their application in manufacturing of the nuclear fuel precursors for new-generation reactors;
- methods for shortening the half-life of the radioactive decay of fission products in the fast neutron reactors by transmutation methods (*i.e.* transition of some elements to another taking place through nuclear reactions);
- development of new technologies for processing and handling of low- and medium-active radioactive waste;
- development of new technologies for reduction of radiotoxicity of radioactive wastes by radiochemical methods;
- development of physicochemical bases of technology for conditioning of radioactive waste and spent nuclear fuel (*i.e.* treatment of materials to achieve the desired effect).

Despite significant increase of the safety in operation of nuclear power plants, management of the spent nuclear waste continues to be a problem. A typical nuclear plant of 1 GW power generates about 35-40 tons of nuclear waste per year. Only about 15% of waste generated worldwide is reprocessed in the plants operating in France, Sweden, Japan, and in the USA and Russia. The remaining part is being stored. Such a mass of the waste is potentially dangerous due to unexpected, long-term environmental impact. In addition, stored waste contains significant amounts of fissible materials and of other valuable materials that may be utilized. On the other hand, it should be emphasized that the current costs of reprocessing of the spent nuclear fuel are high and reach about 1,000 dollars per one kilogram of the material. So, the price for a new nuclear material is much lower than for this obtained from spent nuclear fuels. Therefore, it is important to reduce the reprocessing costs of spent nuclear fuel.

Implementation of the results obtained during realization of the research Task 4 is a multidisciplinary undertaking, encompassing research in the field of chemistry, physics, materials science and technical science. For synthesis of new materials and fuel precursors, patent applications were submitted. It is planned also to submit patent applications for novel solutions in the radioactive waste storage. In the performed studies on the innovative solutions requiring more detailed testing, practical application of results may be expected in the future. Execution of work done within Task 4 includes also strengthen of the cooperation with the domestic industry (*e.g.* the Radioactive Waste Disposal Plant, PGE) as well as with the EU industry (*e.g.* AREVA). Research conducted in collaboration with the Radioactive Waste Disposal Plant creates an opportunity for direct implementation of the effects for expanding the programme for storage of spent fuel and radioactive waste. As a result of regularly performed scientific workshops with the participants of the studies, it was possible to discuss the results and correct directions of the studies.

Results achieved during the project implementation are addressed to the following groups of recipients:

- state administration, persons responsible for decision on the construction of nuclear power plants in Poland and on implementation of domestic technologies for storage of the radioactive waste in Poland;
- centres involved in application of the radioisotopes, producing them as well as the radiolabelled preparates, in nuclear medicine facilities, and in the future – in nuclear power plants, in which the management of liquid, low-activity radioactive waste will be an important problem to be solved.

Results of the project can be implemented to the economic and social practice, resulting in other than the mentioned above prolonged economic effects. Problem of the radioactive waste is a global trouble and despite the fact that Poland does not have at present nuclear power plant, its future acceptance depends, among others, on solving the method of waste management generated by these plants. The economic effects arising from putting into general practice of the results will concern both direct economic effects achieved by implementation of the energy-saving solutions, as well as indirect effects resulting from stimulation of the economy through production of new, innovative products and technologies.

Results of the project implementation are directed also to the producers of equipment for the environmental protection sector, especially manufacturers of the membranes and the membrane modules as well as the systems for membrane filtration and installations for the radioactive waste treatment plants. Results are also directed to the producers of control systems and devices, remote control systems, high-pressure pumps, valves and piping. The effects may be also applied outside the nuclear industry, in sectors generating low-salinity liquid wastes, containing toxic, non-degradable difficult to process matter, designated for temporary storage.

An additional, but important activity undertaken within the research project was education of young scientists which might be future personnel for the nuclear energy programme that starts to be developed in Poland. Some participants have the experience acquired during their long scientific work, especially for the nuclear plant at Żarnowiec. Some of them have gained specific knowledge during their professional visits in the leading nuclear centres throughout the world. They direct this knowledge to the participants of the PhD studies carried out in the Institute of Nuclear Chemistry and Technology as well as students of Warsaw universities in the form of lectures and scientific workshops organized by the INCT. Collective planning and studies carried out within the project, involving students, PhD students, young scientists and experienced employees should result in creating expert groups for the nuclear energy industry that currently restored in Poland.

Main results obtained during realization of Task 4 in the INCT may be summarized as below.

The effect of some hydrophilic ligands on the process of grup extraction of actinides – GANEX

The research was aimed at modification of the 2nd cycle of GANEX process, *i.e.* solvent extraction of actinides from the raffinate remained after separating uranium from spent nuclear fuel dissolved in a few molar HNO_3. Hydrophilic ligands were added to the system in order to suppress unwanted co-extraction of some fission products, *e.g.* Pd, Zr, Tc, *etc.* with a neutral tridentate ligand, *N,N,N',N'*-tetraoctyl diglycolamide (TODGA). Three novel ligands selected from the group of polyamine acetic acids were studied as complexants of the *d*-electron metal ions, and compared with one of the recommended species, diethylenetriamine-*N,N,N',N",N"*-pentaacetic acid (DTPA). An interesting effect was observed, of increased extraction of Am(III) in the presence of hydrophilic ligands studied in the TODGA system. To explain this unexpected synergistic effect a hypothesis has been presented that Am(III) forms mixed ligand complexes, *e.g.* $[Am(TODGA)(DTPA)]^{2-}$, more lipophilic than the $[Am(TODGA)_3]^{3+}$ cation. Our theoretical studies carried out with the use of advanced methods of quantum chemistry confirm that it may be true.

Experimental studies were also performed on the complex formation of actinides with two novel hydrophilic ligands, an anionic (sulphonated) derivative of bis-triazinyl-pyridine (SO_3-Ph-BTP), and a cationic derivative of bis-triazinyl-bipyridine (hydro-BTBP). The determined stability constants show that the SO_3-Ph-BTP ligand forms in acidic aqueous solutions relatively strong complexes, which makes it possible its use for stripping Am(III), Pu(IV) and Np(IV) from the TODGA-containing organic phase and separating them from all lanthanides. On the other hand, the complexes formed by the cationic hydro-BTBP are insufficiently strong to separate Am(III) from all the lanthanides in this system.

Advanced quantum chemistry studies were carried out, aimed at a better understanding of the origin of selectivity of the processes of complex formation and solvent extraction of actinides with some polydentate N- and O-donor ligands. It was concluded that the Am-O bonds in the extracted $[M(TODGA)_3]^{3+}$ complexes are somewhat more covalent than the Eu-O bonds. The reason is a greater shift of electron density from the ligand to the orbital 6*d*(Am) than to 5*d*(Eu), which is due to a greater space extension of the former. The role of the *s* and *f* orbitals of both Am(III) and Eu(III) cations as electron acceptors is much less. Another unexpected conclusion is that – in contrast to the common opinion – the diglycoloamide ligands are not hard (according to Pearson's HSAB conception), but rather soft. Based on that, we have formulated a hypothesis which should allow us designing and synthesis of novel, still softer 'CHON' type ligands of still greater selectivity in the processes of solvent extraction separation of actinides from lanthanides.

Radiation stability of the components of the GANEX extraction systems

Radiation chemical studies of several solutions modelling extraction systems used in the GANEX process have been performed. Nanosecond pulse radiolysis with time-resolved UV-Vis spectrophotometry and steady-state γ-radiolysis coupled with high-performed liquid chromatography (HPLC) were used. Solutions constituting organic phase contained kerosene as a diluent and *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) and/or tri-n-butylphosphate (TBP). Solutions constituting aqueous phase contained 1 M of nitric acid (HNO_3) together with hydrophilic ligands derived from hydroxylamine- and aminopoliacetic acids. Based on the recorded transient absorption spectra, an identification of some intermediates forming in these systems has been performed. Transient absorption spectrum observed in the organic phase was characterized by an absorption band with $\lambda_{max} = 370$ nm and a half-life time ($\tau_{1/2}$) = 200 ns, and was assigned to the radical cation $TODGA^{+\bullet}$. Addition of TBP had no influence on the intensity of that band. Pulse radiolysis of aqueous solutions containing HNO_3 and hydrophilic ligands enabled generation and identification of the main transient species resulting from the reaction of $^{\bullet}OH$, $^{\bullet}H$, $^{\bullet}NO_3$ and $^{\bullet}NO_2$ radicals with hydroxylamine- and aminopoliacetic acids, respectively. In addition, radiation chemical yields of TODGA decomposition in kerosene containing TBP and several modifiers (1-octanol, benzophenone, and acetophenone) and saturated with either Ar or O_2 have been measured.

Radiation stability of ionic liquids applicable for extraction of plutonium and minor actinides

Radiation chemistry of ionic liquids (ILs) is particularly important to investigate because of the possibility of using ILs as new safer solvents in the nuclear fuel cycle (fuel production and reprocessing, nuclear waste reduction, transportation, *etc.*) including actinide separation chemistry. Research in the field of ILs continues to progress towards practical uses and applications for this novel class of solvents. The ability of modification of IL ions as well as various combinations of cations and anions allows us to design the ILs with the required properties. Radiation-induced stable products can severely affect efficiency and loading capacity of extraction systems in nuclear fuel management as well as the safety issues (*e.g.* hydrogen generation). Functional groups purposely introduced into the IL ion structure are capable of improving radiation stability of these solvents or to act as protecting agents for the solutes (ligands).

Benzyl substituent effect on radiation chemistry of the three most popular group of ILs – ammonium, pyrrolidynium and imidazolium salts has been studied. Gaseous products generated during radiolysis induced by an electron beam irradiations of these groups ILs were identified and quantified. An influence of a benzyl substituent in cations of selected groups of ILs, resulting in a substantial reduction of radiation yields of gaseous products, was found and compared with results obtained for ILs based on cations containing only alkyl substituents. Nevertheless, a detailed knowledge of the mechanism of radiation-induced reactions in ILs was essential in clarifying to what extent radiation yields of gaseous products can be used as indicators of ILs degradation. Thus, identification of transient species, evaluation of their radiation yields and investigation of mechanism of radiation-induced reactions were carried out based on the EPR technique and pulse radiolysis method coupled with fast spectrophotometry.

Synthesis of stabilized zirconium dioxide by complex sol-gel process (CSGP)

Novel method of synthesis of stabilized zirconium dioxide by original variant of the sol-gel method has been already elaborated in the INCT in cooperation with the Argonne National Laboratory – complex sol-gel process (CSGP). If combined with the double extraction process (DEP), it allows obtaining different ceramic precursors of nuclear inert matrix fuels, *e.g.* spherical particles of zirconium dioxide with diameter being below $\phi = 100$ μm. In the DEP, ascorbate-zirconyl sols (alkalized by aqueous ammonia) were emulsified in the organic solution of 2-ethylhexanol-1, Primene JMT and 1v/o emulgator SPAN 80. Next, drops of the emulsion were gelled by extraction of water by 2-ethylhexanol-1 accompanied with simultaneous extraction of nitrates by Primene JMT. As a result of applying the combined CSGP-DEP method, perfect spherical particles ($\phi < 100$ μm) of ascorbate-zirconyl gels with stabilizers were obtained. As the last step of synthesis, the calcination process provided spherical grains of the stabilized zirconium dioxide, perfect in shape with a non-cracked surface. Studies on the immobilization in such a material of ^{99m}Tc or ^{241}Am were also carried out. It was shown, that the obtained grains containing radionuclides are homogeneous on the molecular scale.

It may be concluded, that the INCT method is promising for fabrication of advanced precursors of inert matrix fuels for actinide and for other radionuclides transmutation.

Sorption behaviour of the selected radionuclides from industrial waste water by low-cost natural materials of the biological origin

Waste waters that contain radioactive metal ions like Sr(II) or Am(III) are dangerous for the environment. There are several methods to remove them from waste water. All these methods, however, are highly energy consuming thus expensive. Alternative method of eliminating the radioactive metals from the waste water is sorption by low cost natural materials of the biological origin.

Chitosan is derived from an inexpensive material: chitin. The latter is the second most abundant polymer in nature and can be found in the skeletons of insects and shellfish. Calcium alginate is a water-insoluble, gelatinous substance that can be produced through the addition of aqueous calcium chloride to aqueous sodium alginate. The parental substance – alginic acid – is a naturally occurring hydrophilic polysaccharide obtained from various kinds of brown seaweeds.

Sorption of Am(III) or Sr(II) by modified alginates or chitosan was studied as a function different physicochemical parameters and compared with the unmodified materials.

Thermogravimetric analyses of the materials show that some of them decompose at only *ca.* 200°C. This means that energy necessary to reduce the mass of potential solid wastes formed from the latter calcium alginate may be considerably smaller than from the commercial sorbents.

The costless biomass obtained from the dandelion root (DRB) was also investigated as adsorbent for removal of these ions from aqueous solutions. From these results obtained, it is authorized to propose the powdered dandelion root as a perspective material in the decontamination of aqueous radioactive solutions.

Hybrid processes for treatment of liquid radioactive waste

Hybrid processes, which are a combination of different processes performing the same role and running in one apparatus, can be used to process liquid radioactive waste into forms suitable for further conditioning with a view to final disposal. Hybrid processes benefit from the synergy of their components, which results in high rates of decontamination and greater selectivity for certain components, allowing them to be recovered.

Membrane methods, which are economic and flexible, can be easily integrated with the conventional processes. Such processes like microfiltration (MF) or ultrafiltration (UF) combined with sorption or complexation were used in the present work. Two types of adsorbents dispersed in water were applied: biosorbents like alginic acid or baker's yeasts, and inorganic materials – zeolites, bentonite and red clay. Different configurations of membranes were used in the experiments: flat sheet and tubular. The studies were performed with model solutions and samples of original liquid radioactive waste. The results of the experiments confirmed that the proposed hybrid method is effective for radioactive waste processing; it allows obtaining high decontamination factors and a significant reduction of the volume of radioactive material.

Novel nanosorbents for nuclear waste storage

The titanate sorbents are promising materials for sequestration of the radioactive caesium and strontium isotopes from radioactive wastes. The main advantages of these inorganic sorbents are their radiation stability, relatively simple synthesis methods, high selectivity and possibility of their incorporation into existing fixation systems for radionuclides storage.

Hydrothermal procedures for synthesis of the layered sorbents: sodium trititanate ($Na_2Ti_3O_7$), CST – zeolite-like crystalline sodium silicotitanate ($Na_2Ti_2O_3SiO_4·2H_2O$) and of similar structure containing niobium replacement for titanium (Nb-CST) have been developed. Their morphology and structural properties have been characterized by SEM, TEM and XRD. Decreasing temperature and/and applying a shorter synthesis time may provide a less crystalline material of smaller particles. The less crystalline materials exhibit faster ion-exchange kinetics.

The sodium trititanate sorbents show good efficiency in removing strontium even from high ionic strength solutions containing interfering sodium ions. The niobium substitution for titanium in crystalline silicotitanate (Nb-CST) sorbent improves efficiency for caesium ions sequester from strongly basic solutions.

During the thermal treatment at a relatively low (200°C) temperature, the layered structure of sodium trititanate transforms to the tunnel type $Na_2Ti_6O_{13}$ structure giving the possibility of entrapment of sorbed ions inside the tunnels.

By choosing the synthesis conditions and sorption parameters (efficiency and sorption rate) it can be tailored for giving application.

Reducing radiotoxicity of the radioactive wastes by radiochemical methods

Radioactive waste from nuclear power plants may be a source of the radioisotopes used in the nuclear medicine as well as of precious metals from the platinum group. In frame of the project, the following studies were carried out: (a) recovery of the ^{106}Ru – radionuclide applied as the radiopharmaceutical in brachytherapy, as well as (b) isolation and disposal of long-lived radionuclides, such as ^{135}Cs, ^{137}Cs, ^{90}Sr, ^{241}Am, ^{60}Co and ^{65}Zn.

It has been shown that ^{106}Ru may be effectively and selectively extracted to the organic CCl_4 phase from the simulated high-level liquid waste under the oxidizing conditions. After stripping to the aqueous phase, pure ^{106}Ru solution is suitable for production of the radioactive source applicable in brachytherapy.

It was also shown that inorganic ion exchangers based on the Ti(IV) compounds, *e.g.* nanostructures of the titanates and ferrocyanides can be successfully used for isolation of long-lived radionuclides from the radioactive wastes, as well as a matrix for a long-time storage.

Synthesis of silica glasses and Synroc materials for nuclear waste immobilization

Novel methods for synthesis of the silica glasses and ceramics materials (Synroc) designated to solidification of the radioactive wastes have been elaborated. All were based on the sol-gel process. They have several advantages as compared with another, commonly used industrial methods (*e.g.* vitrification or synthesis in the solid phase) and allow to obtain high quality solidifying matrix.

Elaborated methods enable synthesis of various kinds of materials, such as perovskite ($CaTiO_3$), zirconolite ($CaZrTi_2O_7$) and hollandite ($BaAl_2Ti_6O_{16}$) doped with caesium, strontium, cobalt and neodymium – surrogates of the radionuclides present in the nuclear waste. The obtained materials were analysed by XRD, IR, TG-DTA, EDS, BET. Analyses confirmed the structure of the synthesized materials doped with surrogates of nuclear waste to be suitable in the nuclear waste storage. Resistance against leaching of the selected samples was tested. The materials containing nuclear surrogates show leaching resistance comparable to the reference, non-doped, materials.

Practical application of the recovered elements from spent nuclear fuels for production of fuel precursors for reactors of new generation

A method of synthesis of the uranium oxycarbides ($UC\text{-}UC_2\text{-}UO_2$) by novel variant of the sol-gel CSGP method has been elaborated. In combination with the DEP method allows obtaining different ceramic type nuclear fuels, *e.g.* spherical grains containing uranium carbides of the size $\phi < 100\ \mu m$. In the DEP ascorbate-uranyl sols, after addition of black carbon and alkalize with aqueous ammonia solution, were emulsified in the solution of 2-ethylhexanol-1, Primene JMT and 1v/o emulgator SPAN 80. Drops of emulsion were gelled by extraction of water by 2-ethylhexanol-1 accompanied with the extraction of nitrates by Primene JMT. As a result of implementation of such combined CSGP-DEP method, gel spherical grains ($\phi < 100\ \mu m$) of the dispersed carbon black in the uranyl ascorbate were obtained. Finally, thermal treatment (carbonization with carbothermic reduction) was done to obtain the final uranium oxycarbides of spherical shape and with the non-cracked surface. The obtained spherical grains of uranium oxycarbides were nitrided to the uranium nitride.

Equipment for obtaining uranium oxycarbides and uranium nitrides in a mixture with uranium dioxide is available in the INCT and the method is promising for fabrication of the advanced precursors of nuclear fuels.

LIST OF VISITORS TO THE INCT IN 2014

1. **Adliene Diana**, Kaunas University of Technology, Lithuania, *08-09.12.2014*
2. **Al-Khair Saad Salah**, International Atomic Energy Agency (IAEA), Yemen, *23-31.05.2014*
3. **Apel Pavel**, Joint Institute for Nuclear Research (JINR), Dubna, Russia, *05-17.05.2014*
4. **Benderek Anett**, National Research Institute for Radiobiology and Radiohygiene, Hungary, *31.03.-04.04.2014*
5. **Calinescu Ioan**, University Politehnica of Bucharest, Romania, *03-07.11.2014*
6. **Coqueret Xavier**, Université de Reims Champagne-Ardenne, France, *08-09.12.2014*
7. **Dispenza Clelia**, Università degli Studi di Palermo, Italy, *08-09.12.2014*
8. **Dobod Katalin**, National Research Institute for Radiobiology and Radiohygiene, Hungary, *31.03.-04.04.2014*
9. **Dzeba Eva**, Ruđer Bošković Institute, Zagreb, Croatia, *10-25.11.2014*
10. **Gryzłov Anatolij**, TORIJ, Russia, *30.03.-03.04.2014*
11. **Güven Olgun**, Hacettepe University, Department of Chemistry, Ankara, Turkey, *04-10.05.2014*
12. **Himeno Yoshiaki**, Tokyo Institute of Technology, Japan, *14.11.2014*
13. **Hoveé-Levin Chantal**, University of Paris-Sud 11, Orsay, France, *24-26.03.2014*
14. **Jovarauskiene Donata**, Kaunas University of Technology, Lithuania, *08-09.12.2014*
15. **Kalchenko Vitaly**, Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Ukraine, *18-20.03.2014*
16. **Lavric Vasile**, University Politehnica of Bucharest, Romania, *03-07.11.2014*
17. **Nagame Yuichiro**, Japan Atomic Energy Agency, Japan, *19.05.2014*
18. **Nichipor Henrietta**, Belarus, *17-30.08.2014*
19. **Obreja Doina**, Institutul National de Sanatate Publica, Romania, *31.03.-04.04.2014*
20. **Orelovitch Oleg L.**, Joint Institute for Nuclear Research (JINR),Dubna, Russia, *05-17.05.2014*
21. **Parparita Elena**, “Petru Poni” Institute of Macromolecular Chemistry, Romania, *08-09.12.2014*
22. **Peszekanov Vladimir**, Joint Institute for Nuclear Research (JINR), Dubna, Russia, *21-27.09.2014*
23. **Silvestre Clara**, Instituto per i Polimeri, Compositi e Biomateriali, Consiglio Nazionale delle Ricerche (CNR), Italy, *08-09.12.2014*
24. **Solew Saad AL-khair**, International Atomic Energy Agency (IAEA), Austria, *25-31.05.2014*
25. **Şolpan Ozbay Dilek**, Hacettepe University, Turkey, *08-09.12.2014*
26. **Steinbrück Martin**, Karlsruhe Institute of Technology, Germany, *18-20.03.2014*
27. **Torun Murat**, Hacettepe University, Ankara, Turkey, *08-09.12.2014*
28. **Wang Jianlong**, Tsinghua University, China, *13-17.05.2014*

THE INCT SEMINARS IN 2014

1. **Pavel Apel, Ph.D., D.Sc. (Flerov Laboratory of Nuclear Reactions, Joint Institute for Nuclear Research, Dubna, Russia)**
   Asymmetrical track-etched nanopores: fabrication, properties and potential applications
2. **Iwona Bartosiewicz, M.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**
   Badania biogeochemicznych zachowań uranu i pierwiastków towarzyszących w odpadach poeksploatacyjnych rud uranu z bloku izersko-karkonoskiego (Studies of biogeochemical behaviour of uranium and associated elements in uranium mine tailings from Izera-Karkonosze Block)
3. **Prof. Petra Bauer (Institute of Botany, Heinrich Heine University Düsseldorf, Germany)**
   Networks in iron deficiency response regulation
4. **Prof. Ioan Calinescu (Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, Romania)**
   Using microwaves in synthesis and processing of chemical species
5. **Jonathan Coulter, Ph.D. (School of Pharmacy, Queen's University Belfast, Northern Ireland)**
   Enhanced radio-sensitivity of PTEN-deficient prostate carcinomas through the inhibition of treatment induced CXCL8 signalling
6. **Barbara Filipowicz, M.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**
   Nanostruktury ditlenku tytanu jako sorbenty radionuklidów z ciekłych odpadów promieniotwórczych (Nanostructures of titanium dioxide as sorbents of radionuclides from liquid radioactive wastes)
7. **Ewa Gniazdowska, Ph.D. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**
   Projektowanie nowych potencjalnych radiofarmaceutyków receptorowych opartych na analogach peptydów wazopresyny i greliny oraz leku lapatinib (Design of novel potential receptor radiopharmaceuticals based on analogues of the peptides vasopressin and ghrelin and the drug lapatinib)
8. **Prof. Yoshiaki Himeno (Tokyo Institute of Technology, Japan)**
   Nuclear power technology: its progress, challenges and opportunities
9. **Michał Jamróz, Ph.D. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**
   Analiza PED teoretycznych widm oscylacyjnych za pomocą programu VEDA (PED analysis of theoretical oscillation spectra by the VEDA program)
10. **Prof. Vitaly Kalchenko (Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kyiv, Ukraine)**
    Calixarene based binders for metal cations
11. **Piotr Kowalski, Ph.D. (Forschungszentrum Juelich GmbH, Juelich, Germany)**
    Nuclear waste management research on supercomputers
12. **Prof. Vasile Lavric (Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, Romania)**
    Artificial Neural Networks as models in chemical engineering
13. **Prof. Vasile Lavric (Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, Romania)**
    Modeling of flue gas cleaning by high energy electron beam using first principles approach
14. **Prof. Stefan Lis, Ph.D., D.Sc. (Faculty of Chemistry, Adam Mickiewicz University, Poznań, Poland)**
    Nanoluminofory nieorganiczne i ich funkcjonalizowane układy hybrydowe domieszkowane jonami lantanowców (Inorganic nanoluminofors and their functionalized hybrid systems doped with the lanthanide ions)
15. **Prof. Grzegorz Litwinienko, Ph.D., D.Sc. (Faculty of Chemistry, University of Warsaw, Warszawa, Poland)**
    Wpływ rozpuszczalnika na reakcje rodnikowe (Influence of the solvent on radical reactions)

16. **Katarzyna Łuczyńska, M.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**
    Synteza i komplementarne badania strukturalno-spektroskopowe wybranych kompleksów organicznych typu donor-akceptor protonu (Synthesis and complementary structural-spectroscopic studies of selected proton donor-acceptor organic complexes)

17. **Prof. Tetsuro Majima (Research Laboratory for Quantum Beam Science, Institute of Scientific and Industrial Research (Sanken), Osaka University, Osaka, Japan)**
    Recent progress of radiation chemistry using pulse radiolysis and γ-radiolysis

18. **Helen McCarthy, Ph.D. (School of Pharmacy, Queen's University Belfast, Northern Ireland)**
    Nitric oxide mediated radio-sensitivty using novel bio-inspired delivery systems

19. **Prof. Yuichiro Nagame (Japan Atomic Energy Agency (JAEA), Tokai, Japan)**
    Radiochemical studies of the heaviest elements at JAEA

20. **Agata Oszczak, M.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**
    Polisacharydy jako sorbenty w procesach zatężania i składowania nisko- i średnioaktywnych ciekłych odpadów promieniotwórczych (Polysaccharides as sorbents in concentration and components of barriers in the low- and medium-level radioactive waste repositories)

21. **Dariusz Pogocki, Ph.D., D.Sc., professor in INCT (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**
    Wstrząśnienia mózgu a choroby neurodegeneracyjne (Brain concussions and neurodegenerative diseases)

22. **Prof. Javier Romera (Department of Agronomy, University of Córdoba, Spain)**
    Interaction of shoot derived signals with ethylene in the regulation of Fe responses

23. **He Shijun, Ph.D. (Institute of Nuclear and New Energy Technology (INET), Tsinghua University, China)**
    The development of electron beam facility for pilot-scale wastewater treatment in China

24. **Tomasz Smoliński, M.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**
    Synteza metodą zol-żel ceramicznych matryc (Ti) przeznaczonych do zestalania odpadów promieniotwórczych (Method of synthesis titanium ceramic matrixes for immobilization of nuclear waste by sol-gel process)

25. **Martin Steinbrück, Ph.D. (Institute for Applied Materials (IAM), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany)**
    High-temperature oxidation and mutual interactions of materials during severe nuclear accidents

26. **Prof. Jacek Waluk, Ph.D., D.Sc. (Institute of Physical Chemistry, Polish Academy of Sciences, Warszawa, Poland)**
    O rozmaitych sposobach śledzenia pojedynczych cząsteczek (About various methods of tracking of single molecules)

27. **Patryk Wojtowicz, M.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**
    Witryfikacja wysokoaktywnych odpadów promieniotwórczych metodą zol-żel (Vitrification of high-level nuclear wastes by sol-gel method)

LECTURES AND SEMINARS DELIVERED OUT OF THE INCT IN 2014

LECTURES

1. **Brykała M.**
   Młodzież na rzecz energetyki jądrowej (Young people for nuclear energy).
   II Kongres Elektryki Polskiej, Warszawa, Poland, 01-02.12.2014.
2. **Chmielewski A.G.**
   Działania Instytutu Chemii i Techniki Jądrowej w zakresie przygotowania kadr dla energetyki jądrowej (Activities of the Institute of Nuclear Chemistry and Technology in the preparation of specialists for nuclear energy).
   I Edukacyjne Forum Enegetyki Jądrowej, Warszawa, Poland, 02.04.2014.
3. **Chmielewski A.G.**
   Znaczenie dywersyfikacji źródeł energii (Role of energy mix).
   Spotkanie-debata „Rozwój energetyki jądrowej a bezpieceństwo narodowe", Warszawa, Poland, 03.12.2014.
4. **Chmielewski A.G.**
   Energetyka jądrowa w Europie i świecie i jej rola w ograniczaniu emisji zanieczyszczeń atmosfery (Nuclear energy in Poland and Europe and its role in atmosferic pollutant emission reduction).
   II Kongres Elektryki Polskiej, Warszawa, Poland, 01-02.12.2014.
5. **Chmielewski A.G., Palige J., Kryłowicz A., Usidus J., Chrzanowski K.**
   Polska myśl techniczna wykorzystywana przy budowie instalacji do wytwarzania i wykorzystywania biogazu w energetyce, przemyśle i transporcie (Polish developments in the construction of the plant for biogas production and usage in power sector, industry and transportation).
   II Kongres Elektryki Polskiej, Warszawa, Poland, 01-02.12.2014.
6. **Dybczyński R.S., Kulisa K., Pyszynska M., Bojanowska-Czajka A.**
   Nowa metoda rodzielania pierwiastków ziem rzadkich (REE) za pomocą RP-HPLC z wykorzystaniem kompleksów z kwasem nitrylotrioctowym i mechanizmu wymiany anionowej (New method for the separation of rare earth elements (REE) by RP-HPLC with the use of nitrilotriacetate complexes and anion exchange mechanism).
   Konferencja „Chromatografia jonowa 2014", Zabrze, Poland, 09-10.04.2014.
7. **Gajda D., Zakrzewska-Kołtuniewicz G., Kiegiel K., Danko B., Chajduk E., Bartosiewicz I.**
   Oddzielanie związków uranu od metali towarzyszących z roztworów otrzymywanych po ługowaniu piaskowców pochodzących z polskich złóż, metodą chromatografii jonowymiennej (Ion-exchange chromatographic separation of uranium and associated metals from post-leaching solution obtained by Polish sandstones leaching).
   XI Warszawskie Seminarium Doktorantów i Chemików ChemSession'14, Warszawa, Poland, 16.05.2014.
8. **Kiegiel K., Wołoszczuk K., Zakrzewska G., Krajewski P.**
   Licensing framework in Poland.
   ARCADIA 1st Technical Meeting, Bologna, Italy, 11-13.06.2014.
9. **Latek S.**
   O „Postępach Techniki Jądrowej", kwartalniku wspierającym PPEJ ("Postępy Techniki Jądrowej" – quarterly supporting Polish Nuclear Power Programme).
   II Kongres Elektryki Polskiej, Warszawa, Poland, 01-02.12.2014.
10. **Lewandowska-Siwkiewicz H.**
    Omówienie możliwości składania projektu w programie „Biostrateg" (Discussion on the possibilities of applying for the contract in the "Biostrateg" NCBR action).
    Spotkanie grupy roboczej dotyczące planowanego projektu "Wykorzystanie rokitnika do celów przemysłowych i spożywczych", Baranów Sandomierski, Poland, 12-13.06.2014.

11. **Nieścior-Bowińska P.**

    Membrane processes in nuclear technology: the treatment of radioactive waste by using micellar-enhanced ultrafiltration.

    Technical Workshop "LUCOEX (Large Underground Concept Experiments) – installation, closure and initial state", Aspö, Sweden, 13-14.05.2014.

12. **Olszewska W., Zakrzewska-Kołtuniewicz G., Miśkiewicz A.**

    The study of migration of radionuclides in radioactive waste repository surroundings.

    Technical Workshop "LUCOEX (Large Underground Concept Experiments) – installation, closure and initial state", Aspö, Sweden, 13-14.05.2014.

13. **Sommer S.**

    Radiobiologia: dozymetria biologiczna w służbie energetyki jądrowej (Radiobiology: biological dosimetry in the service of nuclear energy).

    Konferencja Naukowa „Nukleonika na początku XXI wieku", Warszawa, Poland, 09.05.2014.

14. **Zakrzewska-Kołtuniewicz G., Głuszewski W.**

    O Polskim Towarzystwie Nukleonicznym i jego roli dla PPEJ (About the Polish Nuclear Society and its role for the Polish Nuclear Power Programme – PPEJ).

    II Kongres Elektryki Polskiej, Warszawa, Poland, 01-02.12.2014.

15. **Zimek Z.**

    Bezpieczeństwo czy ryzyko jądrowe – społeczne aspekty wdrożenia energetyki jądrowej (Safety or nuclear hazard – social aspect of the implementation of nuclear energy).

    II Kongres Elektryki Polskiej, Warszawa, Poland, 01-02.12.2014.

16. **Zimek Z.**

    Układy kontroli i usuwania wodoru z obszaru obudowy bezpieczeństwa reaktora jądrowego (Systems of checking and removal of hydrogen from the reactor containment of a nuclear reactor).

    Konferencja Naukowa „Nukleonika na początku XXI wieku", Warszawa, Poland, 09.05.2014.

SEMINARS

1. **Bilewicz Aleksander**

   New radiopharamceutical precursors for alpha radionuclide therapy.

   Institute of Cancer Research, London, United Kingdom, 17.12.2014.

2. **Cieśla K.**

   Treatment of polymers with inizing radiation technology.

   Swiss Federal Laboratories for Materials Science and Technology (EMPA), Laboratory for Applied Wood Materials, Dubendorf, Switzerland, 27.01.2014.

3. **Chmielewski A.G.**

   Electron beam technology for industrial flue gas treatment.

   University of Pavia, Italy, 14.01.2014.

4. **Chmielewski A.G.**

   Electron beam technology for industrial flue gas treatment.

   University of Pavia, Italy, 15.01.2014.

5. **Chmielewski A.G.**

   Radiation treatment of solid and liquid wastes.

   University of Pavia, Italy, 15.01.2014.

6. **Chmielewski A.G.**

   Electron beam treatment for VOC removal.

   University of Pavia, Italy, 15.01.2014.

7. **Chmielewski A.G.**

   Radiation technology for enhancement of biogas production.

   University of Pavia, Italy, 16.01.2014.

8. **Chmielewski A.G.**

   Radiation methods and applications in nanotechnology.

   University of Pavia, Italy, 16.01.2014.

9. **Gajda D.**
   Zasoby uranu w Polsce (Polish uranium resources).
   Sejm of the Republic of Poland, Warszawa, Poland, 09.07.2014.
10. **Sommer Sylwester**
    Cykl wykładów: Radiobiologia (Series of lectures: Radiobiology).
    University of Warsaw, Faculty of Physics, Warszawa, Poland, February-June 2014.

AWARDS IN 2014

1. The method of disposal of radioactive wastes into structure of silica glasses

   Gold Medal with mention at the International Warsaw Invention Show IWIS 2014, Warszawa, Poland, 14-16.10.2014

   Andrzej G. Chmielewski, Andrzej Deptuła, Magdalena Miłkowska, Wiesława Łada, Tadeusz Olczak

2. Method of obtaining therapeutic amounts of ^{47}Sc

   Gold Medal at the International Warsaw Invention Show IWIS 2014, Warszawa, Poland, 14-16.10.2014

   Aleksander Bilewicz, Barbara Bartoś, Ewelina Chajduk

3. The method of disposal of radioactive wastes into structure of silica glasses

   Gold Medal for the excellent chemical invention at the 3rd World Competition of the Chemical Inventions organized by the International Federation of Inventors' Associations, Warszawa, Poland, 16.10.2014

   Andrzej G. Chmielewski, Andrzej Deptuła, Magdalena Miłkowska, Wiesława Łada, Tadeusz Olczak

4. Precursor of the radiopharmaceutical, the method for producing, radiopharmaceutic and its applications

   Bronze Medal at the International Warsaw Invention Show IWIS 2014, Warszawa, Poland, 14-16.10.2014

   Marcin Kruszewski, Grzegorz Wójciuk

5. A system for studying the tightness in ground and underground industrial installations such as: gas and petroleum pipelines, chemical reactors, rectification and distillation columns 14, etc.

   Distinction at the 12th International Conference and Exhibition OIL & GAS 2014 and the 7th Chemical Industry Fair EXPOCHEM 2014, Warszawa, Poland, 17-18.09.2014

   Institute of Nuclear Chemistry and Technology

6. Merit award of the Ministry of Health "For the service in health protection"

   Andrzej G. Chmielewski

7. Sposób unieszkodliwiania odpadów promieniotwórczych w szkłach krzemionkowych (Method for the disposal of radioactive wastes in structures of silica glasses; authors: A.G. Chmielewski, A. Deptuła, M. Miłkowska, W. Łada, T. Olczak)

   Diploma of the Ministry of Science and Higher Education

   Institute of Nuclear Chemistry and Technology

8. 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; authors: A. Kryłowicz, J. Usidus, A.G. Chmielewski, K. Chrzanowski)

   Diploma of the Ministry of Science and Higher Education

   Institute of Nuclear Chemistry and Technology

9. „Reliable supplier of PKN ORLEN S.A." in the category „Renovation services" – award of PKN ORLEN S.A. for the reliability, solidity and professional cooperation in 2013

   Institute of Nuclear Chemistry and Technology

10. Determination of ^{90}Sr using MSFIA-LOV system with ICP-MS detection (authors: Kamila Kołacińska, Anna Bojanowska-Czajka, Marek Trojanowicz)

    Best oral presentation award for young researcher at the 19th International Conference on Flow Injection Analysis, Fukuoka, Japan, 30.11.-05.12.2014

    Kamila Kołacińska

11. Synteza ziaren ditlenku uranu dotowanych wybranymi pierwiastkami przy zastosowaniu kompleksowej metody zol-żel (CSGP) (Synthesis of uranium dioxides particles doped with selected elements by complex sol-gel process – CSGP)

    Second degree award of the Polish Nuclear Society for the best doctoral thesis in 2013-2014 concerning nuclear sciences

    Marcin Brykała

12. p-Terfenyl jako sonda pierwotnych procesów radiacyjno-chemicznych w wybranej cieczy (p-Terphenyl as a sensor of the primary radio-chemical processes in the selected ionic liquid)

Third degree award of the Polish Nuclear Society for the best doctoral thesis in 2013-2014 concerning nuclear sciences

Rafał Kocia

13. First degree team award of Director of the Institute of Nuclear Chemistry and Technology in 2014 for a series of eight publications concerning physicochemical properties of silver nanoparticles, titanium dioxide and silicon surface-modified and biological effects caused by the nanoparticles

    Marcin Kruszewski, Anna Lankoff, Maria Wojewódzka, Jadwiga Chwastowska, Teresa Bartłomiejczyk, Sylwia Męczyńska-Wielgosz, Iwona Grądzka, Sylwester Sommer, Ewelina Chajduk, Bożena Sartowska, Irena Szumiel

14. Second degree team award of Director of the Institute of Nuclear Chemistry and Technology in 2014 for a series of three publications concerning the radical processes in peptide particles containing sulphur, induced by radioactivity and photochemistry

    Krzysztof Bobrowski, Gabriel Kciuk, Paweł Wiśniowski, Jacek Mirkowski

15. Second degree team award of Director of the Institute of Nuclear Chemistry and Technology in 2014 for the application achievements in 2012-2013 – elaboration of methodology of carrying out and implementing proficiency studies for analytical laboratories conducting research on the content of heavy metals and radionuclides in the environment and in food

    Halina Polkowska-Motrenko, Leon Fuks, Ewelina Chajduk, Jakub Dudek, Paweł Kalbarczyk, Agata Oszczak, Michał Zuba, Marta Pyszynska, Krzysztof Kulisa

16. Second degree team award of Director of the Institute of Nuclear Chemistry and Technology in 2014 for the application achievements in 2012-2013 – elaboration and implementation of the technology of radiation sterilization of new materials

    Zbigniew Zimek, Andrzej Rafalski, Magdalena Rzepna, Sylwester Bułka, Iwona Kałuska

17. Third degree team award of Director of the Institute of Nuclear Chemistry and Technology in 2014 for two publications concerning the bonding of radium radionuclides in nanoparticles and their addition to biologically active particles and labelling of nanoparticles to toxicological studies

    Agata Piotrowska, Edyta Leszczuk, Izabela Cydzik, Aleksander Bilewicz

18. Distinction of the first degree of Director of the Institute of Nuclear Chemistry and Technology in 2014 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

    Łukasz Steczek

19. Distinction of the second degree of Director of the Institute of Nuclear Chemistry and Technology in 2014 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

    Łucja Janiszewska

20. Distinction of the second degree of Director of the Institute of Nuclear Chemistry and Technology in 2014 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

    Konrad Skotnicki

21. Award of Director of the Institute of Nuclear Chemistry and Technology in 2014 for the preparation and obtaining projects in the frame of Erasmus+

    Yongxia Sun

22. Award of Director of the Institute of Nuclear Chemistry and Technology in 2014 for the activities concerning the preparation of territorial plan in the frame of Mazovian Valley of Green Chemistry and Innochem sector project

    Marta Walo, Urszula Gryczka

23. Award of Director of the Institute of Nuclear Chemistry and Technology in 2014 for the activities concerning the promotion of the Institute in the field of invention

    Wiesława Łada

24. Award of Director of the Institute of Nuclear Chemistry and Technology in 2014 for the obtaining award of the Chief Sanitary Inspector

    Wacław Stachowicz, Grzegorz Guzik, Grażyna Liśkiewicz, Kazimiera Malec-Czechowska

25. Award of Director of the Institute of Nuclear Chemistry and Technology in 2014 for the organizing trainings of students in the Institute

    Marta Pyszynska

26. Award of Director of the Institute of Nuclear Chemistry and Technology in 2014 for the excellent conducting of financial matters of the Institute
    Maria Małkiewicz

INDEX OF THE AUTHORS