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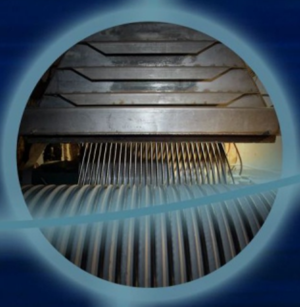

INSTITUTE OF NUCLEAR CHEMISTRY AND TECHNOLOGY

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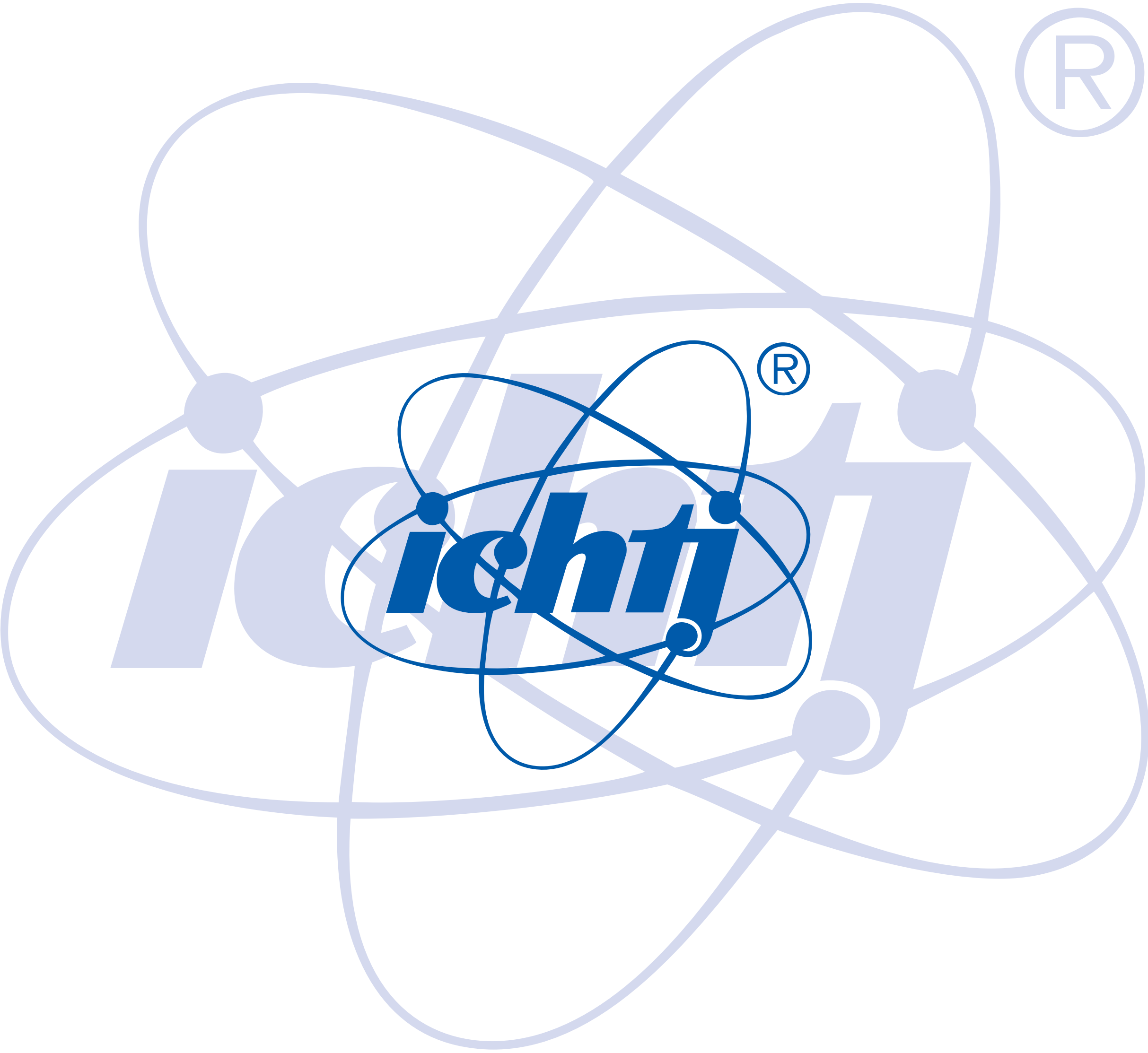
2018



INSTITUTE
OF NUCLEAR CHEMISTRY
AND TECHNOLOGY

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GENERAL INFORMATION

The Institute of Nuclear Chemistry and Technology (INCT) is Poland's leading research institution in the fields of nuclear and radiation chemistry, and radiobiology. Scientific activities of the INCT are dedicated to a wide range of nuclear topics, involving basic and applied research. Basic research is focused on separation processes of actinides and lanthanides, novel radiopharmaceuticals, radiation effects in molecules of biological importance, cells and polymers. With its six electron accelerators, the Institute is one of the most advanced centres in the field of electron beam applications. The various types of accelerators are used for radiation sterilization of medical devices and transplantation grafts, modification of polymers, removal of SO_2 and NO_x from flue gases, and for food irradiation.

The INCT Scientific Council has the right to confer D.Sc. and Ph.D. degrees in the field of chemistry. In 2018, five Ph.D. theses were defended in the INCT.

The Institute's expertise and infrastructure made possible the participation in numerous international and domestic projects. In 2018, the INCT continued research activity in four projects of the EU programme Horizon 2020, in which leading European institutes and industrial companies participate:

- ARIES: Accelerator research and innovation for European science and society;
- GENIORS: GEN IV integrated oxide fuels recycling strategies;
- TeamCABLES: European tools and methodologies for an efficient ageing management of nuclear power plant cables;
- CHANCE: Characterization of conditioned nuclear waste for its safe disposal in Europe.

Besides, four large projects of the National Centre for Research and Development (NCBR) were carried out, including the specially important for environmental protection project TANGO 2 ‘Plasma technology for removal nitrogen oxides from flue gases’.

There were also 16 projects of the National Science Centre (NCN) led by the INCT researchers, majority of them dedicated to the development of new radiopharmaceuticals for medical diagnosis and therapy.

As the Collaborating Centre in Radiation Technology and Industrial Dosimetry of the International Atomic Energy Agency (IAEA), the Institute coordinated a large-scale intercomparison test on alanine dosimetry measurements for electron beam and gamma irradiations. Ten European countries participated in the measurements. Under the framework of the IAEA Coordinated Research Programme, the INCT researchers took part in 11 IAEA projects cooperating with scientists from numerous countries all over the world.

The INCT was granted to carry out the interdisciplinary Ph.D. study project ‘Radiopharmaceuticals for molecularly targeted diagnostics and medical therapy’ (RadFarm) with the National Centre for Nuclear Research, University of Warsaw (Faculty of Chemistry) and Medical University of Warsaw (Faculty of Pharmacy with the Laboratory Medicine Division).

The INCT prepared the report ‘Innowacje dla energii i nie tylko. Zaawansowane materiały polimerowe dla energetyki i innych dziedzin wspomagane technologiami radiacyjnymi’ (Innovation for power engineering sector and more. Advanced polymeric materials for power engineering sector and other industry fields supported by radiation technologies) for the Ministry of Energy.

In 2018, the INCT scientists published 91 papers, including 70 publications in scientific journals indexed in Claritive Analytics JCR.

MANAGEMENT OF THE INSTITUTE

MANAGING STAFF OF THE INSTITUTE

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Deputy Director of Finances
Wojciech Maciąg, M.Sc.

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38. Prof. **Krzysztof Zaremba**, Ph.D., D.Sc.
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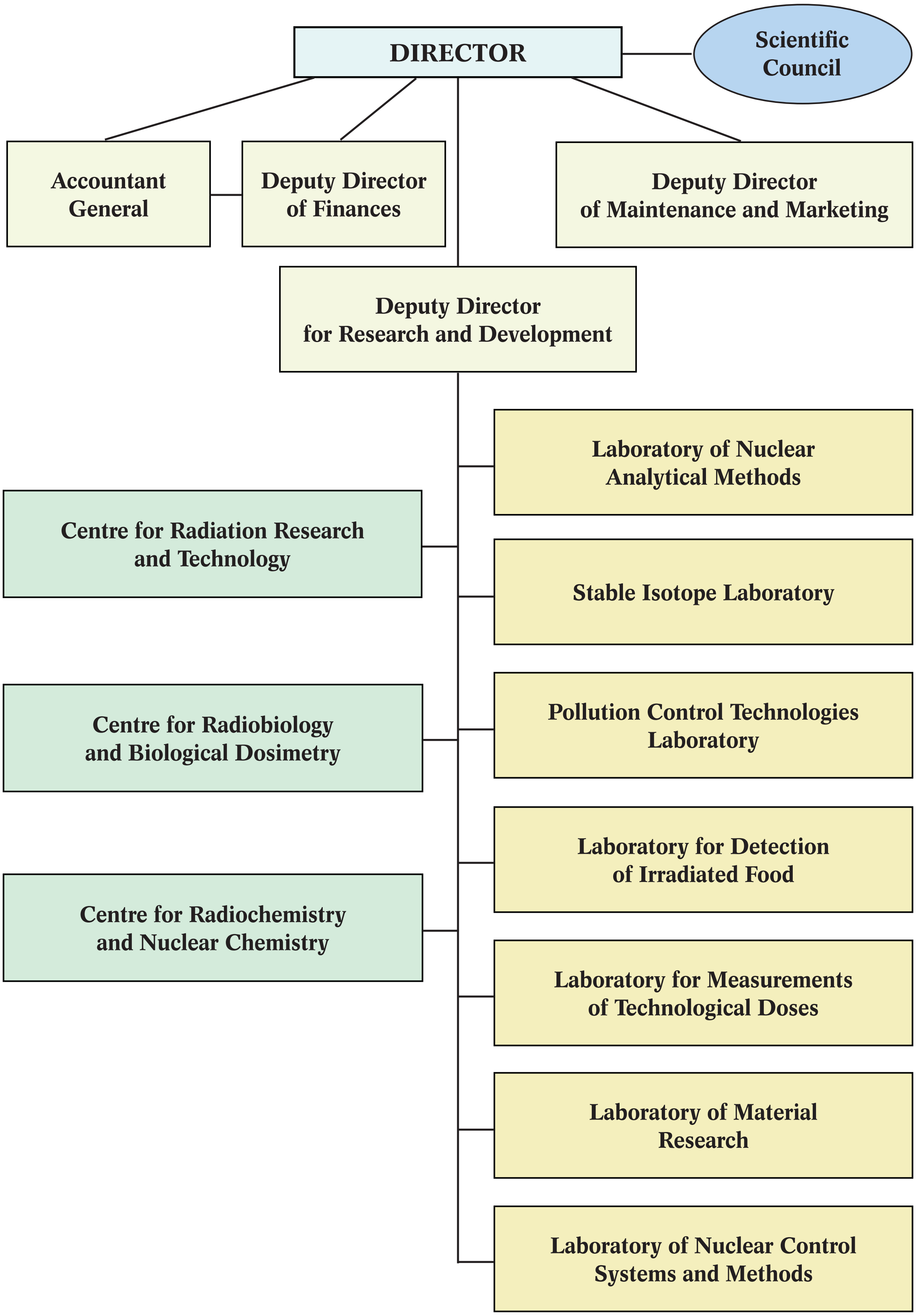
ORGANIZATION SCHEME



SCIENTIFIC STAFF

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3. **Brykała Marcin**
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4. **Chajduk Ewelina**
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7. **Dudek Jakub**
   chemistry
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50. **Zwolińska Ewa**
chemistry

CENTRE FOR RADIATION RESEARCH AND TECHNOLOGY

The 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 study and the applications of radiation technology in various areas.

The Centre, in collaboration with universities in Poland and abroad, applies EB technology to fundamental research on electron beam-induced chemistry and the modification 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 for the direct time-resolved observation of short-lived intermediates (typically within the nanosecond to millisecond time domain) and is complemented by steady-state radiolysis, stopped-flow absorption spectrofluorimetry and product analysis using chromatographic methods. Studies on radiation-induced intermediates concern the processes of energy and charge transfer, radical reactions in model compounds of biologically relevant aromatic thioethers, peptides and proteins, and also the observation of atoms, clusters and radicals by electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR). Furthermore, these studies are also focused on research problems in nanophase chemistry and the radiation-induced crosslinking of selected and/or modified polymers and copolymers.

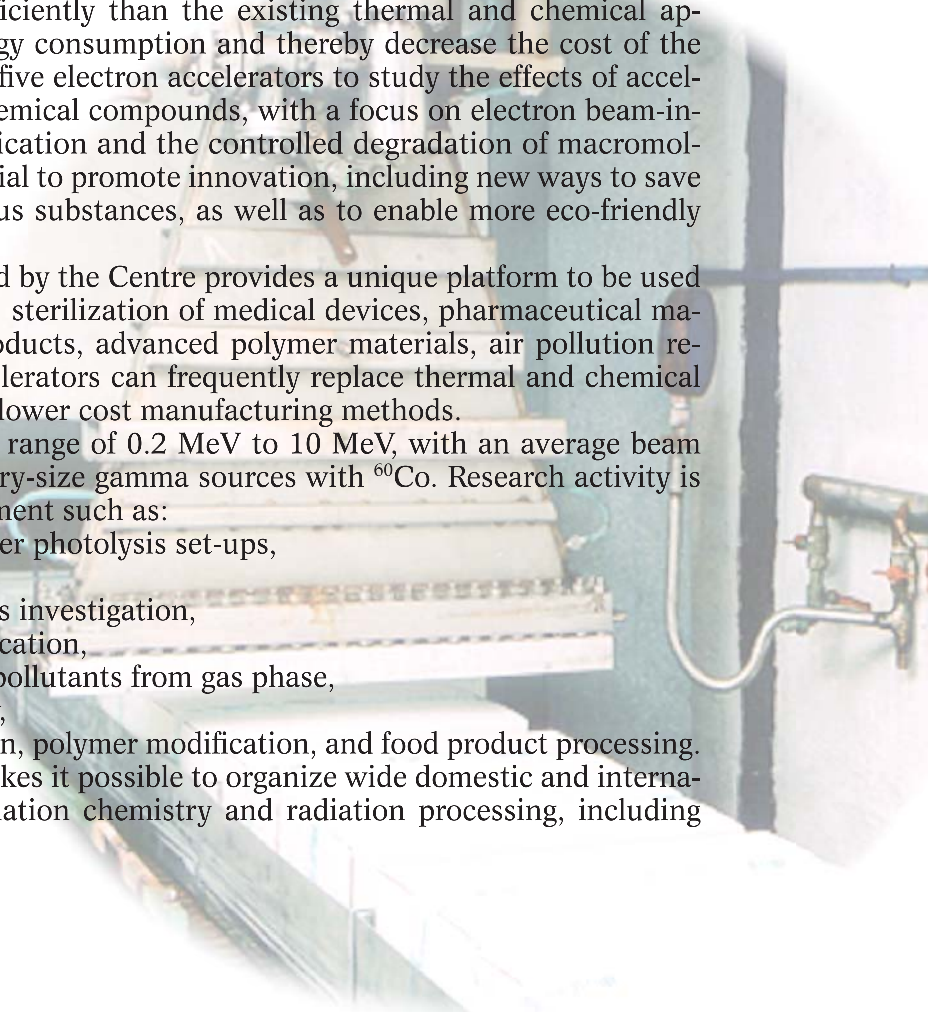
This research has a wide range of potential applications, including creating more environmentally friendly and sustainable packaging, improving product safety and modifying material properties. Electron accelerators provide streams of electrons to initiate chemical reactions or break down chemical bonds more efficiently than the existing thermal and chemical approaches, thus helping to reduce energy consumption and thereby decrease the cost of the processes. The Centre currently offers five electron accelerators to study the effects of accelerated electrons on a wide range of chemical compounds, with a focus on electron beam-induced polymerization, polymer modification and the controlled degradation of macromolecules. EB technology has 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.

The advanced EB technology offered by the Centre provides a unique platform to be used for some of the following applications: sterilization of medical devices, pharmaceutical materials, shelf-life extension of food products, advanced polymer materials, air pollution removal technology and others. EB accelerators can frequently replace thermal and chemical processes with cleaner, more efficient, lower cost manufacturing methods.

The Centre offers EB in the energy range of 0.2 MeV to 10 MeV, with an average beam power up to 20 kW and three laboratory-size gamma sources with ^{60}Co. Research activity is supported by unique laboratory equipment such as:

- nanosecond pulse radiolysis and laser photolysis set-ups,
- stopped-flow experimental set-up,
- EPR spectroscopy for solid materials investigation,
- pilot installation for polymer modification,
- experimental set-up for removal of pollutants from gas phase,
- polymer characterization laboratory,
- pilot facility for radiation sterilization, polymer modification, and food product processing.

The unique technical equipment makes it possible to organize wide domestic 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 noted that currently there are no other suitable European experimental platforms for the study of radiation chemistry, physics and radiation processing covering a full range of electron energy and beam power.

The Centre for Radiation Research and Technology also plays a major role in an IAEA Collaborating Centre for Radiation Processing and Industrial Dosimetry, which has been functioning since being established at the INCT in 2010. That is the best example of the capability and great potential of the equipment, as well as that of the employed methods and staff working towards the application of innovative radiation technology.

To disseminate knowledge and access to the research equipment, the Centre for Radiation Research and Technology organizes, in cooperation with the International Atomic Energy Agency, international courses on radiation technology applications. These include international comparative measurements in the field of technological dosimetry, attended by nearly 20 European countries. Also, the Centre organizes regular training courses for representatives of Polish industry in the fields of radiation technologies, including radiation sterilization and the modification of polymers.

SELECTED REACTION OF PRIMARY SPECIES IN PULSE-IRRADIATED ORGANIC PHASE OF SANEX SYSTEM CONTAINING CyMe$_4$-BTPhen EXTRACTING AGENT

Tomasz Szreder, Holger Schmidt[1/]**, Giuseppe Modolo**[1/]

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The separation of plutonium and uranium from spent nuclear fuel in various versions of the plutonium and uranium recovery by extraction (PUREX) process has been used by the industry in several countries for many years [1, 2]. Such an approach significantly saves energy resources and reduces the potential radiotoxicity hazard of waste from approximately 250 000 to 10 000 years. Further reduction in the radiotoxicity and heat loading, and hence in the footprint of a geological disposal facility, can be achieved by minor actinide transmutation followed by their separation from the PUREX raffinate [3-5].

Bis(triazinyl)pyridine ligands have been proposed for the selective separation of trivalent actinides from lanthanides in the selective actinide extraction (SANEX) process [5-7]. Development of this type of ligand was the first attempt at intentional structural modifications to adapt molecules for the nuclear fuel cycle [8, 9]. A compromise between the stability, extractant solubility and extraction capabilities of the newly designed molecules was found for 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-1,2,4-triazin-3-yl)-2,2'-bipyridine (CyMe$_4$-BTBP) [8]. The CyMe$_4$-BTBP ligand is currently considered as a European standard for the development of selective actinide separation [10]. In addition, it was shown that extraction kinetics of CyMe$_4$-BTBP can be improved by intramolecular pre-organization of the molecule in which the 2,2'-bipyridine moiety was replaced by a 1,10-phenanthroline leading ultimately to 2,9-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)-[1,10]phenanthroline (CyMe$_4$-BTPhen; Fig. 1).

The observed deterioration in the extraction performance in irradiated systems is mainly due to the secondary reactions of radicals, radical ions and permanent products (generated from the diluents) with the ligands. In our current study, we focused on 1-octanol as a simplified model of the SANEX diluent. Knowledge of the mechanism of radiation-induced reactions in the CyMe$_4$-BTPhen/1-octanol system occurring in the early stages was the main aim of this study. The effects of typical scavengers as well as the water content in the system were also considered.

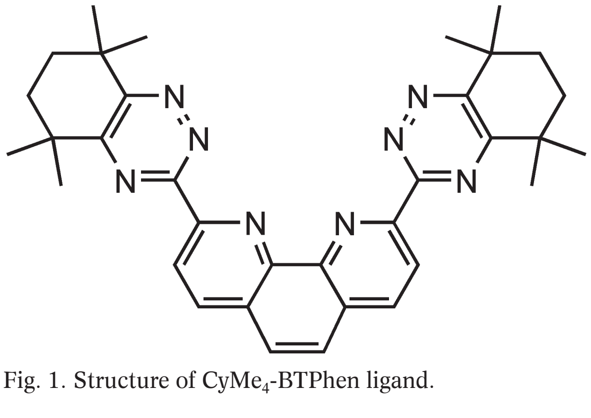

Fig. 1. Structure of CyMe$_4$-BTPhen ligand.

CyMe$_4$-BTPhen (Fig. 1) was obtained from Technocomm Ltd (UK) with a purity of 99% and used as received. All other chemicals were purchased from Sigma-Aldrich with the highest available purity. Water purified using the Direct-Q 3 UV (Merck Millipore) system was used in all experiments.

Pulse radiolysis experiments with fast optical absorption detection were carried out at the Institute of Nuclear Chemistry and Technology (INCT). The pulse radiolysis set-up was based on the LAE-10 linear electron accelerator, delivering 10 ns pulses with an electron energy of about 10 MeV. A 150 W E7536 xenon arc lamp (Hamamatsu Photonics K.K.) was used as a monitoring light source. The respective wavelengths were selected either by an MSH 301 (Lot Oriel Gruppe) monochromator with 2.4 nm resolution or by bandpass filters (Standa Ltd) with a full width at half maximum (FWHM) of about 40 nm above 750 nm. The intensity of the analysing light was measured by means of an R955 photomultiplier (Hamamatsu) below 750 nm, and by a PDA10A Si amplified diode (Thorlabs) up to 1150 nm. The signal from the detector was digitized using a WaveSurfer 104MXs-B (1 GHz, 10 GS/s, LeCroy) oscilloscope and then sent to a PC for further processing. In order to avoid photodecomposition and/or photobleaching effects in the samples, UV or VIS cut-off filters were used. However, no evidence of such effects was found within the time domains monitored. If necessary, a water filter was used to eliminate near IR wavelengths. All the experiments were performed in a standard quartz cell with an optical path length of 1 cm and at a temperature of 22°C.

The total dose per pulse was determined before each series of experiments by a thiocyanate dosimeter (an N_2O-saturated aqueous solution containing 10 mM KSCN) using $G \times \varepsilon = 5.048 \times 10^{-3}$ mol J^{-1} M^{-1} cm^{-1} [11, 12] for the $(SCN)_2^{\bullet-}$ radical anion at 472 nm. Doses absorbed in the 1-octanol systems were corrected for the electron density by a factor of 0.848.

The content of water was determined before pulse irradiation by the Karl-Fischer coulometric titration method (C20 Coulometric KF Titrator, Mettler Toledo). We made an effort to limit the water content in our samples to less than 3% by weight, even though the solubility of water in 1-octanol ranges between 4.7-5.05% [13, 14]. This is because higher concentrations can occasionally cause phase separations during storage or even during experiments.

Quantum calculations were performed using Gaussian 09 software and visualized by an evaluation version of Chemcraft 1.8 on a PC class computer.

Initial stages of 1-octanol radiolysis

The spectrum recorded after an electron pulse in 1-octanol is shown in Fig 2. It is dominated by a broad absorption band in the UV-VIS range (with $\varepsilon_{max} \approx 670$ nm) with a tail in the near IR. This absorption band was unequivocally assigned to the solvated electrons (e^-_s) based on literature data [15-17].

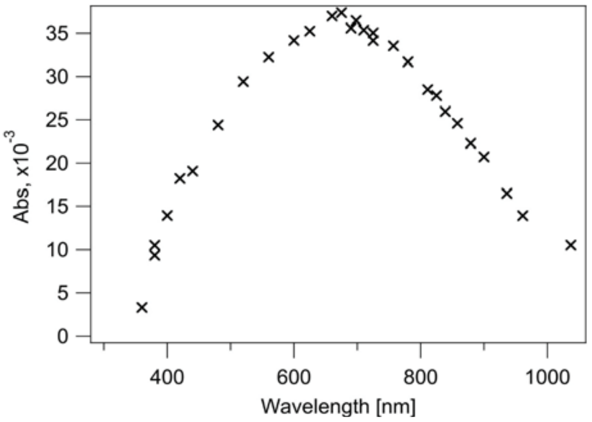

Fig. 2. Transient absorption spectra recorded 50 ns after a pulse in neat 1-octanol purged with Ar, 20 Gy, water content ~ 0.06% by weight.

An initial radiation chemical yield of e^-_s ($G(e^-_s)$) was calculated based on experiments involving pyrene (Pyr). For a short time-scale (up to 150 ns) and a high concentration of Pyr (above 9 mM) reaction (1) can be considered quantitative. Decreasing the e^-_s absorption corresponds quantitatively to increasing the $Pyr^{\bullet -}$ absorption.

$$e^-_s + Pyr \rightarrow Pyr^{\bullet -} \qquad (1)$$

A resulting molar absorption coefficient of e^-_s at 670 nm ($\varepsilon(e^-_s$, 670 nm)) equal to 18 500(700) M^{-1} cm^{-1} was obtained as an average of the data collected from experiments with various concentrations of Pyr (up to 27 mM). The molar absorption coefficient of $Pyr^{\bullet -}$ ($\varepsilon(Pyr^{\bullet -}$, 495 nm)) equal to 4.92×10^4 M^{-1} cm^{-1} used for these calculations was taken from the literature [18]. The value of $\varepsilon(e^-_s$, 670 nm) obtained in this work was in good agreement with those previously reported $\varepsilon(e^-_s$, 670 nm) in 1-octanol, which ranged from 15 000 M^{-1} cm^{-1} to 20 000 M^{-1} cm^{-1} [18, 19]. Eventually, it led to a $G(e^-_s)$ value equal to 130(10) nmol J^{-1}, which was higher than the reported range of 70 nmol J^{-1} to 100 nmol J^{-1} [15, 16, 19]. In part, the difference was due to the fact that the previous results did not take into account the differences in electron density between 1-octanol and water-based dosimeters.

It is worth noting that the organic phase of the extraction system contained a considerable amount of water due to contact with the aqueous phase. The solubility of water in 1-octanol ranges between 4.7-5.05% by weight [13, 14]. A bathochromic shift of the absorption maximum of the e^-_s band from 670 nm to 700 nm, which was accompanied by about 10% increased absorption, was observed in 1-octanol containing 2.9% water. This is not surprising, since the absorption maximum and the corresponding molar absorption coefficient of e^-_s in water are 715 nm and 19 700 M^{-1} cm^{-1}, respectively [20]. Similar effects were reported previously in alcohol/water systems [21, 22]. The experimental error of our method does not allow us to separate the fraction of absorption corresponding to the increase in $G(e^-_s)$ and/or $\varepsilon(e^-_s)$ values.

It is well known from previous studies that the electron-deficient species (often called holes) generated upon ionization of 1-octanol undergo a fast ion-molecule reaction with intact alcohol molecules (reaction 2). This reaction leads mostly to C-centred radicals, including (but not exclusively limited to) α-hydroxyalkyl radicals [9]. These radicals show moderate reducing properties.

$$\begin{aligned} RCH_2OH^{\bullet +} + RCH_2OH \rightarrow R^{\bullet}CHOH + \\ + RCH_2OH_2^{+} \end{aligned} \qquad (2)$$

Reaction of CyMe$_4$-BTPhen with electrons

A faster decay of the transient absorbance at 670 nm (assigned to e^-_s in 1-octanol), compared to neat solvent, was observed in the presence of CyMe$_4$-BTPhen. This was due to the reaction of e^-_s with the ligand (reaction 3).

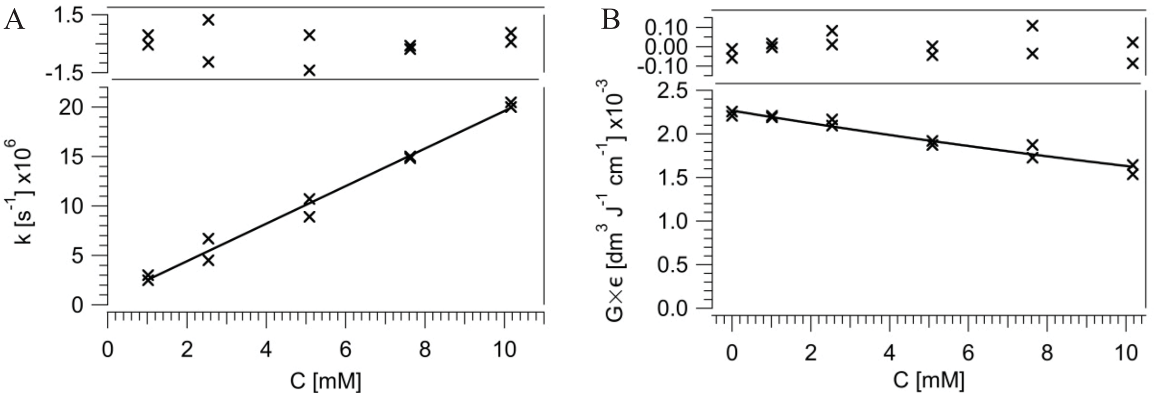

Fig. 3. (A) The dependence of pseudo-first order rate constant of e^-_s decay (measured at 670 nm) on CyMe$_4$-BTPhen concentration, (B) G × ε values calculated based on an initial absorbance at 670 nm as a function of CyMe$_4$-BTPhen concentration (20 Gy, water content – 0.10% by weight, Ar-saturated solution). Straight lines represent fitting to experimental data; residue analysis is shown at the top of plots.

$$e^-_s + CyMe_4\text{-BTPhen} \rightarrow CyMe_4\text{-BTPhen}^{\bullet-} \quad (3)$$

The dependence of the pseudo-first order decay rate constant on the ligand concentration is shown in Fig. 3A. The resulting second order rate constant (calculated from the slope in Fig. 3A) was found to be 1.85(9) × 10^9 M^{-1} s^{-1}. This value is very similar to those previously found for $CyMe_4$-BTP and $CyMe_4$-BTBP, which were equal to 2.4(2) × 10^9 M^{-1} s^{-1} and 1.7(3) × 10^9 M^{-1} s^{-1}, respectively [15]. A value of almost an order of magnitude higher, (1.5-1.8) × 10^{10} $M^{-1}s^{-1}$, was previously found for the reaction of e^-_s with the model compound 1,10-phenanthroline in aqueous solution [23].

Interestingly, a decrease in the initial absorbance of e^-_s with increasing ligand concentration was observed (Fig. 3B), suggesting that the $CyMe_4$-BTPhen ligand reacts with dry electrons (e^-_{dry}). Typically, the scavenging of e^-_{dry} is described by the C_{37} parameter. This parameter corresponds to a concentration of scavenger capable of decreasing the initial $G(e^-_s)$ by a factor of 36.7% (e^{-1}). The C_{37} value for the system studied was found to be 30.4(8) mM, showing moderate scavenging capabilities.

Similar experiments were performed for 1-octanol containing 2.9% of water. In principle, the results were the same within experimental error. The rate constant and C_{37} obtained in this system were 1.7(1) × 10^9 M^{-1} s^{-1} and 31.1(4) mM, respectively.

It is reasonable to assume that the reactions of the ligand with both e^-_{dry} and e^-_s lead to a radical anion of $CyMe_4$-BTPhen ($CyMe_4$-BTPhen$^{\bullet-}$). The structure of $CyMe_4$-BTPhen$^{\bullet-}$ was examined based on the HF 6-311G(d,p) and B3LYP 6-311++(d,p) level of theory. Calculations showed an extended delocalization of the excess electron on the aromatic fragments of the ligand molecule with the highest electron density on the triazine moieties. This effect contributed to the stabilization of the system. In addition, no molecular fragmentation was observed. Thus, it is likely that the lifetime of these species is relatively long, so they may undergo further reactions with other transients (*e.g.* reforming the ligand).

It is worthwhile mentioning that the absorption spectrum of $CyMe_4$-BTPhen$^{\bullet-}$ was not observed, even for a solution containing a relatively high concentration of the ligand (~ 11 mM) and irradiated with a dose as high as 23 Gy per pulse. This is quite surprising, since experimental data for a model molecule, 1,10-phenanthroline [24], as well as theoretical calculations for the radical anion of the ligand ($CyMe_4$-BTPhen$^{\bullet-}$) revealed distinct absorption bands located in the VIS region. The most plausible explanation is a low molar absorption coefficient of the studied species.

Nitric acid effects

Extraction of minor actinides takes place from an aqueous phase acidified by nitric acid (HNO_3). In principle, the concentration of HNO_3 in the aqueous phase is around 1 M [10], which corresponds to 90 mM HNO_3 being in contact with the organic 1-octanol phase [25]. The presence of HNO_3 in the system studied may affect the radiation chemistry of the system due to effective e^-_s scavenging by both protons (H^+) and nitrate anions (NO_3^-), and also by protonation of the ligand.

The reaction of e^-_s with H^+ (reaction 4) was studied in a perchloric acid ($HClO_4$)/1-octanol solution.

$$e^-_s + H^+ \rightarrow H^\bullet \quad (4)$$

The second order rate constant of reaction (4) was measured and was found to be 1.5(3) × 10^9 M^{-1} s^{-1} based on a pseudo-first order rate constant of e^-_s decay dependent on the $HClO_4$ concentration. It is likely that this reaction is reversible, as it was observed in aqueous systems [9, 26]. However, it must be strongly shifted towards the product. In the range of $HClO_4$ concentration investigated (up to 40 mM), no evidence for a reaction of H^+ with e^-_{dry} was found. Neither the rate constant of reaction (4) nor the reactivity towards e^-_{dry} in 1-octanol was affected by a water content of up to 2.9% by weight.

Within experimental error no difference in e^-_s decay kinetics was found when $HClO_4$ was replaced by HNO_3. This is surprising, since the reported reaction of NO_3^- with e^-_s in aqueous systems is relatively fast with a rate constant equal to 9.7 × 10^9 M^{-1} s^{-1} [27]. It seems that this reaction is irrelevant, or full dissociation of HNO_3 is not achieved in the organic phase studied. In part, this observation may be due to a more pronounced ion-ion interaction in non-polar media (dependence of rate constants of charged species on solvent polarity). Moreover, no evidence of a reaction of NO_3^- with e^-_{dry} was found. However, the concentration range of HNO_3 used in our experiment (up to 40 mM) was relatively narrow due to the limitations of the time resolution of the equipment. Thus, it is likely that the C_{37} value was outside the limits of our instrumental technique. This hypothesis is supported by the relatively high C_{37} value in water, which was previously found to be equal to 0.55 M [28, 29].

The first protonation of $CyMe_4$-BTPhen takes place at the phenanthroline ring, with pK_a = 3.1(1) [30]. Subsequent pK_a values are rather low and equal to 0.3(1), 0.2(1) and 0.03(3) for the second, third and fourth protonation, respectively. In the organic phase with an HNO_3 concentration of 90 mM, about 95% of the $CyMe_4$-BTPhen molecules are protonated ($CyMe_4$-BTPhenH$^+$). Taking into account the limited time resolution of our pulse radiolysis set-up, we investigated the reaction of e^-_s with $CyMe_4$-BTPhenH$^+$ (reaction 5) in 1-octanol containing $[H^+]_0$ = 5.8 mM and $[CyMe_4\text{-BTPhen}]_0$ in the range of 0 mM to 5.7 mM.

$$CyMe_4\text{-BTPhenH}^+ + e^-_s \rightarrow CyMe_4\text{-BTPhenH}^\bullet \quad (5)$$

The obtained rate constant of reaction (5) was 1.9(6) × 10^9 M^{-1} s^{-1}. The obtained value was the same (within experimental error) as the rate constant for the respective reaction of the non-protonated ligand, confirming a diffusion-controlled or close to a diffusion-controlled reaction mechanism. It is noteworthy that the relatively high level of uncertainty is due to the narrow concentration range of $CyMe_4$-BTPhen used in our experiments.

Oxygen reaction with solvated electrons

The ability of molecular oxygen (O_2) to react with e^-_s according to reaction (6) is well known. The second order rate constant of this reaction in 1-octanol was calculated by measuring the pseudo-first order rate constants of e^-_s decay as a function of O_2 in the solvent purged by various O_2/Ar mixtures of varying composition. The O_2 concentrations in 1-octanol were calculated by using a Henry fugacity equal to 91.42 MPa [31]. The rate constant obtained $1.0(1) \times 10^{10}$ M^{-1} s^{-1} was independent of water concentration up to 2.9%. As expected, this value is lower than those observed in methanol and ethanol (1.9×10^{10} M^{-1} s^{-1} to 2.1×10^{10} M^{-1} s^{-1} and 1.9×10^{10} M^{-1} s^{-1} to 2.0×10^{10} M^{-1} s^{-1}, respectively). This fact can be rationalized by the higher viscosity of 1-octanol in comparison to methanol and ethanol.

$$e^-_s + O_2 \rightarrow O_2^{\bullet -} \qquad (6)$$

Reaction with $H^\bullet$

The spectrum of an $H^\bullet$ adduct to the model compound 1,10-phenanthroline has been observed in aqueous solution [32]. However, we did not record any absorption which can be assigned to the corresponding $H^\bullet$ adduct with $CyMe_4$-BTPhen. Therefore, it is likely that these species are characterized either by low molar absorption coefficients, or alternatively they are formed on the triazine moieties with no bands in the region studied.

Since Pyr is capable of scavenging $H^\bullet$ forming the adduct $PyrH^\bullet$ with a characteristic band peaking at 400-405 nm [33], we used this feature to study the kinetics of $H^\bullet$ addition to $CyMe_4$-BTPhen by means of a competitive reaction. Our observations did not lead to an exact value, but clearly showed that this reaction is at least 10-fold slower than the reaction leading to $PyrH^\bullet$ formation. The kinetics of $PyrH^\bullet$ formation were not measured in 1-octanol; however, the rate constant of this reaction was found to be 7.2×10^9 M^{-1} s^{-1} in methanol [33].

The transient absorption spectrum recorded in an acidified (80 mM of H^+) 1-octanol solution of $CyMe_4$-BTPhen is shown in Fig. 4. Under these experimental conditions, the ligand exists mostly in a protonated form and e^-_s is converted by forming an additional quantity of $H^\bullet$ (reaction 4).

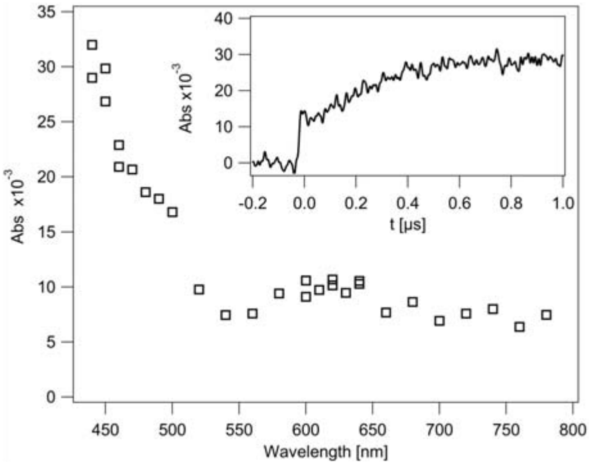

Fig. 4. Transient absorption spectra recorded in irradiated, Ar-saturated, 1-octanol with 80 mM HCl and 8.5 mM $CyMe_4$-BTPhen 800 ns (□) after the electron pulse. Insert shows time profile recorded at 450 nm (19 Gy, water contents – 0.46% by weight).

Two absorption bands can be distinguished in the spectrum recorded 800 ns after the pulse: the first one with $\lambda_{max} \approx 630$ nm and the second one with $\lambda_{max} \approx 450$ nm or below. By comparison with a pulse-irradiated, acidified solution of 1,10-phenanthroline, this spectrum can be assigned to the $H^\bullet$ adduct of a protonated form of the ligand – $CyMe_4$-$BTPhenH_2^{\bullet +}$. The adduct of $H^\bullet$ to protonated 1,10-phenantroline is characterized by similar absorption bands peaking at $\lambda = 430$ nm and 660 nm [23]. The rate constant of $CyMe_4$-$BTPhenH_2^{\bullet +}$ formation (reaction 7) was measured by us and was found to be $4.3(9) \times 10^8$ M^{-1} s^{-1} based on the dependence of a pseudo-first order rate constant signal growing at 450 nm on the concentration of $CyMe_4$-$BTPhenH^+$. For a protonated form of 1,10-phenanthroline in aqueous solution, the rate constant of this reaction was almost one order of magnitude higher and equal to 3.3×10^9 M^{-1} s^{-1} [23].

$$CyMe_4\text{-}BTPhenH^+ + H^\bullet \rightarrow \\ \rightarrow CyMe_4\text{-}BTPhenH_2^{\bullet +} \qquad (7)$$

In conclusion, solvated electrons and hydrogen atoms are the two most reactive species generated during 1-octanol (diluent of r-SANEX extraction system) irradiation. The radiation chemical yield of e^-_s and its molar absorption coefficient in 1-octanol were found to be 130(10) nmol J^{-1} and 18 500(700) M^{-1} cm^{-1}, respectively. Both species undergo fast reactions with the ligand $CyMe_4$-

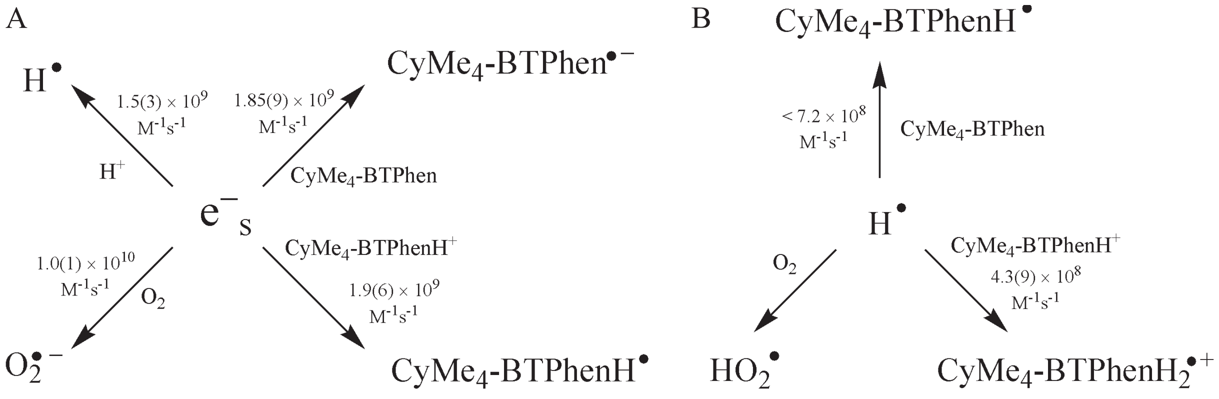

Fig. 5. The reaction scheme involving e^-_s (A) and $H^\bullet$ (B) in 1-octanol–based r-SANEX extraction system containing $CyMe_4$-BTPhen ligand.

-BTPhen and other scavengers present in the extraction system, according to the scheme shown in Fig. 5.

Moreover, the CyMe$_4$-BTPhen ligand is capable of scavenging dry electrons with a C$_{37}$ value equal to 30.4(8) mM.

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EPR RESPONSE OF SELECTED PHENOLIC ANTIOXIDANTS USED IN POLYMER PROCESSING AND DOSIMETRY OF IONIZING RADIATION

Jarosław Sadło, Grażyna Przybytniak

Sterically hindered phenols are a wide group of chemicals used in many areas. They have a hydroxyl group attached to the benzene ring and a specific sequence of substituents. Their structure is characteristic of both natural and synthetic antioxidants. Phenolic compounds that have ortho and para substituents, are particularly important. Bulky substituents, such as tert-butoxyl groups, efficiently stabilize the unpaired spin of phenoxyl radicals, enhancing the antioxidant properties.

Phenolic antioxidants arouse interest in many areas. They are primary antioxidants used in polymer processing to protect materials during manufacture and ageing. Their architecture is tailored to the chemical structure of plastics and to secondary antioxidants to achieve a synergistic effect [1, 2]. When introduced into polymeric materials, they form homogeneous suspensions due to their aliphatic hydrocarbon residues, which increase the compatibility between the components.

Recently, several papers have been published on the use of phenolic antioxidants as dosimeters [*e.g.* 3, 4]. For example, Irganox 1076, which showed a linear response to low doses, was proposed as a dosimeter for clinical applications, appropriate for various types of ionizing radiation [3]. According to the authors, Irganox 1076 in the polymer matrix formed only one stable radical upon irradiation, as observed by EPR (electron paramagnetic resonance) spectroscopy.

However, as seen in Fig. 1, the signals of microcrystalline Irganox 1076 powder are more complex. The spectrum of the antioxidant irradiated with gamma rays at 77 K and recorded at 100 K consists of at least two components. The intensive doublet of hyperfine splitting (hfs) 1.71 mT was assigned to the phenolic radical cation (Scheme 1, R1) formed after electron loss by the hydroxyl group. The intermediate showed a g factor characteristic for this group of radicals (2.0035). The susceptibility of hydroxyl groups to deprotonation depends on the substituents of the aromatic ring and grows with their electron-withdrawing ability. Alkyl groups are considered substituents with moderate electron donor properties, weaker than alkoxyl or amino groups. Due to the rigidity of the crystalline phase, deprotonation in the powdered antioxidant is limited. The presence of a proton in the hydroxyl group significantly changes the distribution of spin density, decreasing the coupling with other substituents [5]. The relatively stable doublet of the radical cation has been found in the past by other research groups [4]. However, at low temperatures we observed additional lines emerging on both sides of the dominant signal. These are components of the spectrum whose internal lines are covered by the intensive doublet. The whole spectrum seems to consist of a quartet of triplets with hyperfine splitting of 2.71 mT and 1.21 mT, respectively. The stick diagram of the signal is marked R2 in Fig. 1.

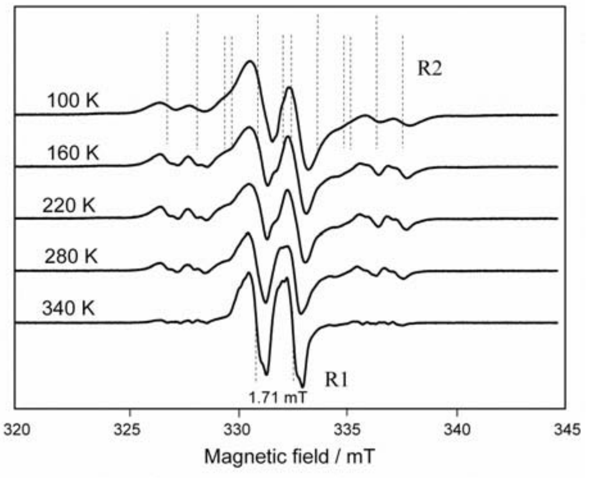
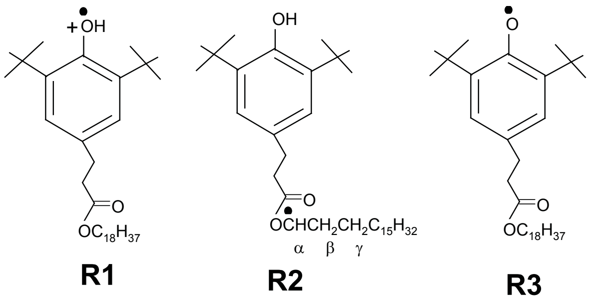


Fig. 1. EPR spectra of Irganox 1076 measured at 1 mW.



Scheme 1. Irganox 1076 radicals found by EPR spectroscopy.

Such a pattern can be attributed to the R2 radical shown in the Scheme 1. The unpaired spin interacts with three equivalent protons, one α and two β protons of the methylene group adjacent to the oxygen of the ester group situated in the para substituent. The hfs of the two γ hydrogens is greater than for typical aliphatic radicals, due to the influence of the neighbouring heteroatom.

Above 340 K the spectrum changed significantly (Fig. 2). A distinctive triplet of triplets appeared, which was attributed to a phenoxyl radical showing spin coupling with the methylene group in the para position (1.20 mT) and the two meta protons (0.15 mT). As can be seen from the evolution of the EPR spectra, the only possible precursor of the intermediate is the radical showing the doublet at lower temperatures. The conversion proves that the two intensive lines were correctly assigned to the phenolic radical cation. Above the melting point (323-328 K), due to the increasing conformational movements of macromolecules, the intermediate was deprotonated. Such a pattern was also found in Irganox 1076 solutions, in which the loss of a proton was facilitated by a hydrogen bonding network.

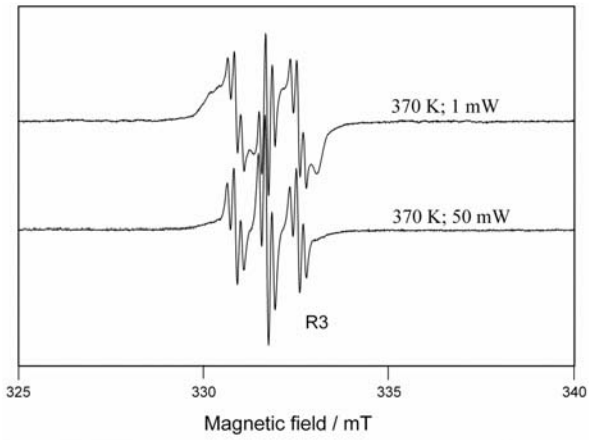


Fig. 2. EPR spectra of Irganox 1076 at 370 K measured at 1 mW and 50 mW.

The observed significant changes in the shape and intensity of the EPR spectra with increasing temperature ought to be taken into account if Irganox 1076 is considered as a dosimeter. At ambient temperatures the experimental signal is a superposition of several resonant lines assigned to two radicals. The spectrum of the alkyl radical R2 gradually decreased over a wide range of temperatures and interfered with the dominant doublet. Thus, the peak-to-peak (Hpp) intensity, measured as the distance between the minimum and maximum of the whole spectrum, decreased during heating. In order to follow the changes, the relative amounts of all radicals were determined by double integration of the experimental signals as well as the 'dosimetric signal' based on a peak-peaking procedure (Figs. 3 and 4). As expected, a gradual decay of all the radicals was confirmed in the range of 100-340 K. However, the relationship between Hpp and temperature has an uneven course. In the range of 100-250 K the Hpp value decreased, but at higher temperatures clearly grew (Fig. 4). Simultaneously, the half-height width and peak-to-peak width increased. These effects can be related to the relaxation of the surroundings of the radical centres. It seems that the population of phenolic radical cations does not change, but the rearrangement of microcrystals modifies the signal. These variations in the intensity of the doublet should be taken into account when the phenolic antioxidant is recommended as an EPR dosimeter.

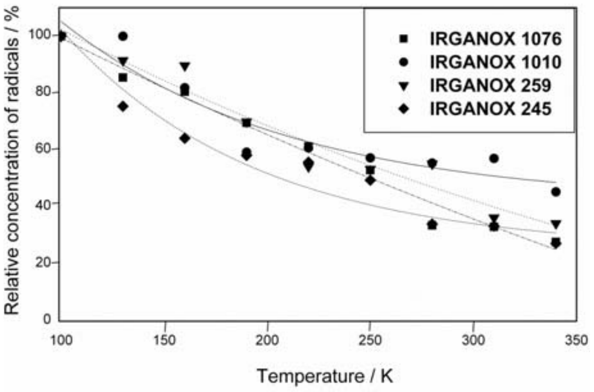


Fig. 3. Changes in the concentration of Irganox radicals with increasing temperature.

The changes in EPR spectra were also studied for other sterically hindered derivatives of 3,5-di-tert-butyl-4-hydroxyphenylpropionate (Irganox 1010, Irganox 245 and Irganox 259; Figs. 3 and 4). In spite of the fact that the population of all types of radicals decreases with increasing temperature, the global Hpp parameter does not follow these changes, as was confirmed for several selected Irganoxes.

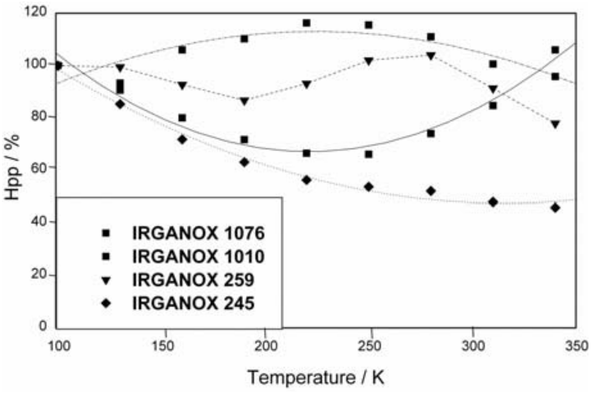


Fig. 4. Changes in the Hpp values of Irganox radicals with increasing temperature.

Summarizing, phenolic antioxidants are widely applied in the plastic industry due to several favourable properties: good compatibility with polymeric matrices, low volatility and effective protection against thermo-oxidative degradation. Nevertheless, their application as EPR dosimeters requires further thorough research. We confirmed that their EPR spectra consist of at least two components. The relationships between the relative concentration of all radicals *vs.* temperature have different profiles than the dependence between global peak-to-peak distance and temperature, as was observed for selected sterically hindered phenols. Such a behaviour does not eliminate this group of compounds from dosimetry applications. However, detailed tests covering the narrow range of temperatures corresponding to the 'ambient conditions' in which ionizing radiation dosimetry is usually performed are required. Another important issue is related to the microstructure of crystalline powders. Their size and distribution influence EPR results. In the past it was found that Irganox 1076 dispersed in a polymer showed a singlet assigned to the phenolic radical, but not the doublet of the radical cation or both if the concentration of the antioxidant was high enough. Thus, the EPR spectra are determined by the distribution of the powdered additives in the matrix. For the above reasons (among others) phenolic antioxidants, although potentially considered an alternative to the alanine dosimeter, require both a well-defined structure and measurement conditions.

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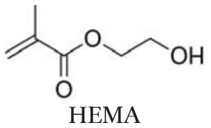
THE EFFECT OF TREATMENT WITH MONOMERS AND GAMMA IRRADIATION ON STARCH:PVA FILMS STUDIED BY DIFFERENTIAL SCANNING CALORIMETRY, THERMOGRAVIMETRY AND FTIR SPECTROSCOPY

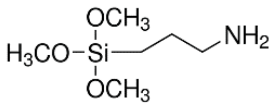
Krystyna Cieśla, Krzysztof Mirkowski, Krzysztof Łyczko, Marcela Grabowska

These fundamental studies are connected to the increasing interest in the use of biopolymers for packaging purposes [1-7]. Polysaccharides, in particular starch, are good candidates for the preparation of cheap biodegradable packaging [1-5]. However, this goal needs additional functionalization of such materials, in regard to their hydrophilicity and minor mechanical properties. Accordingly, various methods have been applied in order to improve the properties of starch films, such as using modified starches, blending starch with other natural polymers or with synthetic biodegradable polymers (such as poly(vinyl alcohol) – PVA) [3-5], and the application of various physical and chemical treatments. Among other chemical methods, procedures that enable various monomers to be grafted onto the polymer backbone have also been explored.

Techniques that apply ionizing radiation have become increasingly implemented for polymer modification in recent years, due to the possibility of initializing processes such as degradation, oxidation, crosslinking and grafting [1]. Previous studies have shown how the properties of films based on the starch:PVA system could be modified [2-6]. These methods have also been successfully applied to the grafting of monomers, such as hydroxyethylmethacrylate (HEMA) or 3-aminopropyltrimethoxysilane (silane) (Scheme 1), onto polysaccharide-based films [7], and an improvement in the films' properties was reported. A good knowledge of the phenomena resulting from the treatment of the polymer with monomers under various conditions should be helpful for the optimization of the preparation procedures.



HEMA



silane (3-aminopropyltrimethoxysilane)

Scheme 1. The structure of HEMA and silane.

At present, our studies are focused on the influence of the treatment with HEMA and silane supported by gamma irradiation on the structural

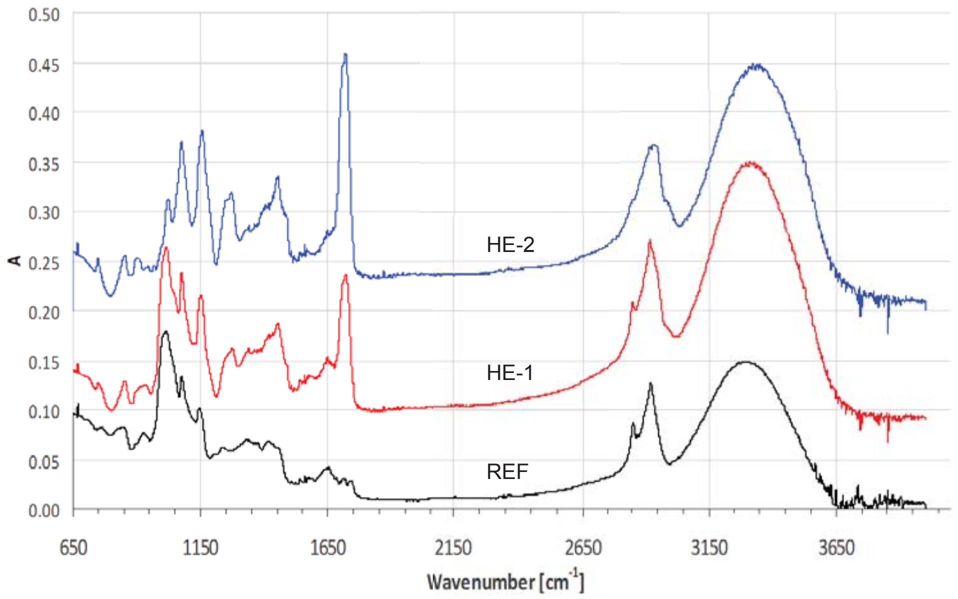


Fig. 1. FTIR-ATR spectra recorded for the reference and the HEMA-treated samples.

properties of starch:PVA films. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and thermal analysis methods, such as differential scanning calorimetry (DSC) and thermogravimetry (TGA, DTGA) have already proved to be useful tools for studying the effects of ionizing radiation in biopolymers [5-6, 8].

Cornstarch (Sigma) and PVA (Aldrich product characterized by a molecular mass of 145 kDa) were used for the films' preparation. The HEMA and silane were Aldrich products. As before [3-4], the starch was pre-irradiated with a dose of 10 kGy before the film preparation.

Films characterized by a starch:PVA ratio equal to 45:55 were prepared by solution casting. Glycerol was introduced at a level of 30% (in relation to the joint starch-PVA mass). The films were dried, peeled from the substrate and stored for a couple of days at a relative humidity of 43% before chemical/radiation treatment and testing.

The obtained film was placed in 10 wt% solutions of HEMA or silane and irradiated in the Gamma Chamber GC 5000 applying a dose of 25 kGy over 5.5 h (at a dose rate of 4.54 kGy/h). The samples were then heated for 2.5 h at 45°C and subsequently stored in the solution at ambient temperature (HE-2 and SI-2 samples) or just stored in the solution at ambient temperature without heating (HE-1 and SI-1 samples). Altogether, each sample remained in contact with the solution for 20 h. Simultaneously, the reference sample (REF) was prepared, applying the same procedure as in the case of the HE-2 and SI-2 samples but with neither monomer being present.

ATR-FTIR spectra were recorded with a Thermo Scientific Nicolet iS10 FT-IR spectrometer. TGA studies were carried out using a TGA Q500 V20.7 thermobalance (TA Instruments) at a temperature range up to 800°C. The measurements were performed under nitrogen, applying a heating rate of 10°C/min, or in oxidative conditions under air (at 5°C/min). DSC studies were performed using heating-cooling cycles (two heating and two cooling cycles) with a heating-cooling rate of 10°C/min using a TA Instruments 2920 V2.6A MDSC.

A clear increase in the intensity of the band at *ca.* 1723 cm^{-1} (stretching vibrations of the HEMA ester groups) was observed after treatment with monomer (Fig. 1). This indicated an effective grafting of HEMA. Besides, an increase in the intensity of the bands at *ca.* 1454, 1277, 1156, 1077 and 843 cm^{-1}, and also the OH bands in the range 3200-3600 cm^{-1}, was noted. The changes in intensity of the bands at *ca.* 2928 cm^{-1} and 2857 cm^{-1} indicated changes in the C-H and C-O-C vibrations of the HEMA ester groups. The stronger treatment seemed to result in the more effective grafting of HEMA onto the starch:PVA film.

The lack of specific vibrations for silane resulted in the small differences noted between the samples subjected to treatment with silane and the reference sample. The spectra of specimens treated with silane could be compared with the ATR spectrum of the sample containing 3% silane (Fig. 2). The occurrence of grafting could be concluded basing the changes in intensities of the bands at 3200-3300 cm^{-1} (vibrations of OH and NH_3 groups), 1103 cm^{-1} and 1380 cm^{-1} (both C-Si-O-C vibrations), as well as those of the bands at 1023, 1012, 1045, 1343, 1420 and 1655 cm^{-1}, and the bands in the range 1570-1590 cm^{-1}.

Several stages of thermal decomposition were observed during heating (Figs. 3 and 4). The first stage was connected to the loss of the volatile and small molecular fractions (in general, water). Due to the fact that it was difficult to control the beginning of this stage, the values of the mass loss occurring in the next stages (the second (II), third (III) and fourth (IV)) were related to the 'dry' mass of the sample obtained above *ca.* 190°C after the evacuation of water.

Three stages of degradation were observed during heating under nitrogen. The major (the second) decomposition stage (*ca.* 190-400°C) occurred at higher temperatures (Fig. 3, Table 1). It exhibited an increase in the DTGA peak temperature

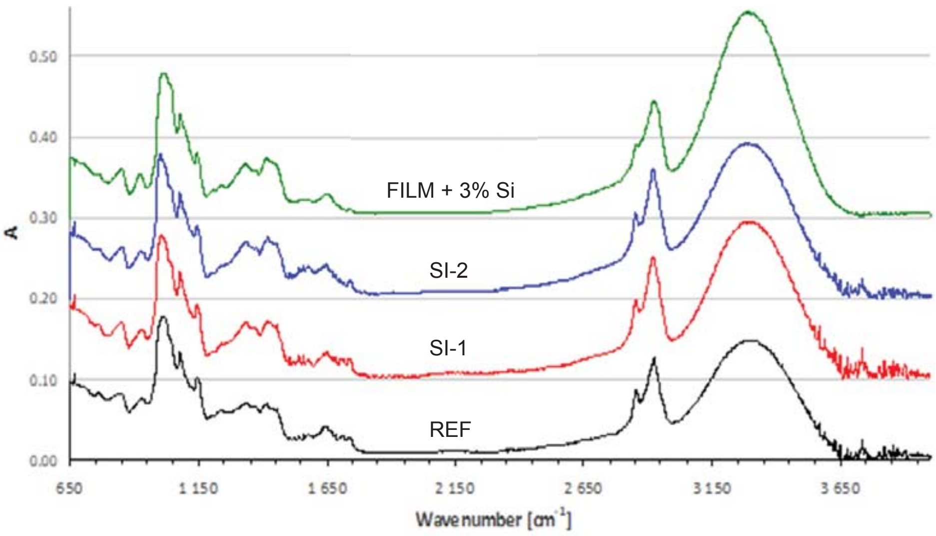


Fig. 2. FTIR-ATR spectra recorded for the reference and the silane-treated samples. The spectrum recorded in the case of the starch:PVA (45:55) containing 3% silane is shown for comparison.

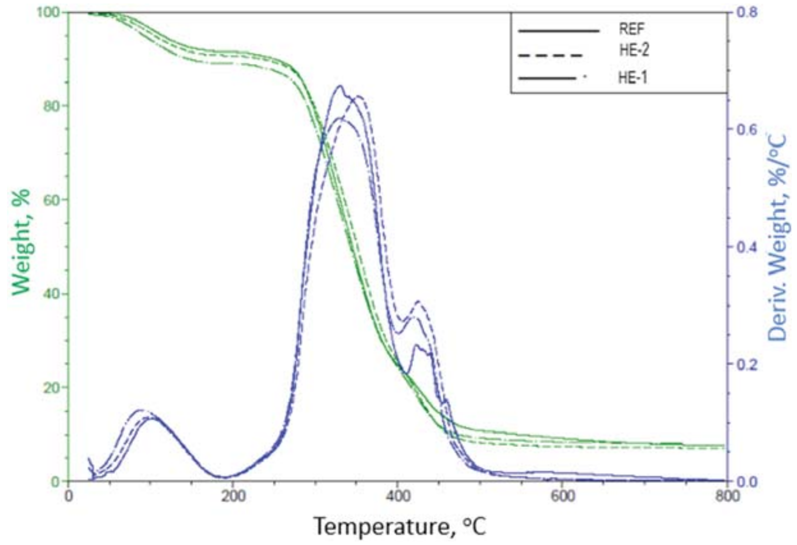


Fig. 3. TGA and DTGA curves recorded under nitrogen (10°C/min) for the reference sample and the samples obtained after treatment with HEMA.

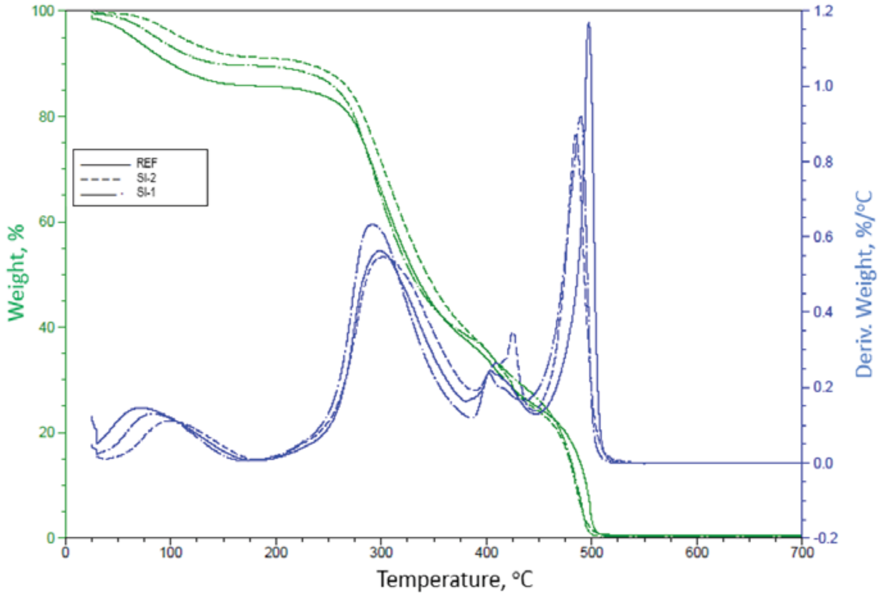


Fig. 4. TGA and DTGA curves recorded under air (5°C/min) for the reference sample and the samples obtained after treatment with silane.

Table 1. Results of TGA carried out under nitrogen (10°C/min). Additional DTGA maxima or shoulders (sh) are shown. The major peak is underlined.

Sample	$T_{fII} = T_{0III}$* [°C]	Stage II			Stage III**	
		Δm_{II} [wt%]	T_p [°C]	Δm at 330.51°C [wt%]	Δm_{III} [wt%]	T_p [°C]
REF	410.0	74.98	330.51 (+350.55 sh)	34.79	14.03	422.95 +435.87 (*ca.* 460.0)
HE-2	405.5	73.44	353.14	30.10	18.00	424.89 (*ca.* 436 sh)
SI-2	408.8	74.73	353.78 (315-318 sh)	28.26	15.56	427.45 439.75 (*ca.* 460 sh, *ca.* 462 sh)
HE-1	399.7	72.55	329.87 (+341.5 sh)	35.73	17.59	420.36 (*ca.* 435.0 sh)
SI-1	406.3	76.07	345.19 (+316-328 sh)	36.83	13.60	428.03

* Temperature of the border between the first and the second stages.
** The value of T_f = *ca.* 545.5°C was arbitrary, being selected based on the data obtained for the REF sample.

(Table 1). Several sub-stages were observed within the third (III) stage of degradation. It was noted that the temperature of the main maximum on the DTGA curves shifted towards higher temperatures in the case of HE-2 and SI-2 samples, as compared to the REF sample and the appropriate HE-1 and SI-1 samples.

The residue at 700°C was determined as being equal to 8.82, 7.93, 8.79, 9.21 and 9.17 wt% for the REF, HE-2, SI-2, HE-1 and SI-1 samples, respectively. Therefore, it was only slightly smaller in the case of the HE-2 sample as compared to the REF sample (Table 1). The heating performed during the preparation procedure also led to a decrease in the residual mass of the monomer-treated samples (Table 1).

An additional stage was observed during the decomposition of the films under air (Fig. 4), with almost no residues at the end of the process (0.28-0.60 wt%). This stage was partially connected to the degradation of the fraction which remained undecomposed in the case of heating under nitrogen and partially due to the decomposition of the fraction which had decomposed within the third stage. The effect of chemical/radiation treatment resulted in an increase in the mass loss occurring during the second stage with a simultaneous increase in the temperature at the end of this stage (Fig. 4, Table 2). A similar increase in the decomposition temperature observed in the case of the third stage resulted in a clear shift of the DTGA peak towards higher temperatures (Table 2). The last (fourth) decomposition stage occurred at lower temperatures compared to the reference and was associated with a smaller mass loss in the case of all the treated samples, showing a simultaneous decrease in the content of the high molecular fraction (Table 2).

The TGA/DTGA data showed the simultaneous formation of both fractions characterized by an increased thermal stability and those characterized by a decreased thermal stability, as com-

Table 2. Results of TGA carried out under air (5°C/min). Additional DTGA maxima or shoulders (sh) are shown. Major peak is underlined.

Sample	The second and the third stages (*ca.* 180-445°C)					The fourth stage (above *ca.* 445°C)		
	$T_{fII} = T_{0III}$* [°C]	The second stage (*ca.* 180-385°C)		The third stage (*ca.* 385-445°C)				
		Δm_{II} [wt%]	T_p [°C]	Δm_{III} [wt%]	T_p [°C]	T_0 [°C]	Δm_{IV} [wt%]	T_p [°C]
REF	379.7	55.99	298.25	14.35	403.45 (*ca.* 418.7 sh)	444.2	29.10	497.3
HE-2	384.8	57.68	301.64	16.11	405.14 423.24	445.9	26.75	479.80
SI-2	385.9	58.56	299.43	15.54	407.61 423.85 (*ca.* 438.6)	447.6	26.03	487.38
HE-1	387.6	58.24	292.0-298.8	13.81	400.21 (*ca.* 414 sh)	444.7	26.21	472.92
SI-1	386.5	57.80	290.90	10.07	402.56 (*ca.* 416 sh)	435.1	31.83	489.41

* Temperature of the border between the first and the second stages.

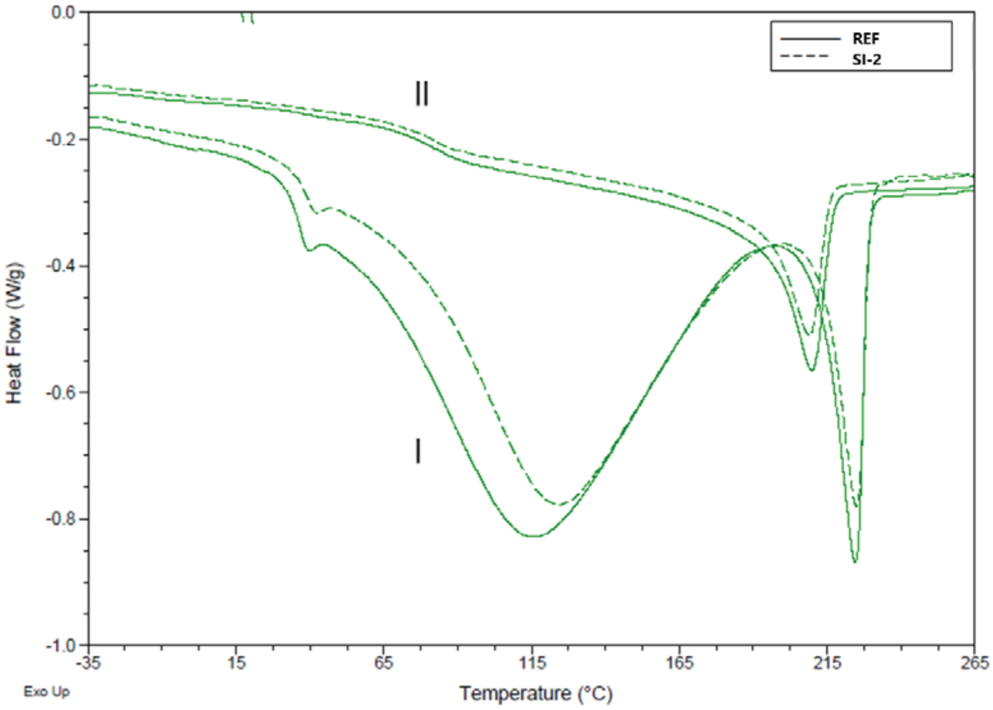


Fig. 5. Comparison of the DSC curves recorded during the first (I) and the second (II) heating of the REF and the SI-2 samples.

pared to the appropriate pristine fractions. These processes can be related both to grafting processes and to a decrease in the content of highly cross-linked fractions due to the monomer treatment.

The effect of melting, connected mainly to the presence of PVA, was detected during the first heating at a temperature above 200°C (DSC; Fig. 5). It was preceded by a glass transition accompanied by a strong effect of structural relaxation in the amorphous phase, taking place due to the presence of both starch and PVA, in the temperature range up to 200°C. The inflection at a temperature of *ca.* 40°C was also connected to glass transition phenomena. The effects of glass transition and melting were detected during the second heating (Fig. 5). The effects of crystallization and glass transition were noted during the first and second cooling (Fig. 6).

Lower values of melting and crystallization enthalpies were determined for the 'grafted' HE-2 and SI-2 samples as compared to the REF sample. Simultaneously, the thermal effects of crystalliza-

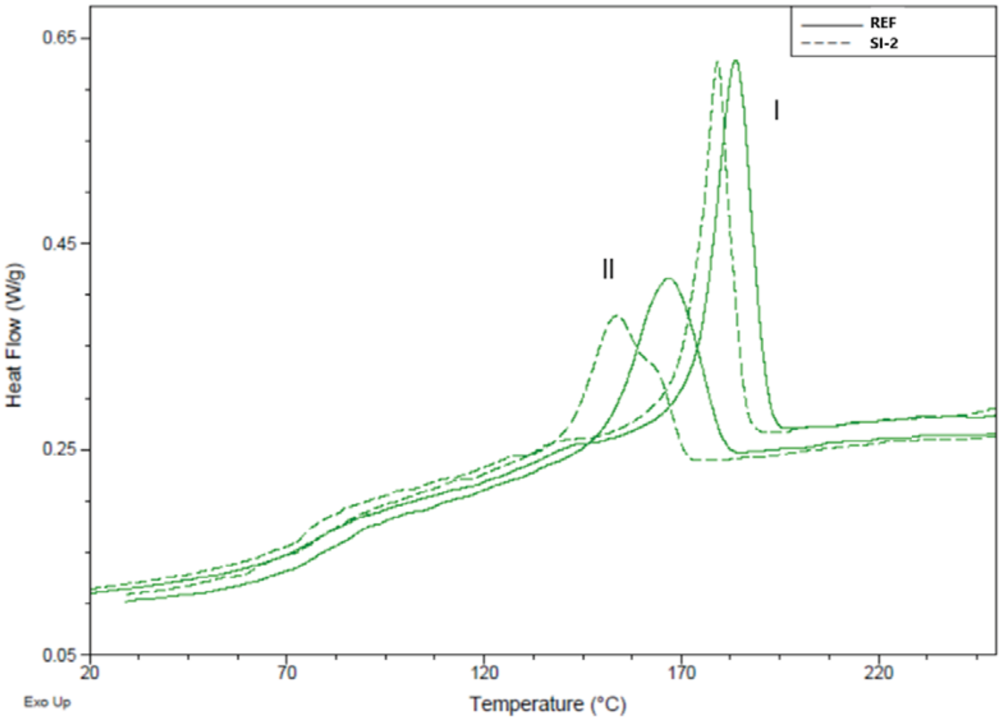


Fig. 6. Comparison of the DSC curves recorded during the first (I) and the second (II) cooling of the REF and the SI-2 samples.

Table 3. DSC results: melting and crystallization.

Sample	T_p [°C]	T_{on} [°C]	ΔH [J/g]	T_p [°C]	T_{on} [°C]	ΔH [J/g]
	Melting					
	I heating			II heating		
REF	224.5	212.2	38.0	209.7	193.2	40.9
HE-2	224.4	211.8	33.9	208.5	192.0	35.7
SI-2	224.9	212.9	32.3	208.9	192.0	32.4
HE-1	224.0	211.7	35.6	209.8	193.3	37.5
SI-1	224.2	212.5	26.7	212.0	196.2	27.3
	Crystallization					
	I cooling			II cooling		
Ref	183.7	191.6	26.8	166.6	180.8	23.9
HE-2	179.3	185.5	23.8	162.9	170.5	21.3
SI-2	179.2	185.0	22.5	153.4	171.0	18.9
HE-1	182.5	189.1	24.3	166.5	175.0	20.6
SI-1	185.1	190.7	21.4	168.0	177.3	17.3

tion were recorded at lower temperatures (Fig. 6, Table 3). Besides, the enthalpy of the structural relaxations observed during the first heating were lower and occurred at higher temperatures due to treatment with the monomer (Table 4). At the same time, the glass transition (during the second heating) as well as an inflection point (during the first heating) were observed at higher temperatures in the cases of the samples subjected to the treatment with both the monomers (Table 4). It was also noted that the heating step performed during the preparation procedures led to an increase in the effect of the monomer action (Tables 3 and 4).

Table 4. DSC results: structural relaxation and glass transition.

Sample	Structural relaxation during the first heating (41-200°C)			Glass transition during the second heating			Inflection point during the first heating [°C]
	T_p [°C]	T_{on} [°C]	ΔH [J/g]	Midpoint [°C]	T_{on} [°C]	T_{end} [°C]	
REF	112.5	64.0	205.7	80.5	65.7	89.7	38.1
HE-2	118.4	67.9	187.1	81.5	68.6	90.4	41.1
SI-2	124.2	73.3	174.6	82.4	71.2	87.9	41.6
HE-1	116.3	60.5	198.4	82.0	67.7	88.7	40.9
SI-1	105.9	56.9	185.0	82.4	64.2	91.9	40.3

The results can be explained in terms of a decrease in crystallinity accompanied by an increase in the ordering of the amorphous phase due to treatment with monomers.

In conclusion, differences were found in the course of thermal degradation carried out under nitrogen and under air, due to the performed treatment showing both the formation of fractions with an increased thermal stability and those with a decreased thermal stability. This can be related to the grafting processes shown by FTIR spectroscopy and to a decrease in the content of the highly crosslinked phase. The modified material is characterized by decreased crystallinity accompanied an increased ordering in the amorphous phase.

The data suggest that it is possible to achieve direct grafting of HEMA and silane onto starch:PVA films by treatment with monomer solution supported by gamma irradiation. Elevation of the temperature during the preparation procedure leads to increased effects of treatment.

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CENTRE FOR RADIOCHEMISTRY AND NUCLEAR CHEMISTRY

Chemical issues in the fields of nuclear power and radiopharmacy are the main research areas of the Centre for Radiochemistry and Nuclear Chemistry. In 2018, the Centre worked on research projects financed by grants from the National Centre for Research and Development (NCBR) and the National Science Centre (NCN), as well as by the funding of the Institute's statutory research, development and international cooperation activities by the Ministry of Science and Higher Education.

The international collaborations of the Centre were focused on the implementation of the European Commission HORIZON 2020 projects, IAEA Coordinated Research Projects or projects framed under state bilateral agreements. The individual projects of young scientists funded under specific subsidies of the Ministry of Science and Higher Education were important elements for the development of the human resources of the Centre.

The Centre's teams have competence in extensive areas, enabling them to participate in the Polish Nuclear Power Programme (PPEJ), involving research works supporting the development of nuclear technologies and the applications of ionizing radiation in the country. Their main fields of competence are the management of spent nuclear fuel and radioactive waste processing, including areas such as:

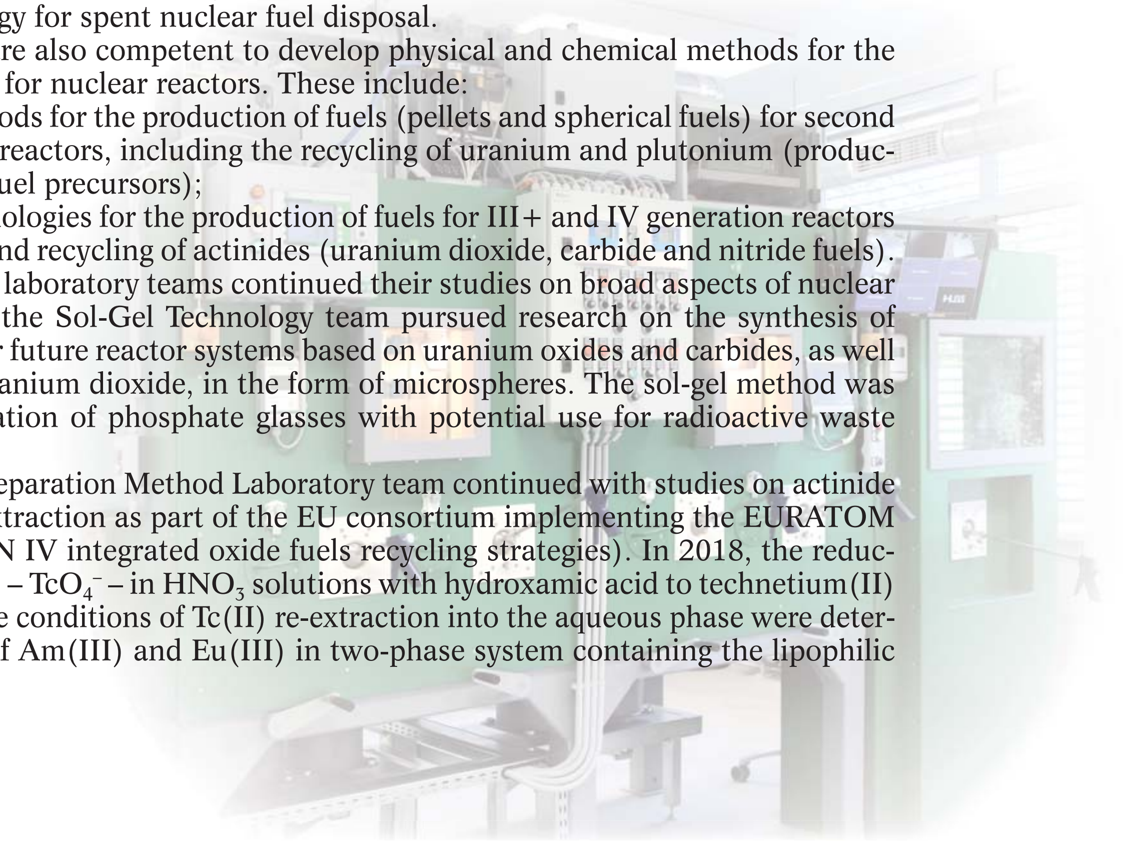
- development of methods for comprehensively managing radioactive waste generated at nuclear power plants, designing optimal recycling strategies and systems;
- purification of coolant from the primary circuit with boric acid recovery;
- research on new methods of liquid waste treatment, reducing radiotoxicity using modern separation processes;
- development of technologies for the storage and disposal of radioactive waste along with research on new protective barriers (chemical, physical and engineering);
- research on modern methods of fuel reprocessing, including the separation of minor actinides;
- elaboration of new ligands, enabling La/Ac separation and the separation of individual actinides (*e.g.* curium and americium);
- research on technology for spent nuclear fuel disposal.

The Centre's teams are also competent to develop physical and chemical methods for the production of new fuels for nuclear reactors. These include:

- development of methods for the production of fuels (pellets and spherical fuels) for second and third generation reactors, including the recycling of uranium and plutonium (production of MOX mixed fuel precursors);
- development of technologies for the production of fuels for III+ and IV generation reactors with the separation and recycling of actinides (uranium dioxide, carbide and nitride fuels).

In 2018, the Centre's laboratory teams continued their studies on broad aspects of nuclear energy. In this respect, the Sol-Gel Technology team pursued research on the synthesis of potential nuclear fuel for future reactor systems based on uranium oxides and carbides, as well as on mixed thorium-uranium dioxide, in the form of microspheres. The sol-gel method was also applied for preparation of phosphate glasses with potential use for radioactive waste stabilization.

The Radiochemical Separation Method Laboratory team continued with studies on actinide separation by solvent extraction as part of the EU consortium implementing the EURATOM GENIORS project (GEN IV integrated oxide fuels recycling strategies). In 2018, the reduction of technetium (VII) – TcO_4^- – in HNO_3 solutions with hydroxamic acid to technetium(II) was investigated, and the conditions of Tc(II) re-extraction into the aqueous phase were determined. The extraction of Am(III) and Eu(III) in two-phase system containing the lipophilic



extractant T-DGA and the hydrophilic ligand SO_3-Ph-BTP^{4-} was investigated. It was shown that this system produces extractable heteroleptic complexes [Am(T-DGA)(SO_3-Ph-BTP)]$^-$. A model was developed including the extraction of such complexes, and a criterion was defined to determine whether, in a given system containing lipophilic and hydrophilic ligands competing for metal ions, complexes are formed.

Advanced quantum chemical calculations were continued, which gave rise to explanations for the actinide selectivity of some ligands used for the solvent extraction separation of actinides from lanthanide fission products. The Group of Spectroscopy and Molecular Modelling has started the implementation of the NCN OPUS project '6xS for chiral naphthalene diimides: synthesis, simulations, structure, spectroscopy, spectroelectrochemistry, sensors'.

The recovery of uranium and accompanying metals from various types of industrial waste, such as phosphogypsum or waste from the flotation of copper ores, was studied within the scope of the IAEA CRP. It was shown that with the use of selected extraction agents it is possible to effectively recover uranium and other metals such as copper, vanadium or rare earth elements.

Various aspects related to the management and storage of spent nuclear fuel and radioactive wastes generated in the course of the exploitation of nuclear power plants were examined. A special emphasis was put on the development of new barrier materials that immobilize radionuclides and prevent their migration. New sorbents of radionuclides based on natural biopolymers and waste material were developed and characterized. Aspects of radioactive waste are addressed by the Euratom Horizon 2020 CHANCE project (Characterisation of conditioned nuclear waste for its safe disposal in Europe). This project is focused on the development of new non-destructive methods of radioactive waste characterization, such as muon tomography, calorimetry and innovative techniques based on laser spectroscopy for the monitoring of gaseous radioactive emissions.

The Membrane Processes group examined novel methods for the treatment of 'problematic' nuclear waste, based on integrated processes (membrane filtration combined with sorption, advanced oxidation-membrane process), as the basis for further technological advancement in the radioactive waste processing field. Research on the phenomena of concentration polarization and membrane fouling in membrane modules was continued within the scope of the NCN research project. The combination of radiotracers with optical techniques, such as SEM (scanning electron microscopy) and FTIR/PAS (Fourier-transform infrared/photoacoustic spectroscopy) gave data for the future elaboration of the methodology of testing membrane units.

Research on radiopharmaceutical chemistry (Laboratory of Radiopharmaceuticals Synthesis and Studies) was focused on obtaining and studying novel potential radiopharmaceuticals, both diagnostic and therapeutic. Novel biomolecules, derivatives of tacrine, agonists (*e.g.* substance P) or antagonists (*e.g.* aprepitant, spantide I (5-11)) of the NK-1 receptor, 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 syndrome, respectively. Radiopharmaceuticals with a synergistic effect based on gold nanoparticles, ^{198}Au, combined with doxorubicin and octreotide, as well as ^{131}I and ^{177}Lu anti-HER2 nanobodies for targeted therapy of breast and ovarian tumours, were among the other subjects of research in the Laboratory. New methods for the cyclotron production of diagnostic radionuclides, for 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 the NCBR.

The development of a new cyclotron method for ^{47}Sc production was continued within the scope of a new IAEA Research Contract. Also, potential therapeutic radiopharmaceuticals were obtained and studied.

The new NCN projects implemented in the Laboratory concern the development of radiopharmaceuticals based on tachykinin-1 receptor antagonists for the diagnosis and therapy of the brain cancer glioblastoma multiforme, and nanostructured liquid crystal lipid carriers of chemotherapeutics and corpuscular radiation emitters for targeted cancer therapy.

In recognition of the achievements of the Centre's researchers, two teams were awarded the Director's prize for publications presented in 2016-2017.

IN VIVO PHARMACODYNAMICS STUDIES OF NOVEL TACRINE DERIVATIVES RADIOCONJUGATES LABELLED WITH ^{68}Ga AND ^{99m}Tc

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Alzheimer's disease (AD), the most frequent cause of elderly dementia, is a complex degenerative disease of the central nervous system, characterized by progressive loss of memory and cognitive functions. The main cause of AD is a decrease in acetylcholine (ACh) neurotransmission level. In order to improve ACh neurotransmission, patients often undergo treatment using acetylcholinesterase (AChE) and butyrylcholinesterase (BuChE) inhibitors [1, 2]. The first clinically applied cholinesterases inhibitor was tacrine, approved by US Food and Drug Administration (US FDA) for palliative treatment of AD. Even though the application of tacrine as a medicine is limited by its side effects, its derivatives are still an interesting subject in the search for novel solutions to AD diagnosis and treatment [3-5].

The issue of effective diagnostic methods for brain cholinergic system needs a selective neuroradiodiagnostics with high affinity for AChE. Therefore, due to tacrine's high cholinoesterases inhibition activity, radiopharmaceuticals based on tacrine structure can enable imaging of body region rich in AChE and BuChE. Furthermore, we assumed that this concept could be involved in the development of early AD diagnosis using commonly applied PET (positron emission tomography) or SPECT (single-photon emission computed tomography) imaging methods [6-8].

As a continuation of our previous project on the synthesis of tacrine derivatives radioconjugates labelled with ^{68}Ga and ^{99m}Tc (Fig. 1) [9], and determination of their biological activity (Table 1), we performed *in vivo* and *ex vivo* pharmacodynamic studies on animal model for the most promising radioconjugates. Our aim was to check and quantify the ability of obtained radioconjugates to cross the blood-brain barrier (BBB) and initially evaluate their utility in cholinergic system neuroimaging.

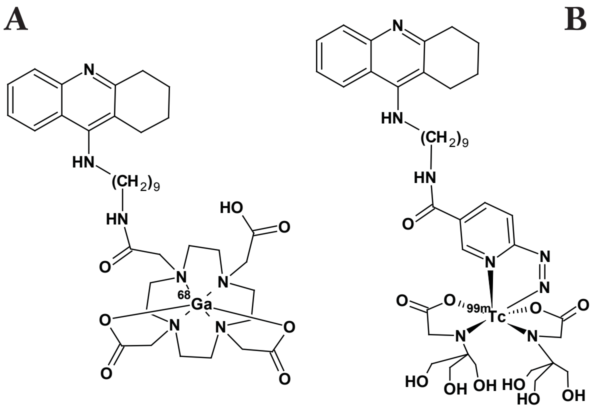

Fig. 1. Structures of tacrine derivatives containing: (A) DOTA chelator labelled with ^{68}Ga isotope, (B) HYNIC chelator in exemplary complex with ^{99m}Tc and two tacrine ligands.

Table 1. Results of inhibition activity against cholinesterases for tacrine derivative conjugates presented as each inhibitor concentration for 50% inactivation of enzymes (IC_{50}).

Inhibitors	IC_{50} ± SD [nM]	
	AChE	BuChE
[^{99}Tc]Tc-HYNIC-(NH(CH_2)$_9$Tacrine)	101 ± 14	1024 ± 160
Ga-DOTA-(NH(CH_2)$_9$Tacrine)	189 ± 20	156 ± 13
Tacrine	306 ± 19	35 ± 3

Previously we have determined very high stability in biological fluids (human cerebrospinal fluid and blood plasma) of both radioconjugates and set their logP values (-1.38 ± 0.01 for ^{99m}Tc-radioconjugate and -1.52 ± 0.01 for ^{68}Ga-radioconjugate), based on these results we suspected that obtained complexes possess sufficient lipophilicity in terms of their ability for BBB transfer [4]. Furthermore, *in vitro* biological studies have shown that both analysed conjugates are more active inhibitors against acetylcholinesterase than tacrine.

Our goal of pharmacodynamic evaluation of both radioconjugates was carried out using two procedures in Wistar rats. The first was based on dynamic PET/CT imaging after intravenous application of [^{68}Ga]Ga-DOTA-(NH(CH_2)$_9$Tacrine in order to register radioconjugate dynamic biodistribution. Whereas the second consisted of each radioconjugate intravenous application, followed by euthanasia of the animal at certain time points in order to perform *ex vivo* radioactivity measurements of desired tissues.

51 Wistar male rats 4-5 weeks of age were obtained from the animal facility at the Mossakowski Medical Research Centre, Polish Academy of Sciences (Warsaw, Poland). All experimental procedures were performed according to the national legislation and were approved by First Local Ethical Committee of the University of Warsaw, Faculty of Biology (Permission No. 510/2018). Rats were kept under constant conditions of 12 h/12 h light cycle, humidity at 55 ± 10%, and temperature at 22 ± 2°C in individually ventilated cages with free access to drinking water and standard laboratory diet. Any procedures were performed after a minimum of 5 days acclimation after travel. All efforts were made to minimize animal suffering.

Dynamic acquisition experiments were performed with 6 rats using Albira PET/SPECT/CT

Preclinical Imaging System (Bruker, Germany). Before each imaging, rats were anaesthetized on a heating pad with 3.5-4% isoflurane (Aerrane, Baxter Polska Sp. z o.o., Poland) in oxygen applied through a nose cone. Prepared rats were placed in the prone position on the suitable bed place in the imager, afterwards 2-15 MBq [^{68}Ga]Ga-DOTA-NH(CH$_2$)$_9$Tacrine was administered intravenously through the tail vein cannula. Through the course of image acquisition respiration was monitored and regulated by adjusting the concentration of the anaesthetic. Spatial resolution of PET measurements was 1.5 mm and scan parameters were set as follows: tube voltage – 45 kV, tube current – 400 μA, projections number – 400. Minimal resolution of CT was 90 μm. The scans from both tomographies were fused and coregistered using PMOD software, since rats remained in the same position on the bed for both PET and CT acquisitions. After acquisitions still anaesthetized rats received a lethal dose of 5% isoflurane until respiratory system completely stopped, they were then decapitated and sacrificed for further radioactivity measurements of internal tissues for the second procedure. Based on six executed PET imaging, mean standardized uptake values (SUVs) for brain, kidneys, lungs, heart and liver were plotted in function of acquisition time (Fig. 2) and a selection of sagittal plane scans were isolated (Fig. 3). This imaging enabled a qualitative view of radioconjugate pharmacodynamics in the tissues of interest and confirmed the ability of [^{68}Ga]Ga-DOTA-NH(CH$_2$)$_9$Tacrine to cross the BBB.

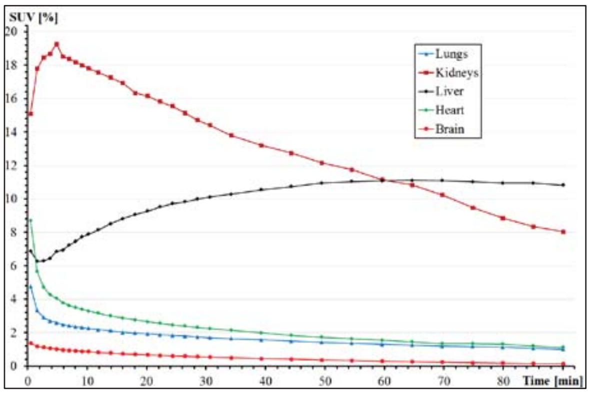

Fig. 2. [^{68}Ga]Ga-DOTA-(NH(CH$_2$)$_9$Tacrine pharmacokinetics determined by PET dynamic imaging.

Static pharmacodynamic analysis was performed for both radioconjuagtes using similarly applied intravenous applications of 2-15 MBq [^{68}Ga]Ga-DOTA-NH(CH$_2$)$_9$Tacrine (20 rats) or 33-62 MBq [^{99m}Tc]Tc-HYNIC-NH(CH$_2$)$_9$Tacrine (25 rats) under anaesthesia. Then in 5th, 15th, 30th, 60th and 150th min (last one only for ^{99m}Tc radioconjugate, additional time points for ^{68}Ga radioconjugate were taken from dynamic PET imaging and classified as 135th min) animals were euthanized by reanaesthetizing using a lethal dose of isoflurane administration followed by decapitation. From each sacrificed animal the whole brain, blood sample (about 5 mL), both kidneys, lungs, heart, spleen and whole liver were isolated and weighed for radioactivity measurements. Each sample was analysed on WIZARD^2 2480 Automatic Gamma Counter (PerkinElmer, Inc., USA) in 60-second triple measurements with decay correlation protocol. Collected radioactivity data was converted into the tissue per cent of initial dose administered into the rat divided by tissue mass in grams (%ID/g), then their statistical relevance was examined in three sigma tests, and finally their averages were plotted in the function of time points in which the animal euthanasia was executed (Fig. 4-11). To each plot an initial point was added of the coordinate system representing the absence of radioconjugate at 0th min time point.

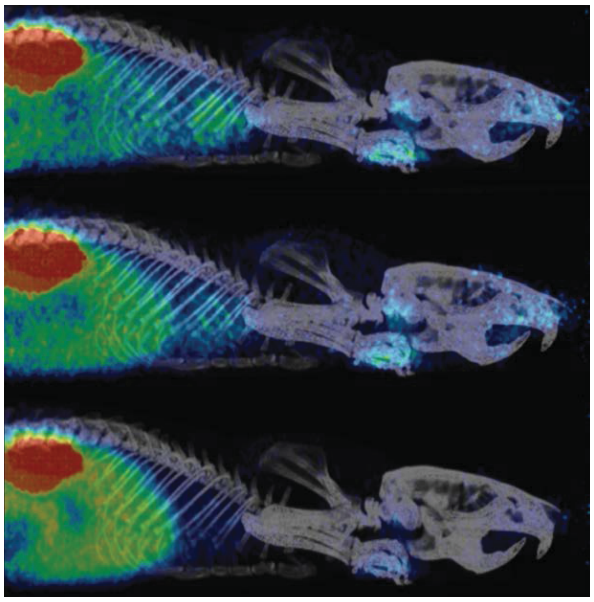

Fig. 3. Three sagittal plane scans (PET dynamic imaging with CT scan fusion) of Wistar rat in 5th (top scan), 15th (medium scan) and 30th min (bottom scan) after injection of [^{68}Ga]Ga-DOTA-(NH(CH$_2$)$_9$Tacrine.

Ex vivo radioactivity measurements provide simple comparison levels of action between both radioconjugates. Crucial differences are presented in uptake levels of radioconjugates in certain regions of interest and in the way of excretion from the body. [^{99m}Tc]Tc-HYNIC-NH(CH$_2$)$_9$Tacrine showed markedly higher uptake in all analysed organs, and had a 4-fold higher brain uptake than gallium-tacrine derivative. Similarly, the blood concentration of first radioconjugate was higher than the second one, due to the longer effective half-life of [^{99m}Tc]Tc-HYNIC-NH(CH$_2$)$_9$Tacrine in rats. Both values of effective half-life were determined theoretically, based on plotted relation of per cent of administrated activity in blood in function of time. Excretion of radioconjugates presumably occurs through involvement of both liver and kidneys, however [^{68}Ga]Ga-DOTA(NH(CH$_2$)$_9$Tacrine showed that the hepatic clearance route had a noticeable greater influence. In general, the changes in radioactivity of both organs were similar in time, and were maintained after 30 min.

In conclusion, we confirmed the ability of analysed radioconjugates to cross BBB into the brain

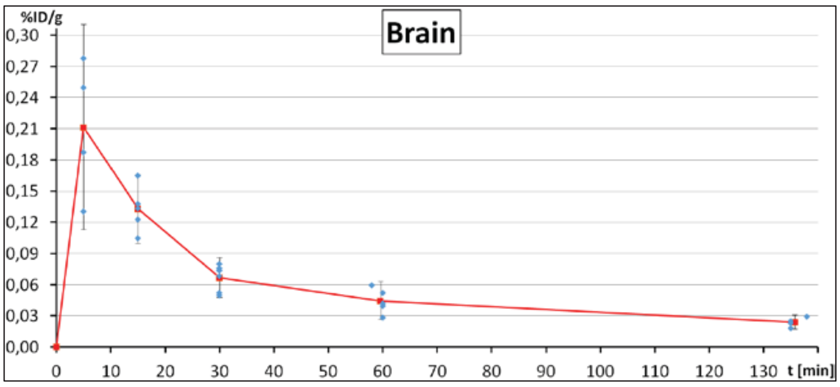

Fig. 4. Results of [^{68}Ga]Ga-DOTA-(NH(CH$_2$)$_9$Tacrine pharmacokinetics in rat brains determined by *ex vivo* radioactivity measurements.

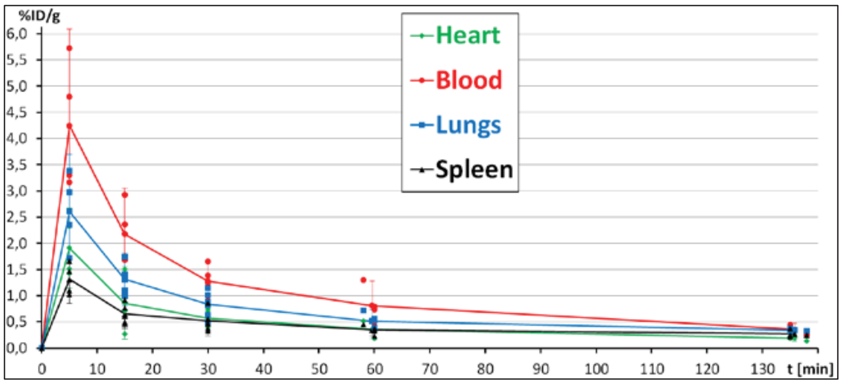

Fig. 5. Results of [^{68}Ga]Ga-DOTA-(NH(CH$_2$)$_9$Tacrine pharmacokinetics in rat blood samples, hearts, lungs and spleens determined by *ex vivo* radioactivity measurements.

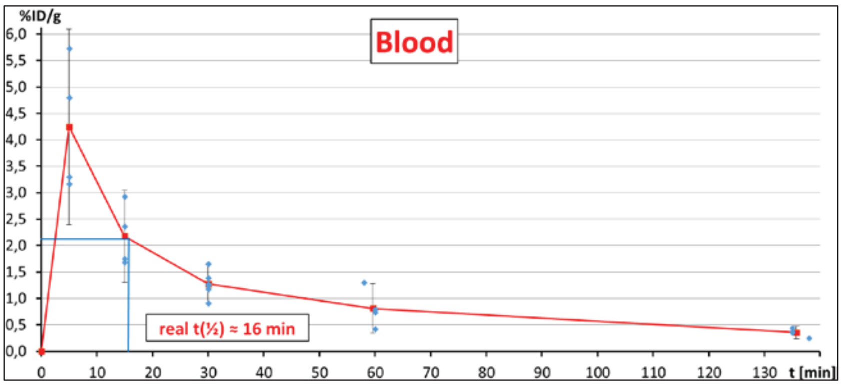

Fig. 6. Results of [^{68}Ga]Ga-DOTA-(NH(CH$_2$)$_9$Tacrine pharmacokinetics in rat blood samples determined by *ex vivo* radioactivity measurements, with a real half-life of radioconjugate determination from the chart.

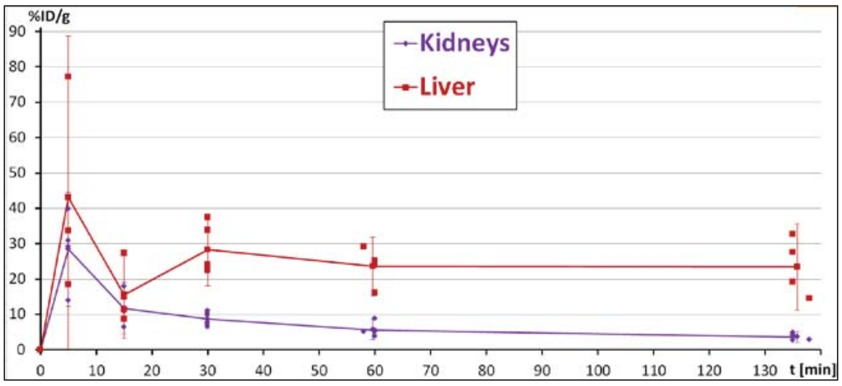

Fig. 7. Results of [^{68}Ga]Ga-DOTA-(NH(CH$_2$)$_9$Tacrine pharmacokinetics in rat livers and kidneys determined by *ex vivo* radioactivity measurements.

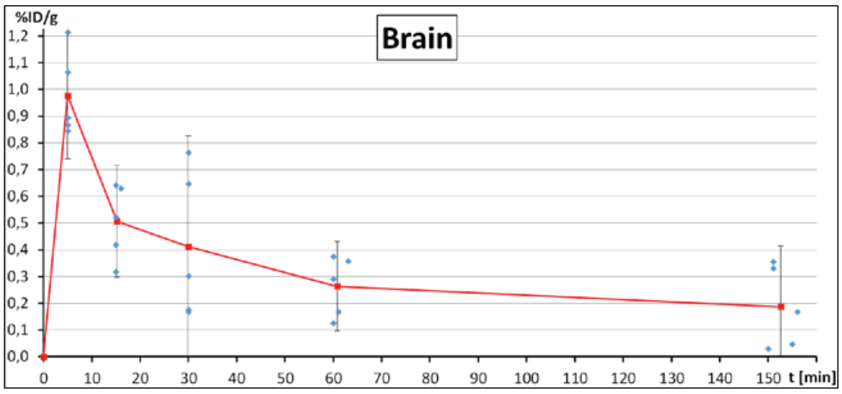

Fig. 8. Results of [^{99m}Tc]Tc-HYNIC-(NH(CH$_2$)$_9$Tacrine pharmacokinetics in rat brains determined by *ex vivo* radioactivity measurements.

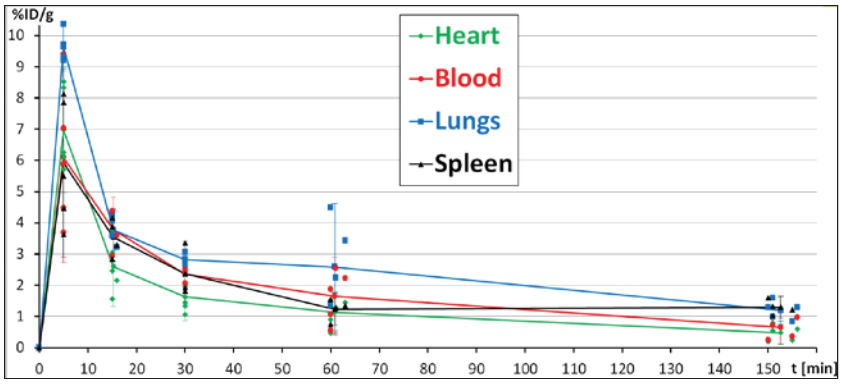

Fig. 9. Results of [^{99m}Tc]Tc-HYNIC-(NH(CH$_2$)$_9$Tacrine pharmacokinetics in rat blood samples, hearts, lungs and spleens determined by *ex vivo* radioactivity measurements.

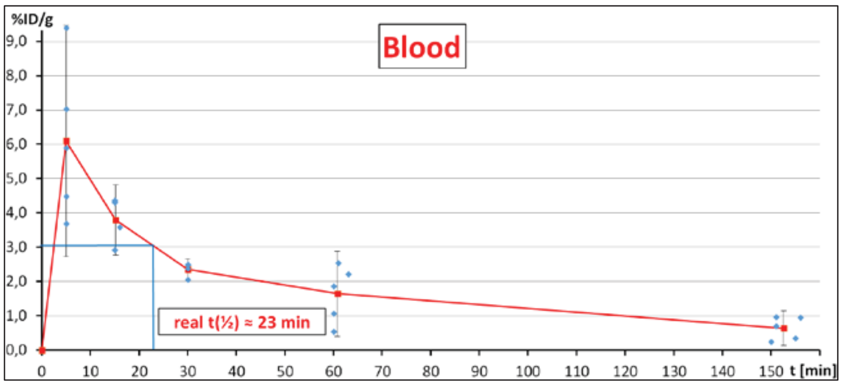

Fig. 10. Results of [^{99m}Tc]Tc-HYNIC-(NH(CH$_2$)$_9$Tacrine pharmacokinetics in rat blood samples determined by *ex vivo* radioactivity measurements, with a real half-life of radioconjugate determination from the chart.

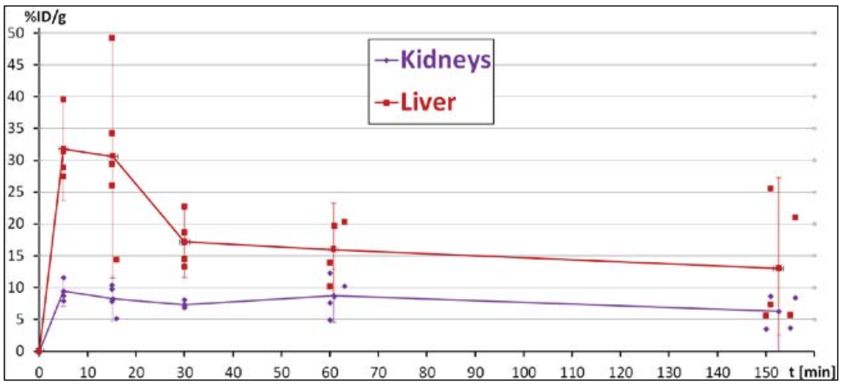

Fig. 11. Results of [^{99m}Tc]Tc-HYNIC-(NH(CH$_2$)$_9$Tacrine pharmacokinetics in rat livers and kidneys determined by *ex vivo* radioactivity measurements.

of rats. Wistar rat model, known as universal, multifunctional and safe, shows its effectiveness in distinguishing and assessing certain regions of interest in dynamic PET imaging. Additionally, all studies were performed using more than year old conjugate kits (sets for in hospital use, containing the lyophilized form of appropriate amounts of reagents needed for the synthesis of a given radiopharmaceutical) reaching labelling yields greater than 95% in every case. From a clinical application point of view we confirmed many crucial aspects of the studied radioconjugates, which must be strictly fulfilled by the potential diagnostic radiopharmaceuticals [10]. Both tacrine derivative radioconjugates show potential applicability in diagnosis of cholinergic neurosystem changes caused by Alzheimer's disease.

The presented work was financial supported by the statutory activity of the Institute of Nuclear Chemistry and Technology.

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APPLICATION OF ELECTRODIALYSIS IN THE PROCESSING OF LIQUID RADIOACTIVE WASTE

Grażyna Zakrzewska-Kołtuniewicz, Agnieszka Miśkiewicz

In this paper, the possibility of using electrodialysis process for the treatment of liquid low-level radioactive waste was investigated. This type of waste creates a considerable problem because of their large volumes, as well as low levels of radioactive substances. The first stage of processing liquid low-level waste is the concentration with volume reduction. In addition to radionuclides, liquid radioactive wastes may also contain high concentrations of inorganic non-active salts and organic compounds (organic solvents, complexing agents, detergents, decontamination liquids, *etc*.). The complex nature of such waste requires sophisticated hybrid techniques for their disposal. Membrane processes employed for liquid radioactive waste treatment offer a number of advantages with high decontamination factors, large volume reduction and low energy consumption [1-3]. Electrodialysis – one of these processes, can be also promising technique due to the possibility of concentration of ionic compounds (*e.g.* inorganic salts, radioactive ions) as well as the separation of ionic from non-ionic substances (*e.g.* organic compounds) [1, 4].

Electrodialysis is a membrane technique using ion-exchange membranes in which the electric potential is the driving force. Such membranes are composed of a polymer network with its associated ionic groups (fixed ions). In cation-exchange membranes, the groups immobilized in the polymer matrix are usually sulphonate groups, with strongly acidic properties or carboxyl groups, of weak acidic properties. In anion-exchange membranes, ion-exchange groups are strongly basic quaternary ammonium groups; amino groups of lower bond order give weakly basic properties to the membranes. Electrodialysis has many advantages, including low-pressure operation, low lifecycle cost, easy maintenance, tunability (easy change of input-output) and adjustable footprint [5]. Therefore, this process has been widely employed across numerous fields, such as the desalination of seawater and concentration of salt solutions, removal or recovery of heavy metals, elimination of hazardous compounds from wastewater, and separation of amino acids and proteins [6-8]. Furthermore, electrodialysis has been also studied as an alternative method for radioactive waste treatment [9-11]. Reports have shown that this membrane process is suitable for removal of ^{137}Cs, ^{90}Sr, ^{106}Ru and fission products from low- and medium-level radioactive waste solutions [9] as well as for removal of iodide ion [10] and uranium separation [11] from radioactive waste.

In the present work the possibility of applying electrodialysis process for the ^{137}Cs and ^{60}Co removal from water solutions has been tested. The first part focused on the investigation of the influence of the electric current value and initial concentration of the feed solutions on the process performance. The effects of the initial salinity of non-radioactive model solutions in the electrodialysis process were tested using three different voltages: 5, 10 and 20 V, and the experimental results are presented in Fig. 1. The results show that the salinity decreases very fast as the process proceeds, the significance of which depends on the voltage applied.

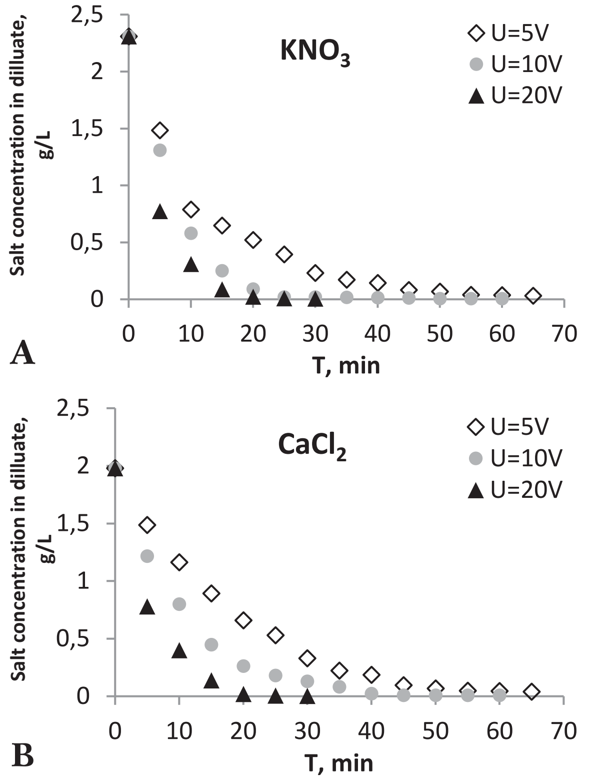

Fig. 1. The variation of salt concentration in diluate during electrodialysis process of model solutions containing salts: KNO_3 (A), $CaCl_2$ (B).

In the next stage, the effect of the initial feed concentration on the efficiency of the electrodialysis process was examined. For this purpose three concentrations of NaCl solutions were used: 1, 2 and 10 g/L and the process was carried out using voltage 20 V. Results of these experiments are displayed in Fig. 2, and show that the initial feed concentration increases, with increasing time necessary to completely remove the ions from solution. For example, for 1 g/L NaCl solution, the time required for effective purification was 15 min, while for solutions with higher concentrations, *e.g.* 2 g/L and 10 g/L, the time was extended to 25 min and 35 min, respectively.

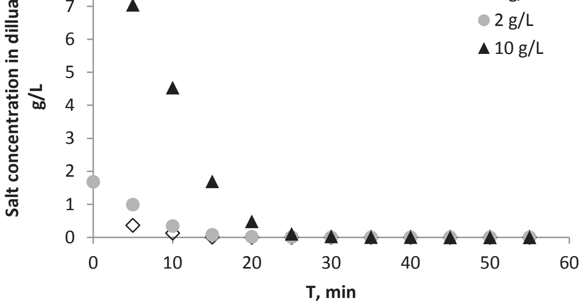

Fig. 2. Variability of salt concentration in diluate during the electrodialysis at various initial concentrations of NaCl; U = 20 V.

Subsequent experimental works were conducted using solutions containing selected radionuclides (^{60}Co and ^{137}Cs), the potential contaminants of effluents from a nuclear power plant. These studies demonstrated the high efficiency of electrodialysis for the decontamination of solutions containing radionuclides (Fig. 3). In the case of ^{137}Cs, its complete removal from solution occurred after 60 min of the process at 20 V. The removal of ^{60}Co required 40 min of the process under the same conditions.

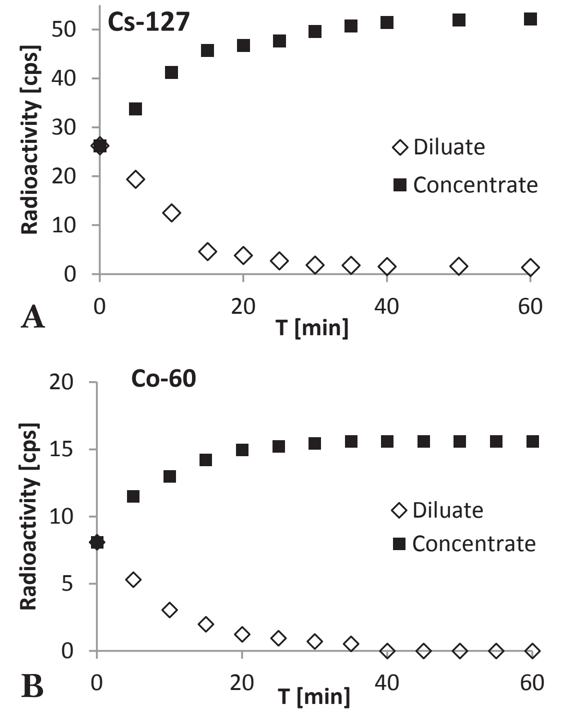

Fig. 3. Variability of radioactivity of diluate and concentrate streams during electrodialysis of model solutions containing ^{137}Cs (A) and ^{60}Co (B) radionuclides; U = 20 V, Fd = Fk = 15 L^{-1} h, I = 0.2 A.

The results of experiments performed proved that electrodialysis can be suitable for liquid radioactive waste treatment, ensuring high desalination and decontamination rates. One of the most important parameters influencing the process is voltage of electric current applied. For experiments conducted at high voltage electrodialysis was faster than those at lower voltage. The results also show the total salinity of the solution affects the duration of electrolysis. Experiments with solutions containing organic contaminants showed their elimination from the concentrate of ionic species remaining in diluate stream. On the basis of this study, it has been found that electrodialysis is a prospective process that can be used for the treatment of liquid radioactive waste with a complex composition.

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RE-USAGE OF WASTE PET CANISTERS BY THE PRODUCTION OF THE ACTIVATED CARBON ADSORBENT FOR REMOVAL OF THE RADIONUCLIDES FROM AQUEOUS SOLUTIONS

Leon Fuks, Irena Herdzik-Koniecko, Marcin Rogowski

Polyethylene terephthalate (PET) is widely used as a raw material for a multitude of products *e.g.* different packaging materials, mainly bottles or containers for food products. However, continuously increasing and improper use of plastics results in serious environmental issues, including adverse effects to human health (*e.g.* the carcinogenicity). Therefore, any novel proposition for the re-usage of plastics, even on small scale, is welcomed.

Carbonization of PET wares results in activated carbon (AC) formation, unique materials of great industrial significance [1-4]. ACs are materials of high specific surface area and great porosity, so are useful in a great number of technological processes [5]. They are used, among others, for removing pollutants (both gaseous and liquid). The advantage of these materials is manifested in high purity of the effluents and extremely low cost of purifying the material. In addition, purification processes based on the application of ACs are simple to design and easy in operation. Finally, ACs are resistant to corrosive (acidic and basic) conditions and non-toxic [6]. Therefore, application of metal solid extraction (sorption) on ACs for management of wastewaters as well as radioactive liquid wastes (RLWs) seems a potential processing method [7, 8].

In this work, a method for obtaining carbonic material by pyrolysis of waste PET canisters was examined and its sorption characteristics described and discussed. Namely, we investigated sorption of Cs(I), Sr(II), Co(II) and Am(III) metal ions in relation to the factors influencing the management of radioactive LWs. Additional physicochemical properties of the expected sorbing material was also determined.

Carbonization of the PET material

Carbon powder was prepared in accordance with the method published in Ref. [4]. Waste mineral water bottles made from PET, were cut into ~ 1 cm^2 segments, and carbonized under a stream of nitrogen (10 $dm^3 h^{-1}$) in quartz crucibles, then placed into a high-temperature vacuum furnace (Nabertherm, VHT series). 5 g samples of PET were heated from room temperature to 1098 K at a rate of 1 K min^{-1}, then were kept at the final temperature for 30 min. Obtained samples of PET carbon were cooled under a nitrogen atmosphere at the same speed, giving a yield of about 20%.

Samples of raw carbon were subjected to chemical activation. Activation of carbon was made with the following activating agents: zinc chloride ($ZnCl_2$), calcium chloride ($CaCl_2$), phosphoric acid (H_3PO_4), potassium hydroxide (KOH), nitric acid (HNO_3) and hydrochloric acid (HCl). In all cases, 3 g of raw carbon were suspended in aqueous solutions containing the activating agent (30% of mass) and stirred at 85°C for 7 h with a magnetic stirrer. Then the samples were filtered, washed with a large amount of deionized water (until the neutral pH was obtained) and dried at 110°C overnight. After drying, the samples were crushed into a fine powder. To make activated carbon, carbon was reacted with hydrogen peroxide [9], ~ 3 g of the crude material was placed into 20 mL of 10% H_2O_2 solution for 2 h at room temperature, then rinsed with deionized water and dried at 80°C overnight and stored.

When checking the homogeneity of the bulk sample of the AC, five randomly selected 50 mg lots of the sorbent were equilibrated with equal volumes of the initial solution containing ^{60}Co radionuclide. It has been found that all values of the solution decontamination factor (DF) did not differ from the median of more than 1%. So, the material was assumed as homogeneous and suitable for further studies.

The obtained AC, after grinding, was also analysed for the total carbon content (TOC), showing 99.32 ± 1.03% carbon content.

Adsorption studies

50 mg of adsorbent was agitated in the polyethylene vials with 10 mL of aqueous solution containing radionuclides for 6 h. When the effect of contact time was studied, solutions were contacted with sorbent for 10 min or 30 min, 1, 2, 3, 6 and 24 h, independently. Then, the system was centrifuged, the supernatant solution was withdrawn and analysed radiometrically to determine the concentration of the radionuclides. Mean values of the radioactivity concentrations were calculated from at least 3-5 independent measurements. The initial solution also was analysed.

Each experiment was made in triplicate, from which the average value was calculated.

Results of sorption the radionuclides were calculated as the decontamination factors (removal effectiveness, DF) expressed in percents.

Commercial Norit CNR116 activated carbon was used as the reference material in the studies of radionuclide sorption. Before use, Norit carbon was demineralized in 10% HCl to remove inorganic impurities, which appeared to be absent in the material obtained from PET.

Results

Activation of the carbon

The production of ACs with the desired pore structure commonly requires using at least one from a large number of activating agents. The purpose of activation is to form and/or increase porosity in AC (both, volume and size), hence enhancing adsorptive properties. All available methods of activation are divided into two groups: physical and chemical activation. Each of these methods have advantages and disadvantages.

Chemical activation, performed in this work, was realized by treating the raw material with certain chemical agents. Solutions of $CaCl_2$, $ZnCl_2$, HNO_3, HCl, H_3PO_4, KOH or H_2O_2, respectively, were tested.

Cumulative graph presenting the decontamination of the radioactively contaminated solutions by the differently activated PET carbon is presented in Fig. 1. We found that the $ZnCl_2$ activation allows sorbent production, which may be compared with production of sorbent commercial Norit CNR116 activated carbon designed for sorption heavy metals from aqueous solutions.

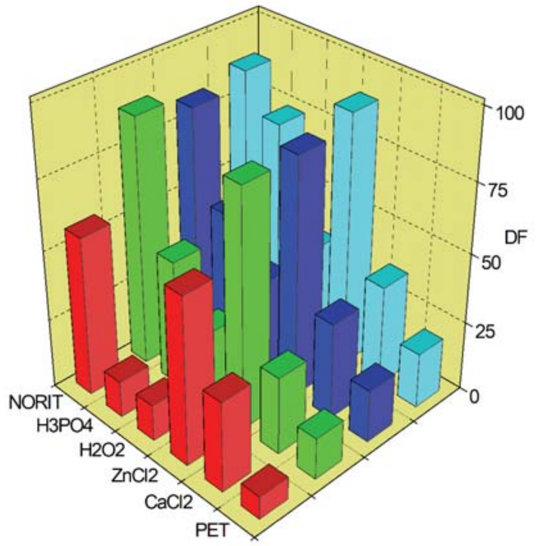

Fig. 1. Removal the radioactive metals on differently activated PET carbon and Norit CNR116 (as a reference material).

The FTIR spectrum registered for AC prepared by $ZnCl_2$ treatment was compared with the raw material. The obtained value of the Pearson's correlation coefficient numerically calculated for the spectra presented is 0.998 and is close to ideal. This value suggests, that no significant change in chemical structure occurs during the activation process.

The carbonaceous materials and coals have specific structural properties, which change from typically amorphous to completely graphitic crystalline structure. X-ray diffractograms (XRD) of PET carbon and Norit CNR116 materials are shown in Fig. 2.

Diffractogram of PET carbon shows two pronounced, but broad, bands placed near $2\Theta = 23.2^{\circ}$ and 43.7°, which are known characteristics of the graphitic structure [10]. The diffraction pattern of Norit CNR116, in turn, shows an amorphous structure.

Impact of the equilibration time on the sorption

Establishing the time needed to reach equilibrium, as well as studies on changes of the radionuclide concentration with increasing equilibration time, is the main factors involved in improving sorption technologies based on newly developed sorbents.

To study the effect of contacting time on sorption efficiency, values of DF were determined for four metal ions. In details, samples were shaken in 10, 30, 60, 120, 180, 360 and 1440 min intervals. All other parameters were kept constant for all samples (nca concentration of the radioactive metal ions; pH 5; sorbent dose – 5 g dm^{-3}). Results

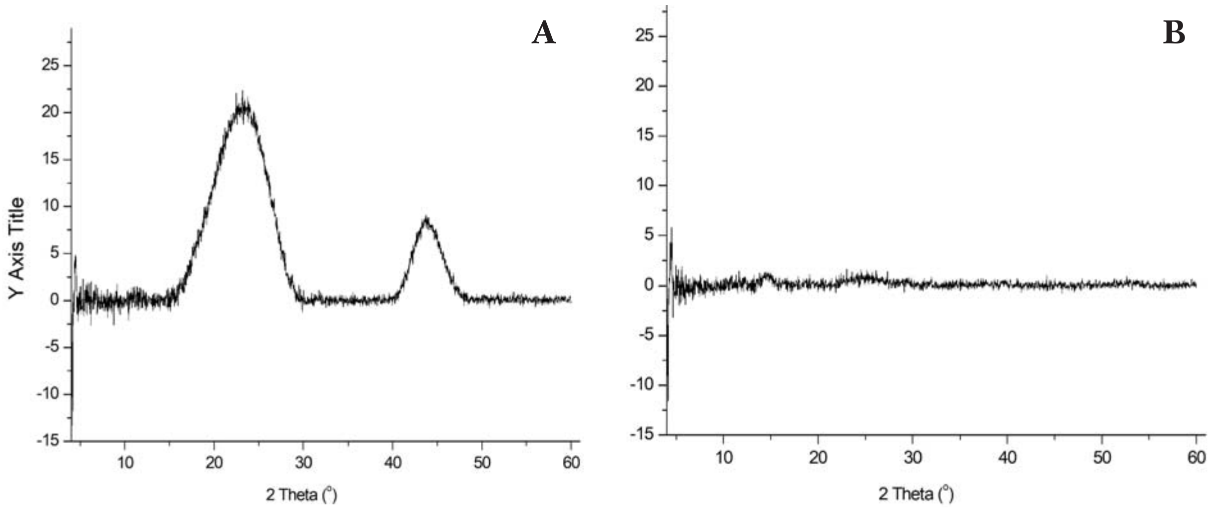

Fig. 2. XRD of PET carbon activated with (A) $ZnCl_2$ and (B) Norit CNR116 reference material.

of sorption efficiency (DF) *vs.* time are shown in Fig. 3. Removal of mono-, di- and trivalent radioactive metal cations by activated carbon reached values of about 80% for Am(III), 70% for Co(II), 50% for Sr(II), but only 15% for Cs(I) within the first 60 min. For all metals, sorption efficiency reached a plateau within 6 h. Prolongation of the shaking-time did not provide any notable DF increase.

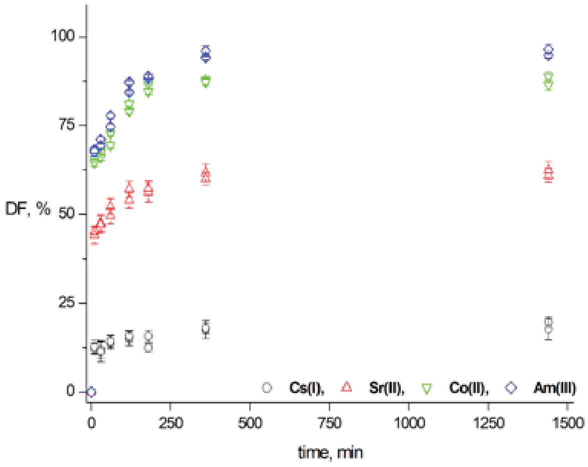

Fig. 3. Effect of contact time on removal of the mono-, di- and trivalent radioactive metal cations by the PET carbon.

As mentioned above, commercial Norit CNR116 activated carbon was used as the reference material for studying sorption of the radionuclides. Mean values of DF after 6 h shaking period were about 90% for Am(III), Co(II) and Sr(II), but only about 60% for Cs(I). All values are higher than the respective values for PET activated carbon. However, it must be noted that both production and activation procedures of the tested in this work carbon sorbent need further optimization.

Comparison of the correlation coefficient values (R2) of fitting experimental data for the increasing part of the curves with the main kinetic equations shows that sorption of any metal ion studied within this work is the best described using the pseudo-second order model. Hence, the rate-limiting step is the surface adsorption based on the chemical bond formation between the sorbate and sorbent [11]. However, the obtained values of correlation coefficients show that intra-particle diffusion model of Weber and Morris cannot be completely excluded.

Effect of the amount of sorbent

To find the mass of sorbent necessary for optimum sorption efficiency of the radiometals, at a constant radionuclide concentration (nca amount) eight different amounts of carbon sorbent was examined ranging from 1-20 g L^{-1}. The results obtained are shown in Fig. 4. As adsorbent dosage increased, whilst all other parameters remained constant, for any radiometal removal efficiency first increased (up to the dosage 5 g L^{-1}) until it reaches a plateau. This trend is attributed to an increase in the number of sorption centres, which (assuming the homogeneity of the material) is proportional to the mass of sorbent. Above 5 g L^{-1} carbon dose, a number of the sorption centres exceed the amount of the sorbate, resulting in the sorption equilibrium depending on the mass low.

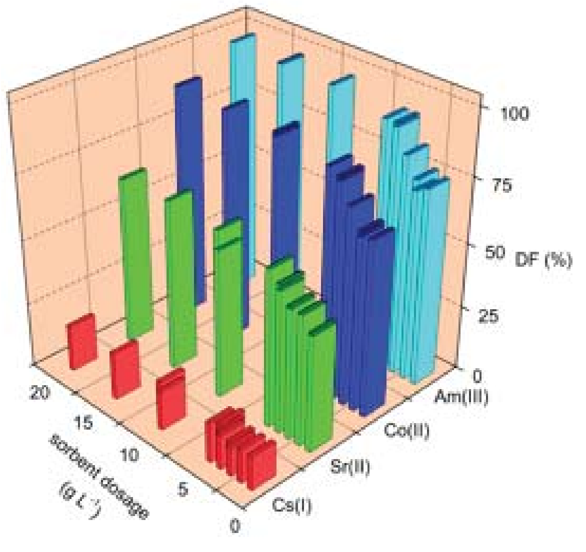

Fig. 4. Effect of the adsorbent dosage on the sorption efficiency of four radioactive metal cations.

Therefore, 5 g L^{-1} of sorbent per litre of purified solution is an adequate amount for the proposed procedure.

Effect of pH

Among the most important factors in metal adsorption is acidity of the solutions. This parameter in many cases determines the surface charge of the adsorbent, as well as the speciation of metals. The effect of pH was studied over a broad range ~ 11 units. Obtained results, presented in Fig. 5, show that the removal efficiency of any radiometal studied in the work passes through a maximum in the region of pH 5-8. This value is in good accordance with the other reports on heavy metal ion sorption.

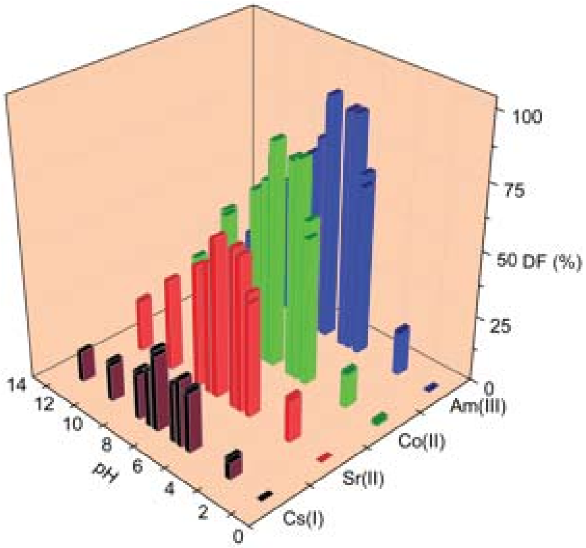

Fig. 5. Influence of pH on the efficacy of PET carbon for the mono-, di-, and trivalent radioactive metal cations.

Desorption (recycling of the sorbent)

The binding strength of the radioactive metals by sorbent was investigated in the consecutive desorption experiments. Samples of the carbon loaded with four radionuclides were shaken with five subsequent portions of fresh water, each portion of the supernatant was centrifuged (20 min, 14 000 rpm) and radiometrically analysed. As shown in Fig. 6, all radionuclides placed in the surface pores of the sorbent were expelled in the first desorption cycle. After three consecutive washing stages of the carbon constant recovery ratio values were achieved. In detail, they appeared to be: 0.52 ± 0.32% for Cs(I), 0.48 ± 0.20% for Sr(II), 0.82 ± 0.20% for Co(II), and 0.64 ± 0.15% for Am(III). Such small values show, that if fixed by AC, all radionuclides may be safely stored as solid phase matter in the radioactive waste repository. The values of Norit reference sorbent are slightly larger, *i.e.* 1.29 ± 0.40% for Cs(I), 0.93 ± 0.26% for Sr(II), 1.21 ± 0.26% for Co(II) and 0.94 ± 0.22% for Am(III).

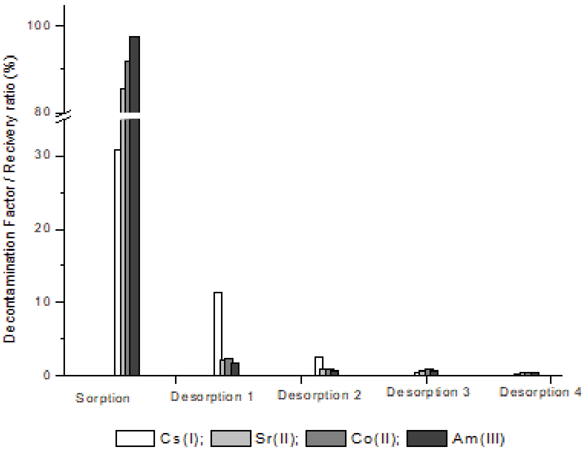

Fig. 6. Desorption of mono-, di- and trivalent radioactive metal cations from PET carbon previously loaded with these metals.

Adsorption capacity

The amount of metal ions that are adsorbed per unit mass of the adsorbent (*i.e.* the adsorption capacity, CEC) for the studied materials was defined using natural strontium chloride ($SrCl_2$; non-radioactive salt) as the chloride source. After shaking the materials with $SrCl_2$ solution and separation of phases, initial and equilibrium solutions were analysed for the content of Sr(II) using ion chromatography method. We found that CEC for the solution at pH 6 is 21 mg g^{-1} for raw carbon and 27 mg g^{-1} for the $ZnCl_2$ AC. For the reference material, Norit CNR116, this value is twice larger (52 mg g^{-1}). Additionally, CEC for Co(II) and Cs(I) of raw carbon are 18 mg g^{-1} and 17 mg g^{-1}, respectively.

One should remember, however, that both procedures of the raw carbon preparation and its activation should be optimized in the future.

Surface area and porosity

Surface area and porosity of the sorbent grains are key properties that determine the metal sorption capacity. In the course of pyrolysis used in the synthesis of the carbon, pores are created in the material varying in size and micropores as a result of dehydration and water loss [12]. Dimension of these pores vary from nano- (< 0.9 nm), through micro- (< 2 nm), up to macro-size (> 50 nm) and dictate metal sorption capacity as the small pores

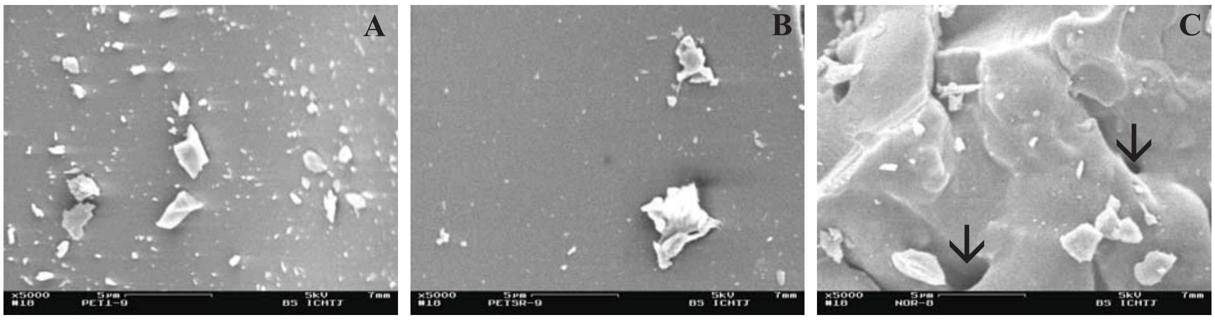

Fig. 7. SEM images (magnification ×5000) of the (A) raw carbon material, (B) AC saturated with $SrCl_2$ and (C) Norit CNR116.

cannot trap large-size sorbate molecules, independent of charge or polarity [13].

Values of the specific surface area and pore volume of the raw carbon, AC $ZnCl_2$ activated and Norit reference materials were determined from low-temperature nitrogen adsorption data. The samples were degassed at 77 K before measurements. The surface area is 0.1048, 0.0454 and 1743 $m^2 g^{-1}$, respectively. The cumulative surface area of pores between 1.7 nm and 300 nm diameter, calculated based on the theory proposed by Barret, Joyner and Halenda (BJH), is 0.117, 0.159 and 616 $m^2 g^{-1}$, respectively. SEM images of AC and Norit materials (Fig. 7) confirm the finding that AC surface is poorly porous.

Conclusions

Decontamination of radioactively contaminated aqueous solutions using activated carbon obtained by carbonization of PET canisters was found to be effective in the case of ^{137}Cs(I), ^{85}Sr(II), ^{60}Co(II) and ^{241}Am(III) radionuclides.

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COMPARISON OF TOA AND D2EHPA FOR EXTRACTION OF MOLYBDENUM, VANADIUM AND URANIUM FROM LEACH SOLUTIONS OF COPPER ORE AND FLOTATION WASTES

Tomasz Smoliński, Marcin Rogowski, Danuta Wawszczak, Tadeusz Olczak, Marta Pyszynska, Marcin Brykała

Hydrometallurgical processes are multistep. Ore or concentrate is crushed and milled, and subjected to enrichment by physical processes and subsequent leaching. At this stage, metal compounds insoluble in water, are converted into soluble salts suitable for other operations. The composition of the leach solution is chosen depending on the type of raw material subjected to leaching, which includes acids – H_2SO_4, HCl, HNO_3; hydroxide – NaOH; chlorides – NH_4Cl, $FeCl_3$; or carbonates – Na_2CO_3, $(NH_4)_2CO_3$ [1-5]. The resulting aqueous solution contains many metal ions, which must be selectively isolated. The extraction of metal ions from aqueous solution is a prospective method for the concentration, separation and preparation of high purity metal. It allows the possibility of utilizing poor mineral resources, semi-finished products and industrial waste containing small quantities of the metals. Isolation and separation of ions is achieved

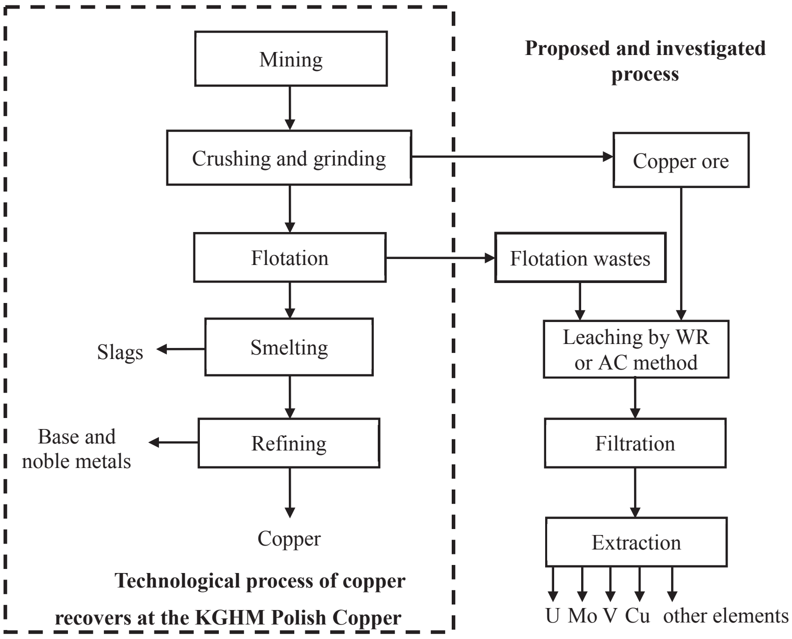

Fig. 1. The proposed process for the processing of flotation wastes.

through particular multiple folded extractants and are useful for process applications [6]. The Institute of Nuclear Chemistry and Technology (INCT) has vast experience in the application of different hydrometallurgical processes for metal recovery is a major advantage [7]. In recent years, the INCT has studied the possibility of uranium recovery, as well as other elements, produced as by-products in the preparation of copper concentrate from copper ore mined in Zagłębie Lubińskie [8-10].

The samples used in the experiments were collected by the Polish Geological Institute – National Research Institute. The main components of the ore samples from deposits in the Lubin region were: chalcocite (Cu_2S, 29.2%), bornite (Cu_5FeS_4, 47.5%) and chalcopyrite ($CuFeS_2$, 23.1%). The sample of flotation wastes was collected from the landfill reservoir in Gilów.

The material samples were ground to a powder and dried at 110°C for 2 h, then analysed using ICP-MS (inductively coupled plasma mass spectrometry). An ICP-MS instrument (ELAN DRC II PerkinElmerTM) with a cross-flow nebuliser and Scott double-pass spray chamber and Ni cones was used for measurements. Standard solutions (1 mg mL^{-1}) used in ICP-MS analyses were supplied by PerkinElmer. For the preparation of the ore samples, analytical grade reagents: Na_2O_2, HNO_3, $Li_2B_4O_7$, $LiBO_2$, were used. The uncertainty of elemental determination was estimated at 5-10% and depended on the elements: uranium – 5%, vanadium – 8%, molybdenum – 10%, due to the high inhomogeneity of the material.

The aim of this study is to develop a process of recovery of various valuable metals from copper ores and waste. The proposed process is illustrated in Fig. 1 with reference to the process of obtaining copper by KGHM. In the case of solvent extraction of metals, optimum leaching conditions were selected [11]. Samples were prepared in accordance with the following procedure: 250 mL of concentrated H_2SO_4 and 10 g of MnO_2 oxidant were added to 500 g of the powdered sample and the mixture was sintered at 150°C for 8 h. Subsequently, leaching was performed using 1000 mL 5% H_2SO_4 for 8 h and then filtered using a Buchner funnel. Sulphuric acid of analytical grade (Sigma-Aldrich) was applied as a leaching agent, and manganese dioxide as an oxidizing agent.

The following extractants were used for the recovery of molybdenum, vanadium and uranium:

- D2EHPA (di-(2-ethylhexyl)phosphoric acid, in toluene) with concentrations of 0.3, 0.2, and 0.1 mol dm^{-3}.
- TOA (trioctylamine) with concentrations of 0.3, 0.2, and 0.1 mol dm^{-3} in toluene.

Each of the three stages of extraction was carried out for 15 min with a 1:1 ratio of organic phase to aqueous phase. For the extraction, 15 mL of sample was taken. The time required to achieve complete separation of the phases was 30 min. The organic phase was back-extracted with 5% Na_2CO_3 for 15 min. Thirty minutes phase separation time, was allowed between each extraction step. The content of uranium, molybdenum and vanadium was chemically analysed by ICP-MS.

In this paper we present the results of extraction of the following elements: molybdenum, vanadium and uranium. ICP-MS analysis showed that copper was present at 44.975 ppm in ores and 12.225 ppm in flotation wastes. Notably, in the process other elements could be recovered as well as copper. These include vanadium, 1370 ppm in ore and 833 ppm in waste, or molybdenum, 358 ppm in ore and 22 ppm in waste (Table 1). Additional data regarding starting materials are presented in Ref. [1].

We compared the results of extraction of various metals from samples (leaching of ore and waste with sulphuric acid) of different D2EHPA and TOA concentrations. The results obtained

Table 1. Analytical data of selected elements in copper ores and flotation wastes.

	Mo [ppm]	V [ppm]	U [ppm]
Cu ore	358 ± 35.8	1370 ± 109.6	27 ± 1.4
Flotation wastes	22 ± 2.2	55 ± 4.4	4.5 ± 0.2

for the extraction of vanadium, molybdenum and uranium are shown in Figs. 2 and 3.

Uranium extraction efficiency as a percentage of element concentration in the leach solution varied in the range of 20% to almost 100%. Much higher extraction yield was observed when TOA was used as the extractant, with the highest recovery rate of metals 99% observed at 0.1 M. Vanadium extraction had greater efficiency than uranium. Extraction from flotation wastes was relatively less than from copper ore, with the highest efficiency observed for D2EHPA – more than 64% for flotation wastes and 70% for copper ore. Similar results were observed for molybdenum – recovery was in the range of 65-90% for D2EHPA and 46-90% for TOA. Comparison of the extractants tested showed that a higher recovery of uranium was obtained using TOA while a higher recovery of vanadium and molybdenum was obtained using D2EHPA.

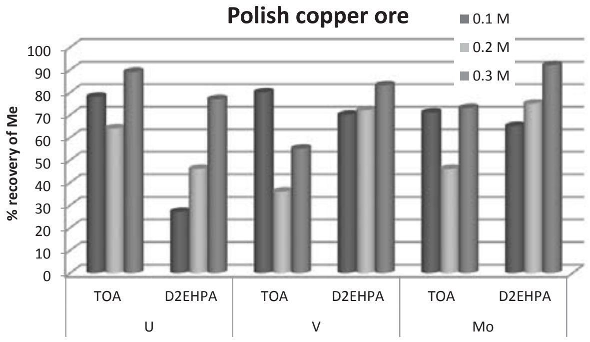

Fig. 2. Comparison of U, V and Mo extraction efficiency from Polish copper ore samples for TOA and D2EHPA, depending on various extractant concentrations.

The waste from a mine still contained vanadium, molybdenum and uranium. Tenths of a percent of copper contained in waste stored in waste reservoirs have no value from the point of view of pyrometallurgy. However, these concentrations are related to millions of tons of waste, and represent thousands of tons of toxic metals making it a kind of deposit of metals, such as molybdenum and other rare metals, for future generations. Therefore, since one of the stages of the process is extraction and cleaning of certain elements, hydrometallurgical methods using properly selected, selectively acting extractants are useful. In the present study, we compared the extraction of various metals from solutions of sulphuric acid that were leached from representative samples of Polish copper ore and flotation wastes from Gilów. Extraction tests of elements such as vanadium, molybdenum and uranium using TOA and D2EHPA were carried out. The results of recovery of these elements in the case of both extractants were satisfactory, but the use of TOA produced the best results.

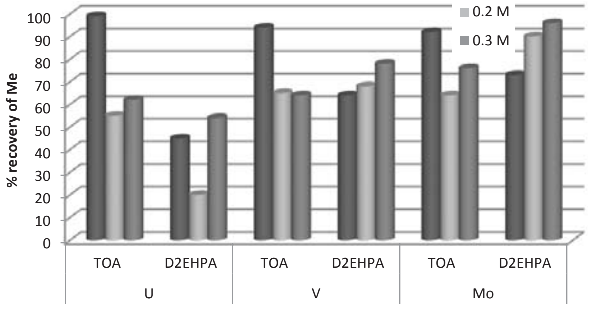

Fig. 3. Comparison of U, V and Mo extraction efficiency for flotation wastes samples for TOA and D2EHPA, depending on various extractant concentrations.

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THE POSSIBILITY OF OBTAINING RARE EARTH ELEMENTS FROM POTENTIAL SOURCES IN POLAND

Katarzyna Kiegiel, Agnieszka Miśkiewicz, Dorota Gajda, Irena Herdzik-Koniecko, Grażyna Zakrzewska-Kołtuniewicz

Rare earth elements (REE) are broadly used in industry. They are constituents of magnets and luminophores used in mobile phones and tablets, as well as in equipment for magnetic resonance, batteries for hybrid vehicles and hydrogen absorbing alloys, energy saving bulbs, *etc*. The applications of REE are really wide and the new ones are still being found. In most cases it is impossibile to replace these metals with other materials [1]. Unfortunately, due to increased demand of REE, their resources are being systematically depleted. From an economic point of view it is important to ensure continuity of REE supply, which can be achieved by exploration and exploitation of new deposits and recovery of REE from waste. In Poland there are some natural sources of REE. Lanthanides (Ln) were found in alkaline intrusive Baltic sands, Elk massif, granite rock of Szklarska Poręba, Huta quarry and Michałowice quarry (Karkonosze massif), Lower Silesia kaolinite and pegmatites of Bogatynia (Sudety mountains) [2-5]. However, these resources do not have a big impact on the national economy because of the relatively low concentration of the metals.

Secondary materials such as phosphogypsum, uranium tailings and the waste electrical and electronic equipment (WEEE) are considered as potential sources of REE.

Uranium mining residues in Poland are also rich sources of lanthanide metals [6, 7], with an average concentration of 64-110 ppm, but in certain post-mining sites even 1000 ppm is achieved [8].

REE can be also recovered from phosphate rocks that are used in phosphoric acid production. The metal content depends on rock type, sedimentary phosphate rocks possess 0.01-0.1 wt%, whereas igneous phosphate rocks have much higher content (1-2 wt%). In technological processes involving phosphoric acid production, *ca*. 70% of REE, present in the phosphate rocks, is transferred to the insoluble by-product – phosphogypsum. Poland imports phosphate rocks from Morocco, Tunisia and Syria, which are used for phosphoric acid production. Phosphogypsum from production of phosphoric acid is stored on the heaps in Police, Wizów and Wiślinka near Gdańsk. It is estimated that yearly, all plants in Poland produce *ca*. 2.2-2.6 mln tonnes of phosphogypsum. Examples of lanthanide concentration in the samples of phosphates of different origin [9] and in phosphogypsum stored on Wiślinka heap [10] are presented in Table 1.

Table 1. Lanthanide concentrations in the phosphates of different origin and phosphogypsum stored on Wiślinka heap.

Raw material	Lanthanide											
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb
	Concentration [ppm]											
Phosphorite from Morocco	90	38	14	62	13	3	18	3	18	4	14	13
Phosphorite from Syria	26	22	4	18	4	1	5	1	4	1	4	3
Phosphorite from Tunisia	64	100	13	55	11	3	12	2	9	2	6	5
Phosphogypsum	40	53	8	34	7	2	9	1	7	2	5	4

Other potential sources of lanthanides include fly ash. Average concentration of lanthanides in Polish fossil fuel, such as coal and lignite, is *ca*. 100 ppm. However, after incineration the total lanthanide concentration increases 3-4 times [11]. Assessment of Polish fly ash showed that REE concentration (including Y and Sc) is 101.1-443.3 ppm [12, 13]. The waste electrical and electronic equipment is also a very good secondary source of the REE. The recovery and processing of WEEE has become important because of the huge amount of collected WEEE in Poland and European Union. In Poland, an overall 1.48 kg per capita of WEEE was collected in 2008, and 4.39 kg in 2014, which is *ca*. 168 900 tonnes of WEEE. In 2021 Poland will be obliged to collect 11 kg per capita [14].

The first step in REE separation is recovery from raw material using the hydrometallurgical process. The technological scheme of REE extraction from minerals usually consists of grinding and cracking mined ore, preliminary enrichment to produce mixed REO (rare earth elements oxides) concentrates, then further concentration, separation, and purification of the oxides [1] (Fig. 1). The obtained concentrate contains other metals apart from REE. For further processing the methods such as leaching, precipitation, solvent extraction, and ion exchange are employed. Inorganic acids, alkalines, electrolytes, and chlorine gas are used as lixiviants. For example, acids are usually used to extract REE from silicate ore mineral, such as gadolinite, eudialite and allanite, and alkaline reagents and sulphuric acid are commonly used to leach REE from phosphate ore minerals like monazite and xenotime. REE from ion-adsorption clay deposits are extracted using electrolyte solutions and chlorination is applied to process the majority of rare earth minerals. The obtained solutions are generally a mixture of various REE and other metals originating from the raw material. This is

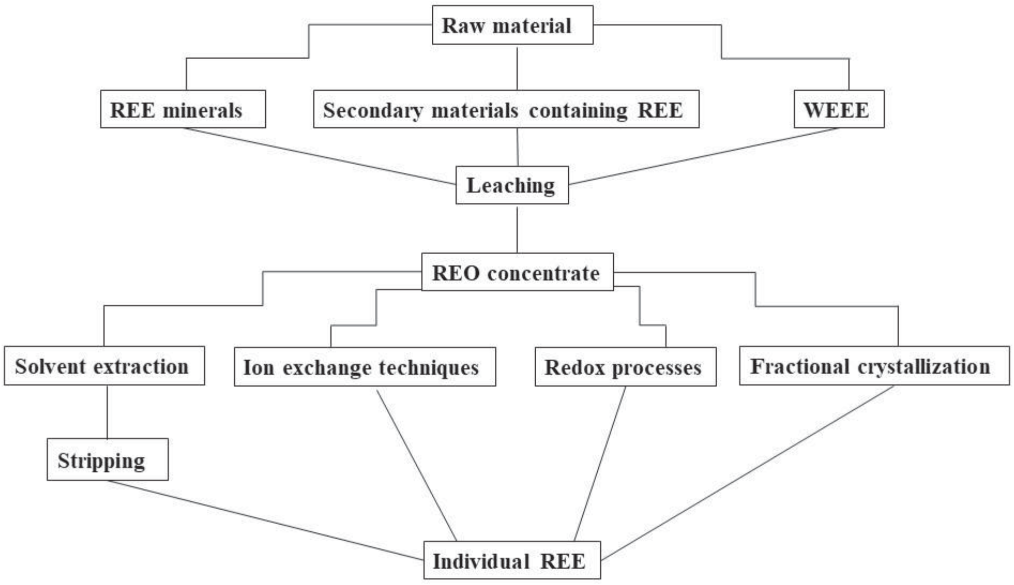

Fig. 1. Treatment of raw materials in the process of REE recovery.

followed by separation of individual metals, which is a highly demanding process in hydrometallurgy. Currently, solvent extraction is the most preferable method of purification because of its continuous nature and possibility to handle large amounts of diluted post-leaching solution. The choice of the ligand used organic soluble metal-ligand complexes, has a significant effect on separation of metals and overall process efficiency, as well as cost. In general there are three major classes of extractants that are used for separating REE, acidic, neutral or basic extractants [15]. In the following scrubbing step, the organic phase obtained from extraction is contacted with the scrubbing solution to remove unwanted solutes, and increase the purity of valuable elements. Scrubbing is usually accomplished with water, dilute acid, or base solution. Notably, a relatively high amount of valuable metals may pass to the scrubbing solution; hence the scrubbing solution should be recycled back to extraction stage and mixed with the feed aqueous solution. The metals extracted to the organic phase are then stripped back to aqueous phase using solutions such as concentrated acid, alkaline, or salt solutions. Likewise with the extraction step, stripping may be performed in one-, two-, or multi-stage process [16]. An alternative method for REE separation is ion-exchange technique. Lanthanides can be separated by using a combination of chelating eluents that are selective for individual lanthanides with resins that are characterized by low selectivity. An alternative method of lanthanide separation is extraction using chemically modified resins, *e.g.* resins coated with extractant [17]. Several REE may be separated using reduction-oxidation reactions [17] or fractional crystallization techniques. The final method is based on the difference in solubility of bromate, nitrate and sulphate complexes of lanthanum, gadolinum, terbium and dysprosium [17 and references therein]. Summarizing, the separation of individual REE is the most challenging aspect of their production. The increasing demand of these metals is the reason for such intensive development and research in this field.

Development of modern technologies is strongly dependent on rare earth elements. Furthermore, in Poland, the constantly growing consumption of REE is observed. Our country does not actually have its own REE natural resources. Further studies of REE recovery from secondary sources are necessary to meet the demand for these valuable and irreplaceable metals in today's life.

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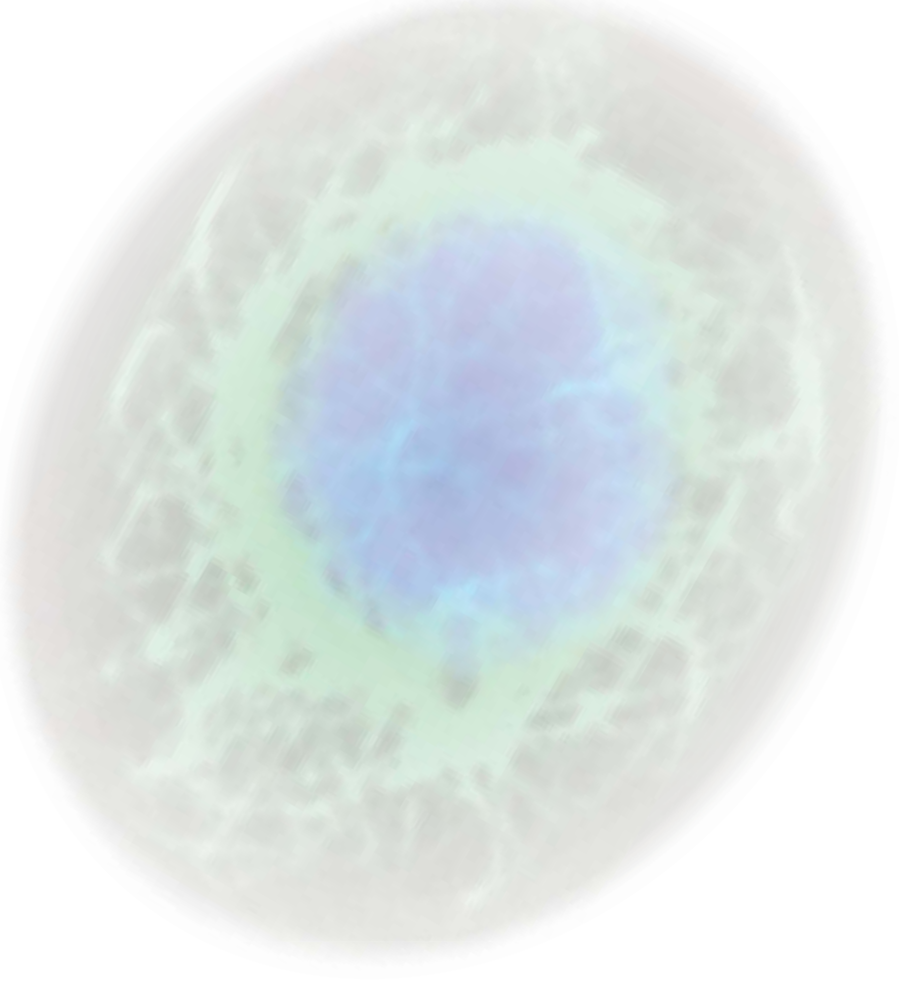
CENTRE FOR RADIOBIOLOGY AND BIOLOGICAL DOSIMETRY

The work carried out at the Centre in 2018 focused on attempts to solve some discrepancies in the micronucleus test, a widely used biodosimetric tool. In addition, a wound healing assay (scratch assay) was implemented in the Centre to study cellular migration ability and metastasis. The accreditation given by the Polish Centre for Accreditation (PCA) to the Laboratory for Biological Dosimetry, established in the Centre in 2015, was sustained for next year. The Laboratory is the only accredited laboratory able to conduct biodosimetrical assays in Poland. The Centre participated in the interlaboratory comparison of the comet assay, organized in the framework of COST action CA15132 ‘The comet assay as a human biomonitoring tool (hCOMET)’. The Laboratory for Biological Dosimetry took part in an interlaboratory comparison of the micronucleus test as a tool for the diagnosis of inherited disorders associated with increased radiosensitivity, organized by Ghent University (Belgium).

An important research topic during the last few years has been nanotoxicology and nanomedicine. The mechanism of toxicity of silver nanoparticles was studied in cell culture in relation to cellular migration ability and metastasis. The Centre has also two ongoing projects on the use of radium-bearing nanozeolite radiopharmaceuticals against prostate and breast cancer.



DIFFERENT PATTERNS OF LYMPHOCYTE STIMULATION, CELL CYCLE ARREST AND INDUCED CELL DEATH – POSSIBLE REASONS FOR THE INTERVARIABILITY OF THE LEVEL OF RADIATION-INDUCED MICRONUCLEUS FORMATION

Sylwester Sommer, Teresa Bartłomiejczyk, Iwona Buraczewska, Iwona Grądzka, Elżbieta Przygoda, Katarzyna Sikorska, Barbara Sochanowicz

The micronucleus test (Mn test) is widely used in genotoxic research and biological dosimetry [1, 2]. In biological dosimetry, the Mn test is performed on human peripheral blood lymphocytes, and the results are compared with calibration curves *in vitro*. The calibration curves are constructed by irradiating lymphocytes with various doses of radiation; however, in a high dose range (above 2 Sv) large differences in the induction of micronuclei between donors are observed (Table 1) [3]. Although no explanation of this phenomenon is offered in the literature, except methodological or probabilistic reasons, it seems that it may be related to two biological phenomena: cell cycle arrest and/or various levels of cell death. Heavily damaged cells, in which DNA repair is underway, stop at the cell cycle checkpoint and will not divide until the DNA damage repair is completed. If the cellular resources to repair DNA damage run out, cells are directed towards the path of programmed cell death (apoptosis) before cell division. Since micronuclei occurrence is observed only in cells that have divided at least once, both cells types are excluded from the assay. The number of cells that are excluded from the counted population may be different. In general, in the range of higher doses the Mn frequency increases with dose, but the dynamics of the increase varies between donors. In some cases only a very slight increase is observed (Table 1).

Interestingly, in the range of low and medium doses, where the effect of cell cycle arrest and apoptosis should not be so significant, we also detected a large variation among donors in the frequency of Mn induced by the same dose of radiation (Table 2). In this case, the offered explanation is based on the differences in stimulation of different lymphocyte populations by phytohaemagglutinin in different donors. In some donors, only 10% of lymphocytes are stimulated to divide, while in others up to 50% do so (Table 2). This can be demonstrated by the ratio of the binucleated cells (after division) to mononucleated (cells that did not divide) calculated as the percentage of binucleated (BN) cells (%BN). The ratio decreases with an increase in the radiation dose, which is likely to depict biological phenomena: cell cycle arrest and cell death.

Human peripheral blood lymphocytes are a gathering of different lymphocyte populations with different radiosensitivity. Therefore, if in one person only 10% of lymphocytes are stimulated to divide in a given population, whereas in the second person 50% of lymphocytes are stimulated in the same population, we can observe differences in radiation sensitivity between these individuals.

In summary, there are biological mechanisms that can account for differences in micronuclei induction by radiation in different donors: cell cycle arrest, different levels of induced cell death, and changes in the stimulation of particular lymphocyte populations. The problem is not often mentioned in the literature and requires further research. One of the questions that needs to be solved is whether these differences would be observed in repeated experiments in one donor.

Huge variations in the Mn frequency changes with increasing dose can be observed, *e.g.* KR: 2.0 Sv – 247 Mn/1000 BN cells, 3.0 Sv – 235 Mn/1000 cells, thus a decrease in the frequency of Mn. Other examples, MK: increase in the frequency of Mn from 178 Mn for 2.0 Sv to 972 Mn

Table 1. The frequency of Mn induced by gamma radiation (^{60}Co) in the dose range from 1.5 Sv to 7.2 Sv; manual Mn scoring.

Donor	Dose [Sv]					
	1.5	2.0	3.0	3.6	4.0	7.2
	Number of micronuclei per 1000 binucleated cells					
AW	95	116	296	-	-	-
GW	145	171	494	-	-	-
KR	109	247	235	-	-	-
GW1	92	160	252	483	-	1516
SS	123	-	-	-	428	-
MK	-	178	-	-	972	-
IB	-	316	-	-	738	-
Mean	113	198	319	483	713	1516
Range	92-145	116-316	235-494	-	428-972	-

Table 2. The frequency of Mn induced by X-rays in the dose range from 0.0 Sv to 1.5 Sv; semi-automatic Mn scoring. Ratio of number of binucleated cells × 100 / number of all cells (%BN) is also shown.

Donor	Dose [Sv]				
	0	0.3	0.5	1.0	1.5
	Number of micronucleus per 1000 binucleated cells. In brackets – %BN				
DK	16 (10)	47 (12)	78 (10)	128 (11)	225 (9)
DS	8 (21)	31 (22)	57 (10)	187 (11)	249 (11)
PM	9 (48)	45 (34)	59 (34)	189 (31)	347 (20)
ZG	7 (21)	29 (23)	46 (16)	118 (16)	208 (17)
SA	7 (21)	13 (21)	43 (25)	134 (22)	207 (19)
WP	13 (29)	21 (29)	50 (24)	131 (25)	329 (27)
SS	18 (10)	30 (14)	43 (12)	109 (9)	189 (9)
Mean	11	31	54	142	251
Range	7-18	13-47	43-78	109-189	189-347

for 4.0 Sv, IB: much lower increase in the frequency of Mn for the same doses – 316 Mn for 2.0 Sv to 738 Mn for 4.0 Sv.

At lower dose ranges the difference in Mn induction between donors is smaller than that for higher dose ranges (Table 1). The ratio of %BN in control cells is the lowest in DK and SS – 10%, and the highest in PM – 48%. In the presented dose range, the ratio of %BN remains stable in some donors: DK, SA, WP and SS, or decreases with increasing doses: DS, PM and ZG.

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COMPARISON OF MIGRATION CAPABILITIES OF A2780 HUMAN OVARIAN CANCER CELL LINE AND 4T1 MOUSE BREAST CANCER CELL LINE BY WOUND HEALING ASSAY USING LIVE-CELL MICROSCOPY

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The *in vitro* wound healing assay (scratch assay) is a well-developed, easy and low-cost method to measure cell migration and cell interactions in culture. The method mimics cell migration during *in vivo* wound healing [1].

The basic steps involve creating a 'wound' in a cell monolayer (the cultures are confluent at the start of the experiment), usually by scratching with a pipette tip and capturing images at the beginning and at regular intervals when cells migrate to close the wound. Comparison of the captured images allows the migration rate to be quantified [2]. During the course of the wound healing assay, the cells will migrate into the gap, but also proliferate. Thus, in most wound healing studies, efforts are made to suppress proliferation, so that it does not interfere with the measurement of migration.

The aim of the present study was to investigate the migration rate of two epithelial cell lines: A2780, a human ovarian cancer cell line, and 4T1, a breast cancer cell line derived from the mammary gland tissue of a mouse. Both cell lines were grown in RPMI-1640 medium with 10% foetal bovine serum (FBS). Cells were seeded into a 24-well tissue culture plate at a density that allowed them to reach confluence as a monolayer after 24 h of growth. Using a 200 μl pipette tip, a straight scratch simulating a wound was made in the monolayer. After scratching, the cells were gently washed twice with medium to remove debris from damaged or dead cells, and the culture medium was replaced. Replacing the growth medium after scratching helps to control the factors available to cells for migration. The 24-well tissue culture plate was then placed in a Nikon Ti microscope equipped with a 'Bold Line CO_2 Incubator System' (Okolab), enabling prolonged observations on biological specimens to be carried out. The automated image acquisition software allows images of multiple positions in a multiwell plate to be taken at regular time intervals as the wound recovers (every 2 h over a 24- to 48-hour period; Figs. 1 and 2).

The cell migration rate was calculated according to the equation below, where the migration speed (v) is the average velocity at which the cells collectively move into the gap. The slope is equal

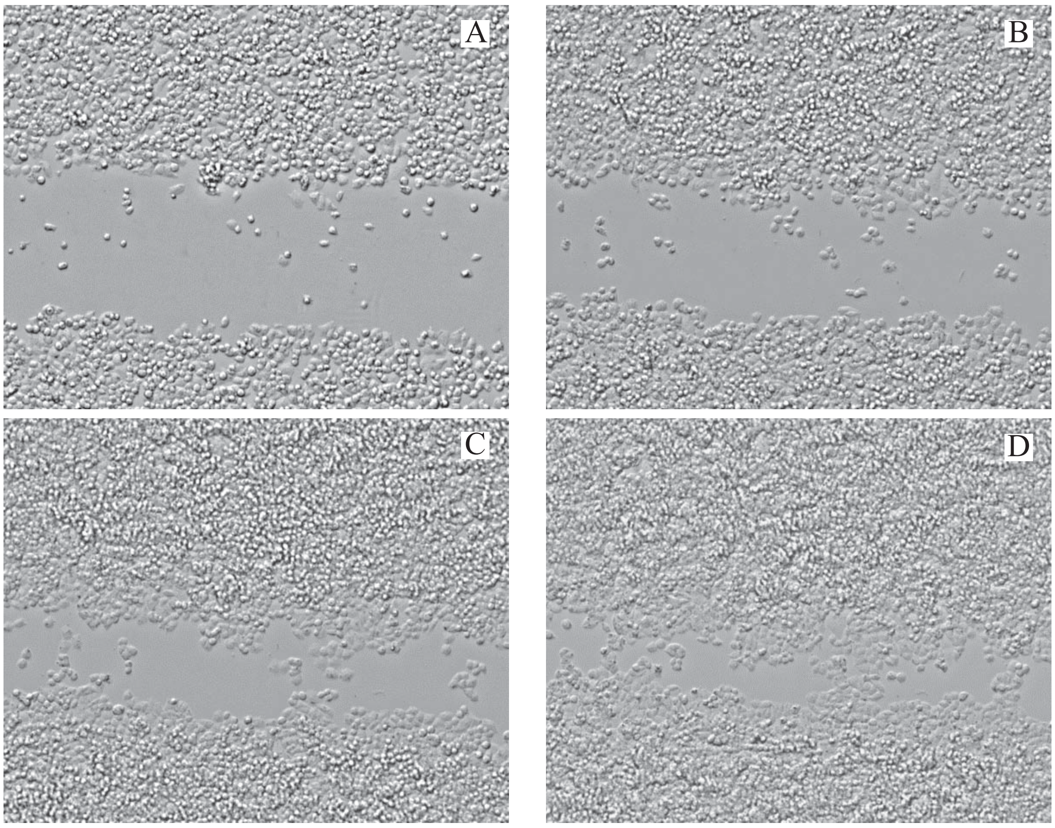

Fig. 1. Images from a scratch assay experiment at different time points. A2780 cells were seeded into a 24-well tissue culture plate, wounded with a p200 pipette tip and then imaged every 2 h overnight. The images in the time series were analysed for gap area over time: A – 0 h, B – 16 h, C – 32 h, D – 44 h. The gap area was detected using Fiji (ImageJ News Version 1.52i 26 November 2018). The slope of the resultant graphs yielded migration rates in μm/h.

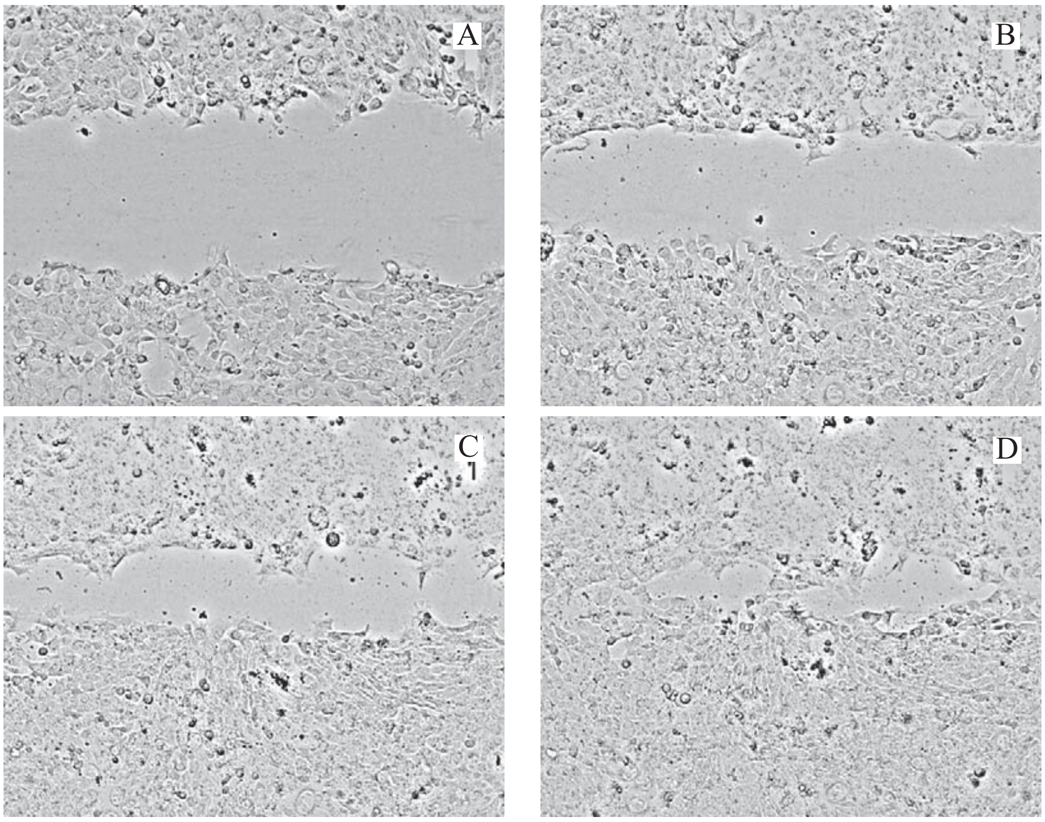

Fig. 2. Images from a scratch assay experiment at different time points. 4T1 cells were seeded into 24-well tissue culture plate, wounded with a p200 pipette tip and then imaged every 2 h overnight. The images in the time series were analysed for gap area over time: A – 0 h, B – 6 h, C – 12 h, D – 18 h. The gap area was detected using Fiji (ImageJ News Version 1.52i 26 November 2018). The slope of the resultant graphs yielded migration rates in μm/h.

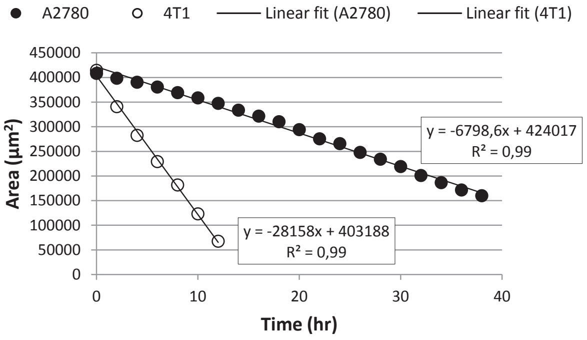

Fig. 3. The wound healing assay can reveal differences in migration rates. As an illustration, the graph shows migration rates of two different cell lines (A2780 and 4T1) determined by plotting the gap area *vs.* time. The slopes of the resultant graphs yield migration rates in μm/h.

to dA/dt, where the area A is the width of the gap (w) multiplied by the length of the gap (l). Assuming that the gap is much longer than the field-of-view, so that cells do not migrate into it from the edges, then the length is constant, so $dA/dt = l \times dw/dt$. Also, the width closes in at twice the rate of the cell migration, so $dw/dt = 2 \times v_{\text{migration}}$. This gives the cell migration rate as:

$$v_{\text{migration}} = \frac{|\text{slope}|}{2 \times l}$$

If the graph is plotted with area in μm and time in hours, then $v_{\text{migration}}$ conveniently can be expressed in units of μm/h [3].

For the experiment shown in Fig. 3, the calculated cell migration rate was 2.88 μm/h for A2780 cells and 11.94 μm/h for 4T1 cells.

To conclude, the results of this study clearly shown that the wound healing assay is a good method to measure cell migration and can reveal differences in migration rate.

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GENOTOXICITY STUDIES OF THE EFFECT OF SELECTED POLYPHENOLS ON FREE RADICAL-INDUCED DNA DAMAGE

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Polyphenols (PPs) are a broad group of chemicals endowed with antioxidant activity, widely distributed in plant-derived food. They are studied as putative cancer-protective agents, potentially contributing to the cancer preventive properties of fruit and vegetables. Human trials and animal experiments that investigated the effects of PPs in combination with known DNA-damaging agents have often shown a decrease in endogenous DNA damage and protection against DNA damage induced by xenobiotics [1-3]. On the other hand, high doses of PPs can induce DNA damage, as demonstrated in numerous cell culture experiments [4]. The aim of this work was to evaluate the genoprotective activity of three PPs commonly found in edible plants: quercetin (Q), curcumin (CUR) and chlorogenic acid (CLA).

In order to estimate the ability of PPs to inhibit reactive oxygen species (ROS)-mediated DNA damage, a plasmid nicking assay was used. The assay is based on an assessment of the abundance of three conformers of a double-stranded plasmid DNA molecule. An initially supercoiled (CCC) molecule becomes open circular (OC) when one DNA strand is nicked or linear (L) if a double-strand break is introduced. All the conformers are easily visualized after electrophoresis, while the band intensity is related to the extent of DNA damage [5, 6] (Fig. 1).

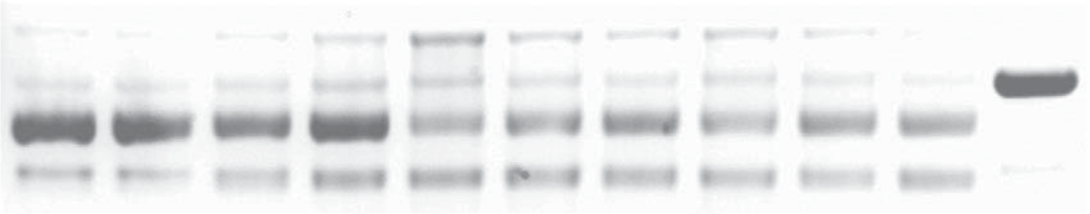
pUC19 plasmid DNA was incubated at 22°C for 10 min in the dark in the presence of 1 mM H_2O_2 and 1 μM Fe^{2+} ions (in order to induce Fenton-type reaction mediated ROS damage of the DNA). The samples were also incubated in the presence of quercetin, curcumin or chlorogenic acid (50 μM or 5 μM). Native pUC19 plasmid (line 1), and pUC19 cleaved to the L form (line 11) were used as a negative and positive controls, respectively. The incubation mixture (5 μL) contained 217 ng pUC19 plasmid DNA. The reaction products were resolved electrophoretically on 1.5% agarose gel containing 0.25 μg/mL ethidium bromide. To obtain a control linear form, the plasmid was cleaved with SmaI endonuclease (Fermentas). The DNA bands were visualized under UV light, photographed and the bands' intensities were estimated by ImageJ software (http://rsbweb.nih.gov/ij/index.html). Figure 1 presents the chart for the sample treatment, the resolved gel and the percentage of each form of the plasmid found in the samples after treatment.

In comparison to the damage induced by Fe^{2+} and H_2O_2 in the absence of PPs, all the PP-containing samples were characterized by a lower (3%

A

Treatment	Line number										
	1	2	3	4	5	6	7	8	9	10	11
pUC19	+	+	+	+	+	+	+	+	+	+	
Fe^{2+}		+		+	+	+	+	+	+	+	
H_2O_2			+	+	+	+	+	+	+	+	
PP					Q (5 μM)	Q (50 μM)	CUR (5 μM)	CUR (50 μM)	CLA (5 μM)	CLA (50 μM)	
pUC19L											+

B



C

OC [%]	1.15	0.29	1.25	4.23	16.75	7.79	4.49	8.52	2.75	0.24	0.00
L [%]	3.24	3.63	5.05	6.80	9.60	6.57	4.67	9.13	5.97	2.46	99.02
CCC [%]	82.35	84.70	74.00	67.19	36.46	47.69	59.61	45.91	64.36	60.87	0.00
CSS [%]	13.27	11.38	19.70	21.79	37.19	37.94	31.23	36.45	26.92	36.44	0.98

Fig. 1. ROS-induced DNA damage caused by Fe^{2+}/H_2O_2 redox system in the presence or absence of PPs: (A) the treatment applied to each sample, (B) representative gel image, (C) values for the band intensities in numerical form; linear form of pUC19 is shown as a reference in line 11. Concentrations: $FeSO_4$ – 1 μM; Q: line 5 – 5 μM, line 6 – 50 μM; CUR: line 7 – 5 μM, line 8 – 50 μM; CLA: line 9 – 5 μM, line 10 – 50 μM; H_2O_2 – 1 mM, where applicable; pUC19 – 44 ng/μl of sample.

to 31%) abundance of the native, undamaged plasmid molecule (CCC form). The presence of a 5 μM concentration of quercetin resulted in an increase in the OC and L forms of the plasmid of 12.5% and 2.8%, respectively. 50 μM quercetin caused an increase of 3.6% in the OC form and a decrease of 0.2% in the L form. 5 μM curcumin caused a 0.3% increase in the OC form and a 2.1% decrease in the L form. 50 μM curcumin caused an increase in both the OC and L forms by 4.2% and 2.3%, respectively. Chlorogenic acid caused a decrease in the oxidatively damaged OC and L forms of 1.5% OC and 0.82% L at 5 μM concentration and 4% OC and 4.3% for L at 50 μM concentration. The single-stranded form of plasmid increased in all the PP-treated samples, as seen in Fig. 1.

In the plasmid nicking assay, the induction of single- and double-strand breaks in plasmid DNA is expressed as an increase in the OC and L forms, respectively. Quercetin promoted the formation of DNA damage (single- and double-strand breaks) at both low (5 μM) and high (50 μM) concentrations. Curcumin also displayed this pro-oxidative effect, but only at the higher concentration (of 50 μM). For the lower, 5 μM, concentration an overall slightly antioxidative effect could be seen, with a considerable reduction in the induction of double-strand brakes (decreased intensity of L form of plasmid) and a negligible increase in the induction of single-strand brakes (OC form) as compared to the control sample. Chlorogenic acid proved to be a potent antioxidant against ROS-induced damage DNA, reducing the amount of OC and L forms of plasmid by 1% each for the lower and 4% each for the higher concentration (Table 1).

The studied PPs displayed a spectrum of mild anti- to pro-oxidative potential, and the final effect

Table 1. Differences in abundance of plasmid forms in samples treated with different concentrations of PPs in comparison to the plasmid damage induced by Fe^{2+} and H_2O_2 in the absence of PPs.

Gel line	5	6	7	8	9	10
Treatment	Q (5 μM)	Q (50 μM)	CUR (5 μM)	CUR (50 μM)	CLA (5 μM)	CLA (50 μM)
OC difference	12.52	3.57	0.27	4.29	-1.48	-3.99
L difference	2.80	-0.22	-2.13	2.33	-0.82	-4.34
CCC difference	-30.72	-19.49	-7.57	-21.27	-2.83	-6.32
CSS difference	15.40	16.15	9.43	14.65	5.13	14.64

depended on their concentration. This is in accordance with the literature (reviewed in [7]). This fact should be considered during trials of elevating PPs' bioavailability in their use as pro-drugs. Apart from the supercoiled, nicked and linear forms of pUC19, in our experimental conditions a certain amount of a dissociated, single--stranded (CSS) form of the plasmid was observed. Interestingly, the presence of PPs significantly increased the amount of the CSS form (26.9-37.9% in PP-treated samples, 13.3% in native, untreated pUc19 preparation and 21% in ROS-treated samples). The pH of the applied PPs' preparations was 6.0, therefore this effect cannot be connected to the alkaline dissociation of DNA strands. The above suggests that the PPs can induce the disruption of hydrogen bonds in DNA, rendering the two DNA strands prone for dissociation. This can have further consequences with respect to PPs' influence on DNA replication and translation kinetics. This particular effect of PPs on DNA has not been considered to date to our knowledge.

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LABORATORY OF NUCLEAR ANALYTICAL METHODS

The Laboratory of Nuclear Analytical Methods specializes in nuclear and nuclear-related analytical methods for applications in many specific fields of high technology, especially nuclear technology, but also health and environmental problems. 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. The Laboratory is the only Polish producer of matrix certified reference materials (CRMs) for the purpose of inorganic trace analysis. Examples of CRMs produced by the Laboratory are Oriental Basma Tobacco Leaves INCT-OBTL-5, Polish Virginia Tobacco Leaves INCT-PVTL-6 and the recently certified MODAS-3 Herring Tissue, MODAS-4 Cormorant Tissue, MODAS-5 Cod Tissue and MODAS-2 Bottom Sediment. In the certification process, unique primary measurement methods, such as RNAA (radiochemical neutron activation analysis), developed in the Laboratory are used. The Laboratory of Nuclear Analytical Methods is also a provider of proficiency testing schemes on radionuclide and trace element 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, liquid chromatography-mass spectrometry, HPLC including ion chromatography, as well as gamma-ray spectrometry and alpha- and beta-ray counting.

The Food and Environmental Laboratory (FEL), which is part of the Laboratory of Nuclear Analytical Methods, provides services to municipal and private customers. The Laboratory specializes in the determination of radionuclides in water and foodstuffs, as well as in environmental samples. Its applied methods of analysis have been approved by the State Sanitary Inspection.

In 2018, the Laboratory of Nuclear Analytical Methods performed a proficiency test (PT) on the determination of ^{137}Cs and ^{90}Sr in water and environmental samples. The PT was provided at the request of the National Atomic Energy Agency (PAA), Poland, for laboratories creating the radiation monitoring network in Poland. Twelve laboratories took part in the PT, including nine laboratories creating the radiation monitoring network in Poland. The proficiency tests were provided in accordance with the requirements of ISO/IEC 17043:2010, ISO 13528:2015 and the IUPAC International Harmonized Protocol (2006).

APPLICATION OF A NEW DIGLYCOLAMIDE SORBENT IN SEQUENTIAL INJECTION ANALYSIS FLOW SYSTEM FOR DETERMINATION OF ^{239}Pu WITH ICP-MS DETECTION

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The extraction and recycling of actinides from spent nuclear fuel is important for reprocessing and radioactive waste disposal. The search for new materials for such processes is challenging from the perspective of the chemical and radiological conditions that the materials are used in. The development of materials for industrial scale as well as analytical separations has been carried out for over half a century. A group of complexing ligands which have been intensively investigated over the last two decades as extractants of lanthanides and actinides are diglycolamides (DGA), invented at the Japan Atomic Energy Research Institute [1]. A particular ligand that has been thoroughly investigated is N,N,N',N'-tetraoctyl-3-oxapentanediamide (TODGA) [2]. With appropriate selection of solvent, it is used for the full recovery of the actinide elements from spent fuel, *e.g.* in the grouped actinide extraction process (GANEX) [3]. It has been reported that Pu(IV) forms a 1:3 complex with TOGDA, with the nitrate ions forced into the outer coordination sphere $[Pu^{IV}(TODGA)_3](NO_3)_4$ [4]. For the analytical separation of Am, the separation of Ra/Ac and that of Ca/Sr/Y, TODGA has been immobilized on the surface of the hydrophobic polyacrylic resin Amberchrom CG-71 [5]; this immobilized form of TODGA is sold commercially as DGA-resin (Eichrom Technologies Inc.).

Up to now, in reported flow analysis methods for the determination of Pu radionuclides, various extraction resins have been employed for the separation of analytes from interfering substances. For instance, in the flow injection determination of ^{239,240}Pu radionuclides with radiometric detection, the commercial resin TRU was employed for the separation of plutonium from trivalent actinides [6]. Recently, in the design of a flow injection analysis (FIA) system with inductively coupled plasma mass spectrometry (ICP-MS) detection for the determination of ^{239,240}Pu and several other actinides, a complex system employing TEVA, TRU and Sr-resins was developed for the fractionation of the determined analytes [7]. Diglycolamide resins have not been employed, so far, in flow systems. A branched commercial resin DGA-b has already been employed for the separation of Pu and U, where Pu(IV) was extracted from a 4 M HNO_3 solution, interfering species, including uranium, were then eluted with 1 M HNO_3 solution, and the subsequent elution of Pu was carried out using various reducing reagents [8].

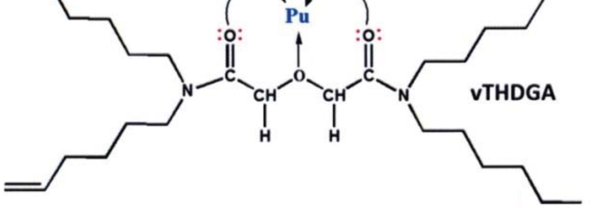

Fig. 1. Structure of vTHDGA ligand with tridentate binding of Pu.

The primary focus of this study was to develop a complexing diglycolamide resin – vinyl-substituted tetrahexyl diglycolamide (vTHDGA), where the DGA ligand is covalently immobilized on a polymeric support. This resin was used in a flow analysis system for the determination of particular Pu radionuclides with ICP-MS detection. The vTHDGA structure, with the expected tridentate binding of Pu, is shown in Fig. 1.

Preparation of vTHDGA resin

Based on reported methods for the N-alkylation of primary and secondary amines [9], several DGA ligands were synthesized with tetra-isobutyl and tetra-hexyl alkyl chains, and additionally with one or two terminal vinyl groups. In 1-octanol : kerosene solution (60:40 volume ratio) at 0.25 mM concentration, the affinity of each synthesized ligand towards plutonium was examined by measuring the extraction efficiency using liquid-liquid extraction. Measurements were carried out using α-spectrometric detection of ^{242}Pu, and the results are shown in Table 1. The largest yield of extraction, counting only those diglycolamides containing one or more vinyl groups, was obtained for the tetrahexyl-derivative with one terminal vinyl group (vTHDGA), so this ligand was used for the preparation of a resin.

Table 1. The efficiency of liquid-liquid extraction of ^{242}Pu from aqueous solution with 25 Bq mL^{-1} ^{242}Pu in 3 M HCl into 1 mL 1-octanol : kerosene (60:40) solution containing different synthesized diglycolamide ligands (0.25 M).

Alkyl group in diglycolamide ligand	Efficiency of ^{242}Pu extraction [%]
Tetraisobutyl-	95.2
Tetraisobutyl-, monovinyl-	69.9
Tetrahexyl-	90.6
Tetrahexyl-, monovinyl-	89.6
Tetrahexyl-, divinyl-	73.1

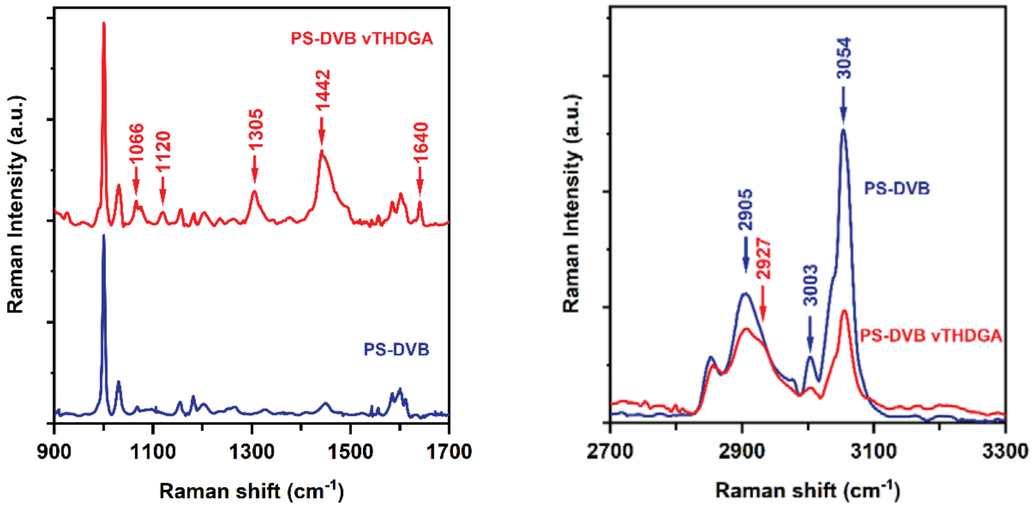

Fig. 2. Raman spectra recorded with 785 nm laser in two different wavelength ranges for PS-DVB copolymer and vTHDGA resin.

Polystyrene-divinylbenzene (PS-DVB) copolymer beads were synthesized in a suspension polymerization process [10]. In a typical synthesis, the organic phase contained styrene (or 4-methyl styrene) monomer (9 mL), divinylbenzene cross-linker (2-3 mL), 4-chloromethylstyrene (CMS) (0.5-3 mL), a mixture of toluene and butanone as a porogen (12 mL), and azobis(isobutyronitrile) (AIBN; 300 mg) as an initiator of polymerization. The aqueous solution contained 300 mg poly(vinyl alcohol) and 2.5 g sodium chloride in 300 mL water. The aqueous and organic solutions were stirred at 200 rpm at 60-75°C for 12 h. The obtained white precipitate was dried, and then sieved to separate polymer beads with a size below 212 μm in diameter. The content of the DVB and CMS components was optimized in separate experiments.

The selected vinyl derivative of the diglycolamide ligand, vTHDGA, was attached to the obtained PS-DVB copolymer by a template polymerization process, in which 1.2 g PS-DVB was added to a mixture of 1.5 mg vTHDGA and 50 mg AIBN in 3 mL chloroform and left unstirred in order for the solvent to evaporate. Elemental analysis of specially prepared beads (using benzoyl peroxide (BPO) as a nitrogen-free initiator) revealed a correlation between the amount of retained vTHDGA ligand and the concentration of CMS groups, giving a proof of the chemical bonding of the ligand to the bead's walls through the chloromethyl functional group. The obtained product was washed with three portions of ethanol to remove adsorbed, but not covalently attached, ligand. After drying, it was then ready for further use.

Spectroscopic characteristics of the synthesized sorbent

Two spectroscopic techniques were used to investigate the properties of the obtained vTHDGA resin with PS-DVB polymeric support, namely Raman spectroscopy and solid-state NMR.

Raman spectroscopy easurements were carried out for the PS-DVB copolymer and the vTHDGA resin using a 785 nm laser, and the obtained spectra in two ranges of wavenumbers are compared in Fig. 2. The spectrum for the vTHDGA resin showed four bands at 1070, 1117, 1304 and 1640 cm^{-1}, which were not seen in the spectrum of the PS-DVB copolymer. The peaks at 1070 cm^{-1} and 1117 cm^{-1} can be assigned to ether group vibrations, while the 1640 cm^{-1} and 1304 cm^{-1} peaks are respectively the amide I band and the amide III band for tertiary amides. These groups are present in the vTHDGA ligand molecules but not in copolymer PS-DVB, which proves the presence of vTHDGA on the final resin. In the spectrum recorded for larger values of wavenumbers, one can find significant changes of the intensity of bands corresponding to C-H vibrations. Above 3000 cm^{-1} the peaks correspond to C-H vibrations in rings (*e.g.* 3054 cm^{-1} in the polystyrene ring), while at lower values they correspond to C-H bonds in aliphatic chains. In the vTHDGB resin spectrum, the ratio of band intensity is different: the intensity of the aliphatic –CH bands increases compared to the aromatic –CH bands, which is due to the larger number of aliphatic chains in the given preparation. This change in the -CH bands is the effect of the vTHDGA added to PS-DVB copolymer; it does not provide information about the character of the binding of vTHDGA to the supporting PS-DVB copolymer.

The solid-state ^{13}C NMR measurements for both materials were carried out with the use of two techniques (Fig. 3). The cross-polarization magic angle spinning (CPMAS) NMR technique is very commonly employed for ^{13}C NMR measurements with solid-state samples because the recorded spectra do not originate from labile molecules (*e.g.* solvent molecules in solvated crystals). The signals at 141.2 ppm and 123.3 ppm recorded for both the investigated materials are from the aromatic ring of polystyrene, namely from the ternary carbon in the aromatic ring and the remaining carbons (-CH). The signals at 41.5 ppm and 35.7 ppm are from the aliphatic carbons of polystyrene (-CH, -CH$_2$). Additionally, in Fig. 3A, a group of signals at 10-30 ppm corresponds to the carbons in the ligand molecule, while the small signal at

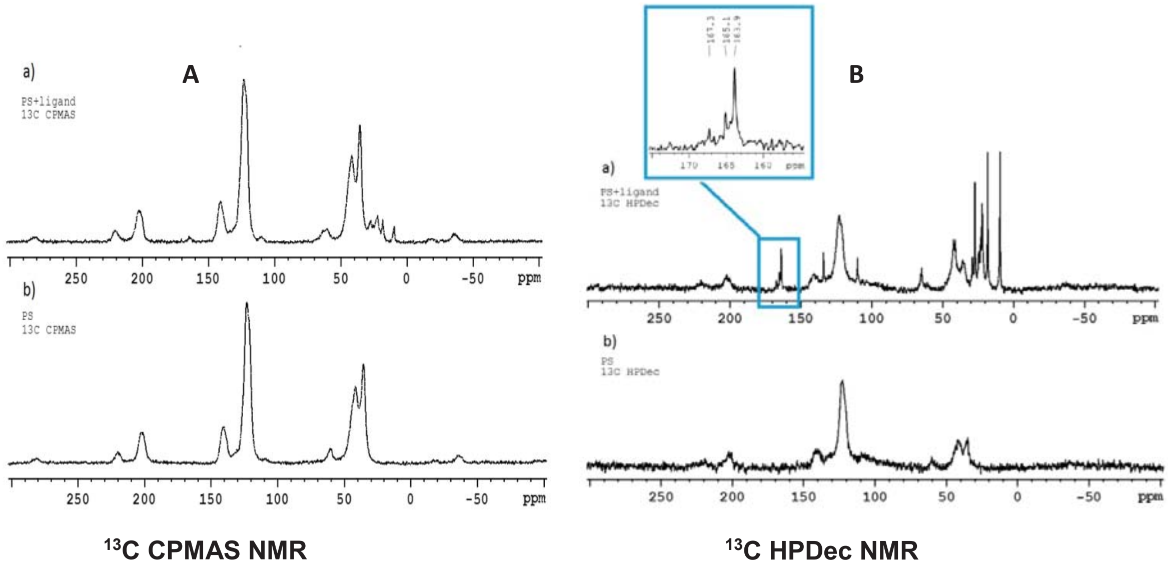

Fig. 3. Solid-state NMR spectra recorded for vTHDGA resin (a) and for PS-DVB copolymer (b), using ^{13}C cross-polarization magic angle spinning NMR (A) and ^{13}C high-power decoupling NMR (B) techniques.

160-170 ppm corresponds to the carbon in C=O. These data indicate the covalent attachment of vTHDGA to the PS-DVB copolymer.

Additional information can be also gained from the spectra of resin obtained by the high-power decoupling (HPDec) NMR technique. Signals in the range 9.5-29.0 ppm correspond to carbons from $–CH_3$ and $–CH_2$ groups, at 64.67 ppm from the $–CH_2$ placed between the C=O and O atoms, at 110.0 ppm from $=CH_2$, and at 134.0 ppm from –CH=, and signals in the range 160-170 ppm from C=O. The latter ones, magnified and indicated by the frame in Fig. 3, can be treated as evidence of the covalent binding of the ligand with the PS-DVB copolymer. This is justified by the presence of three signals from the carbonyl carbon, two of which are of much smaller intensity. In the case of ligand adsorption onto the copolymer only, a single carbonyl carbon signal would be observed. The presence of a signal for $=CH_2$ proves that the ligand is not entirely bound covalently to the copolymer, but is also physically adsorbed.

Optimization of SIA system for sample pretreatment

Flow measurements for sample processing for the plutonium determination carried out in this study were performed in two commercial sequential injection analysis (SIA) systems equipped with advanced multiposition rotary selection/injection valves with built-in microcolumns for mechanized loading/emptying of resin beds, a so-called

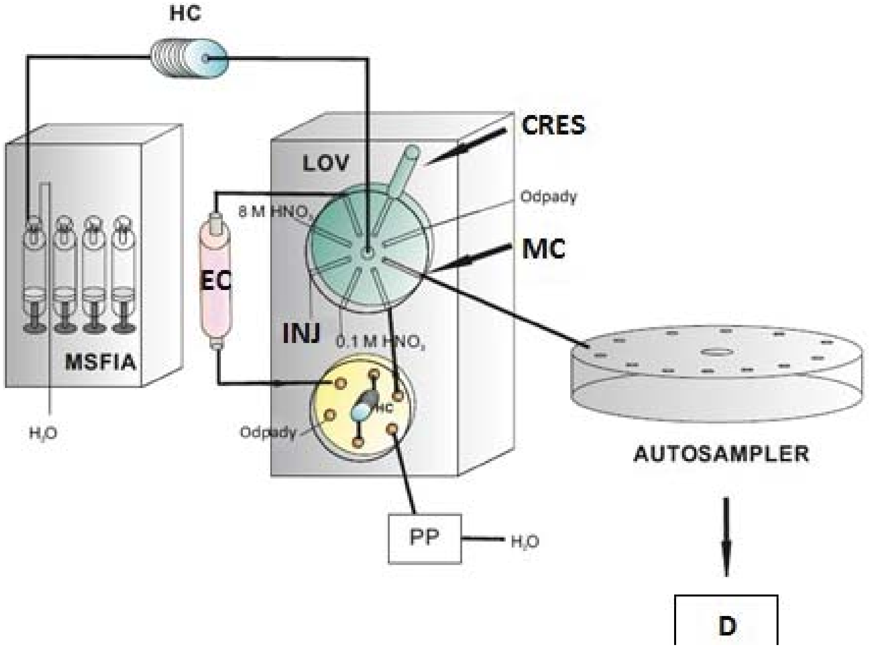

Fig. 4. Schematic diagram of the SIA-LOV system for mechanized sample pretreatment prior to the ICP-MS detection for the determination of ^{239}Pu: HC – holding coil; MSFIA – multisyringe pump; LOV – lab-on-valve rotary, multiposition injection valve with incorporated microcolumn for solid-phase extraction; MC – microcolumn in LOV; EC – optional external column for SPE preconcentration; INJ – sample injection port; CRES – container for resin; PP – peristaltic pump; D – detector (ICP-MS spectrometer or β-spectrometer).

lab-on-valve (LOV). The main part of the optimization work for the SIA system configuration was carried out using a ^{242}Pu radioisotope with α-spectrometric detection, a ProSIA instrument from FIAlab Instruments Inc. (Seattle, USA) and a Tri-Carb 2700TR liquid scintillation detector from Packard Instrument Co. (Meriden, USA). The scintillation cocktail Ultima Gold AB from Perkin Elmer was used in all measurements. Flow measurements for sample pretreatment prior to the off-line ICP-MS detection were carried out with an MSFIA-LOV multisyringe system from Sciware Systems (Bunyola, Spain), and the scheme of its configuration is shown in Fig. 4. The ^{239}Pu radioisotope was used as the analyte to be determined, and detection was carried out using an ELAN 6000 quadrupole ICP-MS spectrometer from Perkin Elmer (USA), which was equipped with a cross-flow nebuliser, a Scott double-pass spray chamber, nickel cones and a DRC module, employing methane as the carrier gas. As an internal standard, ^{115}In was added prior to the ICP-MS measurements.

The first step in the optimization of the SIA measurements was a search for the most suitable conditions for the sorption and desorption of Pu using an LOV microcolumn loaded with 20 mg of vTHDGA resin and using off-line β-spectrometric detection. 1 mL ^{242}Pu solutions of 25 Bq mL^{-1} activity in 0.1 to 8 M HNO_3 were loaded onto the LOV microcolumn, and the most efficient sorption (95 ± 2.8%) was found for the 4 M HNO_3 medium. Therefore, 4 M HNO_3 was also used for the preconditioning of the freshly loaded resin bed in the microcolumn.

Another important factor for the optimization is the volume of solution that can be used for loading the analyte onto the very small resin bed in the LOV microcolumn, and the flow-rate of the loading process, which should not negatively affect the yield of the analyte retention. In order to examine this effect, 100 mL of 10 Bq mL^{-1} ^{242}Pu solution in 4 M HNO_3 was loaded, and each 10 mL fraction of that solution after passing through the column was analysed for Pu content. For each employed flow-rate, 1.0, 5.0 and 10 mL min^{-1}, the sorption yield for the whole volume of the loaded solution was not lower than 94%, which was considered a very satisfactory result. The possibility of loading with a flow-rate of 10 ml min^{-1} shortens the loading of a 100 mL solution to 33 min, instead of 123 min at 1 ml min^{-1}. For the extraction resins employed so far in flow systems for the determination of plutonium, usually the sample volume is limited to 1 mL, with one exception where 10 mL was reported in an FIA system with radiometric detection and a TRU resin for the analysis of soil extracts and biological samples [11].

For the elution of the retained Pu, both less concentrated nitric and hydrochloric acid solutions, as well as reducing reagents were examined. Diluted acids were examined at 0.01, 0.1 and 1.0 M concentrations, and using 1 mL to 10 mL volume. The best elution of Pu elution was obtained for 10 mL 0.1 M HNO_3 (60%), and 5 mL 1.0 M HCl (82%). As shown for DGA resin used for extraction chromatography, trivalent plutonium species have a lower retention on diglycolamide sorbents than Pu(IV) [12]. The reduction of Pu(IV) to Pu(III) as a mechanism to elute the Pu was investigated. Several reducing reagents in different concentrations were examined, including Ti(III) chloride, hydroquinone and acetohydroxamic acid. Oxalic acid, which can be employed as an eluting compound, also exhibits reducing properties, and it was used in early work with DGA resin for Pu elution [5]. Its elution mechanism was attributed to a strong complexation of Pu(IV) [12], although it is also known that plutonium-oxalate chemistry is a very complex area [13]. Experimental data obtained for different eluents (Fig. 5) indicated the following eluting power: oxalic acid ≥ acetohydroxamic acid > hydroquinone > $TiCl_3$. In the case of 0.2 M oxalic acid solution, 1 mL eluted 95 ± 2% of the sorbed plutonium. This solution was further used in an optimized procedure for SIA measurements.

Selectivity towards other radionuclides

In the SIA-LOV flow analysis system used for sample pretreatment prior to the liquid scintillation counting (LSC) determination of ^{242}Pu, ex-

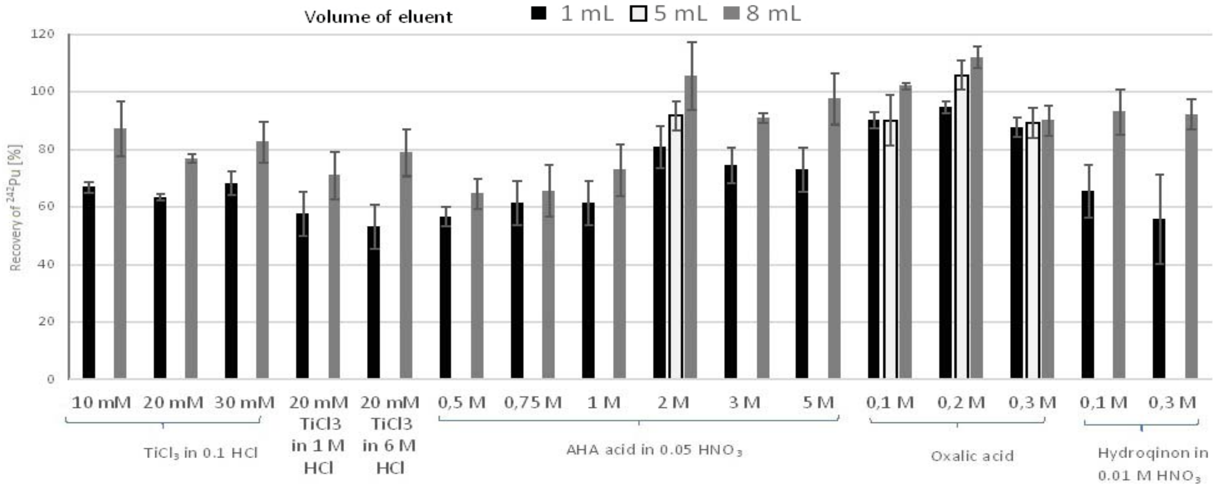

Fig. 5. The efficiency of elution of ^{242}Pu retained on vTHDGA resin using different volumes of various reducing reagents. The LOV microcolumn with 20 mg sorbent bed was loaded with 1 mL 25 Bq mL^{-1} ^{242}Pu in 4 M HNO_3 solution.

perimental optimization studies were also carried out to eliminate the effect of the presence of ^{233}U, ^{230}Th and ^{90}Sr/^{90}Y as potential interferences.

Although uranium's affinity to DGA resin in 4 M HNO_3 is about one order of magnitude weaker than Pu, its interference in ICP-MS determination of ^{239,240}Pu radionuclides can be caused by naturally occurring ^{238}U, because of polyatomic interference from the formation of $^{238}UH^+$. The possibility of separating Pu and U was examined for vTHDGA resin using different volumes of 4 M HNO_3, employed for the elution of retained Pu. The resin bed was loaded with 1 mL of 25 Bq mL^{-1} ^{233}U in 4 M HNO_3, and for comparison also with 1 mL of 25 Bq mL^{-1} ^{242}Pu in 4 M HNO_3. The recovery of elution of uranium was examined in relation to retained U; U retention with 4 M HNO_3 was 41.7 ± 0.7%. As shown in Fig. 6, the optimum volume of HNO_3 solution was 3 mL, using which 100% of the uranium was eluted, while the elution of Pu was only 4 ± 3%, which was taken to be a very satisfactory result.

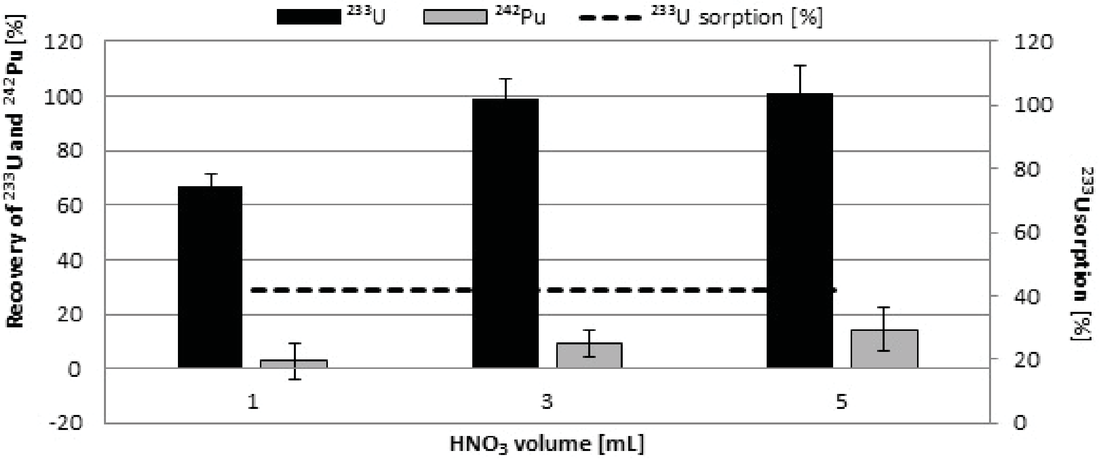

Fig. 6. The effect of the volume of 4 M HNO_3 solution used for the elution of uranium retained on a vTHDGA resin bed in an LOV microcolumn, loaded with 1 mL of 25 Bq mL^{-1} ^{233}U in 4 M HNO_3, or with 1 mL of 25 Bq mL^{-1} ^{242}Pu in 4 M HNO_3. The recovery of eluted ^{233}U is expressed in relation to amount of uranium retained on the sorbent bed (marked by broken line).

Thorium isotopes do not interfere in ICP-MS determinations of Pu radionuclides; however, they may affect radiometric determinations. A similar experimental approach was employed for the removal of interference from ^{230}Th, although in this case several different eluents were examined, including solutions of nitric, hydrochloric and phosphoric acids, and also several of their mixtures. The resin bed in the LOV-microcolumn was loaded with 1 mL of 25 Bq mL^{-1} ^{230}Th or ^{242}Pu, both in 4 M HNO_3, and in this case the yield of ^{230}Th retention was 84%. Phosphoric acid solutions washed out thorium in about 90% yield, but also Pu in 60-70% yield. Much less efficient elution for both radionuclides was observed for 1 M HNO_3 or 6 M HCl. The best results were obtained with a mixture of 8 M HNO_3 with 0.75 M H_3PO_4, where the recovery of Th was about 60%, without elution of Pu. This solution was employed in the final procedure.

The presence of ^{90}Sr and its decay product ^{90}Y does not interfere with ICP-MS detection of Pu radionuclides, but they affect radiometric detection. In a similar manner to the above-mentioned experiments, the separation of ^{242}Pu and ^{90}Sr/^{90}Y was examined using different solutions of HNO_3 and its mixtures with citric acid for the retained analytes. Acidic solutions of citric acid have been previously employed, *e.g.* in innovative SANEX processes based on the use of TODGA, for the residual stripping of lanthanides(III) [14]. The HNO_3 solutions (1 M to 4 M) eluted only 14% to 40% of the retained ^{90}Sr/^{90}Y when the LOV-microcolumn with vTHDGA was loaded with 1 ml of 25 Bq mL^{-1} ^{90}Sr that had not been purified from ^{90}Y. A complete elution of ^{90}Sr/^{90}Y was obtained with 5 mL of a mixture of 4 M HNO_3 and 0.1 M citric acid, with only 8 ± 1% simultaneous elution of Pu under such conditions. The same mixture was also efficient for the elution of retained uranium and thorium, so therefore it was incorporated into the final procedure for the SIA-LOV system (Table 2).

Determination of ^{239}Pu with ICP-MS detection

In ICP-MS determinations of plutonium isotopes, the main problems encountered are the formation of isobaric polyatomic interfering species and the difficulty in stabilizing the signal magnitude for Pu in the mass spectrometer. The list of polyatomic interferences reported in earlier papers for m/z = 239, besides the above-mentioned $^{238}UH^+$, includes $^{208}Pb^{31}P^+$, $^{208}Pb^{16}O^{14}N^1H^+$, $^{207}Pb^{16}O_2{}^+$, $^{207}Pb^{32}S^+$, $^{207}Pb^{16}O^{14}N^1H_2{}^+$, $^{206}Pb^{33}S^+$, $^{204}Hg^{35}Cl^+$, $^{205}Tl^{34}S^+$, $^{204}Pb^{35}Cl^+$, $^{203}Tl^{36}Ar^+$, $^{202}Hg^{37}Cl^+$, $^{201}Hg^{38}Ar^+$, $^{199}Hg^{40}Ar^+$ and $^{199}Hg^{40}Ar^+$ [15, 16], but certainly the most important is $^{238}UH^+$. The latter ion can be eliminated, *e.g.* by the use of collision reaction interface technology with helium gas [17], or by the use of carbon dioxide as the reaction cell gas [18]. In this study, the quadrupole ICP-MS instrument was equipped with a dynamic reaction cell (DRC) and methane was used as carrier gas. The use of methane allowed us to exclude from possible polyatomic interference ions those formed with Ar atoms. Figure 7 shows MS signals for several elements at concentration levels of 50, 250 and 500 μg L^{-1},

Table 2. Scheme of the developed procedure for sample pretreatment in SIA-LOV system in determination of ^{239}Pu with ICP-MS detection. The solid line frame indicates removal of uranium interferences, while the broken line indicates elimination of interferences of U, Th, Sr and Y.

Stage of procedure	Volume [mL]	Flow-rate [mL min^{-1}]
Introduction of THDGA resin		
(I) Aspiration into holding coil	1	5
(II) Loading into microcolumn of LOV	1	1
Conditioning of vTHDGA bed		
(I) Aspiration of 4 M HNO_3 into holding coil	3	5
(II) Rinsing sorbent bed with 4 M HNO_3	3	2
Introduction of sample solution		
(I) Aspiration into holding coil	1-100	5
(II) Loading into microcolumn with vTHDGA resin	1-100	1-10
Washing out spectral interference (U)		
(I) Aspiration of 4 M HNO_3 into holding coil	3	5
(II) Rinsing microcolumn with 4 M HNO_3	3	2
Washing out interferences (U, Th, Sr, Y)		
(I) Aspiration of 0.1 M citric acid in 4 M HNO_3 into holding coil	3	5
(II) Washing microcolumn with 0.1 M citric acid in 4 M HNO_3	3	2
(III) Aspiration of 0.75 M H_3PO_4 in 8 M HNO_3 into holding coil	5	5
(IV) Washing microcolumn with of 0.75 M H_3PO_4 in 8 M HNO_3	5	2
Elution of Pu		
(I) Aspiration of 0.2 M oxalic acid into holding coil	5	5
(II) Washing microcolumn with 0.2 M oxalic acid	5	2
Loading LOV microcolumn with vTHDGA resin		
(I) Aspiration of spent resin into holding coil	1	5
(II) Discarding spent resin to waste	1	10

examined as potential sources of interference in ICP-MS measurements. Practically, as expected, the only strong MS signal was observed for ^{238}U, and its magnitude measured for a 50 μg L^{-1} U concentration corresponded to the signal for ^{239}Pu at an activity concentration of 120 Bq mL^{-1}. Due to this finding, for sample pretreatment in the SIA-LOV system prior to the ICP-MS measurements, only the uranium elution step was used (marked by the solid frame in Table 2). The alternative steps, marked with a broken-line frame in the same table, should be used for radiometric LSC detection.

The instability of the ICP-MS signal for plutonium, especially in the initial stage of measurements, has already been reported in the literature, and it was attributed to a gradual contamination of the internal surfaces of plastic tubing and other instrumental devices by plutonium. Using a method recommended by other authors [19], extended

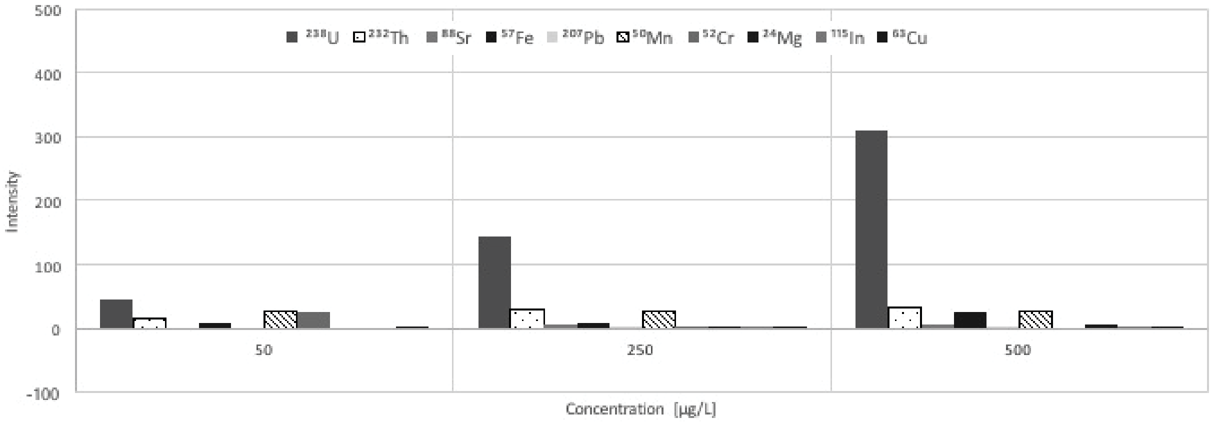

Fig. 7. Magnitude of signals recorded with ICP-MS and methane as carrier gas for m/z = 239 for various isotopes of potential interferences using 50, 250 and 500 μg L^{-1} solutions.

Table 3. Results of determination of ^{239}Pu obtained with the use of ICP-MS detection in natural samples processed in SIA-LOV system employing vTHDGA resin.

Sample	Sample volume [mL]	Added ^{239}Pu [Bq mL^{-1}]	Result	RSD [%] (number of samples)	Recovery [%]
Primary coolant from reactor MARIA	100	-	< MDL	(n = 3)	-
		0.1	72 Bq L^{-1} (31 ng L^{-1})	8.8 (n = 3)	72
Water from spent fuel pool	50	-	< MDL	(n = 3)	-
		0.2	70 Bq L^{-1} (30 ng L^{-1})	5.0 (n = 3)	70

rinsing with oxalic acid and HNO_3 solutions between each measurements was not effective, but we obtained positive results by the stabilization of the MS signal using an initial 20-times injection of 10 Bq mL^{-1} ^{239}Pu solution, and then further measurements were satisfactory for analytical determination.

The value of the instrumental limit of detection (LOD) was evaluated based on multiple (n = 7) measurements of the relative standard deviation for the blank, which was 2% HNO_3 solution containing ^{115}In as internal standard. Its value was 2.35 Bq L^{-1} ^{239}Pu, which corresponds to 1.02 ng L^{-1}. The value of the method detection limit (MDL) was evaluated by measurements of the MS signal for multiple (n = 7) repetitions of the whole sample treatment procedure for 1 mL 4 M HNO_3 solution loaded onto the SIA-LOV system. The obtained MDL value was 9.6 Bq mL^{-1}, which corresponds to 4.2 ng L^{-1}. For 100 mL sample volume, the evaluated MDL value was 96 mBq L^{-1}. These values are evidently much lower than, for instance, the 37 Bq L^{-1} LOD value reported for a system with a coupling of a calix[6]arene-based chromatography column and ICP-MS for on-line actinide analysis [20].

Determination of ^{239}Pu in real samples

The main sources of ^{239}Pu in the natural environment are the nuclear energy industry and the production of nuclear weapon. As it is formed in nuclear reactors by the uptake of neutrons by ^{238}U, its presence in the primary coolant may be evidence of a failure of fuel rods [21]. Those two facts may justify a search for fast and automated methods for ^{239}Pu determination.

The developed method for the SIA-LOV sample processing for ICP-MS determination of ^{239}Pu was used for the analysis of two real samples, namely a sample of primary coolant from the Maria nuclear reactor, and a sample of water from a spent fuel storage pool in the National Centre of Nuclear Research in Świerk. Both samples, prior to their introduction to the SIA-LOV system, were acidified with HNO_3 to a final concentration of 4 M. The processed samples from the flow system (5 mL) were diluted 10 times with 5% HNO_3, containing 50 µg L^{-1} ^{115}In employed as internal standard, and measured with the ICP-MS spectrometer. The dilution was needed to lower the total concentration of ions in the sample prior to their injection onto the ICP-MS, as the maximum concentration of all ions should not exceed 1 mg L^{-1}. The results of the determination are shown in Table 3. The whole process of the sample pretreatment for a 100 mL sample volume took 45 min when the sample loading was carried out with a flow-rate of 10 mL min^{-1}. Although only two samples were analysed, taking into account that in the spiked samples the analyte is at an ultra-trace level (10^{-10} M), the obtained precision expressed in terms of relative standard deviation (RSD) values and the recovery of the analyte were considered as satisfactory. It should also be noted that the developed SIA-LOV sample pretreatment flow system can be directly connected to the ICP-MS spectrometer without any alterations.

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LABORATORY OF MATERIAL RESEARCH

The activities of the Laboratory are focused on:

- studies of coordination polymers built of *s* block metals and azine carboxylate ligands;
- synthesis of nanoscale porous metal organic framework (nanoMOF) materials;
- synthesis of functional materials, *e.g.* silver-modified cotton and cellulose fibres, using radiation beam techniques;
- synthesis of MOF type sorbents for the removal of hazardous elements from water;
- improvement in the usable surface properties of special materials applied in nuclear energy technologies (zirconium alloys, steels) using high intensity pulsed plasma beams (HIPPB);
- characterization of art objects.

Porous coordination polymers, also called metal organic framework materials, have been widely studied in recent years. They exhibit unique pore architecture and a broad range of potential applications. The latter include greenhouse gas removal, storage of gases, selective separation of the components of gaseous mixtures and the removal of hazardous elements, such as heavy metals or radioactive isotopes, from aqueous solutions. In the case of MOFs, the pores' structure and host-guest molecules' interaction can be tailored relatively easily for a potential application by carefully combining the ligand and the type of metallic ion. At present, many potential applications of MOFs require them to be obtained at a nanometre length scale. Nanoscopic dimensions are essential to provide MOFs with high surface areas, which are beneficial, for example, for tuning their properties (catalytic, separation, sensing and sorption) and for mixed matrix membrane synthesis where MOF particles are used as fillers in a polymer matrix. Other applications include MOFs with size-dependent properties (optical, electrical and magnetic) and biocompatible materials for biomedical applications, *e.g.* the encapsulation and transport of drugs. The integration of nanoscale MOFs onto porous supports is advantageous for creating thin-layer membranes. The methods applied for nanoscale MOF synthesis include template synthesis in the pores of track-etched membranes with well-defined cylindrical pores, synthesis in microfluidic flow reactors and synthesis on the surface of porous alumina substrates and also on composites with graphene oxide.

Recently, the possibilities of waste PET (polyethylene terephthalate) utilization for the synthesis of MOFs using recovered terephthalate linkers were reported in the literature. Very robust structures made with that linker, such as UiO-66 or MIL-101, are already known. Moreover, further extending the functionalities of terephthalate MOFs is possible by the covalent grafting of chemical groups directly to the linker or to unsaturated metal sites of existing terephthalate-based MOFs in post-synthetic processes. Work on the depolymerization of PET waste bottles for terephthalic acid (TPA) recovery and on the application of the derived terephthalic acid for the synthesis of valuable metal-organic sorbents has been recently carried out in the Laboratory of Material Research.

Zirconium, due to its good water corrosion and radiation resistance at the normal working conditions of nuclear reactors, is commonly used as a cladding material for fuel elements. However, in the case of LOCA (loss-of-coolant accident) conditions, the possible extremely fast oxidation of zirconium in a steam atmosphere or in an air-steam mixture at temperatures above 800^{o}C results in intense hydrogen generation and a possible hydrogen-oxide mixture explosion. These events, despite being very rare, negatively influence the public acceptance of nuclear energy and result in high restoration costs for the accompanying damage. The development of methods to minimize the risk in the case of design-basis and beyond design-basis accidents is urgently needed. Materials with enhanced tolerance to high temperature oxidation have been already proposed for this purpose, such as silicon carbide, Mo-Zr, FeCrAl claddings, MAX phases and multilayer zirconium silicide coatings.

Zirconium silicide or zirconium silicate coatings are known for having good resistance under high temperature conditions. Up to now, they have been seldom explored for application as corrosion protective coatings for nuclear fuel claddings. However, a review of the existing literature and an analysis of thermodynamic data indicated that silicon-based coatings may offer excellent prospects in this field. In particular, they may provide a more protective barrier than the native ZrO_2 films formed on alloy cladding during routine nuclear reactor operation. Our work in recent years has been focused on the synthesis and the study of the properties of coatings made from a zirconium disilicide target or from two independent Zr and Si targets using magnetron sputtering methods. The studies performed so far have confirmed the protective nature of zirconium silicide coatings in tests in air at high temperatures in the range 900-1200°C. Unfortunately, the results of oxidation tests in an autoclave in an aqueous environment at 360°C were unsatisfactory. However, it was found that around 33% admixture of chromium significantly improves the oxidation resistance of zirconium silicide coatings in autoclave tests.

In order to examine, characterize and analyse cultural heritage artefacts or art objects and their component materials, a conservation scientist requires a palette of non-destructive and non-invasive techniques. This type of research improves our knowledge concerning the elaboration, evolution and degradation of art objects and artefacts over time and provides a basis for their restoration and conservation. Among various methods used for the examination of art objects and artefacts, nuclear techniques are crucial due to their high sensitivity and reproducibility.

The purpose of last year's study related to the cultural heritage framework was the investigation of the La Tène culture's impact on the cultures of ancient Central Europe, especially the Przeworsk culture. The provenance of prehistoric iron is one of the key questions of the archaeology of the Iron Age. A prehistoric burial ground of the Przeworsk culture dated between the 1st century BC and 2nd century AD was excavated near Legionowo. Our study is the first part of a series of such investigations concentrated on iron artefacts from the collection of the Historical Museum at Legionowo. The INAA method was chosen to study the composition of a large number of iron objects. Interpretation of the results based on statistical methods allowed us to differentiate the artefacts in relation to various production centres and production recipes, as well as various raw materials and the methods of their purification. Unique documentation and a database for different types of iron objects are among the results of these studies. Through this research, it will be possible to confirm that objects found in the areas inhabited by the Przeworsk culture are potential imports and to simultaneously provide a new look at intercultural relations in Europe. Moreover, it will allow further assessment of the significance of the La Tène culture in shaping the Przeworsk culture.

The investigation on the chemical composition, chemical durability and technologies employed in the manufacture of historical glass using PGAA (prompt-gamma activation analysis), XRF (X-ray fluorescence analysis) and micro-sample techniques was continued in 2018. The study was focused mainly on 17th and 18th century glass vessels from selected historical collections and on some archaeological findings.

APPLICATIONS OF TEREPHTHALIC ACID RECOVERED FROM WASTE PET BOTTLES FOR SYNTHESIS OF VALUABLE METAL-ORGANIC FRAMEWORK MATERIALS

Wojciech Starosta, Krzysztof Łyczko

Porous coordination polymers constructed from metal-containing nodes and organic bi- or multi-functional linkers, also known as metal-organic frameworks (MOFs), have been actively studied in recent years. Their potential applications in gas storage, separations, catalysis, chemical sensing and drug encapsulation [1] are the main reasons for this interest. The number of MOF structures deposited in the Cambridge Structural Database 2019 edition amounts to 90947. However, progress in the area of applications is much slower, as it is frequently limited by the difficulty of resolving stability issues in the harsh chemical environment used. Therefore, the continuation and extension of application-oriented investigations would be beneficial for the further progress and development of the whole area.

Recently, the possibilities of waste PET (polyethylene terephthalate) utilization for the synthesis of MOFs using recovered terephthalate linker were reported in the literature [2, 3]. By narrowing ourselves down to the terephthalate linker the range of possible structures is limited significantly. However, very robust structures made with this linker, such as UiO-66 or MIL-101, are known. Moreover, extending the functionalities of MOFs is possible by the covalent grafting of chemical groups' functionalities directly to linker, or to unsaturated sites of existing terephthalate-based MOFs in post-synthetic processes, and has been already proven [4-7].

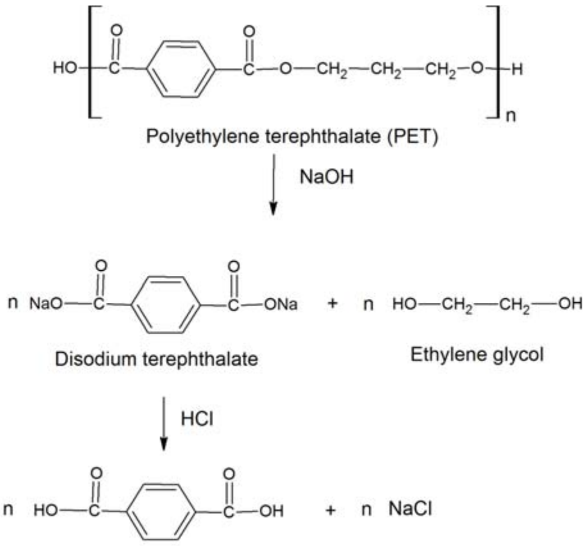

Fig. 1. The general scheme of the PET depolymerization process.

In this paper, experiments conducted recently at the Laboratory of Materials Research on the depolymerization of waste bottle PET for tereph-

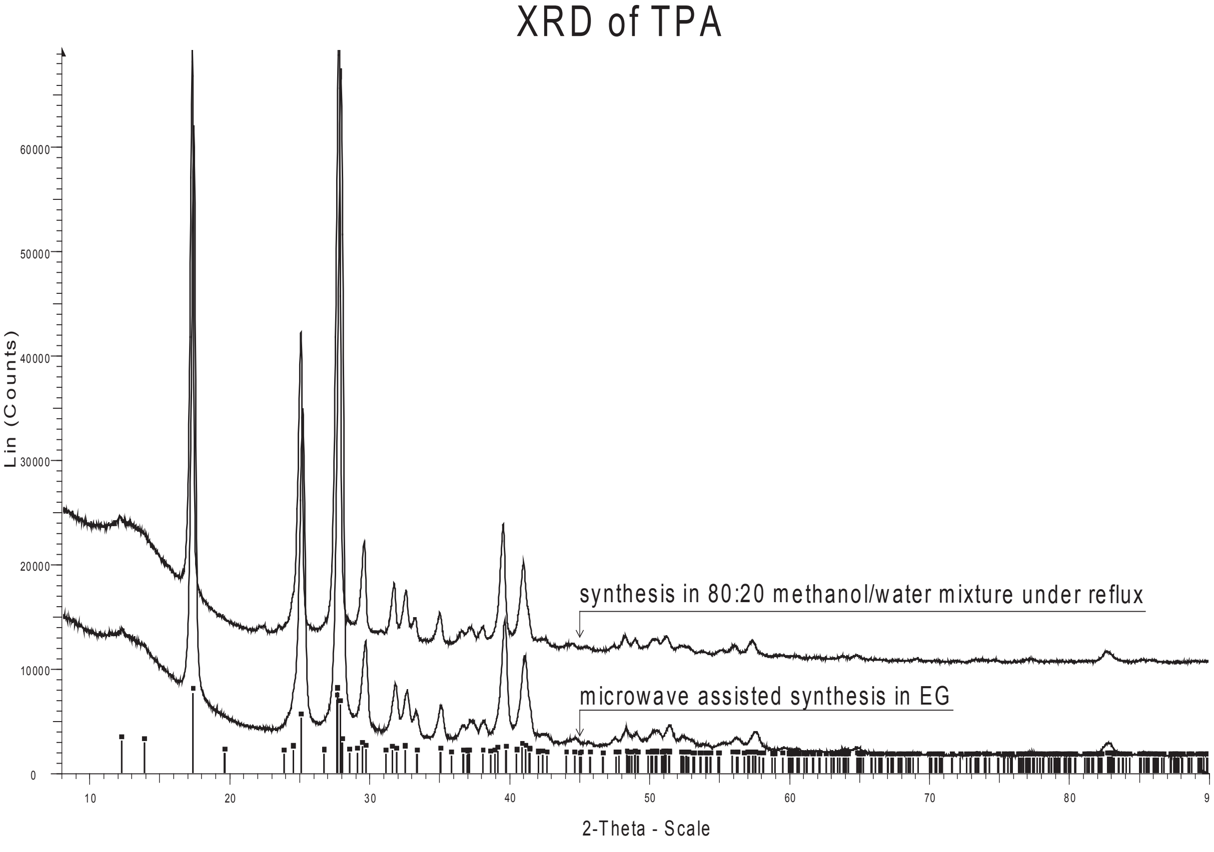

Fig. 2. X-ray diffractograms of terephthalic acid obtained by depolymerization of PET in 80:20 methanol/water solution of NaOH and by microwave assisted depolymerization in ethylene glycol solution of NaOH.

thalic acid (TPA) recovery and on the application of the derived terephthalic acid for the synthesis of valuable metal-organic sorbents are presented.

Waste PET is presently of severe environmental concern due to the large amounts stored every year and the relatively small amount recycled [8]. However, PET can be depolymerized and terephthalic acid recovered by hydrolysis in a concentrated solution of sodium hydroxide. In accordance with the reactions shown in Fig. 1, water-soluble disodium terephthalate is created as an intermediate product. Terephthalic acid can be recovered from this solution by acid precipitation.

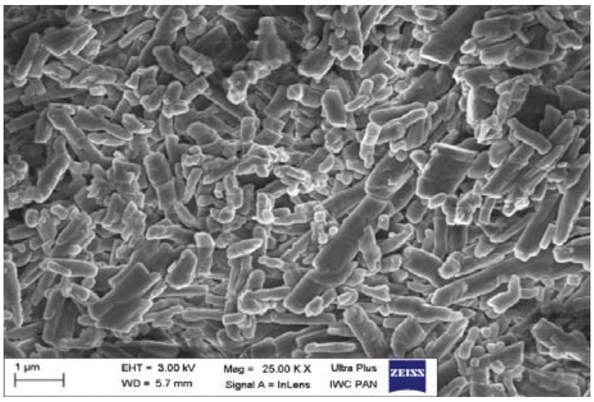

Fig. 3. SEM photo of terephthalic acid obtained by waste PET depolymerization.

We utilized different chemical routes for PET depolymerization such as:

- hydrolysis in a concentrated aqueous solution of NaOH under reflux,
- hydrolysis in an 80:20 methanol/water solution of NaOH under reflux,
- microwave assisted glycolysis (typically, a mixture of 2 g PET flakes and 0.8 g of NaOH in 5 ml of ethylene glycol was treated in a microwave oven at 180 W power for 5 min).

In all cases, an efficiency of depolymerization higher than 90% was obtained. The X-ray diffraction (XRD) spectra of the precipitation product, shown in Fig. 2, confirmed the presence of one of the polymorphs of terephthalic acid. The observed diffraction pattern matches perfectly the terephthalic acid pattern with crystal structure parameters of a = 3.7808 Å, b = 6.44828 Å, c = 7.4083 Å, α = 82.94°, β = 81.01°, γ = 88.98°, space group P-1.

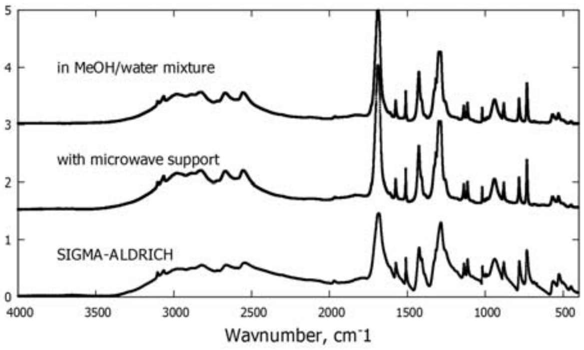

Fig. 4. FTIR spectra of terephthalic acid samples synthesized from waste PET and that supplied by Sigma-Aldrich.

The XRD spectra show also the presence of amorphous phase (the bump at the small angles). It was found that amount of amorphous phase may be decreased by repeating the process (multiple solubilization in alkaline solution followed by precipitation using acid solution). By applying this method the primary product may be purified.

The SEM (scanning electron microscopy) photo of terephthalic acid in Fig. 3 shows the nanocrystalline nature of the material obtained.

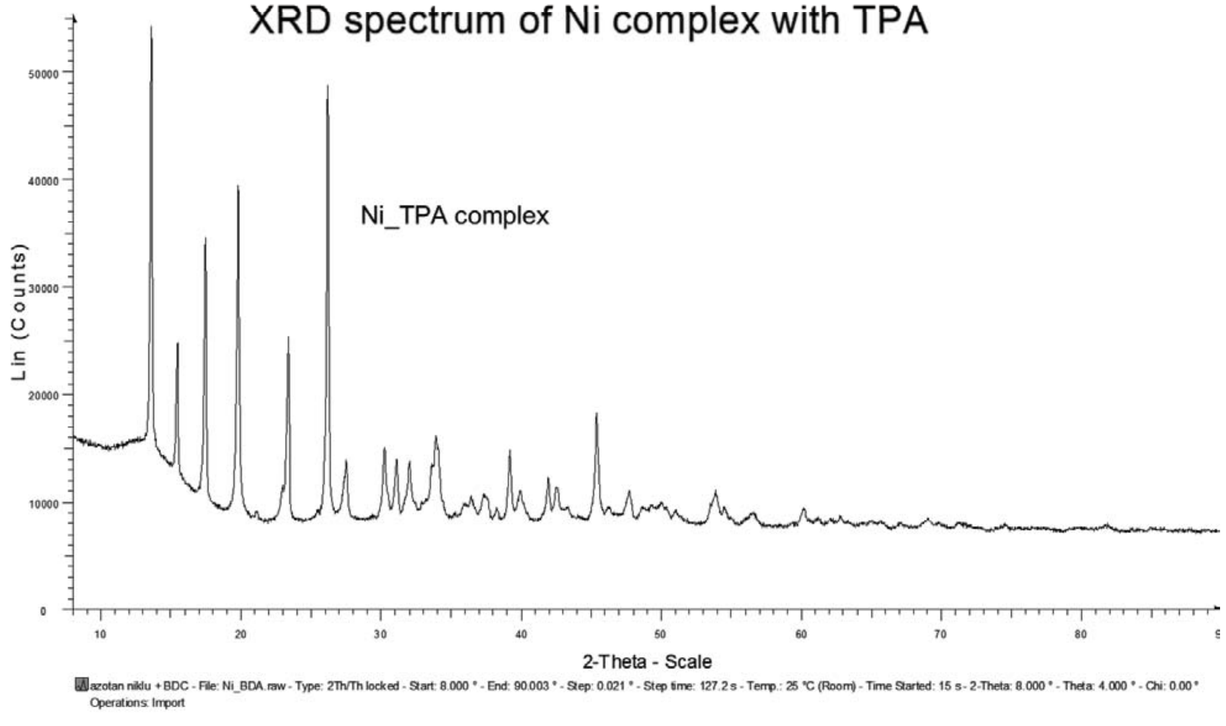

Fig. 5. The XRD spectrum of MOF-type nickel complex with terephthalic acid after 7-day synthesis at room temperature in water.

The infrared absorption spectra were measured with a Thermo Scientific Nicolet iS10 FT-IR spectrometer using KBr pellets. The spectra shown in Fig. 4 confirms the high degree of identity between the terephthalic acid supplied by Sigma-Aldrich and the product synthesized from waste PET bottles.

The terephthalic acid obtained was used for porous MOF synthesis. The nickel complex with terephthalic acid was synthesized by an environmentally friendly, green route at room temperature. Water-soluble disodium terephthalate obtained from waste PET and nickel(II) chloride were applied as substrates. In a typical synthesis, 10 mmol of $NiCl_2$ and 5 mmol of disodium terephthalate were dissolved in 50 ml of water and continuously mixed for around a week. The XRD spectrum shown in Fig. 5 confirms the synthesis of the nickel terephthalate complex. The morphology of the complex is shown in Fig. 6. Recently, this complex has been selected as a green catalyst that can accelerate the decomposition of sodium borohydride and deliver hydrogen to a fuel cell using small amounts of material [9].

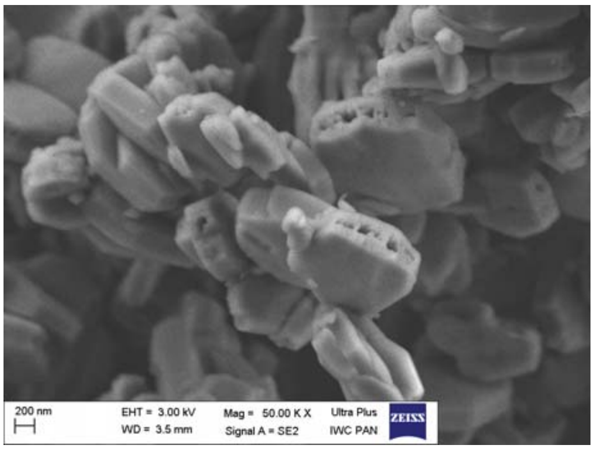

Fig. 6. SEM photo of nickel terephthalate complex.

Another material successfully synthesized with terephthalic acid obtained from waste PET was the well-known UiO-66 (zirconium terephthalate – $Zr_6O_4(OH)_4[C_6H_4(COO)_2]_6$).

The terephthalic acid obtained by the PET depolymerization process was also used for a single crystal synthesis of the terephthalic acid adduct with dimethylacetamide. The molecular structure of the adduct crystallizing in the monoclinic system $P2_1/n$ (a = 10.17915 Å, b = 8.52215 Å, c = 10.71486 Å, β = 110.62°) is shown in Fig. 7.

In conclusion, this study clearly shows that terephthalic acid recovered from waste PET bottles can be used for the cost-effective synthesis of valuable metal-organic framework-type sorbents.

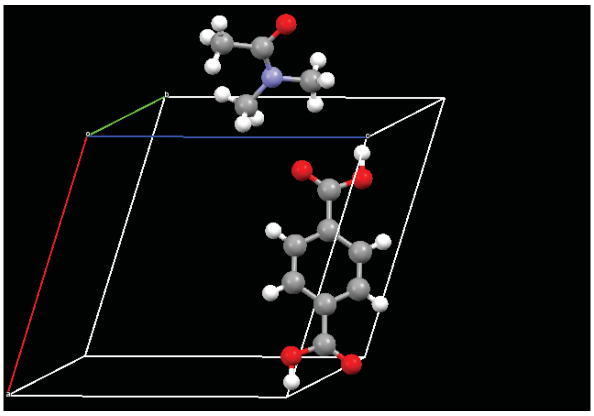

Fig. 7. The molecular structure of 1,4-benzene dicarboxylic acid adduct with dimethylacetamide.

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STUDIES OF ZIRCONIUM ALLOY COATINGS WITH ELEMENTAL COMPOSITION OF Zr, Si AND Cr

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Zirconium (Zr), due to its good water corrosion and radiation resistance under the normal working conditions of nuclear reactors, is commonly used as a cladding material for fuel elements. However, in the case of loss of coolant accident (LOCA) conditions, the extremely fast oxidation of zirconium in a steam atmosphere or air-steam mixture at temperatures above 800°C results in intense hydrogen generation and possible hydrogen-oxide mixture explosions. The concepts of accident tolerant fuels (ATF) and accident tolerant materials (ATM), meaning materials with an increased accident tolerance, have been developed recently to minimize the risk of such accidents [1-4]. The approaches taken can be grouped into two categories: (i) non-zirconium cladding with high strength and oxidation resistance, and (ii) improved high-temperature oxidation resistance and/or strength of the Zr alloy cladding. Coatings based on silicon are one of the investigation directions that have been followed at different institutes, including the Institute of Nuclear Chemistry and Technology [5-9]. These zirconium silicide or zirconium silicate coatings are known for good resistance in high temperature conditions and are applied as environmental barrier coatings for high-temperature gas-turbine components. Silicon-based coatings may provide a more protective barrier than the native ZrO_2 films formed on alloy cladding during routine nuclear plant operations and may provide a protective barrier during high-temperature accident scenarios. Phase diagrams for zirconium-silicon systems show the existence of intermetallic compounds with different Zr/Si ratios and stability regions. For example, $ZrSi_2$ is stable up to 1620°C and ZrSi is stable up to 2210°C [10].

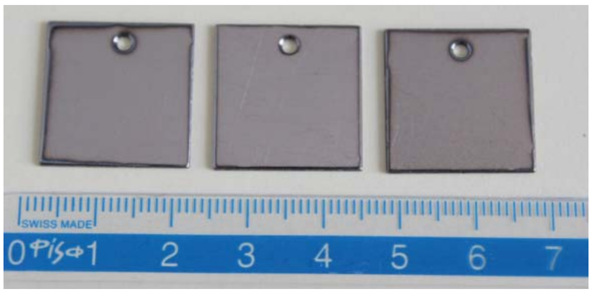

Fig. 1. General view of coated Zry-2.

The material used for our investigations was Zircaloy-2 (Zry-2) from Westinghouse with elemental composition: Sn – 1.3-1.6 wt%, Fe – 0.07-0.20 wt%, Cr – 0.05-0.16 wt%, Ni – 0.03-0.08 wt% and the following impurities: Al, B, Cd, C, Co, Hf, Pb, Mg, Mn, Mo, Si, Ti, W and V. Coatings were formed with a Balzers system – a multi-source plasma magnetron sputtering system with three magnetron plasma sources. The system allows materials to be deposited from separate targets, and multi-elemental coatings to be obtained. Two separate targets (i) composite $ZrSi_2$ and (ii) Cr were used. Samples were coated on both sides. A general view of coated samples is shown in Fig. 1. The samples' surfaces were homogeneous, no characteristic morphological objects being visible. Observations using scanning electron microscopy (SEM) showed details of the surface morphology. It can be seen that samples are coated uniformly, but scratches on the initial material can be distinguished. Agglomerates of deposited material can also be distinguished (Fig. 2). The thickness of the obtained layer was about 2.5 μm.

Energy dispersive spectroscopy (EDS) used for elemental analysis of the coatings confirmed the presence of Zr, Si and Cr. Additionally, the elemental composition homogeneity of the obtained layer was confirmed using EDS point analysis, and depth elemental profiles were in line with the surface analysis results (Fig. 3). Coatings of $Zr_{40}Si_{24}Cr_{36}$ were formed.

Oxidation tests (A1 and A2) on Zry-2 and Zry-2 coated with $Zr_{40}Si_{24}Cr_{36}$ were performed in a PARR 4653 autoclave under the following parameters: 360°C, 195 bar, 21 (A1) and 42 (A2) days.

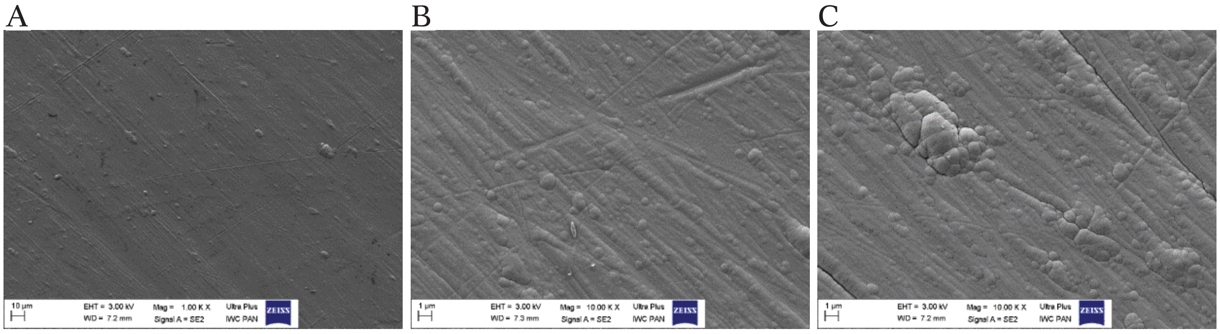

Fig. 2. SEM images of coating surface with different magnifications: (A) ×1000, (B) and (C) ×10 000.

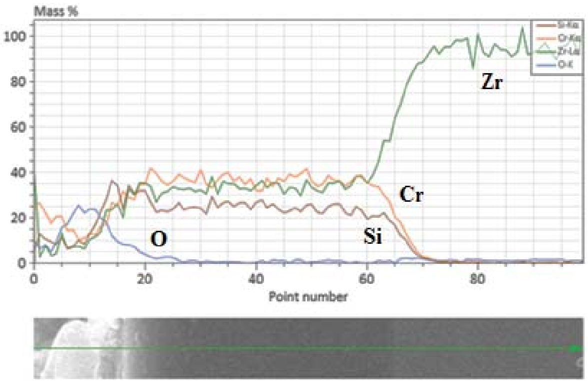

Fig. 3. Elemental concentration in the Zr-Si-Cr coating.

Table 1. Characterization of the water used for autoclave oxidation tests.

	To A1	After A1	After A2
pH	6.74	5.68	6.51
TDO [mg/l]	8.88	7.41	7.32
σ [μS/cm]	11.90	62.3	66.1
Cl^- [mg/l]	0.45	7.5	2.18
NO_3^- [mg/l]	0.033	1.38	0.183
SO_4^{2-} [mg/l]	0.429	9.44	5.35
Na^+ [mg/l]	4.4	3.52	2.14
K^+ [mg/l]	0.4		0.95
Ca^{2+} [mg/l]	2.7	7.09	5.08
Li^+ [mg/l]	0.3	2.08	1.674
Mg^{2+} [mg/l]	0.3	0.25	0.35

The water used in the autoclave experiments was supposed to simulate that from PWR reactors [11], and thus standard conditions for the water were: [Li] = 2-2.2 ppm, [B] = 600-1000 ppm. Changes of water chemistry were studied using ICP-MS (inductively coupled plasma mass spectrometry) with an Elan DRC II spectrometer (Perkin Elmer) and a ProLab 2500 digital meter for IDD sensors (SI Analytics). The results are presented in Table 1. The observed changes in the parameters and chemistry, for example the differences in TDO, σ and the ions' concentrations are connected with the dissolution of substances present in the autoclave (autoclave construction material and investigated samples) and the oxidation process.

Cross-sections of the samples after the A1 and A2 tests showed the presence of oxide layers as well as coating layers (Fig. 4). The oxide layers were formed at the samples' surfaces for the reference Zry-2 and Zry-2 coated with $Zr_{40}Si_{24}Cr_{36}$ (Fig. 4). These layers had the following thicknesses (in μm):

- for Zry-2: 1.488 μm (test A1) and 2.074 μm (test A2),
- for Zry-2 coated with $Zr_{40}Si_{24}Cr_{36}$: 0.5166 μm (test A1) and 1.090 μm (test A2).

In the case of the coated samples, the oxide layer was 35% thinner after the A1 test and 53% thinner after the A2 test. The depth elemental profile changed as compared with the initial ma-

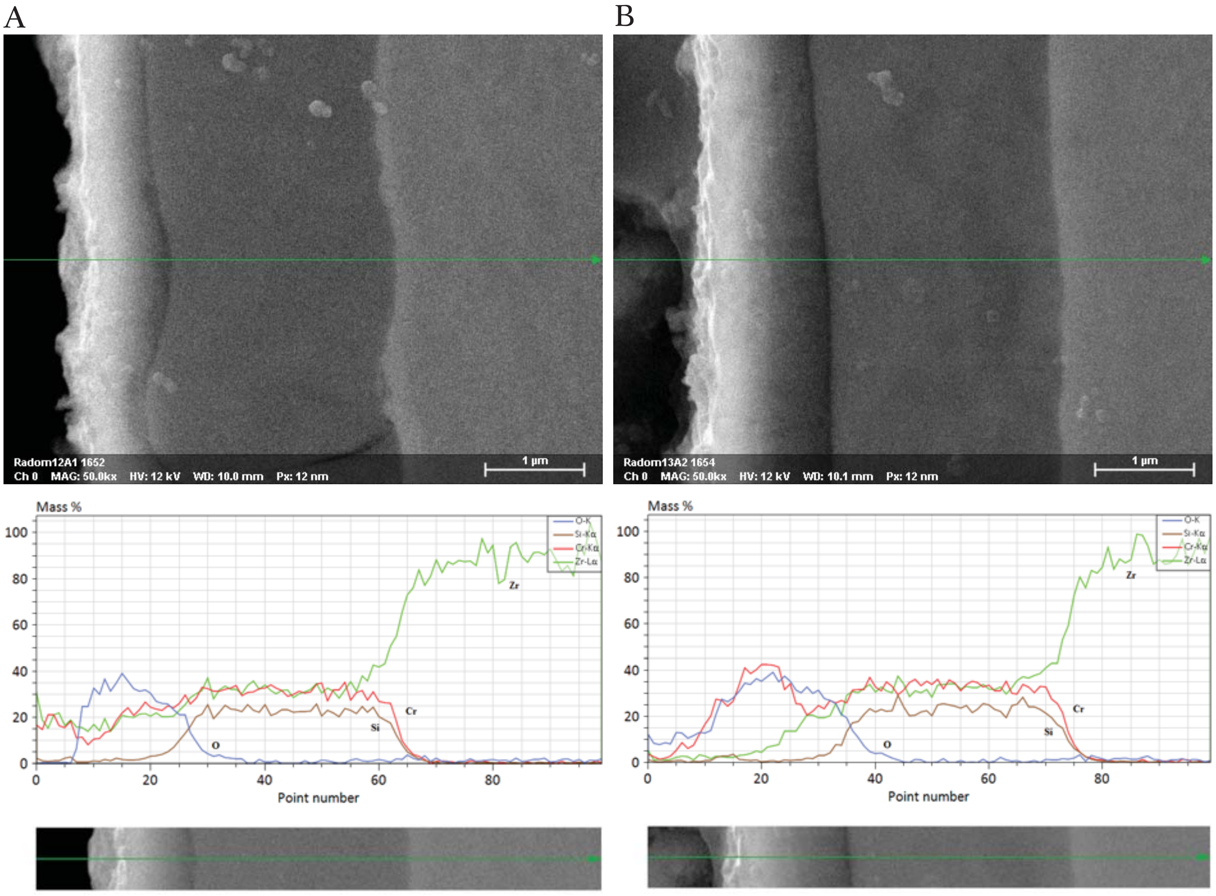

Fig. 4. Elemental concentration in Zry-2 coated with $Zr_{40}Si_{24}Cr_{36}$ after tests A1 (A) and A2 (B).

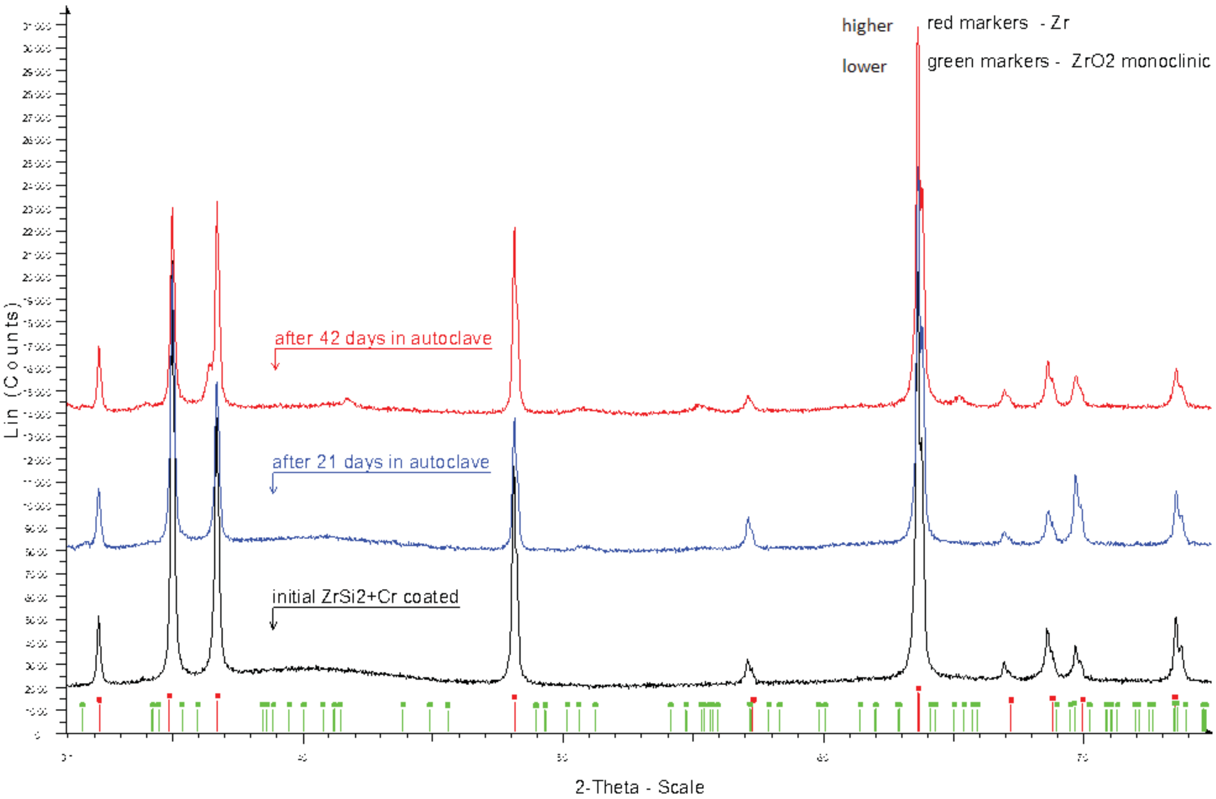

Fig. 5. The set of XRD spectra of the initial material – Zry-2 coated with $Zr_{40}Si_{24}Cr_{36}$ and that after autoclave tests.

terial (Figs. 3 and 4). The most important observation was the presence of Zr and Cr in the oxide layer.

An oxidation process of the $Zr_{40}Si_{24}Cr_{36}$ coatings took place. Due to this fact, the base material (here: Zry-2) remained unoxidized. These results mean that the presence of $Zr_{40}Si_{24}Cr_{36}$ coatings slowed down Zry-2 oxidation, showing the protective character of these coatings.

The phase analysis was performed in Bragg-Brentano geometry with an Advanced D8 X-ray diffractometer (Bruker). The set of XRD (X-ray diffraction) spectra, both Zry-2 coated with $Zr_{40}Si_{24}Cr_{36}$ and after the autoclave tests, confirmed that an oxidation process took place during the autoclave tests. Peaks characteristic for the ZrO_2 monoclinic phase were observed after the A1 test at $2\theta = 51^{\circ}$ and after the A2 test at $2\theta = 34$, 42, 51 (stronger than after A1), 56 and 66°. The observed peak widening was connected with the presence of dispersive phases (grains) (Fig. 5).

Zirconium coatings with the composition of $Zr_{40}Si_{24}Cr_{36}$ were obtained using the PVD (physical vapour deposition) method with $ZrSi_2$ and Cr targets. Surface layers with a 2.5 μm thickness, containing Zr, Si and Cr were obtained. During the autoclave test (360°C, 195 bar, water, 21 and 42 days), the deposited $Zr_{40}Si_{24}Cr_{36}$ layers were oxidized. Thus the base material (in this case Zry-2) was protected from oxygen migration, which confirmed the protective role of the proposed coatings. Further autoclave oxidation tests are planned.

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A CONTRIBUTION OF INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS TO THE CHARACTERIZATION OF DOROGICHIN SMALL LEAD SEALS

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The purpose of this work was to develop a method for the trace element analysis of lead seals using instrumental neutron activation analysis (INAA). The main focus of this study was on early-medieval items, mainly Dorogichin-type seals from their archaeological context as well as from museums'

Fig. 1. Czermno, pow. Tyszowce, Poland. Selected Dorogichin seals (before conservation treatment): No. 1 – Inv. No. MT/1912/19, No. 2 – Inv. No. MT/1912/38, No. 3 – Inv. No. MT/1912/46, No. 4 – Inv. No. MT/1912/54, No. 5 – Inv. No. MT/1912/55, No. 6 – Inv. No. MT/1912/75, No. 7 – Inv. No. MT/1912/76, No. 8 – Inv. No. MT/1912/78, No. 9 – Inv. No. MT/1912/82, No. 10 – Inv. No. MT/1912/83 (photo: M. Wołoszyn, design: I. Florkiewicz) [1].

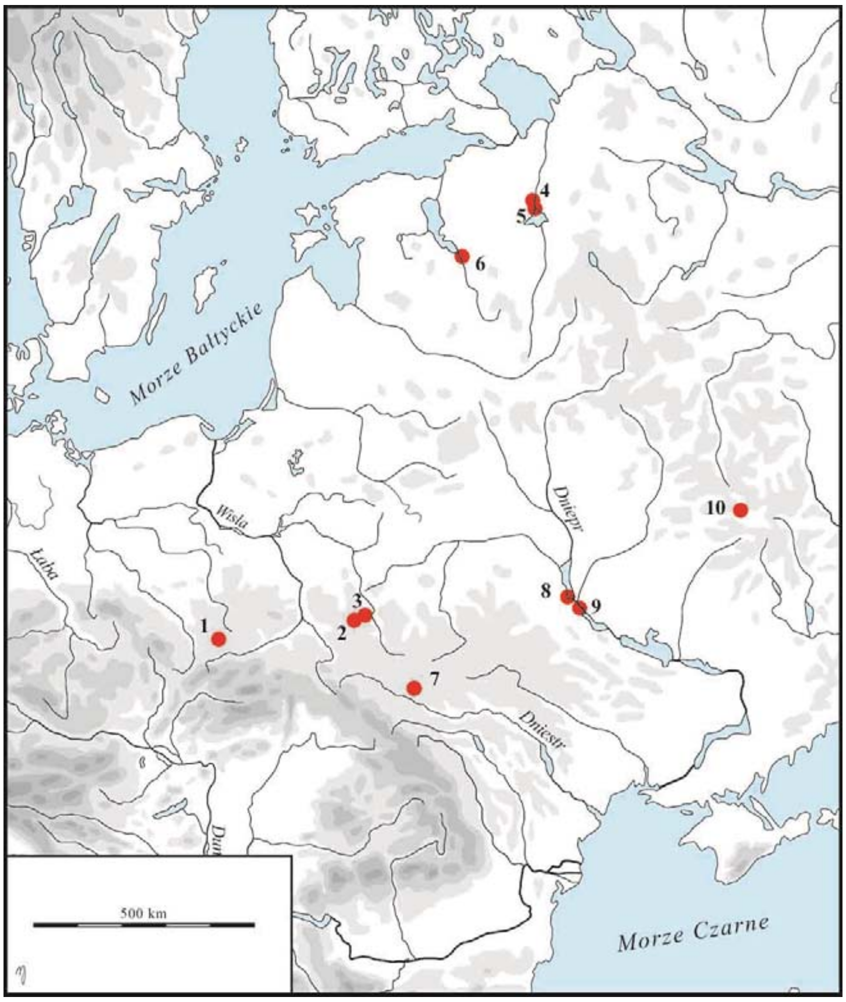

Fig. 2. Distribution of analysed Dorogichin small lead seals.

Table 1. Description of analysed lead seals.

Ordinal number	Description of seals	Sample location	Ordinal number	Description of seals	Sample location
1	U I	Ukraine, Vyshhorod	20	P-Cz-XIX	Poland, Czermno
2	P-Cz-I	Poland, Czermno	21	P-Cz-XX	Poland, Czermno
3	P-Cz-II	Poland, Czermno	22	P-G-I	Poland, Gródek
4	P-Cz-III	Poland, Czermno	23	P-G-II	Poland, Gródek
5	P-Cz-IV	Poland, Czermno	24	P-G-III	Poland, Gródek
6	P-Cz-V	Poland, Czermno	25	P-G-IV	Poland, Gródek
7	P-Cz-VI	Poland, Czermno	26	P-G-V	Poland, Gródek
8	P-Cz-VII	Poland, Czermno	27	P-G-VI	Poland, Gródek
9	P-Cz-VIII	Poland, Czermno	28	P-G-VII	Poland, Gródek
10	P-Cz-IX	Poland, Czermno	29	P-G-VIII	Poland, Gródek
11	P-Cz-X	Poland, Czermno	30	P-DGŁ-IX	Poland, Dąbrowa Górnicza-Łosień
12	P-Cz-XI	Poland, Czermno	31	R-K-I	Russia, Kursk
13	P-Cz-XII	Poland, Czermno	32	R-K-II	Russia, Kursk
14	P-Cz-XIII	Poland, Czermno	33	R-P-III	Russia, Pskov
15	P-Cz-XIV	Poland, Czermno	34	R-P-IV	Russia, Rurikovo Gorodishche
16	P-Cz-XV	Poland, Czermno	35	R-BH-V	Russia, Novgorod
17	P-Cz-XVI	Poland, Czermno	36	U-D-I	Ukraine, Zvenyhorod
18	P-Cz-XVII	Poland, Czermno	37	U-K-I	Ukraine, Kiev
19	P-Cz-XVIII	Poland, Czermno	38	U-K-II	Ukraine, Kiev

collections. The application of INAA allowed some minor and trace elements to be analysed, which provided data reflecting to some extent the method of preparation (purification) or the differentiation of various sources of certain raw materials. A database for different types of lead seals is the result of these studies.

The project aimed to recognize the chemical composition of lead seals selected from the items excavated in the area of the medieval Cherven Towns, with hill-forts at Czermno and Gródek (Poland). The Cherven Towns, an important area coveted by the Piast and the Riurikid rulers, are recorded, under the dates of 1018 and 1031, in the Russian Primary Chronicle. The stronghold of Cherven is mentioned for the first time under the date of 981 [1]. The 2010-2011 finds from Czermno, thanks to their detailed recording, have a special relevance. One highly revealing circumstance is thar nearly all the lead seals, including Dorogichin-type specimens, were recovered at Czermno from the marshy valley of the Huczwa river. It was assumed that knowledge of the chemical composition of the lead seals, including trace element characterization, might help to disclose the origin of objects in the future. Certain lead seal objects from Russia and the Ukraine, which served as comparative materials, were also included to the project. Figure 1 presents Dorogichin-type seals, which have the form of two roughly circular lead discs pressed together with, originally, between them, a piece of string now intimated only by the presence of two holes.

38 samples of historical Dorogichin-type lead seals from four 'regions' were investigated: (I) Piast Poland: No. 1 Dąbrowa Górnicza-Łosień; (II) Russian-Polish borderlands: No. 2 Czermno, No. 3 Gródek, No. 7 Zvenyhorod/Dźwinogród; (III) Northern Ruthenia: No. 4 Novgorod, No. 5 Rurikovo Gorodishche, No. 6 Pskov; (IV) Southern Ruthenia: No. 8 Vyshhorod, No. 9 Kiev, No. 10 Kursk. Distribution of analysed Dorogichin small lead seals is presented in Fig. 2. Table 1 includes a description of collected samples.

For analysis of some minor and trace elements, the INAA method was applied, without chemical separation, using standards of the analysed elements. Samples were also taken with the use of a diamond point tool. After weighing and sealing in quartz ampoules, samples of mass 20-40 mg were packed in packages including eight samples each, together with the CTA-FFA-1 standard (Institue of Nuclear Chemistry and Technology). Additionally, Sc and Au standards were attached to every sample series, to act as monitors of thermal neutron flux.

The irradiation of the samples was carried out in the MARIA reactor at Świerk, at a thermal neutron flux of $8 \cdot 10^{13}$ n/cm^2 s. Samples were irradiated for 0.5 h and cooled for 8 h. Irradiated samples, after being taken out from the package, were washed in 1 M hydrochloric acid and rinsed in alcohol to remove surface contamination.

The radioactivity of the samples and standards was measured by means of an HP-Ge detector (ORTEC) with an active volume of 80 cm^3 and an energy resolution of 1.95 keV for a 1333 keV ^{60}Co source. The detector was coupled to a CANBERRA-System S100 spectrometer, controlled by computer. The analysis of the complex gamma-ray spectra of the samples was carried out using Genie 2000 software. The measurements were repeated five times within the four months after irradiation, while the measurement time varied between 300 s and 7200 s. The lower limits of detection of elements in the lead seals were determined using the Currie method (Table 2) [2].

Table. 2. Lower limit of determination of some elements in lead. Neutron flux – $8 \cdot 10^{13}$ n/cm^2 s, irradiation time – 0.5 h, cooling time – 8 h, counting time – 2 h.

Element	Lower limit of determination [pg]
La, Ir, Au	0.01-0.1
Na, Sc, Sb	0.1-1
Co, Mo, W, As, Ta, Br, Cu, Ag	1-10
K, Cr, Zn	10-100
Ba, Ni (^{58}Co), Fe	100-1000

47 elements were determined in the analysed samples with the use of INAA. The average measured precision, which depends upon the inhomogeneity, variations in the neutron flux and counting errors, was about 10%, ranging from 5% to 17%. Out of 47 determined elements, only the elements identified in all the tested samples were selected for further analysis.

A multi-parameter statistical analysis using STATISTICA (StatSoft) software was applied, using six elements characteristic for the tested samples (Ag, Eu, La, U, Th and Zn) to identify the degree of similarity of the analysed objects. These multivariate analyses (principal component analysis – PCA and clustering analysis) were performed for standardized and logarithmic variables. The results of the principal component analysis are presented in Fig. 3, and the results of the Ward's method cluster analysis of 38 lead seals, described by six features representing six elements, are shown in Fig. 4. Samples are separated into two groups related to the different kinds of seals (Czermno, Gródek and the others).

Trace elements present in the lead seals can help to separate the groups and confirm the affiliations of individual objects. At present, we can point out some groups of seals that were probably melted with the use of certain raw materials that originated from one source.

Trace elements refine this understanding and help to distinguish lead objects according to the sources of the raw materials used for their manufacturing.

Application of INAA in the provenance study of lead objects is not only possible, but provides reliable information about many elements, thus enabling the characterization of the investigated objects.

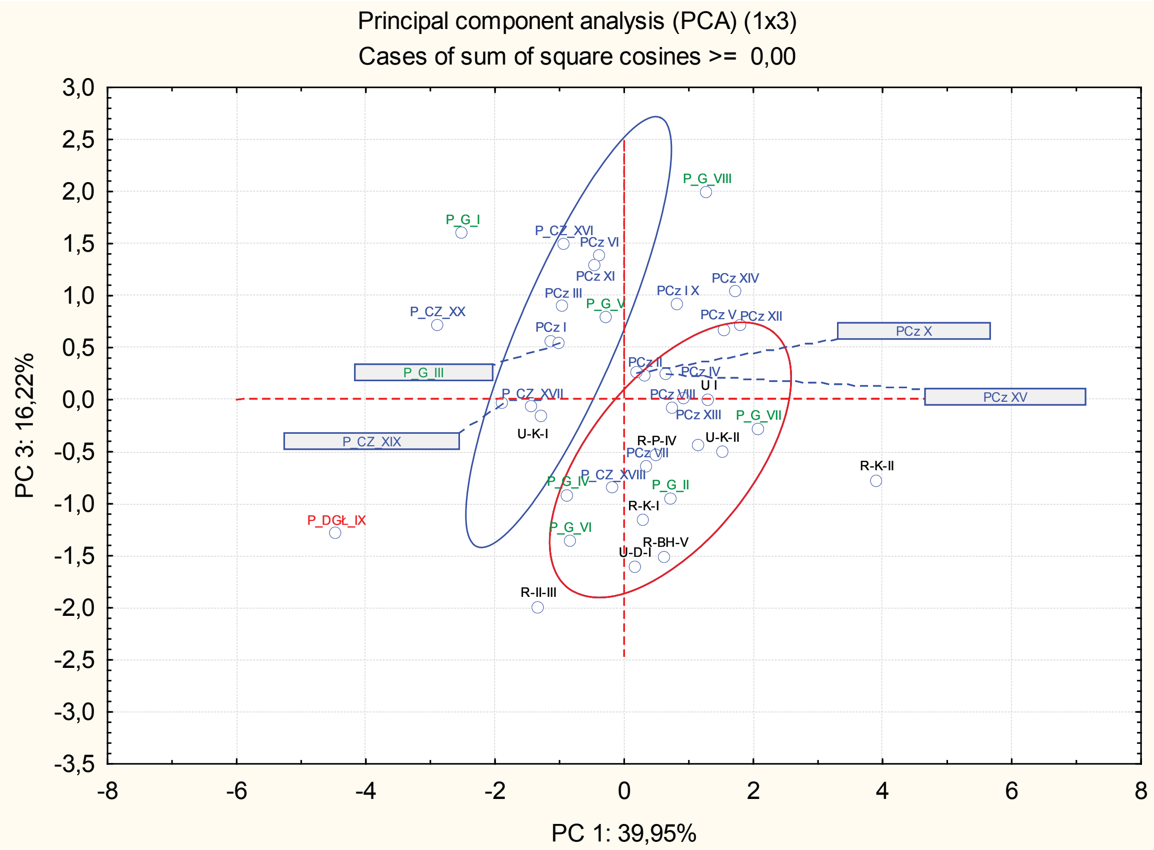

Fig. 3. Principal component analysis (PCA) of lead seals from Czermno, Gródek, Ukraine, Russia and Łosień carried out on set defined by six variables (Ag, Eu, La, Th, U and Zn).

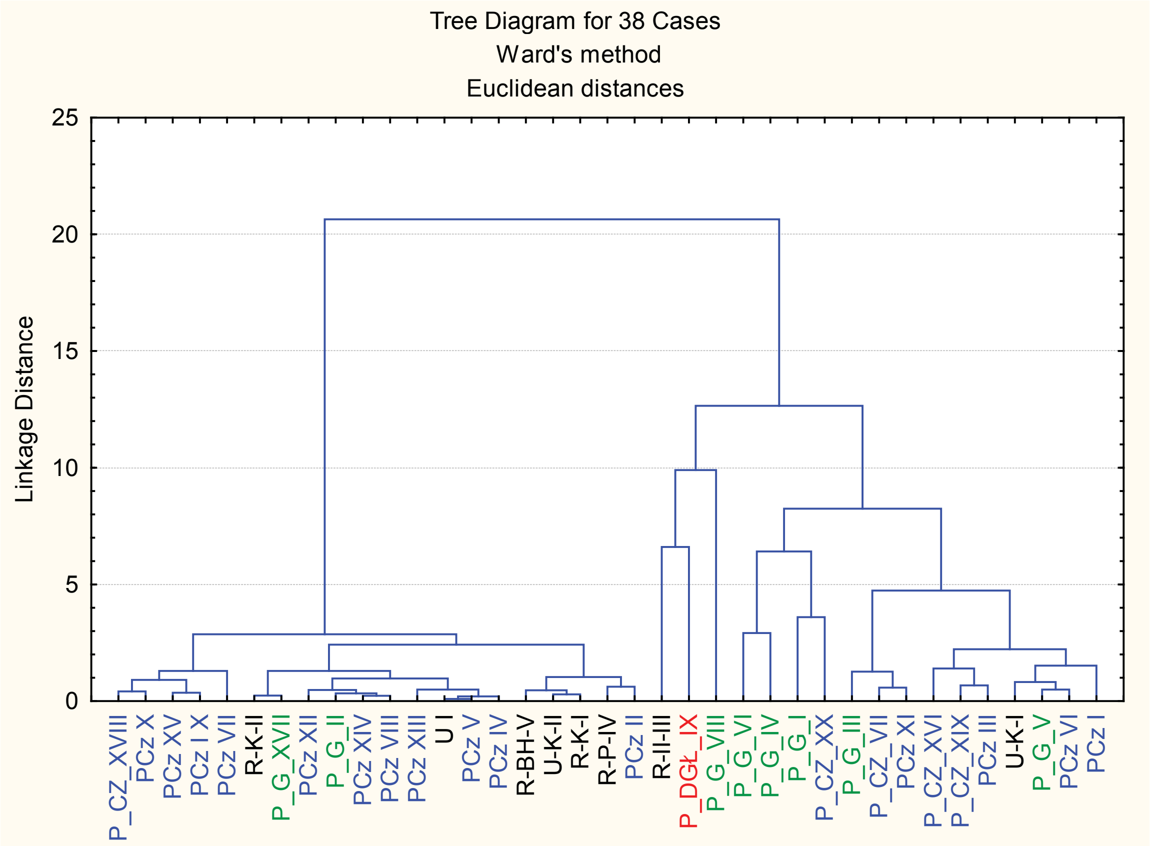

Fig. 4. Cluster analysis of 38 analysed lead seals from Czermno, Gródek, Ukraine, Russia and Łosień describing six features (the number of features was determined by INAA elements: Ag, Eu, La, U, Th and Zn); standardized and logarithmic variables.

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IDENTIFICATION OF GLASS OBJECTS SUSCEPTIBLE TO CRIZZLING. THE CASE OF CENTRAL EUROPEAN BAROQUE POTASSIUM GLASS

Jerzy J. Kunicki-Goldfinger

Crizzling is a phenomenon that has attracted the attention of many glass researchers, curators and conservators for more than a century [1-7]. It is one of the most distinctive symptoms of glass instability for objects kept in the atmosphere. Under normal museum conditions, a major source of the phenomenon is the innate instability of the glass chemical composition. A deficiency of stabilizers (such as CaO) and excess alkali are believed to be the main causes of the phenomenon, which is not reversible and leads to total decay of the glass. It seems that crizzling manifests itself when the hydrated corrosion layers on the surface of the glass shrink and crack. The presence of this hydrated layer constitutes a necessary condition for this process to develop: the thicker the hydrated layer, the greater the chance of cracks developing.

As we cannot change the chemical composition of glass, the only approach to protect these objects is to keep them under the appropriate stable conditions [8]. The deterioration rate can be then significantly reduced. Therefore, the best we can hope to achieve is to identify the objects susceptible to crizzling before the visible symptoms of deterioration occur. These objects could then be stored under specially tailored conditions to slow down the process of their destruction.

We can try to identify the glass objects susceptible to crizzling based on a combined approach consisting of three steps [9]:

- conservation survey,
- chemical characteristics,
- ultraviolet light inspection.

A conservation survey focuses mainly on the characterization of the conditions of outer glass surfaces. Optical coherence tomography (OCT), a completely non-destructive method, seems to be a good auxiliary tool to identify and measure the thickness of the so-called hydrated layer [10]. It also allows the monitoring of its changes with time.

The main factor influencing possible glass deterioration in the atmosphere leading to the appearance of crizzling is the chemical composition of the glass. One of the largest groups of glasses already crizzled throughout galleries around the world are central European potassium glasses from the late 17th and 18th centuries. There are some suggestions that only glasses of the best quality manifest the described symptoms. It is believed that the best glasshouses were attempting new experimental meltings and recipes that have proved to be unstable. Sometimes, we can even point out the specific glasshouses which produced glasses under ‘increased risk’, and the glasshouses in Dresden (Saxony), Zechlin (Brandenburg) and Naliboki (Polish-Lithuanian Commonwealth) are the examples of these. Working on already crizzled glasses, we can identify at least some of these groups, and we can anticipate that other members of these groups are susceptible to crizzling, too. We can try to identify them based on the combined approach of art historians and material scientists. Although, for material characterization of glass, chemical analysis constitutes a crucial method, it seems impracticable – and practically not possible – to carry out the chemical analysis of every glass object. Non-destructive XRF (X-ray fluorescence) analysis may also provide us with very valuable data. The average simplified chemical compositions of five main identified technological groups of potassium glasses melted in central Europe from the late medieval period up to the end of the 18th century are shown in Table 1. They are wood ash glass, potash glass, chalk glass and two groups of crystal glass. The last three groups of the glasses did not appear until the second half of the 17th century. These new groups of glasses were produced, among others, using a number of new raw materials, such as saltpetre and arsenic (without mentioning all). Quantitatively, chalk glasses, which were much cheaper, dominated the market. However, importantly for this topic, all identified crizzled objects fit into the groups of crystal glasses. Crystal glasses are characterized by the lowest concentration of CaO and by a higher than concentration of As_2O_3. The As_2O_3/CaO ratio can therefore serve as an indicator as to whether a specific glass is chemically unstable or not, and hence whether it should be treated as glass susceptible to crizzling or not. Although arsenic does not contribute to glass stability as far as we know, it can be considered as an important technological diagnostic marker. This As_2O_3/CaO ratio can be estimated in most cases on the basis of non-destructive XRF analysis [9, 12].

The blue fluorescence of glass under short-wave fluorescent light (a band with a dominant line of 253.7 nm) can indicate that the examined item might belong to the fifth group shown in Table 1, the 18th century crystal glasses [13], because most 18th century crystal glasses contain lead. This is not a specific feature, as chalk glass also may con-

Table 1. Simplified and averaged chemical compositions of the main technological groups of central European potassium glasses from the post-medieval and baroque periods [11]. Results of EPMA (electron probe microanalysis). If the average values could not be calculated for a whole group, the concentration ranges are given in brackets.

No.	Type of glass	K_2O	Na_2O	CaO	MgO	SiO_2	PbO	As_2O_3	P_2O_5	B_2O_3	As_2O_3/CaO
		[wt%]									
1	Wood ash glass (n = 21)	12.8	1.1	15.9	2.4	62.9	<	<	1.5	<	0
2	Potash glass (n = 12)	17.8	0.8	9.7	(< -0.1)	69.1	<	<	<	<	0
3	Chalk glass, 2nd half of the 17th century and 18th century (n = 111)	15.5	(< -1.9)	9.5	(< -0.8)	71.6	(< -1.5)	0.8	<	<	0.1
4	Crystal glass, 2nd half of the 17th century (n = 10)	17.7	1.0	0.5	<	74.2	(< -9.5)	1.5	<	2.5	4.4
5	Crystal glass, 18th century (n = 22)	17.4	0.5	4.2	(< -0.5)	70.9	4.0	1.7	<	(< -1.1)	0.5

tain PbO; but these are rarer cases, and the PbO content is usually much less in chalk glass.

Summing up, it seems that the high As_2O_3/CaO ratio estimated with the use of XRF analysis and the blue fluorescence of these glasses under UV-C can be considered as important factors allowing us to distinguish at least a proportion of the objects susceptible to crizzling. Additionally, monitoring the thickness of the hydrated layer with the use of OCT may allow us to determine the risk of cracks developing.

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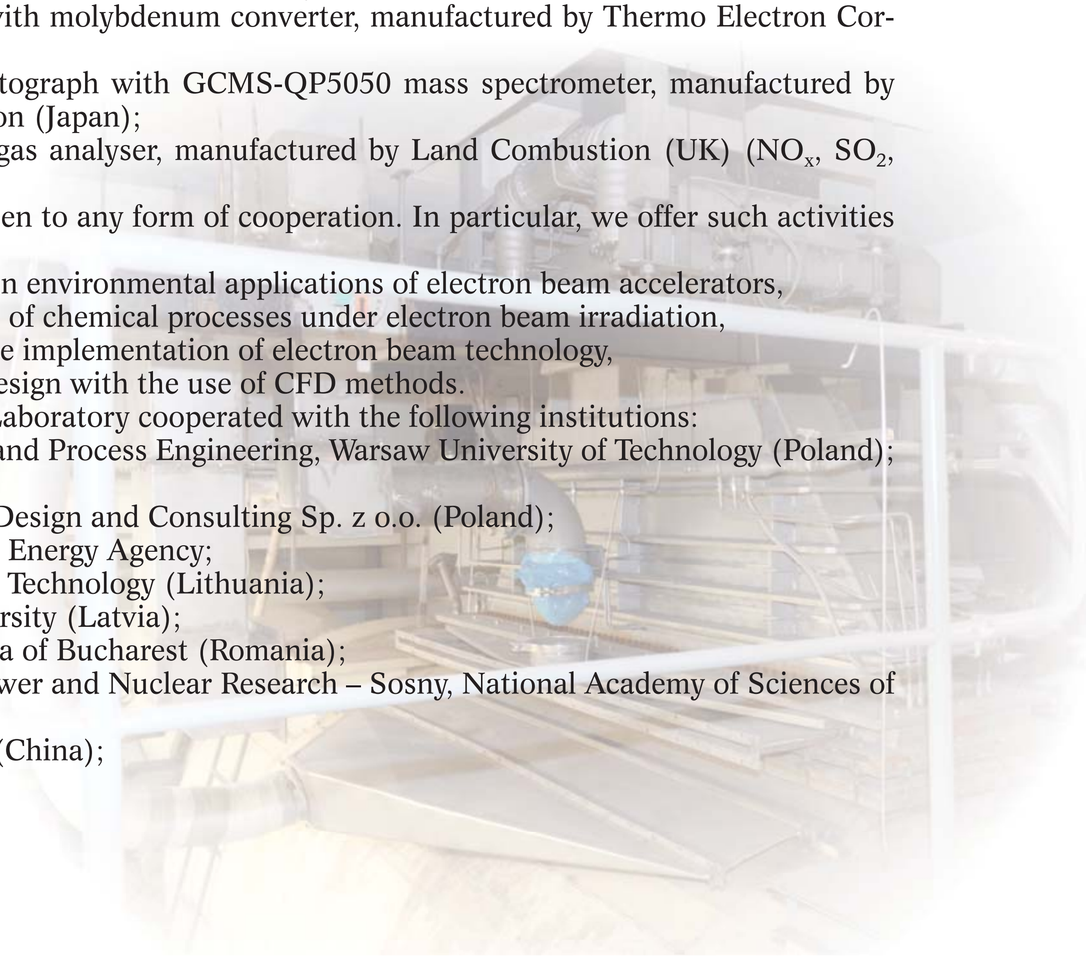
POLLUTION CONTROL TECHNOLOGIES LABORATORY

The research activities of the Pollution Control Technologies Laboratory concern the concepts and methods of process engineering applicable to the environmental area and the mechanism of pollutant removal under electron beam (EB) irradiation. In particular, we participate in research on the application of electron beam accelerators in such environmental technologies as flue gas and water treatment, wastewater purification, the processing of various types of industrial waste, *etc*.

The main aims of the Laboratory's activity 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 cover both basic and applied research. Among them, the most important research fields are:
- development of electron beam flue gas treatment (EBFGT) technology for different emission sources,
- supporting the industrial implementation of EBFGT process,
- investigation of chemical reaction mechanisms and kinetics in the gas phase and aqueous solutions irradiated by electron beams,
- study on the mechanism of the removal of volatile organic compounds (VOCs) from flue gas and PFOA (perfluorooctanoic acid) from aqueous solutions by electron beam excitation,
- process modelling.

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



The Laboratory is open to any form of cooperation. In particular, we offer such activities as:
- laboratory research on environmental applications of electron beam accelerators,
- theoretical modelling of chemical processes under electron beam irradiation,
- concept design for the implementation of electron beam technology,
- process equipment design with the use of CFD methods.

In recent years, the Laboratory cooperated with the following institutions:
- Faculty of Chemical and Process Engineering, Warsaw University of Technology (Poland);
- Biopolinex (Poland);
- Remontowa Marine Design and Consulting Sp. z o.o. (Poland);
- International Atomic Energy Agency;
- Kaunas University of Technology (Lithuania);
- Riga Technical University (Latvia);
- University Politehnica of Bucharest (Romania);
- Joint Institute for Power and Nuclear Research – Sosny, National Academy of Sciences of Belarus (Belarus);
- Tsinghua University (China);

- Xi’an Jiaotong University (China);
- Texas A&M University (USA).

In recent years the Laboratory has focused on developing the technology of SO_2 and NO_x removal from diesel off-gases using combination of electron beam treatments with wet scrubber systems, as well as on the computer simulation of persistent organic pollutant (such as PFOA) removal from aqueous solutions under electron beam irradiation.

NO OXIDATION USING ELECTRON BEAM AND ONE-STAGE ABSORPTION SYSTEM USING NaClO SOLUTION

Liang Zhao, Yongxia Sun, Andrzej G. Chmielewski, Sylwester Bułka, Andrzej Pawelec

The treatment of gases containing NO and NO_2 is an important environmental issue which still needs further study and development. Our previous study [1] showed that an electron beam (EB) hybrid with a wet scrubber is very promising for the simultaneous removal of SO_2 and NO_x from diesel off-gases.

In the current study, we investigated the reduction in the levels of NO_x under an electron beam with the addition of NaClO oxidant in two different scrubber solutions, phosphate buffer (Na_2HPO_4-KH_2PO_4)-salt water solution and NaOH-salt water solution.

The following chemical reagents were used to make scrubber solutions: NaCl (solid, sodium chloride, ACS reagent, Chempur, Poland), NaClO (liquid, sodium hypochlorite solution (6-14% active chlorine), density – 1.22-1.25 g/cm^3, Sigma-Aldrich, USA), NaOH (solid, sodium hydroxide, ACS reagent, Sigma-Aldrich, USA), Na_2HPO_4 (solid, disodium hydrogen phosphate anhydrous, ACS reagent, VWR Chemicals, USA), KH_2PO_4 (solid, potassium dihydrogen phosphate, ACS reagent, VWR Chemicals, USA).

Salt water (3.5% w/w NaCl solution) was prepared by dissolving a certain amount of sodium chloride in distilled water. 0.37 mL NaClO solution as oxidant was added to 1.2 L of scrubber solution. The prepared 1.2 L of solution was kept in two scrubbers connected in series (Scrubber I and Scrubber II), 600 mL in each. Two kinds of scrubber solution were used, one was salt water-NaClO-buffer (Na_2HPO_4 and KH_2PO_4), the other was salt water-NaClO-NaOH. The concentrations of buffer, NaOH and NaClO in the scrubber solution were 5 mM, 0.028% (w/w) and 0.03% (w/w), respectively.

All experiments were carried out using the installation at the Institute of Nuclear Chemistry and Technology (INCT). The set-up of the installation was the same as described by Licki *et al.* [2]. The simulated flue gases were generated by burning Polish light fuel oils in an oil burner. The NO_x concentration in the flue gas was lower than the studied concentration in the experiment, additional NO being added into the flue gas from NO gas cylinders. The desired concentration of NO was regulated by a gas flow meter. A similar method was applied to SO_2. The simulated flue gas (5 Nm^3/h) was irradiated using an ILU-6M accelerator (2 MeV, maximum beam power – up to 20 kW). A CTA gas dosimeter was used to measure the applied dose, which was 10.9 kGy.

A small amount of the flue gas (less than 200 mL/h) remaining after irradiation was passed through the two scrubbers. The rest of the flue gas was discharged into the atmosphere through the stack after the retention chamber.

The concentrations of NO_x and SO_2 before and after the process were analysed by a LANCOM series II Portable Emissions Analyser (LAND Combustion Company, UK).

NO_x removal under solely EB irradiation was studied, and the results are presented in Fig. 1. It can be seen that at process equilibrium only 15.0% of the NO_x was removed from the flue gas with respect to the inlet concentration of NO, with an initial concentration of NO of 1085 ppm at a 10.9 kGy absorbed dose. With an initial SO_2 concentration of 722 ppm, 32.69% of the SO_2 was removed at a 10.9 kGy absorbed dose.

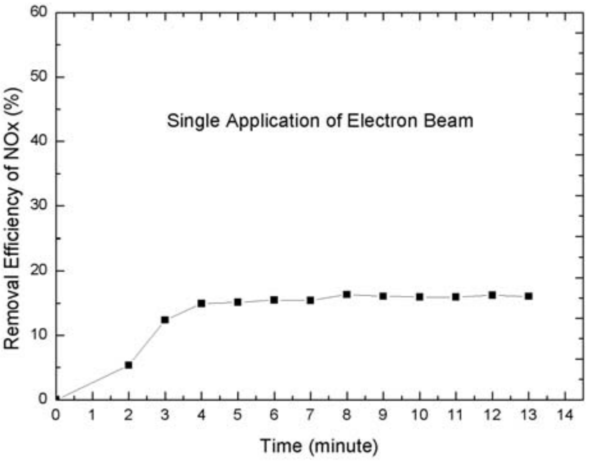


Fig. 1. Removal efficiency of NO_x with electron beam (inlet concentration of NO – 1085 ppm, initial concentration of SO_2 – 722 ppm, dose – 10.9 kGy).

NO reduction was investigated using the EB hybrid with the wet scrubber. The flue gas was first irradiated with the electron beam and then treated by the wet scrubber. Figure 2 shows the whole process during solely EB treatment (first 15 min) and using the electron beam with the wet scrubber (17-25 min). Salt water-0.03% NaClO-buffer (Na_2HPO_4 and KH_2PO_4) was applied as the wet scrubber solution. It can be seen that the NO_x re-

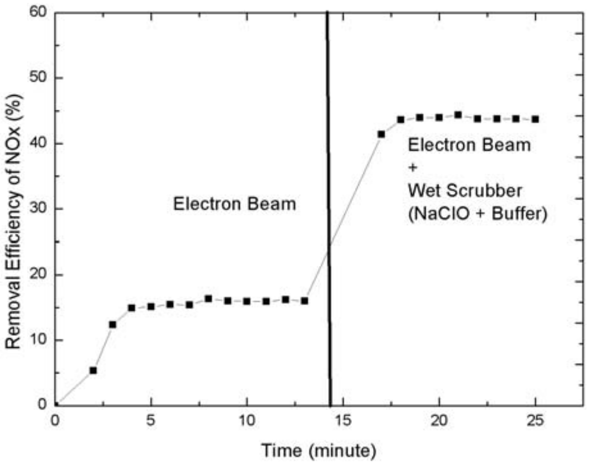


Fig. 2. Removal efficiency of NO_x using electron beam and EB hybrid system using salt water-NaClO-buffer as scrubber solution (inlet concentration of NO – 1085 ppm, inlet concentration of SO_2 – 722 ppm, dose – 10.9 kGy).

moval efficiency was about 15.0% under solely EB irradiation. When the wet scrubber was applied just after EB irradiation, NO_x removal efficiency increased from 15.0% to 43.68%. The pH of the scrubber solution was reduced from 6.290 to 5.932 (Scrubber I) and 6.028 (Scrubber II) after the treatment. In this EB-wet scrubber process, 99.72% of the SO_2 was removed over the same time when the inlet concentration of SO_2 was 722 ppmv.

The EB-absorption system for NO_x removal was further studied. NaOH was used in place of buffer in the wet scrubber solution. A 10.9 kGy dose was applied. The NaOH concentration was about 0.028% (wt/wt). The initial concentration of NO_x was about 1214 ppm. The results are presented in Fig. 3. It can be seen that the NO_x removal efficiency was about 15.0% under solely EB irradiation (5-15 min). When the wet scrubber was applied just after the EB irradiation, the NO_x removal efficiency increased from 15.0% to 46.62% (22-32 min). The pH of the scrubber solution was reduced from 11.487 to 6.214 (Scrubber I) and 6.556 (Scrubber II) after the treatment. The post-process solution could be directly discharged. During this process, SO_2 removal efficiency increased from 27.84% (EB only) to 99.48% (EB-NaClO/NaOH wet scrubber process) for an inlet SO_2 concentration of 776 ppm at a 10.9 kGy absorbed dose.

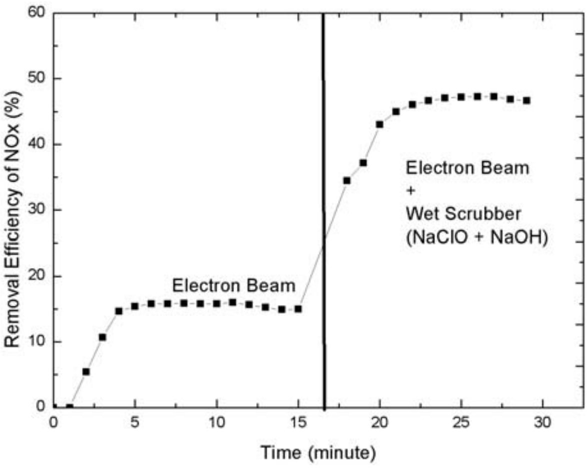


Fig. 3. Removal efficiency of NO_x with electron beam, EB-hybrid system using salt water-NaClO-NaOH as the scrubber solution (inlet concentration of NO – 1214 ppm, inlet concentration of SO_2 – 776 ppm, dose – 10.9 kGy).

In conclusion, the removal of high concentrations of NO_x and SO_2 from flue gas was studied under both an electron beam and an EB-hybrid system with NaClO addition. It was seen that NO_x removal efficiency increased apparently when EB hybrid system was applied, for example, from 15.0% to 43.68% (NaClO-phosphate buffer-salt water), or to 46.62% (NaClO-NaOH-salt water) for an inlet concentration of NO_x of over 1000 ppm. SO_2 removal efficiency increased by over 67% in the EB hybrid system compared with EB irradiation only: about 99.5% SO_2 was removed in the EB hybrid system. The pH of the solution was reduced after treatment. Compared with the results reported by [3], a similar SO_2 removal efficiency (> 99.0%) was obtained due to the good solubility of SO_2 in water. The removal efficiency of NO_x (< 50%) obtained in this work was lower than the results reported in [3], in which about 90% removal efficiency of NO_x was obtained when 25 mM $NaClO_2$ was used in the scrubber solution [3]. The difference may be explained as follows: firstly, the oxidant concentration of $NaClO_2$ (25 mM) used in [3] was higher than the concentration of NaClO (0.03%) used in this work; secondly, $NaClO_2$ is a stronger oxidant than NaClO. The former compound ($NaClO_2$) can work in a wide pH range of the scrubber solution, from pH values of 2.5-7.5 up to 13 [4]. For the latter scrubber (NaClO), the optimal pH value of the scrubber solution to oxidize NO into NO_2 was 5.3 [5], and a NaClO concentration higher than 0.8% by weight percentage is needed to reduce the liquid-film resistance and obtain better absorption efficiency. This value (> 0.8%) is much higher than the concentration (0.03%) tested in this work. It is expected that NO_x removal efficiency will increase with increasing the concentration of NaClO in the wet scrubber solution. In our future work, an electron beam combined with a high concentration of NaClO in NaOH-salt wet scrubber solution will be tested to remove SO_2 and NO_x from off-gases.

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STABLE ISOTOPE LABORATORY

The basic activities of the Stable Isotope Laboratory concern the techniques and methods of stable isotope measurements (H, C, N, O and S) by the use of an isotope ratio mass spectrometer (IRMS). We are also active in the application of IRMS in the environmental area, including determination of the stable isotope composition of hydrogeological, environmental and food samples.

The main aims of the activity of the Laboratory are:

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

The Laboratory is equipped with the following instruments:

- mass spectrometer – DELTA$^{\text{plus}}$ (Finnigan MAT, Germany);
- elemental analyser Flash 1112NC (Thermo Finnigan, 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).

The Laboratory research staff are 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 towards any form of cooperation. We are prepared to undertake any research and development task within the scope of our activity. In particular, we offer our measurement experience, precision and proficiency in the field of stable isotope composition to aid research in various areas. In addition, we are ready to perform any service regarding the control of food authenticity 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 companies,
- food control laboratories,
- private customers

and foreign partners:

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

NITROGEN AND CARBON STABLE ISOTOPIC COMPOSITION IN STUDY OF MUSHROOM ORIGIN

Ryszard Wierzchnicki

For many years the activity of the Stable Isotope Laboratory has been concentrated on the application of stable isotope mass spectrometry for food origin control. In 2018, samples of different species of Polish edible fungi (mushrooms) from various regions of Poland were examined. The products were purchased in a local market in Warsaw.

The aim of the first year of the study was to collect many samples of different species of fungi, with information about their sites of origin. The basic problem was the short season for this activity, which started at the beginning of September and finished at the end of October.

The collected samples (the pilei and stipes were separated) were dried at 60°C for 24 h in a laboratory dryer and then ground in a small laboratory ball mill. Each sample of mushroom (only pilei were used) weighed *ca.* 1.0 mg and was put into a tin capsule. The samples were then put into the autosampler carousel of a Flash 1112 NCS elemental analyser (Thermo Finnigan, Italy). As standards, two reference materials (B2155 protein and Sorghum, IVA Analysentechnik, Germany) for $\delta^{15}N$ and $\delta^{13}C$ measurements were used. The $\delta^{13}C$ and $\delta^{15}N$ isotope analyses were performed on a DELTA^{plus} isotope ratio mass spectrometer (Finnigan MAT, Bremen, Germany), connected to the above-mentioned elemental analyser. The values for the two isotopes (carbon and nitrogen) were simultaneously obtained in one measurement. The standard deviations of the values obtained from the measurements were 0.2‰ for $\delta^{15}N$ and 0.15‰ for $\delta^{13}C$. The values of the isotopic ratios δ are expressed in ‰ and correspond to international standards (PDB for $\delta^{13}C$, and air for $\delta^{15}N$):

- for carbon:

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

- for nitrogen:

$$\delta^{15}N_{vsAIR} = \frac{\left[\frac{^{15}N}{^{14}N}\right]_{SAMPLE} - \left[\frac{^{15}N}{^{14}N}\right]_{STANDARD}}{\left[\frac{^{15}N}{^{14}N}\right]_{STANDARD}} \cdot 1000\text{‰}$$

The number of examined samples (different origin) of mushroom species are presented in Table 1.

Table 1. Number of samples of mushroom species.

Polish name of species	Number of samples
Gąska	5
Gąska szara	2
Jakubek	2
Kania	6
Koźlarz	11
Kurka	5
Maślak	9
Opieniek	5
Podgrzybek	15
Prawdziwek	9
Rydz	8
Sarna	1
Siniak	1
Sitak	2
Zajączek	1
Boczniak	2
Pieczarka	1

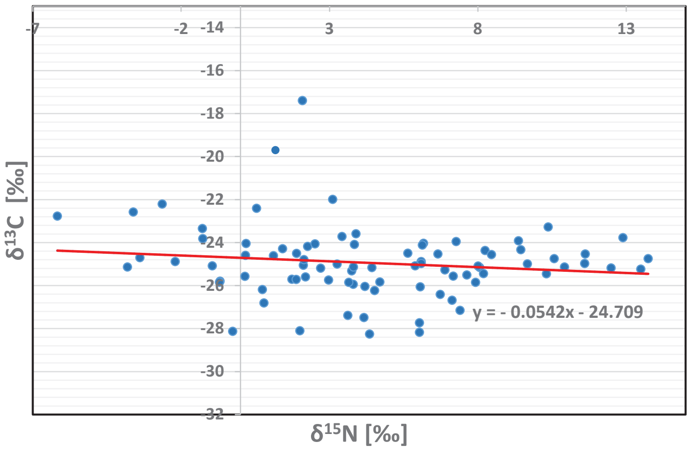


Fig. 1. Isotopic composition of nitrogen and carbon of all collected samples.

Fungi samples from different regions of Poland (85 samples) were collected. The $\delta^{13}C$ and $\delta^{15}N$ values of the samples are presented in Fig. 1. The

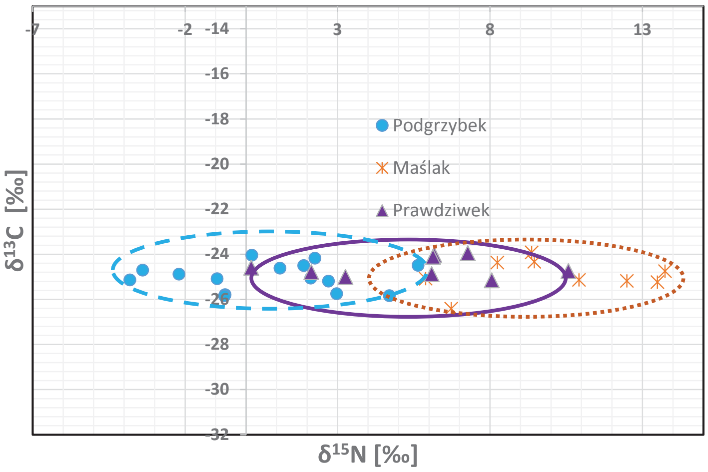


Fig. 2. Isotopic composition of samples of three mushroom species.

results obtained in the Stable Isotope Laboratory showed that the samples had $\delta^{13}C$ values in the range -28% to -22‰ and $\delta^{15}N$ values in the range -7% to +13‰.

For three different species of mushrooms (including all the collected samples of these species), an interesting shift of results along the $\delta^{15}N$ axis was observed (Fig. 2).

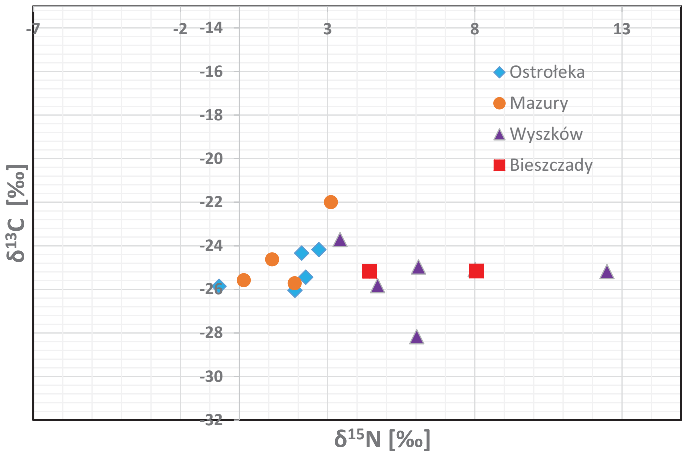


Fig. 3. Isotopic composition of samples from four regions of Poland.

Comparing the results of the isotopic compositions of samples obtained for mushrooms of various species from four regions of Poland, a small concentration of results (in regions) was observed (Fig. 3).

The study of the determination of the isotopic composition of mushrooms from different regions of Poland will be continued with more collected samples. In the next step, our study will be focused on the characteristic of ‘place of origin’ (forest, grassland, mountain or sea region, industrial or clean region, *etc.*). To the best of our knowledge, until now, no research concerning the composition of stable isotopes in mushrooms for various regions of Poland has been conducted.

LABORATORY FOR MEASUREMENTS OF TECHNOLOGICAL DOSES

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

- 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 (1.5-40 kGy),
- irradiation of dosimeters or other small objects with ^{60}Co gamma radiation to strictly define doses,
- irradiation of dosimeters or other small objects with 10 MeV electron beams to strictly define doses.

In accordance with the recommendations of the standard PN-EN ISO/IAC 17025:2005, the Laboratory has established the traceability of its own measurement standards and measuring instruments to the SI by means of an unbroken chain of calibrations or comparisons that links them to the relevant primary standards of the SI units of measurement. The link with the SI units is achieved by referencing to the national measurement standards.

The secondary standards of the dose rate utilized by the LMTD are a ^{60}Co gamma source Issledovatel and a Gamma Chamber 5000. The sources were calibrated in January 2016 and in March 2012, respectively, according to the NPL (National Physical Laboratory, Teddington, UK) primary standard with the use of transfer alanine dosimeters. The uncertainty of the dose rate was estimated to be 3.0% and 3.1% (U, k = 2).

LABORATORY FOR DETECTION OF IRRADIATED FOOD

The Laboratory for Detection of Irradiated Food was established at the Institute of Nuclear Chemistry and Technology in 1994. The adoption of a quality assurance system resulted in the accreditation of the Laboratory in 1999 by the Polish Centre for Testing and Certification (PCBC; at present the Polish Centre for Accreditation – PCA). Since that time, the Laboratory for Detection of Irradiated Food has constantly maintained the status of an accredited R&D unit and is authorized to carry out the examination of food samples and to classify them as being either irradiated or non-irradiated. Every four years, the Laboratory accreditation certificate has to be renewed after successfully passing the PCA audit. The current accreditation certificate, which is the 6th, was received on 24th July 2018 and is valid until 24th October 2022.

Professional and highly experienced staff are engaged in the improvement of irradiation detection methods, which are adapted in the Laboratory to make them more sensitive and reliable for an extended range of food articles. The Laboratory offers analytical services in this field to domestic and foreign customers for a wide variety of food articles with the use of five appropriate and normalized analytical methods. The *Scope of Accreditation*, an integral part of the accreditation certificate, offers customers five methods suitable to detect radiation treatment in almost all types of food available on the open market.

Nowadays, a lot of multi-component food items, such as herbal pharmaceuticals, diet supplements and food extracts, are received by the Laboratory for examination of irradiation from our domestic and foreign customers.

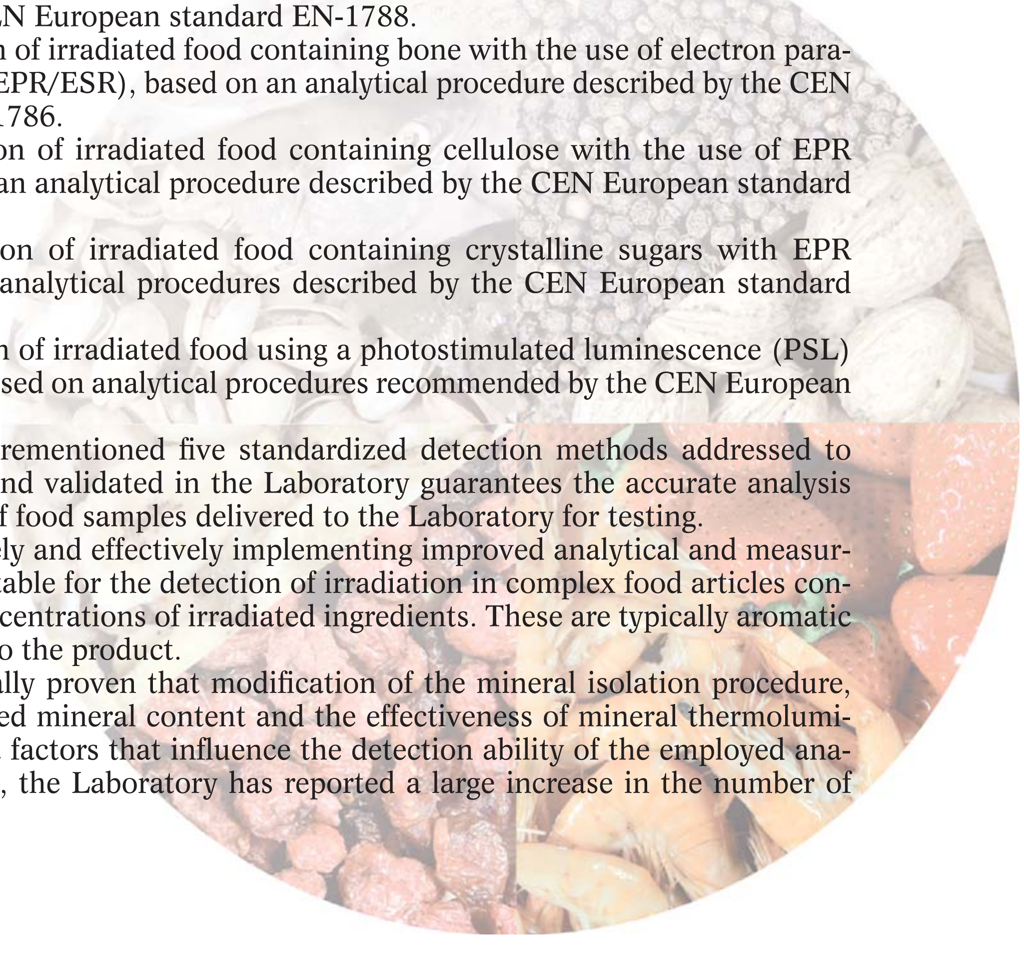
The Laboratory has implemented the following detection methods:

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

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

The Laboratory is actively and effectively implementing improved analytical and measuring procedures that are suitable for the detection of irradiation in complex food articles containing low or very low concentrations of irradiated ingredients. These are typically aromatic herbs and spices admixed to the product.

It has been experimentally proven that modification of the mineral isolation procedure, the determination of isolated mineral content and the effectiveness of mineral thermoluminescence are the important factors that influence the detection ability of the employed analytical method. Since 2016, the Laboratory has reported a large increase in the number of



samples delivered by domestic customers to be analysed. Samples were also delivered by foreign customers from Germany, Italy, Denmark, Latvia, Hungary, Spain, France, Norway, Malta, China and the USA. The assortment of samples received comprised spices, herbs, tea, dried and fresh vegetables, mushrooms, fruit, shrimps, blends of spices and herbs, including food compositions such as souses, dry flavour garnishes, diet supplements, phytopharmaceuticals and plant extracts. In 2018, in total, 1115 samples were tested. All the samples were examined by the thermoluminescence (TL) method, while analytical procedures based on EPR and PSL were used during interlaboratory studies.

In 2018, the Laboratory was invited to join the ‘Intercomparative exercise for quality assurance on TL, PSL and EPR irradiated food detection method’ organized by the Food Technology Department of the Spanish Agency for Food Safety and Nutrition with the participation of specialized analytical laboratories from many countries.

The Laboratory for Detection of Irradiated Food took part in comparative research using the TL method together with the Laboratory of the University of St. Cyril and Methodius in Skopje (Macedonia). The test was carried out with a positive result for both laboratories. The report from the study was the basis for a document supporting the Macedonian laboratory’s application to obtain accreditation.

From 19th June 2012, the Laboratory has held 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 (National Reference Laboratory No. 5). As such, the Laboratory is responsible for the organization of the control and monitoring of irradiated food around the country.

DETECTION OF RADIATION-TREATED WATER-ALCOHOL EXTRACTS OF HERBS WITH TL AND PSL METHODS

Grzegorz Piotr Guzik, Magdalena Miłkowska, Grażyna Liśkiewicz

The extracts obtained from herbs by water-alcohol extraction are widely used in the pharmaceutical and cosmetic industries as important components of popular diet supplements. Normative regulations of the EU Parliament respected in member states and many other countries qualify vegetal extracts as food, following the FAO/WHO Codex Alimentarius classification of diet supplements containing vegetal extracts, vitamins and microelements considered foodstuffs [1]. In order to assure the microbial safety of vegetal extracts and diet supplements, as well as to extend their safe storage time, these food items are subjected to conservation/preservation procedures, preferentially by exposure to ionizing radiation [2, 3]. These food products therefore undergo inspection to determine whether they have been irradiated or not.

Among the ten CEN (European Committee for Standardization) standardized methods for the detection of irradiated food, only two are considered adaptable for the detection of radiation-treated vegetal extracts and food supplements. One is based on the thermoluminescene (TL) released from silicate minerals isolated from vegetal extracts [4], while the other one is based on photostimulated luminescence (PSL) released from the product as a whole [5].

The PPSL (pulsed PSL) method tested in parallel with thermoluminescence in the present study is less time-consuming and markedly faster than the latter. The method is applied in the food industry for the control of crude unprocessed herbs and spices, typically in the form of dried leaves or roots. It has not been reported whether the method is suitable for the detection of irradiation in vegetal extracts or diet supplements. In the present study, 20 kinds of industrially irradiated herbal extracts were examined with both the discussed methods. The aim of the study was to ascertain whether the PPSL method could be suitable for irradiation control of vegetal extracts, which are components of popular diet supplements. The results of the experiment are discussed below. The examined samples were irradiated using real, but unknown, industrial doses.

Table 1. Results of the TL examination of the samples of minerals isolated from 20 vegetal extracts.

Name of sample	TL maximum temperature [°C]		TL intensity (150-250°C)		k_{TL} glow 1/glow 2 (150-250°C)
	glow 1 primary measurement	glow 2 the measurement after 1 kGy re-irradiation	glow 1 primary measurement	glow 2 the measurement after 1 kGy re-irradiation	
Bacopa	206	193	53 887 470	44 985 407	1.1979
Wheat germ extract	208	185	7 114 872	52 669 217	0.1351
Millet grains extract	231	187	31 257 308	126 861 887	0.2464
Guarana seed extract	228	200	2 489 167	6 507 350	0.3825
Parsley extract	217	174	43 622 531	47 263 000	0.9230
Extract from prickly pear	221	183	55 523 481	51 457 932	1.0790
Marsh-mallow	206	189	2 875 177	24 573 679	0.1170
Tomato	214	199	6 352 026	22 279 413	0.2851
Saw palmetto extract	193	182	329 787	84 835	3.8874
Ginseng extract	204	178	49 545	476 275	0.1040
Hoary willowherb extract	215	176	425 682	25 851 312	0.0165
Thyme extract	217	204	189 798 472	217 510 482	0.8726
Green tea extract	204	189	2 021 717	1 709 249	1.1828
Golden root extract	215	200	524 811	26 119 906	0.0201
Puncture-vine extract	232	210	1 508 960	115 754 611	0.0130
Cinnamon bark extract	230	187	1 172 920	38 999 855	0.0301
Schisandra	212	206	87 088 547	55 860 708	1.5590
Milk thistle extract	194	187	826 983	3 626 417	0.2280
Bitter orange extract	196	175	13 492 603	204 952 569	0.0658
Bee putty (propolis)	206	203	70 977 580	91 603 156	0.7748

Thermoluminescence method based on EN-1788 European standard

The results of irradiation detection obtained by the thermoluminescence method based on the TL measurement of minerals isolated from the extracts are shown in Table 1. The TL method was found to be more sensitive than the PSL method and suitable for the routine control of vegetal extracts in specialized laboratories. Silicate minerals isolated from the samples were placed in stainless steel TL measuring cups and heated overnight at 50°C. Thermoluminescence measurements were carried out with a Risø TL/OSL DA-20 reader.

The instrument was run with the following settings:

- initial temperature – 70°C,
- final temperature – 450°C,
- speed of the heating – 6°C/s,
- heating time – 30 s.

Two subsequent TL measurements were conducted with each sample. These were the primary measurement (glow 1) and the calibrated measurement (glow 2), which was carried out after 1 kGy of normalizing ^{60}Co irradiation of the TL measuring cups containing the isolated minerals.

All the examined samples were identified unequivocally using the TL method as irradiated. For five cases (hoary willowherb extract, golden root extract, puncture-vine extract, cinnamon bark extract and bitter orange extract) the examined samples did not fulfill the requirements of two factors in accordance with the EN-1788 European standard (the appearance of the glow 1 and the value of k_{TL}). The positive result for these five samples was established on the basis the appearance of the glow 1 (in compliance with point 9 of the EN-1788 European standard).

Table 2. Operational parameters of PPSL measurements.

Frequency of counting	60 cpm
Lower threshold value of PPSL	700 cpm
Upper threshold value of PPSL	5000 cpm
Light count	17 cpm
Dark count	15 cpm

Photo-stimulated luminescence method based on EN-13751 European standard

The PSL measurement were conducted with the irradiated food screening system (measuring set) by the Scottish Universities Research and Reactor Centre (SURRC) in darkness at ambient temperature with a relative humidity of 85%. The operational parameters of the measuring set were adjusted as presented in Table 2.

The names and the weight of samples measured are given in Table 3. Each sample was measured twice. Firstly untreated and secondly after re-irra-

Table 3. The results of the PPSL measurements of vegetal extracts.

Name of the sample	Weight of the sample [g]	Primary measurement [cpm]	Measurement after 4 kGy re-irradiation [cpm]	Final result of the PPSL measurement
Bacopa	3.0443	830 ± 46	3 940 ± 70	uncertain result*
Wheat germ extract	3.1068	3 845 ± 72	29 238 ± 174	uncertain result*
Millet grains extract	3.0971	889 ± 47	3 400 ± 66	uncertain result*
Guarana seed extract	3.0356	4 314 ± 75	18 753 ± 140	uncertain result*
Parsley extract	3.0575	1 642 ± 54	9 169 ± 100	uncertain result*
Extract from prickly pear	3.0555	1 455 ± 53	16 982 ± 134	uncertain result*
Marsh-mallow	3.0618	791 ± 46	2 328 ± 57	uncertain result*
Tomato	3.0764	466 ± 42	1 243 ± 47	uncertain result*
Saw palmetto extract	3.0352	612 ± 44	28 852 ± 173	unirradiated
Ginseng extract	3.0535	301 ± 40	751 ± 41	uncertain result*
Hoary willowherb extract	3.0412	233 ± 39	1 736 ± 52	uncertain result*
Thyme extract	3.0935	3 108 ± 66	5 228 ± 78	uncertain result*
Green tea extract	3.0488	285 ± 40	463 ± 37	uncertain result*
Golden root extract	3.0423	332 ± 41	1 048 ± 44	uncertain result*
Puncture-vine extract	3.0646	498 ± 43	2 369 ± 57	uncertain result*
Cinnamon bark extract	3.0352	282 ± 40	4 980 ± 77	unirradiated
Schisandra	3.0139	452 ± 42	6 909 ± 88	unirradiated
Milk thistle extract	3.0764	451 ± 42	354 ± 36	uncertain result*
Bitter orange extract	3.0534	225 ± 39	2 467 ± 58	uncertain result*
Bee putty (propolis)	3.0084	10 178 ± 107	55 742 ± 238	irradiated

* Photoluminescence within the range 700-5000 cpm is considered too high to classify the sample as unirradiated, but too low to qualify it as irradiated. According to EN-13751 such a result is not reliable enough, and hence the sample cannot be classified by PPSL, requiring a repetition with the use of the TL method.

diation with a 4 kGy dose of ^{60}Co gamma rays. The results of both measurements are given in Table 3. All measurements were carried out 48 h after radiation treatment at 22.5°C

As seen from the Table 3, the samples of vegetal extracts tested cannot be examined by the PPSL method. The PPSL method was found to be not sensitive enough to deliver reliable results of photoluminescence analysis with one exception. The detection of radiation treatment in 16 extracts was found impossible by this method since the number of counts (PSL flashes) was not sufficiently high. Saw palmetto, cinnamon bark and schisandra extracts delivered faulty results, while the bee putty extract offered the only positive result.

The PPSL method was found to be not sensitive enough to identify radiation treatment of pulverized extracts obtained from water-alcohol solutions. A probable reason was the deep pulverization of the product negatively affecting the shape, the volume and the surface of the mineral crystals, influencing the significant suppression of the total photoluminescence efficiency.

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LABORATORY OF NUCLEAR CONTROL SYSTEMS AND METHODS

The primary focus of the Laboratory's activity in 2018 was the development of methods and equipment, based on the application of ionizing radiation and process engineering, for both measurement and diagnostic purposes. The research programme of the Laboratory was focused on the following topics:

- development of a leakage control method for the testing of industrial installations during their operation using radiotracers (^{82}Br, ^{85}Kr);
- development of measuring devices and systems for industry and for the protection of the environment;
- application of membrane processes for methane enrichment of biogas obtained in fermentation processes on a laboratory and industrial scale;
- identification and optimization of industrial processes using tracer and radiotracer methods;
- elaboration and industrial scale implementation of new methods and technology for biogas production by the fermentation of agricultural substrates and by-products, such as wastewater sediments obtained during wastewater treatment (especially by the dynamic and thermal disintegration of sludge particles);
- development of new radiotracers and radiometric methods for the optimization of hydrometallurgical processes.

In the field of the design of nuclear instrumentation, the work was focused on the detection of radioactive contamination and measurements of the concentration of radon daughter radioisotopes in air and water, especially for medical application (radon bathing).

In all these areas of activity, the Laboratory cooperated with International Atomic Energy Agency (IAEA).

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17. **Dybczyński R.S.**

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24. **Guzik G.P.**

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4. Studies on hydrometallurgical processes using nuclear techniques to be applied in copper industry. I. Application of ^{64}Co radiotracer for investigation of copper ore leaching
   T. Smoliński, M. Rogowski, M. Brykała, M. Pyszynska, A.G. Chmielewski
5. Studies on hydrometallurgical processes using nuclear techniques to be applied in copper industry. II. Application of radiotracers in copper ore leaching from flotation tailings
   M. Rogowski, T. Smoliński, M. Pyszynska, M. Brykała, A.G. Chmielewski

Information

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POSTĘPY TECHNIKI JĄDROWEJ

CONTENTS OF No. 1/2018

1. Centralne Laboratorium Ochrony Radiologicznej: retrospekcja i współczesność – z dr. Pawłem Krajewskim, dyrektorem Centralnego Laboratorium Ochrony Radiologicznej w Warszawie, rozmawia Marek Bielski (Central Laboratory for Radiological Protection: retrospection and the present – the interview with Dr. Paweł Krajewski, Director of the Central Laboratory for Radiological Protection in Warsaw, by Marek Bielski)

   M. Bielski
2. Wspomnienia pierwszego dyrektora CLOR prof. Jerzego Peńsko (Memoirs of the first Director of CLOR professor Jerzy Peńsko)

   J. Peńsko
3. Energetyka jądrowa na świecie i w Polsce w 2017 roku (Nuclear power in the world and in Poland in 2017)

   A. Mikulski
4. Uwagi do Raportu Zespołu Ministerstwa Energii ds. Reaktora Wysokotemperaturowego (Remarks to the Report of the Ministry of Energy Committee on High-Temperature Reactor)

   A. Mikulski
5. Trzy scenariusze energetyki jądrowej w Polsce (Three scenarios for nuclear power in Poland)

   A. Mikulski
6. Exeltium jako jeden ze sposobów finansowania inwestycji w energetyce jądrowej (Exeltium as a way of financing of nuclear power projects)

   Ł. Sawicki, B. Horbaczewska
7. Praca reaktora badawczego Maria w 2017 roku (Research reactor MARIA operation in 2017)

   A. Gołąb
8. Państwowa Agencja Atomistyki wczoraj i dziś (National Atomic Energy Agency – past and present)

   A. Furtek
9. Tajemnicza ciemna materia: aksjony coraz trudniejsze do wykrycia (The mysterious dark matter: axions becoming more and more difficult to detect)

   M. Nowina-Konopka

CONTENTS OF No. 2/2018

1. The cost of new nuclear in France

   D. Beutier, M. Berthelémy, J.-G. Devezeaux de Lavergne, J. David, N. Dellero, V. Faudon, B. Le Ngoc
2. Koszt nowej energetyki jądrowej we Francji (The cost of new nuclear in France)

   D. Beutier, M. Berthelémy, J.-G. Devezeaux de Lavergne, J. David, N. Dellero, V. Faudon, B. Le Ngoc
3. Bezpieczeństwo i ochrona środowiska przy wydobywaniu rudy uranowej (Human health and environment protection at uranium mining)

   A. Strupczewski
4. Zasoby uranu w Polsce – możliwości pozyskiwania uranu ze źródeł niekonwencjonalnych (Resources of uranium in Poland – the possibility of obtaining uranium from the unconventional sources)

   K. Kiegiel, G. Zakrzewska-Kołtuniewicz
5. Obliczenia obszaru ograniczonego użytkowania wokół pierwszej polskiej elektrowni jądrowej (Calculation of the restricted-use area around the first Polish nuclear power plant)

   W. Bielewski, K.W. Fornalski
6. Okresowy układ pierwiastków chemicznych (Periodic system of chemical elements)

   E. Rurarz

7. Radiofarmaceutyki w Instytucie Chemii i Techniki Jądrowej (Radiopharmaceuticals in the Institute of Nuclear Chemistry and Technology)

   R. Walczak, P. Halik, W. Gawęda, Ł. Dziawer, M. Gumiela

CONTENTS OF No. 3/2018

1. Programy badawcze w zakresie energetyki jądrowej – prowadzone obecnie i konieczne do uruchomienia (Research programmes in the field of nuclear energy – currently being conducted and necessary to run)

   S. Latek
2. Pierwsza połowa 2018 roku w światowej i polskiej energetyce jądrowej (Nuclear power in the world and in Poland in the first half of 2018)

   A. Mikulski
3. Dlaczego odnawialne źródła energii nie wystarczą dla Polski (Why renewable energy sources are not sufficient for Poland)

   A. Strupczewski
4. Reaktor dwupłynowy jako nowa i rewolucyjna koncepcja reaktora jądrowego (Dual fluid reactor as a new and revolutionary concept of a nuclear reactor)

   M.P. Dąbrowski
5. Prace modernizacyjne w reaktorze MARIA (Refurbishment acivity in the MARIA reactor)

   A. Mikulski
6. Charakterystyka wybranych typów elektrowni jądrowych generacji III/III+ (Characteristics of selected types of generation III/III+ nuclear power plants)

   M. Klisińska, Ł. Koszuk
7. Ostatnie doniesienia z CERN-u (The latest news from CERN)

   M. Nowina-Konopka

CONTENTS OF No. 4/2018

1. Polska atomistyka – dorobek stulecia (Polish nuclear science – achievements of the century)
2. Twórcy Niepodległej – żołnierze, politycy, uczeni, arytyści, pisarze, ... (Founders of Independent – soldiers, politicians, scientists, artists, writers, ...)

   M. Sobieszczak-Marciniak
3. Nauka w walce o wolność, czyli rewolucja kulturalna w Instytucie Badań Jądrowych (Science in the fight for freedom: cultural revolution in the Institute of Nuclear Research)

   S. Latek
4. Minister Krzysztof Tchórzewski: Energia jądrowa to stabilne dostawy energii elektrycznej (Minister Krzysztof Tchórzewski: nuclear power is a stable supply of electricity)
5. Wywiad z Panią Agnetą Rising dyrektor generalną Światowego Stowarzyszenia Nuklearnego (Interview with Agneta Rising Director General of World Nuclear Association)

   A. Mikulski
6. Prawda o transformacji energetycznej w Niemczech „Energiewende" (The truth about energy transition in Germany 'Energiewende'

   A. Strupczewski
7. Przedłużenie eksploatacji elektrowni jądrowej Pickering w Kanadzie (Ontario, Canada: Pickering NGS extended operations)

   D.W. Kulczyński
8. Pomiary testowe nowych stacji TDPMS3 przeznaczonych do pracy w sieci wczesnego wykrywania skażeń promieniotwórczych (Test measurements performed with the new TDRMS3 stations dedicated for the radiological warning network)

   R. Dąbrowski, K. Wołoszczuk
9. Antyradonowe polimery (Antiradon polymers)

   W. Głuszewski

Information

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THE INCT PATENTS AND PATENT APPLICATIONS IN 2018

PATENTS

1. Sposób wytwarzania węglika uranu o ziarnach sferycznych i nieregularnych jako prekursora paliwa do reaktorów nowej, IV generacji (Method for producing uranium carbide with spherical and irregular grains as a precursor of the fuel for the reactors of new IV generation)

   M. Brykała, M. Rogowski

   Polish Patent 228541

2. Radiofarmaceutyk diagnostyczny do obrazowania infekcji, sposób jego wytwarzania oraz jego zastosowanie (Diagnostic radiopharmaceutical for imaging of infections, method for producing it and applications)

   P. Koźmiński, E. Gniazdowska, M. Chojnowski, A. Kopatys, L. Królicki

   Polish Patent 228617

3. Prekursor radiofarmaceutyku terapeutycznego, przeznaczony do osadzania na nim znanych cząsteczek biologicznie aktywnych naprowadzających radionuklid do chorej tkanki, oraz sposób jego wytwarzania (Precursor of radiopharmaceutical and method for its manufacturing)

   A. Bilewicz, M. Łyczko, A. Piotrowska, E. Leszczuk

   Polish Patent 228716

4. Diagnostyczny i/lub terapeutyczny radiofarmaceutyk receptorowy posiadający powinowactwo do receptora NK-1, sposób jego wytwarzania oraz zastosowanie (Diagnostic and/or therapeutical receptor-specific radiopharmaceutical having the affinity for the receptor NK1, method for producing it and its application)

   E. Gniazdowska, P. Koźmiński

   Polish Patent 229072

5. Sposób otrzymywania ditlenku uranowo-neodymowego o ziarnach sferycznych (Method for obtaining of spherical grains of uranium-neodymium dioxide)

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

   Polish Patent 229092

6. Diagnostyczny lub terapeutyczny radiofarmaceutyk receptorowy posiadający powinowactwo do receptora Her-2, sposób jego wytwarzania oraz jego zastosowanie (Diagnostic or therapeutical receptor-specific radiopharmaceutical having the affinity for the receptor Her-2, method for producing it and its application)

   E. Gniazdowska, P. Koźmiński

   Polish Patent 229139

7. Sposób otrzymywania tlenkowych prekursorów paliw mieszanych typu MOX, w postaci proszków o ziarnach sferycznych (Method for obtaining oxide precursors of blended fuels of MOX type, in the form of powders with spherical grains)

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

   Polish Patent 230331

8. Kompozyt poliuretanowy, zwłaszcza w postaci kształtek do zastosowań w hydrobudownictwie do budowy wałów przeciwpowodziowych i/lub umocnień nabrzeży oraz sposób jego wytwarzania (Polyurethane composite material, preferably in the form of shaped blocks for applications in hydroengineering for construction of flood banks and/or reinforcement of berths and method for producing it)

   P. Kalbarczyk, M. Motrenko, H. Polkowska-Motrenko

   Polish Patent 230343

9. Radiofarmaceutyk diagnostyczny, sposób jego wytwarzania oraz jego zastosowanie do obrazowania infekcji bakteryjnych (Diagnostic radiopharmaceutical for imaging bacterial infections and method for producing it)

   P. Koźmiński, E. Gniazdowska

   Polish Patent 231312

10. Sposób otrzymywania oksywęglika uranu metodą zol-żel (Sol-gel process for synthesis of uranium oxycarbide)

    M. Brykała, M. Rogowski, W. Łada

    Polish Patent 231319

11. Nanokompozytowy wymieniacz jonowy na bazie krzemionki modyfikowanej oraz sposób otrzymywania wymieniacza jonowego (Selective, nanocomposite ion-exchanger based on modified silica and method of its synthesis)

    D. Chmielewska-Śmietanko

    Polish Patent 231413

PATENT APPLICATIONS

1. Urządzenie do jednoczesnego usuwania kwaśnych zanieczyszczeń nieorganicznych i lotnych zanieczyszczeń organicznych ze strumienia gazów odlotowych, zwłaszcza silnika Diesla oraz sposób usuwania zanieczyszczeń (Device for simultaneous removal of acidic inorganic and volatile organic pollutants from the off-gas stream, in particular from Diesel engine)

   A.G. Chmielewski, Z. Zimek, Y. Sun, E. Zwolińska

   Polish Patent Application P-425063

2. Sposób i urządzenie do zabezpieczenia przed niepożądanym oświetleniem fotokatody fotopowielacza zespołu detekcyjnego, z wymienną komorą scyntylacyjną (Method and device to protect the photocathode of the detection unit photomultiplier with the replaceable scintillation chamber against undesirable lighting)

   J. Bartak

   Polish Patent Application P-426013

3. Superparamagnetyczna nanocząstka na bazie tlenków żelaza oraz jej zastosowanie w biotechnologii i medycynie (Superparamagnetic nanoparticle based on iron oxides and its application in biotechnology and medicine)

   P. Krysiński, M. Osiał, P. Rybicka, A. Bilewicz, M. Gawęda

   Polish Patent Application (together with the University of Warsaw)

CONFERENCES ORGANIZED AND CO-ORGANIZED BY THE INCT IN 2018

1. DZIEŃ INFORMACYJNY PROGRAMU EURATOM (EURATOM INFO DAY), 12 FEBRUARY 2018, WARSZAWA, POLAND

Organized by the National Contact Point for Research Programmes of the EU, National Centre for Nuclear Research, Institute of Nuclear Chemistry and Technology

Organizing Committee: Jacek Gajewski, Ph.D., Maria Śmietanka, Ph.D., Aneta Maszewska

2. FIRST COORDINATION MEETING RER1020 'DEVELOPING RADIOTRACER TECHNIQUES AND NUCLEAR CONTROL SYSTEMS FOR THE PROTECTION AND SUSTAINABLE MANAGEMENT OF NATURAL RESOURCES AND ECOSYSTEMS' AND EUROPEAN INTERNATIONAL SEMINAR 'GAMMA SCANNING', 19-21 JUNE 2018, WARSZAWA, POLAND

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

Organizing Committee: Tomasz Smoliński, M.Sc., Marcin Rogowski, M.Sc., Marta Pyszynska, M.Sc., Prof. Andrzej G. Chmielewski, Ph.D., D.Sc., Patrick D.M. Brisset, Tomoko Furusawa

3. WORKSHOP OF THE EMERGING TRENDS IN THE SLUDGE TREATMENT, 27 AUGUST 2018, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Organizing Committee: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc., Yongxia Sun, Ph.D., D.Sc., professor in INCT, Zbigniew Zimek, Ph.D.

4. 9TH PULS CONFERENCE ON PULSE INVESTIGATIONS IN CHEMISTRY, PHYSICS AND BIOLOGY, AND 4TH RKCM CONFERENCE ON REACTION KINETICS IN CONDENSED MATTER, 2-7 SEPTEMBER 2018, ŁÓDŹ, POLAND

Organized by the Institute of Applied Radiation Chemistry of the Łódź University of Technology and the Institute of Nuclear Chemistry and Technology in collaboration with the Polish Radiation Research Society, Society for Free Radical Research – Europe, International Atomic Energy Agency

Organizing Committee: Mariusz Wójcik, Ph.D., D.Sc., Prof. Krzysztof Bobrowski, Ph.D., D.Sc., Piotr Ulański, Ph.D., D.Sc., Agnieszka Dybała-Defratyka, Ph.D., D.Sc., Alicja Olejnik, Ph.D., Bożena Rokita, Ph.D., Lesław Sieroń, Ph.D., Radosław Wach, Ph.D., Paweł Wiśniowski, Ph.D., Ewa Zimna

5. SZKOLENIE „INNOWACJE DLA ENERGII I NIE TYLKO. ZAAWANSOWANE MATERIAŁY POLIMEROWE DLA ENERGETYKI I INNYCH DZIEDZIN WSPOMAGANE TECHNOLOGIAMI RADIACYJNYMI" (TRAINING 'INNOVATION FOR ENERGY AND MORE. ADVANCED POLYMERIC MATERIALS FOR ENERGY AND OTHER FIELDS SUPPORTED BY RADIATION TECHNOLOGIES', 18 OCTOBER 2018, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology, Ministry of Energy

Organizing Committee: Wojciech Głuszewski, Ph.D., Norbert Wróbel, M.Sc., Małgorzata Dąbrowska, M.Sc.

6. INTERNATIONAL ATOMIC ENERGY AGENCY REGIONAL TRAINING COURSE 'RADIATION PROCESSING FOR ADVANCED POLYMERIC MATERIALS' IN THE FRAME OF TECHNICAL COOPERATION PROJECT RER1019 'ENHANCING STANDARDIZED RADIATION TECHNOLOGIES AND QUALITY CONTROL PROCEDURES FOR HUMAN HEALTH, SAFETY, CLEANER ENVIRONMENT AND ADVANCED MATERIALS', 15-19 OCTOBER 2018, WARSZAWA, POLAND

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

Organizing Committee: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc., Grażyna Przybytniak, Ph.D., D.Sc., professor in INCT, Zbigniew Zimek, Ph.D., Marta Walo, Ph.D.

7. PROJECT KICK-OFF MEETING 'DEVELOPMENT OF HYBRID ELECTRON ACCELERATOR SYSTEM FOR THE TREATMENT OF MARINE DIESEL EXHAUST GASES', 11-12 OCTOBER 2018, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Organizers: Prof. Toms Torims and Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.

8. PHOEBE MEETING – H2020 PROPOSAL PREPARATION, 29-30 NOVEMBER 2018, WARSZAWA, POLAND

Organized by the Institute of Nuclear Chemistry and Technology

Organizers: Prof. Rob Edgecock and Zbigniew Zimek, Ph.D.

Ph.D./D.Sc. THESES IN 2018

Ph.D. THESES

1. Justyna Pijarowska-Kruszyna, M.Sc. (National Centre for Nuclear Research, Otwock-Świerk, Poland)
   Innowacyjna metoda syntezy radiofarmaceutyku do obrazowania transportera dopaminy (DAT) w technice pozytonowej tomografii emisyjnej (PET) (The innovative synthesis method of the radiopharmaceutical for the dopamine transporter (DAT) imaging in the positron emission tomography (PET) technique)
   supervisor: Renata Mikołajczak, Ph.D., D.Sc., professor in NCBJ
   Institute of Nuclear Chemistry and Technology, 21.06.2018
2. Konrad Skotnicki, M.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
   Reakcje rodnikowe chinoksalin-2-onów w aspekcie ich zastosowań farmakologicznych (Radical processes involving quinoxalin-2-one derivatives relevant to their pharmacological applications)
   supervisor: Prof. Krzysztof Bobrowski, Ph.D., D.Sc.
   Institute of Nuclear Chemistry and Technology, 29.03.2018
3. Edyta Cędrowska, M.Sc. (INCT Ph.D. student)
   Biokoniugaty nanocząstek tlenków metali jako nośniki emiterów cząstek α w celowanej terapii radionuklidowej (Bioconjugates of metal oxide nanoparticles as carriers of α-emitters in targeted radionuclide therapy)
   supervisor: Prof. Aleksander Bilewicz, Ph.D., D.Sc.
   auxiliary supervisor: Marek Pruszyński, Ph.D.
   Institute of Nuclear Chemistry and Technology, 19.12.2018
4. Łucja Dziawer, M.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
   Biokoniugaty nanocząstek złota jako nośniki ^{211}At w celowanej alfa terapii (Bioconjugates of gold nanoparticles as ^{211}At carriers in targeted alpha therapy)
   supervisor: Prof. Aleksander Bilewicz, Ph.D., D.Sc.
   auxiliary supervisor: Agnieszka Majkowska-Pilip, Ph.D.
   Institute of Nuclear Chemistry and Technology, 19.12.2018
5. Barbara Wiaderek, M.Sc. (INCT Ph.D. student)
   Nanostruktury ditlenku tytanu jako sorbenty radionuklidów z ciekłych odpadów promieniotwórczych (Titanium dioxide nanostructures as new sorbents for separation of radionuclides from nuclear wastes)
   supervisor: Prof. Aleksander Bilewicz, Ph.D., D.Sc.
   auxiliary supervisor: Monika Łyczko, Ph.D.
   Institute of Nuclear Chemistry and Technology, 19.12.2018

D.Sc. THESES

1. Kamil Brzóska, Ph.D. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)
   Sygnalizacja komórkowa związana z rozwojem reakcji zapalnej i apoptozą w odpowiedzi komórki na czynniki wywołujące stres oksydacyjny i uszkodzenia DNA (Cellular signaling associated with inflammation and apoptosis in cell's response to oxidative stress and DNA damage inducing factors)
   Jan Kochanowski University (JKU), Faculty of Mathematics and Natural Sciences, 24.05.2018

EDUCATION

Ph.D. PROGRAMME IN CHEMISTRY

The Institute of Nuclear Chemistry and Technology (INCT) 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 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 2018, the following lecture series were organized:

- The modern methods of organic synthesis – Adam Mieczkowski, Ph.D. (Institute of Biochemistry and Biophysics, Polish Academy of Sciences);
- Chemical aspects in nuclear energy – Prof. Andrzej G. Chmielewski, Ph.D., D.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland);
- Radiobiology – Prof. Marcin Kruszewski, Ph.D., D.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland).

Starting in this (2018/2019) academic year, the INCT is participating in the interdisciplinary Ph.D. study project ‘Radiopharmaceuticals for molecularly targeted diagnostics and medical therapy’, RadFarm. Within the framework of this project, five INCT doctoral students are carrying out doctoral theses related to the use of radioisotopes in medicine.

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: Ewa Gniazdowska, Ph.D., D.Sc., professor in INCT
  (phone: +48 22 504 11 78, e-mail: E.Gniazdowska@ichtj.waw.pl).

TRAINING OF STUDENTS

Institution	Country	Number of participants	Period
AGH University of Science and Technology	Poland	1	3 weeks
École Nationale Supérieure Mines-Télécom Atlantique Bretagne-Pays de la Loire	France	1	2 months

Institution	Country	Number of participants	Period
International Atomic Energy Agency	Kenya	1	1 month
Łódź University of Technology	Poland	2	1 month
Maria Curie-Skłodowska University	Poland	2	4 months
University of Warsaw	Poland	2	1 month
Warsaw University of Technology	Poland	4	1 month
Electric Schools No. 1 in Kraków	Poland	50	one-day course

MASTER'S, BACHELOR'S AND ENGINEER'S THESES

1. Emilia Górzyńska

   Bachelor's thesis: Radiokoniugat ^{198}AuNP-Oktreotyd do celowanej terapii guzów neuroendokrynnych (^{198}AuNP-Octreotide radioconjugate for targeted therapy of neuroendocrine tumours)

   supervisors: Zbigniew Rogulski, Ph.D., D.Sc., Agnieszka Majkowska-Pilip, Ph.D.

   University of Warsaw, Faculty of Chemistry

2. Agnieszka Nowak

   Engineer's thesis: Wykorzystanie membranowych procesów odsalania, jako sposobu dekontaminacji w trakcie normalnej pracy elektrowni i w sytuacjach zagrożenia (The membrane desalination processes as a method of decontamination during normal operation of a nuclear power plant and in emerging situations)

   supervisor: Janusz Sokołowski, Ph.D., D.Sc.

   supervisors in INCT: Prof. Grażyna Zakrzewska-Kołtuniewicz, Ph.D., D.Sc., Agnieszka Miśkiewicz, Ph.D.

   Warsaw University of Technology, Faculty of Chemistry

3. Marta Żuchowska

   Engineer's thesis: Badanie zjawiska foulingu membran stosowanych do oczyszczania ciekłych odpadów promieniotwórczych (Study on the phenomenon of fouling of membranes used for the treatment of liquid radioactive waste)

   supervisor: Ewa Dłuska, Ph.D., D.Sc., WUT professor

   supervisor in INCT: Agnieszka Miśkiewicz, Ph.D

   Warsaw University of Technology, Faculty of Chemical and Process Engineering

RESEARCH PROJECTS AND CONTRACTS

RESEARCH PROJECTS GRANTED BY THE NATIONAL SCIENCE CENTRE IN 2018

1. **Nanobodies labelled with alpha emitters as potential radiopharmaceuticals in targeted radioimmunotheraphy.**
   supervisor: Marek Pruszyński, Ph.D.
2. **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.
3. **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.
4. **Impact of nanoparticles on cellular signalling activated by tumour necrosis factor.**
   supervisor: Kamil Brzóska, Ph.D., D.Sc.
5. **Analytical, kinetic and toxicological study of degradation selected perfluorinated compounds using ionizing radiation.**
   supervisor: Prof. Marek Trojanowicz, Ph.D., D.Sc.
6. **New analytical procedures based on neutron activation analysis for the determination of chosen Se, As and Fe chemical formulae in infant alimentation.**
   supervisor: Halina Polkowska-Motrenko, Ph.D., D.Sc., professor in INCT
7. **Radiation-induced radical processes involving amino acids and quinoxalin-2-one derivatives relevant to their pharmacological applications.**
   supervisor: Konrad Skotnicki, M.Sc.
8. **Bioconjugates of multimodal nanoparticles for targeted alpha and hyperthermia therapy. Synthesis, retention studies of recoiling daughters radionuclides and preliminary cell.**
   supervisor: Edyta Cędrowska, M.Sc.
9. **In vitro and in vivo preclinical studies of NaA nanozeolite funcionalized with antibodies anti-PSMA and labelled with radium radioisotope for targeted prostate cancer therapy.**
   supervisor: Prof. Anna Lankoff, Ph.D., D.Sc.
10. **In vitro studies of NaA nanozeolite functionalized with integrins inhibitor – cilengitide and labelled with radium radioisotope for targeted breast cancer therapy.**
    supervisor: Sylwia Męczyńska-Wielgosz, Ph.D.
11. **Studies on cefepime labelling with Ga-68.**
    supervisor: Przemysław Koźmiński, Ph.D.
12. **Nanostructured lipidic liquid-cystalline carriers for chemotherapeutics and corpuscular radiation emitters in targeted cancer therapy.**
    INCT supervisor: Agnieszka Majkowska-Pilip, Ph.D. (in the framework of a consortium with the University of Warsaw as a leader)
13. **Radiopharmaceuticals based on neurokinin-1 receptor antagonists for the diagnosis and therapy of brain tumour-glioblastoma multiforme.**
    INCT supervisor: Ewa Gniazdowska, Ph.D., D.Sc., professor in INCT (in the framework of a consortium with the Mossakowski Medical Research Centre, Polish Academy of Sciences as a leader)
14. **6xS for chiral semiconducting naphtalene diimides: synthesis, simulations, structure, spectroscopy, spectroelectrochemistry, sensors.**
    supervisor: Prof. Jan Cz. Dobrowolski, Ph.D., D.Sc. (in the framework of a consortium with the Institute of Nuclear Chemistry and Technology as a leader)

15. **Radical reactions in sulphur-substituted nucleobases.**
    supervisor: Konrad Skotnicki, M.Sc.
16. **Superparamagnetic nanoparticles labelled with beta-emitters for simultaneous internal radiotherapy and hyperthermia.**
    INCT supervisor: Prof. Aleksander Bilewicz, Ph.D., D.Sc. (in the framework of a consortium with the University of Warsaw as a leader)

PROJECTS GRANTED BY THE NATIONAL CENTRE FOR RESEARCH AND DEVELOPMENT IN 2018

1. **Plasma technology to remove NO_x from off-gases.**
   (common undertaking of the National Science Centre, and the National Centre for Research and Development "TANGO2")
   supervisor: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.
2. **Syntheses of radiopharmaceuticals based on scandium radionuclides for positron emission tomography (Petscand).**
   supervisor: Prof. Aleksander Bilewicz, Ph.D., D.Sc.
3. **The development of innovative advanced therapy with use of a biological dressing of the human race in the treatment of *epidermolysis bullosa* and other chronic wounds (STRATEGMED).**
   supervisor: Zbigniew Zimek, Ph.D.
4. **Development of the technology for preparation substrates used in methane co-fermentation by disintegration methods.**
   INCT supervisor: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc. (in the framework of a consortium with the Gdańsk University of Technology as a leader)
5. **Radiopharmaceuticals for molecularly targeted diagnostics and medical therapy (RadFarm).**
   INCT supervisor: Prof. Aleksander Bilewicz, Ph.D., D.Sc. (in the framework of a consortium with the National Centre for Nuclear Research as a leader)

IAEA RESEARCH CONTRACTS IN 2018

1. **The study of the influence of the environmental factors on the isotopic compositions of dairy products.**
   No. 18056
   supervisor: Ryszard Wierzchnicki, Ph.D.
2. **Application of low energy electron beam for microbiological control of food and agricultural products.**
   No. 19000
   supervisor: Urszula Gryczka, M.Sc.
3. **Radiometric methods applied in hydrometallurgical processes development and optimization.**
   No. 18945
   supervisor: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.
4. **Silicide/silicate coatings on zirconium alloys for improving the high temperature corrosion resistance.**
   No. 19026
   supervisor: Bożena Sartowska, Ph.D.
5. **Recovery of uranium and accompanying metals from various types of industrial wastes.**
   No. 18542
   supervisor: Katarzyna Kiegiel, Ph.D.
6. **Electron beam for preservation of biodeteriorated cultural heritage paper-based objects.**
   No. 18493
   supervisor: Dagmara Chmielewska-Śmietanko, M.Sc.
7. **New cyclotron method for ^{47}Sc production and conjugation of ^{47}Sc to monoclonal antibodies.**
   No. 20488
   supervisor: Prof. Aleksander Bilewicz, Ph.D., D.Sc.

8. **Cyclic ^{99m}Tc isolation from the gamma irradiated ^{100}Mo target.**
   No. 22521
   supervisor: Przemysław Koźmiński, Ph.D.
9. **A method for hygienization of sewage sludge based on electron accelerator application.**
   No. 22642
   supervisor: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.

PROJECTS WITHIN THE FRAME OF EUROPEAN UNION PROGRAMME HORIZON 2020

1. **Accelerator research and innovation for European science and society (ARIES).**
   GA 730871
   principal investigator: Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.
2. **Characterization of conditioned nuclear waste for its safe disposal in Europe (CHANCE).**
   GA 755371
   principal investigator: Prof. Grażyna Zakrzewska-Kołtuniewicz, Ph.D., D.Sc.
3. **GEN IV integrated oxide fuels recycling strategies (GENIORS).**
   GA 755171
   principal investigator: Prof. Jerzy Narbutt, Ph.D., D.Sc.
4. **European tools and methodologies for an efficient ageing management of nuclear power plant cables (TeamCABLES).**
   GA 755187
   principal investigator: Grażyna Przybytniak, Ph.D., D.Sc., professor in INCT

OTHER INTERNATIONAL RESEARCH PROGRAMMES IN 2018

1. **Nanostructured porous materials with tailored properties – 2018 (MAT-POR).**
   Contract No. 04-4-1131-2017/2021 (with Joint Institute for Nuclear Research, Dubna, Russia)
   supervisor: Bożena Sartowska, Ph.D.
2. **New nanocomposite sorbent for different radionuclides removal (NANO-RAD).**
   Contract No. 04-4-1131-2017/2021 (with Joint Institute for Nuclear Research, Dubna, Russia)
   supervisor: Dagmara Chmielewska-Śmietanko, M.Sc.
3. **The studies on properties optimization of external coatings for zirconium alloys for the increasing of their resistance to oxidation and nuclear irradiation (ZRCRCOAT).**
   No. 254 (with Joint Institute for Nuclear Research, Dubna, Russia)
   supervisor: Wojciech Starosta, Ph.D.

ERASMUS+ PROGRAMME

1. **Mobility for learners and staff higher education student and staff mobility.**
   Key action 103
2. **Inter-institutional agreement 2015-2017 between institutions from programme and partner countries (China).**
   Key action 107
3. **Inter-institutional agreement 2017-2019 between institutions from programme and partner countries (USA).**
   Key action 107

IAEA REGIONAL TECHNICAL COOPERATION PROJECTS

1. **Enhancing standardized radiation technologies and quality control procedures for human health, safety, cleaner environment and advanced materials.**
   IAEA Regional Technical Cooperation Project RER-1019
2. **Developing radiotracer techniques and nuclear control systems for the protection and sustainable management of natural resources and ecosystems.**
   IAEA Regional Technical Cooperation Project RER-1020

WORKS FOR THE MINISTRY OF ENERGY

1. **Organizational support for training seminar presenting the spin-off effects of nuclear energy to Polish industry**
   supervisor: Zbigniew Zimek, Ph.D.
   Contract No. 85/II/P/75001/4300/18/DEJ

LIST OF VISITORS TO THE INCT IN 2018

1. **Buśko Eugeniusz G.**, International Sakharov Environmental Institute, Belarusian State University, Minsk, Belarus, *14-16.11.2018*
2. **Calinescu Ivan**, University Politehnica of Bucharest, Romania, *18-22.06.2018*
3. **Chesori Raphael**, International Atomic Energy Agency, Kenya, *3-31.12.2018*
4. **Edgecock Thomas**, University of Huddersfield, United Kingdom, *4-5.06.2018*
5. **Fuente Julio De la**, Universidad de Chile, Santiago de Chile, Chile, *1-30.09.2018*
6. **Lavric Vasile**, University Politehnica of Bucharest, Romania, *18-22.06.2018*
7. **Lei Lei Oo**, International Atomic Energy Agency, Vienna, Austria, *12-23.11.2018*
8. **Muravsky Oleg**, OM Trading Ltd, Lithuania, *15.03.2018*
9. **Pillai Suresh D.**, Texas A&M University/Texas A&M AgriLife Research, Texas, USA, *27-31.08.2018*
10. **Rowan Scott**, University of Huddersfield, United Kingdom, *4-5.06.2018*
11. **Sevcik Aleksandras**, Kaunas University of Technology, Lithuania, *15.03.2018*
12. **Toson Hassieb Mostafa**, Egyptian Atomic Energy Authority (EAEA), Egypt, *15.10-15.12.2018*
13. **Wang Sheng**, Xi'an Jiaotong University (XJTU), China, *2-6.07.2018*
14. **Wang Zhihong**, The Elementary School affiliated to XJTU, China, *2-6.07.2018*
15. **Zhou Hong**, Xi'an Jiaotong University (XJTU), China, *2-6.07.2018*

THE INCT SEMINARS IN 2018

1. **Prof. Artur Bartkowiak (West Pomeranian University of Technology, Faculty of Food Sciences and Fisheries, Szczecin, Poland)**
   Trendy w opakowalnictwie a badania naukowe – Jak „badać na miarę”? (Trends in packaging and scientific research – How to ‘test for measure’?)

2. **Prof. Joan Calinescu (University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, Bucharest, Romania)**
   Statistical design of experiments (DoE)

3. **Ireneusz P. Grudziński, Ph.D., D.Sc. (Medical University of Warsaw, Faculty of Pharmacy, Warszawa, Poland)**
   Nanomateriały nowej generacji w badaniach onkologicznych (New generation nanomaterials in oncological research)

4. **Sławomir Jednoróg, Ph.D. (Institute of Plasma Physics and Laser Microfusion, Warszawa, Poland)**
   Fuzja jądrowa (Nuclear fusion)

5. **Prof. Vasile Lavric (University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, Bucharest, Romania)**
   Gas-liquid processes to mitigate gaseous pollutants. State of the art

6. **Hanna Lewandowska-Siwkiewicz, Ph.D. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**
   Dinitrozylowe kompleksy żelaza – synteza, struktura i biologia (Dinitrosyl iron complexes – synthesis, structure and biology)

7. **Michał Maurin, M.Sc. (National Centre for Nuclear Research, POLATOM, Otwock-Świerk, Poland)**
   Fragmenty alfa-fetoproteiny (AFP), ludzkiego białka płodowego, jako potencjalne nośniki radioizotopów do diagnostyki nowotworowej (^{99m}Tc) oraz celowanej radioterapii wewnętrznej (^{177}Lu, ^{90}Y) (Alpha-fetoprotein (AFP) fragments, of human fetal protein, as potential radionuclide carriers for tumour diagnostics (^{99m}Tc) and targeted internal radiotherapy (^{177}Lu, ^{90}Y))

8. **Prof. Jerzy W. Mietelski (The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland)**
   Lotniczy napęd jądrowy i zagadkowe skażenie Ru-106 (Aircraft nuclear propulsion and mysterious Ru-106 contamination)

9. **Prof. Suresh D. Pillai (College of Agriculture & Life Sciences, Texas A&M University/Texas A&M AgriLife Research, Texas, USA)**
   Water reuse trends in the United States

10. **Jan Poleszczuk, Ph.D. (The Nalecz Institute of Biocybernetics and Biomedical Engineering, Polish Academy of Sciences, Warszawa, Poland)**
    Nielokalne efekty radioterapii i ich potencjalne wykorzystanie w klinice: perspektywa onkologa matematycznego (Non-tergeted effects of radiotherapy and their potential utilization in clinic; the point of view of mathematical oncologist)

11. **Marek Pruszyński, Ph.D. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**
    Projektowanie, otrzymywanie i charakterystyka nowych radiofarmaceutyków molekularnych do diagnostyki i terapii nowotworów z nadekspresją receptora HER2 (Design, preparation and characterization of new molecular radiopharmaceuticals for diagnosis and therapy of cancers with HER2-receptor overexpression)

12. **Magdalena Rzepna, M.Sc. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**
    Efekty indukowane radiacyjnie w wybranych biodegradowalnych kopolimerach estrów alifatycznych (Radiation-induced effects in selected biodegradable copolymers of aliphatic esters)

13. **Wojciech Starosta, Ph.D., Marcin Brykała, Ph.D. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**

Paliwo dla wysokotemperaturowych reaktorów jądrowych (HTR) – problemy materiałowe (Fuel for high-temperature nuclear reactors (HTR) – material problems)

14. **Marcin Sterniczuk, Ph.D. (Institute of Nuclear Chemistry and Technology, Warszawa, Poland)**
    Radioliza wody w wysokich temperaturach – źródła wodoru molekularnego (Water radiolysis at high temperatures – sources of molecular hydrogen)

LECTURES AND SEMINARS DELIVERED OUT OF THE INCT IN 2018

LECTURES

1. **Chmielewska-Śmietanko D.**
   Electron beam technology for preservation of cultural heritage artefacts.
   ARIES 1st Annual Meeting, Riga, Latvia, 21-24.05.2018.
2. **Chmielewska-Śmietanko D.**
   Radiation methods in nanotechnology.
   IAEA RTC 'Radiation processing for advanced polymeric materials' in the frame of Technical Cooperation Project RER1019 'Enhancing standardized radiation technologies and quality control procedures for human health, safety, cleaner environment and advanced materials', Warszawa, Poland, 15-19.10.2018.
3. **Chmielewska-Śmietanko D., Pańczyk E., Gryczka U., Migdał W., Sadło J., Kopeć K.**
   Zastosowanie wiązki elektronów do dekontaminacji mikrobiologicznej różnego rodzaju papierów (Application of electron beam technology for the microbiological decontamination of different papers).
   3ci warsztat informacyjny oferty MOLAB/FIXLAB PL, Kraków, Poland, 12.06.2018.
4. **Chmielewski A.G.**
   Przykłady zwycięskich projektów (Examples of winning projects).
   Dzień informacyjny programu EURATOM (EURATOM Info Day), Warszawa, Poland, 12.02.2018.
5. **Chmielewski A.G.**
   New applications of low energy electron beams.
   ARIES 1st Annual Meeting, Riga, Latvia, 21-24.05.2018.
6. **Chmielewski A.G.**
   Programy badawcze w ramach energetyki jądrowej – prowadzone obecnie i konieczne do uruchomienia (Polish R&D programmes in the field of nuclear energy – currently run and necessary to start in the future).
   Meeting of the Power Engineering Problems Committee, Polish Academy of Sciences, Warszawa, Poland, 25.05.2018.
7. **Chmielewski A.G.**
   Polish programme in the field of sludge teatment.
   Workshop of the emerging trends in the sludge treatment, Warszawa, Poland, 27.08.2018.
8. **Chmielewski A.G.**
   Comparison of gamma, electron beam and X-ray treatment.
   IAEA RTC 'Radiation processing for advanced polymeric materials' in the frame of Technical Cooperation Project RER1019 'Enhancing standardized radiation technologies and quality control procedures for human health, safety, cleaner environment and advanced materials', Warszawa, Poland, 15-19.10.2018.
9. **Chmielewski A.G.**
   Recent developments in ARIES project WP3 'Industrial and societal applications'.
   IAEA RTC 'Radiation processing for advanced polymeric materials' in the frame of Technical Cooperation Project RER1019 'Enhancing standardized radiation technologies and quality control procedures for human health, safety, cleaner environment and advanced materials', Warszawa, Poland, 15-19.10.2018.
10. **Chmielewski A.G.**
    Preparing for the future: innovation and education. Polish perspective – R&D in nuclar chemistry and radioactive waste.
    Regional Ministerial Meeting on Nuclear Energy Technology and Radioactive Waste Management, Bucharest, Romania, 25-26.10.2018.
11. **Chmielewski A.G.**
    International perspective on ionizing radiation sources development, materials processing and environmental applications.

Corporate Program for ROSATOM Subsidiary Integrator-Company – RUSATOM Healthcare, Skolkovo Village, Russia, 29-30.11.2018.

12. **Chmielewski A.G.**

    Recent progress in the radiation technology development achieved by INCT, Poland – R&D, collaboration, education and promotion.

    IAEA Consultancy Meeting on Review of the Work Plans Being Implemented with Collaborating Centres, Vienna, Austria, 3-6.12.2018.

13. **Chmielewski A.G., Smoliński T., Rogowski M.**

    Application of RT, GS and NCS in an European country – lessons and success' stories.

    Expert Meeting for Promoting Radiotracers and Sealed Sources Technologies and Applications in Industry in the frame of the TC Project RER1020 'Developing radiotracer techniques ane nuclear control systems for the protection and sustainable management of natural resources and ecosystems', Vienna, Austria, 11-13.12.2018.

14. **Cieśla K.**

    Natural polymers modified by ionzing radiation.

    IAEA RTC 'Radiation processing for advanced polymeric materials' in the frame of Technical Cooperation Project RER1019 'Enhancing standardized radiation technologies and quality control procedures for human health, safety, cleaner environment and advanced materials', Warszawa, Poland, 15-19.10.2018.

15. **Głuszewski W.**

    Nowe inicjatywy Międzynarodowej Agencji Energii Atomowej (MEAE/IAEA) w dziedzinie harmonizacji nieniszczących badań (NDT), szkoleń i certyfikacji dla inżynierii lądowej i dziedzictwa kulturowego (New initiatives by the International Atomic Energy Agency (IAEA) in the field of harmonization of non-dectructive testing (NDT), training and certification for civil engineering and cultural heritage).

    II Konferencja „Zastosowanie promieniowania jonizującego w badaniach i konserwacji zabytków", Tczew/Gdańsk, Poland, 10-11.05.2018.

16. **Głuszewski W.**

    Radiacyjna konserwacja obiektów o znaczeniu historycznym – zalety i zagrożenia (Uses of ionizing radiation for tangible cultural heritage conservation – advantages and dangers).

    II Konferencja „Zastosowanie promieniowania jonizującego w badaniach i konserwacji zabytków", Tczew/Gdańsk, Poland, 10-11.05.2018.

17. **Głuszewski W.**

    Radiation treatment of foams, tires and pipes.

    IAEA RTC 'Radiation processing for advanced polymeric materials' in the frame of Technical Cooperation Project RER1019 'Enhancing standardized radiation technologies and quality control procedures for human health, safety, cleaner environment and advanced materials', Warszawa, Poland, 15-19.10.2018.

18. **Gryczka U.**

    Radiation degradation of cellulose.

    IAEA RTC 'Radiation processing for advanced polymeric materials' in the frame of Technical Cooperation Project RER1019 'Enhancing standardized radiation technologies and quality control procedures for human health, safety, cleaner environment and advanced materials', Warszawa, Poland, 15-19.10.2018.

19. **Ostyk-Narbutt J.**

    Am^{III} vs Ln^{III} stripping IChTJ – DM1 WP3 GENIORS.

    First GENIORS Yearly Project Meeting, Würzburg, Germany, 17-18.04.2018.

20. **Pańczyk E., Garbacz-Klempka A., Dudek J.**

    Neutrons and archaeology. A contribution of INAA (instrumental neutron activation analysis) to the characterization of small lead seals of Dorogichin type.

    The Sphinx of Slav Sigillography. Seals of Dorogichin type in the light of interdiscip;linary research, Kraków, Poland, 7-9.05.2018.

21. **Przybytniak G.**

    Cross-linking of electric cables and wires.

    IAEA RTC 'Radiation processing for advanced polymeric materials' in the frame of Technical Cooperation Project RER1019 'Enhancing standardized radiation technologies and quality control procedures for human health, safety, cleaner environment and advanced materials', Warszawa, Poland, 15-19.10.2018.

22. **Przybytniak G.**

    Heat shrinkable tapes and tubing.

    IAEA RTC 'Radiation processing for advanced polymeric materials' in the frame of Technical Cooperation Project RER1019 'Enhancing standardized radiation technologies and quality control procedures for human health, safety, cleaner environment and advanced materials', Warszawa, Poland, 15-19.10.2018.

23. **Przybytniak G.**
    Overview of radiation technologies in polymer processing.
    IAEA RTC 'Radiation processing for advanced polymeric materials' in the frame of Technical Cooperation Project RER1019 'Enhancing standardized radiation technologies and quality control procedures for human health, safety, cleaner environment and advanced materials', Warszawa, Poland, 15-19.10.2018.

24. **Rafalski A.**
    Fundamental aspects of radiation dosimetry: basic principles and methods.
    IAEA RTC 'Radiation processing for advanced polymeric materials' in the frame of Technical Cooperation Project RER1019 'Enhancing standardized radiation technologies and quality control procedures for human health, safety, cleaner environment and advanced materials', Warszawa, Poland, 15-19.10.2018.

25. **Sadło J.**
    Introduction to practical exercises: EPR in radiation chemistry and dosimetry.
    IAEA RTC 'Radiation processing for advanced polymeric materials' in the frame of Technical Cooperation Project RER1019 'Enhancing standardized radiation technologies and quality control procedures for human health, safety, cleaner environment and advanced materials', Warszawa, Poland, 15-19.10.2018.

26. **Sadło J.**
    Radiation curing of polymers. Self-repairing composites.
    IAEA RTC 'Radiation processing for advanced polymeric materials' in the frame of Technical Cooperation Project RER1019 'Enhancing standardized radiation technologies and quality control procedures for human health, safety, cleaner environment and advanced materials', Warszawa, Poland, 15-19.10.2018.

27. **Sudlitz M.**
    Polish and EU regulation of sludge treatment.
    Workshop of the emerging trends in the sludge treatment, Warszawa, Poland, 27.08.2018.

28. **Sudlitz M., Sun Y., Chmielewski A.G., Zwolińska E., Zhao L., Dobrowolski A., Licki J., Pawelec A., Bułka S., Zimek Z., Trojanowicz M., Bojanowksa-Czajka A., Drzewicz P., Głuszewski W., Kulisa K., Łyczko M., Kciuk G., Moskal J., Gryczka U., Chmielewska-Śmietanko D., Edgecock R., Palige J.**
    EB flue gas treatment.
    Project RER1019 'Enhancing standardized radiation technologies and quality control procedures for human health, safety, cleaner environment and advanced materials' – Regional Workshop on the Advantages, Prospects and Potential Applications of Radiation Processing for Environmental Protection, Budapest, Hungary, 11-15.06.2018.

29. **Sudlitz M., Sun Y., Chmielewski A.G., Zwolińska E., Zhao L., Dobrowolski A., Licki J., Pawelec A., Bułka S., Zimek Z., Trojanowicz M., Bojanowksa-Czajka A., Drzewicz P., Głuszewski W., Kulisa K., Łyczko M., Kciuk G., Moskal J., Gryczka U., Chmielewska-Śmietanko D., Edgecock R., Palige J.**
    INCT activities in the field of radiation environment pollution control technologies.
    Project RER1019 'Enhancing standardized radiation technologies and quality control procedures for human health, safety, cleaner environment and advanced materials' – Regional Workshop on the Advantages, Prospects and Potential Applications of Radiation Processing for Environmental Protection, Budapest, Hungary, 11-15.06.2018.

30. **Sun Y.**
    Emerging applications.
    Workshop on Radiation Technology and the Environment, Muscat, Sultanate of Oman, 26-28.02.2018.

31. **Sun Y.**
    Introduction to radiation technology.
    Workshop on Radiation Technology and the Environment, Muscat, Sultanate of Oman, 26-28.02.2018.

32. **Sun Y.**
    Material modification.
    Workshop on Radiation Technology and the Environment, Muscat, Sultanate of Oman, 26-28.02.2018.

33. **Sun Y.**
    Pilot and industrial flue gas treatment plant.
    Workshop on Radiation Technology and the Environment, Muscat, Sultanate of Oman, 26-28.02.2018.

34. **Sun Y.**
    Radiation technology for flue gas treatment.
    Workshop on Radiation Technology and the Environment, Muscat, Sultanate of Oman, 26-28.02.2018.

35. **Sun Y.**
    Treatment of emerging organic pollutants using radiation technology – state of the art.

IAEA Technical Meeting 'Recent advances in the treatment of emerging organic pollutants', Suzhou, China, 8-12.10.2018.

36. **Szreder T.**

    Przetwarzanie wypalonego paliwa jądrowego – efekty radiacyjne (Reprocessing of used nuclear fuel – radiation effects).

    III Akademickie Forum Energii Jądrowej, Kraków, Poland, 16-18.05.2018.

37. **Walo M.**

    Modification of polymeric surfaces by grafting.

    IAEA RTC 'Radiation processing for advanced polymeric materials' in the frame of Technical Cooperation Project RER1019 'Enhancing standardized radiation technologies and quality control procedures for human health, safety, cleaner environment and advanced materials', Warszawa, Poland, 15-19.10.2018.

38. **Zimek Z.**

    Economic aspects of radiation technologies.

    IAEA RTC 'Radiation processing for advanced polymeric materials' in the frame of Technical Cooperation Project RER1019 'Enhancing standardized radiation technologies and quality control procedures for human health, safety, cleaner environment and advanced materials', Warszawa, Poland, 15-19.10.2018.

39. **Zimek Z.**

    Electron accelerators for radiation treatment of polymers.

    IAEA RTC 'Radiation processing for advanced polymeric materials' in the frame of Technical Cooperation Project RER1019 'Enhancing standardized radiation technologies and quality control procedures for human health, safety, cleaner environment and advanced materials', Warszawa, Poland, 15-19.10.2018.

SEMINARS

1. **Chajduk Ewelina**

   Neutronowa analiza aktywacyjna (Neutron activation analysis).

   University of Warsaw, Faculty of Physics, Warszawa, Poland, 13.04.2018.

2. **Chajduk Ewelina**

   Analiza procesów zachodzących przy normalnej eksploatacji obiegów wodnych w elektrowni jądrowej (Analysis of processes during normal operation of water circuits in nuclear power plant).

   University of Warsaw, Faculty of Physics, Warszawa, Poland, 8.06.2018.

3. **Chmielewski Andrzej G.**

   Selected activities of the Institute of Nuclear Chemistry and Technology (Science and education for Polish nuclear power project).

   National Centre for Nuclear Research, Otwock-Świerk, Poland, 29.05.2018.

4. **Kołacińska Kamila**

   Jak pisać pojekty naukowe? (How to write scientific projects?).

   Web seminar, Polish-American Fulbright Commission, Warszawa, Poland, 5.03.2018.

5. **Kołacińska Kamila**

   Energetyka jądrowa oraz Program Polskiej Energetyki Jądrowej (Nuclear power and Polish Nuclear Power Programme).

   SGH Warsaw School of Economics, Warszawa, Poland, 8.03.2018.

6. **Kruszewski Marcin**

   Nanoradioterapia: okno na świat czy ślepy zaułek? (Nanoradiotherapy: a window to the world or a dead end?).

   National Centre for Nuclear Research, Otwock-Świerk, Poland, 25.01.2018.

AWARDS IN 2018

1. Diagnostic radiopharmaceutical for imaging of infections, method for producing it and application
   Platinum medal at the International Warsaw Invention Show IWIS 2018, Warszawa, Poland, 15-17.10.2018
   Przemysław Koźmiński, Ewa Gniazdowska, Marek Chojnowski, Agata Kopatys, Leszek Królicki
2. Precursor of radiopharmaceutical and method for its manufacturing
   Gold medal at the International Warsaw Invention Show IWIS 2018, Warszawa, Poland, 15-17.10.2018
   Aleksander Bilewicz, Monika Łyczko, Agata Piotrowska, Edyta Leszczuk
3. Method for producing uranium carbide with spherical and irregular grains as a precursor of the fuel for the reactors of new IV generation
   Gold medal at the International Warsaw Invention Show IWIS 2018, Warszawa, Poland, 15-17.10.2018
   Marcin Brykała, Marcin Rogowski
4. Diagnostic radiopharmaceutical for imaging of infections, method of its production and its application
   Gold medal at the Seoul International Invention Fair 2018, Seoul, South Korea, 6-9.12.2018
   Przemysław Koźmiński, Ewa Gniazdowska, Marek Chojnowski, Agata Kopatys, Leszek Królicki
5. Method for producing uranium carbide with spherical and irregular grains as a precursor of the fuel for the reactors of new IV generation
   Silver medal at the Seoul International Invention Fair 2018, Seoul, South Korea, 6-9.12.2018
   Marcin Brykała, Marcin Rogowski
6. Leaching of metals from post-flotation copper waste from the pyrometallurgical process of copper production
   Bronze medal at the International Warsaw Invention Show IWIS 2018, Warszawa, Poland, 15-17.10.2018
   Tomasz Smoliński, Marcin Rogowski, Marta Pyszynska, Andrzej Chmielewski
7. Award of the 'Polish Market' magazine and the Main Council of the Research Institutes – 'Innovation Pearl – PROGRESS' in category 'Scientific unit'
   Institute of Nuclear Chemistry and Technology
8. Diagnostic radiopharmaceutical for imaging of infections, method of its production and its application
   Special award of the Indonesian Invention and Innovation Promotion Association (INNOPA) at the Seoul International Invention Fair 2018, Seoul, South Korea, 6-9.12.2018
   Przemysław Koźmiński, Ewa Gniazdowska, Marek Chojnowski, Agata Kopatys, Leszek Królicki
9. Leaching of metals from post-flotation copper waste from the pyrometallurgical process of copper production
   Distinction of the Polish Chamber of Chemical Industry at the International Warsaw Invention Show IWIS 2018, Warszawa, Poland, 15-17.10.2018
   Tomasz Smoliński, Marcin Rogowski, Marta Pyszynska, Andrzej Chmielewski
10. Kwartalnik „Postępy Techniki Jądrowej" nr 4/2017 (Quarterly journal "Postępy Techniki Jądrowej) no. 4/2017)
    The title 'Numerus Primus Inter Pares' awarded by the Society for Technical Culture for the specialist journal best issue in 2017
    Editorial office and publisher – Institute of Nuclear Chemistry and Technology
11. The removal of NO_x and SO_2 from exhaust gases using a hybrid electron beam method
    First degree award of the Polish Nuclear Society for the best doctoral thesis in 2017-2018 concerning nuclear sciences
    Ewa Zwolińska
12. Reakcje rodnikowe chinoksalin-2-onów w aspekcie ich zastosowań farmakologicznych (Radical processes involving quinoxalin-2-one derivatives relevant to their pharmacological applications)
    Distinction of the Polish Nuclear Society for the best doctoral thesis in 2017-2018 concerning nuclear sciences
    Konrad Skotnicki

13. First degree team award of Director of the Institute of Nuclear Chemistry and Technology in 2018 for a series of publications on the aspects of structural research and the application of various methods of quantum chemistry in solving problems in the field of crystallography, oscillation spectroscopy and physical organic chemistry

    Jan Cz. Dobrowolski, Krzysztof Łyczko, Jerzy Narbutt, Sławomir Ostrowski, Joanna E. Rode

14. Second degree team award of Director of the Institute of Nuclear Chemistry and Technology in 2018 for a series of publications on the mechanisms of radical processes in compounds of biological importance induced radiolytically and photochemically

    Krzyszof Bobrowski, Dariusz Pogocki, Konrad Skotnicki

15. Third degree team award of Director of the Institute of Nuclear Chemistry and Technology in 2018 for a series of publications concerning innovative technologies in the field of radiopharmaceuticals, especially nanotechnology for the immobilization of radionuclides

    Aleksander Bilewicz, Edyta Cędrowska, Łucja Dziawer, Jan Cz. Dobrowolski, Przemysław Koźmiński, Marcin Kruszewski, Monika Łyczko, Agnieszka Majkowska-Pilip, Sylwia Męczyńska-Wielgosz, Sławomir Ostrowski, Agata Piotrowska, Marek Pruszyński

16. Second degree team award of Director of the Institute of Nuclear Chemistry and Technology in 2018 for the application achievements in 2016-2017 – Development of silicate minerals separation procedures in food supplements, plant pharmaceuticals and extracts examined using thermoluminescence (TL) method

    Grażyna Liśkiewicz, Grzegorz Guzik, Magdalena Miłkowska

17. Second degree team award of Director of the Institute of Nuclear Chemistry and Technology in 2018 for the application achievements in 2016-2017 – Development of the methodology for implementation of proficiency in the laboratories analysing the content of radionuclides in the environment and foodstuff

    Halina Polkowska-Motrenko, Leon Fuks, Jakub Dudek, Paweł Kalbarczyk, Irena Herdzik-Koniecko, Krzysztof Kulisa, Zdzisław Maciejewski

18. First degree award of Director of the Institute of Nuclear Chemistry and Technology in 2018 for the best presentations at the reporting seminar of the INCT Ph.D. students

    Krzysztof Staszkiewicz, Rafał Walczak

19. Second degree award of Director of the Institute of Nuclear Chemistry and Technology in 2018 for the best presentation at the reporting seminar of the INCT Ph.D. students

    Weronika Gawęda

20. Distinction of Director of the Institute of Nuclear Chemistry and Technology in 2018 for the involvement in the events popularizing the INCT scientific activity

    Paweł Halik, Weronika Gawęda, Marcin Sudlitz, Rafał Walczak

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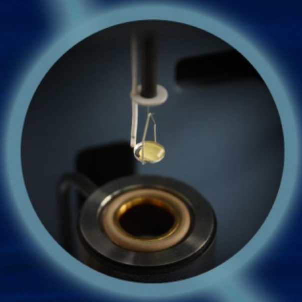

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