ANNUAL REPORT

2011-2012

Nuclear Chemistry

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Czech Technical University in Prague

DEPARTMENT OF
NUCLEAR CHEMISTRY

CENTRE FOR RADIOCHEMISTRY
AND RADIATION CHEMISTRY

NUCLEAR CHEMISTRY
Annual Report 2011-2012

Editors: John, J.; Múčka, V.; Vopálka, D.

EDITORIAL

Dear Reader, this is the third in the series of the CTU Nuclear Chemistry Annual Reports that seem to have reached their maturity with standardised contents, stabilised format, and regular bi-annual periodicity. Similarly to the previous issue, this brochure compiles the achievements of two organisation units of the Faculty of Nuclear Sciences and Physical Engineering (FNSPE) of the Czech Technical University in Prague (CTU) – the Department of Nuclear Chemistry (DNC) and the Centre for Radiochemistry and Radiation Chemistry (CRRC).

On the top of the list of the main events that happened during the period covered (2011 – 2012), the re-accreditation of the master-level study programme connected with significant changes in the structure of both the master and bachelor cycle should be probably listed. The main changes in the master-level study programme include

- The name of the study programme was changed from the original Nuclear Chemical Engineering to the new Nuclear Chemistry. Since the "Engineering" word in the name of the programme was always rather a tribute to the fact that we are a part of the Czech Technical University than a reality, this change only stressed our belonging to the applied sciences orientation of the Faculty of Nuclear Sciences and Physical Engineering.

- The "specialisations" ("minors") were formally abolished. However, the possibility for our students to informally specialise into all the three former fields - Applied nuclear chemistry, Environmental radiochemistry and radioecology, or Nuclear chemistry in biology and medicine was maintained since all the specialisation courses remained available.

- Stronger stress was put on the practical laboratory exercises and their linking to the theoretical education. The former extensive Practical exercises in radiochemistry 1 and 2, covering the entire field, were replaced by a series of shorter practical laboratory exercises attached directly to the respective lecture courses.

- The option to study the master-level nuclear chemistry as a two-year 120 credits programme (designed for the bachelors of nuclear chemistry) or a three-year 180 credits programme (other chemistry bachelors) was abolished. Now, only the two-year option exists and the non-nuclear chemistry bachelors are requested to complete the missed courses as elective studies.

The most important change in the field of research activities concerned the financing. The medium-term Research Programmes of the Czech Ministry of Education Youth and Sports that guaranteed some basic funding of research already since 2005 reached their end and were not continued. Hence, the research activities of the department are now practically fully dependent on standard external project-based financing. This change has not influenced the main direction of the research activities of the DNC and CRRC that still covered the majority of the fields within the traditional definition of nuclear chemistry – radiochemistry including its separation methods, radioanalytical chemistry, radiotracer techniques and chemistry of the actinides, and radiation chemistry including its applications, e.g., in catalysis, environmental protection, radiation iniciated preparation of solids inclusive nanoparticles – as well as radioecology and bioradiation chemistry. In these fields, the CTU has been integrated into several big international EURATOM FP7 integrated projects such as ACSEPT or ASGARD; thus, most of the research is performed in close collaboration and co-ordination with the major European institutes and universities. The main national collaborations included the Nuclear Research Institute Řež plc., Nuclear Physics Institute of the AS CR, both located in Řež near Prague, Radioactive Waste Repository Authority of the Czech Republic (SÚRAO), DIAMO s.p., Stráž pod Ralskem, and many others.

In the period cover by this report, the research in nuclear chemistry at the DNC and CRRC continued to be organised in three research groups that, for the purpose of this Report, may be referred to as "Speciation and Migration", "Separation and Radioanalytics" and „Radiation Chemistry". Selection of short contributions characterising the research topics in more detail forms the body of this Annual Report.

As it has been reported already in the previous Annual Report, attention has been focused recently on the development of radiopharmaceutical chemistry and biomedical applications of radionuclides and ionising radiation. These activities peaked during 2012 when two successful applications were submitted for two large research grants that allowed to establish, starting since the 1st January 2013, a fourth research group – "Radiopharmaceutical Chemistry". For this group, two new researchers were engaged and a new laboratory was set-up for their activities. This laboratory and its activities will be covered in more detail in the next issue of this Annual Report.

Another important event was re-shaping and opening to the general scientific public of the Department Seminar. Since the academic year 2011/2012 it has been planned as a day-long event consisting of an opening lecture by an invited eminent Czech or foreign expert (90 minutes) followed by Ph.D. students' reports of the results achieved during the last year of their study, progress reports of key department grants, and travel reports. In addition to the academic staff, participation in the seminar is mandatory for all doctoral and diploma students. Undergraduate students are highly welcome. The seminar is broadly advertised and well visited by guests from other Czech institutions in the field. A special new section was added to this Annual Report to present this Seminar.

In the field of international cooperation in education, CTU maintained its role of the co-ordinator of the FP7 project CINCH – Cooperation in Education in Nuclear Chemistry (http://www.cinch-project.eu/) that aimed at coordinating the education in nuclear chemistry, both at Ph.D. and undergraduate levels, within the EU, in collaboration with Russia. A separate part of the project was aiming at preparation of the grounds for a significant improvement of the university – industries collaboration in the training programs. The main achievements of the project in the period were significant progress on the way towards establishment of the EuroMaster in Nuclear and Radiochemistry (NRC EuroMaster) and development of distance learning tools NucWik (http://nucwik.wikispaces.com/) and CINCH Moodle (http://cinch.moodlepartner.cz/).

Last but not least it should be noted here that the end of this reporting period marks also the end of one era of nuclear chemistry at the Czech Technical University in Prague – the era of the parallel existence of the DNC and CRRC. Establishment of CRRC back in 2003 significantly contributed to the fact that today, there exists a strong group of highly competent and motivated young nuclear chemists aged 35–40 at the CTU. This team represents one of the most important units of the Czech nuclear community. However, after termination of the extra-budgetary support of the CTU headquarters to the CRRC, the FNSPE management, in agreement with the CRRC and DNC heads, decided to merge the CRRC with its mother Department of Nuclear Chemistry. This change that happened on the 1st January 2013 is expected to simplify the management and administration of the unit. Since it does not have any consequences for the academic staff, the Nuclear Chemistry at the CTU will continue to resemble rather a small research institute than a typical university department.

As usually, we hope that you will find this report interesting, and that it may help to further promote both our national and namely international collaboration. We hope that all potential new collaborators will find the environment in our research groups as convivial and inspiring as our current colleagues do.

Jan John   Václav Čuba
Head, DNC   Head, CRRC

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EDUCATION

- Courses Taught

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Courses Taught

List of Courses in the Academic Years 2011/2012 and 2012/2013

Title, credits (ECTS), semester (W - October to mid-January, S - March to mid-June), cycle (B – bachelor, M – master, D – doctorate), lecturer(s)

Course	Credits	Semester	Cycle	Lecturer(s)
Chemistry for nuclear engineering	4	S	B	Štamberg, K.; Silber, R.
Dosimetry and radiation protection	3	W	B	Martinčík, J.; Hobzová, L.*
Fundamentals of chemistry 1	3	W	B	Motl, A.
Fundamentals of chemistry 2	3	S	B	Motl, A.
Fundamentals of construction and function of nuclear power plants	3	S	B	Otčenášek, P.*
General chemistry	6	W	B	Motl, A.
Instrumental methods of research 1	3	S	B	Pospíšil, M.
Ionising radiation detection	2	S	B	John, J.
Laboratory practice in the instrumental methods of research	2	S	B	Pospíšil, M.; Silber, R.
Measurement and data handling	3	W	B	Vetešník, A.; Vopálka, D.
Nuclear chemistry 1	2	S	B	Beneš, P.
Nuclear chemistry 2	5	W	B	John, J.; Čuba, V.
Numerical methods A	3	S	B	Limpouch, J.*; Vopálka, D.
Physical chemistry 1	5	W	B	Múčka, V.; Silber, R.
Physical chemistry 2	5	W	B	Drtinová, B.; Silber, R.
Practical exercises in ionising radiation detection	3	S	B	Němec, M.; John, J.
Practical exercises in radiochemical techniques	2	W	B	Němec, M.; Čubová, K.
The theory of the electromagnetic field and wave motion	4	S	B	Vetešník, A.
Application of radionuclides 1	3	W	M	Mizera, J.*
Application of radionuclides 2	3	S	M	Mizera, J.*
Applications of radiation methods	2	S	M	Múčka, V.
Chemistry of operation of nuclear power plants	2	W	M	Štamberg, K.; Silber, R.
Chemistry of radioactive elements	2	W	M	John, J.
Chemistry of the pharmaceuticals	3	W	M	Smrček, S.*

* External teacher

• Determination of radionuclides in the environment	2	S	M	Němec, M.
• Environmental chemistry and radioecology	2	W	M	Beneš, P.
• Instrumental methods of research 2	2	W	M	Pospíšil, M.
• Introduction to photochemistry and photobiology	2	W	M	Čubová, K.; Juha, L.*
• Modelling of the migration processes in the environment	2	S	M	Štamberg, K.
• Nuclear materials technology	2	S	M	Štamberg, K.
• Numerical simulation of complex environmental processes	2	W	M	Vopálka, D.
• Physical chemistry 3	2	W	M	Čuba, V.
• Physical chemistry 4	5	S	M	Múčka, V.; Silber, R.
• Physical chemistry 5	2	W	M	Silber, R.
• Practical exercises in nuclear chemistry	4	W	M	Němec, M.; Čubová, K.
• Practical exercises in radiation chemistry	3	S	M	Čuba, V.; Bárta, J.
• Practical exercises in radiation methods in biology and medicine	4	S	M	Čuba, V.; Vlk, M.
• Practical exercises in separation methods in radiochemistry	3	W	M	Němec, M.; Čubová, K.
• Production of radionuclides	2	W	M	Lebeda, O.*
• Protection of the environment	2	W	M	Filipská, H.
• Radiation chemistry	4	S	M	Motl, A.
• Radiation methods in biology and medicine	2	S	M	Čuba, V.; Múčka, V.
• Radiation protection	4	W	M	Vrba, T.*
• Radioanalytical methods	3	S	M	John, J.
• Radiobiology	2	S	M	Davídková, M.*
• Radiopharmaceuticals 1	2	W	M	Lebeda, O.*
• Radiopharmaceuticals 2	2	W	M	Moša, M.*
• Separation methods in nuclear chemistry 1	3	W	M	Němec, M.
• Separation methods in nuclear chemistry 2	2	S	M	Němec, M.
• Technology of the fuel cycles of nuclear power plants	2	W	M	Štamberg, K.
• Waste Management and Treatment	2	W	M	Kubal, M.*

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* External teacher

- Application of large ionising radiation sources
- Applications of radiation chemistry in chemical industry, agriculture and medicine
- Application of radionuclides
- Biosyntheses of labelled compounds
- Chemistry of actinoids and transactinoids
- Experimental nuclear chemistry
- Instrumental radioanalytical methods and their application for monitoring the environmental contamination
- Labelled compounds
- Modelling and simulation of the migration processes in the environment
- Nuclear chemistry
- Nuclear power plants
- Photochemistry and radiation chemistry
- Radioanalytical chemistry
- Radionuclides in biological sciences
- Radiopharmaceuticals
- Separation methods
- Technology of nuclear fuels
- Transport processes

D	Pospíšil, M.
D	Múčka, V.
D	Mizera, J.*
D	Smrček, S.*
D	John, J.
D	John, J.; Němec, M.; Čuba, V.
D	Kučera, J.*
D	Smrček, S.*
D	Štamberg, K.; Vopálka, D.
D	Beneš, P.; John, J.
D	Heřmanský, K.; Štamberg, K.
D	Juha, L.*; Čuba, V.; Čubová, K.
D	Němec, M.
D	Smrček, S.*
D	Lebeda, O.*; Smrček, S.*; Moša, M.
D	Němec, M.
D	Štamberg, K.
D	Štamberg, K.; Vopálka, D.

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* External teacher

Projects

EDUCATION

NEW TASKS FOR PRACTICAL EXERCISES IN RADIOCHEMISTRY TECHNIQUES

Němec, M.; Čubová, K.; Neufuss, S.; Špendlíková, I.

INTRODUCTION

The Department of Nuclear Chemistry, FNSPE CTU in Prague is one of the few institutions in Europe which still provide a full Bachelor, Master, and Ph.D. programme in nuclear chemistry. To meet today's requirements and fundamental knowledge for the work in radiochemical laboratories and to improve laboratory skills of our students several new practical laboratory exercises have been developed. Preparations of radioactive solutions, handling of radioactive liquids, basic liquid-liquid extraction methods, detection of ionizing radiation or surface decontamination are basic procedures students need to familiarize with. The Practical exercises in radiochemistry techniques is a complex course including these basic techniques and its completion is a first step for students to apprehend and get used to the work with open sources of ionizing radiation.

EXERCISE DEVELOPMENT

Contamination control, smears and surface decontamination is laboratory exercise which should teach students proper behaviour in the case of surface contamination by radioactive liquid solutions. It consists of several tasks where a problem of surface contamination survey and surface decontamination has to be trained.

Fig. 1. Contamination control, smears and surface decontamination laboratory task set.
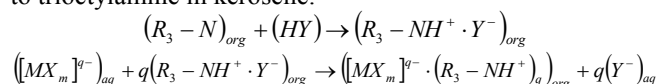
Main goal of this exercise is to teach students:

- to calibrate a surface contamination monitor using proper calibration standards and determine a calibration coefficient
- to determine a surface contamination using wipe tests and detector and using the obtained data to calculate specific surface activity
- to accomplish decontamination of a given surface
- to determine the decontamination efficiency.

Liquid-liquid extraction techniques and their comparison is an exercise where the students should learn differences among liquid-liquid extraction techniques and they should understand their advantages and disadvantages.

Fig. 2. Liquid-liquid extraction techniques and their comparison laboratory task set.

The techniques are simply demonstrated on uranium extraction which is carried out from acidic solution to trioctylamine in kerosene.

$$(R_3 - N)_{org} + (HY) \rightarrow (R_3 - NH^+ \cdot Y^-)_{org}$$

$$([MX_m]^{q-})_{aq} + q(R_3 - NH^+ \cdot Y^-)_{org} \rightarrow ([MX_m]^{q-} \cdot (R_3 - NH^+)_q)_{org} + q(Y^-)_{aq}$$

The main tasks of this exercise are:

- to prepare solutions for extraction systems
- to extract uranium in separatory funnels (hand shaking) and in ampoules using orbital shaker/vortex
- to prepare uranium samples from aqueous and organic phases for measuring and determination of distribution ratios
- to compare distribution ratios and discuss the differences in extraction techniques
- to determine uranium mass present in each phase by measuring its absolute activities and compare it with the uranium mass used in each experiment
- to decide if uranium used in experiments is natural or depleted.

CONCLUSIONS

The new laboratory exercises for Practical exercises in radiochemistry techniques have become, together with other recently developed exercises, an important part of the basic training of our students and contribute to improving their laboratory skills. Moreover, on December 2012, they were successfully employed in the international course Hands-on Training in Nuclear Chemistry in the frame of CINCH project held at the Department of Nuclear Chemistry.

REFERENCES

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CENEN-NET = NEW GENERATION NUCLEAR ENERGY PARTNERSHIP

Dostál, V.[1]; Jiřičková, J.[2]; Katovský, K.[3]; Drtinová, B.; Maliňáková, Š.

[1]CTU in Prague, Faculty of Mechanical Engineering; [2]University of West Bohemia, Pilsen, [3]Brno University of Technology

INTRODUCTION

CENEN-NET project was supported in scope of the European Social Foundation Operational Program Education for competitiveness in Priority axe no. 2 - Tertiary Education, Research and Development and Area of support no. 2.4. - Partnership and networking.

The goal of the project was to intensify collaboration between involved universities which offer education in the field of nuclear energy and are members of CENEN network (Czech Nuclear Education Network).

PARTNERS

Involved organisations: Czech Technical University in Prague (*Faculty of Nuclear Sciences and Physical Engineering* with 3 departments including *Department of Nuclear Chemistry*, and *Centre for Radiochemistry and Radiation Chemistry*, *Faculty of Mechanical Engineering* and *Faculty of Electrical Engineering*), Institute of Chemical Technology Prague, University of West Bohemia Pilsen, VŠB-Technical University of Ostrava, Brno University of Technology, Technical University of Liberec, State Office for Nulear Safety, ČEZ GROUP, Nuclear Research Institute Řež, ŠKODA JS a.s. and VÍTKOVICE ÚAM a.s.

Fig. 1.   CENEN-NET project partners.

OBJECTIVES

Fundamental activities of the project were internships among individual working compartment, together with workshops and conferences which are important to strengthen the contacts and collaboration, and foremost establishing new contacts in national and international academic, state and even industrial bodies. Key part was foundation of a project support office aimed to help CENEN members to prepare domestic and international projects. Activities were focussed to transfer of knowledge and moreover forwarding of contacts to industrial institutions home and abroad from Prague universities to universities outside of Prague. Another part was to arrange sharing of contacts between regional universities themselves. The main output of the project is the tighter collaboration between universities, state and industrial bodies and creating of contacts.

Target group of project are academic workers and students from off-Prague universities involved in nuclear education. Particularly it covers 7 workplaces at the level of departments from 7 different faculties at 4 universities (University of West Bohemia in Pilsen, Technical University of Liberec, VŠB-Technical University of Ostrava and Brno University of Technology).

Fig. 2.   Excursion to uranium milling factory at Rožná.

In addition to many workshops and seminars, 1st International Conference of the CENEN-NET "Partnership in nuclear energy engineering of the next generation" was organized in Prague in October 2012. Next conference will be held at the beginning of 2014.

The *Department of Nuclear Chemistry* (*DNC*) and *Centre for Radiochemistry and Radiation Chemistry* (*CRRC*) participated also in the process of creating the curriculum of nuclear engineer from the perspective of nuclear chemistry.

REFERENCES

[1]   project web site:www.cenen-net.eu

[2]   homepage of CENEN: www.cenen.cz

CINCH: JOINT DEDICATED TRAINING COURSE „HANDS ON TRAINING IN NUCLEAR CHEMISTRY"

John, J.; Němec, M.; Čubová, K.; Špendlíková, I.; Neufuss, S.; Čuba, V.; Maliňáková, Š.

INTRODUCTION

Joint dedicated modular "Hands-on Training in Nuclear Chemistry" course was held at CTU in Prague Czech Republic, on the 3rd-14th December 2012. It was focused on the fundamentals of nuclear chemistry and basic hands-on laboratory training in radiochemistry. This course was a part of the CINCH project workpackage "Joint courses and strategies development". Detailed description of the CINCH project can be found in the previous Annual Report [1].

COURSE ORGANIZATION

The course was organized as a two weeks' course. The basic outline was lectures in the morning and laboratory exercises in the afternoon. All the materials from lectures and for laboratory exercises are available at the CINCH Moodle e-learning platform.

Theoretical part of the course consisted of 40 contact teaching hours including calculation exercises. In addition to the in-house teachers, external teachers were invited to deliver lectures on specific topics. The topics covered were:

- **Fundamentals of nuclear chemistry** 1: Beneš, P.; Omtvedt, J.-P.; Čuba, V.
- **Fundamentals of nuclear chemistry 2**: John, J.; Le Caër, S.; Bonhomme, G.; Čuba, V.
- **Radiation detection and dosimetry, Radiation protection**: John, J.; Martinčík, J.; Čuba, V.
- **Separation methods in radiochemistry**: Ekberg, C.; Němec, M.
- **Radioanalytical chemistry**: Kučera, J.; Lehto, J.

Laboratory exercises consisted of 40 contact teaching hours. They were organised and supervised by four teachers – M. Němec, K. Čubová, I. Špendlíková and S. Neufuss. The trainees were working in four groups of two or three students, each group having a different exercise at a given day. On Friday of the second week, each group prepared a presentation of two selected exercises.

Complete list of the exercises follows:

- Handling of radioactive materials, preparation and dilution of radioactive solution.
- Contamination survey, decontamination of surfaces, smear samples.
- Extraction of uranium in the water-TOA system.
- Preparation of the chromatographic column, ^{234}Th-^{234m}Pa or ^{137}Cs-^{137m}Ba radionuclide generator.
- Liquid scintillation counting, gross alpha and beta measurement.
- Szilard-Chalmers reaction – separation of nuclear isomers.
- High resolution gamma ray spectrometry; determination of ^{137}Cs in natural waters.
- Alpha spectrometry; plutonium determination.

On one of the afternoons, the students performed laboratory exercise in Reactor DNAA (delayed neutron activation analysis) of uranium and thorium samples on the training nuclear reactor Vrabec VR-1 (The Sparrow) operated by CTU.

Fig. 1. Hands-on training in the CTU hot laboratory.

CONCLUSIONS

In total, 10 trainees took part in the course. Three of them were from the University of Leeds (GB), three from Charles University, Prague (CZ), two from Nuclear Research Institute Řež (CZ), one from The National Institute for Nuclear, Chemical and Biological Protection (CZ) and one from Temelín nuclear power plant (CZ).

There were six external teachers coming from Chalmers University of Technology, Gothenburg (SWE), University of Oslo (NOR), University of Helsinky (FIN), CEA INSTN Saclay (FR), Institute of nuclear physics of the AS CR (CZ) and Université de Lorraine (FR) and eight internal teachers from the staff of the CTU in Prague.

The feedback provided by the trainees was mainly positive. Overall feelings expressed that the structure of the course was well set up. The presence of top specialists as teachers was significant highlight of the course. Its structure was well elaborated and time slots for all parts of the course were reasonable. On the other hand recommendations for improvements of laboratory manual, intensity of lectures and content of the calculation exercises have to be taken into account. The feedback received will be used to further improve the content of the course before the future runs.

Detailed information regarding trainees, teachers and lectures, including all presentations and the laboratory manual, are available on CINCH Moodle that is accessible from the CINCH web at http://www.cinch-project.eu.

REFERENCES

[1] Nuclear Chemistry Annual Report 2008–2010, CTU in Prague, http://www.jaderna-chemie.cz/data/documents/vyrocni_zpravy/AR2008-2010.pdf (1.1.2013)

RESEARCH REPORTS

■ Speciation and Migration

■ Separation and Radioanalytics

■ Radiation Chemistry

Speciation and Migration

RESEARCH REPORTS

MODELLING OF KINETICS OF CESIUM, PLUTONIUM AND AMERICIUM SORPTION ON THE BALTIC SEA BOTTOM SEDIMENTS

Štamberg, K.; Lujaniené, G.[1]; Beneš, P.

[1]SRI Center for Physical Sciences and Technologies, Vilnius, Lithuania

INTRODUCTION

Radionuclide sorption to suspended solids and bottom sediments can affect the distribution and behaviour of radionuclides in seas. Here some data are presented on the kinetics of sorption of Cs, Pu and Am to bottom sediments of Baltic Sea, studied in laboratory conditions. The data are evaluated using modelling of the sorption and can be used in the analysis and prediction of behaviour of the radionuclides in the Sea.

EXPERIMENTAL

Bottom sediment samples from Baltic Sea near to Klaipeda were collected using a Van Veen grab sampler on a research vessel during 2009-2011 and characterized by a number of methods [1]. A part of them were separated to several size fractions using wet sieving or column settling technique or membrane filtration. The laboratory batch method described earlier [2] was used for sorption experiments. The Baltic Sea water was mixed with sediments at several values of solid:liquid ratio. Then ^{134}Cs, ^{241}Am or a mixture of ^{238,239,241}Pu were added to achieve the initial total element concentration 4×10^{-10}, 3×10^{-11} or 1×10^{-10} M, respectively. Plutonium used was separated from the Chernobyl highly contaminated soil and adjusted to Pu(IV) or Pu(V) form. After addition of the tracers, the suspensions in PE bottles were shaken for desirable time at room temperature and the distribution of the tracers was determined after centrifugation at 8000 rpm.

RESULTS

Results of the experiments are shown in Figs. 1 and 2, where *F* denotes the fraction of tracer remaining in solution. They indicate rather pronounced effect of grain size on the sorption of radiocesium but only small differences between sorption of the different oxidation states of Pu (Am can be considered similar to Pu(III)). Slightly slower sorption is observed for Pu(V) probably due to a different sorption mechanism [3].
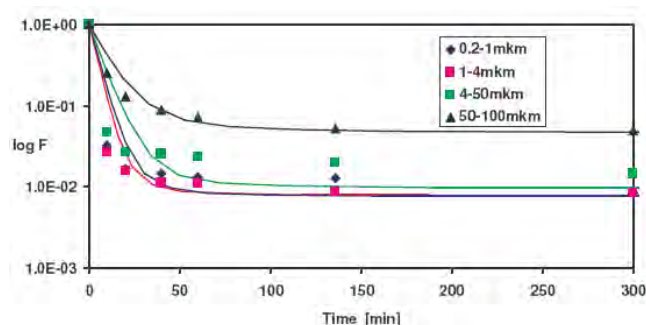

Fig. 1. Time course of radiocesium sorption on bottom sediments separated to several size fractions (at the solid:liquid ratio 0.1 g/ml).

The data obtained were modelled using six differential kinetic equations (models) describing six different control processes (kinetic sorption mechanisms) [4]: the mass transfer or double film model (DM), the film diffusion (FD), the inner layer diffusion (ID), the reacted layer diffusion (RLD), the chemical reaction (CR) and the gel diffusion (GD). Applicability of the models was assessed by goodness of fit of experimental data with the models (WSOS_DF). If the value of WSOS_DF is ≤ 20 the fit is good and the model is applicable [5].
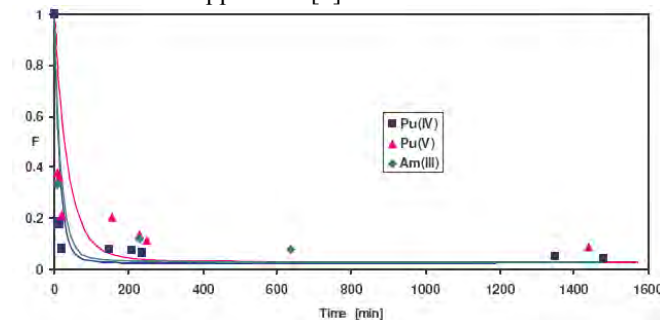

Fig. 2. Time course of Am and Pu sorption on whole bottom sediments (at the solid:liquid ratio 0.001 g/ml).

Tab. 1. Results of modelling of sorption kinetics of Cs, Pu and Am to bottom sediments of the Baltic Sea

Experiment (grain size or valence)	Control process	Kinetic coefficient [min^{-1}]	K_d [mL/g]	WSOS _DF
Cs(0.2-1 µm)	ID	6.21×10^{-2}	1.30×10^3	1.57
Cs(1-4 µm)	ID	9.90×10^{-2}	1.26×10^3	1.71
Cs(4-50 µm)	ID	3.11×10^{-2}	1.02×10^3	4.91
Cs(50-100 µm)	ID	5.12×10^{-2}	2.03×10^2	3.67
Pu(IV)	ID	1.24×10^{-4}	3.90×10^4	24.7
Pu(V)	ID	0.37×10^{-4}	3.35×10^4	15.4
Am(III)	ID	0.54×10^{-4}	3.23×10^4	14.2

As can be seen the ID model best fits all the data obtained. Thus the characteristic parameters (the kinetic coefficient and K_d) for the model were calculated. These parameters can be used for modelling of the sorption.

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SORPTION OF IODINE-125, CESIUM-137, STRONTIUM-85 AND EUROPIUM-152,154 DURING THEIR TRANSPORT IN UNDISTURBED VERTICAL AND HORIZONTAL SOIL CORES UNDER DYNAMIC FLOW CONDITIONS

Palágyi, Š.; Štamberg, K.; Vodičková, H.[1]; Hercík, M.[1]

[1]Nuclear Research Institute Řež, Czech Republic

INTRODUCTION

Laboratory studies of the transport of radionuclides in soils by water are carried out mostly with disturbed core samples, when the soil is homogenized and/or sieved. The homogenization (crushing or even milling) can substantially alter the former macroscopic composition and texture of the soil. Therefore it seems advisable to use undisturbed core samples for this characterization. However, the latter approach may also have some disadvantages as real soils can contain regions of easier or harder accessibility to water movement, which creates preferential flow also influencing transport parameters, this fenomenon has to be taken into account and the results of such observations should be limited to the specific sampling section. The description of this work in detail can be found in [1].

EXPERIMENTAL

Soil samples were taken from the bank of the occasionally dried-up Heřmanický stream, which temporally runs out from vicinity of the Low and Medium Level Radioactive Waste Suface Repository (LMRWR) at Dukovany Nuclear Power Plant in Czech Republic and drains away the collected rainwater of the area. In time of sampling the stream was filled with water only partially. The clover was removed before drilling (ca 0-5 cm). The samples were taken at one location from 5 to 15 cm and from 9 to 100 cm in both vertical and horizontal direction – see Fig. 1. The soil core samples of 9 cm length and 3.8 cm in diameter, by means of special procedure, were put into columns and then used for the dynamic experiments with individual radionuclides.
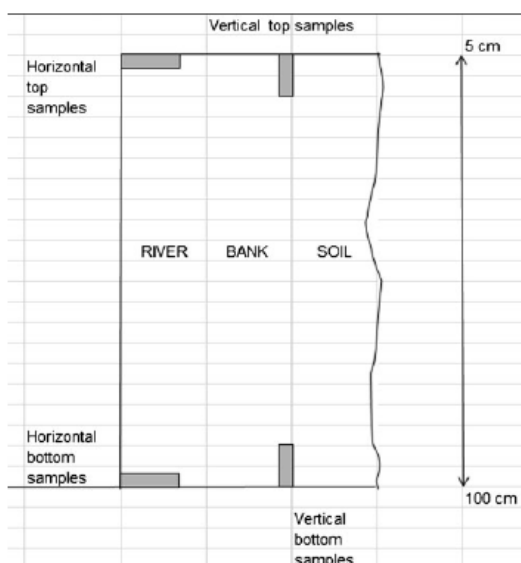

Fig. 1. Vertical cross-sectional representation of the core sampling places from the soil block.

As liquid phase, the solutions in synthetic groundwater of carrier-free ^{125}NaI, or nitrate salts of $^{137}Cs^+$ or $^{85}Sr^{2+}$ or $^{152,154}Eu^{3+}$, and corresponding salts of stable isotopes as carriers in the 10^{-6} M concentration, were used. The flow-rate was adjusted to 1.2 cm³/h. Sorption and desorption of given radionuclides were studied.

RESULTS

From the soil science point of view, the investigated samples can be classified as gleyish cambisol. Their sorption properties are demonstrated in Table 1. It is evident that the anionic iodide is almost not sorbed at all in any type of soil samples. On the other hand, cationic radionuclides according to the expectation are strongly sorbed, namely, in order $^{137}Cs<^{85}Sr<^{152,154}Eu$. The influence of sampling place (top or bottom) and drilling direction (horizontal or vertical) seems to be in some degree important only in a case of cesium and strontium, however, the influence of non-homogeneity of cores can in these results participate, too.

Tab. 1. The behaviour of radionuclides in the sorption process (drilling direction and sampling place: Vt – vertical, top; Vb – vertical, bottom; Ht – horizontal, top; Hb - horizontal, bottom).

Radio-nuclide	Soil sample	Sorption E_S (%)	K_{dS} (cm³/g)
$^{125}I^-$	V_t	4.1	0.3
	V_b	5.2	0.4
	H_t	5.0	0.5
	H_b	5.8	0.5
$^{137}Cs^+$	V_t	84.9	308
	V_b	93.0	642
	H_t	81.4	250
	H_b	91.0	554
$^{85}Sr^{2+}$	V_t	94.1	283
	V_b	89.1	105
	H_t	95.9	379
	H_b	92.3	203
$^{152,154}Eu^{3+}$	V_t	97.0	1,643
	V_b	97.1	1,039
	H_t	97.5	1,967
	H_b	97.1	1,567

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EFFECT OF GRAIN SIZE ON THE SORPTION AND DESORPTION OF CESIUM-137 IN CRUSHED GRANITE COLUMNS AND GROUNDWATER SYSTEM UNDER DYNAMIC CONDITIONS

Štamberg, K.; Palágyi Š.

INTRODUCTION

In this work, the sorption of ^{137}Cs dissolved as ^{137}CsNO$_3$ in the solution of 10^{-6} M CsNO$_3$ in synthetic granitic water (SGW) and the desorption by solution mentioned, were investigated under dynamic conditions in columns with crushed granitic materials of various grain sizes, namely, of pure granite and of corresponding infill material. The model based on the erfc-function was used for fitting of experimental data. The description of this work in detail can be found in [1].

EXPERIMENTAL

Two types of crystalline rocks were used: pure granite coded as PDM1-1 and fracture filling material (infill) coded as PDM1-2. Rocks were sampled from PDM1 borehole, the samples PDM1-1 from 97.5-98.7 m depth and PDM1-2 from 89.7-90.0 m depth. According to the X-Ray analysis, majority phases were quartz, orthoclase and plagioclase, as minority phases mica and chlorite were found. Each sample was crushed and sieved to 0.063-0.125, 0.125-0.630, 0.63-0.80 and 0.80-1.25 mm fractions. The individual fractions were placed into 5 cm^3 suitable adapted plastic columns (medical syringes) of 1.3 cm inner diameter and 5.4 cm height. Experiments were performed using the classical column technique, i.e., the initial activity of the aqueous phase (^{137}CsNO$_3$ in the solution of 10^{-6} M CsNO$_3$ in SGW) and its flowrate (=0.05 cm^3/min) were constant during the process; samples of liquid phase were taken in selected time intervals and their γ activity were measured.

TRANSPORT MODEL

The transport model, by means of which the sorption or desorption breakthrough curves (BTC$_S$ or BTC$_D$) are calculated, is based on complementary error erfc-function. The model description in detail can be found in [2], and therefore, only the basic principles are given below.

Two modifications of given model exist, the first one is characterized by incorporation of linear equilibrium isotherm (so called linear isotherm approach), the second one by incorporation of non-linear equilibrium isotherm (i.e., non-linear isotherm approach).

LINEAR ISOTHERM APPROACH

The so called K_d-model is used: for sorption (1a) and for desorption (1b), where q is concentration in solid phase, C is concentration in liquid phase and $(K_d)_S$ or $(K_d)_D$ are sorption or desorption distribution coefficients. Then, it is necessary, that two important parameters of dynamic process are defined, namely, the sorption and desorption retardation coefficients, R_S (2a) or R_D (2b).

$$q = (K_d)_S \cdot C \quad (1a) \qquad q = (K_d)_D \cdot C \qquad (1b)$$
$$R_S = 1 + \rho \cdot ((K_d)_S / \Theta) \quad (2a) \qquad R_D = 1 + \rho \cdot ((K_d)_D / \Theta) \quad (2b)$$

Where ρ is bulk density and Θ is porosity of the given bed.
Non-linear isotherm approach

The equilibrium state is described with two-parametric (k_S and n_S or k_D and n_D) Freundlich equation, i.e., with Eq. (3a) in the case of sorption or Eq. (3b) in the case

of desorption. As for the retardation coefficients, R_S or R_D, there are two equations at hand:(4a) or (4b).

$$q = k_S \cdot C^{nS} \tag{3a}$$
$$q = k_D \cdot C^{nD} \tag{3b}$$
$$R_S = 1 + (\rho/\Theta) \cdot f'(C)_S \quad (4a) \qquad R_D = 1 + (\rho/\Theta) \cdot f'(C)_D \quad (4b)$$

where f´(C) is the first derivative of the equilibrium isotherm in the point C. It is evident that if the system studied can be described with linear isotherm then it is characterized with constant value of retardation coefficient, if the non-linear isotherm has to be used then different values of retardation coefficients are obtained.

RESULTS

The respective calculated theoretical transports are approximately the same in the linear isotherm and non-linear isotherm approach model. For example, the influence of grain size on the values of R_S or R_D is evaluated in Fig. 1 and on the values of $(K_d)_S$ or $(K_d)_D$ in Fig. 2 (both using linear isotherm approach).
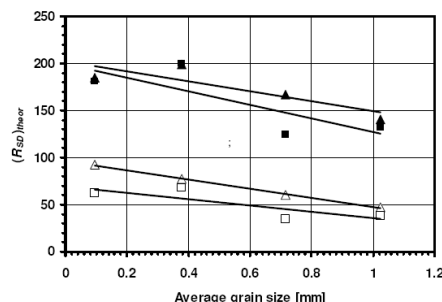

Fig. 1. Effect of the average grain size on the desorption ($\square$, $\blacksquare$) and sorption ($\triangle$, $\blacktriangle$) RS or RD - values of ^{137}Cs+ transport in granite (empty symbols) and fillings (full symbols).
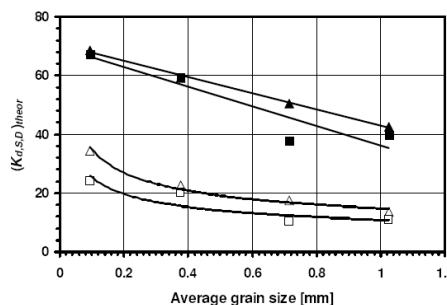
Fig. 2. Effect of the average grain size on the desorption ($\square$, $\blacksquare$) and sorption ($\triangle$, $\blacktriangle$) $(K_d)_S$ or $(K_d)_D$ - values of ^{137}Cs$^+$ transport in granite (empty symbols) and fillings (full symbols).

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EFFECT OF GRAIN SIZE ON THE STRONTIUM-85 SORPTION AND DESORPTION IN COLUMNS OF CRUSHED GRANITE AND INFILL MATERIALS FROM GRANITIC WATER UNDER DYNAMIC CONDITIONS

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INTRODUCTION

In this work, the sorption of ^{85}Sr dissolved as ^{85}Sr(NO$_3$)$_2$ in the solution of 10^{-6} M Sr(NO$_3$)$_2$ in synthetic granitic water and the desorption by the solution mentioned, were investigated under dynamic conditions in columns with crushed granitic materials of various grain sizes, namely, of pure granite and corresponding infill material. The description of this work in detail can be found in [1].

EXPERIMENTAL

Analogous to the study of ^{137}Cs sorption and desorption, two types of crystalline rocks were used, namely, pure granite coded as PDM1-1 and fracture filling material (infill) coded as PDM1-2; the experimental procedure was the same, too (see the contribution from Štamberg, K. and Palágyi, Š. in this report). The experiments were performed using the classical column technique, i.e., the initial activity of the aqueous phase (see above) and its flowrate (0.05 cm^3/min) were constant during the process; samples of liquid phase were taken in elected time intervals and their γ activity were measured.

TRANSPORT MODEL

The transport model, by means of which the sorption or desorption breakthrough curves (BTC$_S$ or BTC$_D$) are calculated, is based on complementary error erfc-function. The model description in detail can be found in [2] and the basic principles are described in the mentioned contribution by Štamberg, K.and Palágyi, Š. We should like only to remind that two modifications of given model exist, the first one is characterized by incorporation of linear equilibrium isotherm (so called linear isotherm approach), the second one by incorporation of non-linear equilibrium isotherm (i.e., non-linear isotherm approach).
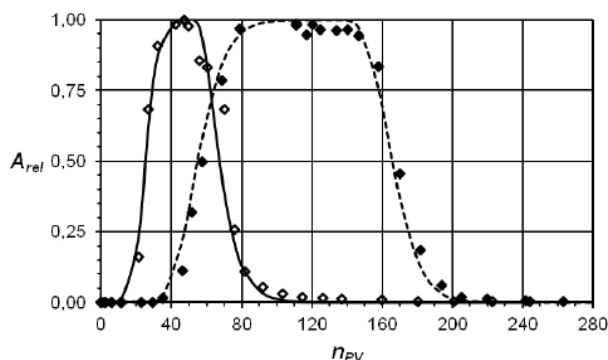
RESULTS

Fig. 1. Experimental (symbols) and calculated (curves) BTCS and BTCD, of ^{85}Sr sorption (ascending edges) and desorption (descending edges) in granite (open diamond, solid line) and fracture infill (filled diamond, dotted line), both of 0.063-0.125 mm grain size.

The respective calculated theoretical transport is approximately the same in the linear isotherm and non-linear isotherm approach model. The results, holding for the linear isotherm approach, are demonstrated: in Fig. 1 as experimental and calculated breakthrough curves; the influence of grain size on the values of retardation coefficients, R_S or R_D, is evaluated in Fig. 2 and on the values of distribution coefficients, K_{dS} or K_{dD}, in Fig. 3. The important influence of grain size is quite evident.
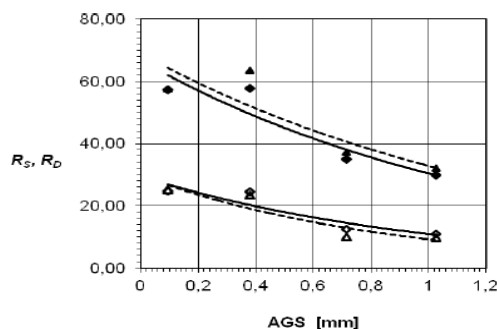

Fig. 2. Effect of the average grain size, *AGS*, on the sorption (open diamond) and desorption (open triangle) retardation coefficients, R_S and R_D - values of ^{85}Sr^{2+} transport in granite (empty symbols) and fillings (full symbols).
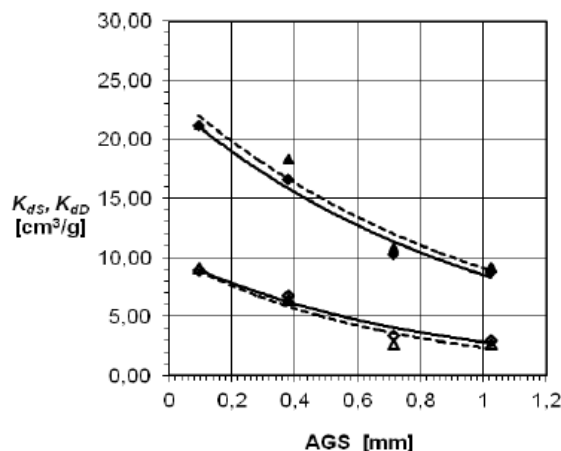

Fig. 3. Effect of the average grain size, *AGS*, on the sorption, K_{dS} (open diamond), and desorption, K_{dD} (open triangle), distribution coefficients of ^{85}Sr^{2+} transport in granite (empty symbols) and fillings (full symbols).

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SORPTION AND DIFFUSION BEHAVIOUR OF SELENITE AND SELENATE ON THE CZECH Ca/Mg BENTONITE

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INTRODUCTION

Isotope [79]Se belongs to critical radionuclides due to its long half-time and limited sorption of its anionic forms. Selenium is redox sensitive element that may exist in four oxidation states. Its mobility strongly depends on in situ speciation affected by pH and redox potential of the geological environment, chemical and mineralogical composition of buffer/backfill materials and host rock. This work focuses on the determination of retarding properties of proposed buffer/backfill material Ca/Mg bentonite for anionic forms of selenium. The sorption and diffusion behaviour of selenite and selenate was studied by static batch and through-diffusion experiments under ambient conditions.

EXPERIMENTAL

Ca/Mg bentonite samples originated from the Rokle deposit (produced by Keramost a.s., Czech Republic) Sodium selenite and selenate (p.a.) in concentration $2 \cdot 10^{-5}$ mol/l was used. Selenium concentration was analyzed by ICP-MS. The sorption of Se(IV) and Se(VI) onto bentonite was investigated as a function of ionic strength, contact time and solid-to-liquid (m/V) ratio. The diffusion behaviour of Se(IV) and Se(VI) was studied by through-diffusion experiments in compacted bentonite (d = 30 mm, L = 15 mm) at dry densities of 1300 and 1600 kg/m^3. Constant concentration in the source reservoir was maintained.

RESULTS

Significant sorption of selenite at alkaline pH (9-10) was observed which contradicts the standard model of non-specific sorption of anions on functional surface SOH groups. The selenite sorption was also supported by increasing ionic strength of liquid phase (Fig. 1). Our experimental results support assumption that selenite sorption at pH above 7 may be caused by formation of ternary surface complexes involving Ca and Mg or by precipitation of Ca/Mg selenites [1,2].
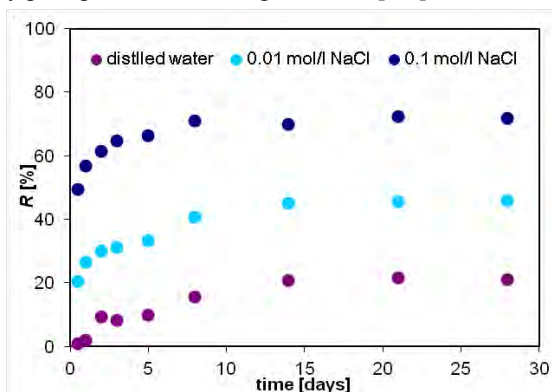

Fig. 1. Effect of contact time and ionic strength of liquid phase on selenite sorption onto bentonite.

In diffusion experiments, the selenite penetration into the output reservoir was not observed after more than 200 days. This finding is consistent with results obtained from selenite batch sorption experiments. On the contrary, selenate diffusion achieved steady state conditions of the diffusive flux into the output reservoir (see Fig. 2). The determination of apparent diffusion coefficient D_a for selenate in compacted bentonite was provided by own module, prepared in the environment of GoldSim programme [3], which simulates diffusion through the homogeneous porous medium, can respect real changes in the concentrations in reservoirs and takes into account the diffusion through separating filters [4]. Examples of fitting by own diffusion module are presented in Fig. 2. Selenate apparent diffusion coefficients: $D_a = (4.41 \pm 0.62) \cdot 10^{-11}$ m^2/s for dry density 1300 kg/m^3 and $D_a = (1.75 \pm 0.33) \cdot 10^{-11}$ m^2/s for dry density 1600 kg/m^3 were obtained.
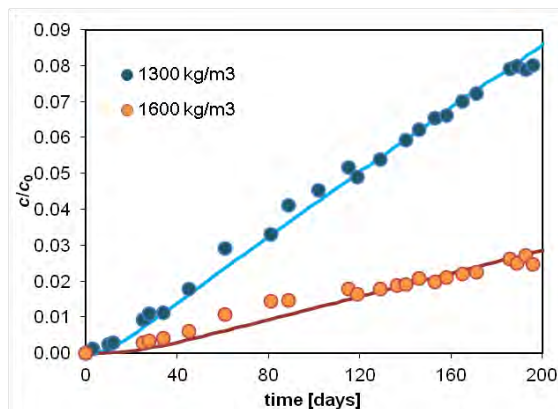

Fig. 2. Selenate cumulative break-through curves and their optimal modelled fits obtained by own diffusion module.

CONCLUSIONS

This work has shown an obvious difference in sorption and diffusion behaviour of selenite and selenate in Ca/Mg bentonite. It can be concluded that a significant role in incorporating selenium species on mineral surfaces may play the three-dimensional molecular structure and geometry. The results of batch sorption experiments indicate significant sorption of selenite at alkaline pH which is supported by increasing ionic strength of liquid phase. In contrast to selenite, selenate sorption was not observed. The obtained apparent diffusion coefficients confirmed high selenate mobility.

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TRANSPORT OF CRITICAL RADIONUCLIDES IN BARRIER MATERIALS: SOME IMPROVEMENTS IN EVALUATION OF DIFFUSION EXPERIMENTS

Drtinová, B.; Vopálka, D.; Monsonis Romero, S.; Hofmanová, E.

INTRODUCTION

Many countries have chosen deep geological repositories as their favoured approach to nuclear waste disposal including spent fuel from nuclear power plants. The modelling of radionuclides transport in the near- and far-field of the proposed repository is necessary for its safety assessment and needs a thorough knowledge of processes taken into account and values of parameters describing them. The diffusion of radionuclides in both: bentonite buffer and host rock; is one of such processes. The sorption and diffusion coefficients of critical radionuclides in barrier materials play a very important role, as their values determinate the rate of radionuclide transport into the food chain. Despite extensive research in these areas, the uncertainties in experimental procedures and in mathematical methods used for evaluation of diffusion experiments mentioned e.g. in [1] seem to be still unclear. The work describes some findings based on the results of modelling of diffusion experiments and evaluation of real diffusion experiments by methods developed in our laboratory [2].

MODELLING

The diffusion model developed was thoroughly checked in order to better understand its behaviour under different conditions and to prepare methods for evaluation of real diffusion experiments. An example of a broad numerical study that helped us in planning real diffusion experiments is presented in Fig. 1. In this case, we modelled the experiments, in which the concentration in the input container was not constant during the experiment. According to the design of our diffusion cell the values of volumes V_1 (input) and V_2 (output) and lengths of compacted bentonite L and of filters LF were selected. The influence of distribution coefficient K_d value on concentrations in both input and output containers was studied.
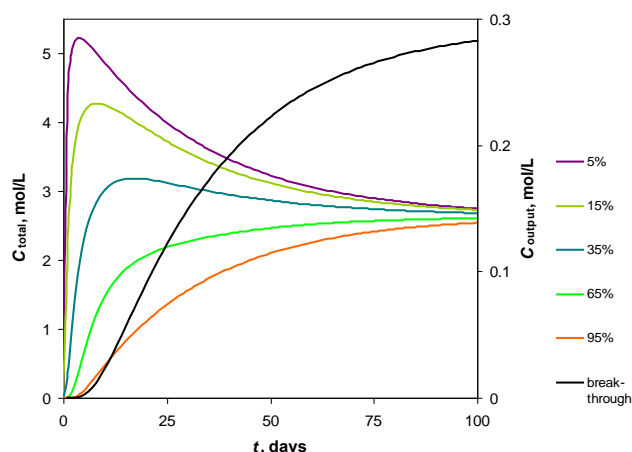

Fig. 1. Results of the numerical diffusion experiment - $V_1 = 0.2$ L, $V_2 = 0.2$ L, $C_0 = 0.001$ mol/L, $K_d = 1$ L/kg, geometrical factor $G = 1$, length of porous layer $L = 0.015$ m, L_F negligible time development of total concentration in the layer and in the output concentration.

EXPERIMENTAL

Diffusion through Ca/Mg bentonite B75 (produced by Keramost a.s., Czech Republic as non-activated crushed bentonite) was experimentally studied. The diffusion experiments consisted of two phases: (1) HTO through-diffusion and (2) Cs in-diffusion. Working solution of $CaCl_2$ with ionic strength $I = 0.1$ was used. In the first step, tritiated water (HTO) was added into the input containers and activity changes in both containers were periodically measured using liquid scintillation counting. The constancy of HTO activity in input containers was not kept in this case. In the second step, solution in the input containers was changed for working solution containing CsCl $(1 \times 10^{-5}$ mol/L) spiked by ^{137}Cs, the output containers were filled by the fresh working solution again. NaI(Tl) scintillation detector was used for determination of Cs concentration in both containers during the through-diffusion experiments as well as in solid phase after termination of experiments. The concentration of Cs in input containers was kept constant during the course of experiments. Simultaneously with measuring Cs activity in thin slices (ca. 0.2-0.5 mm), the humidity was measured enabling determination of total porosity $\varepsilon = 0.43 \pm 0.02$ necessary for mathematical evaluation of experimental results. The value of bentonite density was determined, $\rho = (2730 \pm 103)$ kg/m^3, using measured value of ε and value of dry density ρ_d (1600 kg/m^3).

Some results achieved in works [3] and [4] are shown in Tab. 1. The apparent diffusion coefficients D_a for HTO were evaluated from the change of tritium activity measured in both the input and output containers. The determination of D_a values was performed with own improved method for evaluation of experimental curves.

Tab. 1. Summary of determination of apparent diffusion coefficient (Da) of HTO in compacted bentonite (ρd= 1600 kg/m3).

cells	$D_a \cdot 10^{-10}$ (m^2/s)
A, B, C, D, E (input)	1.60 ± 0.47
A, B, C, D, E (output)	1.71 ± 0.16
F, G, H, J, K (input)	1.79 ± 0.07
F, G, H, J, K (output)	1.52 ± 0.14

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EFFECT OF POROSITY HETEROGENEITY ON THE DIFFUSIVE TRANSPORT THROUGH COMPACTED SWELLING CLAYS

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INTRODUCTION

Compacted swelling clays – especially bentonites – are assumed to be the main engineered barrier in the concept of high level radioactive waste repository (HLWR) in granite host rock due to its favourable physical and chemical properties preventing migration of radionuclides released potentially from the solid waste matrix. Due to the low permeability of the compacted clay, the main process responsible for radionuclides transport in it is molecular diffusion [1]. For the diffusion evaluation by an analytical solution of diffusion equation or modelling, the clay sample is assumed to be homogeneous and isotropic with regard to its transport properties. This approach applied on swelling clays led to some inconsistencies in the evaluation of the results from diffusion experiments. Glaus et al. [2] found that they may be caused by increased porosities at the clay boundaries. The work presents an application of single and multiple porosity models on the results from through-diffusion experiments of tritiated water (HTO) in the bentonite samples compacted to the different bulk densities.

EXPERIMENTAL

The clay powder – activated bentonite Sabenil 65 (S65 - commercial product of Keramost, a.s., Czech Republic) was compacted in the diffusion cell (d = 30 mm, L = 15 mm) to different bulk densities of 1200, 1400, 1600 and 1800 kg/m^3. Stainless steel filters (L = 0.8 mm), were used to prevent the clay swelling. The experiments consisted of two phases: (1) a through-diffusion phase until steady state flux of a tritium tracer into the output reservoir was achieved; and (2) determination of porosity and/or concentration profile in the layer of the compacted bentonite. In cooperation of ÚJV and Czech Technical University, computer module EVALDIFF was prepared in the environment of the GoldSim programme which enables to describe the diffusion in all basic diffusion techniques, including experiments in which the porosity in the layer of studied material is not homogeneous. This module can also respect real changes of the concentrations in reservoirs during the experiment, radioactive decay and influence of separating filters [3].

RESULTS

Measured porosity profiles are shown in Fig. 1. Possible explanation for the increased porosity at the clay boundaries might be the mass redistribution. From the porosity profiles it can be even seen the direction of pressure saturation, especially for bulk density of 1200 kg/m^3. Diffusion experimental data were fitted by model curves while changing geometric factor G, which was assumed to be constant in the layer. Value of G was determined for both the homogeneous (single) and heterogeneous (multiple - based on measured porosity profile) porosity models. The values of apparent diffusion coefficients D_a were obtained on the bases of determined G values, using value of diffusion coefficient of HTO in free water

D_w = 2.3·10^{-9} m^2/s [3] and assuming no retardation corresponding to sorption. Results of G and D_a obtained by single and multiple porosity approach, for the case in which the greatest heterogeneity of porosity was observed, are presented in Table 1.
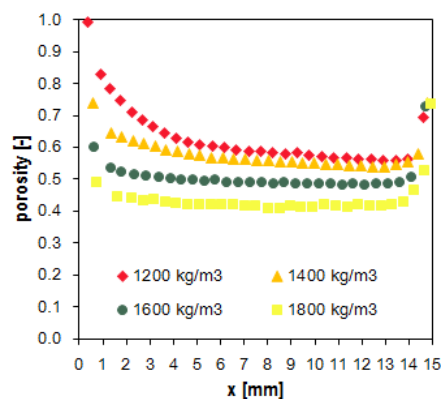

Fig. 1. Porosity profiles for different bulk densities of bentonite samples S65.

Tab. 1. Comparison of HTO diffusion results obtained from both modelling approaches for bulk density 1200 kg/m^3.

porosity model	G	$D_a \cdot 10^{-10}$(m^2/s)
single	0.104 ± 0.016	2.39 ± 0.37
multiple	0.097 ± 0.015	2.24 ± 0.34

CONCLUSIONS

The diffusive behaviour of HTO in bentonite samples was investigated by through-diffusion method at different bulk densities. Apparent diffusion coefficients were evaluated by comparing experimental data with single and multiple porosity model curves calculated by own computer code EVALDIFF. Both approaches were compared. We confirmed that higher porosity at the clay boundaries has an influence on the value of diffusion coefficient. The difference between single and multiple porosity approaches is not significant at the confidence level of 95 %. However, neglecting the effect of porosity heterogeneity results in a systematic error in the determination of the diffusion coefficients, very important parameters for predicting long term safety of HLWR. Prepared module EVALDIFF is an effective tool for modelling and evaluation of real diffusion experiments also on other types of porous materials.

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MODELLING OF CESIUM DIFFUSION IN COMPACTED BENTONITE USING PHREEQC

Vopálka, D.

INTRODUCTION

Understanding of contaminant migration processes at the basic level in a laboratory study can help to develop models, which may be used in transport codes to predict the fate of pollutants on the field scale. Cesium is very well adsorbed by clay minerals and there are many studies concerning adsorption of cesium on different types of clay minerals. On the basis of literature data ([1] and [2]) and experimental findings in our laboratory (e.g., [3]) a model description of cesium sorption on a Ca/Mg bentonite in PHREEQC was prepared. The model respects ion exchange of Cs^+ with Ca^{2+}, Mg^{2+}, K^+ and Na^+, uptake of Cs by surface complexation and cesium sorption on minor sites that are believed to cause the specific Cs sorption in the lower concentration range due to the presence of the Frayed Edge Sites (FES). The complex interaction model, which aimed to take into account qualities of well described FEBEX bentonite and Ca/Mg bentonites of Czech origin, was used for the description of standard types of diffusion experiments in compacted bentonite.

MODELLING

The apparent diffusion coefficient D_a represents the most important parameter in the study of diffusion transport in barriers of final disposal of radioactive waste. Our model realized in PHREEQC enables to predict D_a values for different composition of working solution using obvious *time-lag* method of evaluation of the modelled *through-diffusion* experiments. As can be seen in Fig. 1, the range of cesium D_a values could be relatively broad that accords with experimental findings. The constant concentration $C(Cs)_0$ on the input side and the extend of concentration of FES (Xa) sorption sites in the clay have the greatest effect in the model results.
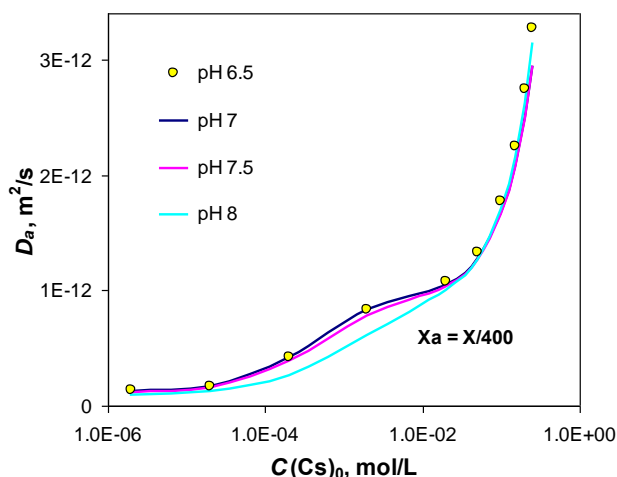

Fig. 1. Model dependence of the apparent diffusion coefficient Da on constant input concentration $C(Cs)_0$ and pH for specified content of minor sorption sites Xa. Results were obtained by evaluation of the modelled through-diffusion experiments using time-lag method.

The model of diffusion realized in PHREEQC with the implementation of the sophisticated description of interaction of species present in the liquid phase with various types of sorption sites enables to model also other types of diffusion experiments. An example of computed profiles of cesium in the layer of compacted bentonites obtained, which were computed for conditions corresponding to the real diffusion experiment, is presented on Fig. 2. From these results, the increase of Cs concentration in the solid phase corresponding to the input boundary with time should be pointed out that is caused by the presence of filters and the non-linear shape of profile corresponding to the stationary state (here 5000 days). The latter effect represents the result of equilibration of studied species with multi-sided sorbing surface of bentonite. Both effects mentioned were observed also in results of real diffusion experiments of cesium in compacted bentonite.
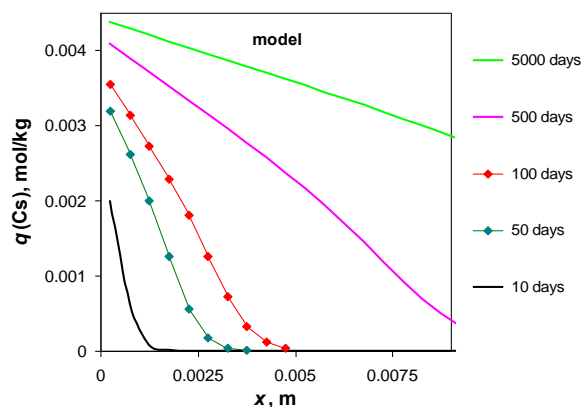

Fig. 2. Modelled cesium concentration profiles in the plug of compacted bentonite for bentonite dry density $\rho_d = 1600$ kg/m^3 and input concentration $C(Cs)_0 = 1\times10^{-4}$ mol/L. Geometrical parameters: diameter $d = 0.03$ m, length of the bentonite plug $L = 0.015$ m, width of the separating filters $L_f = 8\times10^{-4}$ m.

CONCLUSION

A modified method of evaluation of diffusion experiments in homogeneous saturated clays, which was based on sophisticated interaction model of cesium on bentonite, facilitates to shorten substantially the duration of diffusion experiments. The tailoring of it for real clay materials is in progress.

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A STUDY OF METHODS SUITABLE FOR THE SENSITIVITY ANALYSIS OF THE MATHEMATICAL MODEL OF RADIONUCLIDE MIGRATION IN DEEP GEOLOGICAL REPOSITORY

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INTRODUCTION

A deep geological repository shall be selected and designed so as to ensure the safety of its long-term performance. A repository system can be characterized as a complex system whose description requires a number of parameters which is too large for a detailed study and an optimization of each parameter. The performance of a repository system may significantly depend, however, only on a relatively small subset of a whole set of parameters. Such subset can be determined by using the sensitivity analysis. The aim of this work was to select the methods of the sensitivity analysis suitable for the mathematical model of the Czech concept of a deep geological repository of a nuclear waste.

EXPERIMENTAL

Based on the previous studies [1,2], we implemented and subsequently tested screening and variance based methods for the sensitivity analysis. The program for the sensitivity analysis was programmed using the MATLAB® programming environment. Basic algorithms for both types of the sensitivity methods were already implemented in MATLAB® by Saltelli, A. and Tarantola, S [3]. To test the performance of the studied sensitivity methods, there was used a mathematical model of a deep geological repository which was implemented in the simulation software GoldSim [4]. This fact does not bring restriction because it is possible to launch a GoldSim model from the command line. That can be achieved within MATLAB® by using Matlab command 'system'.

In each of the sensitivity analyses, there was selected a group of K uncertain model parameters, an example is shown in Tab. 1 together with assigned probability distribution functions. Each parameter was sampled at randomly selected N_0 values (typically 64) which led to the total number of simulations $N = N_0(K+2)$ necessary for one study. In the course of each simulation, there was mass of selected radionuclides (e.g. ^{129}I, ^{79}Se) at different positions of the radionuclide transport from the source-term the biosphere. In each time point common to N simulations, there were calculated medians, first and ninth deciles of selected observed quantities for the purpose of the uncertainty analysis, and several sensitivity measures for the purpose of the sensitivity analysis.

Tab. 1. Uncertain parameters and their estimated probability distributions (PDF).

Model parameter	PDF
Instant release fraction [**IRF**]	Log-normal
Rate of matrix degradation [**DM**]	Uniform
Diffusion coefficient for bentonite [**DeB**]	Triangular
Diffusion coefficient for granite [**DeG**]	Log-normal
Flow time [**FT**]	Uniform
Inflow [**I**]	Uniform
Dilution [**D**]	Uniform

RESULTS

Fig. 1 illustrates uncertainty (A) and sensitivity (B) analyses of a mathematical model of deep geological repository. The results were obtained at the model position which represents the beginning of bentonite barrier, uncertain parameters used in the simulations are listed in Tab. 1. The relative mass of ^{129}I reaches its maximum relatively shortly after the release of the IR fraction (Fig. 1A). A participation of uncertain parameters on a spread of the ^{129}I relative masses changes with time (Fig. 1B). On the first time interval $(0, 1.5 \times 10^5)$ yr, the most significant source of a spread are uncertainties in IRF; on the subsequent interval $(1.5 \times 10^5, 1 \times 10^6)$ yr, the main contributors to the spread are the diffusion coefficient for granite and the rate of matrix degradation. The reduction of uncertainties of those parameters would lead to the decrease of spread of ^{129}I relative masses.
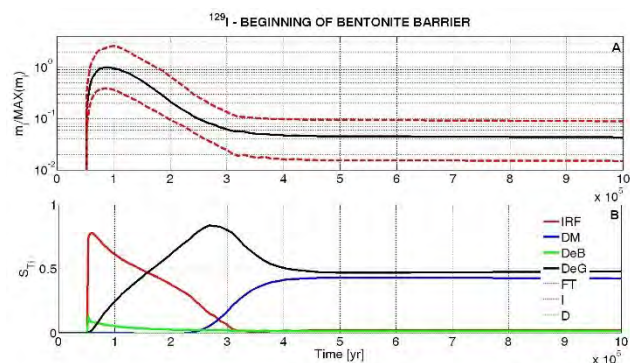

Fig. 1. The uncertainty (A) and the sensitivity (B) analyses of the migration of the radionuclide ^{129}I. A solid black line in A represents median of ^{129}I relative mass, red dashed lines are first and ninth deciles that graphically represents a spread of the relative mass values. Solid color lines in B represent the total order sensitivity index S_{Ti}.

It has been developed and successfully tested the tool for the sensitivity analysis of the mathematical model of deep geological repository of nuclear waste.

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STUDY OF THE SPECIATION IN THE SYSTEM UO_2^{2+} - SO_4^{2-} - H_2O BY MEANS OF THE UV-VIS SPECTROPHOTOMETRY

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INTRODUCTION

The UO_2^{2+} - SO_4^{2-} - H_2O system is important for uranium mining studies, safety studies of radioactive waste repository, geochemical modelling and several other fields. Aim of our work was to obtain parameters of the speciation ($log\ \beta°$ for the individual uranyl-sulfate complexes and SIT coefficients $\varepsilon(i, j)$ where i is an uranyl-specie) by factor analysis based fit of the spectral data.

EXPERIMENTAL

Total uranium concentration $c_U = 0.05$ mol.dm^{-3}, pH = 2, ionic strength $I = 1.5$ mol·kgw^{-1}, c_S varying from 0 mol·dm^{-3} through $c_{S,min} = 1.3 \cdot 10^{-5}$ mol.dm^{-3} up to $c_{S,max} = 0.64$ mol·dm^{-3} (38 solutions prepared). Varian (Cary 100 Conc) spectrophotometer in range 190-900 nm used. $T = 23.4$ °C.
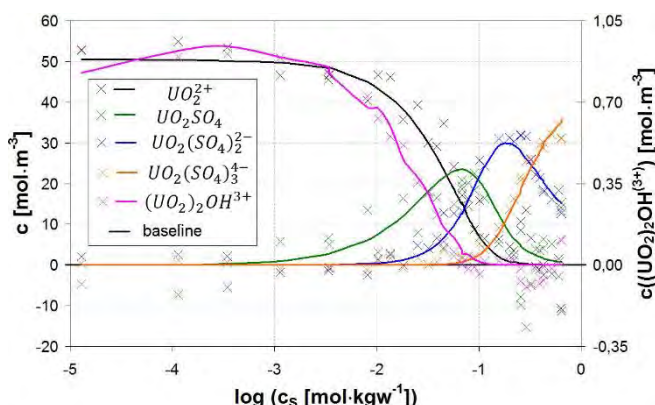

Fig. 1. Speciation diagram resulting from data analysis described below.

DATA ANALYSIS

Measured spectra were corrected for the absorption of background electrolyte, restricted to spectral range 380-480 nm and treated by the weighted Singular Value Decomposition (wSVD). Loadings from six main components were fitted by the maximum likelihood method in order to obtain both absorption spectra of individual species and parameters of speciation model ($log\ \beta°$).

Tab. 1. Decadic logarithms of stability constants extrapolated to zero ionic strength and 298.15K [1,2]

Reaction	$log\ \beta°$			$log\ \beta°_{tab}$		
$2\ UO_2^{2+} + H_2O \leftrightarrow$ $(UO_2)_2OH^{3+} + H^+$	-3.88 -2.61	+ -	0.18 0.77	-2.70	+ -	1.00 1.00
$UO_2^{2+} + SO_4^{2-} \leftrightarrow$ UO_2SO_4	3.40 3.61	+ -	0.46 0.43	3.15	+ -	0.12 0.12
$UO_2^{2+} + 2\ SO_4^{2-}$ $\leftrightarrow UO_2(SO_4)_2^{2-}$	5.12 5.23	+ -	0.58 0.58	4.14	+ -	0.07 0.07
$UO_2^{2+} + 3\ SO_4^{2-}$ $\leftrightarrow UO_2(SO_4)_3^{4-}$	4.07 4.23	+ -	0.53 0.54	3.02	+ -	0.38 0.38

$log\ \beta°$: obtained in this study, $log\ \beta°_{tab}$: data from the literature [1-3]

Unfortunately [1] presents wrong $log\ \beta°$ from MLM fit resulting from the inconsistent combination of input parameters $\varepsilon(i,j)$ and $log\ K°$ of non-uranyl species – those values are written <u>red</u> in the Tab. 1 above together with <u>black</u>-written values corresponding to corrected fitting procedure.
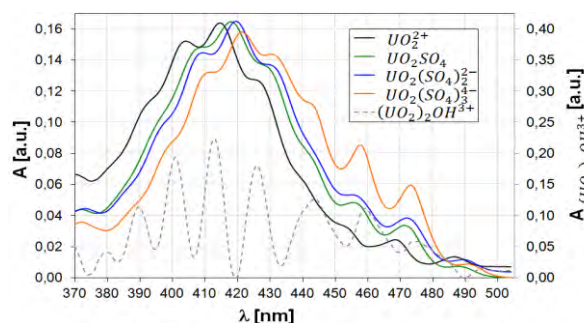

Fig. 2. UV-VIS absorption spectra of individual species

RESULTS

We have obtained $log\ \beta°$ values for uranyl-sulfate complexes by the means of the UV-VIS spectrophotometry. Their discrepancy with respect to [2-3] could be explained by the discrepancy of input speciation parameters of non-uranyl species and by instability of measured solutions. We hope to be able to fix both in later work on this topic.

Tab. 2. Molar absorptivity amplitudes of individual components ε, n-th component of wSVD decomposition singular value Wn and kn (var Vin = kn · meanl(Yli))) obtained by MLM.

n	Wn	kn	Species	ε [dm^3·mol^{-1}·cm^{-1}]
1	49.6783	1.074	UO22+	44.4
2	6.1090	1.023	(UO2)2OH3+	150.5
3	0.6721	0.986	UO2SO4	69.1
4	0.2733	0.923	UO2(SO4)22-	89.8
5	0.1049	0.943	UO2(SO4)34-	88.1
6	0.0182	1.029		

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CHARACTERIZATION OF URANIUM BEHAVIOUR IN THE RUPRECHTOV SITE (CZ)

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INTRODUCTION

Ruprechtov, situated in NW of the Czech Republic in Hroznětín, part of Sokolov basin, was chosen for the study of uranium behavior because of its resemblance with natural analogue systems in Gorleben (Germany) and Mol (Belgium) [1]. Uranium found predominantly in U(IV) form is in the site distributed heterogeneously within volcanodetritic layers in the depth of 10-40 m.

In our previous study [2], the results of sorption and exchange experiments on samples of different mineralogical composition, that could not be described by any formal equilibrium isotherm, were presented. The dissolution of sulfides was assumed as the main reason of the observed behavior. In this study, the surface qualities as layer and edge sites of minerals present in samples were identified by means of evaluation of titration curves. The aim was to prepare a formal sorption model, which will be able to explain the results of interaction experiments with uranium. From the evaluation of sorption and exchange kinetic experiments we expected the formulation of interaction isotherms for different samples. Comparison of determined values of exchangeable uranium using ^{233}U on selected samples with the results of sequential leaching could help in discussion of uranium sorption and/or mineralization in studied rock materials.

EXPERIMENTAL

The kinetics of uranium sorption and isotopic exchange, interaction isotherms and evaluation of titration curves differentiate the qualities of studied types of sedimentary rocks.
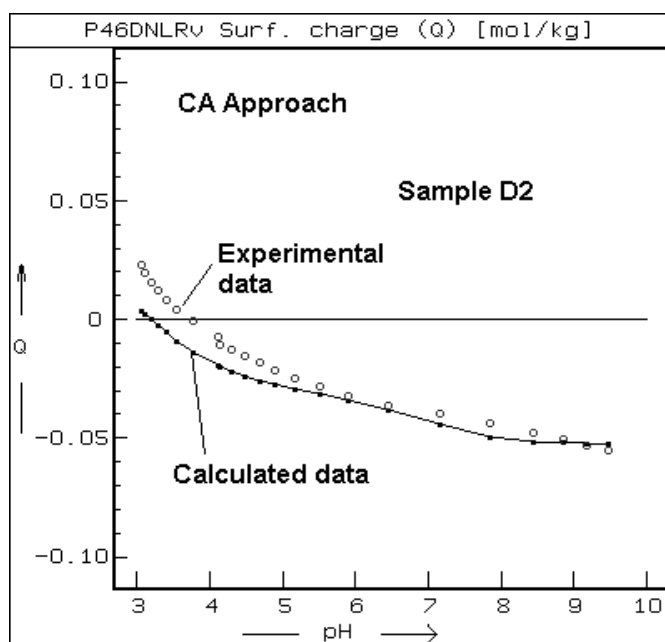

Fig. 1. Calculation of titration curve (total surface charge = f(pH)). CA approach including CEM and IExM models and data from [3] were used.

Samples were selected with respect to the position of uranium mineralization in the borehole profile. Sample D2 represents position with the highest accumulation of uranium (Fig. 1).

An own modification of the KPA method (kinetic phosphorescence analysis) enables the determination of total uranium concentration in leachates.

RESULTS

Titration curves of selected rock samples pre-treated in order to remove carbonates and other impurities using the procedure described in [4] were described by SCM (Surface Complexation Model) using the so called Generalized Composite approach, and the surface sites parameters were determined. In addition, the mineralogical composition of samples was taken into account and the Component Additivity approach (CA Approach) based on literature data characterizing the surface sites of component minerals was successfully applied (Fig. 1). The knowledge of surface sites parameters makes possible the surface complexation modelling of sorption or desorption of radionuclides to be used. Due to the presence of mainly kaolinite and montmorillonite, the mineral surfaces can be characterized by functional groups such as "layer site" and "edge site". These are capable, depending on the pH, of ion exchange mechanism (especially "layer sites") and surface complexation ("edge sites") of ionic and molecular forms present in the liquid phase.

The kinetics of uranium interaction with selected samples was studied under different conditions. The influence of exchangeable uranium present in samples was determined by isotope exchange using ^{233}U.

In some samples the self-leaching of uranium, which would be caused by the oxidation of pyrite, was observed. Unfortunately, it did not enable to formulate the shape of interaction isotherm.

The comparison of the value of exchangeable uranium determined with the use of ^{233}U and by sequential leaching was good.

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Separation and Radioanalytics

FUKUSHIMA RESEARCH CRUISE

K. Šťastná

INTRODUCTION

In response to the Fukushima NPP accident, the Woods Hole Oceanographic Institution (WHOI, Massachusetts, U.S.) initiated the first international, multidisciplinary assessment of the radioactive contamination of the Pacific Ocean. The aim of the project, funded by the Gordon and Betty Moore Foundation, was to determine inventories and pathways of released radionuclides, and their impact on marine life and human health. The essential part of the project was a research cruise in the western North Pacific.

Fig. 1. Research vessel Kai´mikai-o-Kanaloa (University of Hawaii).

ONBOARD

The research vessel (University of Hawaii) departed from Yokohama on June 4, 2011 for 15-day expedition in an area 200 x 200 km off Fukushima, along and across the Kuroshio current, the major ocean current in the area to carry the contamination far into the ocean.

The international research team (17 scientists from U.S., Japan, and Spain), led by Ken Buesseler, Senior Scientist at the WHOI Department of Marine Chemistry and Geochemistry, was concerned with ocean current measurements (using drifters, Acoustic Doppler Current Profiler, Conductivity, Temperature, and Depth sensors) and collecting of samples of seawater (Rosette with Niskin Bottles, in situ pumps) and marine biota (Bongo nets for plankton, Methot trawl for fish) from 32 stations on the cruise track.
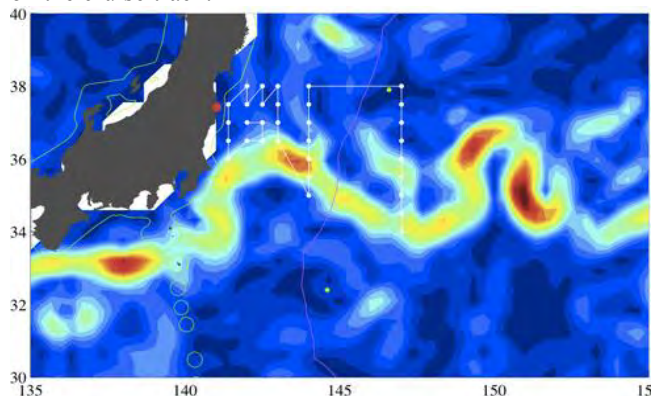

Fig. 2. Cruise track and sampling stations.

Radiation safety was controlled by radiation health physicist by monitoring ambient dose rate levels (Bicron Micro-REM meter, 0.02 to 0.10 µSv/hr), surface contamination (filter paper wipes counted under GM tube, not detected), and cumulative dose (Global Dosimetry DMC 2000 S active dosimeters, 10 µSv total dose for cruise participant) [1].

Cesium radioisotopes and short-lived natural radium isotopes analyses were carried out onboard. Radium from seawater was sorbed on MnO_2 coated acrylic fibers and counted using RaDeCC (delayed coincidence counting system). Short-lived radium isotopes (^{223}Ra, ^{224}Ra) provide information about river and ocean water mixing, submarine groundwater discharges, and water-soil interactions.

The author of this contribution took part in the cruise and carried out onboard cesium concentration from acidified seawater onto the AMP-PAN composite absorber [2] and measurement by gamma spectrometry using NaI(Tl) detector. The onboard determination was just preliminary and for safety purposes but provided contamination relative spreading data. The precise measurements were performed at WHOI laboratory using close-end coaxial well detectors and cesium standards.

RESULTS

The ^{137}Cs and ^{134}Cs highest levels were detected in near-shore areas, although not at stations closest to Fukushima. The highest activity (3.9 kBq·m^{-3}) was found at a semipermanent eddy centered on 37°N 142.5°E. Activities up to 300 Bq.m^{-3} were found at the research area eastern boundary. ^{137}Cs/^{134}Cs activity ratio was close to 1 indicating the Fukushima NPP source. South of the Kuroshio, ^{134}Cs activities were below the limit of detection and ^{137}Cs activities were on levels before the accident (1–2 kBq·m^{-3}). The data show substantial dilution of contamination discharges even at the stations nearest to Fukushima. The activities values averaged 33 kBq.m^{-3} in June at the discharged channels. As a result of ocean stirring and mixing, ^{137}Cs and ^{134}Cs activities offshore decreased far below the Japanese regulatory limits (90 kBq.m^{-3}) and in stations 30 km off Fukushima ranged between 600 to 800 Bq.m^{-3}. These values are even below the levels of the most abundant natural radionuclide in the ocean ^{40}K (12 kBq·m^{-3}) [3].

The seawater and biological samples were analyzed at laboratories in U.S., U.K., Japan, Monaco, Germany, and Slovakia. Contents of many radionuclides (isotopes of cesium, strontium, iodine, ruthenium, promethium, plutonium, radium, uranium, and others) in seawater and their accumulation in phytoplankton, zooplankton and key fish species were determined. Together with ocean current measurements, the data provide input to models describing contamination pathways in the ocean and its transfer up the food chain.

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ESTABLISHING ^{137}Cs AND ^{134}Cs LEVELS IN SEAWATER IN THE PACIFIC OCEAN BETWEEN FUKUSHIMA AND HAWAII

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INTRODUCTION

The Fukushima NPP accident after the March 11, 2011 earthquake and tsunami led to large releases of radioactive contaminants into the ocean. To determine the Pacific Ocean radioactivity spread and levels that might reach Hawaii, seawater samples were collected at eleven stations along the transect from Fukushima to Hawaii from June 21 to July 2, 2011. ^{137}Cs and ^{134}Cs activities in seawater were determined using the concentration on AMP-PAN composite absorber [1,2] followed by gamma spectrometry.

Fig. 1.   Sampling stations

EXPERIMENTAL

The surface seawater samples of about 20 L were pumped through a 1-µm filter, acidified to pH 1 with concentrated nitric acid (6.8 mL/L seawater), and stable cesium carrier was added (approx. 40 µg 133Cs/L seawater). The samples were passed through 10 mL of AMP-PAN composite absorber (0.1 – 0.7 mm diameter, 80 % ammonium phosphomolybdate, stored in 0.1M HNO3, CTU) in a glass column by gravity at flowrates not exceeding 140 mL/min. The loaded AMP-PAN was dried under a heat lamp, put into a Petri dish (35 x 10 mm) and counted placed directly on the top of ORTEC GEM40P4-76 HPGe coaxial detector located in HPLBS-1 High Performance Low Background Lead Shield and coupled with ORTEC DSPEC-LFTM Digital Gamma-Ray Spectrometer. Counting times ranged between 1 to 4 days, giving detection limits of 0.3-1.0 Bq.m^{-3}. The spectra were evaluated using MAESTRO-32 for Windows (Model A65 – B32 Version 6.08) and Hypermet-PC (Version 5.0, Institute of Isotopes, Hungary) software. Cesium activities calculated from the peak areas at 662 keV for 137Cs and 605 and 796 keV for 134Cs were corrected for decay to the date of collection. The counting efficiency was determined using 10 mL AMP-PAN in 0.1M HNO3 spiked with known amounts of standard 137Cs and 134Cs solutions (Eckert & Ziegler Analytics). Chemical recovery, determined from stable cesium concentrations measured by ICP-MS (Element2, ThermoFinnigan) in aliquots of sea water samples taken before and after Cs concentration on AMP-PAN, ranged from 90 to 97 %, with an average of 94 %.

RESULTS

The cesium radionuclide content in seawater samples taken along the transect from Fukushima to Hawaii ranged from background pre-Fukushima levels (1-2 Bq·m^{-3}), calculated using data from Marine Information System and apparent half-residence times in surface waters of Pacific [3], for ^{137}Cs and values bellow the limit of detection for ^{134}Cs south of the Kuroshio current up to 12 Bq·m^{-3} for ^{137}Cs and 10 Bq·m^{-3} for ^{134}Cs at the transect and southern boundary of the current intersection.

Tab. 1. 137Cs and 134Cs activities in surface seawater along the transect Fukushima – Hawaii (combined standard uncertainties in parentheses, bd = below the limit of detection).

Sampling date	Location		^{137}Cs	^{134}Cs
	Latitude	Longitude	activity (Bq.m^{-3})	
21-Jun-11	34°29'N	144°33'E	1.6(0.1)	bd
23-Jun-11	34°18'N	149°53'E	1.8(0.1)	bd
24-Jun-11	34°06'N	154°59'E	5.3(0.2)	3.7(0.2)
24-Jun-11	33°55'N	159°36'E	2.2(0.1)	0.9(0.1)
25-Jun-11	33°44'N	164°27'E	3.5(0.1)	2.1(0.2)
27-Jun-11	33°27'N	169°59'E	11.4(0.3)	9.5(0.4)
28-Jun-11	32°47'N	174°39'E	4.9(0.2)	3.1(0.2)
29-Jun-11	31°27'N	179°38'E	2.2(0.1)	0.7(0.1)
30-Jun-11	29°22'N	174°55'W	1.6(0.1)	bd
1-Jul-11	27°27'N	170°03'W	1.3(0.1)	bd
2-Jul-11	25°34'N	165°16'W	1.4(0.1)	bd

The values observed are far below limits of concern regarding human health, but they give information about the radionuclides pathways in the Pacific Ocean. The results confirm models predicted very little radioactivity spreading south of the Kuroshio current.

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THE EFFECT OF ALKYL SUBSTITUTION IN CyMe₄-BTBP ON ITS EXTRACTION PROPERTIES

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INTRODUCTION

When the spent nuclear fuel is considered to be reprocessed, one of the main chemical tasks, a partitioning of minor actinoids from lanthanoids, is still not complete. This partitioning of the trivalent minor actinoids can be done by solvent extraction using extraction agents such as BTBP molecules. This research was focused on a study of extraction properties of two new derivatives from this family of extractants – MeCyMe₄-BTBP and t-BuCyMe₄-BTBP. Their extraction properties were tested and compared with the extraction properties of their "mother" molecule CyMe₄-BTBP that is also the reference molecule in SANEX process. [1].

EXPERIMENTAL

As an extractant, CyMe₄-BTBP (6,6'-bis (5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzo-tri-azin-3-yl)-2,2'-bipyridine), MeCyMe₄-BTBP (4,4'-dimethyl-6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-2,2'-bipyridine), and t-BuCyMe₄-BTBP (4,4'-di-tert-butyl-6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-2,2'-bipyridine) in cyclohexanone or n-octanol was used. Nitric acid solutions of different concentrations were spiked with ^{152}Eu(III) and ^{241}Am(III) stock solutions. 1 mL of the aqueous phase was contacted with 1 mL of the solvent for 6 hours using an orbital shaker. After the contact, the phases were separated by centrifugation and then samples from each phase were taken for γ-measurement by means of HPGe detector.

RESULTS

On the contrary to the premises, the presence of the additional alkyl groups did not increase the solubility of the MeCyMe₄-BTBP and t-BuCyMe₄-BTBP extracting compounds. Therefore, the alkyl substitution of BTBP ligands does not necessarily improve their solubilities, at least in case of the tested symmetrical MeCyMe₄-BTBP and t-BuCyMe₄-BTBP extractants. Furthermore, the additional substituents slow down the extraction kinetics that is considerably slower than that found for the unsubstituted CyMe₄-BTBP ligand in n-octanol or cyclohexanone diluents. It was also shown that the kinetics of the Am(III) and Eu(III) extraction by t-BuCyMe₄-BTBP ligand in cyclohexanone is slower than the kinetics of the Am(III) and Eu(III) extraction by MeCyMe₄-BTBP ligand in the same diluent. On the other hand, the values of the distribution ratio D(Am) are higher for the t-BuCyMe₄-BTBP ligand in comparison with the MeCyMe₄-BTBP ligand, when both extractants were dissolved in cyclohexanone, as it is shown in Fig. 1.
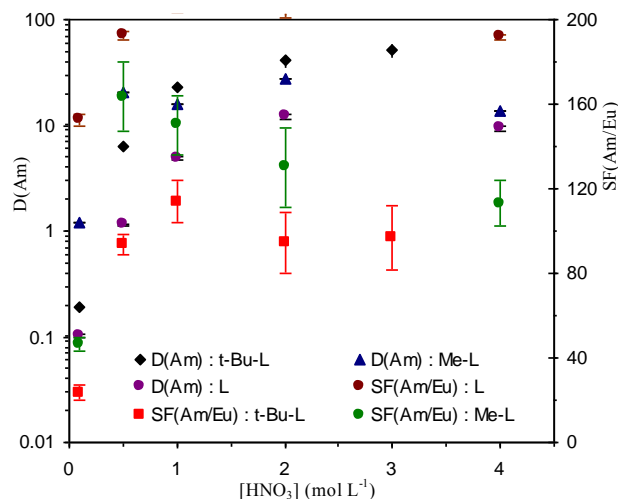
Fig. 1. Comparison of the dependencies of D(Am) and SF(Am/Eu) on HNO₃ initial concentration for MeCyMe₄-BTBP, t-BuCyMe₄-BTBP, and CyMe₄-BTBP, all dissolved in cyclohexanone (each 5 mmol L⁻¹). L represents CyMe₄-BTBP.

Although the MeCyMe₄-BTBP ligand provided higher distribution ratio values of Am and SF(Am/Eu) values in n-octanol at 0.1 – 2 mol L⁻¹ HNO₃ than the t-BuCyMe₄-BTBP ligand did, it could not be recommended for further studies because of the decreased stability incurred by the benzylic hydrogens in the methyl group of this BTBP ligand. The presence of these benzylic hydrogens facilitates chemical attack by free-radical species formed during exposure of the organic and aqueous phases to radiation [2]. The extraction results obtained by these BTBP ligands in n-octanol are important because n-octanol is one of the preferred diluents for process of implementation. The t-BuCyMe₄-BTBP ligand in cyclohexanone provided higher distribution ratio values for americium when compared with the MeCyMe₄-BTBP and CyMe₄-BTBP molecules. Therefore, from all the BTBP molecules compared here, the t-BuCyMe₄-BTBP was chosen as the most prospective both due to its extraction properties and due to its higher stability against free-radical attack.

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KINETIC EFFECTS IN THE Am/Eu SEPARATION WITH BTBP LIGANDS

Distler, P.; John, J.; Harwood, L.M.[1]; Hudson, M.J.[1]; Lewis, F.W.[1]

[1]University of Reading, Department of Chemistry, United Kingdom

INTRODUCTION

The CyMe$_4$-BTBP and its derivatives have been demonstrated to be prospective extractants for the liquid-liquid extraction of minor actinoids over lanthanoids from high-level liquid waste issuing the reprocessing of the spent nuclear fuel [1].

When the extraction system based on BTBP compounds was studied, a significant kinetic effect on separation factor SF(Am/Eu) values was observed. This effect is most probably caused by the usually slower kinetics of Am extraction in comparison with the extraction of Eu. It showed an importance of a detailed study of the extraction system before its implementation on the technological scale.

EXPERIMENTAL

As an extractant, Cy$_5$-S-Me$_4$-BTBP (6,6'-bis(5,5,7,7-tetramethyl-5,7-dihydrothienol[3,4-e]-1,2,4-triazin-3-yl)-2,2'-bipyridine), MeCyMe$_4$-BTBP (4,4'-dimethyl-6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-2,2'-bipyridine), and t-BuCyMe$_4$-BTBP (4,4'-di-tert-butyl-6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-2,2'-bipyridine) in cyclohexanone or n-octanol was used. Nitric acid solutions were spiked with ^{152}Eu(III) and ^{241}Am(III) stock solutions. 1 mL of the aqueous phase was contacted with 1 mL of the solvent on an orbital shaker.

RESULTS

Slow kinetics of Am and Eu extraction from nitric acid solutions by CyMe$_4$-BTBP, t-BuCyMe$_4$-BTBP, and Cy$_5$-S-Me$_4$-BTBP ligands was observed in the systems with n-octanol. The equilibrium was not reached and the separation factor values SF(Am/Eu) did not exceed the value of 100 even after 30 hours of contact of the phases for either of the ligands studied, as it is shown in Fig. 1.
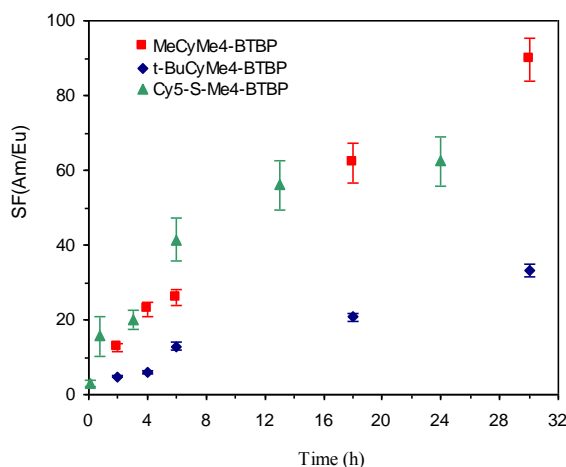
Fig. 1. Comparison of the dependencies of SF(Am/Eu) on the time of contact in the system HNO$_3$ – MeCyMe$_4$-BTBP, t-BuCyMe$_4$-BTBP, or Cy$_5$-S-Me$_4$-BTBP in n-octanol.

The kinetic study revealed that the rates of americium and europium extraction are not the same even in the system of the extractants diluted with cyclohexanone. In the system with cyclohexanone, the equilibrium was reached within 30 minutes for the MeCyMe$_4$-BTBP ligand while around 2 hours were needed to reach equilibrium in the case of the t-BuCyMe$_4$-BTBP ligand. On the other hand, the values of SF(Am/Eu) at equilibrium for the t-BuCyMe$_4$-BTBP molecule are slightly higher than those for the MeCyMe$_4$-BTBP molecule. All the mentioned results are shown in Fig. 2.

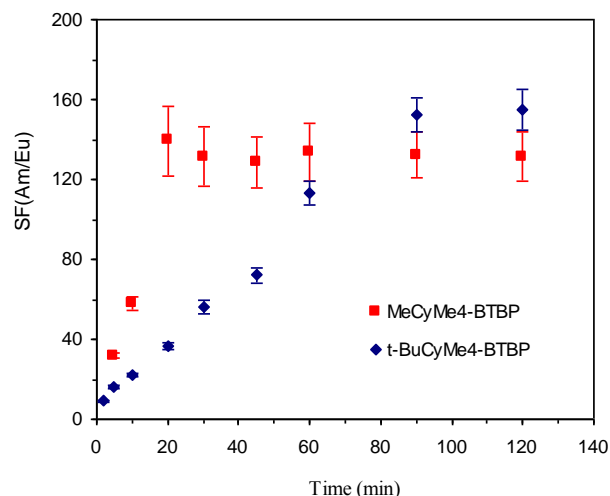**Fig. 2.** Comparison of the dependencies of SF(Am/Eu) on the time of contact in the system HNO3 – MeCyMe4-BTBP or t-BuCyMe4-BTBP in cyclohexanone.

The results of this study demonstrated that a strict control of all parameters of the extraction systems, including kinetics, is needed to reach maximum SF(Am/Eu) values.

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SEPARATION OF CURIUM FROM AMERICIUM USING DMDOHEMA-PAN COMPOSITE ABSORBER AND TEDGA SOLUTION

K. Šťastná, F. Šebesta, M. Vlk, J. John

INTRODUCTION

The EXtraction of Americium (EXAm) process intended as a part of the Partitioning and Transmutation strategy has been used as the basis for development of a chromatographic system for the separation of curium from americium. The liquid organic phase composed of N,N'-dimethyl-N,N'-dioctyl-2-(2-(hexyloxy)ethyl)-malonamide (DMDOHEMA) in alcane was replaced by DMDOHEMA-PAN composite absorber, and N,N,N′,N′-tetraethyldiglycolamide (TEDGA) in nitric acid solution was employed as a masking or eluting agent.

EXPERIMENTAL

In batch experiments, 10 mg of DMDOHEMA-PAN was agitated with 1.0 mL of TEDGA solution spiked with trace amounts of Am and Cm (approx. 4 kBq each) using Rotoratot PTR-30 at 30° and 30 rpm for 10 minutes. Weight distribution ratios and separation factor were calculated from the activities of aqueous phase aliquots taken before (A_0) and after agitation (A) measured by ORTEC Octete Plus Alpha Spectrometer with ULTRA ion implanted silicon detector and evaluated by AphaVision software, the aqueous phase volume (V) and composite absorber weight (m):

$$D_g = \frac{A_0 - A}{A} \times \frac{V}{m} \qquad SF = \frac{D_g(Am)}{D_g(Cm)}.$$

Tab. 1. Characteristics of composite absorber and packed column.

Composite absorber	
Active component	DMDOHEMA
Binding polymer	PAN
Grain size	< 0.3 mm
Active component content	33%
Bulk density	0.14 g/mL
Packed column	
Bed volume	0.82 mL
Bed diameter	0.4 cm
Bed high	6.5 cm
Bed dead volume	0.28 mL
Column dead volume	0.32 mL

In a dynamic experiment, 1mL polyethylene column was filled with 0.12 g of DMDOHEMA-PAN and preconditioned by passing 4mol·L⁻¹ HNO₃. Then 40 μL of 4mol·L⁻¹ HNO₃ containing trace amounts of Am and Cm (approx. 2 kBq each) was pipetted on the top of the bed and eluted with 0.01mol·L⁻¹ TEDGA solution in 4mol·L⁻¹ HNO₃ using gravity at aflowrate of 0.10 mL·min⁻¹. 0.2mL (0.25BV) fractions were collected and measured by alpha spectrometry. Separation factor was calculated from americium and curium elution volumes (V_{Am} and V_{Cm}) and column dead volume (V_d):

$$SF = \frac{V_{Am} - V_d}{V_{Cm} - V_d}.$$

RESULTS
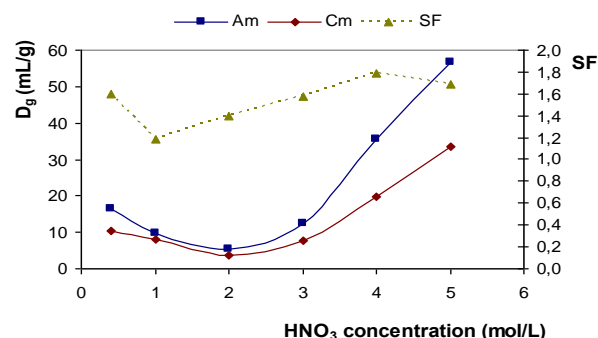
Fig. 1. Sorption of Am and Cm on DMDOHEMA-PAN from 0.01mol·L⁻¹ TEDGA solution at varied nitric acid concentration.
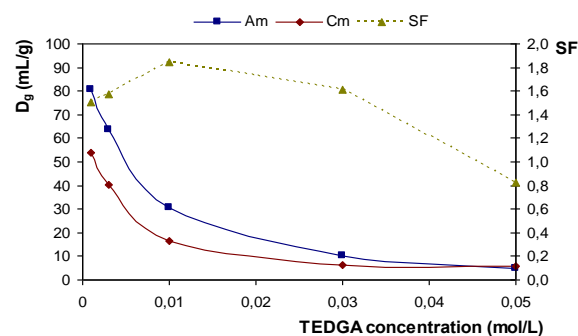
Fig. 2. Sorption of Am and Cm on DMDOHEMA-PAN from 4mol·L⁻¹ HNO₃ solution at varied TEDGA concentration.
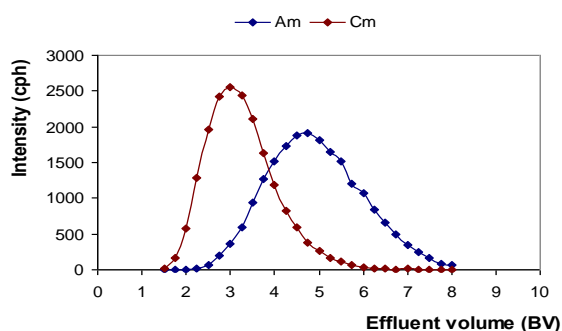
Fig. 3. Chromatogram of Am/Cm separation.

The highest separation coefficient value, reached at 0.01mol·L⁻¹ TEDGA and 4mol·L⁻¹ HNO₃ concentration, from the batch experiments was 1.8 and corresponded to the value obtained in the column experiment.

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DECONTAMINATION OF SPENT DIAMEX SOLVENT CONTAINING CONTAMINANTS DIFFICULT TO STRIP

Mareš, K.V.; John, J.; Šebesta, F.; Vlk, M.; Svobodová, T.

INTRODUCTION

The accumulation of "difficult-to-strip" elements (e.g. Ru, Y, Mo, Pd, Zr, Sr) in spent solvents causes a serious obstacle in industrialization of the DIAMEX process. Materials which can be used for efficient separation of these metals from non-aqueous liquids include various solid sorbents, ion exchange resins, papers impregnated with resins, and (modified) cellulose. The presence of small amounts of water in the system can remarkably influence distribution equilibria, especially in low-polar solvents. Another problem in the identification of potentially suitable materials is the fact that the speciation of some metals like Ru or Pd in the organic phase is hardly predictable. The aim of this study was to evaluate the efficiency of several solid sorbents for decontamination of simulated spent solvents. Spent solvent coming from the TODGA process [1], one of the DIAMEX processes family, was selected as the target organic solution for this study.

EXPERIMENTAL

Simulated spent solvent preparation and composition:
50 mL of the $0.2 mol \cdot L^{-1}$ TODGA extractant in kerosene/octan-1-ol (5 vol.%) solution was contacted with 100 mL of simulated spent PUREX raffinate for 20 hrs using an orbital shaker at 250 rpm. After the contact, the organic phase was scrubbed twice with $0.4 mol \cdot L^{-1}$ $(COOH)_2$ and $0.2 mol \cdot L^{-1}$ EDTA in $1 mol \cdot L^{-1}$ HNO_3, and then twice with $1 mol \cdot L^{-1}$ HNO_3. After the scrubbing, the organic phase was stripped with $0.01 mol \cdot L^{-1}$ HNO_3. The resulting organic solution was pink-coloured due to the presence of Ru. The composition of prepared spent solvent is given in Tab. 1. In total, 12 batches of this simulated spent solvent were prepared for the experiments.

Tab. 1. Composition of the spent solvent

element	this work		Modolo et al. [1]
	c [mg·L⁻¹]	RSD [%]	c [mg·L⁻¹]
Ru	68	2.4	50.6
Y	14	2.6	4.75
Mo	0.05	180	20.4

RSD = relative standart deviation

Ruthenium speciation in spent solvent:
For the preparation of organic solution for the speciation studies, $Ru(NO)(NO_3)_x(OH)_y$, $x + y = 3$ solution in $1 mol \cdot L^{-1}$ HNO_3 was used instead of the PUREX raffinate.
● MS-ESI spectra (positive and negative modes) were measured in methanol or acetonitrile.
● IR spectra were measured using DRIFTS technique in KBr matrix.
● TLC methods using Silica gel 60, Al_2O_3 60, Silica RP-18, Silica RP NH_2, and glass Silica gel (all Merck)

as the stationary phases were tested for the separation of TODGA-Ru complexes.
Determination of the distribution coefficients:
16 mg of sorbent was shaken with 4 mL of spent solvent ($V/m = 250$ mL·g⁻¹; except for the determination of sorption isotherms, where various V/m ratios were used) in 50mL PE bottles for 20 hrs using an orbital shaker at 250 rpm. The supernatant was analysed by XRF. In total, more than 50 various sorbents were tested.

RESULTS

Speciation studies:
● MS-ESI: No Ru inorganic forms were observed. The dominant Ru form represented
$[2TODGA-H+2Ru+2H_2O]^+$, but also the
$[TODGA+Ru+NO+NO_3]^-$ and $[TODGA-H+Ru+NO]^+$
forms were observed.
● IR spectra: Ru-NO bond (1859 cm⁻¹) identified [2].
● TLC: Two single spots occurred in the following systems: Al_2O_3 60 neutral F254 / 10 mL $CHCl_3$ + 1 drop of MeOH and Silica gel 60 RP-18 F254 / 8 or 5 mL THF + 2 or 5 mL 1% AcOH.
Batch sorption studies:
● Distribution coefficients obtained for the most prospective sorbents reached almost 100 mL·g⁻¹ (P2870 dithiocarbamate groups; custom-synthesized) for Ru, and over 1000 mL·g⁻¹ (Amberlyst A26OH, Tulsion A-26OH, Tulsion CH-90, P2870 dithiocarbamate groups, P2848 8-hydroxychinoline groups, P2849 8-hydroxychinoline-5-sulphone groups) for Y.
● In case of P2870, P2848 and P2849, the sorption kinetics is very fast, the equilibrium is reached after approximately 5 minutes. For Amberlyst A26, the apparent equilibrium is reached after approximately 240 minutes, then very slow gradual increase of D_g values was observed for Y and Ru throughout all the 20 hrs of the experiment duration.
● For Amberlyst A26, the sorption isotherm was measured. The maximum sorption capacities obtained are $q(Ru) = 0.083$ mmol·g⁻¹, $q(Y) = 0.096$ mmol·g⁻¹.

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^{236}U DETERMINATION USING AMS

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[1] University of Vienna, Austria

INTRODUCTION

In the environmental studies and also in the nuclear safeguards, determination of low concentrations of uranium, especially ^{236}U, has become important. Natural concentrations of this radioisotope (^{236}U/^{238}U $\sim 10^{-12}$) could be employed in the uranium prospection, on the other hand the athropogenic ^{236}U (concentration of 5-6 orders higher) has already been used during the controls of reprocessing/ handling of spent nuclear fuel.

This study is closely connected with the uranium sorption on TiO-PAN or TiO$_2$ sorbents. The ^{236}U concentrations are determined using the Accelerator Mass Spectrometry (AMS) in cooperation with University of Vienna, VERA facility (Vienna Environmental Research Accelerator).

EXPERIMENTAL AND RESULTS

In the first experiments, TiO-PAN composite sorbent was contacted with tap water with dissolved uranium nitrate and with water from the river Kocába (49°42′5′′N; 14°7′30′′E) collected in the Příbram region. The materials were incinerated at 800°C to get rid of polyacrylonitrile and thus to reduce the volume of the sample. These two incinerated samples together with the incinerated original TiO-PAN were sent to VERA laboratory for the determination of ^{236}U/^{238}U ratio (Tab. 1).

Tab. 1. Anthropogenic contamination by ^{236}U in samples measured by AMS in VERA laboratory (Vienna-KkU – in house standard, uranyl nitrate from pre-nuclear times produced from the Jáchymov ore [1]).

sample	m(U) [µg] *	ratio ^{236}U/^{238}U
Vienna-KkU	1328.2	7.02E-11 ± 2.10E-12
TiO-PAN	0.1	1.80E-07 ± 2.18E-08
TiO-PAN (tap water)	1042.6	1.87E-06 ± 1.84E-09
TiO-PAN (river water)	0.2	6.02E-06 ± 1.04E-07

* mass estimated from AMS measurement

The values of ^{236}U/^{238}U ratios determined in the samples are very high relative to the natural ratio in Vienna – KkU sample which is used as a standard in the ^{236}U-AMS measurements [1]. This means that all the samples are contaminated with anthropogenic uranium and in order to determine ^{236}U in natural waters, it is necessary to eliminate the possiblity of contamination by uranium during any of the procedures used.

After the analysis of possible sources of anthropogenic ^{236}U and in order to prepare pure "uranium free" sorbent, further research was divided into three parts which will be dealt seperately. The first part has focused on identification of a water source not contaminated by anthropogenic uranium and which can be used in further experiments. The second part should deal with the preparation of pure chemicals, since the amount of uranium in commercial chemicals is not monitored and even the distilled water (demi water) used in the laboratory may contain units of micrograms of uranium per litre. And in the last part,

preparation of a pure "uranium free" hydrous titanium dioxides has been planned.

Based on the discussions with hydrogeologists from the Charles University, Děčín thermal water was chosen due to the low level of mineralization (~500 mg L^{-1}) and its classification as a pressurised reservoir. The age of this water was determined by radiocarbon dating, and is estimated to be 24 800 years [2]. This thermal water was distilled in the laboratory and used in further experiments.

New sorption material, modified hydrated TiO$_2$, was prepared by hydrolysis of an organic titanium compound using the prepared distilled water. Then, three samples (1 - pure hydrated TiO$_2$, 2 - TiO$_2$ contacted with thermal water from Děčín, 3 - TiO$_2$ contacted with water from Agricola spring, Jáchymov) were sent to VERA facility to verify the absence of anthropogenic uranium contamination in the new preparation procedure (Tab. 2).

Tab. 2. The values of 236U/238U ratio in paralel samples measured by AMS in VERA facility.

sample	m(U) [µg] *	ratio ^{236}U/^{238}U
pure TiO$_2$	0.005	1.64E-05 ± 2.43E-06
	0.003	2.82E-05 ± 1.59E-05
TiO$_2$ (Děčín water)	0.006	1.21E-05 ± 5.09E-06
	0.001	2.33E-06 ± 5.09E-07
TiO$_2$ (Agricola water)	0.276	2.62E-08 ± 3.50E-09
	0.391	2.96E-08 ± 3.12E-09

* mass estimated from AMS measurement

The absolute amounts of uranium in the pure TiO$_2$ sample and in the loaded TiO$_2$ (Děčín water) are very close to the AMS detection limits and the value of the ^{236}U/^{238}U ratio is determined with very high value of uncertainty (~ 50%). This means that even though the comparison of the results from both ^{236}U-AMS measurements is contradictory, the newly prepared titanium dioxide can be used for the ^{236}U determination in environmental samples. On the other hand, the amount of uranium and the ^{236}U/^{238}U ratio determined in the Agricola spring waters is in an excellent agreement with the former measurements carried out by Steier [3] thus showing the practical applicability of this method for the ^{236}U/^{238}U ratio determination.

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ALTERNATIVE METHODS FOR THE PREPARATION OF PURE TiO₂ SORPTION MATERIAL

Špendlíková, I.; Němec, M.

INTRODUCTION

The first results of ^{236}U determination in TiO₂ (incinerated TiO-PAN sorbent) using AMS (Accelerator Mass Spectrometry) showed the anthropogenic contamination. The sorbent used was prepared from an industrial intermediate of titanium white production and hence it is probably contaminated by uranium already from its origin. Assuming that most organic compounds should not contain uranium and that it is possible to find "anthropogenic uranium free" water, titanium dioxide could be prepared free of anthropogenic contamination. Therefore, an organic compound, TetraButylOrthoTitanate (TBOT), was chosen to be employed in the research project.

EXPERIMENTAL

Titanium dioxides can be prepared via the hydrolysis of titanium compounds, but its properties strongly depend on preparation conditions. First, the hydrolyses were performed with chemicals of analytical grade to optimize the preparation procedure with respect to the sorption properties towards uranium.

In the oxide preparation (Tab. 1), chemical A is added into the beaker with chemical B while placed in an ultrasonic bath. Then, the oxide formed is washed with chemical C.

Tab. 1. List of titanium oxide materials prepared and the chemicals used (IP-isopropanol, W-distilled water, AC-acetone, AM-NH₄OH, EtOH-ethanol).

	chemical A	chemical B	chemical C
TiO₂-A	TBOT	IP+AM	AC
TiO₂-E	TBOT	IPl+AM	EtOH
TiO₂-O	TBOT	W	AC+EtOH+W
TiO₂-S	IP+W	TBOT	-
TiO₂-V	W	TBOT	AC+EtOH+W

The prepared oxides were dried at ≤ 30°C in a vacuum dryer thus preserving crystal water in the structure.

The oxide marked as M was prepared from its suspension in water produced as an industrial intermediate from the sulphate process of titanium white production. The suspension was mixed, filtered and washed with distilled water. This oxide was dried in a furnace at 45-50°C [1].

RESULTS

The sorption on the hydrous titanium dioxides strongly depends on their crystal structure and their capacities increase in the row: rutile < anatase < amorphous [2]. The crystal structure of all prepared oxides was studied using X-Ray Diffraction. The diffraction patterns can be classified into two groups. Group 1 is shown in Fig. 1 where no diffraction peaks of anatase, rutile or brookite can be identified, thus concluding that the oxides A, E and S are amorphous. On the other hand, in the diffraction patterns of group 2 (oxides O, V, M) the diffraction peaks of anatase and brookite can be easily identified, however, showing only a short-range order, which means that the oxides O, V and M

are amorphous anatase. This may already indicate lower sorption capacities when compared with oxides A, E and S.
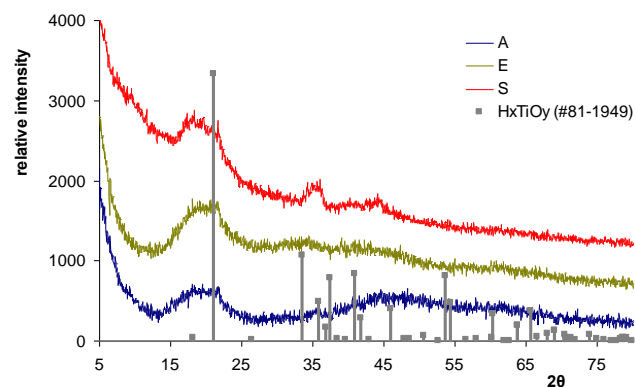

Fig. 1. X-ray diffraction patterns (Cu-K$_\alpha$) of hydrous oxides marked as A, E and S in comparison with hydrous titanium dioxide H$_x$TiO$_y$ (ICDD-PDF-2 Database).

Because the sorption is also influenced by the size of surface area, prepared oxides were also studied with selective sorption of nitrogen gas from catalytically deoxygenated mixture of 5 H₂ : 1 N₂ at the temperature of 77 K. The values can be seen in Tab. 2 and the highest value of the specific surface area (306.6 m² g^{-1}) was measured for oxide A.

In order to study the influence of specific surface area and crystal structure on the sorption properties, batch experiments were performed using the newly prepared oxides with the grain size less than 125 μm. The values of D$_g$ are given in Tab. 2 which shows that the highest value was measured for the oxide A. Comparing the values of specific surface area and weight distribution ratio, it is clear that no correlation exists and that it is the crystal structure that strongly influences the sorption properties.

Tab. 2. Comparison of specific surface area and uranium sorption (V/m = 100 mL g-1, c0(U) = 1.10-3 mol L-1, contact time: 1 hour)

	specific surface area [m² g^{-1}]	D$_g$ [mL g^{-1}]
A	306.6	2310
E	88.9	2307
O	264.5	220
S	14.9	480
V	159.1	271
M	54.8	226

For complete characterization, the properties of the prepared oxides have been further measured also using the thermogravimetry, SEM/TEM and IR methods.

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URANIUM SORPTION ON TiO-PAN ABSORBER AND ITS CHARACTERIZATION

Raindl, J.; Špendlíková, I.; Němec, M.; Zavadilová, A.; Šebesta, F.

INTRODUCTION

Separation of uranium from natural water was studied mainly for industrial acquisition of uranium from sea water. One of the interesting sorbents is TiO-PAN (hydrated titanium dioxide embedded in polyacrylonitrile) which was developed at the Departmant of Nuclear Chemistry in late 80´s and early 90´s [1]. The purpose of this project was the characterization of TiO-PAN sorbent including weight distribution ratios of uranium, sorption isotherm, kinetics of uranium sorption and effects of several ions on the uranium sorption (Ca^{2+}, Mg^{2+}, Fe^{3+}, NO_3^-, SO_4^{2-}) [2]. The uranium concentration was measured by Time Resolved Laser Induced Fluorescence Spectrometry (TRLFS).

EXPERIMENTAL

All experiments were carried out using 20 mg of TiO-PAN in 10 mL of solution (V/m = 500 mL g^{-1}). Concentrations of uranium for sorption isotherm were between 0.001 and 1 mol L^{-1}; in all remaining experiments they were 10^{-4} mol L^{-1}. The effect of interfering ions on uranium sorption was measured at constant ionic strenght (I = 0.01 mol L^{-1}) which was maintained by the solution of $NaClO_4$. The concentrations of interfering ions are shown in Tab. 1. The contact time was 2 hours in all experiments except for the kinetic experiments, where the contact time ranged from 2 to 60 minutes. All samples were shaken at 250 rpm.

Tab. 1. Concentrations of influencing ions in sorption solutions.

$c(Me^{n+}/A^{m-})$ [mol L^{-1}]				
Ca^{2+}	Mg^{2+}	Fe^{3+}	NO_3^-	SO_4^{2-}
0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
8.0E-04	8.0E-04	1.0E-04	1.0E-03	8.0E-04
1.6E-03	1.6E-03	5.0E-04	2.0E-03	1.6E-03
2.2E-03	2.2E-03	9.0E-04	5.0E-03	2.2E-03
2.8E-03	2.8E-03	1.3E-03	8.0E-03	2.8E-03
3.3E-03	3.3E-03	1.7E-03	1.0E-02	3.3E-03

For the measurement of uranium concentration by TRLFS, all samples were diluted 1000x not to overrun upper limit of detection and to suppress the precipitation of uranium complexes. The most intensive fluorescence at the excitation wavelength λ = 412 nm was used for the measurements and the dependence of fluorescence intensity of uranium on its concentration was used for the calibration curves. A relatively high reproducibility of about 3 % and a limit of detection in tenths of micrograms were achieved. For the suppresion of nonradiant processes and for extension of luminescence, samples were mixed with complexing agent Uraplex™ in ratio 2:3 (sample:Uraplex). Before mixing, pH of all samples was lowered to 2 for correct action of Uraplex™.

RESULTS

The kinetic experiments showed very fast kinetics of uranium sorption. The solution was in equilibrium with TiO-PAN sorbent after 5 minutes of contact as can be seen in Fig. 1.
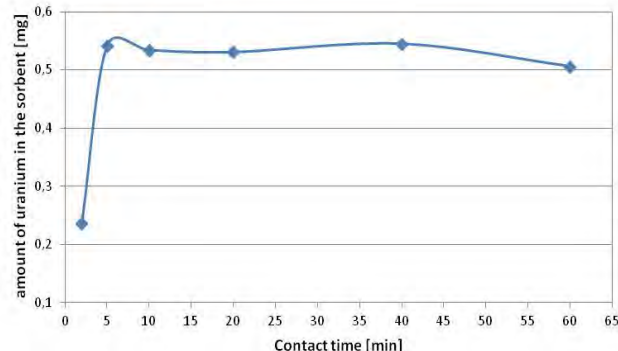
Fig. 1. Sorption kinetics (concentration of uranium 10^{-4} mol L^{-1}, shaken at 250 rpm, V/m = 500 mL g^{-1}).

Preliminary results from sorption isotherm indicated very high sorption capacity of the material for uranium. The effect of additional ions on uranium sorption was found to be strongly dependent on the electric charge of ions. The results obtained are summarised in Fig. 2.
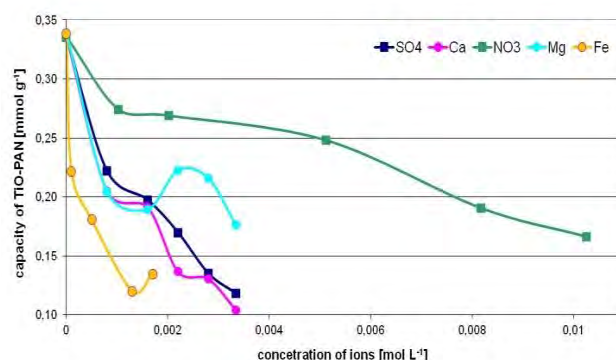
Fig. 2. The effect of additional ions (Ca2+, Mg2+, Fe3+, NO3-, SO42-) on uranium sorption on TiO-PAN sorbent (shaken at 250 rpm for 2 hours at V/m = 500 mL g-1, concentration of uranium 10-4 mol L-1).

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VALIDATION OF THE METHOD FOR NICKEL DETERMINATION IN NPP EVAPORATOR CONCENTRATES

*Šuľaková, J.; Šebesta, F.; Raindl, J.; John, J.*

INTRODUCTION

In this work a procedure developed for determination of radionickel in boric acid containing evaporator concentrate generated at VVER nuclear power plants [1] has been validated for repeatability. For nickel separation, this method uses the composite material PAN-DMG (dimethylglyoxime incorporated in porous beads of polyacrylonitrile) to selectively bind radionickel from the above mentioned concentrate. The PAN-DMG resin was prepared by the methods developed at our Department of Nuclear Chemistry at the Czech Technical University in Prague [2]. The method of ^{59,63}Ni separation on column filled with PAN-DMG from real boric acid concentrates that was validated in this work, has been developed in the thesis of Fišera [3]. In this work the influence of different uncertainty sources on the repeatability of this method has been studied. In addition, properties of various scintillation cocktails for the measurements of ^{63}Ni were compared. Two isotopes of radionickel are determined – ^{59}Ni, which is a X-ray emmiter measured by low energy photon spectrometry (LEPS), and ^{63}Ni, which is a soft β-emmiter measured by the liquid scintillation spectroscopy. Due to these differences, the procedures for ^{59}Ni and ^{63}Ni determination are going to have different sources of uncertainties.

EXPERIMENTAL

Composite material PAN-DMG (20 wt/wt% DMG, grain size ≤ 0.5 mm), used for Ni separation, was prepared by impregnation of ready-made polyacrylonitrile (PAN) beads [2]. Boric acid concentrate (74 g L^{-1} H$_3$BO$_3$, q = 1.15 kg L^{-1}, pH = 11.3) was sampled in 1999 from Dukovany NPP (Czech Republic) waste storage tank. The concentrate was spiked with ^{59}Ni or ^{63}Ni solution. Empty Resorian™ Tube Kit (Supelco, USA) made from polypropylene was used as the column. Liquid scintillation counter TRIATHLER (HIDEX, Finland) and scintillation cocktail Rotiszint Eco Plus (Carl Roth, Germany) was used for ^{63}Ni radioactivity measurement. Low energy photon spectrometry (LEPS) using HPGe detector GL0510P/S (Canberra, USA) with multichannel analyzer ADCAM 926 MCB (EG&G ORTEC, USA) was used for ^{59}Ni counting. Flow rate was controlled by peristaltic pump PCD 22 (Kouril, Czech Republic).

PROCEDURES

The procedure for validation of the repeatability of the yield of nickel separation from boric acid concentrates is presented in Table 1. The procedure for validation of repeatability of ^{59}Ni sample preparation method is presented in Table 2.

Tab. 1. Procedure for Ni separation from boric acid concentrates.

Steps	Description of the step
1st step	Preparation of the sample from 100 mL of boric acid concentrate solution, 1.7 g of ammonium citrate, pH adjusted to pH=9, Ni carrier solution with c(Ni)=10^{-4} mol/l, and ^{59,63}Ni
2nd step	Cooling the sample solution at 6°C overnight
3rd step	Decantation and washing the precipitate formed with 1–2 mL of citrate buffer
4th step	Nickel separation on PAN-DMG column
5th step	Nickel stripping with 3M HNO$_3$
6th step	LSC counting of ^{63}Ni or ^{59}Ni sample preparation for LEPS counting (see Tab. 2)

Tab. 2. Procedure for the 59Ni sample preparation.

Steps	Description of the step
1st step	Sampling 15 mL of stripping solution (3M HNO$_3$, see procedure in Tab. 1., 5th step)
2nd step	Adjusting pH of the stripping solution to the value of 2–3 with NaOH
3rd step	Adding Ni carrier solution, 2 g of urea, and 1 mL of 1% DMG
4th step	Heating the solution at 96°C for 1 hour, then cooling it to the room temperature
5th step	Filtration of the precipitate formed, washing it with distilled water, and drying the filter with precipitate at 100°C for 15 minutes
6th step	LEPS counting of ^{59}Ni

RESULTS AND CONCLUSIONS

The results obtained showed that as well as the whole method also the particular parts of the methods are repeatable. At 100 Bq activities level the repeatability of ^{63}Ni and ^{59}Ni determination is 7.7 % and 8.4 %, respectively.

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ENVIRONMENTAL SAMPLES DIGESTION FOR Sr DETERMINATION

Neufuss, S.; Němec, M.

INTRODUCTION

Determination and monitoring of ^{90}Sr (half-life 28.9 a) as one of the nuclear fission products (yields > 5%) belong among procedures to ensure and provide a radiohygienic safety. ^{90}Sr is studied for its biochemical similarity with calcium and possible consequent incorporation into human body. Main risk represents its daughter product ^{90}Y (half-life 2.67 d), which is a high energy β-emitter ($E_{\beta max}$ = 2.28 MeV). Preparation of liquid ^{90}Sr samples for subsequent extraction is a one of the main steps for ^{90}Sr determination. In this project, the moss samples from surroundings of NPP Temelín have been studied. There are several methods to decompose and to liquidize organic samples. Using traditional ways of "wet" and "dry" chemistry is one of them. These methods (incineration, leaching and evaporation) give us very good results, but they are time consuming and these processes have to be repeated several times to achieve complete dissolution. The application of new decomposition methods, using microwave digestion module, leads to better results. Due to very low concentration of ^{90}Sr in environmental samples, large samples are needed to reach the required detection limit of ^{90}Sr. For such purpose, the combination of incineration and consequent microwave digestion may be advantageous.

EXPERIMENTAL

For full decomposition of moss samples a combination of incineration and microwave digestion has been studied. At first, the moss sample has been incinerated in muffle furnace for 20 hours at the temperature of 800°C. Each sample prepared for subsequent microwave decomposition consisted of moss ash (0.2-1.0 g) and solution of inorganic acids (HCl, HNO$_3$, HF). The samples from 10 to 20 mL have been decomposed in microwave digestion module MAGNUM.

Fig. 1. Moss sample before and after incineration.

After digestion every sample was centrifuged at 3800 rpm. If any undigested fraction occurred, the sample was filtered through glass filter Whatmann C/F, and the residuum was dried and analysed using XRPD.

RESULTS

The Table 1 shows that 95 to 98 % of the organic fraction of moss samples have been incinerated. Ash fraction has been decomposed in solution of HNO$_3$ and HCl (Table 2).

Undisolved fractions were analysed for composition and – as figure 2 shows - they mainly consisted of quartz forms (cristobalite). To get rid of such unwanted undissolved fraction, 4 mL of HF/H$_2$SO$_4$ solution in 1:1 ratio have been added and the sample was decomposed in microvawe digestion module again. As a result clear solution of decomposed moss was obtained.

Tab. 1. Ash fraction after incineration.

sample batch	moss [g]	ash [g]	ash fraction [%]
09S22	76.6	3.5349	4.61
09S6	33.6	0.8280	2.44
09S3	39.6	0.6686	1.69
09S14	23.2	0.4874	2.10

Tab. 2. Digestion mixture composition.

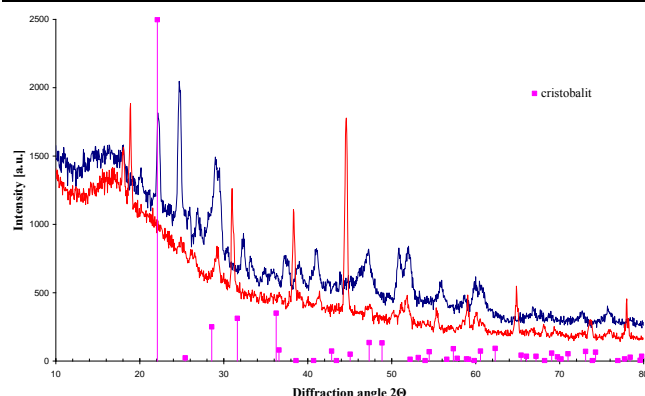| sample batch	moss ash [g]	equivalent moss amount [g]	HNO$_3$ [mL]	HCl [mL]
09S22	0.858	18.5924	15	5
09S22	1.0383	22.4993	3	9
09S22	0.4998	10.8304	7.5	2.5
09S22	0.7986	17.3052	10	10
09S22	0.2974	9.9696	15	5

Fig. 2. Diffraction pattern of undigested fractions with cristobalite diffraction lines (purple).

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COMPARISON OF VARIOUS SAMPLE PREPARATION METHODS FOR ALPHA SPECTROMETRY

Bartl, P.; Fiala, V.; Šťastná, K.; Šuľaková, J.

INTRODUCTION

Alpha-spectrometry requires thin, uniform, and nearly weightless samples because of the energy loss of α-particles by self-absorption [1]. There are three basic methods of alpha-sample preparation: evaporation, co-precipitation, and electrodeposition. In direct evaporation the solution is spread uniformly over counting planchet and solvent is evaporated taking care to prevent splattering and consequent contamination of surrounding work area [2]. Co-precipitation of actinoids with rare-earth fluorides, followed by filtration on a smooth surface membrane filter of small pore size (0.1–0.2 μm) produces good quality alpha sources [3]. In electrodeposition, radioactive material is electrochemically plated from an electrolyte solution onto a polished metal (stainless steel, copper, or other material) cathode planchet, anode being typically platinum wire or gauze [3]. Although the methods of co-precipitation and electrodeposition yield the best energy resolution, they are not always quantitative and are usually relatively demanding and time-consuming. On the other hand, the direct evaporation method has advantage of its simplicity and fastness, but it not always results in thin and uniform sample preparation. In this work three of these methods of sample preparation for alpha-spectrometry performed at the CTU Department of Nuclear Chemistry are compared: direct evaporation, co-precipitation, and electrodeposition.

EXPERIMENTAL

Direct evaporation was based on the results of K. Šťastná et al. [4] who recently compared the quality of alpha-samples prepared by various modifications of the evaporation method such as simple evaporation, evaporation with volatile organic solvent, evaporation in the presence of tensioactive agent and its influence on counting efficiency and energy resolution in order to select the method suitable for screening tests with trace amounts of radionuclides.

In the co-precipitation study, sample for alpha-spectrometry was prepared from a sample of dissolved moss spiked with plutonium and thorium in 3M HNO_3. 100 μL of the dissolved moss was added to 2 mL of 1M HCl in PTFE beaker. 100 μL of 0.5 mg mL^{-1} Ce^{3+} in 1M HCl was also added to the solution. Then, 1 mL of concentrated HF was slowly added drop by drop and the solution was cooled down in cold water for 20 minutes. Then the solution was filtered in PTFE apparatus through membrane filter (pores 0.12 μm). The filter was let to dry and then measured by alpha spectrometry for 3 hours.

As for the electrodeposition, the U and Am sample preparation for alpha spectrometry was performed with two types of electrolytes – Na_2SO_4 + $NaHSO_4$ (sulfate/bisulfate) and $(NH_4)_2(COO)_2$ + $(NH_4)_2SO_4$ + $(NH_3OH)_2SO_4$ (sulfate / oxalate). The conditions of electrodeposition were kept as follows: currency and activity of deposited element were constant, whereas electrodeposition time, voltage, pH, and electrolytic concentration were variable.

RESULTS AND CONCLUSIONS

As it is concluded in the paper by Šťastná [4] the method of simple evaporation of sample without using addition of any substance was evaluated as the fastest and most reproducible for both the aqueous and organic samples. This method was demonstrated to be employable for the evaluation of the distribution ratios of α-nuclides in liquid–liquid extraction studies and was found to perform well for small volumes of diluted or electrolyte/carrier free solutions.

In the case of co-precipitation, the precipitation takes place only in solutions, where the concentration of certain ions is high enough, for the precipitate to be formed. In other words, the solubility product must be exceeded. When working with radionuclides, the concentration of the radionuclide is usually not high enough so a carrier needs to be added. As a carrier one can use a stable isotope. In case of Pu, stable isotope is not available and thus Ce as a chemically similar substance was used here; Pu was then co-precipitated with this carrier. The results of Pu and Th alpha-sample preparation showed the co-precipitation as easy and fast method with high yields.

As for electrodeposition, a significant impact of the electrolyte composition, distance between the electrodes, and time of electrodeposition on alpha-sample deposition yield has been observed. After optimizing the electrodeposition system, the following yields were achived: The highest yield, 91 %, of uranium electrodeposition was reached with deposition time of 2 hours and from solution consisted of 0.068 M Na_2SO_4 + 0.02 M $NaHSO_4$. Because the yield of americium electrodeposition from the sulfate/bisulfate solutions was close to 81 % for the time of deposition 1 hour, another, sulfate/oxalate system was used to increase the yield of electrodeposition. The yield of americium electrodeposition of more than 99 % has been achieved from the solution consisting of 43 g L^{-1} $(NH_4)_2(COO)_2$ + 53 g L^{-1} $(NH_4)_2SO_4$ + 18 g L^{-1} $(NH_3OH)_2SO_4$ and with deposition time of 1 hour.

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DETERMINATION OF LOW ACTIVITIES OF PLUTONIUM USING ALPHA-SPECTROMETRY

Fiala, V.; Němec, M.

INTRODUCTION

This research was concerned with methods of plutonium separation, which is present in low concentrations in the environment. The experiments were conducted as a part of a research project [1]. Plutonium was separated using extraction chromatography from aqueous solutions of dissolved moss in 3M HNO_3. The solution was spiked with ^{239}Pu and Th. Performance of two chromatographic columns for plutonuium separation was compared. Both solid extractants contained Aliquat-336 as a mobile phase but they varied by the supports used. The first one was TEVA column, which is commercially available from Eichrom. The second column contained PAN-A336 material - Aliquat-336 supported on modified polyacrylonitrile beads, which was prepared by Šebesta [2].

For the detection, liquid scintillation counting was used to analyze the eluate. Samples for alpha-spectrometry were prepared from eluate fraction containing the highest alpha activity. Co-precipitation with CeF_3 was used for the sample preparation for alphaspectrometry.

EXPERIMENTAL

Four separations using extraction chromatography were executed. In the first three experiments, TEVA column was used for the separation. In the last experiment, PAN-A336 column was used. The procedure was same for both columns. A sample of dissolved moss in 3M HNO_3 was spiked with ^{239}Pu and Th. The oxidation state of Pu was adjusted to Pu(IV) by the addition of Fe^{2+} and NO_2^-. After every step, the solution was slightly heated and stired for 5 min. Then the solution was loaded on the column. The column was rinsed with 5 bed volumes (BV) of 3M HNO_3. Then, 5 BV of 8M HCl was used for the elution of Th. The column was again rinsed with 5 BV of 3M HNO_3. Pu was eluted by 10 BV of 0.02M HNO_3/0.002M HF. The eluate was being collected by 0.5BV fractions. Samples for liquid scintillation counting were prepared from the eluate. Samples for alpha-spectrometry were prepared from eluate fraction containing the highest alpha activity by co-precipitation with CeF_3. 100 μl of the eluate fraction was added to 2 ml of 1M HCl and then 100 μl of 0.5 mg/ml of Ce^{3+} in 1M HCl was added. Then 1 ml of HF (conc.) was slowly added drop by drop. The solution was then cooled down in cold water for 20 min. The precipitate was then filtrated on the Pragopor 10 filters using PTFE filtration apparatus. The membrane filter was let to dry and then measured with alpha-spectrometry.

RESULTS

The result of each separation is shown as elution curve, where the x-axis shows the eluate volume and the y-axis shows the counts detected by liquid scintillation counting from the elute fractions.

In future, the research will focus on the determination of detection limits and other statistical quantities for both columns to determine which column is more suitable for the separation of Pu in low concentrations.
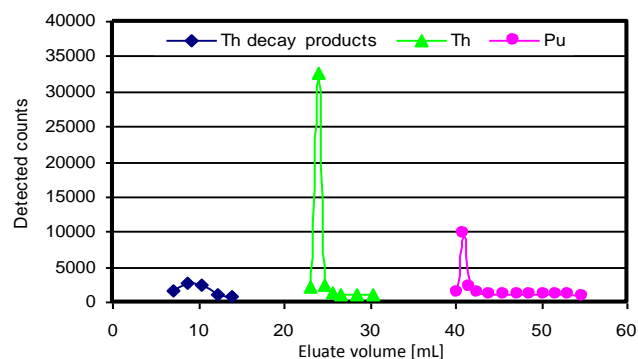
Fig. 1. Elution of Pu and Th from the TEVA column from the sample of spiked dissolved moss.
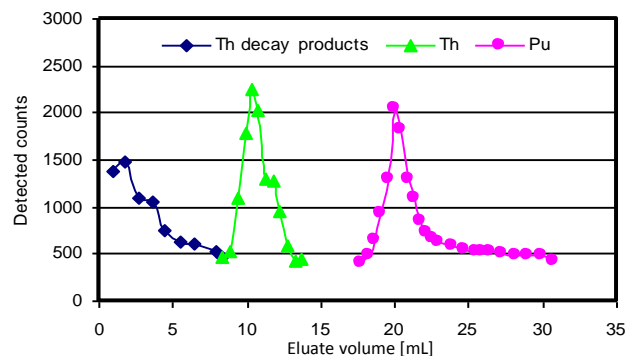
Fig. 2. Elution of Pu and Th from the PAN-A336 column from the sample of spiked dissolved moss.
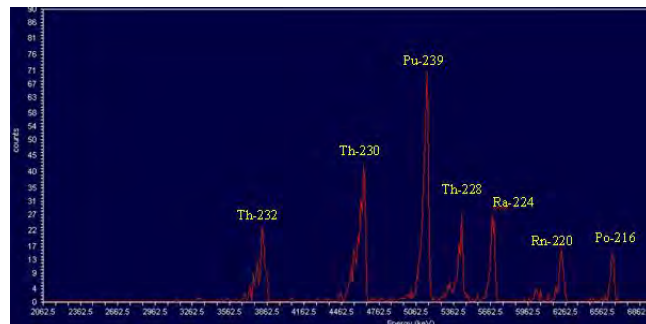
Fig. 3. Alpha spectrum of Th and its decay products and 239Pu. The sample was prepared by co-precipitation.

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VERIFICATION AND CHARACTERISATION OF XRF-ANALYSIS OF THE SPENT ORGANIC SOLVENT FROM DIAMEX PROCESS

Mareš, K.V.; John, J.; Němec, M.

INTRODUCTION

For the study of decontamination of the spent organic solvent from DIAMEX process, a suitable analytical method for determining concentrations of the "difficult-to-strip" elements in the organic solution was needed. Therefore, X-ray fluorescence spectrometry method was characterised and verified for the direct determination of concentrations of problematic elements in this type of solutions.

EXPERIMENTAL

To verify the possibility of using the XRF method for spent solvent analyzis, ruthenium was selected as an analyte. Micro X-Cells (SPEX CertiPrep Group) with one side covered by 4 microns thin polypropylene foil (Premier Lab Supply) were filled with 250 µL of spent solvent and measured using Niton XL3t XRF analyser (Thermo Fisher Scientific) set to "Mining mode Cu/Zn" for 100 s (25 seconds for each filter configuration: main, low, high and light). Because the instrument was not equipped with a built-in calibration for this type of samples, the measured spectra were exported to PC and evaluated using the GamaVision spectroscopic software (ORTEC). All other measurements were made with a filter configuration "Main Range".

To evaluate the repeatability of the method, Micro X-Cells samples measurement was compared with the XRF Universal Sample Cells (Premier Lab Supply; sample volume 1.4 mL) – one micro or universal sample was measured 12 times always removing the sample from the analyzer between the measurements. The further measurements were carried out only in universal cells. One sample was measured 12 times without removing from the analyzer between measurements. Then, 12 samples were prepared by pippeting the spent solvent into the cell and measured. After the measurements, the results were evaluated by calculating the overal uncertainity of the measurement from individual contributions of sample preparation, geometry measurement, instrument measurement repeatability and peak evaluation (GamaVision). The minimum detectable number of pulses A_{min} was calculated as $3\sigma_{IZ}$, where σ_{IZ} was determined from measurements of the pure solvent, i.e. 5 vol% octan-1-ol in kerosene.

The calibration curve was plotted using measurements of the samples prepared by successive dilution.

RESULTS

The overall combined uncertainty of ruthenium determination in the simulated spent organic solvent from DIAMEX process was determined as σ_{XRF} = 1.3 %. The experimentally determined contributions of individual sources of uncertainties such as sample preparation, geometry of the measurement, and instrument measurement repeatability to the overall uncertainty are given in Table 1. The value σ_{IR} is obtained from the GamaVision

programme and is given by peak evaluation (peak area calculation) and the statistical character of radioactive decay.

Tab. 1. Experimentally determined contributions to the overall uncertainty of sample measurement of Ru in spent solvent.

origin of uncertainty	partial relative standard deviation [%]
peak evaluation	σ_{IR}
instrument measument repeatability	0.40
geometry	0.89
sample preparation	0.90

Calibration curves were determined for Ru and Y in the next phase. Both calibration curves were linear (see Figure 1) therefore it was concluded that the XRF is a suitable method for the analysis of spent solvents from DIAMEX process and for the decontamination studies of these solvents.
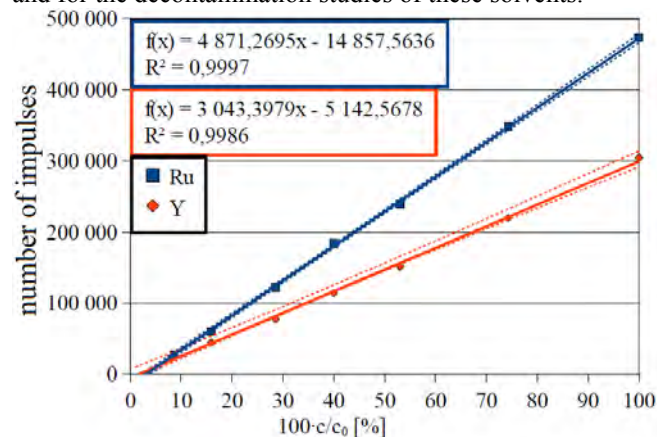
Fig. 1. Calibration curves of Ru and Y. Uncertainties plotted at the significance level 0.95.
(100 % Ru = 68 mg·L^{-1}, 100 % Y = 14 mg·L^{-1}; measurement time 1000 s)

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X-RAY FLUORESCENCE ANALYSIS OF SMALL SAMPLES OF MIXED URANIUM, CERIUM AND EUROPIUM OXIDES

Sajdová, A.; Šebesta, F.

INTRODUCTION

In scope of the European project ACSEPT (2008 – 2012) a new method of preparation of mixed uranium and minor actinides oxides was developed at the Department of Nuclear Chemistry. These materials should be used as precursors for the Generation IV nuclear reactor´s fuel manufacture. Cerium and europium were utilized as the analogues of plutonium and americium in model preparation of the above mentioned mixed oxides. There was a need to control a composition of mixed oxides during development of the method for U, Ce and Eu conversion from solutions to solids (mixed oxides). The aim of this work was to develop and verify a routine method for the determination of composition of small amounts of the powder samples of mixed oxides.

EXPERIMENTAL

NITON XL3t portable XRF analyser (Thermo Fisher Scientific) with 40 kV X-Ray lamp and 20 kV Cu filter was used for the measurements. Measurements were performed in the „Mining mode Ta/Hf" for the time of 300 sec. Micro X-Cell (SPEX CertiPrep Group) plastic ampoules of the respective diameter covered with 4 μm polypropylene foil (Premier Lab Supply) were used. For the calibration curves preparation oxides U_3O_8, CeO_2 a Eu_2O_3 of an analytical purity were used. Mixtures of oxides were prepared by the following procedure: weighted amounts of the respective oxides were carefully pulverized in an agate mortar, chosen amount of the sample was regularly spread on the foil and pressed with a glass stick of the suitable diameter.The measured spectra were exported to PC and evaluated in Maestro software (EG&G Ortec). The content of cerium and europium in the samples was determined from calibration curves constructed as the dependence of the peak area on the amount of CeO_2 or Eu_2O_3 in the sample.

RESULTS

XRF spectra of CeO_2, Eu_2O_3 a U_3O_8 were measured in the introductory experiments and the appropriate energetic peaks for the quantification of cerium and europium oxides admixtures in uranium oxide were chosen. The 4.84 keV peak was used for the quantification of the cerium oxide while the 5.85 keV peak was used for the quantification of the europium oxide admixture in uranium oxide. The 6,85 keV peak can be used for the quantification of the europium oxide in cerium oxide matrix. Uranium content could be estimated with the use of the 13,61 keV peak. From the measured spectra, it was found that it is not possible to determine simultaneously the content of europium and cerium oxides in the mixture with the uranium oxide.

Since only minimal amount of the sample could be utilized, preparation of pellets from the oxides was not considered. The factors possibly influencing analytical reproducibility were monitored in the following experiments. Above all, a minimal amount of the sample providing a saturated layer for the measurements was determined. Further, the influence of the compression of the sample before measuring was studied. It was found that compression of the sample significantly influences the peak area in the XRF spectra and improves the reproducibility of the analyses. The samples were therefore pressed and fixed in the position before each measurement. The uncertainty of the count rate associated with the counting statistics only was 4.5 %, it increased to 6 % when combined with the uncertainty of the position of the sample in the analyser during repeated insertions and removals of the samples to/from the measurement position. The uncertainty of 4.5 % was sufficient for this study and therefore three types of calibration curves were prepared for the analysis of mixed oxides. 30 mg samples (saturated layer) with the content of minor compound from 3 to 30 w/w % were used for the preparation of standards for the determination of the calibration curves. The calibration curves measured were characterized by linear regression (**y** represents the peak area and **x** represents the content of the minor oxide in the analysed sample).

$y = 1.2533x – 0.6741$ ($R^2 = 0.9987$)
for Eu_2O_3 in the mixture with U_3O_8

$y = 0.9325x – 0.4795$ ($R^2 = 0.9889$)
for CeO_2 in the mixture with U_3O_8

$y = 0.1139x – 0.1859$ ($R^2 = 0.9928$)
for Eu_2O_3 in the mixture with CeO_2

The established procedure was applied to the analysis of the samples of mixed oxides prepared by the developed method. Within the accuracy of the measurement, the results for the minor components of the oxides were in good agreement with the compositions expected based on the compositions of the starting solutions. Hence, the above described method may suit its purpose. However, it cannot be used for the analysis of samples containing all the three oxides, since the characteristic peaks overlap. The results also showed that this method is not suitable for the determination of the major component of the mixtures.

SELECTIVELY LABELLED HETEROCYCLIC BETULIN AND BETULINIC ACID DERIVATIVES

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Palacký University Olomouc

INTRODUCTION

Triterpenoids are a large group of natural compounds that are found in numerous living organisms, and are particularly prevalent in plants. They often have a variety of biological activities.[1] Betulinic acid (**2**) has strong anti-HIV [1] and anti-cancer [1] activities and belongs to a group of the most interesting lupane derivatives.

The aim of this work was to synthesize a set of derivatives of lupane, lup-20(29)-ene, and 18α-oleanane, and to investigate their cytotoxic activity. Some of those heterocycles were previously known in the oleanane (allobetulin) group; however, to our knowledge the syntheses and biological activities of lupane heterocycles have not been reported before.

EXPERIMENTAL

Among hundreds of new compounds, we have synthesized several derivatives of lupane that are highly cytotoxic in a variety of cancer cell lines *in vitro*, including those that are resistant against current chemotherapy.[1] Previously, we described partial synthesis of triterpenic heterocycles,[2] in which a pyrazine ring was connected to the A-ring and ¹⁵N-labelled analogues of lupane derivatives. Within this set of pyrazines, three compounds were significantly cytotoxic *in vitro* to warrant the extension of the *in vitro* studies to *in vivo* testing in mice. All of the active compounds have a single pyrazine ring that is connected to the A-ring of **2**.
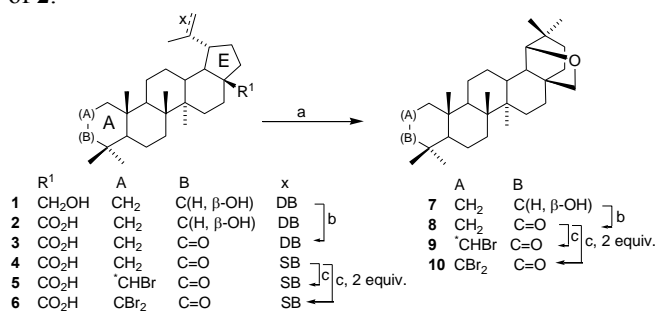

	R¹	A	B	x		A	B	
1	CH₂OH	CH₂	C(H, β-OH)	DB		**7**	CH₂	C(H, β-OH)
2	CO₂H	CH₂	C(H, β-OH)	DB		**8**	CH₂	C=O
3	CO₂H	CH₂	C=O	DB		**9**	*CHBr	C=O
4	CO₂H	CH₂	C=O	SB		**10**	CBr₂	C=O
5	CO₂H	*CHBr	C=O	SB				
6	CO₂H	CBr₂	C=O	SB				

Fig. 1. Preparation of starting material for the synthesis of heterocycles. Reagents and conditions: (a) Montmorillonite, CHCl₃, reflux; (b) CrO₃, DMF; (c) Br₂, AcOH, AcON

The promising cytotoxicity of triterpenic pyrazines,[2] nonterpenic heterocycles, and pyrrole and indole derivatives of **2** [3] encouraged us to synthesize several different types of heterocycles. Except for a few cases,[3] most efforts to modify **2** have focused on heterocycles, wherein a heterocycle is condensed with the A-ring.

Starting from betulin (**1**) and betulinic acid (**2**), we prepared 3-oxocompounds and 2-bromo-3-oxocompounds **3 – 10**.

By the condensation of these intermediates with ethylendiamine (resp. ¹⁵N-ethylendiamine dihydrochloride) or thiourea, pyrazines **11** and **12** (resp. ¹⁵N – analogues) and thiazoles **13 - 16** have been synthesized.

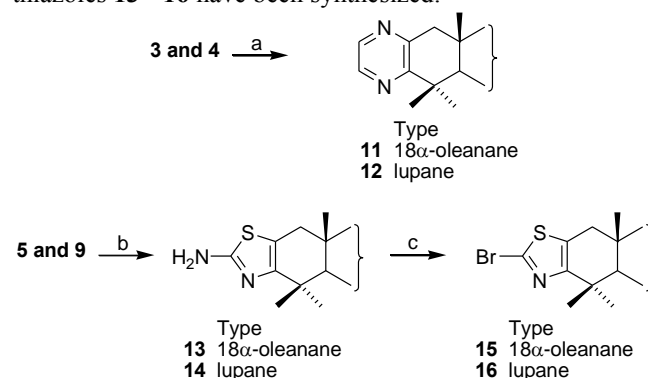**Fig. 2.** Reagents and conditions: (a) Ethylendiamin (resp. 15N-ethylendiamin dihydrochloride, morpholin, sulfur, reflux; (b) Thiourea, morpholine, reflux; (c) Isoamylnitrite, TBAB, CHCl3.

The reaction of both 2-bromoketones **5** and **9** with thiourea gave the best yield of the corresponding aminothiazoles **13** and **14** in morpholine at reflux, whereas larger amounts of the side-product diosphenol were obtained when other solvents were used. Amines **13** and **14** were further modified into the bromo derivatives **15** and **16** by converting them into the corresponding diazonium salts.

The cytotoxic activity of all the compounds that were synthesized was measured in T-lymphoblastic leukemia CEM cells.

RESULTS

In this study, we prepared triterpenes with heterocycles condensed to the A-ring of betulonic acid (**3**), dihydrobetulonic acid (**4**), and allobetulone (**8**). To increase the number of compounds for biological testing, we also included several known heterocycles. All of these compounds were tested for cytotoxicity in T-lymphoblastic leukemia CEM cells *in vitro*; however, these compounds were not as active as previously prepared derivatives of pyrazines.[2] Poor solubility of the heterocyclic derivatives in water-based media and other solvents might be the main reason for their low cytotoxicity.

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Radiation Chemistry

RADIOLYTIC FORMATION OF FERROUS AND FERRIC IONS IN CARBON STEEL - DEAERATED WATER SYSTEM*

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INTRODUCTION

Processes occurring at the steel-water interface in the presence of ionizing radiation (IR) might significantly threaten the stability of steel spent nuclear fuel containers in a deep geological repository after groundwater leakage. The rate and mechanism of corrosion processes and the formation of protective layers on the surface of steel are predominantly affected by the concentration of dissolved oxygen in water, the presence of various ions/minerals, and pH values (Sunder et al., 2004, Smart et al., 2008).

The primary motivation of the work presented in here was (a) to investigate the impact of radiation on formation of Fe^{2+} and Fe^{3+} ions in deaerated steel/water system with respect to corrosion of steel spent nuclear fuel containers after groundwater leakage into deep repository, (b) to characterize formed solid crystalline corrosion products.

EXPERIMENTAL

The influence of gamma irradiation on the formation of Fe-ions was investigated, with respect to the expected ingress of groundwater into the disposal site with spent nuclear fuel containers. Steel plates submerged in deionized water were irradiated using ^{60}Co gamma source. Deaerated conditions were ensured by working in an inert atmosphere. The kinetics of Fe^{2+} and Fe^{3+} formation in the presence of ionizing radiation was studied. Characterization of crystalline solid corrosion products using X-ray powder diffraction was performed.
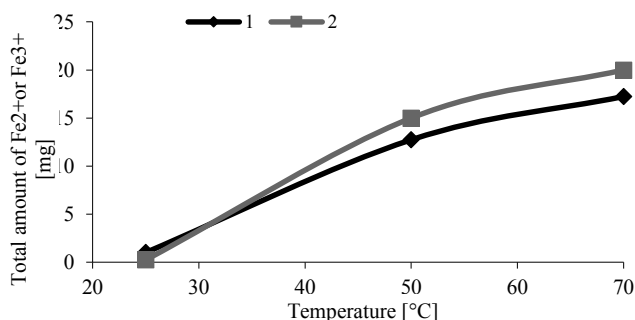

Fig. 1. Dependence of total amount of 1 – Fe^{2+} or 2 – Fe^{3+} ions found in solid and liquid phase on temperature of irradiation (dose 90 kGy) in deionized water saturated with nitrogen.
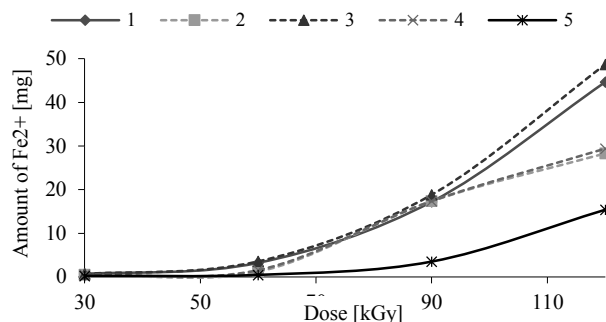
Fig. 2. Dependence of Fe^{2+} formation on the dose at 70°C in granitic water and deionized water; comparison of non-deaerated system with systems saturated with nitrogen or helium. 1 - deionized water; 2 - deionized water deaerated with nitrogen; 3 – granitic water; 4 - granitic water deaerated by nitrogen; 5 – granitic water deaerated with helium.

RESULTS

In the absence of oxygen, or after consumption of oxygen by corrosion in a closed system, corrosion in the presence of γ-radiation proceeds mainly via reaction with the intermediate products of water radiolysis (mainly OH, H_2O_2, HO_2· radicals). The radiation increases amount of corrosion products; it affects their composition mainly via radiation oxidation of ferrous to ferric ions. Under given conditions, the composition of solid crystalline corrosion products does not depend on temperature, but rather on the presence of other compounds in water. On the other hand, the amount of corrosion products in an irradiated system does depend on the temperature and on the dose; other compounds present in water affected the total amount of corrosion products only marginally. In the solid phase formed during contact with deionized water, the predominant crystalline corrosion products were magnetite and lepidocrocite.

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PHOTOCHEMICAL PREPARATION OF ZINC OXIDE NANOPARTICLES*

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INTRODUCTION

Zinc oxide, commonly occurring as hexagonal wurtzite, is the n-type semiconductor with large direct band gap (~ 3.4 eV) and large exciton binding energy 60 meV. It has been intensively studied due to its piezoelectric, pyroelectric, photocatalytic and conductive properties and it has currently wide range of possible applications, including acoustic wave devices, optical waveguides, LED diods, solar cells, chemical sensors, photovoltaic devices (Tak and Yong 2008; Yuan et al. 2010).

The aims of presented work were (a) to prepare crystalline zinc oxide, both pure and doped with lanthanum, from aqueous solutions via UV irradiation; (b) to characterize formed solid phase; (c) to study the effect of heat treatment on the solid phase; (d) to study the scintillation properties of prepared pure and doped zinc oxide.

EXPERIMENTAL

Solution **a**: zinc nitrate dissolved in aqueous solution of 1.3 mol dm^{-3} propan-2-ol.

Solution **b**: zinc formate dissolved in aqueous solution of 1 mol dm^{-3} hydrogen peroxide.

Solution **c**: zinc formate dissolved in aqueous solution of 1 mol dm^{-3} hydrogen peroxide and 10^{-5} mol dm^{-3} polyvinylalcohol (PVA).

Medium pressure mercury lamp UVH 1016-6 (UV Technik Meyer GmbH) emitting photons at wavelengths 200-580 nm, with variable power output 140-400 W, was used. The lamp in quartz tube was immersed in 2 dm^3 of solutions in glass reactor with thermometer. During irradiation, the solutions were continually stirred and the reactor was cooled with water, so that the temperature of irradiated solution did not exceed 45°C.

After irradiation, the finely dispersed solid phase was separated via microfiltration (Millipore HAWP 0,45 μm), dried at 40°C to the constant weight and treated 2h at temperatures 250, 650 or 1000°C in air using Clasic 0415VAK oven. Additionally, some samples were treated 0.5 h at 800°C in the stream of H$_2$/Ar mixture (1:20), to evaluate the effect of annealing in reduction atmosphere on radioluminescence spectra.

RESULTS

Crystalline zinc oxide was prepared by UV irradiation of aqueous solutions containing zinc nitrate and propan 2 ol, or zinc formate and hydrogen peroxide at ambient temperature. Solution containing zinc formate, hydrogen peroxide and polyvinyl alcohol yields pure zinc peroxide. Calculated size of the crystallites depends on the initial solution and varies between 1 nm and 70 nm. Calcination at 650 and 1000°C leads to further increase in particle size up to hundreds of nm and to the decrease of specific surface area of the material.
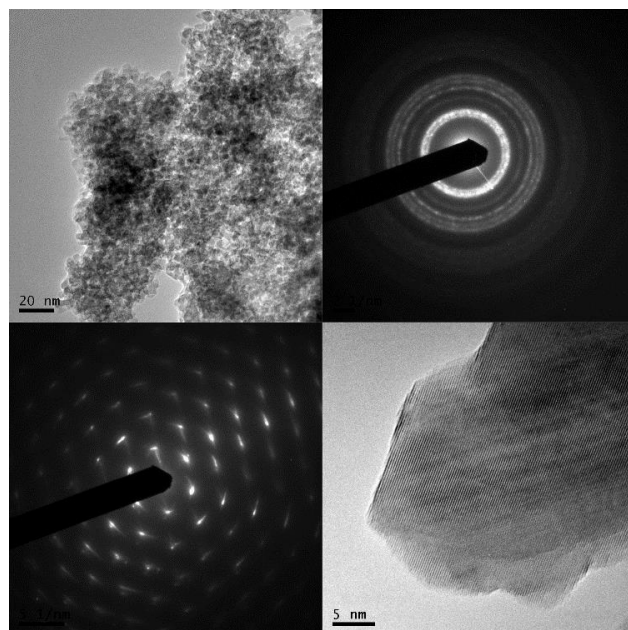
Fig. 1. Upper left HRTEM image of sample b dried at 40°C; upper right SAED image of sample b dried at 40 °C; lower left HRTEM image of sample b calcinated at 1000 °C; lower right SAED image of sample b calcinated at 1000 °C.

Zinc oxide was successfully doped with lanthanum by adding lanthanum acetate to irradiated solutions. Scintillation properties depend strongly on initial precursors, calcination temperature and doping with foreign ions; all prepared materials calcinated at 650 and 1000°C show well shaped visible luminescence. Most intensive UV luminescence at 395 nm showed materials prepared from aqueous solution containing zinc formate, lanthanum acetate and hydrogen peroxide, treated at 1000°C. Further enhancement of UV emission was achieved by the subsequent annealing in reduction H$_2$-containing atmosphere at elevated temperature.

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RADIATION INDUCED SYNTHESIS OF POWDER YTTRIUM ALUMINIUM GARNET*

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INTRODUCTION

Yttrium aluminium garnet $Y_3Al_5O_{12}$ (YAG) is synthetic crystalline material with cubic structure. Powder YAG may be used for preparation of transparent optical ceramics. When doped with luminescent ions (e.g. trivalent lanthanides), such ceramics may serve as cheaper alternative to monocrystalline YAG for applications in solid-state lasers, as phosphor in cathode ray tubes (Zhou et al., 2002), in radiation dosimetry or as a scintillating material also in an optical ceramic form. Recently, also the application of YAG:Ce phosphor in white LED light source R&D was reported (Mueller-Mach et al. 2005).

We report simple method for YAG synthesis via irradiation of precursors in aqueous solutions. The aim of this work was (a) to prepare solid phase from aqueous solution containing YAG precursors, using ionizing or non-ionizing radiation (b) to prepare and characterize YAG after calcination (c) to perform preliminary study of termoluminescence and radioluminescence properties of prepared material.

EXPERIMENTAL

Yttrium-aluminium garnet powders were prepared from aqueous solutions containing yttrium nitrate and aluminum chloride or nitrate via irradiation with accelerated electrons or UV light and via consequent calcination of formed solid phase.
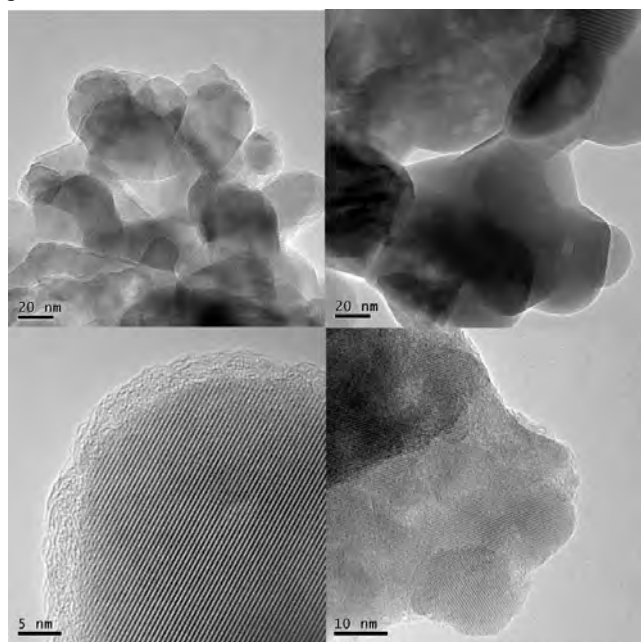

Fig. 1. TEM images of solid phase formed under irradiation and calcined at 1000°C. Upper and lower left – formed under UV irradiation; upper and lower right - formed under accelerated electrons irradiation.

RESULTS

Irradiation route presents simple method for powder YAG synthesis. The preparation enables fast production of good amounts of powder material. Moreover, no strict control of experimental conditions is required. Powder YAG was successfully prepared from aqueous solutions containing yttrium nitrate, aluminium chloride or nitrate and potassium formate, using UV or accelerated electrons irradiation. The former is more convenient for YAG synthesis; YAG phase was first observed in material formed under UV irradiation of solution containing yttrium nitrate, aluminium chloride and potassium formate, after calcination for 1h at 900°C; calcination of the same material for 1h at 1000°C yields pure powder YAG with well developed single crystals.

After accelerated electrons irradiation, YAG phase is still the major component of prepared material, but some amounts of yttrium oxide or alpha-aluminium oxide were also detected after 1h calcination at 1000°C or 1300°C.

All prepared materials show leading radioluminescence peak at 530 nm typical for the Ce^{3+} doped YAG structure. Materials formed under UV irradiation have more intensive radioluminescence in both visible and UV area than those formed under accelerated electrons irradiation. RL intensity of the best prepared material exceeds several times RL intensity of BGO standard. Thermoluminescence glow curves show distinctive peaks at 135 - 140°C and 240 – 250°C which are most probably due to oxygen vacancy-based electron traps. Again, the most intensive thermoluminescence is shown by materials prepared under UV irradiation.

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* Full article in: Radiat. Phys. Chem. 80 (2011) 957‑962

PHOTO- AND RADIATION INDUCED PREPARATION OF Y$_2$O$_3$ AND Y$_2$O$_3$:Ce(Eu) NANOCRYSTALS*

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INTRODUCTION

A convenient method for preparation of pure and doped yttrium oxide was developed, which is based on irradiation of solutions containing yttrium nitrate and ammonium formate with UV light or accelerated electrons.

Radiation-induced reduction of metal ions in the presence of ·OH radical scavengers (e.g. formates or propan-2-ol) is an efficient method for the preparation of nanocrystalline metals [1] or metal oxides [2]. UV irradiation may be used with similar results for this purpose [3].

Porous yttrium oxide with high surface area is used as a selective catalyst for various reactions; pure or doped Y$_2$O$_3$ is used to manufacture phosphors and ceramics [4].

EXPERIMENTAL

Aqueous solutions containing 5×10^{-3} mol dm^{-3} yttrium nitrate tetrahydrate, 0.15 mol dm^{-3} ammonium formate and, for preparation of doped oxides, also 5×10^{-6} to 10^{-4} mol dm^{-3} cerium nitrate or 2.5×10^{-5} europium nitrate were irradiated by UV light or accelerated electrons.

UV irradiation was performed using medium pressure mercury lamp UVH 1016-6. Solutions were irradiated for 60 min with photon flow 2×10^{19} hv s^{-1}.

High-energy electron irradiation was performed using pulse linear electron accelerator LINAC 4-1200. Applied dose was 80 kGy.

After irradiation, the finely dispersed solid phase was separated via microfiltration, washed with water, dried at room temperature and then calcined for 2 hours at temperatures 500 - 1200 °C in air.

The solid phase was characterized via X-ray powder diffraction (XRPD), mass spectrometry coupled with thermal analysis (TGA-MS), specific surface area (SSA), X-ray fluorescence (XRF), selected area electron diffraction (SAED) and scanning or high resolution transmission electron microscopy (SEM, HRTEM).

Radioluminescence spectra were measured at room temperature under the excitation by X-ray tube. To evaluate the scintillation performance, the Bi$_4$Ge$_3$O$_{12}$ (BGO) standard scintillator was used for quantitative comparison.

RESULTS

Both photochemical and radiation techniques present simple alternative methods for yttrium oxide preparation. Similarly to other techniques, thermal treatment is necessary to obtain material with good crystallinity. Yttrium oxide nanocrystals were first observed after annealing of solid phase for 1 hour at 500 °C in air (Fig. 1). At 500 °C, material prepared under UV radiation shows better developed crystals than material prepared under accelerated electrons.

Prepared yttrium oxide has high specific surface area (up to 58 m^2 g^{-1}) and contains nanoparticles of 25 to 100 nm in diameter depending on preparative conditions, and with narrow size distribution. SEM images show that after irradiation and subsequent calcination, particles with uniform size and roughly spherical shapes are formed.
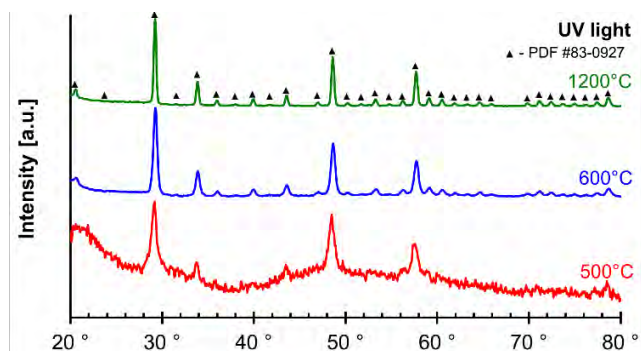
Fig. 1. XRPD patterns of the solid phase formed under UV irradiation, calcined at 500, 600 or 1 200 °C for 1 h and compared to Y$_2$O$_3$ standard (PDF #83-0927).

Addition of small amount of cerium(III) or europium(III) nitrates to irradiated solutions resulted in doping of yttrium oxide with Ce(III) or Eu(III) ions.

In Y$_2$O$_3$:Ce,Eu materials, only XRPD lines corresponding to yttrium oxide were found and no presence of separate phases of dopants was observed. With increasing concentration of Ce^{3+}, low angle shift of diffraction lines was observed, and with increasing temperature of calcination the monotonous increase in particle size of both pure and doped materials occurs.

In the doped oxides Y$_2$O$_3$:Eu, intensive radioluminescence spectra typical for Eu^{3+} doped oxide structures were observed, whereas only weak Ce^{3+} band was observed for Y$_2$O$_3$:Ce.

Photochemical variant of preparation is simpler, as the irradiation equipment is easily accessible; however, accelerated electrons offer two important advantages – quantitative yield of solid phase and superiority with respect to the doping with foreign ions.

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RADIATION-INDUCED PREPARATION OF PURE AND Ce-DOPED $Lu_3Al_5O_{12}$ AND ITS LUMINESCENT PROPERTIES*

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INTRODUCTION

In recent decades, ionizing radiation has been successfully employed for the preparation of various metallic, alloyed or core-shell nanoparticles [1]; however, papers dealing with radiation-induced formation of oxides or other compounds are rather scarce. Our research group prepared a multitude of different compounds [2], including amorphous or weakly crystalline precursors for mixed oxides such as garnets.

The aim of this work was to investigate the potential indirect synthesis of nanocrystalline $Lu_3Al_5O_{12}$ (LuAG). This garnet, when doped with $5d – 4f$ emitting ions (Ce^{3+}, Pr^{3+}), features very intensive and fast scintillation and is suitable for many applications including fabrication of optical ceramics [3].

EXPERIMENTAL

The aqueous solutions containing 3 mmol dm^{-3} $Lu(NO_3)_3$ or $LuCl_3$, 5 mmol dm^{-3} $Al(NO_3)_3$ or $AlCl_3$ and 0.1 mol dm^{-3} ammonium formate $HCOONH_4$ were irradiated by UV light (medium pressure mercury lamp) or accelerated electrons (mean energy 4.5 MeV). Formed gelatinous solid phase was filtered using microfiltration cell and Millipore 0.45 μm filter, dried and then calcined at various temperatures in air. Formed solid phase was characterized by X-ray powder diffraction (Cu-K$_\alpha$), X-ray fluorescence spectroscopy (Niton XL3t 900), thermal analysis (Setaram Labsys Evo) and electron microscopy (JEOL 3010). The luminescence of powders prepared from solutions doped by $Ce(NO_3)_3$ was studied using X-ray, deuterium lamp or LED excitation.

RESULTS

Solid phase prepared using electron-beam irradiation and calcination at $\geq$ 1000 °C consisted of Lu_2O_3, $Lu_3Al_5O_{12}$ and perovskite $LuAlO_3$, whereas in the powder formed using UV light only pure garnet phase was present. The minimum temperature needed for LuAG crystallization was ca. 900°C (Fig. 1, confirmed by thermal analysis).
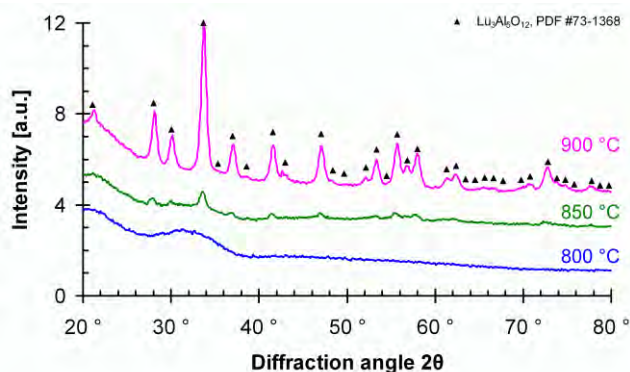
Fig. 1. Diffraction patterns of $Lu_3Al_5O_{12}$ precursor prepared by UV light and calcined at different temperatures.

The size of formed nanoparticles was calculated from the diffraction profiles and accounted for ~17 nm at 950 °C, ~36 nm at 1200°C. Rounded nanoparticles of corresponding dimensions were observed by high-resolution transmission electron microscopy, with slight intergrowth only at higher

temperatures; nanocrystalline LuAG phase was confirmed by electron diffraction patterns as well.

Prepared LuAG nanoparticles doped by Ce ions exhibit properties typical for bulk LuAG:Ce crystal (Fig. 2, double emission band of Ce^{3+} $5d – 4f$ transition at ca. 510 nm, two $4f – 5d$ excitation bands at 347 and 450 nm). However, the measured mean lifetime (decay time) of this transition was significantly higher than ~58 ns observed in single crystals and changed with the technique used for sample preparation (Tab. 1). This behaviour was successfully explained by the influence of surrounding medium on local refractive index (scale ~150 nm) and therefore on luminescence decay times [4], independently confirming the nanoparticle character.
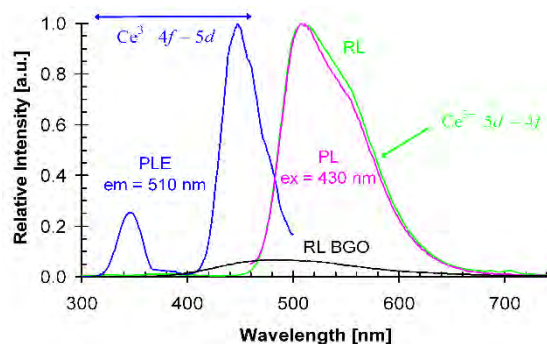
Fig. 2. Photoluminescence excitation (PLE), emission (PL) and radioluminescence (RL) spectra of compacted $Lu_3Al_5O_{12}$:Ce 0.5% calcined at 1400 °C, compared to the RL spectrum of the BGO reference scintillator.

Tab. 1. Luminescence decay times of Ce^{3+} 5d – 4f transition influenced by medium surrounding the nanoparticles.

Sample preparation	Surrounding medium	n_{med}	τ_{decay} Ns
Powder in glue	nitrocellulose	?	87
Free-standing powder	air	1.00	117
Powder in oil	immersion oil	1.52	67.4
Compacted powder	~ bulk crystal	1.84	58.3

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CATALYTIC PROPERTIES OF RADIATION-INDUCED NANOSILVER

Zdychová, V.; Silber, R.

INTRODUCTION

Nanosilver is due to its unique physical and chemical properties suitable material usable in many scientific applications (optics, electronics, catalysis). Therefore, considerable attention is devoted to methods of preparation of silver nanoparticles and studies of their properties. In recent years increased attention is paid also to the method of radiation-induced preparation of nanoparticles.

EXPERIMENTAL

Nanosilver was prepared by irradiation of aqueous silver nitrate ($0,1$ mol.dm^{-3}) and Triton X-100 (reducing agent, stabilizer) solution with fast electrons (4.5 MeV) up to doses of 24 kGy. Samples were characterized by UV/VIS spectroscopy and TEM (Fig. 1). Quantity of prepared nanosilver was determined by potentiometric method. Changes of pH values of irradiated solutions were also measured in dependence on applied doses.

RESULTS

Fig. 2 presents the dependence of amount of nanosilver produced by reduction of Ag$^+$ ions on the applied dose.

It was found that the pH value of prepared solutions decreased with increasing radiation dose from pH=5 (non-irradiated sample) up to 2,5 (sample irradiated by dose of 24 kGy).
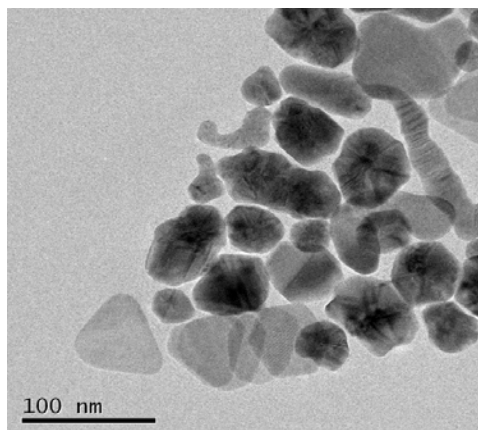
Fig. 1. Size of irradiation induced silver nanoparticles fixed on $CaSO_4.2H_2O$ and measured by TEM.

Furthermore, the reaction of hydrogen peroxide decomposition was selected for study of the influence of applied irradiation dose on catalytic activity of silver nanoparticles themselves (Fig. 3). The rate of H_2O_2 decomposition was detected by measuring the pressure increase in a closed system with sensitive manometer.

At the reaction temperature of 25 °C it was showed that the stabilization of nanoparticles is needed. Owing to this, method of nanoparticles fixation onto the solid support – $CaSO_4.2H_2O$ from solution was selected. Catalytic activity of samples prepared by this method was expressed as a rate constant k_m corresponding to the reaction order 1.5, related to the weight of catalyst.
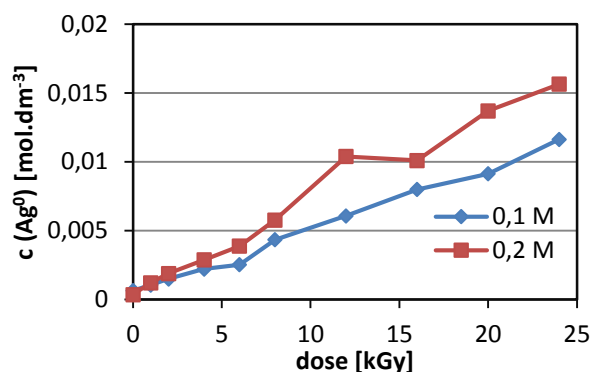
Fig. 2. Dependence of amount of nanosilver produced by reduction of Ag$^+$ ions on the applied dose. (0.1 and 0.2 M – initial concentrations of H_2O_2 solution
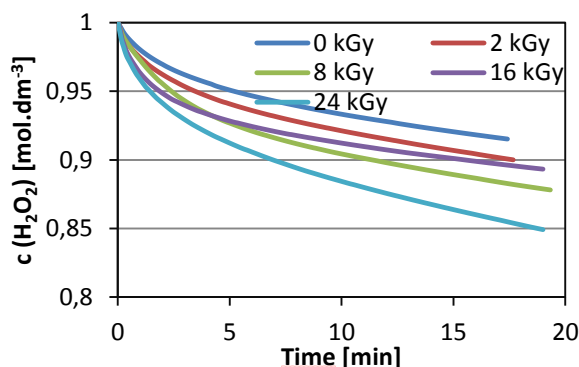
Fig. 3. Dependence of catalytic activity of fixed nanosilver on applied dose.

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METHOD FOR INDICATIVE DETERMINATION OF THE SOIL OR WATER CONTAMINATION WITH POLYCHLORINATED BIPHENYLS AND EQUIPMENT

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TECHNICAL FIELD

The invention relates to the determination of soil or water contamination with polychlorinated biphenyls (PCBs) or other chlorinated hydrocarbons and equipment for its implementation.

BACKGROUND OF THE INVENTION

Existing methods of determining soil or water contamination of PCBs or other chlorinated hydrocarbons depend on the matrix samples and generally consist of the following steps: a) sampling and drying (except liquid and oil samples), b) adaptating, granulating and homogenizing the sample, c) extracting into an appropriate organic solvent (usually hexane or a mixture of hexane and diethylether is used), d) separating the extract from the soil or water d) removing interfering substances from the extract, e) analysing chromatograms, f) evaluating chromatograms.

Technical PCB mixtures contain tens of congeners with different numbers of chlorine atoms in the molecule in varying proportions, so the determination of PCBs is a rather difficult analytical problem. For the analysis of these compounds gas chromatography (GC) with an electron capture detector (ECD) is almost exclusively used.

The results are in accordance with the methodology of Ministry of the Environment of the Czech Republic given as the sum of the contents indicator congeners (PCB 28, 52, 101, 138, 153, 180). Quantitative evaluation of the results of the analysis is carried out by comparing the peak areas of indicator congeners and external standard with known concentration. Calculation of PCB concentration is done for each indicator congener and the sum of the values obtained for all indicator congeners is given as a result.

Such a method of PCB determination is obligatory. The above-mentioned method is not suitable as a test procedure for tentative determination of PCBs or other chlorinated hydrocarbons, which should be rapid and easy to use, because of the following shortcomings.

Firstly, it is necessary to perform the extraction of chlorinated hydrocarbons, particularly PCBs from dried soil samples or contaminated water into hexane, or a mixture of it and diethyl ether, which are according to Regulation EC 1907/2006 volatile, harmful (Xn), highly and extremely flammable (F , M+) and environmentally harmful (hexane) organic substances.

Secondly, it is necessary to dry the contaminated soil samples, which extends the analytical procedure. When testing samples of contaminated soil the residual water can still reduce extraction efficiency, which results in lower determined levels of contamination.

Thirdly, an expensive and time-consuming analysis - gas chromatography with ECD - with a relatively complex evaluation of the measured chromatograms is needed. These draw-backs of the current technology for the determinination of the total organic chlorine content are largely removed (for the determination of soil or water contamination by PCBs or other chlorinated hydrocarbons) by the procedure and equipment according to the current invention.

PRINCIPLE OF INVENTION

The subject of the invention is a method of determining contamination of soil or water with PCBs or other chlorinated hydrocarbons, whose principle is based on a) the tested sample of soil or water contaminated with PCBs or other chlorinated hydrocarbons is contacted with excess of solubilisation agent comprising an aqueous solution of ethoxylated alkyl phenols with the number of ethylene oxide units in the range of 7-20, preferably an aqueous solution of Triton X-100 ($C_{14}H_{22}O$ $(C_2H_4O)_n$, 4 - (1,1,3,3-tetramethylbutyl)-phenyl polyethylene oxide, n = 9,5 ethylene oxide units) at a concentration of 0.5 to 5 wt. % (non-volatile, water-soluble) to convert chlorinated hydrocarbons in a micellar system,

b) the resulting aqueous phase is separated from the soil,

c) pH in the separated phase, which contains PCBs or other chlorinated hydrocarbons, is adjusted to pH 8.2-11.9 by a carbonate / hydrogen carbonate buffer,

d) the prepared aqueous phase is placed into glass ampoules, in which it is irradiated by a beam of accelerated electrons with doses ranging from 1 to 100 kGy at a dose rate of 10 to 10^3 kGy.s^{-1} to form the reaction product - inorganic chloride ions created by reactions of organically bound chlorine atoms with radiation induced reactive particles coming out of the water and the surfactant Triton X-100 dissolved in the extracted phase,

e) determination of the content of radiolytically produced chloride ions using a chloride electrode potentiometry or by liquid chromatography with spectrophotometric or potentiometric detection.

For the determination, the present invention preferably utilizes a beam of electrons from 1 to 250 µA accelerated to an energy level of 4 MeV.

When determined in accordance with this invention, the content of the products of radiolysis - inorganic chloride determined potentiometrically using chloride electrodes - allows to determine chloride concentration down to 10^{-5} mol.l^{-1} in the aqueous phase in conventional arrangement.

THE METHOD OF RADIATION DECHLORINATION OF POLYCHLORINATED BIPHENYLS AND OTHER CHLORINATED ORGANIC COMPOUNDS

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BACKGROUND OF THE INVENTION

Existing disposal of chlorinated organic compounds is performed classically by their combustion (e.g. PCBs are burned in special furnaces at temperatures higher than 1100 °C). The alternative methods are their biodegradation or chemical degradation and their radiation degradation.

The disadvantages of combustion methods are their economic costs and in particular the risk that the incomplete combustion of chlorinated hydrocarbons creates more toxic substances, e.g. dioxins and benzofurans for PCBs, which may be dispersed in the atmosphere. Biodegradation has another serious problem – the need for a microbial culture, which would be able to consistently and with satisfactory rate degrade chlorinated derivatives. The chemical degradation has problems connected to the relatively high stability of the chlorinated derivatives, especially of PCB.

Radiation degradation of PCBs can be successfully performed in certain alcoholic solutions (e.g. alkaline 2-propanol) using gamma radiation from Co-60 or electrons with an energy of about 4 MeV from a linear pulse accelerator (Patent No. 283198, Prague 1998). Owing to PCB solubility in 2-propanol (unlike aqueous solutions) and relatively high yield of dechlorination (due to the chain mechanism) this procedure can be used mainly for technical disposal of PCBs and PCB-containing oils. Disadvantage of this method is a decreasing efficiency of PCB dechlorination process with increasing dose resulting in long irradiation times

The destruction of PCBs in an aqueous environment was also studied. In the case of irradiation methods it was found that dechlorination of PCBs in alkaline aqueous solution of Triton X-100 (butyl-phenyl polyethylene oxide, n = 9,5) by gamma rays from Co-60 takes place. Radiation yield of dechlorination compared with the yields of primary radicals from water radiolysis was lower and it decreased with the increasing concentration of the surfactant which indicates scavenging of reactive radicals by Triton X-100.

PRINCIPLE OF INVENTION

The above-mentioned shortcomings in the disposal of polychlorinated biphenyls, or other chlorinated compounds by radiation technologies, are removed by the invention, which rely on the fact that the PCBs or other chlorinated compounds are solubilised into aqueous ethoxylated alkyl phenols (alkyl = octyl-or nonyl-) with the number of ethylene oxide units in the range 7-20, with the solution pH ranging from 5 to 12, preferably from 7.5 to 8.5, is irradiated with accelerated electrons of an energy of 1-5 MeV, preferably 4 MeV with dose rates of 10 to 10^3 kGy / s preferably 102 kGy / sec, and a total dose of 1 to 100 kGy.

Irradiation is performed in a device which consists of the electron accelerator, an irradiation and a separation circuits. The circulation and flow irradiation circuits consist of a reservoir 1 for the medium containing chlorinated compounds, a pump 2, the irradiation cell 4 and a reservoir for the irradiated medium 5. Behind the output of the irradiation cell 4 is a three-way valve 3, which allows its connection to the irradiated medium tank 5 or to the tank 1. The irradiation circuit can work in a flow-mode, when the irradiated medium is piped into the irradiated medium tank 5 or in circulation-mode, when the irradiated solution flows back into tank 1 during the time necessary to achieve the desired degree of dechlorination. Fig. 1 shows the diagram of the circuit and the irradiation cell. The solution of chlorinated compounds is pumped from tank 1 into the irradiation cell 4 located below the electron exit window of the accelerator 6, The electrons entry window is formed by thin metal foil perfectly sealing the space of the cell.

The irradiated solution is then collected for further processing in the storage medium tank 5, the solution processed by irradiation circulates through irradiation circuit for the time necessary to achieve the desired degree of dechlorination. Circulation speed of the solution can be varied depending on the dose rate so that the treated solution gains desired dose. Sampling for the current analysis can be done in tank 1, in the flow regime in the tank 5.
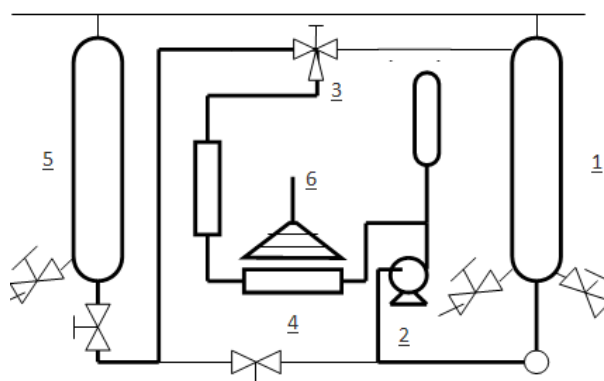
Fig. 1. Diagram of the circulation and flow irradiation circuits. Comment in text.

The high degree of dechlorination of PCBs which can be achieved by irradiation with accelerated electrons in an aqueous solution of ethoxylated alkylphenols is probably due to the increased concentrations of PCBs solubilised in the micelles of surfactants..

Not only polychlorinated aromatic compounds but also such volatile chlorinated compounds as dichloroethane and tetrachlorethylene can be dechlorinated by the method according to the current invention after solubilization directly in aqueous solution.

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Čuba, V.; Bárta, J.; Múčka, V.; Pospíšil, M.: **Aluminium oxide preparation method.** Patent Úřad průmyslového vlastnictví, 302753. 2011-09-07. (in Czech).

Čuba, V.; Gbur, T.; Múčka, V.; Pospíšil, M.: **Method for preparation of nanoparticle scintillator based on zinc oxide.** Patent Úřad průmyslového vlastnictví, 302443. 2011-04-08. (in Czech).

Čuba, V.; Indrei, J.; Pavelková, T.; Pospíšil, M.; Múčka, V. et al.: **Method for preparation of powder ceramic material Y3Al5O12 (YAG).** Patent Úřad průmyslového vlastnictví, 302642. 2011-06-30. (in Czech).

Čuba, V.; Pavelková, T.; Múčka, V.; Pospíšil, M.: **Method for preparation of yttrium oxide nanoparticles.** Patent Úřad průmyslového vlastnictví, 302700. 2011-07-27. (in Czech).

Čuba, V.; Pavelková, T.; Pospíšil, M.; Múčka, V.: **Method for preparation of nickel oxide nanoparticles with high catalytic activity.** Patent Úřad průmyslového vlastnictví, 302445. 2011-04-12. (in Czech).

Šarek, J.; Vlk, M.: **Topical product. Patent European Patent Office**. EP20110003689 20110505.

Pavelková, T.; Čuba, V.: **Irradiation device for study of UV-light effects on biological activity of enzymes.** [Funkční vzor]. 2011. (in Czech).

Přidal, P.; Mašek, P.; Kouba, P.; Bukový, M.; Štekl, I. et al.: **Tunable source of electrons.** [Funkční vzor]. 2012.

Přidal, P.; Valach, O.; Kouba, P.; Štekl, I.; Fajt, L. et al.: **Device for testing of scintillating detector.** [Funkční vzor]. 2012.

THESES

Author, **Title**, *Supervisor, Year*

HABILITATION

Čuba, V.

Radiation Preparation of Inorganic Compounds

2011

Silber, R.

Radiation Dechlorination of Organic Compounds

2010

Vopálka, D.

Modelling of Radioactive Contaminants Migration in Nuclear Waste Repositories

2010

DOCTORAL / DISSERTATION

Landa, J.

Mathematical and Computer Modeling of the Anticipated Deep Geological Repository Concept

Vopálka, D., 2012

Seifert, D.

Optimization of the Radiosynthesis of [18]Fluoroethylspiperone Using Commercially Available Automated Synthesis Modules

Lebeda, O. (Nuclear Physics Institute AS CR), 2012

Beckford, V.

Synthesis and Evaluation of Radioconjugates Formed with Selected Trivalent Radiometals

Melichar, F. (Nuclear Physics Institute AS CR), 2011

Fikrle, M.

Development of Methods for Determination of ^{99}Tc in Environmental Samples

Kučera, J. (Nuclear Physics Institute AS CR), 2011

Ráliš, J

Study of Production of ^{86}Y and ^{124}I on the Cyclotron U-120M

Lebeda, O. (Nuclear Physics Institute AS CR), 2011

Tomeš, M.

Study of Lutetium-177-Labelled Compounds

Melichar, F. (Nuclear Physics Institute AS CR), 2011

MASTER / DIPLOMA

Davídková, Z.

Radiation Dechlorination of Micellar Systems Based on Triton X-100

Silber, R., 2012

Ficenzová, K.

Development of a New Radiodiagnostic Specimens Based on Human Immunoglobuline

Viklický, V. (Nuclear Resear Institute Řež), 2012

Romero, S. M.

Diffusion of Radioactive Contaminants in Barrier Materials

Drtinová, B., 2012

Štika, M.

Analysis of the Fuel Cycle of Molten Salts Reactor System with Thorium Fuel and Single-Fluid vs. Double-Fluid Reactor Core Design

Uhlíř, J., 2012

Zdychová, V.

Preparation and Properties of Radiation Induced Nanosilver

Silber, R., 2012

Bláha, P.

Study of Radiation Sensitivity of Selected Microorganisms

Múčka, V., 2011

Mareš, K. V.

Verification of the Possibility to Decontaminate Spent Solvents Issuing the DIAMEX and/or SANEX Processes

John, J., 2011

Višňák, J.

Faktorová analýza časových řad jako nástroj pro analýzu spekter z časově rozlišené laserem indukované spektrometrie

Vetešník, A., 2011

BACHELOR

Bartl, P.

Separation and Determination of Transplutonium Elements

Šuľaková, J., 2012

Červenák, J.

Modification of Radiation Sensitivity of Microorganisms

Múčka, V., 2012

Mičolová, P.

Synthesis of Biological Degradable Esters of Triterpenic Acid

Vlk, M., 2012

Raindl, J.

Separation of Uranium from Natural Waters for Development of Uranium Sample Preparation Method for Accelerator Mass Spectrometry (AMS)

Němec, M., 2012

Řibřidová, E.

Study of Speciation of Uranium in Natural Waters by TRLFS

Zavadilová, A., 2012

Švehláková, T.

Synthesis of Oleanane and Ursane Derivatives with Modified A-cycle

Vlk, M., 2012

Distler, P.

Study of Extraction Properties of BTBP-Compounds

John, J., 2011

Fiala, V.

Determination of Low Activities of Plutonium

Němec, M., 2011

Procházková, L.

Photochemical Removal of Selected Toxic Metals from Aqueous Solutions

Pospíšil, M., 2011

Svobodová, T.

Determination of ^{90}Sr in Environmental Samples from the Surrounding of the Nuclear Power Plant Temelín

John, J., 2011

Bělohlávek, T.

Electrochemistry Study of Fe–UO$_2$ System in Spent Fuel Disposal Conditions

Silber, R., 2010

Pisch, J.

Study of the Effect of Chemical Mining of Uranium on Fucoide - sandstone in Stráž pod Ralskem

Kraus, L., 2010

PROJECTS AND GRANTS

Title, Code, Donator/Contractor; Chief Scientific Investigator(s)

Safety of Nuclear Installations, MSM6840770020, Ministry of Education, Youth and Sports, Czech Republic; John, J. and Vopálka, D.

Application of Radionuclides and Ionising Radiation, MSM6840770040, Ministry of Education, Youth and Sports, Czech Republic; John, J. and Pospíšil, M.

ACSEPT - Actinide reCycling by SEParation and Transmutation, EC FP7 CP 211267, Euratom; John, J. and Šebesta, F.; co-financed as 7G08075 by the Ministry of Education, Youth and Sports, Czech Republic

ASGARD - Advanced fuleS for Generation IV reActors: Reprocessing and Dissolution, EC FP7 EK7G 295825, Euratom; John, J.

CINCH - Coordination of Education In Nuclear Chemistry, CA 249690, Euratom FP7; John, J.

Synchronously pumped optical parametrical oscillator for sensors, P102/12/P645, GACR; Zavadilová, A.

Nanocomposite, Ceramic and Thin-layer Scintillators, KAN300100802, Grant Agency of the Academy of Sciences of the Czech Republic; Múčka, V.

Research and development of the radwaste treatment technologies and of the system of radwaste management for nuclear new builds, FR-TI3/245, Ministry of Industry and Trade, Czech Republic; Němec, M.

Research into the Properties of Materials for Safe Disposal of Radioactive Waste and the Development of Evaluation Procedures, FR-TI1/362, Ministry of Industry and Trade; Vopálka, D.

Support of the Activities in the Division of Nuclear and Radiochemistry (DNRC) EuCheMS, LA09023, Ministry of Education, Youth and Sports, Czech Republic; John, J.

Determination of important radionuclides and their correlation coefficients in the environmental samples, 7AMB12SK028, Ministry of Education, Youth and Sports, Czech Republic; Němec, M.

Development of sample preparation methods for minor uranium isotopes determination in the environment, 7AMB12AT022, Ministry of Education, Youth and Sports, Czech Republic; Němec, M.

The use of isotopes in research of drugs, SGS11/133/OHK4/2T/14, CTU Prague; Vlk, M.

Photochemical and Radiation Synthesis of Inorganic Materials, SGS11/163/OHK4/3T/14, CTU Prague; Pavelková, T.

Separation of Actinoids from Spent Fuel Reprocessing Solution and Their Conversion to Oxides, SGS11/071/OHK4/1T/14, CTU Prague; Šťastná, K.

Methods for the Determination of Radionuclides in the Environment, SGS11/164/OHK4/3T/14, CTU Prague; Špendlíková, I.

Chemical Aspects of Advanced Nuclear Fuel Cycles Development, SGS12/199/OHK4/3T/14, CTU Prague; Sajdová, A.

Mathematical modelling as a tool for studies on selected chemical systems, SGS11/136/OHK4/2T/14, CTU Prague; Vetešník, A.

RESEARCH FELLOWSHIPS / VISITING SCIENTISTS

OUTGOING:

Distler, P.; Špendlíková I.

Study of the DTPA and Malonic Acid Solution for the Selective Am Stripping in the CEA EXAm Process (internship)

CEA, Marcoule, France, January – March 2011

John, J.

Education and R&D in Nuclear Chemistry / Spent Nuclear Fuel Recycling Studies at the CTU in Prague (invited lecture at the department seminar)

Paul Scherrer Institute, Laboratory of Radiochemistry and Environmental Chemistry, Villigen, Switzerland, March 2011

Šťastná, K.; Špendlíková, I.

8th School on the Physics and Chemistry of the Actinides

Institute of Experimental Physics SAS, Stará Lesná, Slovakia, April 2011

Pavelková, T.; Špendlíková, I.

6th Summer School on Actinide Science and Applications

JRC-ITU, Karlsruhe, Germany, June 2011

Drtinová, B.; Sajdová, A.; Svobodová,T.

Technical Trip of the French Nuclear Facilities

AREVA, France, July 2011

Bárta, J.

Gamma-ray Induced Preparation of Oxide Materials (experimental activity)

Chalmers University of Technology, Gothenburg, Sweden, April 2012

Bárta, J.; Gbur, T.; Neufuss, S.; Pavelková, T.; Špendlíková, I.

2012 Actinet Plutonium Futures Summer School

UK National Nuclear Laboratory, Whitehaven, Cumbria, U.K., July 2012

Zavadilová, A.

Research Based on Time Resolved Laser Induced Fluorescence for the Speciation of Americium(III) in Solutions.

Commissariat à l'énergie atomique et aux énergies alternatives (CEA), ATALANTE, Marcoule, France, September – November 2012

John, J.

Introduction to Radiochemistry (invited lecture at the "Experimental Radioecology" course)

Norwegian University of Life Sciences, Aas, Norway, October 2012

Raindl, J.

Experimental Radioecology

Norwegian University of Life Sciences, Aas, Norway, October 2012

INCOMING:

Navratil, J. D.

Molten Salt Technology for the Treatment of Organic Radioactive Waste

Clemson University, Department of the Environmental Engineering and Earth Sciences, Clemson, SC; and Hazen Research Inc., Colorado, U.S.A., May 2012

Noseck, U.; Britz, S.

Advanced Methods of Description of Selected Critical Radionuclices Interaction with Barrier Materials

GRS Braunschweig, Germany, May 2012

Lehto, J.

Sorption of Trivalent Actinides and Lanthanides on Clay and Oxide Minerals

University of Helsinki, Laboratory of Radiochemistry, Helsinki, Finland, September 2012

Paulenova, A.

Chemistry of the Actinoids

Oregon State University, Radiation Center, Corvallis, OR, USA, September - October 2012

Omtvedt, J. P.

Nuclear Reactions (teaching in the CINCH course Hands-on Training in Nuclear Chemistry)

University of Oslo, Department of Chemistry, Oslo, Norway, December 2012

Le Caër, S.

Preparation of Joint Experiment Focused on the Transfer of Radiation Generated Charge through the ZnO Nanoparticle – Water Interface

Institut Rayonnement Matière de Saclay, Saclay, France, December 2012

Ekberg, C.

Separation Methods (teaching in the CINCH course Hands-on Training in Nuclear Chemistry)

Chalmers University of Technology, Gothenburg, Sweden, December 2012

Lehto, J.

Determination of Radionuclides from Nuclear Waste and Environmental Samples (teaching in the CINCH course Hands-on Training in Nuclear Chemistry)

University of Helsinki, Laboratory of Radiochemistry, Helsinki, Finland, December 2012

DEPARTMENT SEMINAR

Below, the overwiev is given of invited opening lectures and the respective speakers at the Department seminar in 2011 and 2012. Full programme of the seminars, including all the contributed lectures and their authors can be found at the Department web at http:// http://www.jaderna-chemie.cz/?vv=seminar_en

2011

Kučera ,J.

Neutron Activation Analysis and its Applications in Chemical Metrology, Biomedicine, Geo- and Cosmo- Chemistry

Nuclear Physics Institute ASCR, Řež, Czech Republic, October 2011

Macášek, F.

Quality Assurance for PET Radiopharmaceuticals Development and Production

Biont, a.s. Bratislava, Slovakia, November 2011

Hůlka, J.

Radiation Monitoring Network Activity and CR National Radiation Protection Institute

National Radiation Protection Institute, Prague, Czech Republic, December 2011

2012

Uhlíř, J.

Pyrochemical Methods for Reprocessing Irradiated Nuclear Fuel for Fuel Cycles in Fourth Generation Reactors

Nuclear Research Institute, Řež, Czech Republic, February 2012

Stegnar, P.

Legacy of uranium extraction and environmental security in Central Asia

Jožef Stefan Institute, Ljubljana, Slovenia, March 2012

Nikl, M.

Physical Problems and Applications in the Field of Scintillation Materials

Institute of Physics ASCR, Prague, Czech Republic, April 2012

Navratil, J.D.

Development of Aqueous and Organic Radioactive Waste Treatment Processes at Hazen Research Inc., USA

Clemson University, Department of the Environmental Engineering and Earth Sciences, Clemson, SC; and Hazen Research Inc., Colorado, U.S.A., May 2012

Britz, S.

Determination and Evaluation of Surface Complexation Parameters for Eu^{3+} on Muscovite and Orthoclase

GRS Braunschweig, Germany, May 2012

Paulenova, A.

Recent advances in separation Chemistry at Oregon State University

Oregon State University, Radiation Center, Corvallis, OR, USA, October 2012

Hrubý, M.

Radiochemistry for biomedical application on Institute of Macromolecular Chemistry ASCR

Institute of Macromolecular Chemistry AS CR, Prague, Czech Republic, November 2012

Caër, S. Le

Radiation Chemistry of Divided Systems: The Role of Interfaces and of Confinement

Institut Rayonnement Matière de Saclay, Saclay, France, December 2012

PERSONNEL

DEPARTMENT OF NUCLEAR CHEMISTRY

Head:

prof. Ing. Jan John, CSc.

Vice head:

doc. Mgr. Dušan Vopálka, CSc.

Secretary:

Marie Kotasová

CENTRE FOR RADIOCHEMISTRY AND RADIATION CHEMISTRY

Head:

doc. Ing. Václav Čuba, Ph.D.

Vice head:

doc. Ing. Ferdinand Šebesta, CSc.

Secretary:

Mgr. Štěpánka Maliňáková

SEPARATION AND RADIOANALYTICS

prof. Ing. Jan John, CSc.

Ing. Kateřina Čubová, Ph.D.
Ing. Alois Motl, CSc.
Ing. Mojmír Němec, Ph.D..
doc. Ing. Ferdinand Šebesta, CSc.
RNDr. Jana Šuľaková, Ph.D.
Ing. Alena Zavadilová, Ph.D.

Ph.D. students:

Ing. Kamil V. Mareš
Ing. Soběslav Neufuss
Ing. Aneta Sajdová
Ing. Irena Špendlíková
Mgr. Kamila Šťastná
RNDr. Martin Vlk

Technician:

Jana Steinerová

SPECIATION AND MIGRATION

Doc. Mgr. Dušan Vopálka, CSc.

prof. Ing. Petr Beneš, DrSc.
Ing. Barbora Drtinová, Ph.D.
doc. Ing. Karel Štamberg, CSc.
Mgr. Aleš Vetešník, Ph.D.
Ing. Alena Zavadilová, Ph.D.

Part-time:

Ing. Helena Filipská, Ph.D.

Ph.D. students:

Ing. Eva Hofmanová
Ing. Jakub Višňák

Technicians:

Ing. Šárka Hráčková
Olga Múčková

RADIATION CHEMISTRY

prof. Ing. Viliam Múčka, DrSc.

doc. Ing. Václav Čuba, Ph.D.
prof. Ing. Milan Pospíšil, DrSc.
doc. Ing. Rostislav Silber, CSc.

Ph.D. students:

Ing. Jan Bárta
Ing. Tomáš Gbur
Mgr. Daniel Kobliha
Ing. Tereza Pavelková

Technician:

Alena Matyášová