Department of Nuclear Chemistry
Břehová 7
115 19 Praha 1
Phone: +420 224 358 207
Fax: +420 222 317 626
E-mail: kjch@fjfi.cvut.cz
http://www.jaderna-chemie.cz/
NUCLEAR CHEMISTRY
Annual Report 2013-2014

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

Reports are available from: Marie Kotasová (kotasova@fjfi.cvut.cz), Břehová 7, 115 19 Praha 1, Czech Republic or download from: http://www.jaderna-chemie.cz/
Dear Reader, this is the fourth in the series of the CTU Nuclear Chemistry Annual Reports. Similarly to the previous issues, the bi-annual periodicity is preserved as well as the structure and format of the report. After the merger of the two earlier 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) – that took place on the 1st January 2013, this brochure compiles and will continue compiling the achievements of DNC only.

On the top of the list of the main events that happened during the period covered (2013 – 2014), we have to share a sad news – Prof. Petr Beneš, the former head of the department, disciple of Vladimir Majer and a renowned radiochemist passed away on the 7th June 2013 at the age of 75. More details can be found below in a eulogy in the section Education and Management.

From the point of view of the DNC operation, the most important event was establishment of the fourth research group – “Radiopharmaceutical Chemistry”. For this group, two new researchers were engaged and a new laboratory was set-up for their activities. The new laboratory and its activities are described in the editorial of the respective section below. Hence, unlike earlier, in the period cover by this report, the research in nuclear chemistry at the DNC was organised in four research groups that, for the purpose of this Report, may be referred to as “Speciation and Migration”, “Separation and Radioanalytics”, „Radiation Chemistry” and “Radiopharmaceutical Chemistry”. Selection of short contributions characterising the research topics in more detail forms the body of this Annual Report.

Another important event during the period covered was the leading role of DNC in co-organisation of the international 17th Radiochemical Conference held in 2014 traditionally in the Western Bohemian spa of Mariánské Lázně (http://www.radchem.cz/). For the second time, the conference was organised as a part of the regular bi-annual series of pan-European nuclear chemistry conferences guaranteed by the Division of Nuclear and Radiochemistry of the EuCheMS. The largest ever audience – 320 participants from 43 countries – made the conference a clear success. The Booklet of Abstracts, published by the Czech Technical University in Prague, can be freely downloaded from http://www.radchem.cz/babstr/Babstr14.pdf. The RadChem 2014 Proceedings, compiled from the 68 accepted full papers, have been published in the Journal of Radioanalytical and Nuclear Chemistry (Volume 304, 2015, Issue 1). More details on the conference can be found in the respective article below.

During this reporting period the main direction of the research activities of the DNC continued to cover 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 initiated preparation of solids inclusive nanoparticles, as well as radioecology and bioration- and newly also radiopharmaceutical chemistry. In these fields, the CTU has been a partner in several big international EURATOM FP7 integrated projects such as SACSESS or ASGARD; thus, most of the research is performed in close collaboration and co-ordination with the major European institutes and universities. As usually, 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.
The Department Seminar, re-shaped and opened to the general scientific public since the academic year 2011/2012, continued its proven successful scheme as a half-day event consisting of an opening lecture by an invited eminent Czech or foreign expert followed by Ph.D. students’ reports, progress reports of key department grants, and travel reports. The invited speakers and the topics of their talks are listed in a dedicated section of this Annual Report.

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 that aimed at coordinating the education in nuclear chemistry, both at Ph.D. and undergraduate levels, within the EU, in collaboration with Russia. Immediately after the end of the project in mid 2013, it was succeeded by a follow-up project CINCH-II - Cooperation in education and training In Nuclear CHEmistry (http://www.cinch-project.eu/). The CINCH-II project was built around three pillars - Education, Vocational Education and Training (VET), and Distance Learning - supported by two cross-cutting activities – Vision, Sustainability and Nuclear Awareness that included also dissemination. More details about the main achievements of the projects in the period are summarized in a dedicated article in the Education section below.

Similarly to the conclusion of the editorial of the previous Annual Report, it can be concluded that there exists a strong group of highly competent and motivated young nuclear chemists aged 35–40 at the CTU who are slowly taking over the leadership but remain backed by the older generation. This team represents one of the most important units of the Czech nuclear community. Taking in account the variety and number of research grants, the Department of Nuclear Chemistry at the CTU continues 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 especially 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
Head, DNC
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EDUCATION AND MANAGEMENT

Courses Taught

Projects and Management
Courses Taught

List of Courses in the Academic Years 2013/2014 and 2014/2015

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

<table>
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<tr>
<th>Title</th>
<th>Credits (ECTS)</th>
<th>Semester</th>
<th>Cycle</th>
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<tr>
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<tr>
<td>Dosimetry and Radiation Protection</td>
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<td>W</td>
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<tr>
<td>Exercises in General Chemistry</td>
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<td>B</td>
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<tr>
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<td>Motl, A.</td>
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<td>Instrumental Methods of Research 1</td>
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<td>B</td>
<td>Pospíšil, M.</td>
</tr>
<tr>
<td>Ionising Radiation Detection</td>
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<td>S</td>
<td>B</td>
<td>John, J.</td>
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<tr>
<td>Laboratory Practice in the Instrumental Methods of Research</td>
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<td>Measurement and Data Handling</td>
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<tr>
<td>Practical Exercises in Radiochemical Techniques</td>
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<td>The Theory of the Electromagnetic Field and Wave Motion</td>
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* External teacher
- 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 Můčka, 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.*
- Determination of Radionuclides in the Environment
  - 2 S M Němec, M.
- Environmental Chemistry and Radioecology
  - 2 W M Filipská, H.; Vopálka, D.
- Instrumental Methods 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.; Vopálka, D.
- Nuclear Materials Technology
  - 2 S M Drtinová, B.; 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 Můčka, 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 Kozempel, J.; Vlk, M.
- Practical Exercises in Radioanalytical Methods
  - 4 S M Němec, M.; Čubová, K.; John, J.
- Practical Exercises in Separation Methods in Radiochemistry
  - 3 W M Němec, M.; Čubová, K.; John, J.
- 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.
- Radioanalytical Methods
  - 3 S M John, J.

* External teacher
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<td>Radiopharmaceuticals 1</td>
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<tr>
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<td>2</td>
<td>W</td>
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</tr>
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<td>Separation Methods in Nuclear Chemistry 1</td>
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</tr>
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<tr>
<td>Technology of the Fuel Cycles of Nuclear Power Plants</td>
<td>2</td>
<td>W</td>
<td>Drtinová, B.; Štamberger, K.</td>
</tr>
<tr>
<td>Theoretical Basics of Radiation Chemistry</td>
<td>2</td>
<td>W</td>
<td>Juha, L.*</td>
</tr>
<tr>
<td>Trace Radiochemistry</td>
<td>3</td>
<td>S</td>
<td>Filipská, H.; John, J.</td>
</tr>
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</table>

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* External teacher
- Application of Large Ionising Radiation Sources  
  D Pospíšil, M.
- Applications of Radiation Chemistry in Chemical Industry, Agriculture and Medicine  
  D Můčka, V.
- Application of Radionuclides  
  D Mízera, J.*
- Biosyntheses of Labelled Compounds  
  D Smrček, S.*
- Chemistry of Actinoids and Transactinoids  
  D John, J.
- Experimental Nuclear Chemistry  
  D John, J.; Čuba, V.; Němec, M.
- Instrumental Radioanalytical Methods and their Application for Monitoring the Environmental Contamination  
  D Kučera, J.*
- Labelled Compounds  
  D Smrček, S.*
- Modelling and Simulation of the Migration Processes in the Environment  
  D Štamberg, K.; Vopálka, D.
- Nuclear Chemistry  
  D John, J.
- Nuclear Power Plants  
  D Heřmanský, K.*; Štamberg, K.
- Photochemistry and Radiation Chemistry  
  D Juha, L.*; Čubová, K.; Čuba, V.
- Radioanalytical Chemistry  
  D Němec, M.
- Radionuclides in Biological Sciences  
  D Smrček, S.*
- Radiopharmaceuticals  
  D Lebeda, O.*; Moša, M.*
- Separation Methods  
  D John, J.; Němec, M.
- Technology of Nuclear Fuels  
  D Štamberg, K.
- Transport Processes  
  D Štamberg, K.; Vopálka, D.

* External teacher
# Projects and Management

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Prof. Petr Beneš, a renowned radiochemist, our friend and dear colleague, spent all his professional life at the Faculty of Nuclear Sciences and Physical Engineering (FNSPE) of the Czech Technical University in Prague. He was an active member of the Department of Nuclear Chemistry over five decades, since 1960 when he, as one of the very first group of graduates from this department, was hired and stayed involved till his death. During that period, he became a worldwide recognised authority in the field of nuclear chemistry. He headed the Department of Nuclear Chemistry for 17 years (in 1986–2003) and successfully led it through the difficult period of the financing system transformation of the Czech universities and research. He had held also numerous positions in both the research and education fields at FNSPE. Since 1970s his research was devoted to the development of methods for speciation studies and to the behaviour of toxic elements and radionuclides in surface waters and other compartments of the biogosphere. Petr Beneš is ranked among the pioneers in this research area all over the world. Towards the end of his career he became interested in the applications of spectroscopic methods in speciation analyses and initiated the introduction of Time resolved laser fluorescence spectroscopy at FNSPE. He authored several monographs and chapters in monographs. The best known is the “Trace Chemistry of Aqueous Solutions” which won the creative award of the Czech Literary Fund.

As a university teacher, he was a gifted educator, and he is fondly remembered by several generations of students, namely with his profile lecture course in “Nuclear Chemistry”. From seven additional courses he taught during his professorship at CTU, the most notable was “Trace Chemistry of Aqueous Solutions: General Chemistry and Radiochemistry” which was essential topic of both his educational and research interest. He supervised numerous diploma and doctoral students.

The international acknowledgement of his creative capabilities resulted in invited editorial board memberships of several international scientific journals, including Radiochimica Acta. In 1989 he became a member and in 1998–2001 he served as the Secretary of the IUPAC Commission for Radiochemistry and Nuclear Techniques. For many years, he was an active member of the International Union of Radioecology (IUR) that appointed him an Honorary Member of the IUR for his merits.

With Petr Beneš, we have lost an unforgettable teacher, colleague, and friend. He will remain in our minds and memories. He will be missed, and remembered fondly by the whole nuclear chemistry community.

God rest his soul!
CINCH – II PROJECT – NEXT STEP IN THE COORDINATION OF EDUCATION IN NUCLEAR- AND RADIOCHEMISTRY IN EUROPE


1CHALMERS University, Sweden; 2University of Helsinki, Finland; 3National Nuclear Laboratory Ltd., Warrington, United Kingdom; 4University of Hanover, Germany; 5Loughborough University, Great Britain; 6Commissariat à l’énergie atomique et aux énergies alternatives, France; 7Leeds University, United Kingdom; 8Norwegian University of Life Sciences, Aas, Norway; 9University of Oslo, Norway

MOTIVATION

Any of the potential scenarios for the nuclear power industry – both the renaissance, if any, or the phase out – will require significant numbers of the respective specialists, amongst others the nuclear and/or radiochemists. In parallel, a significant demand exists for these specialists in non-energy fields, such as environmental protection, radiopharmacy, nuclear medicine, biology, authorities, etc. Since the numbers of staff in teaching and the number of universities with facilities licensed for the work with open sources of ionizing radiation has decreased to or sometimes even below the critical level, coordination and collaboration are required to maintain the necessary teaching and training capabilities.

In 2010, the series of CINCH projects was started by a Euratom FP7 project aiming at the “Coordination of education In Nuclear Chemistry in Europe (CINCH)”. After a successful completion, it was succeeded by the CINCH-II project (2013–2016) “Coordination of education and training In Nuclear Chemistry in Europe”. The main public outcomes of both the projects are available at the project webpage at http://www.cinch-project.eu.

CINCH ACHIEVEMENTS

The CINCH project aimed at the coordination of the rather diverse situation in nuclear chemistry education and training in Europe. The project also aimed at providing a common basis to the fragmented activities in this field and thus moving the education and training in nuclear chemistry to a higher level. The main target groups were not only the doctoral students and research workers but also students at the Master level.

The CINCH consortium included both academia and ‘future employers’, thus representing all the key players in the field. A big benefit was the participation of a Russian partner (Moscow State University) in the project that added the considerable Russian expertise in this field. The experience gained by former Euratom FP6 projects like EURAC, ENEN II, ENETRAP etc. and ENEN association during the coordination of nuclear engineering education was directly applied.

The main results of the project with the broadest impact to students, teachers, industries, and research community are a set of compact joint modular courses developed in different branches of modern nuclear chemistry, an electronic tool in the form of a virtual educational platform developed and demonstrated for both education and training, and a long-term sustainable strategy for the nuclear chemistry education. These results are described in detail in a paper in the proceedings of RadChem 2014 conference [1].

CINCH – II OBJECTIVES

The CINCH-II project has been built around three pillars - Education, Vocational Education and Training (VET), and Distance Learning - supported by two cross-cutting activities – Vision, Sustainability and Nuclear Awareness that includes also dissemination, and Management. Its main objectives, expected to have the broadest impact to the target groups, are

- further development and implementation of the EuroMaster in Nuclear Chemistry,
- completion of a pan-European offer of modular training courses for the customers from the end users,
- development of a Training Passport in Nuclear Chemistry and preparing the grounds for the European Credit system for Vocational Education and Training (ECVET) application in nuclear chemistry,
- implementation of modern e-learning tools developed in CINCH and further development of new tools for the distance learning,
- laying the foundations of a Nuclear Chemistry Education and Training Platform as a future sustainable Euratom Fission Training Scheme (EFTS) in Nuclear Chemistry,
- development of a Sustainable Systems for Mobility within the Nuclear Chemistry Network, or
- development of methods of raising awareness of the possible options for nuclear chemistry in potential students, academia and industry.

CONCLUSIONS

The CINCH-II project should mobilize the identified existing fragmented capabilities to form the critical mass required to implement the courses and meet the nuclear chemistry postgraduate education and training needs, including the high-level training of research workers, of the European Union. Networking on the national level and with existing European as well as international platforms is an important feature of the project.

REFERENCES


These activities have been supported by the Euratom FP7 grants FP7-CA-249690 and FP7-CA-605173.
INTRODUCTION
In accordance with the objectives of CENEN (Czech Nuclear Education Network), the goal of the CENEN-NET project was to intensify collaboration between involved universities which offer education in the field of nuclear energy. CENEN is a voluntary academic association, whose principal activity is to provide high-quality and sustainable education in the field of nuclear engineering. By the effective cooperation of universities and commercial partners, high quality education can be achieved. The transfer of information between students and academic staff is being improved by organizing workshops, seminars and discussions with experts from the Czech Republic and abroad. Foreign cooperation is being extended thanks to the inclusion of ENEN, the European Nuclear Education Network, and cooperation with WNU – the World Nuclear University. The CENEN association was founded in May 2005, and since then the membership has grown to 17 members from academic institutions, with 4 associated commercial partners. The CENEN-Net project was solved within the scope of Operational Programme Education for Competitiveness in priority axes no. 2 - Tertiary Education, Research and Development and area of support no. 2.4. - Partnership and Networking.

PARTNERS
Target group of project includes academic workers and students from out off-Prague universities (University of West Bohemia Pilsen, VŠB-Technical University of Ostrava, Brno University of Technology, and Technical University of Liberec).
Other involved universities were Czech Technical University in Prague (Faculty of Nuclear Sciences and Physical Engineering including Department of Nuclear Chemistry, and Centre for Radiochemistry and Radiation Chemistry, Faculty of Mechanical Engineering, and Faculty of Electrical Engineering) and Institute of Chemical Technology Prague. State Office for Nuclear Safety, ČEZ GROUP, Nuclear Research Institute Řež, ŠKODA JS a.s., and VÍTKOVICE ÚAM a.s. were also connected to the project.

REFERENCES

This project was supported from European social foundation and Czech Republic state budget, grant No. CZ.1.07/2.4.00/17.0116
INTRODUCTION
Power engineering is one of the strategic sectors of the government and training and education of new young specialists mainly in the area of nuclear power engineering is of the fundamental importance. The lack of the technically educated specialists is the problem concerning the whole Europe. There are two main reasons responsible for the current situation. The first is lack of interest of the potential students in the study in technical fields. The second one is the long term problem related to the generation exchange of the specialists.

SOLUTION
Four Czech technical institutions - Faculty of Mechanical Engineering CTU (CTU FME), Faculty of Nuclear Sciences and Physical Engineering CTU (CTU FNSPE), Brno University of Technology (BUT) and VSB Technical University of Ostrava) in cooperation with Research Centre Rez (RCR) and National Training Fund (NTF) decided to solve this situation by establishing the Central European Energy Institute. Idea of the common education of the students opens a space for innovation of study programmes, engagement of Czech and external specialists and possibility of education of foreign students. The main aim of this institution was to provide a sustainable, interdisciplinary and practical teaching programme for highly educated specialists in nuclear power engineering. Such concept is supported in the framework of Operational Programme Education for Competitiveness supported by the Czech Ministry of Education, Youth and Sports.

KEY ACTIVITY
In the framework of the project, study programmes of the nuclear power engineering were innovated. This innovation concerns all three levels (Bc, MSc and PhD) and includes formation of new educational materials and introduction of E-learning system. The innovated study programmes were prepared in Czech and English languages.

THE ROLE OF NUCLEAR CHEMISTRY
An integral part of the educational programmes of the Institute is the curriculum in nuclear chemistry. It will aim to give the students – future engineers – indispensable radiochemical background with the emphasis on the chemistry of operation of nuclear power plants, technology of the fuel cycle of nuclear power stations and the waste management and treatment. For the necessity of the institute, the new educational materials focused on chemical aspects of nuclear fuel cycle, technology of nuclear fuel, detection of ionizing radiation and also some practical exercise in detection were contemporary prepared at the Department of Nuclear Chemistry FNSPE CTU.

This research has been supported by the Ministry of Education, Youth and Sport of the Czech Republic under contract OP VK No. CZ.1.07/2.2.00/28.0256
SECONDARY SCHOOL STUDENTS
AT THE DEPARTMENT OF NUCLEAR CHEMISTRY

Distler, P.; John, J.

INTRODUCTION
Academic staff and doctoral students at the DNC provide opportunities for talented secondary school students. They can try working in the radiochemistry labs and present their results in various students’ competitions or at students’ conferences.

STUDENTS’ PROFESSIONAL ACTIVITIES
“Students’ professional activities” (Středoškolská odborná činnost - SOČ) is an activity for the secondary students interested in science. They do research, write “theses” and defend them in front of a scientific panel. This competition has different rounds: a school one, the regional one, and, finally, a national round for the best students. [1] Among the recent successful students who did their work at the DNC, Anna Červenková from the Gymnázium Sokolov can be named. She was awarded the 8th place in Chemistry at the SOČ National Round in 2013 for her work Characterization of bentonite and their usage in nuclear waste repository. Her supervisor was Eva Hofmanová, Ph.D. student at the DNC.

In June 2014, Martin Palkovský from the Gymnázium Jakuba Škody Přerov won the 4th place in Chemistry at the SOČ National Round. The title of his work was Preparation of functionalized nanoparticles used in photodynamic therapy. Martin’s supervisor was Dr. Martin Vlk.

The DNC usually offers the following projects for students:
- Making of nanosilver by a radiation-chemical way
- Preparation and control of radiopharmaceuticals
- Green fluorescence light that can identify uranium ions (TRLFS)
- Work in a radiochemical laboratory – determination of half-lives of short-lived radionuclides

THE WEEK OF SCIENCE AT FNSPE
Every spring, secondary school students are welcome to come to our faculty to spend here 5 days doing science. They attend a series of lectures, participate in one excursion outside FNSPE and can choose a “mini-project”, which they solve with a help of their supervisor. At the end of the “Week of Science at FNSPE” (Tyden vědy na jaderce), there is a students’ conference, where they inform other participants about their research done. [2]

In addition to the activities described above, the DNC members deliver lectures for the students participating in the Chemistry Olympiad during the dedicated summer holidays youth chemical camp in Běstvina. The support of these activities enables the DNC to address the secondary school students interested in science and motivate them to study at the FNSFE.

REFERENCES
The 17th Radiochemical Conference – RadChem 2014, was held in the Casino conference centre in Mariánské Lázně, Czech Republic, on the 11-16th May 2014. As usual in its more recent history, the conference was co-organized by the Department of Nuclear Chemistry, Czech Technical University in Prague (DNC), Czech Chemical Society, and Ioannes Marcus Marci Spectroscopic Society. Together with the “International Conference on Nuclear and Radiochemistry (NRC)” series, the RadChem series form the pillars of the pan-European conference series organised on behalf of the Division of Nuclear and Radiochemistry of the European Association for Chemical and Molecular Sciences (DNRC EuCheMS).

Traditionally, RadChem 2014 was organized in cooperation with the International Atomic Energy Agency (IAEA) and was sponsored by the International Union of Pure and Applied Chemistry (IUPAC). Over its 50+ years long tradition, it has gained a good reputation as a platform for the presentations of research results and for the discussions about current issues.

The conference was attended by 320 participants from 43 countries, from which the most represented countries were the Czech Republic, Russia, Germany, Poland, the USA, Japan and Korea. In total, 413 contributions were accepted for the presentations.

The scientific programme was accomplished, except for the plenary lectures, in two parallel sessions. The programme of most of the sessions was opened with invited lectures. The poster presentations were organised into topical sessions and spread over three days to give the participants ample time for the discussion with the authors.

The conference was organised in eight technical sessions covering all the fields of the current nuclear- and radiochemistry and a session on the education of new professionals. Two of the sessions were dedicated to the memory of our colleagues who have recently passed away, and who had participated in the RadChem conference organization for many years. The session “Radionuclides in the Environment and Radioecology” was dedicated to the memory of the late Prof. Petr Beneš and the session “Separation methods and speciation” to the memory of the late Prof. Věra Jediničková-Křížová.

The full conference programme is available at the conference web page (http://www.radchem.cz) together with freely accessible booklet of all accepted abstracts. The 68 contributions that have been selected based on the results of a standard double-blind peer-review procedure were published as Vol. 304, Issue 1, of the Journal of Radioanalytical and Nuclear Chemistry.

A rich social and cultural programme was organised. Monday sounded with the piano recital “Radiochemist plays Chopin” performed by Marek Bystran, a talented student of DNC CTU interpreting selected Chopin's compositions in an exceptional way. On Tuesday, all participants were offered a chance to relax during the evening programme “Wellness Night” where they could enjoy selected spa treatments in the conference host - Marienbad Kur & Spa Hotels - facilities. Wednesday afternoon was dedicated to a pleasant trip to the historical centre of town Cheb. The guided tours were followed by the conference dinner in Metternich Castle Hotel in the spa Lázřně Kynžvart. The social programme was concluded with an unusual fusion of fire show, theatre, acrobatics and expressional dance performed by the Amanitas Fire Theatre group. Traditionally, Thursday evening was devoted to the Singing Fountain performance at the spa colonnade which was preceded by another musical surprise – “Radiochemistry Jam Band Session”, a performance of an amateur musician group composed of the conference participants presenting a programme rehearsed on-site during the conference.

Two prestigious scientific awards were presented during the conference. The first was the premier international George Hevesy Medal Award for excellence in radioanalytical and nuclear chemistry, named after George de Hevesy (*18. 8. 1885, †5. 7. 1966), a Hungarian radiochemist, and Nobel prize laureate for chemistry in 1943. Prof. Heino Nitsche received the George Hevesy Medal Award 2014 in recognition of his contributions to heavy element chemistry and actinide environmental chemistry.

The second appraisement was the new Vladimír Majer Medal Award presented by the Nuclear Chemistry working group of the Czech Chemical Society to scientists who significantly contributed to the development of nuclear chemistry and/or played a decisive role in the development of some its area. The first ever medal was awarded at RadChem 2014, in memoriam to the late Prof. Petr Beneš, former professor and head of the DNC CTU, for his lifelong contribution to the nuclear chemistry development in Czechoslovakia and the Czech Republic.

Prof. Dr. Vladimir Majer (*19. 3. 1903, †5. 7. 1998) was a prominent Czech nuclear and physical chemist, one of the pioneers of the Czech radiochemistry. He authored the first Czech monograph “Radiochemistry” (1942) and most importantly the still unsurpassed textbook Fundamentals of Nuclear Chemistry (in Czech 1961, 2nd edition 1981; in German 1982).
RESEARCH REPORTS

- Speciation and Migration
- Separation and Radioanalytics
- Radiation Chemistry
- Radiopharmaceutical Chemistry
Speciation and Migration

Lujaniene G., Štamberg K., Pakštas V., Juškénas R., Kulakauskaité I., Šemčuk S., Mažeika K., Vopálka, D: **Study of Pu Sorption Behaviour in Natural Clay**

Adam R., Štamberg K., Drtinová B.: **Characterization of Clays by Titration Curves – Possibilities of Fitting Parameters of Titration Curves**

Štamberg K., Palágyi S., Videnská K., Havlová V.: **Interaction of $^3$H$^+$ (as HTO) and $^{36}$Cl$^-$ (as Na$^{36}$Cl) with Crushed Granite and Corresponding Fracture Infill Material Investigated in Column Experiments**

Hofmanová E., Vopálka D., Rosendorf T.: **Comparative Study of Chloride and Iodide Diffusion in Compacted Bentonite**

Vopálka D., Vetešník A., Hofmanová E.: **Some Uncertainties in Evaluation of Diffusion Experiments with Compacted Bentonite**


Hofmanová E., Maes N.: **Development and Testing of Electromigration Technique to Study Radionuclide Transport in Compacted Bentonite**


Višňák J.: **Quantum Algorithms for Computational Nuclear Physics**
INTRODUCTION
Plutonium is the most toxic element ever introduced into the environment, its behavior and redistribution is rather complicated and still not completely understood. The behavior of plutonium can be strongly dependent on the redox reactions that can lead to changes in its speciation, solubility and transport. The most common oxidation states are Pu(IV) and Pu(V). The environmental behavior of plutonium can be strongly affected by the hydrolysis, complexation and by redox reactions especially if various iron oxides, carbonates and humic substances etc. are present. Clay minerals are the most common components of environmental systems, the particles of which are coated with above mentioned iron oxides having the sorption properties, too. The aim of this work was to study sorption and reduction/oxidation of Pu isotopes in the natural clay–groundwater systems [1].

EXPERIMENTAL
The experimental part of the study consists of the three sections: sorption experiments, sample characterization and sequential extraction (SE), and oxidation state distribution. Here, the consideration will be given to the sorption kinetics and oxidation state distribution results. Three well-characterized clay samples (denoted as S; 6; 7), taken from the industrial exploitation site Šaltiškiai in North Lithuania, were used to study Pu(IV),V) sorption kinetics and oxidation state distribution (+ SE). Sorption was studied using natural groundwater (pH 7.16, HCO$_3^-$ - 517 mg/L, Ca$^{2+}$ - 139 mg/L) by batch method (liquid-to-solid ratio = 1000 mL/g). Plutonium isotopes of Pu(IV) or Pu(V) as a mixture of $^{238}$Pu, $^{239}$Pu, $^{240}$Pu and $^{241}$Pu were added to achieve their initial concentration of 1∙10$^{-10}$ mol/L. After selected sorption time the solid phase was separated from the liquid phase by centrifugation at 10$^4$ G.

As for the determination of oxidation state distribution, the liquid extraction by means of different extraction agents was used. In detail, it is described in [1].

RESULTS
The sorption kinetic data, depicted in Fig.1., were evaluated by fitting with six different types of kinetic models [2] derived for the following six control processes: mass transfer (DM), film diffusion (FD), diffusion in the inert layer (ID), diffusion in the reacted layer (RLD), chemical reaction (CR) and gel diffusion (GD). The best fit was obtained for ID-model in case of S-clay, and for RLD-one in case of 6- and 7-clays. But the differences between clays studied were not important and the ID-control process can be attributed to all three clays studied. As a fitting criterion, the quantity WSOS/DF (Weighted Sum of Squares divided by the Degrees of Freedom) [3] was used.

![Fig. 2. Distribution of different binding forms of Pu(IV) and Pu(V) sorbed on clays after 7 days contact; F1-exchangeable; F2-carbonate bound; F3-oxides; F4-organic matter; F5-acid soluble; F6- residual.](image)

Results of SE studies from two sets of experiments – with Pu(IV) and Pu(V) – are presented in Fig. 2. It can be seen that in experiments with Pu(V) the largest portion of Pu is bound to carbonate fractions (F2) in clay S (79±5 %) and clay 6 (83±6 %). As for the Pu(IV), Pu isotopes are mainly associated with oxides and organic matter in a case of all three clays studied. More information can be found in [1].

REFERENCES
CHARACTERIZATION OF CLAYS BY TITRATION CURVES – POSSIBILITIES OF FITTING PARAMETRES OF TITRATION CURVES

Adam, R.; Drtinová, B.; Štamberg, K.

INTRODUCTION

To develop a safe radionuclide repository, it is necessary to characterize all possible processes in its barriers. In the case of migration, there are four types of processes: diffusion, advection and convection, decay of radionuclides and interactions. This work focuses on interactions, especially on bentonite sorption properties. Sorption of radionuclides is usually described by sorption isotherms. For better understanding of sorption processes it is useful to use more complex models of surface interactions. In model utilized in this work two processes are assumed: surface complexation due to the edge-sites (=S), and ion exchange due to the layer-sites (=X).

For correct characterization of bentonite surface, the equations (1)-(8) should be used.

\[ \equiv S^- + H^+ \leftrightarrow \equiv SH \] (1)

\[ \equiv SH + H^+ \leftrightarrow \equiv SH_2^+ \] (2)

\[ \equiv XNa + H^+ \leftrightarrow \equiv XH + Na^+ \] (3)

\[ K_1 = \frac{[\equiv SH]}{[\equiv S^-][H^+]^{\frac{1}{2}}} \] (4)

\[ K_2 = \frac{[\equiv SH_2^+]}{[\equiv SH][H^+]^{\frac{1}{2}}} \] (5)

\[ K_{ex} = \frac{[\equiv XNa][H^+]^{\frac{1}{2}}}{[\equiv X][Na^+]^{\frac{1}{2}}} \] (6)

\[ SS = [\equiv SH] + [\equiv SH_2^+] + [\equiv S^-] \] (7)

\[ SX = [\equiv XNa] + [\equiv XH] \] (8)

For the determination of parameters mentioned in equations (4)-(8), evaluation of titration curves can be used. There are two titration approaches, semicontinuous method, where it is assumed that equilibrium is reached if pH changes by less than 0.01 pH unit in 5 minutes [1], and batch titration, where solid and liquid phases are in contact for a time long enough to reach the equilibrium in the system [2]. It is assumed that in semicontinuous system dissolution of solid material may be neglected, but it cannot be ensured, that the system reached the true equilibrium. In batch system, the dissolution of solid material has to be taken into account. This effect can be partially eliminated by back titration.

This work compares differences between these two methods, and two different evaluations of titration curves on bentonite B75.

EXPERIMENTAL

All experiments were carried out under N₂ atmosphere. Bentonite was pretreated by Wanner’s way [1]. For this material, its surface was characterized by BET technique. The liquid-to-solid ratio of 250 ml·g⁻¹ was used in interaction experiments. As the liquid phase, 0.1 M NaNO₃ solution was used. Acidic titration was carried out by 0.1 M HNO₃, base titration was carried out by 0.1 M NaOH.

Semicontinuous titration was carried out according to [1] by automatic titrator TIM 845. Batch titration experiments were carried out in the following way: the mixture was shaken for two weeks with defined amount of titration agent, then it was centrifugated for 3 minutes at 3000 rpm and finally titrated to pH 7 by 0.01 M NaOH or 0.01 M HNO₃.

Evaluation of the titration curves was carried out by two non-linear regression methods. The first calculation was done by own code prepared in Famulus, where Newton-Raphson regression method was used. The second one was done by connection of PHREEQC v.3 and UCODE_2005, where Gauss-Newton modified regression method was used. Goodness-of-fit was characterized by criterion WSOS/DF (sum of weighted squared residuals divided by degrees of freedom) adapted from FITEQL [3].

RESULTS

As presented in Table 1, there are differences between parameters achieved from semicontinuous and batch type of experiments. Especially there are differences in total amount of edge sorption sites. All fits have criterion of goodness-of-fit between 0.2 and 20, that means that fits are good [3].

Tab. 1. Fitted parameters of titration curves. Labeling used in this table: U = PHREEQC v.3+UCODE_2005, F = Famulus, Ct = continuous titration, w2 = 2 week contact time.

<table>
<thead>
<tr>
<th>Method</th>
<th>K₁</th>
<th>K₂</th>
<th>Kex</th>
<th>SS</th>
<th>SX</th>
<th>WSOS/DF</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCt</td>
<td>5.76×10⁻⁶</td>
<td>7.98×10⁻⁶</td>
<td>5.95×10⁻⁶</td>
<td>5.88×10⁻⁶</td>
<td>8.94×10⁻⁶</td>
<td>13.1</td>
</tr>
<tr>
<td>UCl</td>
<td>9.85×10⁻⁶</td>
<td>9.19×10⁻⁶</td>
<td>8.53×10⁻⁶</td>
<td>8.70×10⁻⁶</td>
<td>7.46×10⁻⁶</td>
<td>3.54</td>
</tr>
<tr>
<td>F2w</td>
<td>1.16×10⁻⁹</td>
<td>2.00×10⁻⁹</td>
<td>2.22×10⁻⁹</td>
<td>5.19×10⁻⁹</td>
<td>9.87</td>
<td></td>
</tr>
<tr>
<td>U2w</td>
<td>5.90×10⁻⁹</td>
<td>5.25×10⁻⁹</td>
<td>2.31×10⁻⁹</td>
<td>4.20×10⁻⁹</td>
<td>8.09</td>
<td></td>
</tr>
</tbody>
</table>

Although Wanner et al. [1] expected that in continuous method equilibrium of layer-sites is not achieved, Table 1 shows that there are differences in equilibrium on edge-sites. From results of evaluation by PHREEQC+UCODE and Famulus some differences could be seen, that could be neglected in many cases. These differences may be explained by different regression methods and by the use of slightly different databases.

REFERENCES


This research was supported by the Grant Agency of the Czech Technical university in Prague, grant No. SGS13/224/OHK/3T/14.
INTERACTION OF $^3$H (AS HTO) AND $^{36}$Cl (AS Na$^{36}$Cl) WITH CRUSHED GRANITE AND CORRESPONDING FRACTURE INFILL MATERIAL INVESTIGATED IN COLUMN EXPERIMENTS

Štamborg, K.; Palágyi, Š.; Videňská, K.; Havlová, V.

1ÚJV Řež, a.s., Husinec-Řež, Czech Republic

INTRODUCTION

The granitic rock is investigated as a potential host rock, being considered as one of the safety barriers for high-level radioactive waste disposal in a number of countries, including Czech Republic. Migration of radionuclides is described by the transport parameters such as the retardation and distribution coefficients ($R$ and $K_d$), Peclet number ($Pe$) or hydrodynamic dispersion coefficient ($D$). These parameters can be determined using dynamic column technique, which has many advantages in comparison with static batch experiments. The present work [1] investigated sorption and desorption of tracers HTO and $^{36}$Cl (as Na$^{36}$Cl) in columns filled with crushed pure granite and corresponding infill materials. Experiments were focused on the study of the effect of grain size; firstly, on the values of Peclet numbers, hydrodynamic dispersion coefficients and bed porosity, secondly, on the influence of grain size on the values of retardation and distribution coefficients. The transport model, based on the erfc-function, assuming a linear equilibrium sorption/desorption isotherm, was used for the description and modeling of experimental data.

EXPERIMENTAL

Analogous to the previous studies, see e.g. [2], two types of crystalline rocks were used: pure granite, coded as PDM1-1 (from 97.5 to 98.7 m depth), and fracture infill material, coded as PDM1-2 (from 89.7 to 90.0 m depth). Each rock sample was crushed and sieved to 0.063, 0.125, 0.630, 0.63, 0.80 and 0.80-1.25 mm fractions. The fractions were placed into 5 cm$^3$ adapted plastic columns of 1.3 cm inner diameter and 5.4 cm height. Tracer solution was obtained by adding appropriate aliquots of the above mentioned tracers into synthetic groundwater (SGW) – this solution was used in the sorption phase of given study. To the desorption of tracers mentioned, pure SGW was used. In both the cases, the dependences in the form of breakthrough curves (BTC) were obtained, BTC being the dependence of the output relative activity ($A_{rel}$) of the given radionuclide on the number of bed pore volumes ($n_{PV}$) outgoing from the column.

RESULTS

The experimental points and calculated lines of BTCs of $^3$H (as HTO) obtained with crushed pure granite and corresponding infill material are demonstrated in Fig. 1. The BTCs for other grain sizes, including the BTC of $^{36}$Cl, are similar or practically the same. It is evident that it deals with the non-interacting (non-sorbing) tracers because the points of inflection of BTCs are around the value $n_{PV} = 1$, and the retardation coefficients have the same values [1]. Therefore, such tracers are appropriate for the determination of $Pe$ number characterizing the flow pattern (flow character) in the bed. In this case, $Pe$ is a function of the grain size (see Fig. 2). It corresponds well with the theory [3], according to which such phenomenon depends on bed height, particles size and shape, their arrangement, seepage velocity, etc.

REFERENCES


This research has been supported by the Ministry of Industry and Trade of the Czech Republic under contract No. FR-T11/362.
COMPARATIVE STUDY OF CHLORIDE AND IODIDE DIFFUSION IN COMPACTED BENTONITE

Hofmanová, E.; Rosendorf, T.; Vopálka, D.

INTRODUCTION
In many concepts of high level radioactive waste repository, compacted bentonite is planned as a buffer/backfill material due to its very low permeability and high sorption capacity. However, anionic species such as $^{36}\text{Cl}^-$, $^{129}\text{T}$ are not retarded due to their negligible interaction with engineered and/or natural barriers and may migrate to the biosphere much faster than cationic species. Chloride and iodide are the most stable species under in situ conditions of the deep repository and thus significantly contribute to the potential overall long-term dose. The transport of chloride and iodide ions in the bentonite barrier can be reduced by anion exclusion effect, which occurs due to the electrostatic repulsion of anions from negatively charged surfaces of clay minerals. Therefore, this work was focused on the fundamental understanding of diffusive behavior of chloride and iodide anions in compacted bentonite. In order to demonstrate the anion exclusion effect, chloride and iodide diffusion experiments were further compared with diffusion experiments performed with neutral species in the form of tritiated water.

EXPERIMENTAL
A set of through-diffusion experiments on the compacted bentonite B75 (commercial milled and homogenized bentonite originating from Rokle deposit, Czech Republic) of $L = 15 \text{ mm}$ at different dry densities was performed. Water, chloride and iodide in trace concentration (as HTO, $^{36}\text{Cl}$ and $^{129}\text{T}$; radioanalytical detection) as well as in non-active form in concentration of 0.01 mol/L (ion selective electrode detection, ISE) were used. All experiments were performed under ambient conditions and at the ionic strength of 0.1 mol/L in order to compare diffusive behavior of these species.

![Fig. 1. Schematic representation of the objectives and the experimental conditions of this study.](image)

After the through-diffusion step, the bentonite sample was cut into thin slices and concentration profile in the layer was determined. Apparent and effective diffusion coefficients were evaluated from two types of data sets (break-through curves and concentration profiles), using own computer module EVALDIFF [1].

RESULTS
HTO profiles in Bentonite layer showed that separating filters (stainless steel membranes of $L_d = 0.8 \text{ mm}$) have high diffusive resistance. By simultaneous fitting of break-through curves and concentration profile, filter parameters were obtained, $D_{eff} = (3.4 \pm 0.4) \times 10^{-11} \text{ m}^2$/s, which were used for the evaluation of chloride and iodide experiments.

No significant effect of background electrolyte on iodide diffusive behavior was found, see Fig. 2.

![Fig. 2. Concentration profiles and break-through curves of iodide and corresponding fits.](image)

Slightly lower apparent diffusion coefficients were found in case of $^{129}\text{T}$ experiments than for stable iodide experiments. This might support a weak retardation at low iodide concentrations [2-4]. Stable chloride diffusion into the target reservoir was faster than in the case of $^{36}\text{Cl}$. Bentonite sample contained more chloride when stable chloride in initial concentration of 0.01 mol/L was used. It seems that chloride was not completely removed by saturation with 0.1 mol/L NaNO₃. Finally, although different exclusion was expected based on different ionic radius and therefore different charge density, no significant difference in diffusive behavior of chloride and iodide was observed. Both anions enter only ca. 20 ± 5 % of the total bentonite pore space under initial strength of 0.1 mol/L.

REFERENCES

This work was supported by the Ministry of Industry and Trade of the Czech Republic under Project No. FR-T11/362 and by the Grant Agency of the Czech Technical University in Prague, grant No. SGS13/224/OHK4/3T/14.
INTRODUCTION

The determination of parameters characterizing the diffusion transport in barrier materials is an important tool for prediction of the behavior of critical radionuclides in both near- and far-field of the final disposal of radioactive waste. The evaluation of laboratory diffusion experiments can supply values of effective diffusion coefficient \( D_e \) and apparent diffusion coefficient \( D_a \) that enable to model the transport of radionuclides in a barrier system. The connected parameters are distribution coefficient \( K_d \) and/or retardation coefficient \( R \) of species interacting with the surface of a barrier material. The systematic errors in determination of these parameters could be caused by improper methods of evaluation of diffusion experiments, e.g., (i) in case when the standard time-lag method is being used for evaluation of experiments in which the diffusion resistance of separating filters is important, and (ii) heterogeneity of samples not taken into consideration by the evaluation. The model of diffusion experiments prepared in GoldSim [1] enabled to quantify the influences errors mentioned. The retardation of interacting species in their diffusion transport in porous media can be connected by a sophisticated description of their interaction with the surface of a solid phase by means of a geochemical code. We used the ability of PHREEQC to model the diffusion transport in multicomponent heterogeneous systems to the development of a model of through-diffusion experiments.

RESULTS

The use of the models of diffusion experiments in compacted bentonite prepared in GoldSim environment enabled to take into account the presence of filters and concentrations changes in working reservoirs that helped us to improve laboratory procedures. The numerous simulations performed with the models gave us a better knowledge about the diffusion of various species in the layer of compacted bentonite under different conditions. The influence of the higher bentonite porosity on the contact with filters (by about 20% higher than in the middle) on the modeled concentration profile in the stationary state of diffusion experiment is presented in Fig. 1 as an example.

Three types of sorption sites (for ion-exchange X and Xa), for surface complexation HfoO) in bentonite were assumed in our interaction model, the set of their characteristic data and their interaction with the Cs\(^+\) ion were based on data in [2-3]. The uncertainties of 6 parameters of the interaction model developed were used for the assessment of the uncertainty of cesium retardation in the layer of compacted bentonite. Uniform probability density function (for logarithms of interaction constants \( \log K(CsX) \), \( \log K(CsXa) \) and \( \log K(HfoO) \)) and triangular distribution (for concentrations of sorption sites X, Xa and Hfo) were supposed for the description of uncertainties of parameters taken into account. The uncertainty analysis predicted uncertainty of retardation coefficient \( R \) (see Fig. 2). From the sensitivity analysis performed for two concentrations in the input reservoir it was concluded that, for intervals chosen for the description of uncertainties of individual parameters, the most important are uncertainties of log \( K(CsX) \) and log \( K(CsXa) \). The uncertainties of concentrations of X and Hfo were of minor importance. The results of the study performed can help to explain qualitatively the observed variability of diffusion coefficients determined from the results of diffusion experiments.

Fig. 1. Influence of the inhomogeneity in the porosity on the profile of the total concentration in the bentonite layer for different distribution coefficients \( K_d \).

Fig. 2. Histograms (model of probability distributions function) of computed retardation coefficient \( R \) related to diffusion transport of Cs in the layer of compacted bentonite for two input concentrations. Six uncertain parameters are mentioned in the text; in the case of four parameters, the uncertainty of X and Hfo concentrations were not taken into account.

REFERENCES


The research was supported by the Ministry of Industry and Trade of the Czech Republic under contract FR-T11/362 and by SÚRAO.
INTRODUCTION
The aim of this work was to perform the sensitivity and probability analyses of a new version of the model of the Czech safety concept of deep geological waste repositories [1] taking into account a limited set of critical radionuclides ($^{39}$Cl, $^{73}$Se, $^{129}$I, $^{226}$Ra and its daughter products $^{210}$Po and $^{210}$Pb). The repository is in the model considered as a connected system of engineered and natural barriers. The fuel matrix consisting of uranium dioxide ceramics, in which minor actinides and fission products are incorporated, forms the first barrier. Released radionuclides will diffuse through the layer of compacted bentonite and rock (granite) matrix and will reach the flowing water in granite rock fractures. We focused mainly on conducting safety and uncertainty analyses for parameters which can be affected by design, research and development activities. These include the lifetime of disposal canisters and the characteristics of the bentonite buffer. Parameter uncertainties were modelled via probability density functions which were assigned on the basis of available data by expert judgment.

EXPERIMENTAL
The sensitivity analysis of $^{79}$Se concentration, presented here as an example, used the variance-based method, which allows one to perform both analyses in a single set of Monte Carlo simulations [2].

Fig. 1. Probability analysis of $^{79}$Se concentrations at the end of the model of a host rock.

The variance-based method provides two quantitative sensitivity measures: the first order sensitivity coefficient, $S_i$, and the total effect of a parameter, $S_{i,t}$; which are based on the Hoeffding decomposition scheme of a function of $K$ input parameters. Coefficients $S_i$ and $S_{i,t}$ were calculated simultaneously using Monte Carlo estimators that require two independent sampling matrices A and B of uncertain parameters. We used the Sobol’ quasi-random generator to build these matrices.

RESULTS
We performed two parallel analyses with two different geosphere parameter settings. We considered seven model parameters as uncertain. Each analysis was comprised by 2304 model simulations. Fig. 1 illustrates the methodology of the probability analysis performed in our study. Panel A is devoted to the descriptive statistics of concentrations at the end of a network of fractures of host rock model. The 0.25th, 0.50th, 0.75th, 0.975th quantiles and mean values (black dashed line) were calculated separately for each time point. Consequently, displayed time profiles cannot be identified with the time courses of $^{79}$Se concentrations corresponding to any individual combination of uncertain parameters. Concentrations of $^{79}$Se are widely spread at the beginning (4 000, 11 000) [a] and constant on the time interval (1·10$^5$, 1·10$^6$) [a], the latter is caused by a restricted solubility limit of granite layer.

Variance-based sensitivity measures used in our work are not suitable for the cases when values of examined output $Y$ vary over several orders of magnitude [3], as it occurs at the beginning interval of $^{79}$Se concentration profiles. In such cases it is necessary to transform $Y$ before calculating $S_i$ or $S_{i,t}$. Our sensitivity analysis identified four main contributors that caused a wide spread of concentrations at the beginning time interval.

We concluded that if model output is properly transformed before performing sensitivity analysis, the calculated sensitivity coefficients serve as robust indicators of the importance of uncertainty of selected parameters. We plan to use the proposed methodology to develop an updated model of deep geological waste repository.

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This research has been supported by the Ministry of Industry and Trade of the Czech Republic under contract No. 1H-PK/25 and by SURAO.

Vetešník, A.; Landa, J.; Vokál, A.; Vopálka, D.

1ÚJV Řež, Czech Republic, 2SURAO, Czech Republic

NUCLEAR CHEMISTRY ● ANNUAL REPORT

26
INTRODUCTION
Classical migration experiments are used to obtain diffusion and sorption parameters but they require long experimental time periods (months to years). The electromigration (EM) technique uses an electrical gradient as driving force to force ionic species to move, hence these data can be obtained in days. This technique was developed to determine diffusive properties for different radionuclides in Boom Clay (e.g. [1-2]), extended for use on compacted sodium montmorillonite [3-4], and in crystalline rocks [5]. The aim of this study was to develop an EM cell for compacted bentonite and to test the applicability of EM technique to study radionuclide transport in it.

EXPERIMENTAL
The EM cell design was based on a mix of the design of [1,3]. The newly developed EM cell represents a modular system consisting of two or three bentonite plugs in series; and in between an aliquot of studied tracer is spiked. The bentonite specimen is separated by glass filters from the reservoirs filled with an electrolyte in which Pt electrodes are immersed to provide an electrical field over the specimen. When electric field is applied, electrolysis of the electrolyte solution occurs with creation of protons and hydroxyls at the anode and cathode sides, respectively, which induces pH changes over the sample that can negatively influence the EM experiment. In order to mitigate these effects, different set-ups were tested, see Fig. 1 (with intermixing of both electrode sides in one (A) or two neutralisation reservoirs (B), without intermixing (C) and with salt bridges (D)).

A  
\[ \text{Anode side} \]

B  
\[ \text{Cathode side} \]

C  
\[ \text{Anode side} \]

D  
\[ \text{Cathode side} \]

Fig. 1. The tested EM set-ups.

Plugs of the Czech commercial bentonite B75 were compacted to a dry density of 1300 kg/m³ and fully saturated with 0.033 M CaCl₂ (which suppresses the swelling). Two or three bentonite plugs were combined in an EM set-up and in between an aliquot of ¹²⁵I tracer was spiked. After the test, the bentonite was sliced and tracer activity in each slice was measured.

In order to demonstrate that the EM technique provides comparable values as classical diffusion tests, through-diffusion experiments were performed in parallel.

RESULTS
EM revealed that the purchased ¹²⁵I spiking solution was not pure in terms of a speciation (Fig. 2), namely iodide as declared on the specification sheets provided by the producer. This was not evident from classical diffusion experiments. EM profiles were deconvoluted in order to determine apparent diffusion velocity \( V_D \), apparent dispersion coefficient \( D \) and also the proportion of iodide to total initial ¹²⁵I activity in the spiking solution. Thereafter, results of through-diffusion experiments were interpreted taking into account the presence of two iodine species and an iodide apparent diffusion coefficient \( D_{DIF} \) was determined.

\[ D_{DIF} = (3.0 \pm 0.5) \times 10^{-10} \text{ m}^2/\text{s} \]

In order to remove less mobile iodine species (probably iodate), a reductive treatment of ¹²⁵I spiking solution with Na₂S₂O₃ under acidic conditions was carried out. Only the faster iodine species (iodide) was indentified in the EM experiment. From a series of iodide EM experiments, an apparent diffusion coefficient \( D_{EM} \) was determined which is consistent with the value obtained from through diffusion experiments.

REFERENCES

This work originated from an apprenticeship at SCK•CEN with the purpose of developing and testing the electromigration technique on compacted clay materials.
SPECIATION IN THE UO$_{2}^{2+}$ - XO$_{4}^{2-}$ - H$_{2}$O SYSTEMS (X=S, Se) BY SPECTROSCOPICAL MEANS, INTERPRETATION OF THE INDIVIDUAL COMPONENT LUMINESCENCE SPECTRA.

Višňák, J.; Vetešník, A.; Kuba, J.; Sladkov, V.; Bok, J.; Štamberk, K.

INTRODUCTION
Complex species [UO$_{2}$(XO$_{4}$)](H$_{2}$O)$_{n}$XO$_{4}$ (X = S, Se) formation is of importance for geochemical studies (of, e.g., uranium mining and radioactive waste repositories – including safety studies). Time-resolved Laser-induced Fluorescence Spectroscopy (TRLFS) and UV-VIS absorption spectrophotometry speciation studies provided individual species luminescence and absorption spectra, luminescence life-times and complex stability constants $\beta_{n}$. Luminescence spectra can be interpreted in terms of adiabatic excitation energy $T_{0,0}$ and uranyl group symmetric mode vibrational frequency $\omega_{gs}$ ($\omega_{es}$) – see Fig. 1.

EXPERIMENTAL
Experimental solutions were prepared from UO$_{2}$ ($c_{UO_{2}}$ = 0.05 M for spectrophotometry and from 10$^{-3}$ M to 10$^{-5}$ M for TRLFS), and Na$_{2}$XO$_{4}$ (the ligand concentrations $c_{X}$ were chosen to equidistantly span log $c_{X}$ axis), pH 2 was fixed by HClO$_{4}$ and ionic strength $I$ by NaClO$_{4}$. TRLFS spectra were measured by tunable Nd:YAG laser-pumped laser system VIBRANT$^\text{TM}$ 355 II.

RESULTS
The spectroscopic properties of uranyl-selenates are almost identical with those of uranyl-sulfates. Stability constants of uranyl-selenates are slightly lower according to selenate being softer base than sulfate [1].

EXPERIMENTAL solutions were prepared from UO$_{2}$ ($c_{UO_{2}}$ = 0.05 M for spectrophotometry and from 10$^{-3}$ M to 10$^{-5}$ M for TRLFS), and Na$_{2}$XO$_{4}$ (the ligand concentrations $c_{X}$ were chosen to equidistantly span log $c_{X}$ axis), pH 2 was fixed by HClO$_{4}$ and ionic strength $I$ by NaClO$_{4}$. TRLFS spectra were measured by tunable Nd:YAG laser-pumped laser system VIBRANT$^\text{TM}$ 355 II.

RESULTS
The spectroscopic properties of uranyl-selenates are almost identical with those of uranyl-sulfates. Stability constants of uranyl-selenates are slightly lower according to selenate being softer base than sulfate [1].

REFERENCEs

This research has been supported by the Ministry of Education of the Czech Republic under contract MSM 6840770020 and SÚRAO ČR.
**THE MATRIX INFLUENCE ON THE DETERMINATION OF LOW URANIUM CONCENTRATIONS BY LASER INDUCED FLUORESCENCE METHOD**

Zavadilová, A.; Drtinová, B.

---

**INTRODUCTION**

A measurement technique enabling the determination of low uranium concentrations utilizing tunable laser system used for TRLFS (time resolved laser induced fluorescence spectroscopy), based on a commercially available KPA method (kinetic phosphorescence analysis) was carried out. KPA is a fast, sensitive, and non-destructive method, allowing the uranium concentrations determination in the order of ng L\(^{-1}\) [1]. In our laboratory, the concentration of U is determined mainly in samples relating to uranium mining and processing where the concentration of uranium is in the order of μg L\(^{-1}\).

Our interest was therefore focused on verifying the applicability of the modified method for samples with this level of U concentration and also for matrices of higher ionic strength that could potentially influence the determination of uranium concentration. The effect of the matrix, complexing agent, and the level of acidification on the recorded fluorescence spectrum shape and integral intensity was studied.

**EXPERIMENTAL**

Tunable laser system commonly utilized for TRLFS measurement was used. In order to determine the concentration of uranyl in the tested samples, the relation between the concentration and the intensity of the detected fluorescence was measured. Calibration measurements were performed for solutions of known concentrations (0.5 - 2000 μg L\(^{-1}\)). For each complexing agent, the excitation wavelength in the absorption maxima was used, i.e. 416 nm for Uraplex (Chemchek Instruments) and 418 nm for H\(_2\)PO\(_4\). The resulting value of fluorescence intensity for the concentration calculation is taken as the sum of the averages of the measured intensities of the spectra for every wavelength in the emission spectra. Besides the intensity measurement the method enabled the study of the emission spectral characteristics and the detail measurement of potential complexes wavelength shift.

Uranium solutions were prepared by dissolving UO\(_2\)(NO\(_3\))\(_2\).6H\(_2\)O, G.R.; for samples containing UO\(_2\)Cl\(_2\) or UO\(_2\)SO\(_4\), already available pure stock solutions were used, in which the U concentration was confirmed by ICP-MS. To simulate the matrix in the samples, simple salts were tested: NaOH, NaCl, NaNO\(_3\), Na\(_2\)SO\(_4\).10H\(_2\)O, NaHCO\(_3\), CH\(_3\)COONa.3H\(_2\)O, KCl, KNO\(_3\) and Ca(NO\(_3\))\(_2\).4H\(_2\)O. Samples containing simulated groundwater NA6 (Ruprechtov site, Czech Republic) were also used [2].

During the “concentration” measurements slight fluctuations of spectral characteristics in wavelength as well as the intensity were observed. The formation of different complexes could be responsible for this phenomenon. The method of time resolved laser induced fluorescence spectroscopy was used to confirm or refute the presence of different complexes. Based on measured spectra, lifetimes of different complexes were calculated.

**RESULTS**

For most of the investigated matrices, the described method for concentration measurements offered sufficient precision of the U concentration determination if the samples differ from the calibration standards only in the added salt. Then merely the presence of nitrates and chlorides was problematic. In case of nitrates, even the method of standard addition has not offered satisfactory results. Determination of uranium concentration turned out to be more complicated if its starting salt was chloride or sulfate while the calibration with uranium nitrate was performed.

**Tab. 1.** Effect of added salt on fluorescence intensity of the sample, c(U)=100 μg L\(^{-1}\).

<table>
<thead>
<tr>
<th>added salt, c=0.01 mol L(^{-1})</th>
<th>UO(_2)(NO(_3))(_2)</th>
<th>UO(_2)Cl(_2)</th>
<th>UO(_2)SO(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>×</td>
<td>100.1 ± 1.6</td>
<td>120.3 ± 30.9</td>
<td>115.2 ± 19.5</td>
</tr>
<tr>
<td>Na(^+) (NaOH)</td>
<td>98.7 ± 5.5</td>
<td>134.1 ± 35.2</td>
<td>121.6 ± 26.2</td>
</tr>
<tr>
<td>Na(^+) (NaHCO(_3))</td>
<td>103.7 ± 3.1</td>
<td>166.7 ± 0.6</td>
<td>141.1 ± 1.1</td>
</tr>
<tr>
<td>NaNO(_3)</td>
<td>102.5 ± 6.3</td>
<td>207.7 ± 152.4</td>
<td>140.1 ± 45.8</td>
</tr>
<tr>
<td>Na(_2)SO(_4)</td>
<td>98.5 ± 9.9</td>
<td>154.6 ± 0.6</td>
<td>144.4 ± 0.7</td>
</tr>
<tr>
<td>NaCl</td>
<td>71.8 ± 1.9</td>
<td>96.0 ± 23.5</td>
<td>98.1 ± 9.5</td>
</tr>
<tr>
<td>CH(_3)COONa(_4)</td>
<td>99.0 ± 3.4</td>
<td>164.4 ± 3.4</td>
<td>145.6 ± 0.8</td>
</tr>
</tbody>
</table>

To better understand these results, the concentration measurements were extended and TRLFS method was used. From the obtained data it is evident, that the complexing agents could form different complexes for different matrices. In the case of chlorides it is possible to distinguish their presence by TRLFS first and then use the method of standard addition which provides good results in this case. If another substance able to cause the quenching effect is present, either several different complexes will be formed and different appropriate fluorescence lifetimes could be measured, or only one complex (chloride and substance) will exist, but the lifetime and spectral characteristics will be certainly different from those of the chloride complex.

Given the interest in the subject work, studies aimed at improving the methodology are still in progress.

**REFERENCES**


This research was supported by the Ministry of Education of the Czech Republic under contract MSM 6840770020.
DETERMINATION OF THE TOTAL MERCURY IN CONTAMINATED SOILS BY DIRECT SOLID SAMPLING ATOMIC ABSORPTION SPECTROMETRY USING AN AMA-254 DEVICE AND RADIOCHEMICAL NEUTRON ACTIVATION ANALYSIS

Sysalová, J.¹; Jan Kučera, J.²; Fikle, M.²; Drtinová, B.

¹Institute of Chemical Technology, AAS Laboratory, ²Nuclear Physics Institute AS CR

INTRODUCTION
Reliable procedures for the determination of total mercury are in demand according to increased attention recently paid to the determination of Hg species in environmental and biological samples. However, such procedures usually involve sample digestion as the first step.

One of the exceptions is simple direct solid sampling atomic absorption spectrometry method using an AMA-254 (Advanced Mercury Analyser) device for the determination of total mercury content in soils highly contaminated from different pollution sources. Excellent accuracy of the total mercury determination at the level up to 25 mg kg⁻¹ using AMA-254 was demonstrated by analysis of several US NIST soil standard reference materials (SRMs) and by a comparison with results of radiochemical neutron activation analysis RNAA achieved for the same contaminated soil samples and NIST SRMs.

EXPERIMENTAL
Samples of contaminated soils from two localities with different pollution sources were analyzed. The first site was an abandoned waste storage ground of a former incineration plant in the suburb of Hradec Králové, Czech Republic, where the Hg content in several soil samples exceeded the maximum permissible limit of 0.8 mg kg⁻¹ [1] and in separate experiments Hg⁰ and methyl mercury CH₃Hg⁺ were identified as the dominant species there. The second sampling site was selected in the vicinity of a former phenyl mercury chloride-based fungicide production plant next to Příbram, Czech Republic, with Hg content reaching up to 10 mg kg⁻¹. Additional two species were identified there - inorganic Hg²⁺ and phenyl mercury PhHg⁺.

The soil samples were collected from the upper layer (0-20 cm), air-dried at laboratory temperature, sieved through a nylon 2mm screen and 5g sample portions were further subjected to cryogenic grinding at liquid nitrogen temperature to achieve a degree of homogeneity as high as possible and also to prevent possible losses of volatile mercury forms. Control samples of NIST SRMs were analyzed without any treatment.

Samples of contaminated soils and quality control materials with masses of 10-25 mg were inserted into the AMA-254 spectrometer in a nickel boat, dried at 120°C for 70 s, and combusted in the oxygen atmosphere at 650°C for 150 s. For quantification, a mercury reference standard solution 1000 mg L⁻¹ ±10 mg L⁻¹ as Hg²⁺ in dilute nitric acid was used to prepare aqueous calibration solutions in the range of 0–200 μg L⁻¹ using deionized water. Each calibration solution contained 1% (v/v) HNO₃, 0.1% (v/v) HCl and mercury-free 0.01% (m/v) K₂Cr₂O₇.

In the case of RNAA, a slightly modified procedure [2] was used. The samples were irradiated in the LVR-15 reactor in Řež (at a thermal modified procedure [2] was used. The samples were irradiated in the LVR-15 reactor in Řež (at a thermal neutron fluence rate of 3×10¹⁷ cm⁻² s⁻¹ for 10 h).

RESULTS
The agreeable results of the total mercury determination obtained by analysis of rather low, up to 20mg sample portions by AMA-254 and approximately 150mg sample portions by RNAA, are compared in Tab. 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>AMA-254 x ± s (N=3)</th>
<th>RNAA x ± ua</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hradec Králové F5A</td>
<td>2.42 ± 0.22</td>
<td>2.48 ± 0.08</td>
</tr>
<tr>
<td>Hradec Králové F5D</td>
<td>24.5 ± 0.8</td>
<td>25.3 ± 0.8</td>
</tr>
<tr>
<td>Hradec Králové F5E</td>
<td>11.5 ± 1.0</td>
<td>12.2 ± 0.4</td>
</tr>
<tr>
<td>Příbram 1</td>
<td>2.11 ± 0.03</td>
<td>2.25 ± 0.07</td>
</tr>
<tr>
<td>Příbram 12</td>
<td>4.17 ± 0.09</td>
<td>4.55 ± 0.15</td>
</tr>
<tr>
<td>Příbram 15</td>
<td>9.76 ± 0.003</td>
<td>9.88 ± 0.32</td>
</tr>
<tr>
<td>2711 Montana Soil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NIST value</td>
<td>6.18 ± 0.41</td>
<td>6.22 ± 0.05</td>
</tr>
<tr>
<td>2711a Montana II Soil</td>
<td>7.19 ± 0.25</td>
<td>7.16 ± 0.25</td>
</tr>
<tr>
<td>NIST value</td>
<td></td>
<td>7.42 ± 0.19</td>
</tr>
<tr>
<td>1648a Urban Particulate Matter</td>
<td></td>
<td>1.42 ± 0.12</td>
</tr>
</tbody>
</table>

Value ± combined uncertainty (coverage factor k = 1).

Commercially available devices, such as AMA-254 or DMA-80 spectrometers, have been specifically designed for mercury determination at trace and ultratrace levels. It should be carefully observed that the upper limit of their working range (0.5 μg or 1.2 μg for AMA-254 and DMA-80, respectively) is not exceeded in analyzing samples with high mercury contents, because this would lead to negatively biased results. Unlike other authors, who employed the dilution of high contents of Hg in heavily polluted samples with an inert matrix, we used low masses (10-25 mg) of well homogenized, yet representative samples to comply with requirements for accurate Hg determination using AMA-254. We have also found that NIST SRM 2711 and 2711a (Tab. 1) are sufficiently homogeneous with respect to Hg to allow accuracy testing at the low-mass sample intakes. The new total mercury value determined in NIST SRM 1648a is of importance for quality control of air pollution studies.

REFERENCES

This research was supported by the Czech Science Foundation - projects P503/12/0682 and P108/12/G108.
INTRODUCTION
The Quantum computer as a computational model seems to be a permissive tool for breaking the limits of asymptotical computational costs derived for classical algorithms for classical computers. Quantum algorithms may be particularly efficient for many-body quantum system simulation (e.g. eigenvalue finding) [1]. While for molecular systems (quantum chemical case) this was already done [2-5], I suggest this technique for the computational nuclear physics case for the first time. The aim of the article prepared [6] was to perform the first steps to the simulation of a quantum algorithm based on modified first-quantized Weisner and Zalka’s formulation [7,8] and exploiting the Iterative Phase Estimation Algorithm [4,9-11] for deuterium Hamada-Johnson (or Argonne) Hamiltonian ground state energy estimation to test its applicability and possible extensions to larger nuclei. In this case, second-quantized Abrams-Lloyd variant was suggested. Excited states energy estimation, nuclear potential optimizations and Quantum Chromodynamical calculations via quantum algorithms are mentioned briefly in [6] as well.

PROBLEM FORMULATION
For a given Hamiltonian \( \hat{H} \), the problem is to find the ground state energy \( E \) (the lowest eigenvalue of \( \hat{H} \))

\[
\hat{H}|\psi\rangle = E|\psi\rangle.
\]

The (Iterative) Phase Estimation Algorithm needs an initial guess of the eigenvector \( |\psi_0\rangle \) (which can be derived as a solution of (1) restricted to small model function space) and lower and upper bounds to \( E \): \( E_{\text{min}} \leq E \leq E_{\text{max}} \), the latter might be a variational value of \( E \) connected to \( |\psi_0\rangle \) and the former could be constructed from \( \hat{H} \) and \( |\psi_0\rangle \) as described in [12]. The deuterium Hamiltonian in position representation has a form

\[
\hat{H} = \frac{\hat{p}^2}{2 \mu} + \frac{\hat{r}^2}{2 \mu r^2} + \hat{V},
\]

where \( \mu \) is proton-neutron reduced mass, \( r \) is radial coordinate (distance between proton and neutron), \( \hat{p}^2 = -r^{-1}\partial_r^2 r \) is square of radial momentum operator, \( \hat{L} \) is angular momentum operator and \( \hat{V} \) is either Hamada-Johnson [13] or Argonne [15] potential. The Trotter-Suzuki approximation for the evolution operator is used,

\[
\hat{U} = \exp(i \Delta t \hat{H}) = \left[ \exp\left(i \frac{\Delta t}{m} \hat{L} \right) \exp\left(i \frac{\Delta t}{m} \hat{V}_{\text{eff}} \right) \right]^{n} + O\left(\frac{1}{m} \right),
\]

where \( \hat{L} = \hat{p}^2 / 2 \mu \) (radial kinetic energy) represents the first term in (2) and \( \hat{V}_{\text{eff}} \) (effective potential) the second and third ones. The latter is diagonal in radial coordinate representation (but mix the S and D states), the former in the “dual” representation. The wave function can be written as

\[
\langle \alpha | \psi \rangle = \sum_{a=0}^{1} \frac{R_a(\alpha)}{r} |a\rangle,
\]

where

\[
|S\rangle = |J = 1, m_j = 0, l = 0, s = 1\rangle_{L_{\text{spin}}},
\]

\[
|D\rangle = |J = 1, m_j = 0, l = 2, s = 1\rangle_{L_{\text{spin}}},
\]

therefore, \( |\psi\rangle \) is represented by 1 qubit for SJD part and b qubits for radial part \( R_a(r) \). The most economical use of all b qubits is supposed encoding equidistant radial grid on \( 2^b \) points with minimal element \( dr > 0 \) and maximal \( 2^b dr \).

\[
|\psi\rangle \approx \sum_{a=0}^{b} \sum_{j=1}^{b} R_a(\langle j dr \rangle) |a, j\rangle.
\]

While the action of \( \exp\left(i \Delta t / m \hat{V}_{\text{eff}} \right) \) on (7) is an action of block diagonal quantum gate operator (2x2 blocks are spanned by \( |0, j\rangle, |1, j\rangle \), the \( \exp\left(i \Delta t / m \hat{L} \right) \) can be represented by a diagonal quantum gate if inserted between quantum sine transforms [6,14] and therefore can be implemented by \( O(\beta^2) \) elementary quantum gates. The number of elementary gates for implementing \( \exp\left(i \Delta t / m \hat{L} \right) \) is at least \( O(b) \) and at most \( O(b^2) \), depending on algorithm details (the former variant suppose several additional working registers where binary represented parts of [13] potential will be computed, a large multiplicative factor is expected).

RESULTS
The first, preliminary, steps for the simulations of quantum algorithms for bounded state energy calculation for the smallest nuclei (in particular, deuterium) were presented [6].

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Němec, M.; Čubová, K.: Determination of Uranium Isotopic Composition Using LSC for Screening and Education Purposes
SEPARATION OF CURIUM FROM AMERICIUM USING TODGA-PAN COMPOSITE SORBENT AND (PhSO₃H)₂-BTPhen SOLUTION

Šťastná, K.; Šebesta, F.; John, J.

INTRODUCTION
The Americium Selective Extraction (AmSel) process [1] has been used as the basis for development of a chromatographic system for separation of Cm from Am. The liquid organic phase (N,N,N’,N’-tetraoetyl diglycolamide (TODGA) in TPH + 5 % 1-octanol) was replaced by TODGA-PAN composite sorbent, and 3,3’,3’’,3’’’-[3-(1,10-phenanthroline-2,9-diyl)-1,2,4-triazine-5,5,6,6-tetrayl] tetrabenzensulfonic acid ((PhSO₃H)₂-BTPhen) in nitric acid solution was employed as a masking or eluting agent.

EXPERIMENTAL
In batch experiments, 10 mg of TODGA-PAN (33 % active component, grain size < 0.3 mm) was shaken with 1 mL of (PhSO₃H)₂-BTPhen in HNO₃ solution spiked with trace amounts of Am and Cm using Rotorator PTR-30 at 360° and 30 rpm for 60 minutes (unless otherwise stated) at room temperature. Weight distribution coefficients (Dₜ) and separation factor (SF) were calculated from the alpha activity of aqueous phase aliquots taken before (Aₕ) and after shaking (Aₜ) and the aqueous phase volume (V) and composite sorbent weight (m) as:

\[ Dₜ = \frac{Aₜ - Aₕ}{Aₕ} \quad SF = \frac{Dₜ(Cm)}{Dₜ(Am)} \]

For extraction chromatography experiments, plastic column was filled with 60 mg of TODGA-PAN to form 0.50mL bed (0.47 cm diameter and 2.9 cm height). 500 μL of 0.3M nitric acid with trace amounts of Am and Cm was placed on the column and eluted with 0.003M (PhSO₃H)₂-BTPhen solution in 0.3M HNO₃ at a flow rate of 0.6 ml h⁻¹. Fractions of 0.6 mL were collected and measured by alpha spectrometry. Separation factor was calculated from curium and americium effluent volumes (Vₐₐ and Vₐₘ) and column dead volume (Vₜₜ) as:

\[ SF = \frac{Vₐₐ - Vₜₜ}{Vₐₘ - Vₜₜ} \]

RESULTS

![Fig. 1. Sorption of Am(III) and Cm(III) on TODGA-PAN from 0.003M (PhSO₃H)₂-BTPhen in 0.3M HNO₃ solution at varied shaking time.](image1)

![Fig. 2. Sorption of Am and Cm on TODGA-PAN from 0.003M (PhSO₃H)₂-BTPhen at varied c(HNO₃).](image2)

![Fig. 3. Sorption of Am and Cm on TODGA-PAN from 0.3M HNO₃ at varied c((PhSO₃H)₂-BTPhen).](image3)

![Fig. 4. Elution chromatogram of Cm/Am separation in TODGA-PAN = 0.003M (PhSO₃H)₂-BTPhen in 0.3M HNO₃ system.](image4)

REFERENCES

This research has been supported by the Grant Agency of the Czech Technical University in Prague, grant No. SGS12/199/OHK4/3T/14.
HYDROPHILIC SULFONATED BIS-1,2,4-TRIAZINE LIGANDS: EFFECTIVE REAGENTS FOR EFFICIENT ACTINIDE-LANTHANIDE SEPARATIONS VIA SELECTIVE FORMATION OF AQUEOUS ACTINIDE COMPLEXES

Distler, P.; John, J.; Lewis, F.W.; Kozhevnikov, V.N.; Harwood, L.M.; Hudson, M.J.; Geist, A.

1Northumbria University, Newcastle, United Kingdom; 2University of Reading, United Kingdom; 3Karlsruhe Institute of Technology, Germany

INTRODUCTION
In order to overcome the limitations of the TALSPEAK processes, the water-soluble hydrophilic derivatives of the highly effective bis-1,2,4-triazine N-donor ligands have been developed. Furthermore, it is worth noting that the highly selective BTP, BTBP, and BTPhen ligands retain their actinide binding selectivity when dissolved in aqueous solutions. [1]

Therefore, it has been reasoned that hydrophilic sulfonated bis-1,2,4-triazine ligands could be promising reagents for selective actinide complexation even at the high HNO₃ concentrations usually found in genuine waste solutions without the need for additional buffers.

The results of our studies on sulfonated bis-1,2,4-triazine ligands as highly effective reagents for carrying out actinide-lanthanide separations via selective actinide aqueous complexation are presented.

EXPERIMENTAL
Each of the sulfonated ligands was added to HNO₃ solutions and spiked with Am(III) and Eu(III) tracers. The distribution ratios D and separation factors SF were measured after contacting the aqueous phases with the organic solutions containing 200 mmol/L TODGA in kerosene:octanol mixture (95:5 volume ratio). The concentration of each sulfonated ligand in aqueous phase was 10 mmol/L. Obtained results were compared with those of a blank sample, which did not contain any sulfonated ligand in the aqueous phase.

RESULTS
The results of 4 tetrasulfonated bis-1,2,4-triazine ligands are shown in Fig. 1.

The structure of one of the promising ligands (PhSO₃H)₂-BTPhen is shown in Fig. 2. Dependence of distribution ratios on HNO₃ concentration for this molecule is shown in Fig. 3.

![Fig. 2. Structure of (PhSO₃H)₂-BTPhen](image)

![Fig. 3. Extraction of Am(III) and Eu(III) from HNO₃ by TODGA in the presence of (PhSO₃H)₂-BTPhen in the aqueous phase](image)

It was shown that disulfonated bis-1,2,4-triazine ligands cannot suppress extraction of either Am(III) or Eu(III) by TODGA. On the other hand, the results showed that the tetrasulfonated bis-1,2,4-triazine ligands can selectively complex Am(III) and prevent its extraction by TODGA agent across a wide range of HNO₃ concentrations, in contrast to the TALSPEAK process which operates within a very narrow pH range. These ligands can be used as selective masking agents for Am(III) and Eu(III) separation in processes currently being developed for the selective extraction of actinoids from high level waste, such as the i-SANEX process.

REFERENCES

This study has been supported by Euratom FP7 Projects SACSESS, "Safety of ACtinide SEparation ProceSSes" (FP7-CP-SP5-323 282).
INTRODUCTION
In the frame of the development of the French CEA EXAm process (Am selective separation from a PUREX raffinate by solvent extraction), the selective stripping of Am(III) from lanthanides was studied using a solution of DTPA and malonic acid. This step is similar to a reverse-TALSPEAK system developed for Am/Ln separation.

EXPERIMENTAL
Organic phase containing 0.3 mol/L HDEHP and 0.6 mol/L DMDOHEMA in TPH was first loaded with the aqueous phase containing Am and lanthanides. The loaded organic phase was then contacted with the aqueous solution of DTPA and malonic acid at pH around 2.0-2.5.

RESULTS
Dependence of log(D*[H₄DTPA]) on pH is shown in Fig. 1.

From obtained data shown in Fig 2, thermodynamic parameters were calculated and are shown in Tab. 1

<table>
<thead>
<tr>
<th>Element</th>
<th>ΔH [kJ/mol]</th>
<th>ΔS [J/mol∙K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>-33.3 ± 1.0</td>
<td>86.3 ± 3.1</td>
</tr>
<tr>
<td>Eu</td>
<td>-7.2 ± 1.1</td>
<td>16.8 ± 3.7</td>
</tr>
<tr>
<td>Am</td>
<td>-20.5 ± 0.2</td>
<td>85.7 ± 0.6</td>
</tr>
</tbody>
</table>

Moreover, DTPA stability constants were determined. The dependences are shown in Fig. 3. From obtained results, the following DTPA stability constants were calculated. Am: Log β = 23.45; Eu: Log β = 22.93; and Ce: Log β = 21.65.

The impact of DTPA and malonic acid concentrations, pH dependence, kinetic and thermodynamics were studied on Am(III) and lanthanides extraction. In addition, the stability constants of DTPA with Am(III), Eu(III) and Ce(III) were determined in process conditions. These results showed that DTPA and malonic acid extraction system can selectively strip Am(III) over lanthanides (Ce(III) and Eu(III)). The results are important for a better understanding of the process chemistry and are used for the modelling and the simulation of this step of the EXAm process.

This study has been supported by Euratom FP7 Projects ACSEPT, "Actinide reCycling by SEParation and Transmutation" (FP7-CP-2007-211 267).
INTRODUCTION
Recently, magnetic separation technology has again attracted attention in the area of irradiated nuclear fuel reprocessing.\cite{1} It is proposed that when magnetic nanoparticles (MNPs) are combined with prospective ligands such as CyMe$_2$-BTPhen, these functionalized MNPs could be used to extract the minor actinides and the radioactive material could then be collected magnetically in preference to centrifugation. Finally, the MNPs could be recycled by stripping the radioactive elements from the conjugates, generating a very small amount of secondary waste.

EXPERIMENTAL
The aqueous solutions for extraction experiments were prepared by spiking HNO$_3$ solutions (0.001 – 4 mol/L) with stock solutions of $^{241}$Am, $^{152}$Eu, and $^{244}$Cm; and then by adding 600 µL of spiked aqueous solution into CyMe$_2$-BTPhen-functionalized silica-coated MNP (Fig. 1) to create a 10 mmol/L concentration of CyMe$_2$-BTPhen. The suspension was sonicated for 10 minutes and shaken at 1800 rpm for 90 minutes. After centrifuging for 10 minutes, aliquots of supernatants were separated and taken for measurements.

RESULTS
High mass distribution ratios ($D_m > 700$ mL/g) were obtained (Fig. 2) for both Am(III) and Eu(III) at 0.001 mol/L HNO$_3$ solution with no significant selectivity for Am(III) over Eu(III). At 0.1 mol/L HNO$_3$, the $D_m$ value for Am(III) remained high ($D_m$(Am) = 1857 ± 154), but the $D_m$ value for Eu(III) was significantly lower ($D_m$(Eu) = 101 ± 2), resulting in lower separation factor. Decreases in the $D_m$ values for both Am(III) and Eu(III) were observed also at 1 mol/L HNO$_3$ solution, resulting in a higher separation factor (SF$_{Am/Eu}$ = 65 ± 5).

Finally, at 4 mol/L HNO$_3$ a further decrease in $D_m$ value for Am(III) gave $D_m$(Am) = 55.4, but $D_m$(Eu) = 0.03. This means that only Am(III) was retained on the tested MNP. The resulting separation factor (SF$_{Am/Eu}$ estimated to be > 1300) is far superior to that observed for CyMe$_2$-BTPhen ($SF_{Am/Eu} = 400$) in solvent extraction experiments.\cite{2}

In summary, the CyMe$_2$-BTPhen ligand has been covalently bound to SiO$_2$-coated MNPs by a phenyl ether linkage after functionalization at C-5 of the phenanthroline. This MNP exhibits very high selectivity for Am(III) over Eu(III) at 4 mol/L HNO$_3$ (with a separation factor in excess of 1300). This MNP also shows a small but significant selectivity for Am(III) over Cm(III) with a nominal separation factor of around 2 at 4 mol/L HNO$_3$.

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This study has been supported by the CTU in Prague, grant No. SGS12/199/OHK4/3T/14 and Euratom FP7 project SACSESS (FP7-CP-SPS-323 282).
INTRODUCTION
CyMe$_4$-BTBP and CyMe$_4$-BTPhen are prospective extractants for the European SANEX and/or GANEX processes for the recovery of minor actinides from a genuine spent nuclear fuel solution. [1,2] In such applications, it is necessary to demonstrate not only good extraction properties of the solvent, but also radiation stability of the extractants and the influence of solvent irradiation on its extraction properties. [3]

EXPERIMENTAL
The solutions of the CyMe$_4$-BTBP (6,6’-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazine-3-yl)-2,2’-bipyridine) and CyMe$_4$-BTPhen (2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazine-3-yl)-1,10-phenanthroline) ligand dissolved in cyclohexanone or alkylated cyclohexanone derivatives were irradiated by gamma source ($^{60}$Co - Gammacell 220, 14.5kGy/h, Chalmers University) in presence/absence of 2mol/L HNO$_3$ by the doses of 100kGy and 400 kGy. The solutions of 5 mmol/L CyMe$_4$-BTBP and CyMe$_4$-BTPhen (0.85 mL) were shaken with 1 mL of HNO$_3$ solutions for 6 hours. Extraction properties of irradiated and non-irradiated solvents were compared. Nitric acid solutions were spiked with $^{152}$Eu(III) and $^{241}$Am(III) stock solutions. Samples were analyzed using HPLC system LaChrom series 7000 (Merck-Hitachi).

RESULTS
In the case of CyMe$_4$-BTBP and in absence of the acid, a visible increase of stability was observed for system containing 2,6-dimethylcyclohexanone diluent. However, preliminary results indicate that this protective action is probably lost in presence of the acid. From this point, the system containing 3-methylcyclohexanone seems better due to uniform stability in presence/absence of the acid.

The first results on radiation stability of CyMe$_4$-BTPhen in three different solvents indicate comparatively similar stability of this ligand in cyclohexanone, but only in absence of aqueous phase. Lower stability was observed in both remaining solvents. In presence of acid, a significant drop in residual concentration in cyclohexanone and 2,6-dimethylcyclohexanone was observed even after applying dose 100 kGy. The system with 3-methylcyclohexanone didn’t prove any sensivity to acid.

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This study was supported by Euratom FP7 Projects SACESS, "Safety of ACtinide SEparation ProcессEs" (FP7-CP-SP5-323 282) and TALISMAN FP7- 323 300 and a partialy also from Ministry of Education project No. 7G13003 and the project RVO 61389830 from the Academy of Sciences of the Czech Republic.
INTRODUCTION
For the transmutation of minor actinides, various targets are proposed. Due to the small fraction of delayed neutrons, the criticality of the conventional reactor zone is a technical issue. Moreover, high level of helium production causes subsequent swelling during the fission of americium. One of the promising strategies to operate fission system containing minor actinides in a safe way is to use the accelerator driven system (ADS) using inert matrix fuel (IMF). Because the costs of ADS operation are high, suitable neutron balance is necessary. For this purpose, various matrices were designed for the IMF: MgO (CerCer), Mo, Al, SiAl, Zirkaloy-4, Inox 304 (CerMet) etc. [1]

Molybdenum based IMF uses significant amount of isotopically enriched $^{92}$Mo. Special head-end treatments for and after dissolution are necessary (Fig. 1). Firstly, it is necessary to remove main activity of the fission products to simplify the next separation steps of isotopically tailored molybdenum. Secondly (the part which is described here), it is necessary to purify the recovered molybdenum from the remaining traces of radionuclides and stable impurities prior its conversion to the metal and recycling.

![Figure 1. Possible flowsheet for the reprocessing of ADS fuel with molybdenum inert matrix](image)

EXPERIMENTAL
Molybdenum solution was prepared from dianmonium dimolybdate (Alfa Aesar) and caesium nitrate (Dorapis) or strontium nitrate (Lachema). The basic simulant solution for caesium or stroncium sorption studies had 100 g·L⁻¹ Mo, $10^5$ mol·L⁻¹ Cs or Sr and pH = 9.1 (adjusted by ammonia). The solutions were spiked by $^{137}$Cs (Institute for Research, Production and Use of Radioisotopes) or $^{85}$Sr (Perkin Elmer) for gamma spectrometric measurements.

**Determination of the kinetics:**
100 mg of the tested sorbent was shaken with 4 mL of molybdenum solution ($V/m = 250$ mL·g⁻¹) in 30mL PE bottles for 6 hrs using an orbital shaker at 250 rpm.

**Determination of the mass distribution coefficients:**
16 mg of sorbent was shaken with 4 mL of molybdenum solution ($V/m = 250$ mL·g⁻¹) in 30mL PE bottles for 6 hrs using an orbital shaker at 250 rpm.

**Column experiments:**
Supelco PP cartridge (bed volume, $BV = 1.27$ mL) was used as a column. The column was filled with the KNiFC with polyacrylonitrile (PAN) binding matrix (composite adsorber is referred to as KNiFC-PAN) for Cs separation or Ba(Ca)SO₄ with PAN binding matrix (referred to as Ba(Ca)SO₄-PAN) for Sr separation that has been wetted prior to the experiment by sucking distilled water. The molybdenum solution was passed through the column in upward direction by a peristaltic pump.

RESULTS

- In the case of KNiFC and Ba(Ca)SO₄ the sorption kinetics is fast, the equilibrium is reached after approximately 60 minutes. For composite sorbents, the apparent equilibrium is attained after approximately the same time (or even earlier in the case of Ba(Ca)SO₄-PAN with grain size < 0.3 mm).
- For KNiFC and Ba(Ca)SO₄, the dependences of $D_S$ on molybdenum concentration and pH were determined. Influence of pH around a value 9.1 and of molybdenum concentration around 100 g·L⁻¹ Mo was very low. Also the sorption isotherm was measured. The maximum sorption capacity obtained in batch experiments was 0.454 mmol·g⁻¹ for Cs (for Sr the maximum sorption capacity has not been reached).
- Dynamic column tests for Cs separation were performed with the KNiFC-PAN material. The column experiment was done with caesium concentration set to $10^2$ mol·L⁻¹. 100% breakthrough (BT) was achieved, but symmetric S-curve was not observed in this experiment. Possible reasons could be either molecular sorption of caesium molybdate on the KNiFC-PAN (similar phenomenon was observed earlier for the sorption of caesium chromate on the same material [2]). The calculated practical weight capacities $Q_m$ of Cs = $10^{11}$ mol·L⁻¹ ~ 0.418 mmol·g⁻¹.
- The dynamic column tests for Sr separation were performed with the Ba(Ca)SO₄-PAN material. The Sr concentration was set to the upper limit of the temporal stability of the solution, i.e. to $10^4$ mol·L⁻¹. The Sr breakthrough did not reach 10% BT even after processing of 5,000 BV of the surrogate solution. At this volume of the feed, problems with blockage of the column occurred and therefore this experiment was finished after the treatment of almost 7,000 BV (~ 1,600 mL) of the feed. At that moment, the experiment has been running for ~ 1,100 hours (one and half months).

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This work has been supported by the GA of the CTU in Prague, grant No. SGS12/199/OHK4/3T/14 and EU FP7 grant ASGARD (FP7-CP-2007-211 267).
AMERICIUM DETERMINATION IN BORIC-ACID CONTAINING NUCLEAR POWER PLANT EVAPORATOR CONCENTRATE

Bartl, P.; Němec, M.; John, J.; Šuľaková, J.

INTRODUCTION

Americium determination in technological solutions has been studied for many years. Most of the work has been, however, focused on spent nuclear fuel reprocessing, i.e. liquid-liquid extractions from very acidic nitric acid solutions. The $^{241}$Am is significantly produced during nuclear fuel irradiation, and thus it is vital, with regard to nuclear safety, to monitor this nuclide both in spent nuclear fuel and in NPP operational wastes. Given the origin of americium, wastes coming from a primary circuit cooling solution, such as very basic boric acid concentrate, are crucial for monitoring of this element.

For reaching our goal, extraction chromatographic separation method was utilized. Several extraction chromatographic materials suitable for americium separation were developed, but only DGA Resin showed good separation properties for americium even at pH value around 2 [1,2], and thus DGA and DGA-like materials were chosen.

EXPERIMENTAL

In this method, extraction-chromatographic separation using TODGA incorporated in PAN matrix developed at the Department of Nuclear Chemistry, CTU in Prague [3] was utilized. The boric acid concentrate coming from Dukovany NPP with pH 11.3 was used as the initial solution.

The pre-treatment of the initial solution was the subject of a recent work [4]. With the optimized sample solution, kinetic experiments in batch arrangement using 2mL Eppendorf vials (1 mL of the sample solution and 4 mg of a sorbent) were performed. According to the sorption kinetics found, the following column experiments used bed volume (BV) of 0.24 mL and flow rate of 2 BV/hour.

All the samples (100 µL fraction) were measured by a Liquid Scintillation Counter (LSC) Triathler (Hidex Oy, Finland)

RESULTS

Optimal parameters of pH 2.1 – 2.3 and 40% dilution of concentrate for Am sorption from the concentrate were determined with regards to resin properties and initial solution parameters. The kinetics experiments revealed that not only the kinetics of the process is very fast, which is not a common attribute for extraction chromatography, but also TODGA-PAN is even faster than the commercial DGA Resin. As shown in Fig. 1, about 97% americium uptake has been reached after half an hour of phase contact with TODGA-PAN.

Next, the capacity of our 0.24mL column was tested. It was found that only 1% of americium has broken through after loading 238 BV of the work solution (40% diluted concentrate, pH of 2.2).

Naturally, the last experiment was focused on the validation of this method with regard to repeatability. Fig. 2 and Table 1 show elution profiles and total amounts of eluted americium respectively, in three experiments conducted under exactly same conditions. Given the results, a very good repeatability of the method has been demonstrated.

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INTRODUCTION
For determination of $^{238}\text{U}/^{235}\text{U}$ ratios in environmental samples by accelerator mass spectrometry, the uranium oxide targets and UO$^+$ beam are usually used. However, uranium fluoride targets containing no oxygen and hydrogen may offer higher molecular isobar suppression together with a higher accuracy and sensitivity of uranium isotope analysis. In order to implement this kind of matrix into routine analyses, its preparation has to be studied in more details. In this work, several prepared targets were tested in the CENTA laboratory, Bratislava and VERA laboratory, Vienna. More details can be found in Povinec et al. [4].

EXPERIMENTAL
For the preparation of uranium tetrafluoride, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, HF, HCl, $\text{NH}_2\text{HF}$, and hydrazine hydrate solution (24-26%) of p.a. grade were used. The preparation of anhydrous uranium tetrafluoride was carried out following the published procedures - digestion of $\text{UO}_2$ with concentrated HF in 2M HCl [1], melting of $\text{UO}_2$ with $\text{NH}_2\text{HF}$ [2], or melting of $\text{UO}_2(\text{NO}_3)_2$ with hydrazine difluoride [3].

RESULTS
A set of uranium fluoride samples was produced using the above mentioned procedures and analysed for their purity using X-ray powder diffraction method. The diffraction patterns of these first prepared materials were compared with the diffraction lines of uranium dioxide and uranium tetrafluoride obtained from ICDD-PDF-2 database. Sharp peaks pertaining to uranium dioxide diffraction lines and uranium tetrafluoride were easily identified in all samples. In addition, the instability of the prepared uranium tetrafluoride in time was observed which is also undesirable in future applications (Fig. 1). To prevent any additional oxidation during the sample heating, reducing atmosphere was introduced into the used preparation methods.

![Fig. 1. Diffraction patterns of uranium tetrafluoride (procedure [1]) immediately after the preparation (red line) and after 41 days (blue line)](image)

Even though all these methods of anhydrous uranium tetrafluoride presented pure product [1–3] and additionally, the combustions were carried out under Ar or even Ar/H$_2$ atmosphere, the evaluation of the measured diffraction patterns of all prepared materials still revealed the presence of uranium dioxide and even the presence of U(VI). This lead to question the purity of the reactant, uranium dioxide, which was then checked using XRPD method. The diffraction patterns of this material showed not only the lines of uranium dioxide but also the lines of metaschoepite (($\text{UO}_2$)$_2\text{O}($OH$)_6$($\text{H}_2\text{O})_3$)) in which uranium is partially oxidised to higher oxidation state. This could partially cause the presence of U(VI) in all amoles of anhydrous uranium tetrafluoride prepared from stock $\text{UO}_2$.

Anhydrous uranium tetrafluoride prepared according to Wang et al. [1] was measured using AMS. The mass scan clearly showed several peaks related to oxide molecular ions (Fig. 2). The UF$_5^-$ ion current from uranium fluoride sample was in average higher by about 50 % than the UO$^+$ current from the uranium oxide samples. The targets were completely shattered away, and the estimated ionization yields of UO$^+$ and UF$_5^-$ were of the order of $10^{-3}$.

The development of uranium tetrafluoride targets for AMS analysis of $^{238}\text{U}/^{235}\text{U}$ U mass ratio in environmental samples has shown promising results, but more work is needed to master this technique.

![Fig. 2. Comparison of uranium oxide and fluoride ion currents in the Faraday cup.](image)

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This work was supported by the Grant Agency of the CTU in Prague, grant No. SGS 11/164/OHK4/3T/14, SGS 14/154/OHK4/2T/14, by the MIT CR under contract No. FR-T13/245 and grant No. 7AMB 12AT022.
INTRODUCTION
Many current AMS methods employ the uranium oxides as the most common matrix for \(^{238}\text{U}\) determination. However, one of the biggest disadvantages of this matrix is the presence of the isobaric interferences of more abundant molecular ions. Recently, the mostly desired improvements of the AMS sample matrix are suppression of isobaric interferences, increase in ion source yields or the improvements in the stability and durability of the sample in the ion source.

EXPERIMENTAL
In the basic studies of homogeneous precipitation, tetra-n-butylorthotitanate (TBOT, \(\text{C}_{16}\text{H}_{36}\text{O}_{4}\text{Ti}\)) and \(\text{UO}_2(\text{NO}_3)_2\cdot6\text{H}_2\text{O}\) of p.a. grade were used. As the commercial uranyl salts often contain high \(^{238}\text{U}/^{235}\text{U}\) isotopic ratio, uranium from Vienna KkU in-house standard with the \(^{238}\text{U}/^{235}\text{U}\) isotopic ratio at the level of \((6.1 \pm 0.4) \times 10^{-11}\) was used for AMS measurements [1]. TBOT (50, 100 and 200 \(\mu\)L) was added dropwise into the uranium solutions (0.5, 5 and 20 mmol L\(^{-1}\)) and mixed for 2 hours. Afterwards, the suspension was filtered and the aliquots of the filtrate and the original solution were taken for uranium measurements. The residue was dried at 30 °C in a vacuum kiln (\(p \sim 0.5\) kPa) before weight determination. To compare this matrix with classical oxide one, similar experiment was performed with Vienna-kKU uranyl nitrate to prevent the anthropogenic contamination. Into 10 mL of uranium solution (~1.9 mmol L\(^{-1}\)) 100 \(\mu\)L of TBOT was added dropwise, the suspension was stirred for one hour and then filtered. The residue was placed into a crucible and combusted at 900°C. Aliquots of the solutions before and after precipitation were taken for the alpha measurement using LSC.

RESULTS
The hydrolysis reaction between TBOT and water results in the hydrous titanium oxide formation accompanied by the ion sorption. The performed experiments showed consistent results and the mass of the formed solid material is proportional to the added volume of TBOT. The slope of the fitted curve was equal to 0.319±0.004 and had high accuracy. The value of the slope agrees with the fact that approximately two thirds of the TBOT mass comes from aliphatic chains and only the last third forms the mass of hydrous titanium oxide.

The sorption of uranium from aqueous solutions is also proportional to the added TBOT amount and it decreases with increasing uranium concentration. Solutions before and after the precipitation were checked for the change in pH. With increasing added amount of TBOT into the uranium solution, pH slightly reduces. The applicability of this sorption method is also supported by the promising results obtained in the experiments with a real water sample from the inlet to the mine water treatment plant placed in Dubenec, Bytíz, CZ (CDV PB II). This water sample was not acidified and after spontaneous iron precipitation, the uranium concentration was determined to be 5.29 mg L\(^{-1}\). The experiment was performed with 750 mL of the water sample into which only 1 mL of TBOT was added dropwise. The calculated uranium uptake of 56% is sufficient and promising also for other possible applications.

From the combusted residue of homogeneous precipitation, three sputter targets of different masses were prepared. For comparison, three other sputter targets of oxide matrix and also of different masses were added into the sample holder for \(^{238}\text{U}/^{235}\text{U}\) isotopic ratio measurements which was performed at VERA facility (Vienna, Austria).

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This work was supported by the Grant Agency of the CTU in Prague, grant No. SGS 11/164/OHK4/3T/14, SGS 14/154/OHK4/2T/14, by the MIT CR under contract No. FR-T13/245 and MEYS grant No. 7AMB 12AT022.
MEASUREMENT OF $^{99}$Tc VIA CHERENKOV COUNTING

Čubová, K.; Němec, M.

INTRODUCTION

Separation of $^{99}$Tc from the radioactive waste and nuclear industry operational matrices is a problem being solved for a long time. The ultimate goal of our work has been to test options of separation and measurement of $^{99}$Tc from NPP operational evaporator concentrates and/or from the concentrated solutions of molybdenum salts potentially issuing the GEN IV reactor fuels reprocessing. In the first phase, it was decided to test the possibility to measure $^{99}$Tc via Cherenkov counting after its selective extraction. The idea was to find a system allowing a one-step extraction and measurement in a scintillation vial.

EXPERIMENTAL

Cherenkov counting is usually not recommended for the $^{99}$Tc measurement because of low efficiency of the method [1]. Besides, following the literature data [1], the Cherenkov counting strongly depends on the refractive index of the respective solution. To test the possibility of $^{99}$Tc measurement using a Cherenkov counting, experiments were performed aiming at finding a system for the extraction of $^{99}$Tc into organic phase with high refractive index.

RESULTS

It was proven that the measurement of $^{99}$Tc via Cherenkov counting should be possible. Despite the fact that Cherenkov radiation is generated, the system is unstable. It was shown that the reason of the gradual decrease of the measured count rates is the fact that in a short time $^{99}$Tc is re-extracted back to the aqueous phase. This happens despite the fact that pH of aqueous phase is stable in case of CCl$_4$ system. In the CS$_2$ system, pH decreased in time from the original values (10-11) to pH ~ 7. Because of this unexpected behavior, detection efficiency of the Cherenkov counting could not be determined. From the values measured, we are estimating the detection efficiency to be higher than 40% for CS$_2$ system and at least 10% for CCl$_4$ related to the LSC measurement using Ultima Gold AB. Another set of experiments is planned to identify stable extraction system conditions.

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This work was supported by grant project of the Ministry of Industry and Trade of the Czech Republic MPO TIP FR-T13/245.
DETERMINATION OF URANIUM ISOTOPIC COMPOSITION USING LSC FOR SCREENING AND EDUCATION PURPOSES

Němeč, M.; Čubová, K.

INTRODUCTION
Fast, simple and effective method for determination of enrichment/depletion of uranium samples that can be used not only in the laboratory but also for unknown samples at inspections outdoors, was proposed for screening and education purposes. The technique of liquid scintillation counting (LSC) in the mobile mode represented by Triathler LSC Counter (Hidex Oy) could be a valuable tool for this type of measurement. Application (usage) of this equipment allows several advantages: determination of enrichment or depletion under off-lab conditions, combination of alpha, beta and Cherenkov counting (gives a complete picture required), milligram or even sub-milligram amounts of the sample (comparing e.g. to gamma-ray spectrometry), and easy preparation of the sample by mixing the U-salt with scintillation cocktail (comparing to e.g. alfa-spectrometry). The method can be used as the final step of a suitable separation/concentration method.

EXPERIMENTAL
How to rapidly determine the isotopic composition of uranium in “mg” amounts of uranium salt?

EDUCATION ASPECT
The method was also adjusted as a task for students in “Practical exercises in radiochemistry techniques” in the educational programme “BSc in Nuclear Chemistry”. The subject of this practical exercise is to determine the distribution ratios of uranium using different extraction techniques. The uranium extraction is carried out from an acidic solution to triocetylamine (TOA) in kerosene. The uranium concentration is measured using the liquid scintillation spectrometry with alpha-beta separation.

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Fig. 1. Procedure of rapid determination of the isotopic composition of uranium in uranium salts

Fig. 2. Uranium purification via amine extraction
Radiation Chemistry

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**NANOSILVER PREPARATION BY IRRADIATION METHODS IN MICELLAR SYSTEMS**

Wangle, T.; Silber, R.

**INTRODUCTION**
This work deals with the preparation of silver nanoparticles using ionizing radiation. The nanosilver was prepared from aqueous solutions of silver nitrate with either Triton X-100 or Brij L4 as the stabilizer and reducing ‘OH radical scavenger. The effects of AgNO$_3$ concentration, dose and type of deposited energy – accelerated electrons, gamma rays or UV – were studied. UV-Vis spectrophotometry was used to determine the concentration of silver nanoparticles. Photon Cross-correlation Spectroscopy was used to determine particle size in dispersions. The nanosilver was also separated by solvent extraction with chloroform.

**EXPERIMENTAL**
Triton X-100 and AgNO$_3$ were purchased from Merck. Brij L4 was purchased from Sigma-Aldrich. All chemicals purchased were of analytical grade and were used without further purification.

Sample Preparation
An aqueous solution of the desired surfactant was prepared at the desired concentration (1% for Brij L4 and 2% for Triton X-100) by adding the liquid surfactant to water and continuously mixing it either until a homogenous emulsion was formed (Brij L4), or until the gel formed in the solution was dissolved (Triton X-100). This process usually took about one hour. Solid AgNO$_3$ was then dissolved in the continuously stirred solution (emulsion) and modified by adding small amounts (up to 1 vol%) of modifier ions. Samples were stored in the dark to shield them from the effects of UV light present in natural sunlight.

Electron Irradiation
A 10 mL sample of the prepared solution was irradiated in 10 or 20 mL ampoules secured with parafilm. The ampoules were placed on a tray on a conveyor and irradiated with 4.5 MeV electrons from a linear accelerator with doses ranging from 1 to 32 kGy. The samples were placed on the tray all at once and irradiated until a sample was to be taken, then the irradiation resumed. If the jump between doses increased, then the dose rate was adjusted accordingly. An identical sample containing all the components except the silver nitrate was also irradiated at 24 kGy. This was then used as a standard for taking base readings. This standard was chosen over an unirradiated sample because of the quick effects of any UV radiation which, though not significant enough for concentration measurements in UV-Vis spectrophotometry, plays havoc with results from photon cross-correlation spectroscopy, where a very wide range of concentrations is detectable and it is more difficult to establish a good baseline. The other advantage being the possibility to, at least partially, control for the chemical changes undergone during radiolysis.

UV Irradiation
A 2 L solution was prepared and then transferred into a 2.8 L glass sulphonation flask (photochemical reactor). A medium-pressure mercury discharge was submerged into the solution and the output on the power source was set to 400 W.

Irradiation with Gamma Rays
Samples prepared for gamma irradiation were also taken into ampoules just as those for electron irradiation were. The samples were then placed into a $^{60}$Co gamma radiation source.

**RESULTS**
The dependence of measured nanosilver concentration on dose and results of nanoparticle size distribution measurement are shown in Figure 1 and 2.

![Fig. 1. Optical absorption spectra for a 0.1 mol/L AgNO$_3$ sample irradiated with various doses](image1.png)

![Fig. 2. Size distribution for 0.01 mol/L AgNO$_3$ in Brij L4 irradiated at 24 kGy](image2.png)

This work has been performed under the auspices of Ministry of Education, Youth and Sports project MSM 68-4077-0040 and it was passed as patent application number PV 2012-690.
PROTECTIVE EFFECT OF SOME OH RADICAL SCAVENGERS ON THE IRRADIATED CELLS UNDER BOTH NORMOXIC AND HYPOXIC CONDITIONS

Múčka, V.; Reimitz, D.

INTRODUCTION
High attention has been devoted to the action of various radioprotectors in many studies of bioradiation chemistry [1]. The action of some protectors may depend, among others, on the concentration of oxygen during the course of irradiation [2]. According to the paper [2], the OH radicals may cause up to 45% of cell damage, especially if the irradiation was performed in the nitrogen atmosphere. From the earlier study [3], it seems to be clear that the oxygen plays a large role in the indirect processes and their contribution to the cells killing reaches from 55 to 76% and from 20 to 50% under normoxic and hypoxic conditions, respectively [4].

EXPERIMENTAL
The yeast cells Saccharomyces cerevisiae were used in the study. The incubated cells were irradiated (60Co, 50 Gy h\(^{-1}\), 150 and 350 Gy) in the salt solutions containing various concentrations of scavengers (methanol, ethanol and potassium formate). Before irradiation, the suspension was bubbled with the nitrogen gas. The hypoxic samples (0.3 mg O\(_2\) / L) were irradiated in airtight test tubes. After a suitable dilution an aliquot part of the irradiated and non-irradiated cell suspension was plated on the complete nutrient agar. Incubation at 30° C for 4–5 days gave rise to colonies. Every measurement was repeated independently three times. Each colony represents one living cell. All colonies were counted up. The samples were evaluated according to the paper [1].

RESULTS
The slopes k of the linear dependences \(\sigma = \ln S_o/\ln S = f(Q)\) \((S_o\) and \(S\) are the parts of surviving cells without and with scavengers, respectively, and \(Q\) is the scavenging efficiency) for three different scavengers are given in Table 1. These values were compared with those obtained earlier [1] under the normoxic conditions. From the data given in the Table 1 is clear that the \(k\) values obtained under the hypoxic conditions are lower than those obtained under normoxic conditions at all irradiation conditions and for all three scavengers. The highest difference was found for methanol (factor 17.3) at the lowest dose. The decrease in the \(k\) values is due to the hypoxic conditions under which the sensitivity of the protection on the changes in scavenging efficiency is much lower than under the normoxic conditions. This statement is valid despite the fact that the dose rate for normoxic irradiation was about 70 Gy h\(^{-1}\) because the \(k\) values probably decrease with increasing dose rates in the range above 50 Gy h\(^{-1}\) [5]. Under this assumption, we can conclude that the participation of scavenging of OH radicals on the radiation protection of living cells seems to be lower under the hypoxic conditions than under the normoxic ones.

Tab. 1. The slopes \(k = d\sigma/dQ\) for various scavengers at different doses \(D\) under the hypoxic \((k_h)\) and normoxic \((k_N)\) conditions as well as the factor \(f = k_N/k_h\)

<table>
<thead>
<tr>
<th>Scavenger</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>Potassium formate</th>
</tr>
</thead>
<tbody>
<tr>
<td>D [Gy]</td>
<td>150</td>
<td>350</td>
<td>150</td>
</tr>
<tr>
<td>(k_h \times 10^{11}) [s]</td>
<td>9.0</td>
<td>10.1</td>
<td>4.2</td>
</tr>
<tr>
<td>(k_N \times 10^{11}) [s]</td>
<td>14.9</td>
<td>10.9</td>
<td>9.0</td>
</tr>
<tr>
<td>(f = k_N/k_h)</td>
<td>1.73</td>
<td>1.1</td>
<td>2.1</td>
</tr>
</tbody>
</table>

REFERENCES

This work was supported by the Grant Agency of the Czech Technical University in Prague, grant No. SGS14/207/OHK4/3T/14.
SYNTHESIS OF (Ni,Zn)O SOLID SOLUTIONS OR MIXED OXIDES VIA RADIATION METHODS

Procházková, L.; Pavelková, T.; Čuba, V.; Múčka, V.; Pospíšil, M.; Jakubec, I.¹

¹Institute of Inorganic Chemistry, AS CR, v. v. i., Husinec-Rež 1001, 250 68 Rež, Czech Republic

INTRODUCTION
Nickel oxide is a p-type semiconductor crystallizing in cubic rock-salt structure, whereas zinc oxide is n-type semiconductor crystallizing in the hexagonal wurtzite structure. Powders of ZnO:Ni were studied for ferromagnetic behaviour and photocatalytic activity [1]. Metal oxides prepared via radiation methods feature high chemical purity, nanometre-sized particles and high surface area, which may affect some properties, e.g. the enhancement of catalytic activity. A set of ZnO, NiO, mixed oxides and (Zn,Ni)O solid solutions was prepared by irradiation of aqueous solutions of Ni²⁺ and Zn²⁺ salts, based on the method described in [2].

EXPERIMENTAL
Aqueous solutions with various concentrations of Zn(NO₃)₂·6H₂O (from 0.005 to 0.02 mol dm⁻³), Ni(NO₃)₂·6H₂O (from 0.01 to 0.02 mol dm⁻³) and HCOOK (0.03 mol dm⁻³) as OH radicals scavenger were used. Medium pressure mercury lamp (200–580 nm) and high frequency linear accelerator with electron energy 4.5 MeV were used as sources of radiation. Characterization of powders was performed by X-ray powder diffraction (XRPD), X-ray fluorescence (XRF) was used for elemental analysis. Specific surface area (SSA) was measured by selective adsorption of N₂ from the mixture of H₂/N₂ at the temperature of liquid nitrogen.

RESULTS
Both UV and e-beam irradiation lead to the precipitation of weakly crystalline solid phase, identified as nickel hydroxide carbonate tetrahydrate and/or zinc hydroxide carbonate. After annealing at temperatures in the range of 300–600 °C, corresponding oxides were observed (Fig. 1).

![Fig. 1. Diffraction patterns of solid phase formed under UV irradiation in solution with molar ratio Ni:Zn = 1:0.5; annealed at various temperatures for 1 h. [4]](image-1.png)

The XRPD and XRF analyzes showed that Ni²⁺ transition from solution to solid phase is much less quantitative than for Zn²⁺. Formation of (Ni,Zn)O solid solutions in the cubic structure of NiO concurrently with hexagonal ZnO was observed in all cases, when the molar ratio of Ni:Zn in the solution was ≥0.5. For (Ni,Zn)O solid solutions, lattice parameter a was determined and practically linear dependence of a on the molar % of Zn in the NiO structure was observed. According to the Vegard’s rule [3], the Zn⁺⁺ content in the NiO phase was calculated (Fig. 2). From the comparison of calculated values of Zn content in the NiO phase with the molar % Zn in the material, it seems that the amount of Zn in the solid solution increases with decreasing overall molar fraction of Zn in the sample. The SSA increases with the increasing content of Ni²⁺ in the solid phase in samples annealed at 300 °C. This trend is caused by the much lower SSA of ZnO.

![Fig. 2. Dependence of lattice parameter on the molar % of Zn the samples and molar % of Zn in the NiO phase [4]](image-2.png)

REFERENCES

*Results were presented at the RadChem 2014 conference and published in [4].
INTRODUCTION
In last decades, fiber lasers have been established as an inherent part of a number of advanced photonic devices, including data transfer and processing. Optical fibers, namely erbium doped fiber amplifiers, have a crucial role as key components of optical networks. The design of fiber lasers widely exploits luminescence properties of rare earth ions located inside the optical fiber core. These ions or their combination primarily determine the operating wavelength of the fiber laser, e.g. a combination of erbium and ytterbium ions is used in lasers for telecommunication at 1.55 μm [1]. Conventional preparative process combines modified chemical vapor deposition, to prepare porous silica frit of ultra high purity, with solution-doping approach. An active lasing element (i.e. Er), is introduced into the laser material as an inorganic salt dissolved in an appropriate solvent [1]. One of the modifications of solution-doping approach is based on the replacement of inorganic salts by inorganic nanoparticles. Such a simple modification can significantly improve properties of glass matrix [2], thus improving the optical properties of optical fibers.

EXPERIMENTAL
Nanocrystals of erbium-doped yttrium aluminium garnet were prepared by photo-induced synthesis according to the published procedures [3]. Optical fibers were prepared by drawing from preforms manufactured by MCVD method combined with a solution-doping technique.
A refractive index profile of preform and the local chemical composition of the preforms was determined. Spectral attenuation and steady-state luminescence properties of the fiber were measured. The lasing properties of prepared fiber were measured in the ring arrangement depicted in Fig.1.

RESULTS
Maximal difference of refractive indexes between the preform core and preform cladding was 0.0092. The refractive index profile followed the concentration profile of the dopants inside the fiber core. The concentration ratios between particular dopants corresponded to the composition of incorporated ceramic nanocrystals. The maximal concentration of the aluminium ions was about 1 at % and corresponding concentration of erbium ions was 0.011 at % only. The crystallite size of prepared YAG nanocrystals was smaller than 30 nm, but the nanocrystals formed aggregates with average size around 300 nm.
Emission spectrum of the fiber excited at 976 nm by a laser diode is demonstrated in Fig. 2. The overall shape of the emission band is similar to that of the fibers prepared by conventional solution doping methods. Intensity of the emission linearly increased with increasing excitation power. A lifetime of Er\(^{3+}\) \(I_{15\mu\text{m}}\rightarrow I_{155\mu\text{m}}\) transition was 10.2 ms.
Optimal laser properties were achieved for a fiber length of 20 m. The slope efficiency of the fiber laser was about 15 %.

REFERENCES

*Full paper in [4].
X-RAY DIFFRACTION ANALYSIS OF TERNARY RARE-EARTH SULPHIDES

Bártá, J.; Jarý, V.; Havlák, L.; Nikl, M.

1Institute of Physics, AS CR, v.v.i., Cukrovarnická 10, 162 00 Prague 6, Czech Republic

INTRODUCTION

Ternary rare-earth sulphides with the general formula ALnS₂ (A = alkali metal, Ln = La-Lu,Y) are long-known materials either with a rhombohedral α-NaFeO₂ structure (Fig. 1), cubic NaCl structure (several Na, Li sulphides) [1] or hexagonal β-RbScO₂ structure (most Cs sulphides). Structural and luminescence properties of ALnS₂ materials started to be studied recently in a cooperation between the Department of Nuclear Chemistry, FNSPE and the Institute of Physics, AS CR [2,3]. This new family of inorganic scintillating materials with high Zeff possesses a narrower band gap relative to oxides. The suitably-sized lanthanide site with D₃d symmetry enables heavy doping by rare-earth ions. This contribution summarizes several main observations and results obtained during the structural study of this material family.

EXPERIMENTAL

Ternary rare-earth sulphides ALnS₂ were synthesized at the Institute of Physics by heating mixtures of lanthanide oxides Ln₂O₃ and a large excess of alkali metal carbonates A₃CO₃ in the flow of hydrogen sulphide gas H₂S and argon. The phase composition of the formed hexagonal-shaped platelets was analyzed by X-ray powder diffraction using either HZG-3 goniometer (TUR-62) or the Rigaku MiniFlex 600 diffractometer, both equipped with copper X-ray tubes and NaI:Tl scintillation counters. The measured diffraction patterns were compared to the ICDD PDF-2 structural database and the lattice parameters of the observed phase were calculated. The elemental composition was determined by X-ray fluorescence analyzer Niton XL3t 900 GOLDD.

RESULTS

In all studied samples containing either Rb or K, a single rhombohedral α-NaFeO₂-type phase was found by X-ray diffraction. No significant phase or elemental impurities were found in the prepared crystals. During preliminary experiments, the formation of very stable Ln₂O₃S phases was observed, but this impurity was avoided by proper synthetic conditions. The lattice parameters a and c of all prepared compounds corresponded to the literature values sufficiently well – several examples are shown in Fig. 2.

Due to the flat shape of the crystals, a very strong preferred orientation resulted in increased intensity of (0 0 3n) lines. In all ALnS₂ sulphides, the parameter a changes mainly with the type of Ln ion, whereas c reflects the alkali metal ion.

In the RbGdS₂ ternary sulphides doped up to 20 at. % of Pr [3], the lattice parameter a approximately linearly increased with Pr content (Fig. 3), indicating complete incorporation of the Pr ions into the Gd position, i.e. a substitutional solid solution. Similar behaviour may be expected for different lanthanide dopants in other ALnS₂ sulphides as well.

REFERENCES


This research has been supported by the Technology Agency of the Czech Republic (grant no. TA01011017) and by the Czech Science Foundation (grant no. GA13-09876S).

Fig. 1. Structure of the rhombohedral KLuS₂ sulphide and the microphotograph of prepared hexagonal-shaped KLuS₂ platelet (~ 1×1×0.1 mm).

Fig. 2. Measured diffraction patterns of different ternary sulphides KLnS₂ [2] compared to the expected positions of diffraction lines according to [1].

Fig. 3. Evolution of lattice parameter a in Pr-doped RbGdS₂ [3] compared to the literature values.
INTRODUCTION
In recent years, much attention has been drawn to the photo- and radiation-induced synthesis of various materials. In presented work, radiation-induced synthesis of nanocrystalline uranium and/or thorium oxides has been investigated. Uranium(IV) oxide is widely used as a fuel in various types of nuclear reactors [1]; thorium(IV) oxide and mixed uranium-thorium oxides are currently tested as a promising alternative [2].

EXPERIMENTAL
The principle of performed experiment is shown in Fig. 1.

Fig. 1. Radiation-induced synthesis of UO₂/ThO₂

All irradiated solutions were prepared in deionized water (conductivity ≤ 1 μS cm⁻¹) and they contained 0.1 mol dm⁻³ ammonium formate and 0.005–0.01 mol dm⁻³ uranyl and/or thorium nitrate. All prepared solutions were irradiated without any further adjustments. Irradiation was performed using UV radiation (low- / medium-pressure mercury lamp) or ionizing radiation (accelerated electrons). Changes in the solutions were evaluated by UV-Vis spectrophotometry and pH measurement.

Finely dispersed solid phase formed under irradiation was separated via microfiltration (Millipore HAWP 0.45 μm), washed with deionized water, dried at room temperature and then studied as is or heated at temperatures up to 800 °C in air or in argon + hydrogen (ratio 10:1, Ar+H₂) atmospheres.

Solid phase was characterized by thermal analysis (TGA), elemental (C, H, N) analysis, X-ray powder diffraction (XRD) and specific surface area (SSA) measurement. High resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) were employed as additional methods for solid phase characterization.

RESULTS
In all prepared solutions, finely dispersed solid phase (precursor) was formed under irradiation; the pH of irradiated solutions (~ 4.5) did not change significantly during irradiation. UV-Vis measurements of uranium solutions showed the typical spectra of uranyl nitrate with maxima at 427, 477 and 495 nm; the maxima gradually disappeared during irradiation, due to the precipitation of solid phase. Absorption spectra of thorium solutions showed the presence of nitrates (peak at 300 nm); due to photoreduction of nitrate to nitrite ions, peak at 365 nm emerged during irradiation. Filtered and dried solid precursors formed under irradiation in all solutions were amorphous. Importantly, results of elemental analysis indicated that there were only negligible amounts of carbon (≤ 0.3 %) in solid precursors, which makes it possible to prepare pure crystalline nanomaterials containing U(IV) oxide or U(IV) and Th(IV) oxide solid solution from (amorphous) solid precursors directly via treatment in Ar+H₂ atmosphere without pre-treatment in air.

Heat treatment of solid precursor formed in solution of uranyl nitrate under Ar+H₂ atmosphere resulted in formation of pure nanocrystalline UO₂ with well-developed crystals at 550 °C; yield was determined as 75 %.

In the solid precursor formed from solution of thorium nitrate, XRD lines of ThO₂ were first detected at 450 °C in air; at 500 °C, pure ThO₂ phase with well-developed nanocrystals was formed. Yield of ThO₂ was determined as 75–95 %, depending on the source of irradiation.

In the solid precursor prepared via irradiation of solution containing both uranyl and thorium nitrates at U:Th molar ratio 1:1, heat treatment under Ar+H₂ atmospheres resulted in the formation of solid (Th,U)O₂ solution (documented by the shift of XRD lines) already at 300 °C and the formation of well-developed crystals at 450 °C. Yield was determined as 75 %.

The materials consisted of nanoparticles ranging from 3 to 30 nm in diameter and with narrow size distribution, which was confirmed by HRTEM. Proposed method for uranium and/or thorium oxides synthesis is fast, simple and prepared oxides fulfill the prerequisites for the production of the high-quality nuclear fuel.

REFERENCES

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* Full paper in [3].
Radiopharmaceutical Chemistry

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NEW LABORATORY OF RADIOPHARMACEUTICAL AND ORGANIC CHEMISTRY

Kozempel, J.; Vlk, M.

INTRODUCTION

Even though the chemistry of labelled compounds and general interest in radiopharmacy have long tradition in the Czech Republic, the education in this field was formerly held only at the Department of Organic and Nuclear Chemistry of the Faculty of Sciences of the Charles University in Prague. Recently, the education in this field transferred to the Department of Nuclear Chemistry of the Faculty of Nuclear Sciences and Physical Engineering of the Czech Technical University in Prague. An independent research group focused in the main topic of radiopharmaceutical chemistry was established by appointing RNDr. J. Kozempel, Ph.D. as assistant professor starting since the 1st January 2013, together with RNDr. M. Vlk, Ph.D., who was previously a member of the separation chemistry group at the same department (both graduated from the Faculty of Sciences of the Charles University in Prague under the supervision of the late Doc. RNDr. Ladislav Lešetický, CSc.). During the 2013 the new laboratory of radiopharmaceutical chemistry opened in a refurbished space and starting from this year, many laboratory instruments and equipment were acquired.

![Fig.1. Members of the radiopharmaceutical group](image)

Most of the equipment is located in class I. and II. radiochemical laboratories allowing to handle the open sources of ionising radiation (license of the Czech State Office for Nuclear Safety No.: SUJB/RCAB/13262/2016). The key equipment includes:

- FT-IR spectrometer
- HRMS with collision cell equipped with APCI and ESI ion-sources
- single-qadrupole LC-MS system
- radiometric detectors (α and γ spectrometry, ionization chamber, \( A_{\text{max}} = 250 \text{ GBq} \))
- laboratory microbalances (\( d_{\text{min}} = 1 \mu g \))
- gloveboxes, laminar boxes and radiochemical hoods

Medical and material research is supported by analytical background based on various mass spectrometry systems, molecular spectroscopy techniques, magnetic resonance as well as radioanalytical techniques. From the early beginning, up to 95% of the group budget originates from various competitive sources. Close collaboration with academic, industrial and commercial partners is also very important.

CURRENT RESEARCH

Current research focuses on several areas of medicinal and nanomaterial chemistry. First is the development of medicinal radionuclides for diagnosis and therapy. One of the main fields of interest are the \(^{223}\text{Ra}\) labelled nanoparticles for targeted alpha-particle therapy and study of nanoparticles as carriers based on various bio-degradable or inert materials (e.g. hydroxyapatite, titanium dioxide, etc.). Our activities are focused also on multimodal imaging/therapy nanoprobes and theranostics, where superparamagnetic iron oxide nanoparticles (SPIONs) are being studied as contrast agents for MRI as well as carriers of \(^{223}\text{Ra}\) besides the SPECT (\(^{99m}\text{Tc}\)) and PET (\(^{18}\text{F}, \, ^{68}\text{Ga}\)) application. This part is closely related to the structural modification of nanoparticle surface as well as their electrostatic stabilisation and their \textit{in vivo} evaluation. Part of our research is also devoted to \(^{68}\text{Ga}\) chemistry and labelling condition and stability tests of bifunctional DOTA and NOTA analogues as a PET tracers.

Secondly, our activities are traditionally focused on chemistry of \(^{3}\text{H}, \, ^{2}\text{H}, \, ^{15}\text{N}, \, ^{13}\text{C}, \, ^{14}\text{C}\) or \(^{31}\text{P}\) labelled analogues of biologically active compounds, especially terpenes, steroids and auxines which show significant cytotoxic, antiviral or anti-neoplastic activities \textit{in vitro} and \textit{in vivo} on various tumour cell lines including multi drug resistant ones.

The third part of our research is devoted to material sciences, mostly synthesis and study a new materials for radionuclide separation and retention based on covalently bound extraction agents (e.g. PAN-DGA) with potential use in nuclear medicine.

REFERENCES


ACKNOWLEDGEMENTS

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Envinet a.s., Czech Republic
Eckert-Ziegler AG
Watrex Praha, s.r.o.
INTRODUCTION
Precipitation and dissolution of $^{226}$Ra$\text{BaSO}_4$ belong to basic radium chemistry operations. One of the methods involves the reduction of sulphates into sulphides, which can be dissolved in some mineral acids. Generally known route to sulphides is the thermal reduction of sulphates at high temperature with carbon.[1] Some subsequent operations may interfere with chelators or reagents added into the Ba/Ra samples, thus reagents like hydrazine hydrate or NaBH$_4$ offer an alternative. Reduction of sulphates to sulphides by sodium borohydride under microwave irradiation was already successfully used (80-90% conversion of sulphate).[2] For the purposes of further processing, the Na$_2$CO$_3$ method seemed to be advantageous for us, since the quite insoluble $^{226}$Ra$\text{BaCO}_3$ allows simple wash-out of bulk amount of Na$_2$CO$_3$ without significant losses of activity.

EXPERIMENTAL
Dissolution experiments were performed with non-labelled BaSO$_4$ or in some cases, with low-activity sintered radiobarite. Generally, the material was suspended in a solution of the corresponding reagents mixture and heated for a defined time period, cooled, washed with deionized water and finally let to react with diluted HCl, to convert Ba and Ra into soluble chlorides. Reaction mixtures in the experiments employing microwaves were not stirred. Experimental details are summarized in Tab. 1. and Tab. 2 together with results. Three reaction routes were selected - conversion to carbonates, conversion to sulphides and chelation with Na$_2$EDTA as a method of reference. A set of experiments for each route was performed in order to determine optimal conditions. Mainly, dissolution was performed at 85 °C for 1 hour.

Tab. 1. Summary of dissolution experiments with reducing agents. a time was 48 h., b temperature gradient and microwave power were used.

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>17$^a$</td>
<td>10</td>
<td>1:3 NaBH$_4$</td>
<td>1 mL water</td>
<td>lab.t.</td>
<td>partial</td>
</tr>
<tr>
<td>18$^a$</td>
<td>11</td>
<td>1:3 NaBH$_4$</td>
<td>1 mL water</td>
<td>80</td>
<td>partial</td>
</tr>
<tr>
<td>19</td>
<td>20</td>
<td>1:150 NaBH$_4$</td>
<td>15 mL water</td>
<td>120-160$^b$</td>
<td>not dissolved</td>
</tr>
<tr>
<td>20</td>
<td>104</td>
<td>1:12 NaBH$_4$</td>
<td>15 mL water</td>
<td>100-140$^b$</td>
<td>partial</td>
</tr>
<tr>
<td>21</td>
<td>99</td>
<td>1:13 NaBH$_4$</td>
<td>15 mL water + 0.2 % NaOH</td>
<td>85-90$^b$</td>
<td>partial</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^a$</td>
<td>20.8</td>
<td>1:172</td>
<td>10 mL 1.5M Na$_2$CO$_3$</td>
<td>quantit tive</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>109</td>
<td>1:172</td>
<td>50 mL 1.6 M Na$_2$CO$_3$</td>
<td>quantit tive</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>203</td>
<td>1:86</td>
<td>50 mL 1.5 M Na$_2$CO$_3$</td>
<td>quantit tive</td>
<td></td>
</tr>
<tr>
<td>8$^a$</td>
<td>130</td>
<td>1:85</td>
<td>30mL 1.6M Na$_2$CO$_3$</td>
<td>quantit tive</td>
<td></td>
</tr>
<tr>
<td>10$^b$</td>
<td>100</td>
<td>1:55</td>
<td>30 mL 0.75M Na$_2$CO$_3$</td>
<td>quantit tive</td>
<td></td>
</tr>
<tr>
<td>11$^b$</td>
<td>300</td>
<td>1:16</td>
<td>25 mL 0.8M Na$_2$CO$_3$</td>
<td>quantit tive</td>
<td></td>
</tr>
<tr>
<td>13$^a$</td>
<td>100</td>
<td>1:9</td>
<td>40 mL 0.1M Na$_2$EDTA 0.9M NH$_4$OH</td>
<td>quantit tive</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>250</td>
<td>1:3</td>
<td>30 mL 0.1M Na$_2$EDTA 1.7M NH$_4$OH</td>
<td>quantit tive</td>
<td></td>
</tr>
<tr>
<td>16$^b$</td>
<td>100</td>
<td>1:9</td>
<td>40 mL 0.1M Na$_2$EDTA 0.9M NH$_4$OH</td>
<td>quantit tive</td>
<td></td>
</tr>
</tbody>
</table>

RESULTS
$^{226}$Ra$\text{BaSO}_4$ was successfully dissolved at relatively mild conditions. Both Na$_2$CO$_3$ (a method of our main interest) and Na$_2$EDTA+NH$_4$OH methods brought good results. Application of a microwave power speeded-up and facilitated the conversion significantly. Several alternative methods were tested, however with low (if any) yields. Thus, depending on further use and intended processing of final $^{226}$Ra/Ba solution, both abovementioned methods could be applied in the recycling of aged $^{226}$Ra sources containing $^{226}$Ra$\text{BaSO}_4$.

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Authors are grateful to the Ministry of Education Youth and Sports of the Czech Republic for the support of this project (grant No.: LK21310).
INTRODUCTION

Increasing attention is paid to alpha emitters in cancer therapy including clinical trials and clinical applications. Hydroxyapatite is a material with natural affinity to the bones [1] and therefore could be good candidate for the construction of targeted carriers for radionuclide therapy and diagnosis in nuclear medicine. Moreover, hydroxyapatite was already approved by Food and Drug Administration (FDA) to be used in biomedical applications e.g. as bone implants material.

EXPERIMENTAL

Stock $^{223}$Ra was prepared from $^{227}$Ac/$^{227}$Th/$^{223}$Ra generator (Dowex-1×8, 0.7M HNO$_3$ in 80% CH$_3$OH) prepared according to Guseva et al.[2] Stock $^{99m}$Tc was obtained from commercial $^{99}$Mo/$^{99m}$Tc generator (DRYTEC™, GE Healthcare) and was eluted with 0.9% saline. Radionuclidic purity was checked by γ-spectrometry and in case of $^{223}$Ra also by α-spectrometry. Nano-hydroxyapatite particles were prepared by precipitation of 1.2M Ca(NO$_3$)$_2$·2H$_2$O with 0.8M (NH$_4$)HPO$_4$. The pH value of the reaction mixtures was maintained at 11. The prepared HA-NPs were filtered through 0.22 μm filter, dried under vacuum and characterised by FT-IR spectrometry (Fig. 1) and X-ray powder diffraction (Fig. 2). [3]

Two strategies were chosen for HA-NPs labelling [4]; surface sorption of radionuclides (S) and intrinsic incorporation of radionuclides into HA structure (V). In surface sorption, HA-NPs were dispersed in physiological saline and subsequently incubated with the eluate (in the case of $^{99m}$Tc reduction with SnCl$_2$ was necessary). The yields are shown in the tables (Tab. 1 and Tab. 2).

**Tab. 1. Preparation of $^{223}$Ra HA-NPs.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type of labelling</th>
<th>Weight [mg]</th>
<th>Initial activity [kBq]</th>
<th>Activity of lab.HA-NPs [kBq]</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S</td>
<td>5</td>
<td>17.6</td>
<td>14.6</td>
<td>84</td>
</tr>
<tr>
<td>2</td>
<td>S</td>
<td>5</td>
<td>17.5</td>
<td>14.3</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>V</td>
<td>5</td>
<td>17.7</td>
<td>17.0</td>
<td>97</td>
</tr>
<tr>
<td>4</td>
<td>V</td>
<td>5</td>
<td>17.6</td>
<td>17.0</td>
<td>98</td>
</tr>
</tbody>
</table>

**Tab. 2. Preparation of $^{99m}$Tc HA-NPs.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type of labelling</th>
<th>Weight [mg]</th>
<th>Initial activity [kBq]</th>
<th>Activity of lab.HA-NPs [kBq]</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S</td>
<td>5</td>
<td>160</td>
<td>90</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>S</td>
<td>5</td>
<td>140</td>
<td>90</td>
<td>94</td>
</tr>
<tr>
<td>3</td>
<td>V</td>
<td>5</td>
<td>230</td>
<td>160</td>
<td>94</td>
</tr>
<tr>
<td>4</td>
<td>V</td>
<td>5</td>
<td>140</td>
<td>82</td>
<td>93</td>
</tr>
</tbody>
</table>

RESULTS

Surface-labelled HA-NPs were obtained with yields ranging from 82 to 94 % both for $^{99m}$Tc and $^{223}$Ra. In the latter strategy, the corresponding radionuclide was precipitated together with 1.2M Ca(NO$_3$)$_2$·2H$_2$O and 0.8M (NH$_4$)HPO$_4$. These intrinsically labelled HA-NPs were obtained in the yields of 93-98 %. Labelling yields of intrinsically labelled $^{223}$Ra]HA-NPs were slightly higher than surface-labelled HA-NPs. The obtained labelling yields of $^{99m}$Tc]HA-NPs were comparable in both methods.

REFERENCES


This research has been partially supported by the Ministry of Education Youth and Sports of the Czech Republic (grant No. LK21310) and Technology Agency of the Czech Republic (grant No. TA03010027).
PREPARATION OF $^{227}$Ac FOR $^{227}$Ac/$^{223}$Ra GENERATOR BY NEUTRON IRRADIATION OF $^{226}$Ra

Kukleva, E.; Kozempel, J.; Vlk, M.; Mičolová, P.; Vopálka, D.

INTRODUCTION

The development of nuclear medicine involves the use of alpha particle emitting radionuclides like $^{223}$Ra and its decay products, which can be used for the targeted therapy of bone metastases. High total released energy (of about 27 MeV), high linear energy transfer (LET) of alpha particles and therefore short range in tissues make $^{223}$Ra and its decay chain very useful in the targeted therapy of small tumors. The most convenient method is the use of a $^{223}$Ac/$^{227}$Th/$^{223}$Ra generator. The $^{223}$Ac can be obtained in the $^{226}$Ra(n,$\gamma$) $^{227}$Ra $\rightarrow$ $^{227}$Ac activation/decay sequence (Fig. 1.).[1] This method is the most feasible for large scale production of $^{227}$Ac. The aim of this work was to verify the effective production cross section value and the irradiation yield of $^{227}$Ac.

EXPERIMENTAL

Radium-226 sample (190 kBq of $^{226}$RaCl$_2$ that equals to 5.135 $\mu$g of $^{226}$Ra) was prepared by the evaporation of standardized solution of $^{226}$RaCl$_2$ (Czech Metrological Institute, Czech Republic) under infrared lamp. The dry sample was flame-sealed in a quartz ampoule and irradiated in the LVR-15 reactor (Research Centre Rež, Czech Republic) for 11.7 effective days at a neutron flux density of $1.09 \times 10^{18}$ n/cm$^2$/s (0–10 keV group). The yields of products were determined several weeks after the end of bombardment (EOB) by the evaluation of $\gamma$-spectra recorded on a calibrated $\gamma$-spectrometer (Ortec, USA). The activity of $^{227}$Ac was determined by back-calculation from activities of its decay products to EOB.

The theoretical calculations were made with an in-house designed program based on differential equations that includes decay corrections and neutron reactions.

Despite worse resolution and quality of the spectra, good agreement between the experimental and the predicted values was observed. The effective cross section of $^{227}$Ac production was determined empirically by the activity measurements of the $^{227}$Th and $^{223}$Ra daughter nuclei in partial equilibrium with $^{227}$Ac using back-calculation to EOB. The activation intermediate $^{223}$Ra was neglected in the cross section determination. The effective cross section value of $^{227}$Ac production was then estimated to $14 \pm 4$ b. This value is in good agreement with available literature data (8–23 b) (Tab. 1).

![Fig. 1. Simplified reaction scheme of $^{226}$Ra under neutron irradiation. The effective cross section for the $^{227}$Ac production reaction was taken from [4], those for $^{226}$Ra and $^{227}$Ra production reactions were fitted empirically. Decay data were taken from [5].](image)

**Fig. 1.** Simplified reaction scheme of $^{226}$Ra under neutron irradiation. The effective cross section for the $^{227}$Ac production reaction was taken from [4], those for $^{226}$Ra and $^{227}$Ra production reactions were fitted empirically. Decay data were taken from [5].

![Fig. 2. Fit of experimental data measured in two intervals after EOB (88 and 136 days). Curves represent the calculated values, points represent experimental data.](image)

**Fig. 2.** Fit of experimental data measured in two intervals after EOB (88 and 136 days). Curves represent the calculated values, points represent experimental data.

**Tab. 1.** Comparison of recent data on $^{227}$Ac production.

<table>
<thead>
<tr>
<th>Yield (EOB) [Ci/g $^{226}$Ra]</th>
<th>Irradiation conditions</th>
<th>Calc. $\sigma_{\text{eff}}$ [b]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>$1.09 \times 10^{15}$ n/cm$^2$/s</td>
<td>14</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>11.7 days</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.7</td>
<td>$1.0 \times 10^{15}$ n/cm$^2$/s</td>
<td>12</td>
<td>[2]</td>
</tr>
<tr>
<td></td>
<td>24 days</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>$1.5 \times 10^{15}$ n/cm$^2$/s</td>
<td>9</td>
<td>[3]</td>
</tr>
<tr>
<td></td>
<td>25 days</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

REFERENCES


This work was partially supported by the Ministry of Education Youth and Sports of the Czech Republic and the Technology Agency of the Czech Republic under grant agreements No.: LK21310 and TA03010027 respectively.
INTRODUCTION
Application potential of radionuclides (RN) in medicine is wide, but possibilities of use are controlled by strict rules. One of them is the radionuclide purity control. For its determination alpha or gamma spectroscopy is usually used.[1] In case of RN generator more attention should be paid onto this purity in order to limit radiation exposure of a patient by leak of parent nuclei (in our case $^{227}$Ac and $^{227}$Th).[2]

EXPERIMENTAL
Radium-223 was eluted from $^{227}$Ac/$^{227}$Th/$^{223}$Ra generator, which was prepared by sorption of $^{227}$Ac solution onto Dowex-1.[3] Mixture of 0.7M HNO$_3$ and CH$_3$OH (2:8) with or without 0.9% NaCl was used as the eluent. The eluates were evaluated by gamma spectroscopy with no further adjustment. Samples for alpha spectroscopy were prepared by evaporation of an aliquot on the metal pad.

RESULTS
Under optimal elution conditions (0.7M HNO$_3$ and CH$_3$OH (2:8)) only $^{223}$Ra and its daughter nuclei ($^{219}$Rn, $^{215}$Po, $^{211}$Pb and $^{211}$Bi) were detected (Tab. 1 and Fig. 1).

In case of other elution conditions (with 0.9% NaCl) sorption stability was disrupted, so parent nuclei were found in the eluate ($^{227}$Ac and $^{227}$Th) (Tab. 1 and Fig. 2).

It is important to note, that in all experiments the activity of impurities did not exceed 5%. Purity of $^{223}$Ra eluate under optimum conditions was 98%.

REFERENCES

This research has been partially supported by Ministry of Education Youth and Sports of the Czech Republic (grant No.: LK21310), Technology Agency of the Czech Republic (grant No.: TA03010027) and Czech Technical University in Prague (grant No.: SGS14/084/OHK4/1D/14).

<table>
<thead>
<tr>
<th>Eluent</th>
<th>NaCl (%)</th>
<th>$^{223}$Ra (%)</th>
<th>$^{227}$Th (%)</th>
<th>$^{227}$Ac (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7M HNO$_3$-MeOH (2:8)</td>
<td>0.0</td>
<td>89.0</td>
<td>0.2</td>
<td>n.d.</td>
</tr>
<tr>
<td>0.7M HNO$_3$-MeOH (2:8)</td>
<td>0.9</td>
<td>92.0</td>
<td>5.9</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

Fig. 1. Elution of $^{223}$Ra, eluent 0.7M HNO$_3$ and CH$_3$OH (2:8), fraction volume 1.5 ml. The arrow points on relative activity of $^{227}$Ac on column.

Fig. 2. Elution of $^{223}$Ra, eluent 0.7M HNO$_3$ and CH$_3$OH (2:8) and 0.9% NaCl, fraction volume 1.5 ml. The arrow points on relative activity of $^{227}$Ac, $^{227}$Th on column.

Tab. 1. Percentages of nuclei in eluates. n.d. - not detected.
INTRODUCTION
Revision of the synthetic methods of cisplatin, or cis-diamminedichloroplumium(II) with an outlook to the preparation of $^{195m}$Pt-labelled complex was made. Historically cisplatinum was the first member of platinum-containing cytostatic drugs. Nowadays carboplatin and oxaliplatin are also being used as the non-specific anticancer drugs. Cisplatin is used widely especially in the combination with other drugs in the treatment of testicular cancer, ovariya cancer, bladder cancer, breast cancer, osteosarcoma etc. Since cisplatin acts non-specifically its use is universal; however, it has several drawbacks and side effects such as nephrotoxicity and sickness. [1] Also transformation from cis to trans isomer is possible due to light sensitivity.

Use of $^{195m}$Pt instead of stable Pt allows to prepare small amounts of high cytotoxic preparation, which seems to be more effective in cancer treatment. Disruption of DNA in target tissue is provided by 33 emitted Auger electrons.

Preparation of n.c.a. $^{195m}$Pt by neutron irradiation of $^{195}$Ir (Fig. 1.) is a promising method for further synthesis.

EXPERIMENTAL
Two synthetic methods [2,3] were tested (Fig.2.) and compared. Both conclude two main steps, while the first step is similar. First step: Approx. 30 µg of Pt foil was dissolved in hot aqua regia (cca. 5 ml), nitric acid was removed by repeated dissolution with HCl and evaporation. pH was adjusted to neutral by 0.5M K$_2$CO$_3$. Reduction of Pt$^{IV}$ to Pt$^{II}$ was made by diluted hydrazine solution (0.1M). Hydrazine was added drop-wise into reaction mixture, which was stirred for 2 hours. Reduction was accompanied by color change to orange. Second step: (a) According to one method [2] cisplatin is synthetized by adding aqueous ammonia (0.5M) into reaction mixture containing NH$_4$Cl as a buffer (pH neutral). Separation of the product was made by centrifugation and following dissolution in 0.1M HCl under heating. b) In another method [3] before the synthesis potassium iodide was added in order to convert chloride complex to iodide. Then ammonia solution was added. To convert iodide complex back to chloride AgNO$_3$ was added. Precipitate of AgI was separated by centrifugation and washed with water. NaCl was added into supernatant under stirring to convert aqua complex into bright yellow precipitate of cisplatin. Separation was provide by centrifugation. The first step (a) was tested with both stable and radioactive platinum. The active tracer was prepared by neutron irradiation of Pt foil on microtrone MT-25 in Dubna.

RESULTS
After testing the two described synthetic methods on stable Pt, it was shown that the method b was not successful on such small amount of source material (20 mg). AgI precipitate contained too much [Pt(NH$_3$)$_2$Cl(H$_2$O)$_2$][NO$_3$], even after washing. The yield determined by gravimetric analysis was 50%, but structure analysis (by MS spectroscopy) showed, that no cisplatin was obtained.

Method a eliminates the step with chloride replacement, but it needs more time for crystallization. However, this method was successful. Structure analysis of obtained product was performed by MS spectroscopy. Yields of this synthesis were not satisfactory, mainly because of problematic reduction of Pt(IV). Platinum(II) is unstable compared to metallic platinum and platinum(IV). The best results of reduction were obtained, when the reaction was left to proceed at laboratory temperature.

Yield of cisplatin, as obtained by gravimetric analysis and radioactive tracer technique, was 34% and 60% respectively. These results correspond with the literature data very well (43% [3] and 60% [2]). Final time spent for synthesis took about 2-3 days. With the comparison to half-life $^{195}$Pt, which is 4.02 days, whole cisplatin synthesis requires significant acceleration.
BIOLGOCALY DEGRADABLE LABELLED ACETOXYMETHYL ESTERS


1IMTM, Faculty of Medicine and Dentistry, Palacky University in Olomouc; 2Institute of Organic Chemistry and Biochemistry AS CR, v.v.i., Prague

INTRODUCTION

Triterpenes and its derivatives are studied for their biological properties, especially for their cytotoxicity. For research and better understanding of biochemical processes, metabolic pathways or problems in live systems, synthesised selectively labelled compounds with Hydrogen-2, Hydrogen-3, Carbon-13, Carbon-14 and Nitrogen-15 are used.

Triterpenic acids are well-known cytotoxic representatives. To increase the cytotoxicity while retaining their other properties, their esters were prepared. Acetoxyethyl-esteric group (Acm) was chosen because its cytotoxicity is comparable or even higher than that of the starting acid. For this reason the Acm-esters are suitable prodrugs and were chosen as candidates for the selective labelling.[1]

EXPERIMENTAL

Acm-esters were selective labelled in position 3α with hydrogen isotopes by reduction of 3-ketones of prepared Acm-esters (1, 5, 9 and 13) by enriched NaBH₄ (Fig. 1). [2]

RESULTS

Four deuterated Acm-esters (2, 6, 10 and 14) and 4 tritiated Acm-esters (3, 7, 11 and 15) were prepared. Tab. 1 shows the enrichment yields of prepared deuterated esters determined by MS and radiochemical yields of tritiated esters determined by TLC.

Tab. 1. Yields of deuteration and tritiation of esters.

<table>
<thead>
<tr>
<th>Esters</th>
<th>Y₀ [%]</th>
<th>Esters</th>
<th>Yₚ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>98</td>
<td>3</td>
<td>25</td>
</tr>
<tr>
<td>6</td>
<td>94</td>
<td>7</td>
<td>15</td>
</tr>
<tr>
<td>10</td>
<td>93</td>
<td>11</td>
<td>9</td>
</tr>
<tr>
<td>14</td>
<td>91</td>
<td>15</td>
<td>17</td>
</tr>
</tbody>
</table>

During labelling of esters by tritium, labelled free acids (4, 8, 12 and 16) were acquired because of instability of esters. Percentage ratio between esters and free acids is given in Tab. 2 (measured by RP-HPLC Fig. 3).

Tab. 2. Percentage ratio and activity of esters and acids.

<table>
<thead>
<tr>
<th>Esters [%]</th>
<th>A [MBq/mg]</th>
<th>Esters [%]</th>
<th>A [MBq/mg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>68</td>
<td>18.9</td>
<td>27</td>
<td>7.5</td>
</tr>
<tr>
<td>72</td>
<td>11.9</td>
<td>26</td>
<td>4.5</td>
</tr>
<tr>
<td>50</td>
<td>6.9</td>
<td>35</td>
<td>4.9</td>
</tr>
<tr>
<td>49</td>
<td>13.0</td>
<td>44</td>
<td>11.7</td>
</tr>
</tbody>
</table>

Fig. 2. Acm esters and their labelled analogues.

REFERENCES


This research has been partially supported by Czech Technical University in Prague (grant No. SGS14/084/OHK4/1T/14), Technology Agency of the Czech Republic (grant No.: TA03010027), Ministry of Education Youth and Sports of the Czech Republic (grants No.: LK21310 and C262d).
INTRODUCTION

Natural triterpenoids together with their semisynthetic derivatives form basis for extensive medicinal research, because they have shown various biological activities [1], e.g.: antineoplastic, antiviral, anti-inflammatory, antimicrobial activities, heptato- and cardioprotective effects; and revealed a great potential for pharmaceutical applications when their cytotoxic and anti-HIV activities were described. Betulinines, as we named the group of semisynthetic derivatives, have proven multispectral cytotoxic activity on the panel of several cell tumor lines of different histogenetical origin, including multidrug resistance.[1,2,3]

One of our leading compounds, 3β,28-diacetoxy-18-oxo-19,20,21,29,30-pentanorlupan-22-oic acid, shows fast and selective apoptosis of tumor cells [3], comparable to conventional anticancer drugs – paclitaxel.

During the past years, several labelled derivatives have been synthesized that have been used for investigation of mechanism, labelled by deuterium, tritium, carbon-13, carbon-14 and nitrogen-15. Recent interest of our research is synthesis of heterocyclic labelled derivatives of selected acids, e.g. compounds labelled on A-ring and esters.

EXPERIMENTAL

Set of labelled esters

Esters 1-12 were synthesized via reaction of corresponding acids and labelled diazomethane-d_2 or iodomethane (C^3H)_2I or [^13C](H)_2I.

![Fig. 1. Labelled esters I.](image1)

Set of ^3H/^4H-3α analogues

Compounds 14 – 17 were obtained by a reduction of 13 with NaB[^3H]_4 or NaB[^4H]_4 (molar activity 6.4 Ci/mmol) in a mixture of tetrahydrofuran and methanol. Tritium atom in position 3α of 15 and 17 was confirmed by ^3H NMR with signals at δ ≈ 3.47 ppm for 15 and δ ≈ 4.47 ppm for 17.

![Fig. 3. Reduction of esters a: NaB[^3H]_4 or NaB[^4H]_4/ THF, CH_3OH.](image2)

Set of labelled heterocyclic compounds

Reaction of corresponding 3-oxo acids with ethylenediamine or ^15N-ethylendiamine (released in situ) in morpholine yields pyrazines 18 - 21.

![Fig. 4. Labelled heterocycle compounds.](image3)

RESULTS

Selectively labelled analogues of the most cytotoxic active compounds are used for the investigation of mechanism of reaction and binding interactions and/or as a standard for mass spectroscopy. Altogether, 33 deuterated and C-13 labelled methyl esters were synthesized and fully characterized by spectral data. Also, a unique family of pyrazines were synthesized (18 - 21).

Selectively labelled [3α^-H] and [3α^-3H] methyl-3β-acetoxy-21,22-dioxolup-18-en-28-oates (16 and 17) show cytotoxicity against human T-lymphoblastic leukemia CEM of IC_{50} 10 µmol/L. The group of pyrazines shows cytotoxicity against CEM of IC_{50} 20 µmol/L and compound 18 shows cytotoxicity on human neuroblastoma cells SK-N-MC IC_{50} 7.6 µmol/L.

REFERENCES


This research has been partially supported by Czech Technical University in Prague (grant No. SGS14/084/OHK4/1T/14), Technology Agency of the Czech Republic (grant No.: TA03010027), Ministry of Education Youth and Sports of the Czech Republic (grants No.: LK21310 and C262d).
INTRODUCTION
Series of indole-3-acetic acid derivatives substituted in the benzene ring belongs to the natural plant growth hormone – auxines, with interesting biological activities (e.g. specific antigen stimulation in atopic allergic disease by interleukin 4 and 5). They have recently been synthesized via Fisher ring closure of the succinic-aldehydeic acid phenylhydrazones obtained from glutamic acid or by a direct method where intermediate phenylhydrazones carry out the cyclization in one step employing corresponding acetics (e.g. ethyl γ,γ-dimethoxybutyrate) as a starting material.

EXPERIMENTAL
Synthesis of 7-bromo-5-chloroindole-3-acetic acid (5) and its analogues was described via cyclization of substituted phenylhydrazine 1 with methyl 4,4-dimethoxybutyrate (2) in two steps: the first is addition of acetel 2 on phenylhydrazine 3 in acetic acid the second is intramolecular cyclization of intermediate 3 in ethanol catalyzed by addition of concentrated sulphuric acid resulting in 4a, eventually 4b when methanol is used, during 3 h under reflux. Both steps were also carried out in closed microwave reactor with focused power. Reaction times were shortened dramatically for both steps to less than 20 min. Conditions of hydrolysis of obtained esters 4a and 4b were studied under alkaline and also acidic conditions. Acidic catalysed hydrolysis was employed to obtain 5 as an optimal. Finally, selective dehalogenation was studied as a method for introduction of 1H or 3H to location 7 of indole-3-acetic acid (6).

RESULTS
Synthesis of indole-3-acetic acid derivatives and its labeled analogues was described via cyclization of substituted phenylhydrazine with methyl 4,4-dimethoxybutyrate in two step. The reaction was also carried out in microwave reactor with focused power. The obtained esters were hydrolyzed and optimal conditions of dehalogenation were studied.

Tab. 1. Condition of dehalogenation and yields.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate</th>
<th>Substrate</th>
<th>Pd/BaSO4</th>
<th>Et3N</th>
<th>MeOH</th>
<th>EtOH</th>
<th>Time</th>
<th>Debromination</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4a</td>
<td>2</td>
<td>8</td>
<td>10.38</td>
<td>300</td>
<td>10</td>
<td>180</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>1</td>
<td>3</td>
<td>10.38</td>
<td>300</td>
<td>15</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>1</td>
<td>3</td>
<td>10.38</td>
<td>300</td>
<td>20</td>
<td>70</td>
<td>10</td>
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<td>6.5</td>
<td>10.38</td>
<td>300</td>
<td>20</td>
<td>70</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>2</td>
<td>6</td>
<td>1.038</td>
<td>300</td>
<td>10</td>
<td>20</td>
<td>50</td>
</tr>
</tbody>
</table>

Optimisation of synthesis of 7-bromo-5-chloroindole-3-acetic acid (5) was studied. Obtained esters 4a and 4b were hydrolyzed under acidic condition with excellent yield. Also optimal conditions of dehalogenation were studied (Tab.1). All prepared compounds were characterized by spectral data.

REFERENCES

This research has been partially supported by Czech Technical University in Prague (grant No. SGS14/084/ OHK4/1T/14) and by the Ministry of Education Youth and Sports of the Czech Republic (grant No. C262d).

Fig. 1. Synthesis of indolyi-3-acetic acid.

Fig. 2. Microwave reactor.
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BOOK CHAPTERS


PROCEEDINGS


PAPERS


Štamberg, K. - Palágyi, Š. - Videnská, K. - Havlová, V.: Interaction of $^3$H$^+$ (as HTO) and $^{34}$Cl$^-$ (as Na$^{34}$Cl) with Crushed Granite and Corresponding Fracture Infill Material Investigated in Column Experiments. Journal of Radioanalytical and Nuclear Chemistry. 2014, vol. 299, no. 3, pp. 1625-1633. ISSN 0236-5731.


CONFERENCE CONTRIBUTIONS


REPORTS


PATENTS


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Múčka, V., 2014

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**Radiation-induced preparation of synthetic garnets**

Bárta, J., 2013

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Silber, R., 2013
PROJECTS AND GRANTS

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

**ASGARD** - Advanced fuels for Generation IV reActors: Reprocessing and Dissolution, EC FP7 CP 295825, Euratom; John, J. and Šebesta, F.; co-financed as 7G12092 by the Ministry of Education, Youth and Sports, Czech Republic

**SACSESS** - Safety of ACtinide Separation proceSSes, EC FP7 CP 323282, Euratom; John, J.; co-financed as 7G13004 by the Ministry of Education, Youth and Sports, Czech Republic

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

**CINCH-II** - Cooperation in education and training In Nuclear Chemistry, EC FP7 CA 605179, Euratom; John, J.

Preparation and radiochemical separation of $^{195m}$Pt isomer for the use in nuclear medicine, JINR 04-5-1076-2009/2014, Joint Institute for Nuclear Research, Dubna; Kozempel, J.

Inorganic nanoscintillators: Novel synthesis and size-dependent characteristics, GA13-09876S, Czech Science Foundation; Čuba, V.

Damage to model biomembranes and living cell surfaces induced by extreme ultraviolet laser radiation, GA13-28721S, Czech Science Foundation; Můčka, V.

Synchronously pumped optical parametrical oscillator for sensors, GPP102/12/P645, Czech Science Foundation; Zavadilová, A.

**Ra-226 recycling and Ac-227 applications**, TA03010027, Technology Agency of the CR; John, J. and Kozempel, J.

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 of the properties of materials for safe disposal of radioactive waste and the development of methods for their assessment, FR-TI1/362, Ministry of Industry and Trade, Czech Republic; Vopálka, D.

Research and development of storage container for underground storage of spent nuclear fuel into the phase of implementation of the sample, Ministry of Industry and Trade, Czech Republic; Silber, R.

Use of nanotechnology for minimization of radionuclide contamination of environment, VG20132015132, Ministry of the Interior of the CR; Čuba, V.

Study of transmutation of Ra-226 and separation of the irradiation products, LK21310, Ministry of Education, Youth and Sports, Czech Republic; Kozempel, J.
Development of sample preparation methods for minor uranium isotopes determination in the environment, 7AMB12AT022, Ministry of Education, Youth and Sports, Czech Republic; Němec, M.

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

Support of the activities in the Division of Nuclear and Radiochemistry (DNRC) EuCheMS, LG13016, Ministry of Education, Youth and Sports, Czech Republic; John, J.

Laboratories for labelled compounds and radiopharmaceuticals education, C120d, Ministry of Education, Youth and Sports, Czech Republic; Kozempel, J.

Inter-universities laboratory for in-situ education of transport processes in the real rock environment, C27-2-2d, Ministry of Education, Youth and Sports, Czech Republic; Hofmanová, E., Vopálka, D.

Material research for InovaSEED, VaVpI CZ.1.05/3.1.00/14.0301, Ministry of Education, Youth and Sports, Czech Republic; Čuba, V.

Upgrade of practical training of students in nuclear at CTU-FNSPE, OPPA CZ.2.17/3.1.00/36038, Ministry of Education, Youth and Sports, Czech Republic; Čubová, K.

Central European Energy Institute, OPVK CZ.1.07/2.2.00/28.0256, Ministry of Education, Youth and Sports, Czech Republic; Čubová, K.

CENEN-NET - New generation nuclear energy partnership, OPVK CZ.1.07/2.4.00/17.0116, Ministry of Education, Youth and Sports, Czech Republic; Drtinová, B.

Study of migration of selected critical radionuclides in repository barriers, SGS13/224/OHK4/3T/14, CTU Prague; Hofmanová, E.

Preparation of theranostic radionuclides carriers for nuclear medicine, SGS14/084/OHK4/1T/14, CTU Prague; Kozempel, J.

Separation and determination of significant radionuclides, SGS14/154/OHK4/2T/14, CTU Prague; Neufuss, S.

Photo- and radiation-induced synthesis of inorganic materials, SGS11/163/OHK4/3T/14, CTU Prague, Pavelková, T.

Advanced methods of inorganic materials synthesis, SGS14/207/OHK4/3T/14, CTU Prague, Pavelková, T.

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


Radium interactions with cementitious materials, SÚRAO ČR; Filipská, H.

Support of preparation of Ruprechtov Experience Report, ÚJV Řež a.s.; Vopálka, D.

Research of uncertainty assessment of safety analysis of deep geological repository of radioactive waste, SÚRAO ČR; Vetešník, A.
RESEARCH FELLOWSHIPS / VISITING SCIENTISTS

OUTGOING:

Mareš, K.V.

Chemistry of the nuclear fuel cycle (CINCH course)
ENSCP Paris, France, January 2013

Mareš, K.V.

Joint ASGARD, FAIRFUELS and CINCH Winterschool 2013 "Fabrication methods & Irradiation performance"
NRG, Petten, The Netherlands, January 2013

Bláha, P.

Radiobiological and radiation chemical aspects of chromosome instability in mammalian cell subclones irradiated with ionizing radiation of different LET (PhD stay)
Joint Institute for Nuclear Research (JINR) Dubna, Russia, January 2013 – December 2014

Mareš, K.V.

7th Summer School on Actinide Science & Applications (Actinides 2013)
JRC-Institute for Transuranium Elements, Karlsruhe, Germany, July 2013

Zavadilová, A.

Time Resolved Laser Induced Fluorescence for the speciation of selected actinides and lanthanides in solutions (experimental stay - Talisman)
Commissariat à l’énergie atomique et aux énergies alternatives (CEA), ATALANTE, Marcoule, France, September – November 2013
Hofmanová, E.

**Development and testing of electro-migration for clay-based systems**
*(Apprenticeship - Erasmus Programme - student mobility for placement, 2013/2014)*

**SCK-CEN Mol, Belgium, October 2013 – March 2014**

Mareš, K.V.

**ASGARD Course on Fuel Characterization and Isotope Separation**

*KTH Stockholm, Sweden, January 2014*

John, J.

**Radioanalytical Methods** *(course at the TALISMAN – CEA Marcoule Summer School 2014 “Actinide Chemistry for Future Fuel Cycle”)*

*CEA, Marcoule, France, June 2014*

Pavelková, T.

**Photo and radiation induced preparation of uranium/thorium oxides** *(experimental stay - Talisman)*

*Chalmers University of Technology, Gothenburg, Sweden; June 2014*

J. Višňák

**Uranyl – Selenate Interactions Studied by the Time Resolved Laser Induced Fluorescence Spectroscopy** *(experimental stay – BFG 2014 from the French Institute in Prague and Campus France)*

*Institute de Physique Nucléaire (IPN), Orsay, France, September-October 2014*
INCOMING:

Keçeli, G.

**Preconcentration of radionuclides from surface water samples by homogeneous precipitation with hydrated titanium dioxide**

*University of Istanbul, Istanbul, Turkey, July – September 2013*

Gelis, A.V.

**Microfluidic systems for liquid-liquid extraction of actinides**

*Argonne National Laboratory, USA, April 2014*

Kalmykov, S. N.

**Radiochemical studies in Moscow State University**

*Lomonosov Moscow State University, Moscow, Russia, December 2014*

Santos-Oliveira, R.

**Radiopharmacy in Brazil**

*Universidade Estadual da Zona Oeste, Rio de Janeiro, Brazil, December 2014*
DEPARTMENT SEMINAR

Below, the overview is given of invited opening lectures and the respective speakers at the Department seminar in 2013 and 2014. Full programme of the seminars, including all the contributed lectures and their authors can be found at the Department web at http://www.jaderna-chemie.cz/?vv=seminar_en

2013

Aksenov, N.

Radiochemical investigations at the Flerov Laboratory of Nuclear Reactions, JINR Dubna

Joint Institute for Nuclear Research, Russia, February 2013

Štekl, I.

Double Beta Decay Studies

Institute of Experimental and Applied Physics, Czech Technical University in Prague, March 2013

Pražská, M.

The Advanced Technologies for Radioactive Waste Treatment issuing the Decommissioning of Nuclear Installations

AMEC Nuclear Czech Republic, a.s., Czech Republic, April 2013

Beele, B.

Complexation and Separation Performance of N- and O- Donor Ligands Used in Actinide Separation

INE - KIT, Karlsruhe, Germany, May 2013
Panak, P.

**Time-resolved Laser Fluorescence Spectroscopy - A Valuable Tool for Actinide Speciation**

INE - KIT, Karlsruhe, Germany, May 2013

Smrček, S.

**Application of Labeled Compounds in the Studies of Behaviour of the Residues of Pharmaceuticals in the Environment**

Department of Organic Chemistry, Faculty of Science, Charles University, Prague, Czech Republic, October 2013

Eigl, R.

**AMS-application at VERA**

University of Vienna, Austria, November 2013

Kameník, J.

**Nuclear Chemist at Hawaii aka Around the World in 667 Days**

Nuclear Physics Institute, ASCR, Řež, Czech Republic, November 2013

Hanuš, V.

**Nothing is Perfect, or Power Plant is not as Simple as a Grinder of Money or There is Never Shortage of Surprises**

ČEZ a. s., NPP Temelín, Czech Republic, December 2013
2014

Juha, L.

**Thermal and Non-thermal Effects of Intense XUV / X-rays**

*Institute of Physics, ASCR, Prague, Czech Republic, October 2014*

Moša, M.

**Current Radiopharmaceuticals Topics from the Point of View of Nuclear Medicine**

*IMUNA s.r.o., Prague, Czech Republic, March 2014*

Gelis, A.V.

**Microfluidics in Actinide Solvent Extraction**

*Argonne National Laboratory, USA, April 2014*

Mizera, J.

**Geochemical Studies of Tektites and Impact Glasses Using Activation Analysis**

*Nuclear Physics Institute, ASCR, Řež, Czech Republic, October 2014*

Světlík, I.

**Radiocarbon Dating**

*Nuclear Physics Institute, ASCR, Řež, Czech Republic, November 2014*

Santos-Oliveira, R.

**Radiopharmacy in Brazil**

*Universidade Estadual da Zona Oeste, Rio de Janeiro, Brazil, December 2014*

Kalmykov, S. N.

**Radiochemical Studies in MSU**

*Lomonosov Moscow State University, Russia, December 2014*
PERSONNEL

Head of the department:
prof. Ing. Jan John, CSc.

Vice head:
doc. Mgr. Dušan Vopálka, CSc.

Registrar:
Ing. Alois Motl, CSc.

Project Manager / Economist:
Mgr. Štěpánka Maliňáková

Secretary:
Marie Kotasová

SEPARATION AND RADIOANALYTICS

prof. Ing. Jan John, CSc.
Ing. Kateřina Čubová, Ph.D.
Ing. Alois Motl, CSc.
Ing. Mojmir Němec, Ph.D.
doc. Ing. Ferdinand Šebesta, CSc.
RNDr. Jana Šulaková, Ph.D.
Ing. Alena Zavadilová, Ph.D.

Ph.D. students:
Ing. Pavel Bartl
Mgr. Barbara Basarabová
Mgr. Yulia Buchatskaya
Ing. Mgr. Petr Distler
Ing. Kamil V. Mareš
Ing. Soběslav Neufuss
Ing. Aneta Sajdová
Mgr. Jana Sočuvková
Ing. Irena Špendlíková
Mgr. Kamila Šťastná

Technician:
Jana Steinerová

SPECIALIZATION AND MIGRATION

doc. Mgr. Dušan Vopálka, CSc.
Ing. Barbora Drtinová, Ph.D.
doc. Ing. Karel Štamberg, CSc.
Mgr. Aleš Vetešník, Ph.D.
Ing. Alena Zavadilová, Ph.D.

Ph.D. students:
Mgr. Rostislav Adam
Ing. Eva Hofmanová
Ing. Iveta Holánová
Mgr. Lucie Ramešová
Ing. Jakub Višňák

Part time:
Ing. Helena Filipská, Ph.D.

Technician:
Olga Múčková

RADIATION CHEMISTRY

prof. Ing. Viliam Múčka, DrSc.
Ing. Jan Bártta
doc. Ing. Václav Čuba, Ph.D.
prof. Ing. Milan Pospíšil, DrSc.
doc. Ing. Rostislav Silber, CSc.

Ph.D. students:
Ing. Tomáš Gbur
Ing. Tereza Pavelková
Ing. Lenka Procházková

Technician:
Alena Matyášová

RADIOPHARMACEUTICAL CHEMISTRY

RNDr. Ján Kozempel, Ph.D.
RNDr. Martin Vlk

Ph.D. students:
Ing. Petra Mičolová

Technician:
Ing. Šárka Hráčková

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