

ANNUAL REPORT

2015-2016



Nuclear Chemistry

Czech Technical University in Prague

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DEPARTMENT OF NUCLEAR CHEMISTRY

# NUCLEAR CHEMISTRY

## Annual Report 2015-2016

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

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# EDITORIAL

Dear Reader, this is the fifth in the series of the CTU Nuclear Chemistry Annual Reports that is slowly becoming a well-established periodical with bi-annual periodicity and established structure and format. The period covered by this issue (2015 – 2016) can be generally rated as one of the more quiet periods in the life of the department with only evolutionary developments.

From the point of view of the operation of the Department of Nuclear Chemistry (DNC), the most important fact is that the fourth research group – “Radiopharmaceutical Chemistry” (established in 2013) – demonstrated clearly its viability and successfully develops even after the end of the series of the initial grants secured for its establishment. Hence, most developments in this period regard the department personnel. Two long-time members of the department – Professor Milan Pospíšil and Associate Professor Karel Štamberg – decided to retire by the end of 2016 after having spent whole or larger part of their carriers, respectively, at the DNC. On the one hand, we wish them a happy and restful retirement, but on the other hand we hope that we will be able to continue using their extensive experience for a long time. After his retirement, Prof. Štamberg was appointed one of the first Honorary academic staff members at the Faculty of Nuclear Sciences and Physical Engineering and thus he stays closely connected with the department life. Two young assistant professors were recruited to fill these vacancies; additional recruitment is planned for the near future. From the qualification structure point of view, promotion of Mojmír Němec to the associate professor should be mentioned here.

Similarly to the previous period, 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 reports characterising the research topics in more detail forms the body of this Annual Report. To summarise briefly, one can state that 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 or in environmental protection, radiation initiated preparation of solids inclusive nanoparticles, as well as radioecology, bioradiation chemistry, and radiopharmaceutical chemistry. In these fields, the CTU has been a partner in several big international EURATOM FP7 integrated projects such as CEBAMA, 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 ÚJV Řež a.s., Nuclear Physics Institute of the AS CR, or Research Centre Rez, all three located in Řež near Prague, Radioactive Waste Repository Authority of the Czech Republic (SÚRAO), DIAMO s.p., Stráž pod Ralskem, and many others. Full list of publications, conference contributions, and research reports can be found in the respective section below.

The Department Seminar, re-shaped and opened to the general scientific public since the academic year 2011/2012, was raised to a new level by combining our efforts with the Working Group of Nuclear Chemistry (WGNC) of the Czech Chemical Society – the seminar is run now in collaboration of DNC with WGNC and attracts an average of 30–40 participants each month. If approved by the speaker, opening lectures by invited eminent Czech or foreign experts are now recorded and archived using the SlidesLive™ system. These recordings are publicly available at <https://slideslive.com/seminar-kjch/prednasky> and contribute tremendously to the visibility of our department and nuclear chemistry in general. For the 12 lectures, delivered between April 2015 and December 2016, the system registers more than 10,000 views (as of 10/06/2017). 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, the role of DNC CTU as the co-ordinator of the FP7 project CINCH-II – Cooperation in education and training

In Nuclear Chemistry (<https://meet-cinch.codeart.cz/cinch2/>), peaked in mid-2016 when this, second in the series, project finished. As explained in the previous issues of this Annual Report, these projects aimed at coordinating the education, vocational education and training (VET), and distance learning in nuclear chemistry. More details about the main achievements of these projects are summarized in a dedicated article in the Education section below. In the next period, these projects will be succeeded by the MEET-CINCH project aiming at setting-up "A Modular European Education and Training Concept In Nuclear and Radio Chemistry" (<http://www.cinch-project.eu/>). In this project, CTU will remain the partner under coordination of the Gottfried Wilhelm Leibniz University Hannover (Germany). A very useful offspring of these projects is a set of modular hands-on courses in nuclear chemistry for the customers from both academia (e.g. Intercontinental Nuclear Institute - <http://www.intercontinental-nuclear-institute.com/>, or Charles University, Prague) and industry (e.g. Czech nuclear power plants chemists) that can be run both in English and Czech. One of these courses – a "blended-learning" course "Hands-on Training in Radiochemistry" combining the distance-learning theoretical part (on CINCH-Moodle learning platform) with the on-site laboratory experimental part – will become one of the cornerstones of the joint CINCH portfolio of training and education courses.

Similarly to the previous Editorials, it can be concluded that the department is marching on strongly and the core activities and productivity are slowly taken over by a strong group of highly competent and motivated young nuclear chemists in their late 30s or early 40s who still 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 2015/2016 and 2016/2017

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

• Chemistry for Nuclear Engineering	4	S	B	Štamberg, K.; Silber, R.
• Dosimetry and Radiation Protection	3	W	B	Martinčík, J. *; Pašková, P.*
• Fundamentals of Construction and Function of Nuclear Power Plants	3	S	B	Otčenášek, P.*
• General Chemistry	6	W	B	Motl, A.
• General Chemistry 1	3	W	B	Motl, A.
• General Chemistry 2	3	S	B	Motl, A.
• Instrumental Methods of Research 1	3	S	B	Zavadilová, A. ; Vlk, M.
• Ionising Radiation Detection	2	S	B	John, J.
• Laboratory Practice in the Instrumental Methods of Research	2	S	B	Zavadilová, A. ; Vlk, M.
• Measurement and Data Handling	3	W	B	Vetešník, A.; Vopálka, D.
• Nuclear Chemistry 1	3	S	B	John, J.; Čuba, B.
• Nuclear Chemistry 2	4	W	B	John, J.; Čuba, V.
• Physical Chemistry 1	5	W	B	Múčka, V.; Silber, R.
• Physical Chemistry 2	5	W	B	Drtinová, B.; Silber, R.
• Practical Exercises in Ionising Radiation Detection	3	S	B	Němec, M.; Čubová, K.; Špendlíková, I.
• Practical Exercises in Radiochemical Techniques	2	W	B	Čubová, K.; Němec, M.
• The Theory of the Electromagnetic Field and Wave Motion	4	S	B	Vetešník, A.

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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 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.
• Environment 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.; Vlč, 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.
• Protection of 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.
• Radionuclide Production	2	W	M	Lebeda, O.*
• Radiopharmaceuticals 1	2	W	M	Lebeda, O.*
• Radiopharmaceuticals 2	2	W	M	Kozempel, J.; Moša, M.*; Vlč, M.

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\* External teacher

• Separation Methods in Nuclear Chemistry 1	3	W	M	Němec, M.; John, J.
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• Separation Methods in Nuclear Chemistry 2	2	S	M	Němec, M.; John, J.
• Technology of the Fuel Cycles of Nuclear Power Stations	2	W	M	Drtinová, B.; Štamberg, K.
• The Chemistry of Operation of Nuclear Power Plants	2	W	M	Štamberg, K.; Silber, R.
• Theoretical Basics of Radiation Chemistry	2	W	M	Juha, L. *
• Trace Radiochemistry	3	S	M	Filipská, H.,; John, J.

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\* External teacher

• Advanced Nuclear Chemistry	D	John, J.; Čuba, V.
• Applications of Radiation Chemistry in Chemical Industry, Agriculture and Medicine	D	Můčka, V.
• Application of Radionuclides	D	Mizera, J.*
• Biosyntheses of Labelled Compounds	D	Smrček, S.*
• Chemistry of Actinoids and Transactinoids	D	John, J.
• Experimental Nuclear Chemistry	D	John, J.; Čubová, K.; Němec, M.
• Instrumental Radioanalytical Methods and their Application for Monitoring the Environmental Contamination	D	Kučera, J.*
• Labelled Compounds	D	Smrček, S.*; Kozempl, J.
• Modelling and Simulation of the Migration Processes in the Environment	D	Vetešník, A.; Vopálka, D.
• Nuclear Data, Targetery and Preparation of Radionuclides	D	Lebeda, O.
• Nuclear Power Plants	D	Sklenka, L.; Bílý, T.
• Photochemistry and Radiation Chemistry	D	Juha, L.*; Čubová, K.; Čuba, V.
• Radiation Removal of Liquid and Gaseous Contaminants	D	Můčka, V.
• Radioanalytical Chemistry	D	Němec, M.; John, J.
• Radionuclides in Biological Sciences	D	Smrček, S.*
• Radiopharmaceuticals	D	Lebeda, O.*; Moša, M.*
• Separation Methods	D	Němec, M.
• Technology of Nuclear Fuels	D	Štamberg, K.; Čubová, K.
• Transport Processes	D	Vopálka, D.

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\* External teacher

## Projects and Management

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# CINCH-PROJECTS SERIES – A MILESTONE IN THE COORDINATION OF EDUCATION IN NUCLEAR AND RADIOCHEMISTRY IN EUROPE

*John, J.; Němec, M. (on behalf of the CINCH consortium)*

## INTRODUCTION

As explained in the previous issues of this Annual Report, a sequence of broad international projects was initiated in 2010 to maintain the fading expertise and skills in nuclear and radiochemistry by launching the 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>.



## SUMMARY OF THE CINCH ACHIEVEMENTS

The projects aimed at mitigating the special skill-based deficits within nuclear chemistry at masters and doctorate levels and the decline of number of staff qualified in this field. The projects were built around the well-proven five-phase (Analysis, Design, Development, Implementation, Evaluation) Systematic Approach for Training (SAT) developed by IAEA; while CINCH-I dealt with the first three phases of the process, CINCH-II concentrated on the Implementation. The main results obtained by these projects can be summarized as follows:

- The European Master in Nuclear Chemistry (NRC EuroMaster) quality label aiming at the mutual recognition of the scope and level of master-level education in NRC was implemented. To achieve this, the minimum requirements and evaluation criteria for NRC EuroMaster were finalized and the Division on Nuclear and Radiochemistry (DNRC) of EuCheMS became a guarantor of the NRC EuroMaster label.
- A set of the Vocational and Educational Training (VET) courses was developed for customers from the end-users and is summarized in CINCH VET Courses Prospectus, its commercialized version, and in the Syllabi for the CINCH-II VET Courses. These documents contain a list of short or detailed descriptions, respectively, of each of the VET courses produced through CINCH-II; it includes the knowledge, skills and competencies that would be gained by someone doing the course. Various pedagogical tools are used in these courses – e.g. hands-on courses, distance learning courses, or combination of both. In parallel, training passport requirements and assessment criteria for hands-on courses were designed and set.
- During the work in the field of “Modern E-learning Tools to Enhance Teaching in Nuclear Science”, a NRC study material database NucWik was set-up at the public server wikispaces.com (<http://nucwik.wikispaces.com/>). NucWik is an open platform for sharing teaching material and to promote active collaboration across institute/university borders. Most of the teaching materials developed in CINCH projects are available at this platform. All the materials at NucWik is open-access,

the platform aims at free global exchange of teaching materials among the NRC university teachers.

- The most innovative result in the E-learning field are the RoboLab remote controlled exercises. These allow students anywhere in the world to perform experiments in a real radiochemistry laboratory through the use of a web control panel and watching what is going on in the laboratory through a live video feed. Six such experiments were developed and set up (available through NucWik).
- For the stand-alone E-learning courses that include students’ registration, quizzes and evaluations, the student management platform CINCH Moodle was set-up (<http://moodle.cinch-project.eu>). It hosts not only “our own” courses but it also serves as a host to a suite of recorded lectures and courses developed by other Euratom FP7 projects – Talisman, ASGARD, SACSESS.
- As a major step towards the sustainability of the results achieved in CINCH projects, the “European Network on Nuclear and Radiochemistry Education and Training (European NRC Network)” was established as a new Euratom Fission Training Scheme (EFTS) (<http://nrc-network.org/>). The current number of members of this network is twenty three.



## THE FUTURE – MEET-CINCH

Even though a major step towards the sustainability was done well before the end of CINCH-II project, some support is still needed during the period of transition to real sustainability. This is why a new Euratom H2020 project “A Modular European Education and Training Concept In Nuclear and RadioCHEmistry – MEET-CINCH” will commence in June 2017. Among the biggest challenges in this project developing a MOOC – Massive Open On-line Course in nuclear and radiochemistry, setting-up a “CINCH VET e-shop”, or investigating the applicability of the modern Flipped (Inverted) Classroom concept in the nuclear chemistry teaching and training field may be listed.

# A NEW BLENDED-LEARNING HANDS-ON TRAINING COURSE IN NUCLEAR CHEMISTRY

Němec M.; Čubová K.; Špendlíková I.; John J.; Čuba V.; Procházková L.; <sup>1</sup>Martinčík J.;  
<sup>2</sup>Omtvedt J-P.; <sup>3</sup>Evans N.; Maliňáková Š.; Kotasová M.

<sup>1</sup>Department of Dosimetry and Application of Ionizing Radiation, CTU in Prague; <sup>2</sup>University in Oslo, Norway; <sup>3</sup>University of Loughborough, United Kingdom

## INTRODUCTION

The lack of trained nuclear chemical specialists has been identified in all branches of nuclear industry and other areas where skills in NRC are required, such as radiopharmacy, nuclear medicine, radiation protection and radioecology, and many others. Retraining general chemistry graduates is one of the options for mitigating this problem.

Hands-on Training in Nuclear Chemistry (HOT in NRC) aims at efficient delivering the basics of nuclear and radiochemistry to trainees with chemical background at Master level, who need to extend their skills and knowledge to the field of nuclear and radiochemistry. It provides fundamental theoretical knowledge of principles and concepts in nuclear chemistry necessary for understanding the processes and methods in radiochemistry, and practical hands-on training required for the work with open ionizing radiation sources (handling of radioactive materials, application of radionuclides and ionizing radiation...).

The course was developed by Department of Nuclear Chemistry, CTU in Prague in collaboration with CINCH consortium during the CINCH I and CINCH II projects [1].

## EXPERIMENTAL

The original structure of the course designed in CINCH I consisted of 1 week theoretical part of lectures and exercises (40 hours) covering the fundamentals of nuclear chemistry and related fields followed by 1 week (40 hours) of practical laboratory exercises. In CINCH II, new version of Hands-on Training in Nuclear Chemistry with re-designed structure meeting better the needs of industrial end-users was demonstrated. The theoretical part of the course was used to record and finalize the future distant learning option. The course took place on January 6-14 at the Department of Nuclear Chemistry of the CTU in Prague.

For the course, both theoretical and practical parts were modified to get reasonable schedule and relevant materials available. Prior to attending the course, the participants had to pass distant-learning radiation protection courses related to a) general radiation protection and b) radiation protection rules and restrictions of the laboratory controlled area.

The newly created e-learning “Radiation Protection Course” created by IRS on CINCH Moodle together with embedded CTU course “Radiation protection minimum” were used as one of the obligatory prerequisites for the admission to the course. Participants had to successfully finish theoretical and radiation protection parts before entering the on-site course as well as an interview on the principles and procedures of each of the tasks before starting the practical/laboratory work.

## RESULTS

Based on the experience and feedback obtained during the course, all the course materials were updated and finalized after the end of the course. All the lectures delivered during the theoretical part of the course were

recorded, post-produced using the SlidesLive™ technology, and e-learning materials for the theoretical parts of the future re-runs of the courses were produced. All the materials and the course are available at <https://moodle.cinch-project.eu/>, additional study materials including the living textbook at <https://nucwik.wikispaces.com/>.

**The contents of the theoretical part includes:**

**Fundamentals of nuclear chemistry:** Structure and properties of atomic nuclei. Classification of radionuclides. Kinetics of radioactive decay. Radioactive equilibria. Binuclear reactions. Yield of nuclear reactions. Natural radioactivity. Radioactive decay chains. Nuclear fission, fission products. Hot atoms chemistry. Szilard-Chalmers system. Radiation chemistry. Actinides and transactinides.

**Radiation detection and dosimetry:** Interaction of IR with matter ( $\alpha$ ,  $\beta$ ,  $\gamma$ , neutrons). Detection of ionizing radiation (detector types, principles). Dosimetry of ionizing radiation.

**The practical exercises included have been:**

1. Handling of radioactive materials - pipetting, work behind shielding and in glove box.
2. Preparation of working solutions with required activity.
3. Contamination survey, decontamination, preparation of wipe smear samples.
4. Radionuclide generator preparation and milking. Radioactive equilibria.
5. Sample activation via neutron irradiation.
6. Decay curve measurement and deconvolution, half-life determination.
7. Gamma-ray spectrometry – calibration, efficiency, measurement.
8. Liquid-liquid extraction of uranium. Uranium specific activity, estimation of its isotopic abundance.
9. Liquid scintillation counting.



Fig. 1. HOT in NRC brochure – title page.

## REFERENCES

- [1] [www.cinch-project.eu](http://www.cinch-project.eu)

CINCH-II – “Cooperation in education and training In Nuclear Chemistry” has been supported by the European Atomic Energy Community's 7<sup>th</sup> FP (EURATOM FP7 2007-2011) under grant agreement No. 605173

## RESEARCH REPORTS



Speciation and Migration



Separation and Radioanalytics



Radiation Chemistry



Radiopharmaceutical Chemistry



## Speciation and Migration

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# MODELLING OF ACID-BASE TITRATION CURVES OF MINERAL ASSEMBLAGES

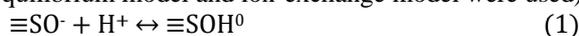
Štamberg, K.; Drtinová, B.; Filipská, H.; Vopálka, D.

## INTRODUCTION

The modelling of acid-base titration curves [1] can be, in principle, explored using two methods; namely, by the so-called component additivity (CA) and generalized composite (GC) approaches. The first one is based on the assumption that the resulting sorption, adsorption or chemical properties of given assemblage are additive functions of relative amounts or surface areas of all minerals. In the case of GC-approach, it is supposed that the studied mineral mixture is characterized by the overall surface area value and the averaged sorption properties of all function groups (sites) presented. The modelling by CA-approach requires the knowledge of the constants and parameters characterizing sorption on individual minerals to be available from literature (e.g., [2]). In the case of GC-approach, the determination of over-all constants or other parameters, valid for the whole system, must be based on the evaluation of experimental data obtained for the given samples of the assemblage studied.

## THEORY

The mineral components contain at least two types of surface groups, namely, the so called layer-sites ( $\equiv X$ ) where the cation-exchange proceeds, and the edge-sites ( $\equiv SOH$ ) where the protonation or deprotonation takes place (or complexation, as well). Consequently, the titration curve of a mineralogical component can be described by means of the reactions (1-3). For these reactions, the equations defining the equilibrium constants ( $K_1$ ,  $K_2$ ,  $K_3$ ) can be derived in a common way (in our case, the chemical equilibrium model and ion-exchange model were used).



Of course, three balance equations complete the description of the given system by means of which the total concentration of sites,  $\sum SOH$  and  $\sum X$ , can be calculated.

The modelling of the titration system, characterized by reactions (1-3), is described elsewhere [3]. In short, the goal of the modelling is to construct the relations (equations) for the calculation of the surface charge [ $mol\ kg^{-1}$ ],  $Q_{cal}$  ( $= Q_{ES} + Q_{LS}$ ), consisting of the charge of the edge-sites  $Q_{ES}$  and of the charge of the layer-sites  $Q_{LS}$ .

Then, in the case of GC-approach, the function  $(Q_{cal})_i = (Q_{ES})_i + (Q_{LS})_i = f([H^+]_i)$  has to be derived, which is applicable for the fitting of experimental data evaluated as  $(Q_{exp})_i = f([H^+]_i)$ ,  $i = 1, 2, 3, \dots, n_p$ , where  $n_p$  is the number of experimental points of the given titration curve, and for the determination of the values of  $K_1$ ,  $K_2$ ,  $K_3$ ,  $\sum SOH$  and  $\sum X$ .

For the case of the mineral assemblage consisting of  $J$  components, each of which has weight percentage  $mP_j$  ( $j = 1, 2, 3, \dots, J$ ), the calculation algorithm of the corresponding CA-approach proceeds according to eq. (4).

$$((Q_{cal})_{total})_i = \sum_j \{ (mP_j / 100) \cdot [(Q_{ES})_{ij} + (Q_{LS})_{ij}] \} \quad (4)$$

$(i = 1, 2, 3, \dots, n_p; j = 1, 2, 3, \dots, J)$

The experimental data were fitted by the Newton-Raphson non-linear regression procedure, and the  $WSOS/DF$

quantity (based on  $\chi^2$ -test) was used as a criterion of goodness-of-fit.

## EXPERIMENTAL

The following mineral assemblages were studied: **MA-F** (fucoïdic sandstone sampled from Cenomanian age deposit in Stráž pod Ralskem (CZ)), **MA-R** (sedimentary rock-clay formation sampled in the Ruprechtov site (CZ)), and **MA-B/M** (bentonite (CZ) + magnetite (Bayer Chemicals) mixture, where magnetite was used as a representative of corrosion products of storage containers).

As for the CA-approach, the most important input data were the mineralogical composition and the corresponding values of the surface sites parameters. For example, sample **MA-R-D2** consisted of (% by weight): montmorillonite (26.4), kaolinite (36.3), anatase (4.3), illite (7.6), quartz (15.0) and pyrite (2.8). The parameter values of individual components were taken from [2].

## RESULTS

For example, the results obtained with the sample **MA-R-D2** are demonstrated in Fig. 1. Not only in this case, but also in others, the GC-approach method proves to be better for the fitting of experimental data than the CA-one. Of course, the agreement is generally better in the case of CA-approach, if we judge the most interesting pH interval from 5 to 8. In particular, there were only two titration curves in our study, namely of **MA-R-D5** and **MA-F-48544**, having the  $WSOS/DF > 20$  (the acceptable values range is 0.1 to 20). On the basis of this study, the substitution of the experimental titration curve by CA-approach method seems to be possible.

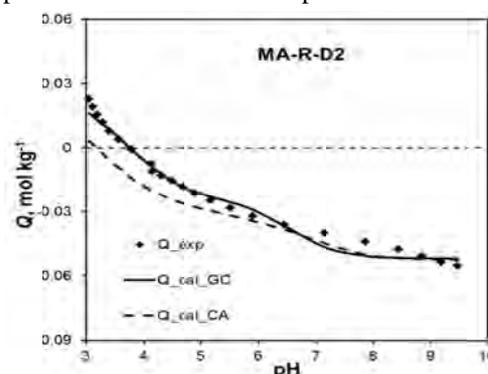


Fig. 1. **MA-R-D2** sample – titration curves evaluated using GC- and CA-approach method

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# CESIUM UPTAKE BY Ca/Mg BENTONITE: EVALUATION OF SORPTION EXPERIMENTS BY A MULTICOMPONENT TWO-SITE ION-EXCHANGE MODEL

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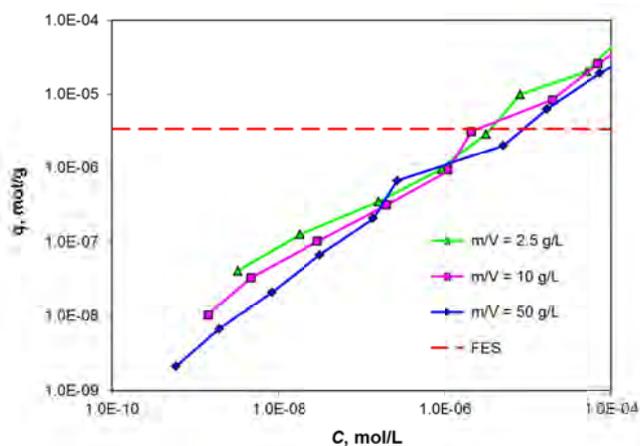
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## INTRODUCTION

Understanding the migration processes at the basic level can help to develop models, which may be used in transport codes to predict the migration in the field scale. Cesium is well adsorbed by clay minerals and many studies concerning adsorption of cesium on different types of clay minerals have been published so far, e.g. [1-2]. Because usage of local bentonite is proposed in Czech project of deep underground repository, cesium adsorption on Czech Ca/Mg bentonite (Rokle deposit, NW Bohemia) was studied in this work. As reported in [3], a substantial content of micas and mica-type clay minerals (about 19 wt. %) caused the specific Cs sorption in the lower concentration range due to the presence of the Frayed Edge Sites (FES). This contribution aims mainly at construction of an ion-exchange model that would take into account the presence of four dominant cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ) sorbed initially on the studied bentonite, and at elaboration of a formal study of the importance of cesium selective sites.

## EXPERIMENTAL

The phase ratio  $m/V$  used for the determination of equilibrium isotherms in the stirred reactor varied from 2.5 to 80.0  $\text{g}\cdot\text{L}^{-1}$ . Initial concentrations of Cs in solutions ranged from  $10^{-7}$  to  $10^{-1}$   $\text{mol}\cdot\text{L}^{-1}$ . The cesium concentration in equilibrium solution has been determined using AAS and ICP-MS. The concentrations of released cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) have been determined using ICP AES and AAS.  $^{137}\text{Cs}$  tracer has been used in experiments with trace concentrations of Cs and also as a spike in a set of experiments with higher cesium concentrations; its activity was measured using NaI(Tl) detector. The stable solution of silver thiourea (AgTU) necessary for the determination of FES concentration was prepared from  $\text{AgNO}_3$  and thiourea.



**Fig. 1.** Cesium sorption isotherms for three values of phase ratio  $m/V$ . Capacity corresponding to FES is indicated.

## RESULTS

The excess of selective agent in the liquid phase, e.g. Cs, AgTU or Cu-trien can successfully replace most of initially sorbed ions. The divalent  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  cations dominated in the initial occupancy of the studied bentonite (determined cation exchange capacity CEC:  $0.505 \text{ equiv}\cdot\text{kg}^{-1}$ ; initial occupancy:  $\text{Ca}^{2+}$  - 34.6 %,  $\text{Mg}^{2+}$  40.4 %,  $\text{Na}^+$  - 10.2 %,  $\text{K}^+$  - 14.7 %). Our older ion exchange model [1] was extended into the model that would respect the cesium exchange with all four cations mentioned on dominant (planar) sorption sites. On the basis of the evaluation of two sets of equilibrium concentrations in the solution, the equilibrium constants for the description of the interaction of cations, which was taken into account with the studied bentonite, were determined using a simple fitting procedure applied on the equilibrium modelling performed in PHREEQC (see Table 1).

**Tab. 1.** Determined surface chemical parameters of the Czech Ca/Mg bentonite.

Surface chemical parameters (planar sites)		
Species	$\log_{10} K_0$	
ZNa	20.00	by definition
ZCs	20.85	
ZK	20.35	
Z <sub>2</sub> Ca	40.30	Gaines-Thomas convention
Z <sub>2</sub> Mg	39.45	
Z(AgTU)	22.24	
(ion exchange master species: Z)		
Frayed edge sites		
FES capacity	0.0034 $\text{equiv}\cdot\text{kg}^{-1}$	

The developed multicomponent ion exchange equilibrium model prepared in the environment of PHREEQC described the non-linear character of equilibrium sorption isotherm very well. The new model was used for the prediction of cesium interaction in dynamic experiments, in which the phase ratio  $m/V$  is greater than that in batch experiments. Modelling of cesium diffusion transport in PHREEQC in the layer of porous material also qualitatively indicated the observed decrease of diffusion flow with the increase of either cesium concentration and/or dry density of the solid in the modelled layer.

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# CRITICAL INSIGHT INTO METHODOLOGY OF THROUGH-DIFFUSION EXPERIMENTS AND THEIR EVALUATION

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The diffusion of radionuclides in clay (bentonite buffer and argillaceous host rock) is an important process that needs to be precisely described with the aim to correctly model the radionuclide transport in the near- and far-field of the proposed final repository of radioactive waste. Through-diffusion (TD) technique is the most widely used method for studying diffusion in porous materials. The species migrates through the porous sample driven by the concentration gradient; its increasing concentration in the target reservoir is monitored.

In order to evaluate diffusion experiments, usually a simple evaluation procedure based on the analytical solution of diffusion equation derived for the specific initial and boundary conditions is applied even though these conditions are not fully accomplished. When filters are not taken into account in the evaluation of diffusion of tracers entering the total pore space, a systematic error in diffusion coefficient determination up to 50 % may arise (depending on the dry density, see [1]). On the other hand, the effect of filters on anionic conservative tracers is negligibly small and can be neglected at high dry densities.

There are several approaches how to deal with the separating filters: (i) by using new type of diffusion cell with advectively flushed filters [2, 3], the influence of filters can be minimized; (ii) filter parameters can be determined independently and used for the steady-state flux correction through the system filter-sample-filter [4, 5]; (iii) filter parameters can be implemented in the numerical modelling, e.g. [6].

In the field of radionuclide diffusion in porous media, some improvements of experimental procedure and evaluation of TD experiments were performed in our laboratory. The first results of these attempts showed that the new evaluation program realized in the GoldSim environment enabled to take into account the diffusion in filters separating clay specimen from the liquid phase [1]. This module can also respect real concentration changes in both reservoirs and thus eliminates the need to replace the target reservoirs (to keep the concentration close to zero) and/or to have a big source reservoir (to keep “essentially” constant concentration). The next upgrade of the module consisted in making it possible to simulate diffusion in the layer with heterogeneous porosity profile. The model, named EVALDIFF, was thoroughly tested and successfully verified against the results of analytical solutions for specific boundary conditions.

We use a static diffusion cell with thin stainless steel membranes [7]. Tracer concentrations in both reservoirs are not kept constant. We take into account all experimental outputs, i.e. concentration evolution in both reservoirs in time and a tracer concentration profile in the sample layer determined after the termination of TD experiment. Procedure for obtaining concentration profiles enables to determine the value of grain density, dry density

and total porosity for each experiment. In case of non-sorbing tracers, also rock capacity factor can be determined independently from the break-through curve fitting, as shown in Fig. 1. In addition, apparent filter length could be discussed from HTO concentration profiles.

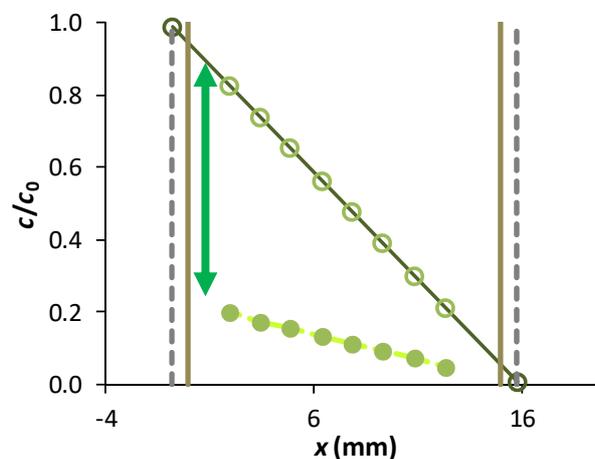


Fig. 1.  $^{36}\text{Cl}$  profile on Bentonite 75 (compacted to  $1600\text{ kg/m}^3$  and saturated with  $0.1\text{ M NaNO}_3$ ) after three weeks of TD experiment: rock capacity factor determination.

However, still at least 3 (for non-sorbing tracers) or 4 (for sorbing tracers) parameters remain generally unknown. Therefore, we make an effort to apply a multi-parametric curve fitting using Box's method in GoldSim that would enable to determine simultaneously all unknown parameters by fitting of all types of output datasets.

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# MIGRATION BEHAVIOUR OF STRONTIUM IN CZECH BENTONITE CLAYS

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## INTRODUCTION

This study is a part of a research on reactive transport of radioactive contaminants in barrier materials of a deep geological repository of radioactive waste in the Czech Republic. Diffusion of cationic species through the porous material is influenced by their interaction with the charged surface of the material and by its physical properties. Physico-chemical properties of bentonite material may be altered in the compacted state (as in the diffusion experiment) compared to the loose state (as in the batch experiment). Therefore, this study shows and compares data obtained for these two types of experiments under various conditions.

## EXPERIMENTAL

A series of sorption and diffusion experiments with Sr and non-activated Ca/Mg bentonite B75 produced in the Czech Republic were performed in two background solutions (CaCl<sub>2</sub> and NaCl). The standard batch method was used for the study of Sr sorption kinetics and equilibrium characteristics. The range of solid-to-liquid ratio (*m/V*) was varied from 0.005 to 0.2 g/mL. The experiments were performed with two values of Sr concentration, 10<sup>-3</sup> mol/L and 10<sup>-5</sup> mol/L of SrCl<sub>2</sub> spiked with radioactive tracer <sup>85</sup>Sr (*T*<sub>1/2</sub> = 64.8 d).

Diffusion experiments were carried out in a diffusion cell (the set-up is described in [1]). Diffusion cells with bentonite plugs of two widths (5 and 15 mm) and two bulk densities (1300 and 1600 kg/m<sup>3</sup>) were prepared. The compacted bentonite was initially saturated with the studied background solution (0.033 mol/L CaCl<sub>2</sub> or 0.1 mol/L NaCl). Diffusion experiments lasted from 21 to 42 days.

## RESULTS

It was confirmed that the sorption of Sr on bentonite is fast, which indicates that the main mechanism of Sr sorption is ion exchange. The sorption kinetics of Sr was faster and values of *K*<sub>d</sub> were generally higher in the NaCl environment compared to the CaCl<sub>2</sub> environment. This could be attributed to the effect of the weaker competitive strength of Na relative to Ca ion [2].

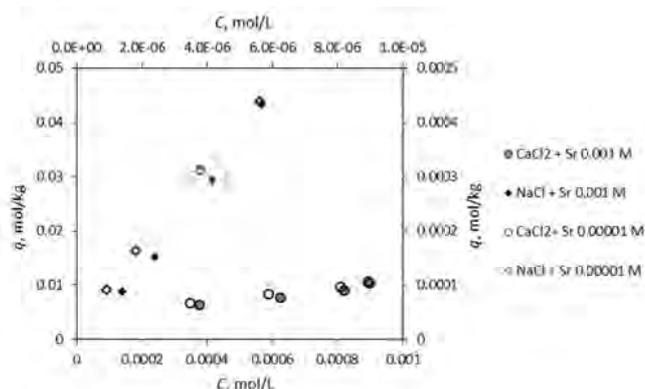


Fig. 1. Sorption isotherms of Sr on bentonite B75 for four types of initial solution.

As shown in Fig. 1, the linear isotherm is applicable for sorption of Sr. Some data, especially from CaCl<sub>2</sub> solution, showed rather non-linear trend. This may be caused by relatively high concentration of Sr combined with competition with Ca ion. Therefore, in some cases Freundlich isotherm was applied.

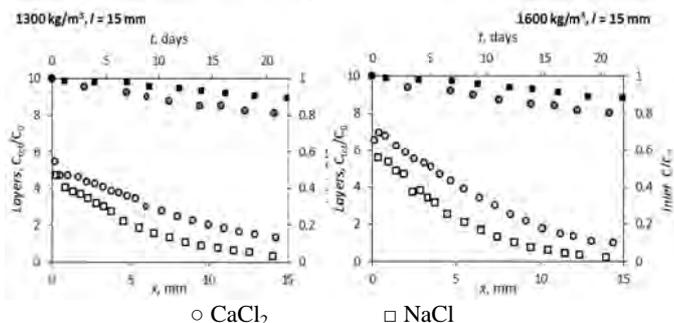


Fig. 2. Data obtained from diffusion experiments with Sr and bentonite B75 compacted to 1300 kg/m<sup>3</sup> (left) and 1600 kg/m<sup>3</sup> (right) in two types of background solution (CaCl<sub>2</sub> and NaCl) which lasted for 21 days. Solid points represent Sr concentration decrease in the inlet reservoirs during the experiment duration. Open points represent Sr concentration profile in the bentonite plug after the experiment termination.

In Fig. 2, it is shown that the course of the diffusion experiments differs significantly for both background solutions. *K*<sub>d</sub> values obtained from sorption and diffusion experiments were compared and significant discrepancies between *K*<sub>d</sub> values obtained from these two types of experiments were observed. Whereas *K*<sub>d</sub> values of Sr obtained from sorption experiments in NaCl environment were approximately 7 times higher compared to CaCl<sub>2</sub> environment, the ratio was opposite in diffusion experiments. This was attributed to different physical conditions of bentonite during these two types of experiments. Moreover, the diffusion of Sr was slower in NaCl environment than in CaCl<sub>2</sub> environment, which may be explained by higher tortuosity of bentonite with dominating Na ion. The developed original method of evaluation of diffusion experiments which are not led to the stationary state does not require long duration of experiments, which is very valuable in terms of minimization of time necessary for migration data acquisition.

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# INFLUENCE OF HOST ROCK AND CEMENT MATERIALS ON DIFFUSION OF RADIOCONTAMINANTS THROUGH COMPACTED BENTONITE

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## INTRODUCTION

Diffusion coefficients of radionuclides obtained in laboratory experiments are fundamental for the performance assessment of radioactive waste disposal in deep geological repositories (DGR). During the long-term evolution of DGR, the alkali-leachates from cementitious materials will induce changes in compacted bentonite affecting radionuclides migration (such as mineralogy, cation exchange capacity and population of exchangeable cations, swelling, hydraulic conductivity) [1-3].

## EXPERIMENTAL

Bentonite powder – unactivated Mg/Ca-bentonite BaM (commercial product of Keramost, a.s., Czech Republic) was compacted in the diffusion cell (length  $L = 1.5$  cm, diameter  $d = 3$  cm) to bulk density  $1600$  kg/m<sup>3</sup>.

The diffusion experiments consisted of three steps:

(1) Compacted bentonite was equilibrated by synthetic groundwater SGW-UOS [4] or evolved portlandite cement water ECW for 6 weeks. In order to maximize the equilibration of bentonite with the liquid phase, the solution was exchanged weekly for fresh.

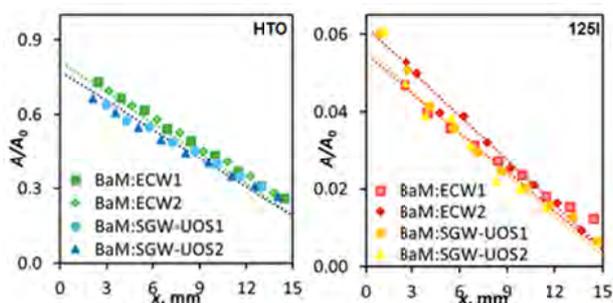
(2) Realization of through-diffusion experiments of HTO and iodide (<sup>125</sup>I) lasting 14 days; determination of porosity, real bulk density, concentration profile (HTO / I) in the layer of the compacted bentonite.

(3) Evaluation of diffusion experiments using the module EVALDIFF, prepared in the environment of GoldSim based on the cooperation between ÚJV Řež, a.s. and Czech Technical University.

(4) Determination of cation exchange capacity and population of exchangeable cations (using Cu<sup>II</sup>-trien method) and XRD analysis of the bentonite after diffusion experiment to rule out mineralogical changes.

## RESULTS

Determined relative volume activities of <sup>3</sup>H and <sup>125</sup>I in pore water for both series are shown in Fig. 1.



**Fig. 1.** The relative volume activities of <sup>3</sup>H and <sup>125</sup>I in pore water for series BaM:SGW-UOS and BaM:ECW after 14 days.

Experimental data were fitted by model curves dependent on the geometric factor  $G$  and effective porosity  $\epsilon_{\text{eff}}$  (real porosity for HTO) in two-parametric regression. The values of effective diffusion coefficients  $D_e$  were obtained on the bases of determined  $G$  and  $\epsilon_{\text{eff}}$  for reference diffusion coefficient in free water  $D_w = 2.3 \cdot 10^{-9}$  m<sup>2</sup>/s. Results are presented in Table 1.

**Tab. 1.** Determined  $\epsilon_{\text{eff}}$  and  $D_e$  values of HTO and <sup>125</sup>I for conditions of realized diffusion experiment.

Liquid phase	species	$\rho_d$ kg/m <sup>3</sup>	$\epsilon_{\text{eff}}$ -	$D_e$ m <sup>2</sup> /s
SGW-	HTO	1530	0.46	$1.1 \cdot 10^{-10}$
UOS	<sup>125</sup> I	1550	0.03	$2.3 \cdot 10^{-12}$
ECW	HTO	1490	0.48	$1.4 \cdot 10^{-10}$
	<sup>125</sup> I	1510	0.03	$4.8 \cdot 10^{-12}$

Faster diffusion of HTO in the ECW water in comparison with the SGW-UOS water is in the agreement with similar experiments on the bentonite MX-80 [1]. Differences in bulk density (ie. total porosity) may have less significance, the main factor is the greater diffusivity  $D_w$  in ECW (+12 %) than in the SGW-UOS (estimated from diffusion experiments through glass frit plates).

Another important factor is that the equilibration process is influenced by the ion exchange of Ca<sup>2+</sup> ions for other cations (primarily monovalent Na<sup>+</sup>); this results in differences in pore size, in spite of the same total porosity. For this reason, the diffusion path is less tortuous ( $G$  is greater).

Similarly, diffusion of iodide through bentonite equilibrated with the ECW water is faster. Despite the fact that the ionic strength in the environment of ECW is higher (ca. 38 mmol/l) than in the environment of SGW-UOS (ca. 3 mmol/l), approximately seven percent of the total pore space is open to a diffusion in both cases. The similar effective porosity at various ionic strength is in a disagreement with the theory of anionic (Donnan) exclusion, described in [5].

After a short contact (about 8 weeks) of bentonite and liquid phases, no significant mineralogical changes were observed by XRD analysis.

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# A KINETIC STUDY OF Sr UPTAKE ON MIXTURES OF BENTONITE AND CRUSHED HYDRATED CEMENT PASTE

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## INTRODUCTION

Radionuclide waste repository should confine radionuclides for million years. Interactions on the interface of different natural and engineering barriers are a serious problem. One of important interfaces is the interface between hydrated cement and bentonite. There are big differences between hydrated cement and bentonite, which could change both materials on their interface in million years. The interface of hydrated cement and bentonite can be divided into 'hydrated-cement-like' part and 'bentonite-like' part. There are three ways how to study this interface: geochemical modelling; comparison with natural and/or industrial analogues; experimental study of changes of both materials in contact. Our study evaluates a short-time (until 96 hours) change of Sr sorption in different mixtures of hydrated cement and bentonite used as an analogue of hydrated cement-bentonite interface.

## EXPERIMENTAL

In this work, hydrated cement was prepared from cement CEM II/A-S 42.5 R by hydration for 19 days. The bentonite used was Czech type BaM. Characterization of mixture is defined by  $Ce/So$  quantity (mass of hydrated cement versus total solid phase mass). Sorption of Sr was studied for  $Ce/So$  equal to 0, 0.1, 0.25, 0.5, 0.75, 0.9 and 1. As contact solutions, (A) 0.001 M  $SrCl_2$  and (B) Artificial Cement Water (ACW) prescribed by Wieland [1] (0.14 M NaOH, 0.18 M KOH and 0.002 M  $Ca(OH)_2$ ) in equilibrium with  $SrCl_2$  of chosen concentrations ( $1 \cdot 10^{-3}$ ,  $2 \cdot 10^{-3}$ ,  $5 \cdot 10^{-3}$ ,  $7 \cdot 10^{-3}$  and  $1 \cdot 10^{-2}$  M) were used. Working solutions were labelled by  $^{85}Sr$  and Sr concentrations were determined on the basis of  $^{85}Sr$  activity measurement using NaI(Tl) detector. Three solid-to-liquid ratios were used for the study of Sr uptake on mixtures of hydrated cement and bentonite: 0.3, 0.5 and 1.0 g to 8 mL. The systems were shaken with frequency of  $120 \text{ min}^{-1}$ . The activity of  $^{85}Sr$  in the liquid phase, after centrifugation at 3000 rpm for 10 minutes, was determined for experiments lasting 2, 4, 7, 24, 30, 48, 72 hours. The influence of the  $CO_2$  presence in working solutions was not taken into account.

## RESULTS

The evolution of  $^{85}Sr$  relative activity in the liquid phase (see Fig. 1) shows that 96-hours experiments seem to approach the equilibrium, although in [2] it was stated that changes in sorption behaviour of such systems can be observable up to four months.

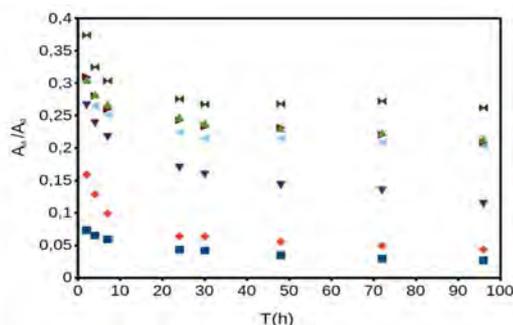


Fig. 1. Development of Sr uptake for different ratios  $Ce/So$ .

As shown in Fig. 2, the dependence of measured  $K_D$  on the presence of hydrated cement in the solid phase is not linear, which indicates mineralogical changes of bentonite in contact with highly alkaline solution ( $pH > 13$ ). Such results were observed for both working solutions and all phase ratios studied. The interpretation of results is in an agreement with leaching experiments made in [3].

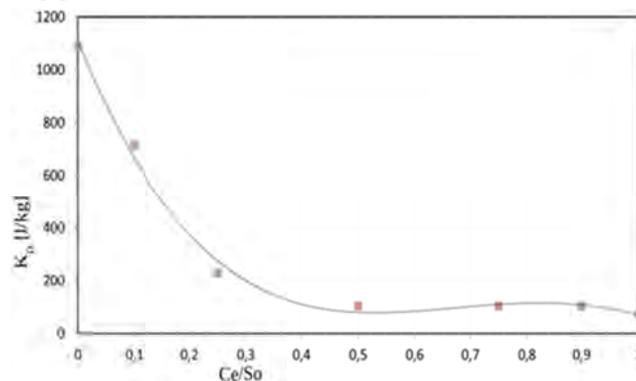


Fig. 2. Dependence of distribution coefficient  $K_D$  on  $Ce/So$  after 96 hours. The working solution was ACW with initial Sr concentration of  $10^{-3} \text{ mol/L}$ .

With regard to the non-linear shape of  $K_D$  as a function of ratio  $Ce/So$  presented on Fig. 2, it should be noted that mineralogical changes of bentonite influencing the Sr in the complex system are difficult to detect [4]. In the further study, the presence of exchangeable strontium in the cement phase should be taken into account, as it makes it impossible to derive from obtained data the shape of the interaction isotherm of strontium on the mixture of barrier materials containing crushed hydrated cement phase.

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# CHARACTERIZATION OF HYDRATED CEMENT PASTE (CEM II) BY SELECTED INSTRUMENTAL METHODS AND A STUDY OF Sr-85 UPTAKE

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## INTRODUCTION

For the safety assessment of the repository Bratrství, it is necessary to collect characteristics of applied barrier materials. As barriers in this repository are based on cementitious materials and  $^{226}\text{Ra}$  is the main contaminant of interest there, SURAO (the Czech Radioactive Waste Repository Authority) aims to study systems radium – hydrated cement materials.

An introductory methodological study with Sr, which can be considered in some aspects chemically similar to Ra, was carried out to gain experience and knowledge about optimal experimental conditions and procedures while working with hydrated cement pastes. This study also dealt with the description of interaction of radionuclides with cement materials, which are essential for modelling the transport of Ra in the storage environment.

## EXPERIMENTAL AND RESULTS

Two cementitious materials of CEM II grade, A: CEM II / A-S 42.5 R (produced by Lafarge Cement, a. s.) and B: CEM II / B-M (S-LL) 32.5R (Českomoravský cement, a. s. – Heidelberg Cement Group) have undergone testing by instrumental methods (more in [1]). With the hydrated cement paste of cement A, a preliminary study of the interaction using  $^{85}\text{Sr}$  tracer was carried out.

### Characterization of cementitious materials

Values of density of hydrated cement paste were determined by the pycnometric method on crushed materials. For cement A, a value of  $2177 \pm 44 \text{ kg/m}^3$  was measured, and  $1998 \pm 29 \text{ kg/m}^3$  for cement B.

Specific surface areas of both materials were measured by  $\text{N}_2$  adsorption at  $\sim 77 \text{ K}$  (Quantachrome Monosorb MS-22 device, single-point method). Obtained values were  $20.1 \pm 0.3 \text{ m}^2/\text{g}$  and  $48.5 \pm 0.3 \text{ m}^2/\text{g}$  for cements A and B, respectively.

FTIR spectra were measured for two blocks of cement B differing in time of contact with water by a Nicolet iS 50 FT-IR spectrometer using the Attenuated Total Reflection (ATR) technique in the scan range of  $400 - 4000 \text{ cm}^{-1}$ . Leaching of hydrated cement caused only a very small change of the FTIR spectrum.

Both cementitious materials were studied by X-ray diffraction (Rigaku Mini Flex 600 with ICDD PDF-2 database (version 2013)). Four mineral phases, namely calcite  $\text{CaCO}_3$ , hydrotalcite  $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4(\text{H}_2\text{O})$ , portlandite  $\text{Ca}(\text{OH})_2$  and ettringite  $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$  were identified in hydrated cement A, but only calcite and portlandite in cement B. It could be also proven that the content of  $\text{Ca}(\text{OH})_2$  decreased significantly in the bulk of the cementitious block by leaching of hydrated cement in water.

### Sorption experiments with $^{85}\text{Sr}$

In a set of kinetic experiments, crushed hydrated cement A (grain size  $\leq 0.71 \text{ mm}$ ) was contacted with a cement leachate (distilled water contacted with crushed hydrated cement A for 1 month at  $m/V = 0.2 \text{ kg/L}$  -  $\text{pH} = 12.8$ ). Strontium ( $1 \cdot 10^{-7} \text{ mol/L}$ ) traced by radioactive isotope  $^{85}\text{Sr}$  was added as  $\text{SrCl}_2$ . Its activity was monitored by a  $\text{NaI}(\text{Tl})$  detector. The  $m/V$  ratio used was in the range from 0.033 (1:30) to 0.33 (1:3)  $\text{kg/L}$ .

The observed kinetics of  $^{85}\text{Sr}$  uptake was relatively fast – after two days, the equilibrium was reached.

An extensive set of equilibrium experiments was performed, in which the initial total concentration of Sr in the liquid phase was varied between 0.35 and 1  $\text{mmol/L}$ . The lower limit of concentration range corresponds to the content of Sr in cement A itself. The experiments were carried out for 6 different  $m/V$  ratios (from 1:100 to 1:3). The distribution coefficient  $K_d$ , obtained from the balance evaluation of  $^{85}\text{Sr}$  activity in the liquid phase as the measure of the  $^{85}\text{Sr}$  uptake, was used. No influence of the total initial Sr concentration on the  $^{85}\text{Sr}$  uptake was observed.

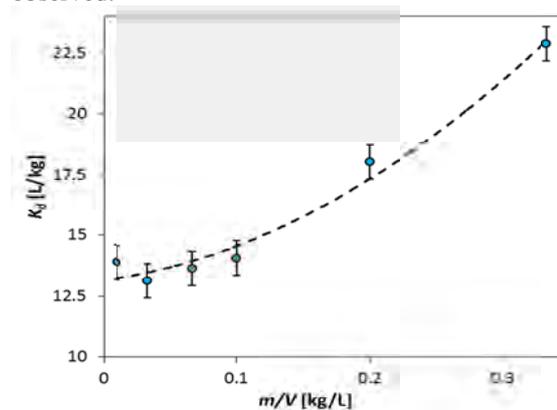


Fig. 1. Dependence of determined  $K_d$  values describing  $^{85}\text{Sr}$  uptake on hydrated cement A on the phase ratio  $m/V$ .

The increase of  $K_d$  values with increasing  $m/V$  is unexpected if the ion-exchange is taken into account as an important mechanism of the uptake (e.g. [2]). The presence of Sr in both working solution and solid phase at the beginning of sorption experiment needs to be taken into account. The content of the so-called exchangeable Sr in the solid phase  $q_0$  was determined as  $4.04 \pm 0.26 \text{ mmol/kg}$ .

As Sr and Ra are similar to some extent, the performed study of Sr uptake will help us with the planned study of Ra uptake on the same material.

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# QUASIRELATIVISTIC QUANTUM CHEMICAL CALCULATIONS OF URANYL(VI)-SULFATES SPECTROSCOPIC PROPERTIES

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## INTRODUCTION

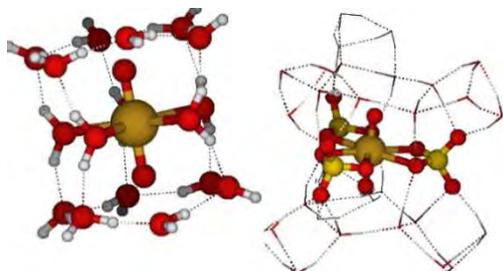
Uranyl(VI) – sulfate system in aqueous solutions ( $\text{UO}_2^{2+}$  -  $\text{SO}_4^{2-}$  -  $\text{H}_2\text{O}$ ) is of great importance for both nuclear industry and environmental safety studies. In previous studies, experimental values for spectroscopic and thermodynamic properties (in particular stability constants) have been presented. Quantum Chemical Estimates for the former can be used to check the self-consistency of previous speciation studies.

## COMPUTATIONALS

The first calculations of  $\text{UO}_2^{2+}$  -  $\text{SO}_4^{2-}$  -  $\text{H}_2\text{O}$  system performed have been quasirelativistic (60 uranium inner electrons have been replaced by an effective core pseudopotential (ECP) including important part of scalar relativistic effects, other electrons have been treated as in non-relativistic case). For the electron correlation, DFT/B3-LYP method has been employed, with def-SVP and def-TZVPP atomic basis sets. Explicit hydration model has been applied [1,2]. For dispersion forces DFT-D3 a correction has been used. Excitations have been described on RPA/TDDFT level. The above mentioned calculations were performed in Turbomole [3].

## RESULTS

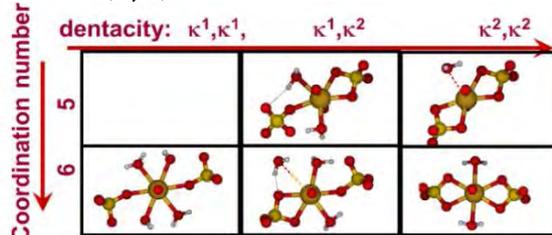
From spectroscopic constants important for luminescence and UV-VIS absorption spectra, the  $0' \rightarrow 0$  excitation energies ( $T_{00}$ , the transition between lowest lying vibrational levels of ground and excited electronic states), uranyl group symmetric mode vibrational frequency ( $\omega_{\text{gs}}$  for ground state together with  $\omega_{\text{e}}$  for excited state) and  $\Delta R$  ( $\text{U-O}_{\text{yl}}$  excitational elongation) were determined. We predicted e.g.  $\Delta R = 4.6$  pm for  $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+} \cdot n\text{H}_2\text{O}$  and  $\Delta R = 3.7$  pm for  $[\text{UO}_2(\kappa^2\text{-SO}_4)_2(\text{H}_2\text{O})]$  in vacuum) from a quasirelativistic study. Values for the former two are presented in Tab. 1. Some of the simple molecular models used are presented in Fig. 1. Fig. 2 shows the plethora of possible isomers for bis(sulfate)uranyl complex. Further details are presented in [1,2].



**Fig. 1.** Explicit hydration molecular models, hydrated uranyl  $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+} \cdot 12 \text{H}_2\text{O}$  (left) and tris(sulfate) uranyl  $[\text{UO}_2(\kappa^2\text{-SO}_4)_3]^{4-} \cdot 30 \text{H}_2\text{O}$  (right).

The electronic excited state corresponds here to the lowest lying triplet state ( ${}^3\Delta_{\text{g}}$  for bare uranyl ion;  ${}^3\Phi_{\text{g}}$  is close as well). Both all-electron and RECP DFT and *ab initio* calculations with fully relativistic Dirac-Coulomb(-Gaunt) Hamiltonian (which mix singlet and triplet states so the excited state in question will have a singlet

component as well) are in preparation – they will be compared with the presented results and excitation probabilities ( $\sim \mu_m$ ).



**Fig. 2.** All possible isomers/structures of bis(sulfate) uranyl,  $\text{UO}_2(\text{SO}_4)_2^{2-}$ , for which ground state PES minimum has been found

**Tab. 1.**  $[\text{UO}_2(\text{SO}_4)_m(\text{H}_2\text{O})_n]^{2-2m}$  properties – Quantum chem. estimates (calc.) and experimental data (exp.)

$m$	calc. $T_{00}$ [ $10^3 \text{ cm}^{-1}$ ]	exp. $T_{00}$ [ $10^3 \text{ cm}^{-1}$ ]	calc. $\omega_{\text{gs}}$ [ $\text{cm}^{-1}$ ]	exp. $\omega_{\text{gs}}$ [ $\text{cm}^{-1}$ ]
0	$20.3 \pm 0.4$	$20.49 \pm 0.20$	$900 \pm 20$	$873 \pm 10$
1	$19.6 \pm 0.2$	$20.36 \pm 0.20$	$880 \pm 30$	$860 \pm 10$
2	$18.7 \pm 0.2$	$20.27 \pm 0.20$	$860 \pm 20$	$854 \pm 10$
3	$20.0 \pm 0.6$	$20.20 \pm 0.20$	$860 \pm 20$	$850 \pm 30$
$1^{\text{Se}}$	$17.4 \pm 0.3$	$20.29 \pm 0.20$	$880 \pm 10$	$850 \pm 10$

Values for uranyl monoselenate (denoted  $1^{\text{Se}}$ ) are presented for comparison. Uncertainties for calc. data correspond to the averaging over explicitly hydrated models and/or denticity ( $\kappa^1\text{-SO}_4^{2-}$ ,  $\kappa^2\text{-SO}_4^{2-}$ ) isomers. For  $T_{00}$  calculations, smaller number of explicit water molecules was used in our model for uranyl monosulfate/selenate and bis(sulfate) (since, unlike vertical excitation energy  $T_e$ ,  $T_{00}$  need normal mode vibrational analysis to be done for both ground and excited electronic states). This explains the higher discrepancy in prediction of both  $T_{00}$  and  $\omega_{\text{gs}}$  for cases  $m = 1, 2$  and  $1^{\text{Se}}$ .

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## INTRODUCTION

Compared to most common oxide matrices used for determination of anthropogenic  $^{236}\text{U}$  in natural samples by Accelerator Mass Spectrometry (AMS), fluoride matrices promise to significantly reduce the occurring isobaric interferences. In this respect,  $\text{UF}_4$  compound appeared to be the most promising as a target sample for AMS [1]. The preparation of the compound in a pure form without oxygen has, however, proven to be rather complicated and significantly reliant on the reaction conditions [2, 3]. In addition, the common preparation methods include reactants containing uranium in IV+ oxidation state, whereas the uranium eluted from usual processing methods occurs in VI+ form. Therefore, a series of experiments was carried out to suggest a suitable method of fluoride-matrix target preparation, involving a reduction step and carrier addition.

## EXPERIMENTAL

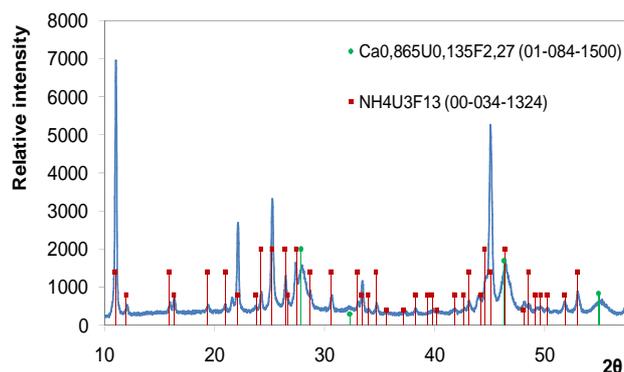
For the reduction of hexavalent uranium in aqueous solutions of  $\text{UO}_2\text{SO}_4$  and  $\text{UO}_2(\text{CH}_3\text{COO})_2$ , several various reducing agents including  $\text{SnCl}_2$ ,  $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ ,  $\text{NH}_2\text{OH}$  and  $\text{Na}_2\text{S}_2\text{O}_3$  were tested at different conditions (see [4] for more details). Subsequently,  $\text{Ca}^{2+}$  or  $\text{Nd}^{3+}$  was added to the solution as a carrier. After addition of a concentrated hydrofluoric acid and a consequent reaction, a precipitate was isolated from the solution. The precipitate was dried and analysed using X-ray powder diffraction method. Selected samples were also heated under a reducing argon-hydrogen atmosphere at a temperature of  $310\text{ }^\circ\text{C}$ .

## RESULTS

From all the reducing agents tested, tin dichloride and hydrazine dihydrochloride were selected as the most effective, combined with a copper catalyst and increased temperature. Most experiments were carried out at  $80\text{ }^\circ\text{C}$ . Decreasing the temperature or excluding the catalyst apparently leads to a significant reduction of the reaction rate.

Independently on the carrier used, both the tin dichloride and hydrazine dihydrochloride methods provided a green precipitate. None of the resulting compounds could be identified using the X-ray diffraction, however the alpha activity of the supernate, determined by liquid scintillation counting, greatly decreased.

In addition, heating the precipitate obtained by the hydrazine dihydrochloride method at  $310\text{ }^\circ\text{C}$  under the argon-hydrogen atmosphere provided a mixture of clearly defined compound  $\text{NH}_4\text{U}_3\text{F}_{13}$  and  $\text{Ca}_x\text{U}_y\text{F}_z$  (identified by XRD method; see Fig. 1). In this sample, no additional oxidic impurities were found.



**Fig. 1.** Diffractogram of the product obtained by heating the precipitate at  $310\text{ }^\circ\text{C}$  under argon-hydrogen atmosphere.

Further heating at the temperatures exceeding  $400\text{ }^\circ\text{C}$  led to decomposition of  $\text{NH}_4\text{U}_3\text{F}_{13}$ , resulting in  $\text{UF}_4$  contaminated by  $\text{UO}_2$ . The occurrence of the  $\text{UO}_2$  compound is in contradiction with data found in literature [5].

In conclusion, the  $\text{NH}_4\text{U}_3\text{F}_{13}$  compound could potentially be used as a target sample for AMS analysis as it contains the uranium incorporated in a non-oxygen matrix. Further research in this field is necessary.

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# DETERMINATION OF KINETIC PARAMETERS OF SELECTED AN/LN LLE SYSTEMS USING MICROFLUIDIC SLUG-FLOW TECHNIQUE

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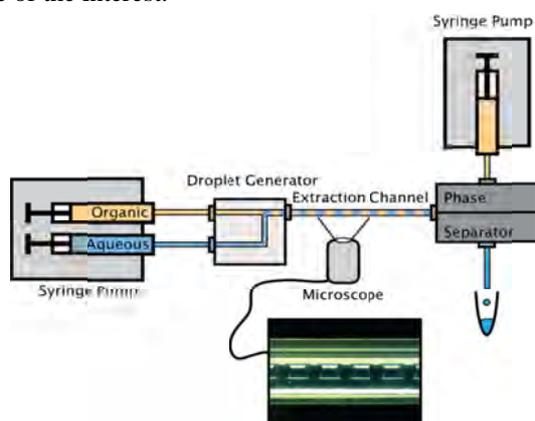
## INTRODUCTION

One of the approaches to closing the nuclear fuel cycle may involve the partitioning and transmutation of irradiated nuclear fuel. Within this approach, a key step is to selectively separate minor actinides (Am and Cm) from chemically very similar trivalent lanthanides. For successful non-equilibrium modelling of such separation systems, mass-transfer data is of utmost importance [1]. To gain such data, slug-flow microfluidic extraction technique was utilized. In the slug-flow regime, the advantage of well-defined interfacial area, high mixing velocity and fast phase separation is what we benefit from, unlike within other conventional methods [1, 2].

In this work, we studied few LLE systems that are taken into account for An(III)/Ln(III) separation processes, such as 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) used within ALSEP process [3] and N,N,N',N'-tetraoctyl diglycolamide (TODGA) used within both ALSEP and SANEX processes [3, 4].

## EXPERIMENTAL

In this method, microfluidic slug-flow method developed at the NE Division, ANL (Fig. 1) was utilized. As a liquid media, HEH[EHP] in dodecane (org) – HEDTA (aq), and TODGA in octanol + dodecane (org) – HNO<sub>3</sub> (aq), were of the interest.



**Fig. 1.** Experimental setup – microfluidic parts by Dolomite Microfluidic, USA; a microscope by Aven, USA

Experiments regarding HEH[EHP] were carried out in cooperation with ANL, IL under previously defined optimal conditions, i.e. 0.75M HEH[EHP] in *n*-dodecane with pre-extracted <sup>241</sup>Am and <sup>147</sup>Pm (org), 0.125M HEDTA + 0.20M (NH<sub>4</sub>)<sub>3</sub>Cit of pH ca 2.75 (aq) and temperature of (22.0 ± 1.0) °C.

The system TODGA – HNO<sub>3</sub> was tested for various concentrations of agents, i.e. 0.025-0.200M TODGA in 5% octanol and *n*-dodecane, 1-3M HNO<sub>3</sub> spiked with <sup>241</sup>Am or <sup>242</sup>Pu, and temperature of (23.0 ± 1.0) °C.

First, specific interfacial area was measured for each system in question and for various retention times, which were controlled by syringe pumps, varying from 2.5-14.0 s. The area was measured using pixel analysis of static pictures taken by a microscope.

After collecting separated phases for each retention time, samples (50 or 100 μL fraction) were measured by a Liquid Scintillation Counter (LSC) Tricarb (Perkin Elmer, USA).

## RESULTS

Experiments with previously tested HEH[EHP] – HEDTA system showed, according to expectations, repeatable linear dependency and relatively constant specific interfacial area dependency on retention time (i.e. flow rate). Kinetic equation of pseudo-first order, thus, plotted data perfectly. As shown in Tab. 1, Am(III) back-extracts faster than Pm(III), however, because of higher selectivity of HEDTA to Pm(III), its total extraction half-time is higher.

**Tab. 2.** Am(III) and Pm(III) mass-transfer coefficients of forward ( $k_{ao}$ ) and backward ( $k_{oa}$ ) extraction, observed kinetic constants ( $k_{obs}$ ) and extraction half-times ( $t_{1/2}$ ) for system 0.75M HEH[EHP] in *n*-dodecane – 0.125M HEDTA + 0.20 (NH<sub>4</sub>)<sub>3</sub>Cit of pH ca 2.75.

	Am(III)	Pm(III)
$k_{ao}$ [mm/s]	$(2.07 \pm 0.11) \times 10^{-3}$	$(1.06 \pm 0.07) \times 10^{-2}$
$k_{oa}$ [mm/s]	$(7.53 \pm 0.40) \times 10^{-3}$	$(1.44 \pm 0.09) \times 10^{-3}$
$k_{obs}$ [1/s]	$(7.02 \pm 0.67) \times 10^{-2}$	$(8.80 \pm 0.90) \times 10^{-2}$
$t_{1/2}$ [s]	$9.9 \pm 1.0$	$7.9 \pm 0.8$

The kinetic experiments with TODGA – HNO<sub>3</sub> showed, on the other hand, many drawbacks. Not only the extraction of both Am(III) and Pu(IV) was extremely fast, but also specific interfacial area dependency on retention time was not linear for all systems tested. The non-linear specific interfacial area dependence on retention time resulted in non-linear data curve. Hence, the kinetic order of extraction must have been determined. Using *n*-th order kinetic equation plotting, a pseudo-1.5<sup>th</sup> order was found to fit best the experimental data.

These results indicate that TODGA-HNO<sub>3</sub>-Am/Pu create undefined interfacial species, because the radionuclide of interest does not approach the interface from one phase in the same kinetic regime as it withdraws from the interface within the other phase. Such a regime corresponds to the film-penetration model. However, to validate this theory, mechanism of interfacial transfer needs to be further studied.

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# RADIATION INFLUENCING OF THE EXTRACTION PROPERTIES OF THE CyMe<sub>4</sub>-BTBP AND CyMe<sub>4</sub>-BTPPhen SOLVENTS WITH FS-13

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## INTRODUCTION

Liquid high radioactive waste generated from nuclear fuel reprocessing still contains long-lived actinides. If these actinides are separated from the rest of waste, long term radiological risks of the high radioactive waste would be reduced very effectively. So reprocessing of the used nuclear fuel could decrease the long-term radiotoxicity, reduce the heat load of the waste and shorten the storage time of waste [1]. Partitioning and Transmutation (P&T) is an advanced reprocessing option focusing primarily on decreasing the long-term radiotoxicity [2].

## EXPERIMENTAL

The solutions of the CyMe<sub>4</sub>-BTPPhen and CyMe<sub>4</sub>-BTBP ligands dissolved in FS-13 (phenyl trifluoromethyl sulfone) were irradiated by pulse linear electron accelerator LINAC 4-1200 (Tesla v.t. Mikroel) in presence/absence of 1 mol/L or 2 mol/L HNO<sub>3</sub>. The maximum total dose was 200 kGy. Samples were analyzed for the presence of degradation products using HPLC system LaChrom series 7000 (Merck-Hitachi). The extraction properties of irradiated and non-irradiated solvents were compared. The respective organic phases were contacted for 6 hours with nitric acid solutions spiked with <sup>152</sup>Eu(III) and <sup>241</sup>Am(III) stock solutions. Activity measurements of <sup>241</sup>Am and <sup>152</sup>Eu were performed with a  $\gamma$ -ray spectrometer EG&G Ortec.

## RESULTS

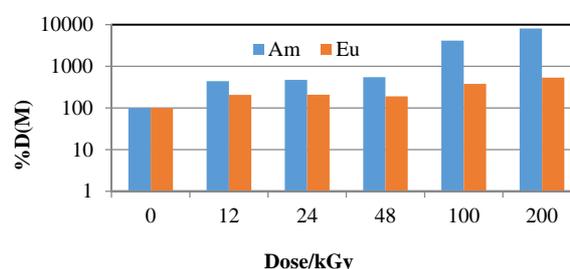
The data on stability of the irradiated CyMe<sub>4</sub>-BTBP and CyMe<sub>4</sub>-BTPPhen ligands in FS-13 indicate their higher stability in the FS-13 diluent than that observed previously in the cyclohexanone-type diluents. From the residual concentrations of the ligands, it follows that the presence of HNO<sub>3</sub> in the system slightly increases the stability of CyMe<sub>4</sub>-BTBP ligand at higher radiation doses. In case of CyMe<sub>4</sub>-BTPPhen, the ligand was found rather sensitive to the presence of aqueous phase.

**Tab. 1.** Residual concentration (c) of CyMe<sub>4</sub>-BTBP and CyMe<sub>4</sub>-BTPPhen after irradiation in FS-13. Initial concentration - 5 mmol/L.

Contact Y/N HNO <sub>3</sub> /conc.	Dose [kGy]	c [mmol/l] CyMe <sub>4</sub> -BTPPhen	c [mmol/l] CyMe <sub>4</sub> -BTBP
N	12	4.91	4.63
N	24	4.73	4.51
N	48	4.49	4.09
N	100	3.43	3.27
N	200	2.88	2.61
Y/ 1M	12	4.62	4.44
Y/ 1M	24	3.82	3.90
Y/ 1M	48	1.98	4.12
Y/ 1M	100	2.76	3.01
Y/ 1M	200	1.66	2.86
Y/ 2M	12	4.53	3.80

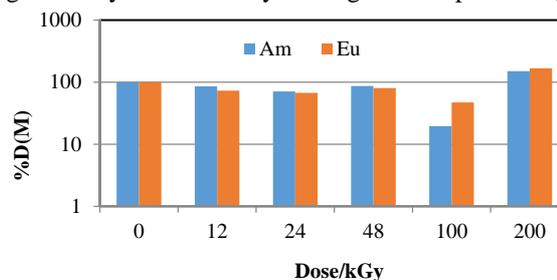
Y/ 2M	24	3.81	4.02
Y/ 2M	48	2.49	3.72
Y/ 2M	100	2.90	3.58
Y/ 2M	200	1.78	3.17

For the system with CyMe<sub>4</sub>-BTPPhen dissolved in FS-13, the distribution ratios for americium and europium increase with the increasing absorbed dose. The dependences of the relative D(Am) and D(Eu) values on the absorbed doses are shown in Fig.1. The highest D(Am) and D(Eu) values were determined in the sample irradiated by the dose of 200 kGy. It seems that degradation products positively influence the extraction properties in this system.



**Fig. 1.** Dependences of relative D(Am) and D(Eu) values on doses (CyMe<sub>4</sub>-BTPPhen in FS-13).

The dependences of the relative D(Am) and D(Eu) values on the absorbed doses for the system with CyMe<sub>4</sub>-BTBP in FS-13 are shown in Figure 2. It can be concluded that contrary to the system of CyMe<sub>4</sub>-BTPPhen in FS-13, the extraction properties of CyMe<sub>4</sub>-BTBP in FS-13 are not significantly influenced by the degradation products [3].



**Fig. 2.** Dependences of percentage D(Am) and D(Eu) values on doses (CyMe<sub>4</sub>-BTBP in FS-13).

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# SOLVENT EXTRACTION OF EUROPIUM (III) FROM COMPLEXING SOLUTIONS INTO ROOM TEMPERATURE IONIC LIQUIDS USING CMPO EXTRACTANT

Basarabová, B.; Němec, M.; Čubová, K.

## INTRODUCTION

Room temperature ionic liquids (RTILs) are organic salts with a melting point below 100 °C, made of bulky organic cations and organic/inorganic anions. Currently, RTILs are considered as promising media for L-L extraction separations. Therefore, they are investigated as possible replacements of volatile organic compounds in decontamination of liquid radioactive waste with a possibility of their recycling. Their properties (negligible vapour pressure, high ionic conductivity, high thermal and radiation stability, tuneable hydrophobicity etc.) are advantageous for the field of radioactive waste treatment and radionuclide separations. Although RTILs provide enormous variety of structures, extraction studies predominantly concern the imidazolium RTILs family. Hydrophobic methylimidazolium RTILs  $[C_2mim][NTf_2]$  and  $[C_4mim][NTf_2]$  have been selected as extraction media for Eu (III) extraction, as a representative of lanthanides, from various aqueous solutions.

Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) has been selected as an extractant dissolved in RTIL.

## EXPERIMENTAL

Aqueous phase (AP) has been prepared as a solution of  $HNO_3$  ( $c = 10^{-3}, 10^{-2}, 10^{-1} \text{ mol.dm}^{-3}$ ), with constant nitrate concentration of  $1 \text{ mol.dm}^{-3}$ . Citric or oxalic acids were dissolved in AP with constant concentration  $10^{-2} \text{ mol.dm}^{-3}$ . Organic phase (OP) has been prepared by dissolving CMPO in RTIL, using ultrasonic bath (30 min at 60°C), to concentrations 0.5, 1, or 5  $\text{mmol.dm}^{-3}$ . OP was pre-equilibrated with non-spiked AP at volume ratio 1 : 1 for 12 hours. Prior to contacting, AP has been spiked with Eu stock solution in carrier free form. After spiking, an aliquot of AP was taken for later determination of activity balance A%. Spiked AP and pre-equilibrated OP were contacted for 12 h at volume ratio 1 : 1, the phases were then separated by centrifugation for 5 min at 2500 rpm (MPW-350). After centrifugation, another aliquot of AP was taken and diluted with distilled water, while an aliquot of OP was taken using glass microcapillary and diluted with acetone. Sampled aliquots were measured on well type NaI(Tl) scintillation detector.

## RESULTS

A series of L-L extraction experiments have been carried out to determine the ability of  $[C_2mim][NTf_2]$  and  $[C_4mim][NTf_2]$  to extract Eu from  $HNO_3$  solutions ( $10^{-3}, 10^{-2}, 10^{-1} \text{ mol.dm}^{-3}$ ) containing constant concentration ( $c = 10^{-2} \text{ mol.cm}^{-3}$ ) of oxalic or citric acid. Pure  $[C_2mim][NTf_2]$  and  $[C_4mim][NTf_2]$  did not extract Eu from the above described extraction systems, therefore CMPO was added into the RTILs. The presence of CMPO has significantly increased the Eu extraction. Eu extraction has been also increasing with the increase of CMPO concentration (Fig. 1., Fig. 2.), when at 5  $\text{mmol.cm}^{-3}$  the extraction per-cent E% reaches ~99% for each of the studied extraction system. In  $HNO_3$  solutions, lower concentrations of CMPO showed more efficient extraction from the oxalic acid than from the citric acid.

The  $[C_2mim][NTf_2]$  and  $[C_4mim][NTf_2]$  containing CMPO have shown promising results for Eu extraction from decontamination solutions, but more detailed research is needed.

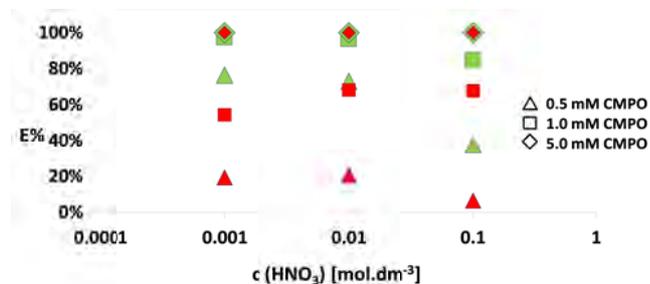


Fig. 1. Solvent extraction of  $^{152}\text{Eu}$  from  $HNO_3$  solutions ( $c(HNO_3) = 10^{-3}, 10^{-2}, 10^{-1} \text{ mol.dm}^{-3}$ ) containing oxalic acid (red) or citric acid (green) into pre-equilibrated  $[C_2mim][NTf_2]$  containing CMPO ( $c(\text{CMPO}) = 0.5, 1, 5 \text{ mmol.dm}^{-3}$ ).

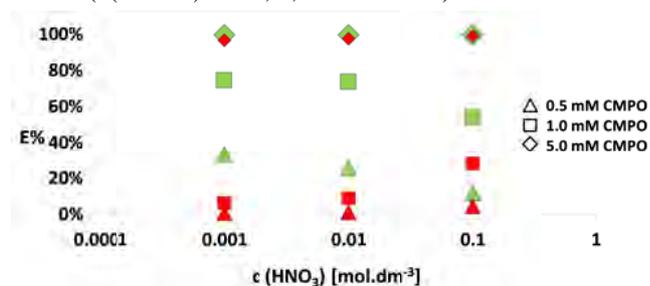


Fig. 2. Solvent extraction of  $^{152}\text{Eu}$  from  $HNO_3$  solutions ( $c(HNO_3) = 10^{-3}, 10^{-2}, 10^{-1} \text{ mol.dm}^{-3}$ ) containing oxalic acid (red) or citric acid (green) into pre-equilibrated  $[C_4mim][NTf_2]$  containing CMPO ( $c(\text{CMPO}) = 0.5, 1, 5 \text{ mmol.dm}^{-3}$ ).

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# SCREENING OF CyMe<sub>4</sub>-BTBP LIGANDS MODIFIED BY SUBSTITUTION OF H WITH NO<sub>2</sub> OR Br FOR ACTINIDE AND LANTHANIDE SEPARATION IN NUCLEAR WASTE TREATMENT

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## INTRODUCTION

Effects of nitro/bromo group substitution at the 4-position of pyridine ring of CyMe<sub>4</sub>-BTBP have been studied with regard to the extraction of Am(III) from Eu(III) from 0.1 - 3 M HNO<sub>3</sub>. Similar to CyMe<sub>4</sub>-BTBP, a highly efficient ( $D_{Am} > 10$  at 3 M HNO<sub>3</sub>) and selective ( $SF_{Am/Eu} > 100$  at 3 M HNO<sub>3</sub>) extraction was observed for NO<sub>2</sub>-CyMe<sub>4</sub>-BTBP and Br-CyMe<sub>4</sub>-BTBP in 1-octanol, however even in the absence of a phase-transfer agent.

## EXPERIMENTAL

Solvent extraction experiments were carried out to determine the ability of NO<sub>2</sub>-CyMe<sub>4</sub>-BTBP and Br-CyMe<sub>4</sub>-BTBP to extract Am(III) and Eu(III). Solutions of both extraction compounds in 1-octanol (0.03 M) were contacted (200 min) with nitric acid solutions (0.1 - 3 M) spiked with <sup>241</sup>Am and <sup>152</sup>Eu radiotracers. The structures of CyMe<sub>4</sub>-BTBP derivatives are shown in Fig. 1.

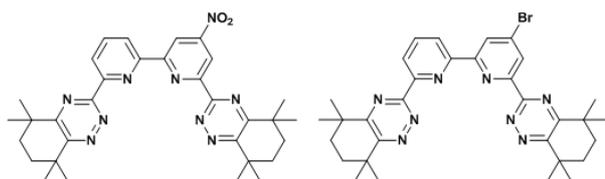


Fig. 1. Structural formulae of NO<sub>2</sub>-CyMe<sub>4</sub>-BTBP (left) and Br-CyMe<sub>4</sub>-BTBP (right).

## RESULTS

Quite expectedly, both ligands showed higher solubility than CyMe<sub>4</sub>-BTBP in both 1-octanol (> 170 mM) and cyclohexanone (> 230 mM), because nonsymmetrical ligands possess a far higher solubility than symmetrical due to its higher entropy of dissolution [1].

The distribution ratios for Am(III) and Eu(III) and the separation factors for Am(III) over Eu(III) for NO<sub>2</sub>-CyMe<sub>4</sub>-BTBP in 1-octanol as a function of nitric acid concentration are shown in Fig. 2.

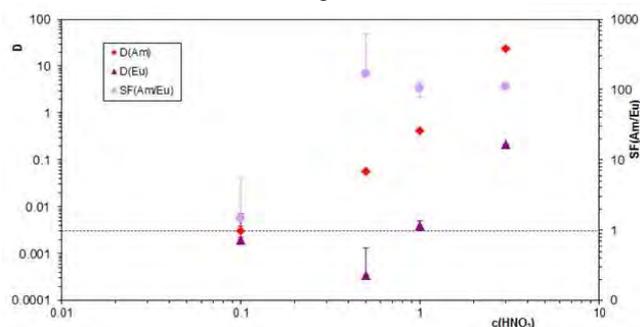


Fig. 2. Extraction of Am(III) and Eu(III) by NO<sub>2</sub>-CyMe<sub>4</sub>-BTBP in 1-octanol as a function of nitric acid concentration.

The highest  $D_{Am}$  value observed was  $28 \pm 3$  at 3 M HNO<sub>3</sub> and the highest separation factor obtained was  $124 \pm 12$  at 3 M HNO<sub>3</sub>. The  $D_{Eu}$  values remained less than 0.3 over most HNO<sub>3</sub> concentrations. The  $D$  values for both Am(III) and Eu(III) increased with increasing nitric acid concentration and this trend is also observed with CyMe<sub>4</sub>-BTBP and other BTBPs [2].

The extraction of Am(III) and Eu(III) from nitric acid by Br-CyMe<sub>4</sub>-BTBP in 1-octanol is shown in Fig. 3. The  $D$  values for Am(III) and Eu(III) increased with increasing nitric acid concentration in the aqueous phase resulting in a maximum separation factor of  $112 \pm 11$  at 3 M HNO<sub>3</sub>.

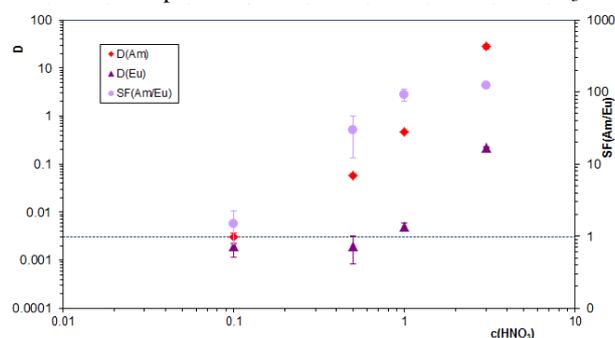


Fig. 3. Extraction of Am(III) and Eu(III) by Br-CyMe<sub>4</sub>-BTBP in 1-octanol as a function of nitric acid concentration.

In summary, extraction of Am(III) and Eu(III) from HNO<sub>3</sub> by the two new BTBP ligands NO<sub>2</sub>-CyMe<sub>4</sub>-BTBP and Br-CyMe<sub>4</sub>-BTBP was described. Compared to CyMe<sub>4</sub>-BTBP, a better solubility in 1-octanol and cyclohexanone was observed. The distribution ratios and separation factors for Am(III) over Eu(III) obtained without using a phase transfer agent for new derivatives were similar to that observed for the non-substituted ligands with use of a phase transfer agent.

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# COMPARING THE EXTRACTION OF Am(III), Cm(III) AND Eu(III) BY CyMe<sub>4</sub>-BTPHEN-FUNCTIONALIZED SiO<sub>2</sub> AND ZrO<sub>2</sub>-COATED MAGNETIC NANOPARTICLES

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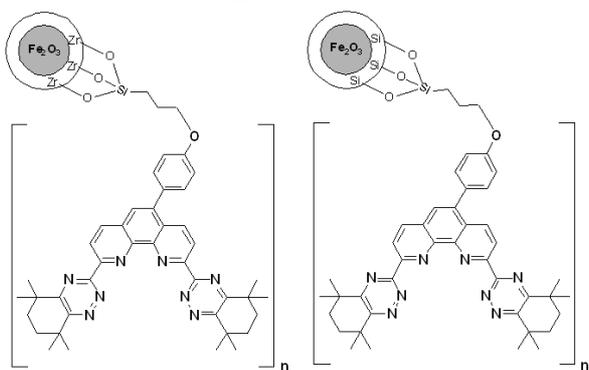
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## INTRODUCTION

We report the extraction properties of CyMe<sub>4</sub>-BTPHEN-functionalized zirconia-coated (ZrO<sub>2</sub>) maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) magnetic nanoparticles (MNPs) and their ability to extract Am(III) from Eu(III) and Am(III) from Cm(III) in a range of HNO<sub>3</sub> concentrations (0.001 – 4 M). Their extraction behavior is compared to our previously tested model based on silica-coated (SiO<sub>2</sub>) MNPs [1]. Extraction of Am(III) and Eu(III) is reported, but little or no selectivity can be seen between Am(III) and Cm(III) at concentrations of 4 M HNO<sub>3</sub>.

## EXPERIMENTAL

A new immobilised CyMe<sub>4</sub>-BTPHEN was tested for its ability to catch Am(III), Eu(III) and Cm(III) from HNO<sub>3</sub> solutions by the method of solid-liquid extraction. Its structure is shown in Fig. 1.



**Fig. 1.** Structure of CyMe<sub>4</sub>-BTPHEN-functionalized ZrO<sub>2</sub>-MNPs (left) and previously tested CyMe<sub>4</sub>-BTPHEN-functionalized SiO<sub>2</sub>-MNPs.

Aqueous solutions were spiked by tracers of Am(III), Eu(III) and Cm(III) and 600  $\mu$ l of spiked aqueous phase was added to 34 mg of the MNPs. Suspension was sonicating for 10 minutes, followed by shaking for 90 minutes and centrifuging for 10 minutes. The corresponding V/m ratio was 56 mL/g.

## RESULTS

The extraction results showed good weight distribution ratios for both Am(III) ( $D_w$ Am =  $142 \pm 4$ ) and Eu(III) ( $D_w$ Eu =  $9.7 \pm 4.2$ ) at 0.001 M HNO<sub>3</sub> with a separation factor of  $SF_{Am/Eu} = 14.7 \pm 1.4$  (Table 1). However, these values are much lower than those obtained for the same ligand covalently bound in the same manner to SiO<sub>2</sub>-MNPs ( $D_w$ Am =  $1169 \pm 79$  and  $D_w$ Eu =  $701 \pm 32$ ).

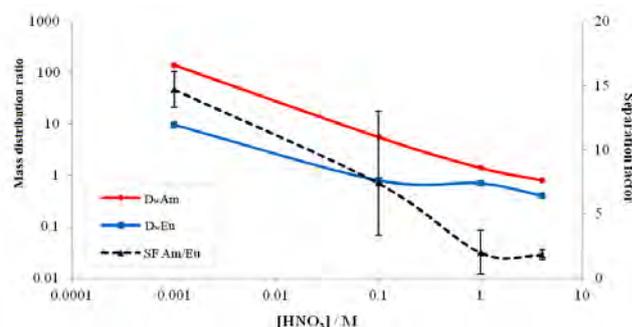
Increasing HNO<sub>3</sub> concentration to 0.1 M showed a dramatic decrease in both Am(III) extraction ( $D_w$ Am =  $5.6 \pm 1.0$ ), and Eu(III) extraction ( $D_w$ Eu =  $0.8 \pm 0.1$ ) giving a separation factor of  $SF_{Am/Eu} = 7.4 \pm 7.5$ . In the case of the CyMe<sub>4</sub>-BTPHEN-functionalized SiO<sub>2</sub>-MNPs, however, an increase

in the extraction of Am(III) at 0.1 M HNO<sub>3</sub> was reported  $D_w$ Am =  $1857 \pm 154$  whilst Eu(III) extraction decreased to  $D_w$ Eu =  $101.1 \pm 2.3$  giving a  $SF_{Am/Eu} = 18.4 \pm 1.6$ .

**Tab. 2.** Extraction of Am(III) and Eu(III) by CyMe<sub>4</sub>-BTPHEN ZrO<sub>2</sub>-MNPs as a function of nitric acid concentration

[HNO <sub>3</sub> ]	$D_w$ Am	$D_w$ Eu	$SF_{Am/Eu}$
0.001	$142 \pm 4.0$	$9.7 \pm 4.2$	$14.7 \pm 1.4$
0.1	$5.6 \pm 1.0$	$0.8 \pm 1.0$	$7.4 \pm 7.5$
1	$1.4 \pm 0.9$	$0.7 \pm 0.9$	$2.0 \pm 1.7$
4	$0.8 \pm 0.9$	$0.4 \pm 0.9$	$1.8 \pm 0.4$

A linear decrease in both Am(III) and Eu(III) extraction was observed upon increasing HNO<sub>3</sub> concentration to both 1 M and 4 M. Although  $D_w$ Am remained greater than  $D_w$ Eu in both cases, the selectivity was lost at 4 M HNO<sub>3</sub> solution with  $D_w$ Am =  $0.8 \pm 0.9$  and  $D_w$ Eu =  $0.4 \pm 0.9$  resulting in  $SF_{Am/Eu} = 1.8 \pm 0.4$  (Fig. 2). This is significantly lower than the results obtained for ligand on SiO<sub>2</sub> at 4 M HNO<sub>3</sub> where a  $SF_{Am/Eu} \approx 1700 \pm 300$  was obtained.



**Fig. 2.** Extraction of Am(III) and Eu(III) by CyMe<sub>4</sub>-BTPHEN ZrO<sub>2</sub>-MNPs as a function of nitric acid concentration.

Reported MNPs co-extracted both Am(III) and Eu(III) from solutions up to 4 M HNO<sub>3</sub>, with lower selectivity ( $SF_{Am/Eu} = 1.8$ ) when compared to that previously for reported SiO<sub>2</sub>-coated MNPs ( $SF_{Am/Eu} \approx 1300$ ). Extraction of both actinides Am(III) and Cm(III) is also noted, again without any selectivity; whereas previously reported SiO<sub>2</sub>-coated MNPs exhibited at least some selectivity for Am(III) over Cm(III) ( $SF_{Am/Cm} = 2.2$  at 4 M HNO<sub>3</sub>).

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# COLUMN STUDIES FOR THE SEPARATION OF $^{99m}\text{Tc}$ USING ACTIVATED CARBON

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## INTRODUCTION

Activated carbon (AC) is an organic material with a large surface area and network of pores where adsorption takes place. In this study, AC has been used for investigation, as a potential candidate for laboratory separation process for technetium. The  $\text{TcO}_4^-$  sorption mechanism on AC may differ according to the functional group. It involves ion-exchange reaction between AC surface and  $\text{TcO}_4^-$  anions, chemical bond or reduction of  $\text{TcO}_4^-$  on the surface [1-4].

## EXPERIMENTAL

50 g of fibrous cellulose was heated at 700 °C for 1 h in a closed vessel. The internal volume of the column used (ID=10 mm, height 15 mm) allowed 0.2 g of AC. The columns were placed in a NaI(Tl) detector. 21 mL of each solution was prepared by labelling with  $^{99m}\text{TcO}_4^-$ . 1 mL sample was taken for counting of original radioactivity ( $A_0$ ) and 20 mL of aqueous solution of  $\text{TcO}_4^-$  (pH 2) was passed through the column and activity was measured. From the eluate, 1 mL sample was withdrawn for obtaining the percentage of adsorption.  $\text{TcO}_4^-$  was eluted with different stripping solutions. From the eluates, 1 mL sample was always withdrawn for counting of radioactivity and desorption percentage calculation. Adsorption and desorption processes were measured with NaI(Tl) gamma counter at the same time. From the volume activity and volume of eluate from adsorption and desorption experiments, adsorption and desorption yields were calculated. The count rates were normalized to  $A_0$ .

## RESULTS

Adsorption and stripping of  $\text{TcO}_4^-$  for sample A are shown on Fig. 1. The X-axis corresponds to the experiment time, while the count rate on Y-axis is normalized to  $A_0$  for better clarity. Each streak corresponds to one experiment and zigzag shape of the streaks is caused by statistical character of radioactive decay. The measurements were monitored continuously with integration time of 5 s. From volume activity measurements of the eluate, yields of adsorption were calculated and were found to be nearly 100 % as can be seen from the straight line plateaus of the adsorption curves, typical for all figures presented in this paper concerning the adsorption experiments. The adsorption is quantitative as was confirmed by measuring of volume activity.

As is shown on Fig. 1, desorption decreases in the order  $1 \text{ mol}\cdot\text{dm}^{-3} \text{ NaClO}_4 > (\text{pretreated with } 10 \text{ mL of } 1 \text{ mol}\cdot\text{dm}^{-3} \text{ NaClO}_4) > 1 \text{ mol}\cdot\text{dm}^{-3} \text{ NaNO}_3 > 70 \text{ }^\circ\text{C } 0.1 \text{ mol}\cdot\text{dm}^{-3} \text{ NaClO}_4 \geq 0.1 \text{ mol}\cdot\text{dm}^{-3} \text{ NaClO}_4 > 0.1 \text{ mol}\cdot\text{dm}^{-3} \text{ NaNO}_3 > 0.01 \text{ mol}\cdot\text{dm}^{-3} \text{ NaClO}_4 > 0.01 \text{ mol}\cdot\text{dm}^{-3} \text{ NaNO}_3 > 0.01 \text{ mol}\cdot\text{dm}^{-3} \text{ EDTA} + 10 \text{ mg SnCl}_2 > \text{NaOH (pH 12)} > 1 \text{ \% NaCl} > 95 \text{ }^\circ\text{C dist. H}_2\text{O}$ . At the  $\text{NaClO}_4$  pretreatment, the column was conditioned with 10 mL of  $1 \text{ mol}\cdot\text{dm}^{-3} \text{ NaClO}_4$  (pH 2) before adsorption and subsequently the column was washed with the same solution. This treatment before the adsorption has no significant influence on the desorption. The  $\text{ClO}_4^-$  has a very similar structure with  $\text{TcO}_4^-$ , therefore its behaviour during the surface adsorption processes will be the same. The solutions of  $\text{NaNO}_3$  were chosen due to its second highest standard absolute molar enthalpy of hydration, which is  $-316 \text{ kJ}\cdot\text{mol}^{-1}$  (for  $\text{TcO}_4^-$   $-205 \text{ kJ}\cdot\text{mol}^{-1}$ ). In consideration with the resonance structure of  $\text{NO}_3^-$  it is possible that the surface configuration during the stripping of  $\text{TcO}_4^-$  will be as follows:  $\text{R}-\text{C}=\text{O}\cdots\text{H}^+ + \text{NO}_3^- \rightarrow \text{R}-\text{C}=\text{O}\cdots\text{H}\cdots\text{ONO}_2$ . The concentration of those ions plays also significant role during desorption processes of  $\text{TcO}_4^-$ . This work was supported by VEGA Project No. 1/0507/17.

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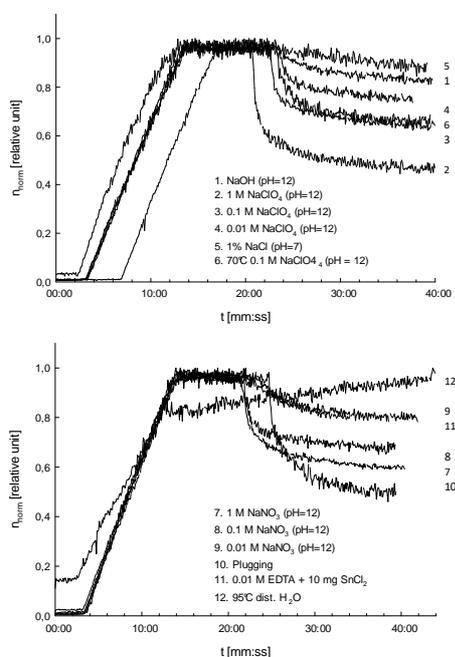


Fig. 1. Adsorption and desorption of  $\text{TcO}_4^-$  from activated carbon (flow rate = 2.4 BV/min)

# REDUCTIVE SEPARATION OF Tc-99

Pokorný M.; Čubová K.; Němec M.

## INTRODUCTION

The isotope  $^{99}\text{Tc}$  is generated in nuclear power plants with the fission yield of approximately 6% as a fission product of  $^{235}\text{U}$ . Significant activities of  $^{99}\text{Tc}$  were released to the environment from the fallout from nuclear weapons testing, nuclear power plant accidents, and nuclear fuel reprocessing plants such as Sellafield or La Hague. Due to the worldwide use of  $^{99\text{m}}\text{Tc}$  generators, some amounts are also released from nuclear medicine sources. Technetium main specie in wide range of conditions is pertechnetate  $\text{TcO}_4^-$ , which is characterized by a high mobility in the environment and therefore  $^{99}\text{Tc}$  belongs among frequently monitored radionuclides in the environment. Tc-99 is a pure beta emitter, for radiometric measurement its beta emission with a maximum energy of 294 keV is usually detected using gas ionization detector or more often liquid scintillation counting (LSC).

Several widely-used methods exist for the separation of technetium. Their application follows chemistry and composition of the sample matrix. The procedures always consist of several steps because technetium should be fully separated from any interfering radionuclides [1-3]. However, in the final step of the procedures, technetium is usually eluted with 8-10M  $\text{HNO}_3$  from an extraction-chromatographic material based mainly on Aliquat336. In such case, determination of  $^{99}\text{Tc}$  by means of widely used LSC is problematic because of quenching and subsequent decrease in detection efficiency. Several steps including evaporation of eluate and dissolution of the residue in a diluted acid are often applied. Those steps are time consuming and decrease the yield of the separation. Also, concentrated  $\text{HNO}_3$  can damage the matrix of the extraction-chromatographic material.

The main aim of this work was to find a solution containing reducing and complexing agents that would elute technetium from the extraction-chromatographic material by reduction to lower oxidation states and stabilize it in proper complex. Chemical system selected should also show minimum quenching in the radiometric step and it also should not damage inert matrix of the sorbent. Reduction of  $\text{Tc(VII)}$  is a required step as  $\text{TcO}_4^-$  is quite strongly bound to Aliquat336 and it does not form suitable complexes; on the other hand complexation of the formed reduced low-valence technetium species is necessary to prevent their hydrolysis. This work is also related to the separation of technetium from decontamination solutions and waste streams of the nuclear power plants and the reductive method was developed to support determination of  $^{99}\text{Tc}$  when testing its extraction to the ionic liquids from the real liquid radioactive wastes.

## EXPERIMENTAL

Extraction chromatography followed by LSC measurement was used in this work. Elution of  $^{99}\text{Tc}$  by means of solutions containing reducing and complexing agent

in a proper solvent from extraction-chromatographic material prepared by impregnation of Aliquat336 onto a matrix of polyacrylonitrile (PAN-A336) [4] was studied. Stannous ions, hydrazine, ascorbic acid and sodium dithionite were tested as reducing agents in combination with citric acid, trisodium citrate, diammonium tartrate and potassium sodium tartrate as complexing agents. Both the bench and dynamic sorption experiments were performed. Hidex 300SL liquid scintillation counter was used for the measurement.

## RESULTS

The most effective solutions consisted of 15-25 mg of  $\text{SnCl}_2$  and 100-150 mg of  $\text{H}_3\text{Cit}$  per 10 mL of 0.1M  $\text{HNO}_3$ . As for the batch experiments – by the application of  $\text{SnCl}_2$  in the  $\text{HNO}_3$  and citric acid solution  $82.8 \pm 1.6\%$  of desorption was achieved. In dynamic experiments, almost 92% of  $^{99}\text{Tc}$  was eluted with solution containing higher concentration of  $\text{SnCl}_2$  in the  $\text{HNO}_3$  and citric acid solution. From the results obtained it can be concluded that combination of reduction and complexing agent is a promising way for elution of  $^{99}\text{Tc}$  from Aliquat336-based solid extractants.

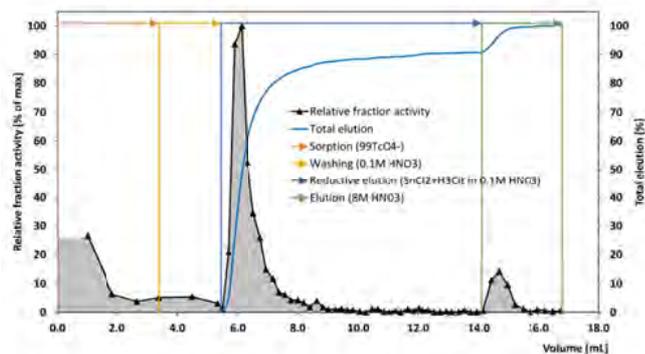


Fig. 1. Elution of  $^{99}\text{Tc}$  from PAN-A336 column (5 BV.h<sup>-1</sup>, mixed solution of  $\text{SnCl}_2 + \text{H}_3\text{Cit}$  in 0.1M  $\text{HNO}_3$ )

Nevertheless, the results show that some of technetium is still remaining in the column and 8M  $\text{HNO}_3$  is needed to fully elute it. Such behaviour may be caused by complex chemistry of technetium at lower valence states and additional research is needed to find more suitable elution solution.

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# THE EFFECT OF COUNTING CONDITIONS ON PURE BETA EMITTER DETERMINATION BY CHERENKOV COUNTING

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## INTRODUCTION

In the past few decades, the Cherenkov counting technique for high energetic beta emitters has drawn considerable attention due to several advantages over liquid scintillation counting (LSC). Its widespread application is primarily due to simplicity of sample preparation [1]. Most frequent application of Cherenkov counting is the analysis of <sup>89</sup>Sr and <sup>90</sup>Sr via <sup>90</sup>Y as their determination is a part of routine environmental radiological monitoring programs. Nowadays Cherenkov counting can be successfully used in quantitative determination of isotopes of interest in wide range of activities by using modern commercial LSCs.

As quantitative determination requires accurate and precise determination of the detection efficiency, the first goal was to examine dependence of Cherenkov counting efficiency for several pure beta emitters on key parameters having crucial influence (type of solvent, volume, colour, etc.).

The first commercially available TDCR (triple-to-double coincidence ratio) instrument Hidex 300SL utilizes TDCR technique for obtaining counting efficiency without any external or internal standard sources [2]. However, only few papers were published on using TDCR for quantitative measurements using Cherenkov counting. Therefore, the second goal was to show possibility of using TDCR Cherenkov counting for routine quantitative determination of high energetic beta emitters. In addition, Cherenkov counting properties of commercially available instruments with one-, two- and three photomultiplier tubes (PMT) were compared and their main benefits were highlighted.

In general, the purpose of this work [3] was to show how experimental conditions influence the measured count rates or detection efficiencies, and suggest possible applications in analysis of radionuclides.

## EXPERIMENTAL

Measurements were carried out in 20 mL polyethylene plastic and low-potassium borosilicate glass scintillation vials, and 5 mL polyethylene plastic minivials. For Cherenkov efficiency determination, beta emitters with different energy of electrons – <sup>36</sup>Cl, <sup>89</sup>Sr, <sup>32</sup>P and <sup>90</sup>Sr/<sup>90</sup>Y – were used in different counting conditions.

Minivials with radionuclide solutions were inserted into empty larger glass vials and counted. In such arrangement, contribution of various surroundings to total Cherenkov radiation was investigated [3]. In addition, effects of the sample volume, type of solvent and various instrumental setup were investigated using three instruments - Triathler Multilabel Counter (Hidex, Oy, Finland; 1 PMT), Tri-Carb 3180 TR/SL (Perkin Elmer, Waltham, MA, USA; 2 PMT), and Hidex 300 SL (Hidex, Oy, Finland; 3 PMT).

## RESULTS

The obtained results show that the Cherenkov counting efficiency increases with the sample volume on all the tested instruments and reaches the maximum value between 8 ml and 16 mL. The highest detection

efficiencies for all the tested radionuclides, solvent and geometries were achieved on the Hidex 300 SL, with maximum ( $0.7656 \pm 0.0032$ ) for <sup>90</sup>Sr/<sup>90</sup>Y samples in methanol. The TDCR Cherenkov efficiency in glass vials is lower than in plastic vials and the discrepancy between the true and TDCR Cherenkov efficiencies for <sup>90</sup>Y is above 14 % in glass, while it is below 5 % in plastic vials.

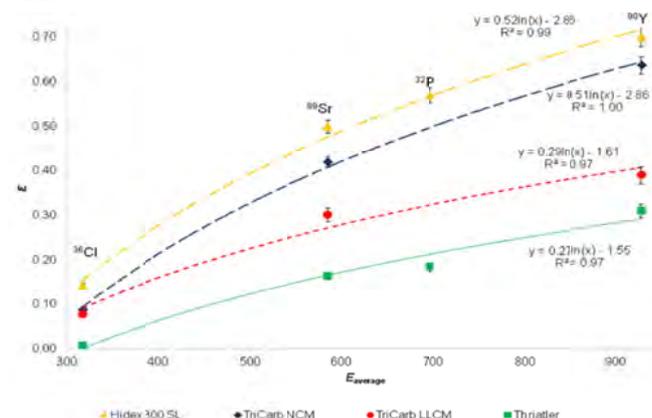


Fig. 1. Cherenkov detection efficiency of radionuclides ( $A \sim 100$  Bq) as a function of their  $E_{\text{average}}$ .

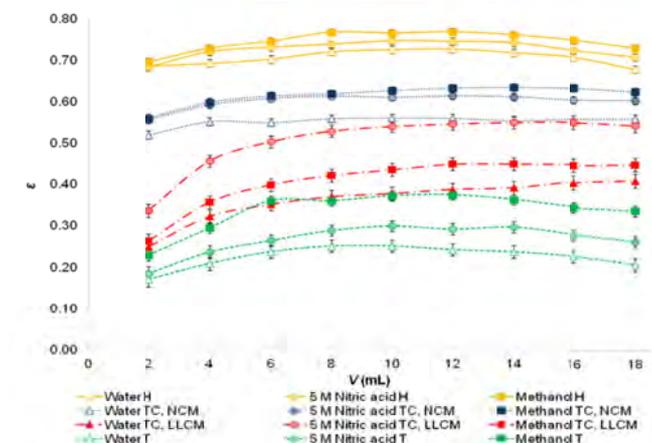


Fig. 2. Dependence of Cherenkov detection efficiency of <sup>90</sup>Sr/<sup>90</sup>Y ( $A \sim 60$  Bq) on volume of different solvents in glass vials. Hidex 300 SL (H), Tri-Carb (TC) in LLCM and NCM and Triathler (T) were used.

Based on the overall results obtained it can be concluded that similarly to standard Cherenkov counting the TDCR Cherenkov counting is well suited for routine quantitative determination of low activities of high energetic beta emitters, such as e.g. <sup>90</sup>Sr/<sup>90</sup>Y.

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# RADIATION INDUCED DECHLORINATION OF SOME CHLORINATED HYDROCARBONS IN AQUEOUS SUSPENSIONS OF VARIOUS SOLID PARTICLES\*

Můčka, V.; Buňata, M.; Čuba, V.; Silber, R.; Juha, L.<sup>1</sup>

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## INTRODUCTION

Halogenated organic compounds may cause, besides many other damages, modifications of the function of impregnating substances in the cell walls, disorders in a cell-division leading to the cancer development [1]. That is a reason why various alternative and effective methods for their destruction are needed [2]. A special attention has been devoted to solid modifiers of radiation-induced degradation of chlorinated hydrocarbons (CHC) such as Cu<sub>2</sub>O, PbO or NiO oxides or zeolites. The aim of this work was to examine the impact of both cupric oxide (CuO) and active carbon (AC) on the dechlorination of trichloroethylene (TCE) and tetrachloroethylene (PCE) caused by irradiation of the system with accelerated electrons.

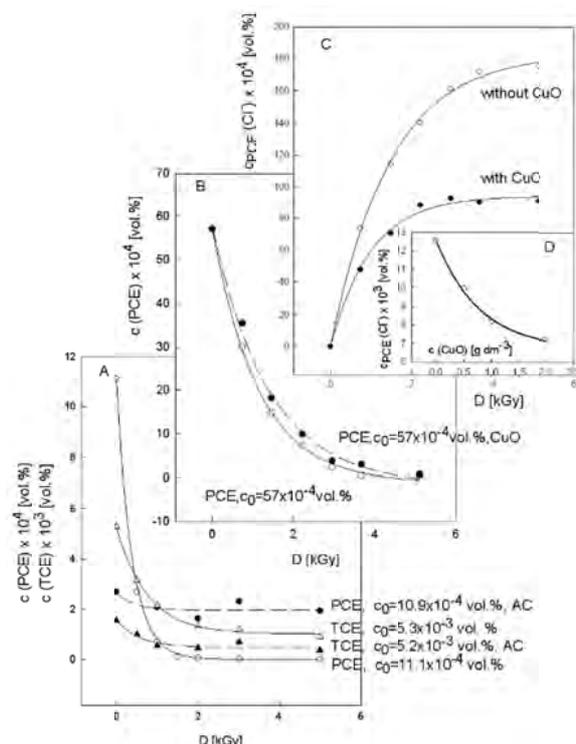
## EXPERIMENTAL

Aqueous solutions of TCE and PCE with concentrations ranging from  $1.6 \cdot 10^{-4}$  to  $405 \cdot 10^{-4}$  vol. % and from  $2.7 \cdot 10^{-4}$  to  $94 \cdot 10^{-4}$  vol. %, respectively, were irradiated with accelerated electrons ( $E = 4.5$  MeV, dose rate  $D^* 1.5$  kGy s<sup>-1</sup> and doses  $D$  from 0.5 to 5.0 kGy) with different amounts of active carbon (AC) or cupric oxide (CuO). The concentrations of solid modifiers ranged from 0.1 to 5.0 g dm<sup>-3</sup>. The concentrations of chloride ions and hydrocarbons were determined electrochemically and by gas chromatography, respectively. Following quantities have been calculated: *the degrees of dechlorination*  $\alpha(\text{CHC})$  (degradation) or  $\alpha(\text{Cl}^-)$  (mineralization); *the relative radiation chemical yields*  $G(\text{-CHC})$  or  $G(\text{Cl}^-)$ ; and *the reaction order*, which was evaluated according to the earlier published method [2].

## RESULTS

The obtained results gave evidence that the radiation-induced dechlorination of both TCE and PCE hydrocarbons proceeds regardless of the presence of the modifiers. It was also evident that both hydrocarbons under study were significantly adsorbed on the active carbon, whereas no adsorption was observed on the CuO. The CuO oxide was found to be inhibiting the mineralization of the hydrocarbon (Fig. 1). The AC modifier caused a large decrease in the degree of dechlorination of PCE, whereas only a slight decrease was found in the case of dechlorination of TCE. These differences may be connected with a different adsorption ability of the two hydrocarbons. The shape of the dependence of degree of dechlorination on the dose implies that the radiation-induced dechlorination may be affected both by recombination reactions between the products of radiation reactions and by the solvent presented in irradiated system. The evaluation of the efficiency of dechlorination by means of the radiation chemical yields of reactions showed that both modifiers under study decrease the efficiency of both degradation and mineralization of hydrocarbons, while the mineralization of the PCE proceeds much more effectively (by a factor 1.7) than that of the TCE.

The efficiency of mineralization increases with the initial concentration of the hydrocarbon. The measured values of radiation chemical yields enable us to estimate the energies needed for a separation of one Cl<sup>-</sup> ion from the molecule of hydrocarbon. This value is about 67 and 40 eV for TCE and PCE molecules, respectively. No influence on the reaction order of radiation induced dechlorination was found in either of both modifiers under study.



**Fig. 1.** A: Dependence of concentrations of TCE and PCE both with and without active carbon (0.5 g dm<sup>-3</sup>) on the dose; B: As in A, but for the PCE both with and without cupric oxide (2.0 g dm<sup>-3</sup>); C: As in B but for the Cl<sup>-</sup> ions from dechlorination of PCE (initial concentration of  $5.7 \cdot 10^{-3}$  vol. %); D: Dependence of  $\alpha(\text{Cl}^-)$  on the concentration of the CuO modifier for PCE with initial concentration of  $5.6 \cdot 10^{-3}$  vol. % irradiated with the dose of 5 kGy

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\*Full paper in [3].

# DETERMINATION OF THE SURVIVAL OF YEAST AND BACTERIA UNDER THE INFLUENCE OF GAMMA RADIATION IN PRESENCE OF SOME SCAVENGERS OF $\cdot\text{OH}$ RADICALS\*

Múčka, V.; Červenák, J.; Čuba, V.; Bláha, P.

## INTRODUCTION

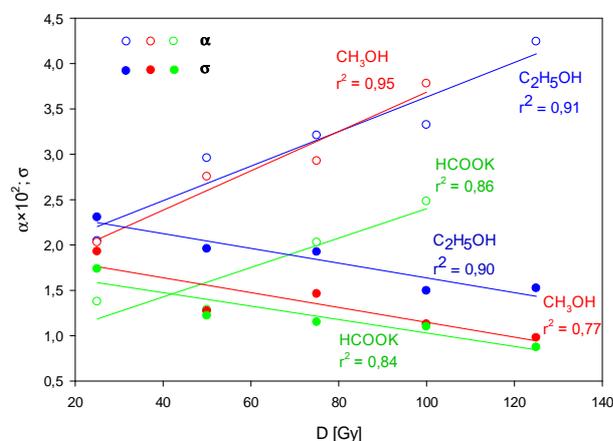
The extent in which the scavenging of  $\cdot\text{OH}$  radicals participates on the cell protection may be expressed by the slopes  $k$  or  $h$  of two different dependences: The first one is the linear dependence  $\sigma = \ln S_0 / \ln S_S = f(Q)$  and the second one is the dependence  $\alpha = (S_S - S_0) / S_0 = f(Q)$ , where  $S_0$  and  $S_S$  are the fractions of surviving cells after irradiation without and with the scavenger, respectively and  $Q$  represents the scavenging efficiency of the scavenger [1, 2]. The first aim of this work was to mutually compare these two quantities  $h$  and  $k$  and the second aim was to find their dose dependences.

## EXPERIMENTAL

Two different microorganisms were used in the study: the yeast cells *Saccharomyces cerevisiae* and the *Escherichia coli* bacteria taken from a stationary state of the 3-5 days old culture. The cells were introduced into the isotonic salt solutions containing various concentrations of  $\cdot\text{OH}$  radicals scavengers (ethanol, methanol or potassium formate). The suspension was irradiated with gamma radiation ( $^{60}\text{Co}$ ) in polypropylene ampoules so that the doses ranged from 20 to 130 Gy at a dose rate of  $60 \text{ Gy h}^{-1}$ . The gamma doses were determined using the Fricke dosimeter. After a suitable dilution, aliquots of the irradiated and non-irradiated cell suspensions were plated on the complete nutrient agar. Incubation at  $30^\circ \text{C}$  for 4-5 days gave rise to colonies, which were then counted. Every measurement was repeated three times and the mean value of the counted colonies was taken into account

## RESULTS

Both abovementioned quantities  $\alpha$  and  $\sigma$  increase linearly with increasing scavenging efficiency of all scavengers under various irradiation conditions for both yeast *Saccharomyces cerevisiae* and bacteria *E. Coli*. The slopes of both dependences are unique for each scavenger. Similarly to the  $k$  quantity, also the  $h$  values are several times higher for bacteria than for the yeast. On the other hand, the following properties are different: Unlike the  $k$  values, the  $h$  quantity increases with the dose. Therefore, the characterization of the scavengers by the  $\alpha$  values should be performed at the same dose. The  $h$  values for the yeast are about 4.6 times higher than are the  $k$  values and, conversely, the  $k$  values are about twice as higher as the  $h$  values for bacteria. The  $\alpha$  values increase with the dose, whereas the  $\sigma$  values decrease (Fig. 1). Therefore, the use of the  $\sigma$  and  $\alpha$  quantity should be advantageous for low and high doses, respectively. The sensitivity of the  $\alpha$  value on the changes in the dose is about fifty times smaller than is the sensitivity of the  $\sigma$  values. Therefore, the use of the  $\sigma$  values and then the  $k$  values is, in general, more advantageous for characterization of the protection of cells by the scavengers of  $\cdot\text{OH}$  radicals.



**Fig. 1.** Dependences of the differences  $\alpha$  and the ratios  $\sigma$  on the dose  $D$  for the bacteria *Escherichia coli* in the presence of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), methanol ( $\text{CH}_3\text{OH}$ ) and potassium formate ( $\text{HCOOK}$ ) as scavengers at the  $\gamma$ -dose rate  $60 \text{ Gy h}^{-1}$  and the scavenging efficiency  $3 \cdot 10^9 \text{ s}^{-1}$  ( $r^2$  – determination factor)

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This research has been supported by the Czech Science Foundation grant no. GA13-28721S.

\*Full paper in [3].

## INTRODUCTION

This report is focused on the pelletizing of photochemically prepared  $\text{UO}_2$ ,  $\text{ThO}_2$  and  $(\text{Th,U})\text{O}_2$  powders. Preparation of nano-particles of  $\text{UO}_2$ ,  $\text{ThO}_2$  and  $(\text{Th,U})\text{O}_2$  by photochemical method using mercury UV lamps as the radiation source has been reported recently [1,2]. Amorphous solid precursors formed under the irradiation were subsequently heat treated between 300 and 550 °C to convert them to nano-crystalline oxides. Photochemical methods typically produce nano-sized powder with high specific surface area. Such kind of materials can be usually sintered at lower temperature when compared to materials with larger particle size. The method produces solid precursors that are nitrogen and carbon free, thus allowing direct heat treatment in reducing atmosphere without pre-treatment in air.

## EXPERIMENTAL

Nano-crystalline  $\text{UO}_2/\text{ThO}_2$  powders were prepared following the previously described procedure [1].

Powder  $\text{UO}_2$  and/or  $\text{ThO}_2$  nanoparticles were pressed into pellets without addition of any lubricant or additives to the oxide powder. The powders have been pressed by a manual laboratory press, using stearic acid as die-wall lubricant (e.g. by pressing the stearic acid powder into pellets). The powders were compacted at the pressure of 500 MPa for 30 min into a pellet of 10 mm in diameter and 1 mm in theoretical height.

The prepared green pellets without any further treatment were additionally characterized using porosimetry (immersion into chloroform) and scanning electron microscopy (SEM). SEM images were taken from the unpolished surface of the green pellet. The geometric densities of the pellets were obtained by weighing and by measuring the pellet diameter and height with a digital calliper. Pellets were subsequently sintered at relatively low temperatures up to 1300 °C (temperature ramp 2 °C min<sup>-1</sup>) for 3 hours under Ar:H<sub>2</sub> (20:1) mixture ( $\text{UO}_2$  and  $(\text{U,Th})\text{O}_2$ ) or 1600 °C (ramp 2 °C min<sup>-1</sup>) for 6 hours in ambient air ( $\text{ThO}_2$ ). Sintered pellets were consequently characterized in the exactly same manner as described for green pellets. Moreover, SEM images of polished sintered pellets were taken.



**Fig. 1.** Sintered pellets; pellets are approximately 8.5 mm in diameter and 1.5 mm in height. Left:  $\text{UO}_2$  sintered at 1300 °C; middle:  $\text{ThO}_2$  sintered at 1600 °C and right:  $(\text{Th,U})\text{O}_2$  sintered at 1300 °C [2]

## RESULTS

The obtained nano-powders are carbon free, allowing direct heat treatment in reducing atmosphere without pre-treatment in air. The EXAFS analyses of the amorphous precursors indicate that the Th-containing precursors probably contain  $\text{ThO}_2$  (direct formation of  $\text{ThO}_2$ ), whereas the U-containing precursors are a mixture of uranium(IV) and uranium(VI) compounds.

No binder was used during the pelletizing and comparatively low sintering temperature was sufficient for  $\text{UO}_2$  (and  $(\text{Th,U})\text{O}_2$ ) pellets preparation.

The densities of green pellets reached values from 37 to 54 % theoretical density (TD), sintered pellets reached values from 91 % to 97 % TD.

The prepared green pellets are highly durable. Based on the obtained results, the photochemical method offers promising alternative route for preparation of both single and mixed oxide fuel pellets.

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# PHOTOCHEMICAL PILOT PLANT FOR LARGE-SCALE PREPARATION OF OXIDE NANOMATERIALS

Čuba, V.; Procházková, L.; Bárta, J.; Pavelková, T.

## OVERVIEW

The pilot plant, which was constructed at the Department of Nuclear Chemistry, presents a technical solution for the manufacture of metals or metals oxides in the form of nanopowders from aqueous or organic solutions via irradiation of photosensitive metal compounds. The irradiated solutions often contain scavengers of  $\cdot\text{OH}$  radicals. The apparatus consists of a photoreactor with UV irradiation sources and a device for concentrating and separation of solid nanoparticles (Fig. 1). The device for water purification is also part of the system.

## DESCRIPTION OF THE TECHNOLOGY

In principle, the technical solution relies on a circulating sedimentation tank attached to the output of photoreactor with the irradiation sources. Both sedimentation tank and photoreactor are interconnected in a circuit for circulation of the irradiated solution. The circulation is ensured by a peristaltic pump. A reservoir for water or fresh solution for irradiation is attached via another valve. The circulation, product separation and addition of fresh solution ensure that the plant can be run in continual operation mode.

To prevent temperature increase and to regulate temperature during irradiation, the photoreactor itself is a double-surface glass vessel for easy cooling using water coolant in the outer layer. Therefore, no undesired heating of irradiated solution occurs during operation.

The irradiation source consists of a set of submersible low-pressure mercury UV lamps, whose length covers roughly the upper two thirds of the photoreactor. Inflow of circulated liquid is also placed in the upper part, whereas the outflow is placed at the bottom. A separate valve for influx of fresh solution is also placed at the bottom of the photoreactor. Irradiated liquid with nanoparticles in the photoreactor is continually stirred and circulated into the sedimentation tank. Circulation of the non-sedimented part of nanoparticles in the irradiated solution from the sedimentation tank back to the photoreactor is crucial for the continual operation.

The upper part of the photoreactor is sealed with a lid with holes for insertion of UV lamps into the solution. Continual irradiation of photosensitive compounds and metal salts soluble in water initiates the formation of metallic or metal oxide nanoparticles.

The sedimentation tank is equipped with a valve at its bottom for continual or semi-continual removal of the sedimented nanoparticles.

The reservoir vessel is also equipped with a lid and an intake valve for refilling with a fresh solution to be irradiated, pure water or cleaning solution. The refilling can be done in the continual mode as well.

The water purification apparatus consists of water filters, a reverse osmosis membrane, ionexes, pumps and a reservoir for deionized water. This setup ensures continual inflow of fresh pure water into the system when necessary.

All parts of the device are attached to a supporting construction. As a safety measure, a large plastic vessel is placed under the pilot plant in case of any damage to the photoreactor or sedimentation tank. It ensures that any leakage of the solution is captured. This convenient setup prevents any losses during the production as well as any damage to the surroundings due to the leakage of irradiated solution.

## ADVANTAGES OF THE PILOT PLANT

The pilot plant for photochemical preparation of nanoparticle metals or metal oxides has several advantages. The process itself is very simple, largely independent of temperature (which can also be controlled), a high level of interaction between individual components in precipitated solid phase can be expected and the yield of nanomaterials is close to 100% under optimized conditions. The prepared materials are of high purity and with relatively narrow size distribution of particles. The process is comparatively cheap and it allows for rather high production rates.

In several testing runs, the pilot plant successfully produced nanomaterials in very large amounts in the order of several hundreds of grams per batch. Their properties were found to be consistent with materials prepared using small-scale laboratory synthesis.

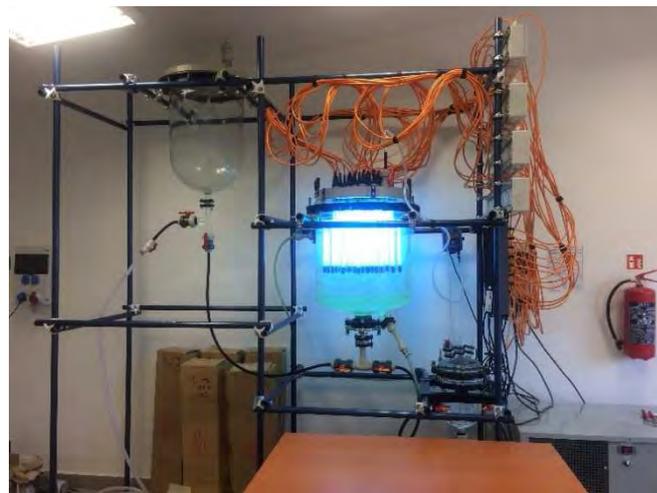


Fig. 1. Photochemical pilot plant.

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This research has been supported by the Ministry of Education, Youth and Sports of the Czech Republic, project no. CZ.1.05/3.1.00/14.0301.

# IRRADIATION METHODS OF NANOSILVER PREPARATION IN MICELLAR SYSTEMS

Zdychová, V.; Silber, R.

## INTRODUCTION

Nanosilver is a material useable in many scientific applications (optics, electronics, catalysis) due to its unique physical and chemical properties. Therefore, considerable attention is devoted to the methods of preparation of silver nanoparticles and to the studies of their properties. This work compares the silver nanoparticles preparation using ionizing radiation (fast electrons, 4.5 MeV) with synthesis using UV radiation.

## EXPERIMENTAL

**Sample preparation:** An aqueous solution of the desired surfactant was prepared at the desired concentration (2% Triton X-100 and either 0.1 or 0.2 mol/L silver nitrate) by continuously mixing the solution for about one hour. Samples were stored in the dark to shield them from the effects of UV light present in natural sunlight.

**Electron irradiation:** The prepared solution was transferred into 10 or 20 mL ampoules (aliquot volume 10 mL), which were sealed with parafilm. The ampoules were placed on a tray on the conveyor and irradiated with 4.5 MeV electrons from a linear electron accelerator, the doses ranging from 1 to 32 kGy.

**UV Irradiation:** For UV photolysis, UVH-1016-16 medium-pressure mercury discharge from UV Technik Meyer GmbH was used. The lamp emits photons in the range of 200-580 nm, where 70% of the intensity is within the 200-400 nm UV range. The output of the lamp can be regulated within the 140 to 400 W range. During irradiation, the mercury lamp was submerged into the solution (volume 2 L) in a photochemical glass reactor. Samples were characterized by UV/VIS spectroscopy (Fig. 1). The quantity of prepared nanosilver was determined potentiometrically – the decrease in the concentration of  $\text{Ag}^+$  ions was determined from the silver electrode potential.

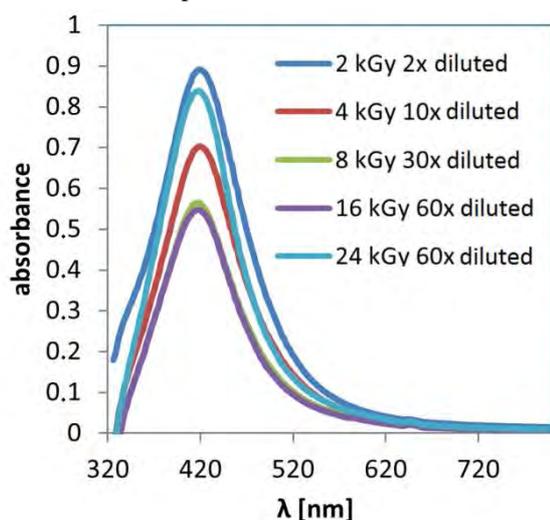


Fig. 1. Optical absorption spectra for a 0.2 mol/L  $\text{AgNO}_3$  sample irradiated at different doses

## RESULTS

The plot of absorbance at the wavelength of 420 nm versus the dose is shown in Fig. 2.

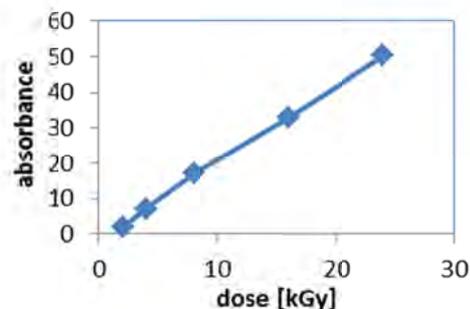


Fig. 2. Dependence of absorbance at 420 nm (multiplied by the dilution factor) on dose.

The comparison of production efficiency of the radiation induced nanosilver realized by accelerated electrons irradiation (characterized by dose) and by UV irradiation (characterized by irradiation time) is shown in Fig. 3 and Fig. 4.

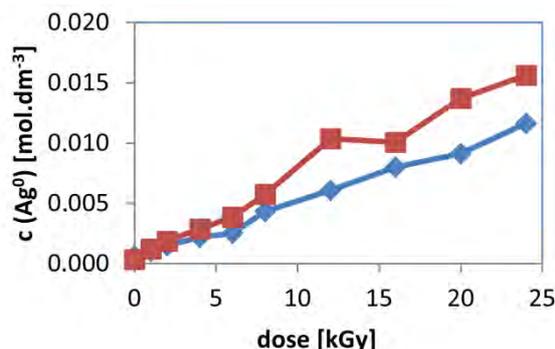


Fig. 3. Nanosilver concentration versus dose (initial concentrations of silver nitrate: 0.1 mol/L (blue points) and 0.2 mol/L (red points)) for electron irradiation

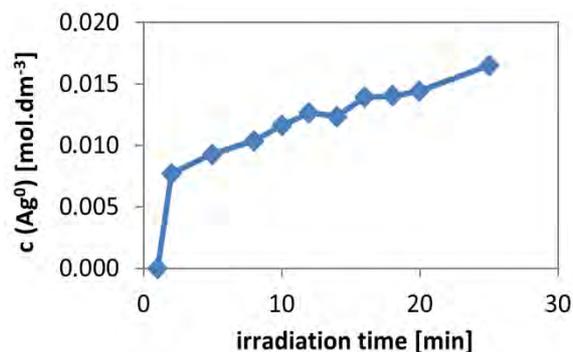


Fig. 4. Nanosilver concentration versus UV irradiation time (initial concentration of silver nitrate: 0.2 mol/L)

This work has been performed under the auspices of Ministry of Education, Youth and Sports project MSM 68-4077-0040.

# Ce-DOPED (Lu/Y)AG NANOMATERIALS AND FABRICATION OF CERAMICS USING SPARK PLASMA SINTERING\*

Bárta, J.; Pejchal, J.<sup>1</sup>; Beitlerová, A.<sup>1</sup>; Kučerková, R.<sup>1</sup>; Čuba, V.; Nikl, M.<sup>1</sup>

<sup>1</sup>Institute of Physics, AS CR, Prague

## INTRODUCTION

Radiation- and photo-induced preparation of luminescent nanomaterials with garnet structure has been studied at the Department of Nuclear Chemistry for many years. These materials could be utilized in the form of scintillating nanopowder for X-ray induced photodynamic therapy or liquid scintillation counting and as a suitable precursor for fabrication of optical (i.e. transparent) ceramics. In most applications, the most useful doping ion is the Ce<sup>3+</sup> ion with fast (~tens of ns) green emission. Optical ceramics might offer comparable properties to single crystals with the benefit of cheaper production and lesser amount of defects. Synthetic garnets also have the potential for their properties to be finely tuned by changes in composition.

## EXPERIMENTAL

The solid precursors for (Lu,Y)<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (LuAG, LuYAG, YAG) have been prepared by gamma (<sup>60</sup>Co, 80 kGy) or UV irradiation of aqueous solutions containing soluble salts of Al<sup>3+</sup>, rare-earth ions and formate anions. The dried solid precursors were calcined usually at 1200 °C for 2 hours in mild vacuum and then characterized by X-ray powder diffraction using Rigaku MiniFlex 600 and X-ray fluorescence analysis using Niton XL3t 900 GOLDD analyzer. The luminescence properties were measured at the Institute of Physics, AS CR. Spark plasma sintering (SPS) as a potential method for fabrication of ceramics was studied by J. Pejchal during his stay at the Tohoku University in Sendai. During SPS, the powder was simultaneously pressed in a graphite die (up to 100 MPa) and rapidly heated (up to 1700 °C) by electrical current passing through the die.

## RESULTS

After calcination of gamma-ray induced solid precursors at 1200 °C or more, the cubic garnet phase was present in all the solid materials (Fig. 1) as a major component. Its lattice parameter shifts according to the material composition.

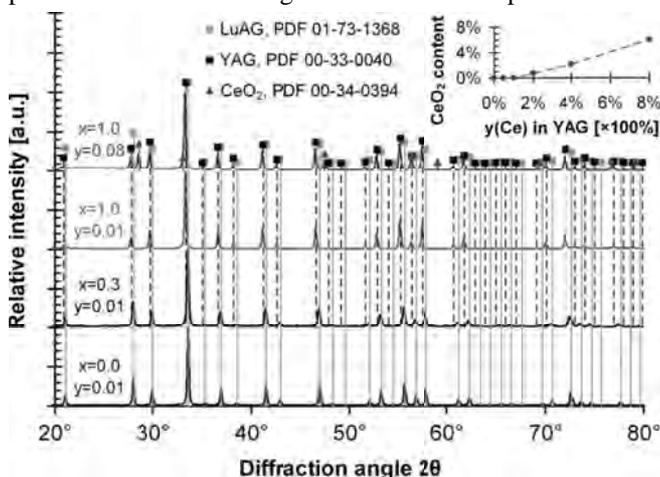


Fig. 1. Diffractograms of Lu<sub>3(1-x-y)</sub>Y<sub>3x</sub>Ce<sub>3y</sub>Al<sub>5</sub>O<sub>12</sub> samples prepared using <sup>60</sup>Co gamma irradiation; inset: amount of CeO<sub>2</sub> present in YAG (x = 1) samples [1]

In samples with very high Ce concentration, a separate CeO<sub>2</sub> appeared, probably due to a lower solubility in such garnet materials (Fig. 1 inset). The precursors also contained the specified amounts of rare-earth metals with no segregation. This was confirmed for Ce in YAG:Ce, Ce in LuAG:Ce and Lu/Y in LuYAG:Ce. All samples featured very intense broad emission at ~ 520 nm, consistent with Ce<sup>3+</sup> in garnets.

The LuAG:Ce ceramics prepared by the SPS method were rather opaque and only slightly transparent due to graphite / soot inclusions (Fig. 2). The undoped sample, however, was nearly transparent, which may imply that only a very small dopation (0.2 % Ce) has tremendous effect on the sintering process. Despite the dark colour and large opacity, the produced pellets had luminescence properties comparable to a LuAG:Ce single crystal with a much smaller amount of Lu<sub>Al</sub> defects (Fig. 3, ~300 nm). Apart from the Ce<sup>3+</sup> 5d – 4f emission, Gd<sup>3+</sup> and Cr<sup>3+</sup> impurity lines were visible in the radioluminescence spectrum. A new kind of defect was observed at 400 nm, probably related to oxygen vacancies.



Fig. 2. Photographs of ceramics made by SPS method [2] sintered at 1700 °C; left to right: LuAG:Ce, rapidly pre-heated LuAG and rapidly pre-heated LuAG:Ce

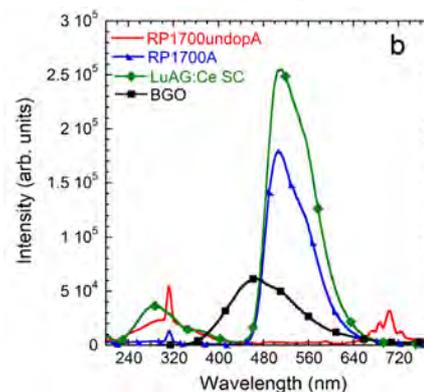


Fig. 3. Radioluminescence spectrum of LuAG:Ce ceramics (RP1700A) compared to a single crystal (SC) and Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub> reference scintillator (BGO) [2]

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This research was supported by the Czech Science Foundation project no. GA 13-09876S.

\* Compilation based on papers [1] and [2]

# PREPARATION OF LuAG:Eu AND LuAG:Pr NANOPARTICLES, DOPANT CONCENTRATION EFFECTS AND LUMINESCENCE DECAY\*

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<sup>1</sup> Institute of Physics, AS CR, Prague

## INTRODUCTION

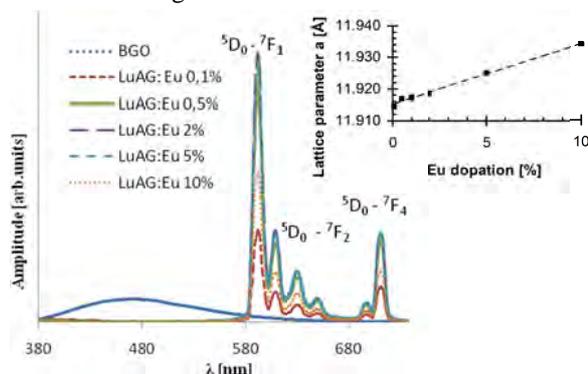
Many different trivalent ions can be incorporated into the synthetic garnet materials with general formula  $A^{III}_3B^{III}_5O_{12}$ , resulting in completely different luminescent properties. The main aim of this work was to investigate the possibility to prepare the  $Lu_3Al_5O_{12}$  garnet (LuAG) doped with some selected lanthanides with interesting properties –  $Eu^{3+}$  is a structural probe and red-emitting optical centre, while  $Pr^{3+}$  was chosen due to its very fast decay and emission in the UV, utilizable in the X-ray induced photodynamic therapy.

## EXPERIMENTAL

Solid precursors to the LuAG samples doped with Eu or Pr were prepared using the UV-light irradiation of aqueous solutions containing  $Lu^{3+}$ ,  $Al^{3+}$ ,  $Eu^{3+}$  /  $Pr^{3+}$  and  $HCOO^-$  ions based on [1]. The precursors were calcined at 1200 °C for 2 hours in air and then characterized by X-ray diffraction analysis (XRD; phase composition) using Rigaku MiniFlex 600 diffractometer and X-ray fluorescence analysis (XRF; elemental composition) using Niton XL3t 900 GOLDD analyzer. The radio- and photoluminescence properties as well as decay were measured at the Institute of Physics.

## RESULTS

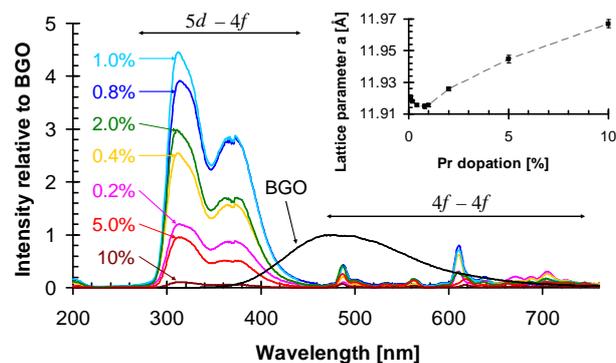
In both sets of prepared LuAG samples, the XRF analysis confirmed the intended elemental composition. All samples calcined at 1200 °C contained a cubic phase consistent with the LuAG phase; in some samples, also a very small amount of  $Lu_2O_3$  phase was found. The radioluminescence spectra of LuAG:Eu (Fig. 1) feature very intense  $4f - 4f$  transitions originating from the  $Eu^{3+} {}^5D_0$  excited state with a maximum intensity at ~2% Eu. Lattice parameters of LuAG:Eu (Fig. 1, inset) increase linearly with Eu content according to the Vegard's rule due to the larger diameter of  $Eu^{3+}$  relative to  $Lu^{3+}$ .



**Fig. 1.** Radioluminescence (RL) spectra of  $(Lu,Eu)_3Al_5O_{12}$  samples; inset: measured lattice parameters [2]

The luminescence of LuAG:Pr was dominated by broad  $Pr^{3+} 5d - 4f$  transitions in the UV region; however, some  $Pr^{3+} 4f - 4f$  lines in the visible range were present as well (Fig. 2). Both the very fast UV and the rather slow visible emissions reached their maximum intensity at ~ 1% Pr doping and then decreased significantly with further increase in Pr doping due to concentration quenching.

The lattice parameters of LuAG:Pr (Fig. 2, inset) had a distinct minimum around 1% Pr, which was probably caused by calcination of the samples in air. This resulted in the formation of rather small  $Pr^{4+}$  ions; at high Pr content, the prevalence of larger  $Pr^{3+}$  ions caused a sharp increase in  $a$ .



**Fig. 2.** Radioluminescence (RL) spectra of  $(Lu,Pr)_3Al_5O_{12}$  samples; inset: measured lattice parameters [3]

In both materials (measured as free-standing powder), the decay times of their photoluminescence transitions were significantly higher than in the corresponding single crystal (Tab. 1) because of the influence of surrounding medium on nanoparticle scintillators [1]. As a result, the evaluation of concentration quenching as a decrease in the decay times is rather imprecise. Nevertheless, the decay times shorten with the dopant content similarly to the decrease of RL intensity.

**Tab. 1.** A selection of photoluminescence decay times for the Eu- and Pr- doped LuAG samples, compared to the values from a single crystal (SC) [2,3]

$\lambda_{ex}$ [nm]	225	$\lambda_{ex}$ [nm]	280
$\lambda_{em}$ [nm]	592 710	$\lambda_{em}$ [nm]	310
% Eu	$\tau$ [ms]	% Pr	$\tau$ [ns]
0.1	10.3 10.2	0.1	28.3
0.5	10.7 10.2	0.2	32.7
1.0	10.5 10.3	0.4	34.2
2.0	9.9 9.8	0.8	33.1
5.0	9.9 9.8	2.0	26.2
10	9.0 8.9	5.0	13.3; 42.8
SC	~3.8	10	3.8; 12.6
		SC	~20

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This research was supported by the Czech Science Foundation project no. GA 13-09876S.

\*Compilation based on papers [2] and [3].

# STRUCTURAL AND LUMINESCENCE INVESTIGATION OF $\text{Eu}^{2+}$ -DOPED $\text{ALnS}_2$ TERNARY SULPHIDES\*

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## INTRODUCTION

Ternary sulphides of alkali metals and rare-earth elements with  $\text{ALnS}_2$  stoichiometry are prospective scintillators and phosphors, which are currently studied in a cooperation of the Institute of Physics, AS CR and the Department of Nuclear Chemistry. Since the observation of a very intense luminescence of  $\text{Eu}^{2+}$  in this host [1] that can be excited by light in the blue region, the possibility of their application in solid state lighting has been considered as well.

Most  $\text{ALnS}_2$  compounds crystallize in the same structure type (rhombohedral  $\alpha\text{-NaFeO}_2$ ), but possess widely differing lattice parameters due to large size variations among both  $\text{A}^+$  and  $\text{Ln}^{3+}$  ions. This also enables to use these materials as structural probes to observe changes in various properties caused by their composition and structure parameters.

## EXPERIMENTAL

Crystalline ternary rare-earth sulphides were synthesized at the Institute of Physics by heating rare-earth oxides with a large excess of alkali metal carbonates in an  $\text{Ar} + \text{H}_2\text{S}$  atmosphere to both form sulphides and prevent their oxidation to a much more stable  $\text{Ln}_2\text{O}_2\text{S}$  phase. The phase composition was confirmed by X-ray diffraction using Rigaku MiniFlex 600 or, for older samples, HZG-3. The elemental composition was investigated by X-ray fluorescence analysis using Niton XL3t 900 GOLDD; the Na content (outside the measurable energy range) was estimated from the content of other elements. Luminescence properties and EPR characterization of the crystals were measured at the Institute of Physics.

## RESULTS

All studied  $\text{ALnS}_2$  ternary sulphide samples apart from  $\text{NaLaS}_2$  (cubic) had a rhombohedral crystalline structure with lattice parameters consistent with literature. Their RL spectra were dominated by the  $\text{Eu}^{2+} 5d - 4f$  emission, whose position strongly depended on the composition (Fig. 1); some impurity emission lines are present as well. A strong correlation was found between emission band maximum and the ratio of the lattice parameters  $c/a$  [2], which was explained by a model based on crystal field considerations.

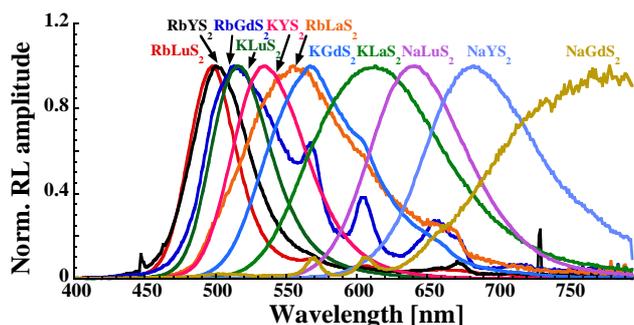


Fig. 1. Room-temperature radioluminescence (RL) spectra of  $\text{ALnS}_2\text{:Eu}$  crystals with different composition [2]

Additionally, the possibility to influence the emission band maximum by incorporation of two different alkali metals was investigated [3]. In all samples, only a single phase was detected. It was found that  $\text{ALuS}_2$  ternary sulphide greatly prefers Na over K as only small amounts of  $\text{Na}_2\text{CO}_3$  in the melt had large effect both on lattice parameters (Fig. 2) and on the content of K in the solid phase. As can be seen in the inset of Fig. 2, both lattice parameters depend linearly on the composition with a small bend of  $c$  at high K content.

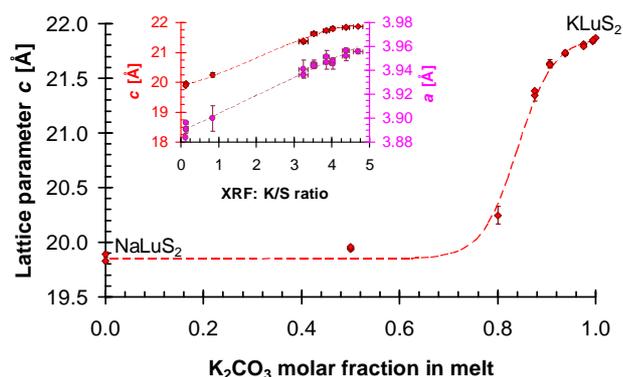


Fig. 2. Dependence of  $(\text{K,Na})\text{LuS}_2\text{:Eu}$  lattice parameters on the melt composition ( $\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$ ). Inset: plot of  $c$  and  $a$  on the determined K content in solid [3]

Radioluminescence spectra of these solid solutions (Fig. 3) showed that the  $\text{KLuS}_2$ -like emission center redshifts with Na addition until a transitory region is reached ( $\sim 70\%$  K), where a  $\text{NaLuS}_2$ -like emission center appears. The very wide emission observed in this region might be utilized in lighting applications when combined with a blue excitation diode to produce white light.

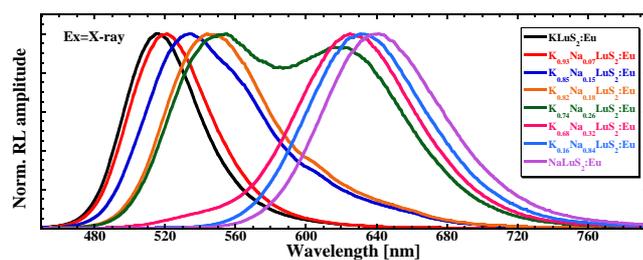


Fig. 3. RL spectra of  $(\text{K,Na})\text{LuS}_2$  samples with different composition (left to right:  $\text{KLuS}_2$  to  $\text{NaLuS}_2$ ) [3]

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- [3] Havlák, L. et al. (2016) Mater. Design 106, 363–370.

\*Compilation based on papers [2] and [3]

# ZnO:Ga-PS: AN ULTRAFAST SCINTILLATING COMPOSITE

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## INTRODUCTION

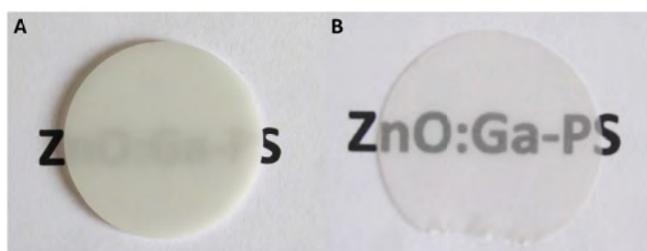
ZnO:Ga is known as an ultrafast scintillator with sub-nanosecond decay. Despite many disadvantages such as low stopping power and light yield, ZnO:Ga embedded in appropriate matrix is one of the most promising materials for next-generation scintillators used in high energy physics (HEP) and time of flight positron emission tomography (TOF-PET). Bringing the ZnO:Ga nanocrystal's timing performance to radiation detectors could pave the research path towards sub-20 ps time resolution.

## EXPERIMENTAL

The highly luminescent ultrafast ZnO:Ga powder was prepared using photochemical method [1]. ZnO:Ga nanopowder was dispersed within a polystyrene (PS) host matrix, following the drying and heating procedure described in [2]. ZnO:Ga@PS nanocomposite contained 10 weight % of ZnO:Ga with an average density of  $1.5 \text{ g cm}^{-3}$ . Samples were characterized using laser-initiated pulsed X-rays up to 40 keV and a Hamamatsu C10910 streak camera with an intrinsic time resolution of 18 ps. The instrumental response function (IRF) of the system has been determined as 75 ps. Coincidence time resolution (CTR) measurements using 511 keV annihilation photons ( $^{22}\text{Na}$  source) were performed with ZnO:Ga@PS sample of  $3 \times 3 \times 1 \text{ mm}^3$  dimensions. A  $2 \times 2 \times 10 \text{ mm}^3$   $\text{Lu}_2\text{SiO}_5:\text{Ce,Ca}$  (0.4% Ca; LSO) reference crystal was used as the second detector. Stated CTR values were corrected for the time resolution of the reference detector (70 ps FWHM) in order to obtain a CTR value as if two identical ZnO:Ga@PS detectors were operated in coincidence.

## RESULTS

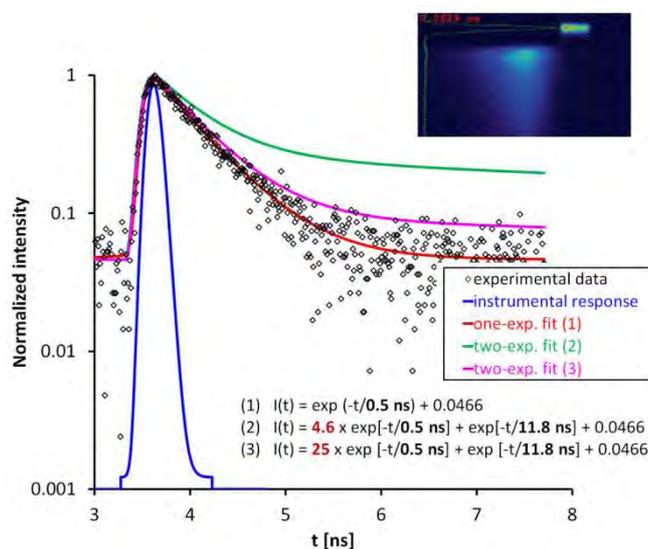
ZnO:Ga-PS composite with 10 wt% of ZnO:Ga in the form of 1 mm and 0.17 mm thick plate is shown in Fig. 1.



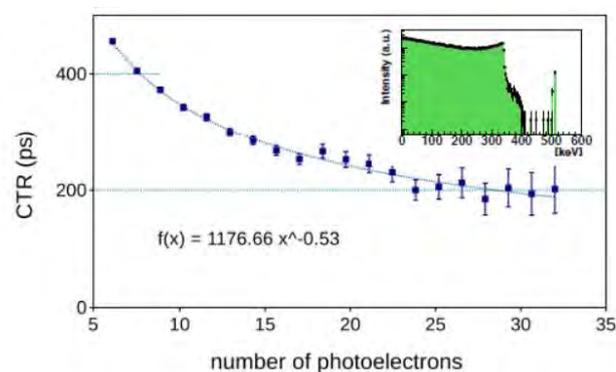
**Fig. 1.** Image of A) 1 mm and B) 0.17 mm thick ZnO:Ga-PS composite [2]

Spectrally and time-resolved radioluminescence data are shown in Fig. 2. Light is emitted between 380 and 420 nm with no presence of the polystyrene host radioluminescence emission between 300 and 350 nm. The decay curve measured with the 75 ps IRF had a mono-exponential character with a decay time of  $500 \pm 5 \text{ ps}$ . Measurements using 511 keV excitation present a minimum FWHM of  $200 \pm 30 \text{ ps}$  for events with maximum energy deposition. When compared

to the timing performance of LSO:Ce,Ca, the ZnO:Ga@PS showed a time resolution deteriorated by a factor 2, which was caused by the poor light output of the sample combined with a low stopping power and no energy resolution.



**Fig. 2.** ZnO:Ga@PS spectrally resolved radioluminescence decay measurement using 2 ns sweeping range. The laser IRF is shown to the right of the ZnO:Ga@PS emission [2, 3]



**Fig. 3.** CTR of the ZnO:Ga@PS as a function of the number of photoelectrons detected; inset: simulations for 511 keV photon energy deposition [3]

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This research has been supported by the the Grant Agency of the Czech Republic, grant no. GA13-09876S and by the Grant Agency of the Czech Technical University in Prague, grant no. SGS14/207/OHK4/3T/14.

# PRELIMINARY STUDY ON SINGLET OXYGEN PRODUCTION USING $\text{CeF}_3:\text{Tb}^{3+}@\text{SiO}_2$ -PORPHYRIN NANOCOMPOSITES\*

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<sup>1</sup>Institute of Physics, AS CR, Prague

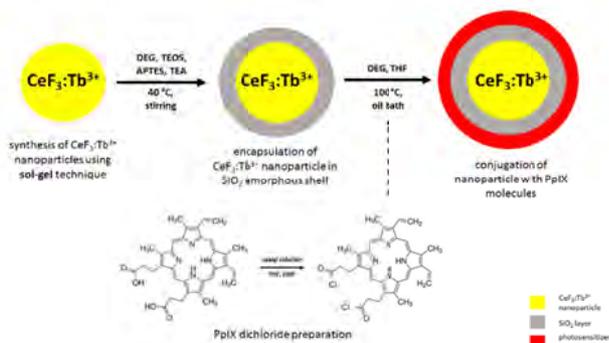
## INTRODUCTION

X-ray induced photodynamic therapy (PDTX) is a novel method for cancer treatment. It uses composite nanomaterials, based on the nanoparticles conjugated with a photosensitizer molecule, as a tumor-destroying agent [1]. The PDTX agent accumulates preferentially in target cells; subsequently, the external X-ray irradiation excites the scintillating nanoparticles emitting secondary radiation, which activates the photosensitizer (PS) molecules. Their deexcitation via the non-radiative energy transfer leads to the production of reactive oxygen species (ROS), where the singlet oxygen is widely believed to be the most cytotoxic agent [2].

This work presents a proof-of-concept research focused on the preparation and study of the luminescent properties of a composite nanomaterial based on  $\text{CeF}_3:\text{Tb}^{3+}$  nanoparticles prepared via sol-gel route and modified with  $\text{SiO}_2$  and protoporphyrin IX (PpIX), having their prospective application in PDTX in mind.

## EXPERIMENTAL

The synthesis of the  $\text{CeF}_3:\text{Tb}^{3+}@\text{SiO}_2$ -porphyrin nanocomposite material includes three main steps (Fig. 1): synthesis of the nanoparticle via sol-gel route, surface covering with an amorphous silica shell using polycondensation reaction between tetraethoxysilane (TEOS) and (3-aminopropyl)triethoxysilane (APTES), and finally conjugation of the nanoparticle with protoporphyrin IX molecules (biofunctionalization) [3].

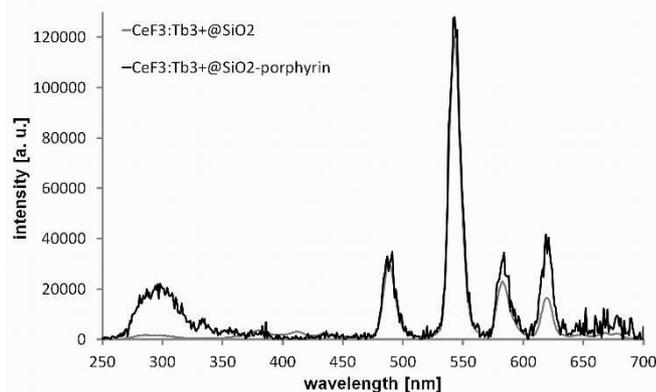


**Fig. 1.** Preparation of the  $\text{CeF}_3:\text{Tb}^{3+}@\text{SiO}_2$ -porphyrin nanocomposite material for PDTX

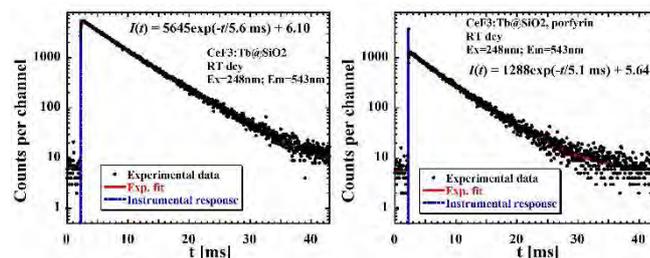
## RESULTS

Radioluminescence spectra (Fig. 2) of the samples indicate the presence of broad emission band around 280 – 300 nm due to  $\text{Ce}^{3+}$   $5d - 4f$  transition and typical narrow lines of the  $\text{Tb}^{3+}$  emission in the green spectral part. In biofunctionalized sample, a significantly higher emission intensity of  $\text{Ce}^{3+}$  at 300 nm compared to  $\text{Tb}^{3+}$  lines was observed, which may suggest an energy transfer from  $\text{Tb}^{3+}$  center towards PpIX layer. We suppose that the increasing relative intensity of the line at 620 nm in the  $\text{CeF}_3:\text{Tb}^{3+}@\text{SiO}_2$ -porphyrin spectra may be caused by the emission of PpIX.

Photoluminescence decay measurements (Fig. 3) for  $\text{Tb}^{3+}$  are qualitatively consistent with the conclusions drawn from the radioluminescence spectra. A reduction of about 10% in the PL decay time of  $\text{CeF}_3:\text{Tb}^{3+}@\text{SiO}_2$ -porphyrin in comparison to  $\text{CeF}_3:\text{Tb}^{3+}@\text{SiO}_2$  sample evidenced the energy transfer between nanoparticles and PpIX outer layer; as a consequence, the singlet oxygen production may be expected.



**Fig. 2.** Room temperature radioluminescence spectra of the  $\text{CeF}_3:\text{Tb}^{3+}@\text{SiO}_2$  and  $\text{CeF}_3:\text{Tb}^{3+}@\text{SiO}_2$ -porphyrin samples



**Fig. 3.** Room temperature photoluminescence decay curves of the  $\text{CeF}_3:\text{Tb}^{3+}@\text{SiO}_2$  and  $\text{CeF}_3:\text{Tb}^{3+}@\text{SiO}_2$ -porphyrin samples. The excitation at 248 nm and emission at 543 nm was used

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This work was supported by the Czech Science Foundation, projects GA13-09876S and GA13-28721S, and by the Grant Agency of the Czech Technical University in Prague, grant No. SGS14/2070HK4/3T/14.

\*The results were presented at the LUMDETR 2015 conference and published in [3].

# INTERACTION OF EXTREME-ULTRAVIOLET RADIATION WITH PLASMID DNA\*

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## INTRODUCTION

DNA molecule is believed to be the most sensitive target for the deleterious effects of all types of ionizing radiation (IR) in living organisms.

Final products in the interaction process of IR with DNA are the single (SSBs) and double-strand breaks (DSBs), abasic sites and modified sugars or bases. Among all of the products, the double strand breaks are the most lethal ones since their repair in the cell often leads to a chromosomal aberrations and ultimately to cell death.

The energy deposition process of the IR is mediated mainly by the electrons liberated in the irradiated material by Compton effect (photons) or Coulombic interactions (charged particles). In a certain approach, the interaction of electrons can be described by the energy loss function, which describes the most probable energy that can be transferred to the medium by the energetic electrons. For most materials including DNA, this function has a maximum at 22 eV.

Effects of such energetic electrons on the DNA can be effectively simulated by interaction of the extreme ultraviolet radiation (XUV) due to the photoelectric effect and relatively low ionization potential of DNA, i.e. 7-10 eV.

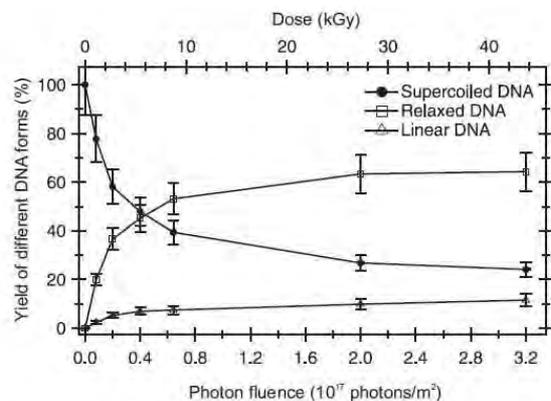
We have exploited the XUV radiation with energy of 26.5 eV generated by a capillary-discharge Ne-like Ar laser (CDL) [1] to study direct effects of such radiation on the strand breakage in the plasmid DNA.

## EXPERIMENTAL

Thin films containing 110 ng of plasmid DNA (pBR322) and buffer salt (Tris, EDTA) were prepared by depositing on coverslip in a volume of 5  $\mu$ l and left to evaporate. Samples were transferred to a vacuum interaction chamber evacuated to  $10^{-5}$  mbar ( $10^{-3}$  Pa). Samples were irradiated by pulsed laser radiation (3 Hz) up to a dose of 46 kGy. Energy deposited in the DNA sample was controlled by insertion of Al filters with various thicknesses into the beam path. After irradiation, the samples were removed from the chamber and retrieved from the coverslip for the agarose gel electrophoresis. After separation in agarose gel stained with SYBRGreen I, three separate bands were identified by UV transillumination. These bands correspond to the plasmid conformational change during irradiation, i.e. supercoiled (S), closed circular (C) and linear (L) form. The relative distribution of these forms as a function of the photon fluence or the dose was calculated from the measured fluorescence intensities. Fractions of plasmid DNA forms as a function of photon fluence are shown in Fig. 1.

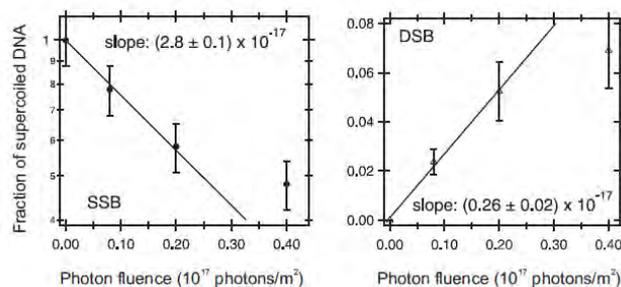
Yields of SSBs and DSBs per plasmid per Gy as well as action cross section can be obtained from the initial slope of the dose (fluence) response curve by assuming Poisson distribution of strand break induction. Radiation chemical yields ( $G$  value) in  $\text{nmol J}^{-1}$  can be calculated as  $1/(D_0/M_{\text{plasmid}})$ , where  $D_0$  represents the dose required to

induce, on average, one SSB or DSB per plasmid molecule.



**Fig. 1.** Forms of plasmid DNA as a function of photon fluence as detected by agarose gel electrophoresis.

The entrance dose in Gy can be estimated as a product of the mass absorption coefficient of the sample based on its stoichiometric composition, the photon energy and the photon fluence if all quantities are expressed in SI units.



**Fig. 2.** Initial slopes of the fluence response curves determining the action cross section for SSB (left) and DSB (right).

## RESULTS

Action cross sections for SSB and DSB induction were determined to be  $2.8 \times 10^{-17} \text{ m}^2$  and  $2.6 \times 10^{-18} \text{ m}^2$ , respectively.

The  $G$  values obtained for the direct effect of 26.5 eV pulsed laser radiation were  $29.6 \pm 3.2$  and  $3.1 \pm 0.7 \text{ nmol J}^{-1}$ , respectively. These  $G$  values as well as action cross sections are in a good agreement with similar experiments conducted using synchrotron radiation as a source of XUV photons.

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\*Full text available in [2].



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# PREPARATION OF OXIDIZED CARBON NANOSTRUCTURES BASED SORBENTS FOR RADIONUCLIDE CAPTURE

Kománková, L.; Kozempel, J.; Vlk, M.

## INTRODUCTION

Uniqueness of carbon nanomaterials enables their application in a wide range of disciplines, e.g. the sorption of radionuclides from waste solutions. This work was focused on the preparation of sorbent based on graphene oxide (GO) [1] and its composite with hydroxyapatite (HAp) and their sorption properties [2].

The experiments were conducted with a mixture of  $^{227}\text{Ac}/^{227}\text{Th}/^{223}\text{Ra}$ . Such mixture may be used in  $^{227}\text{Ac}/^{227}\text{Th}/^{223}\text{Ra}$  generators. However, the dose rate in close vicinity of such sources requires sorbents with high radiation stability and selectivity.

## EXPERIMENTAL

GO was prepared by graphite oxidation by Tour method [3] (Fig. 1). Composite GO-HAp (Fig. 2) were synthesized by low-temperature (I) and high-temperature (II) hydrothermal reaction from exfoliated GO and HAp precursor solution.

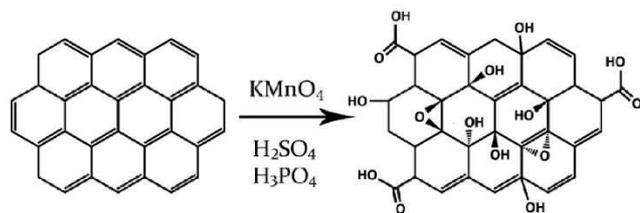


Fig. 1. GO synthesis from graphite – Tour method.

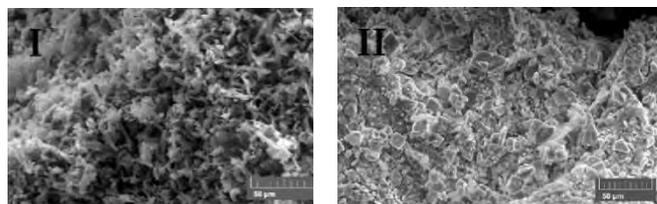


Fig. 2. GO-HAp composite (SEM). I – low-temperature, II – high-temperature.

Materials were granulated into PAN matrix. (Fig. 3 and 4).

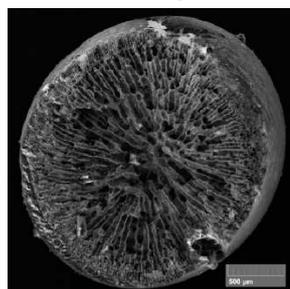


Fig. 3. GO-PAN granule.

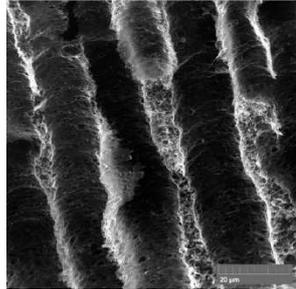


Fig. 4. Internal structure of GO-PAN composite.

Sorption experiments on composites were carried out by static method where the aqueous suspension of composite was mixed with  $^{227}\text{Ac}/^{227}\text{Th}/^{223}\text{Ra}$  solution. Distribution coefficient was calculated from the results of static experiments (Tab. 1 and 2).

Tab. 1. Values of  $D_g$  for each radionuclide sorbed on GO-PAN. Calculated from measured activities of solid and liquid phase.

pH	$D_g$ [mL/g]		
	$^{223}\text{Ra}$	$^{227}\text{Th}$	$^{211}\text{Pb}$
11,0	560	120	440
9,8	12000	80	1700
3,9	4500	970	2600
1,2	70	360	80
0,2	20	190	20
0	20	3100	20

Tab. 2. Values of  $D_g$  for each radionuclide sorbed on GO-HAp-PAN. Calculated from measured activities of solid and liquid phase.

GO-HAp-PAN	pH	$D_g$ [mL/g]		
		$^{223}\text{Ra}$	$^{227}\text{Th}$	$^{211}\text{Pb}$
I	7	160	5600	150
	9	500	510	470
	11	1600	1800	1300
II	7	430	4000	400
	9	490	670	440
	11	3900	350	4700

## RESULTS

The values of distribution coefficient ( $D_g$ ) for GO-PAN composite were highest for Ra-223 and at pH = 9,8 and for Th-227 in the range from 0 to 3,9.

For samples GO-HAp-PAN with increasing pH the sorption of Ra-223 increases and simultaneously the sorption of Ac-227 and Th-227 decreases.

Also the method of composite synthesis (GO-HAp-PAN) has the influence on yield.

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This research has been supported by the Technology Agency of the Czech Republic and Czech Technical University in Prague under contract No.: TA03010027 and SGS16/251/OHK4/3T/14.

# PLANT UPTAKE AND TRANSLOCATION OF HYDROXYAPATITE NANOPARTICLES LABELLED WITH $^{223}\text{Ra}$

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## INTRODUCTION

Nanoparticles appear in the environment from many aspects of our life, especially during manufacturing and fossil fuels combustion. These particles have both positive and negative impact on our environment. In the case of negative impact, the particles should be removed from the surroundings. There are many various ways and one of them is phytoremediation. That means use of plants for transforming, accumulation or removal of pollutants, such as heavy metals, pesticides, explosives, dyes, radionuclides or nanoparticles.

The study of plant uptake and translocation of hydroxyapatite nanoparticles labelled with  $^{223}\text{Ra}$  in plant *Zea mays* was performed.

## EXPERIMENTAL

The plants were grown in Murashige and Skoog medium in a culture room at 25 °C and a daily cycle of 16 hours light and 8 hours darkness for 14 days (Fig. 1.). The plant uptake and translocation of [ $^{223}\text{Ra}$ ]nanohydroxyapatite was studied on the set of 10 plants by phytoextraction. A sample of [ $^{223}\text{Ra}$ ]nanohydroxyapatite (3 mg) was prepared with a specific activity of 25.0 kcps/mg. Labelled nanoparticles were applied to each plant with activity approximately 500 cps. After 7 days of cultivation of the plants the distribution of accumulated activity in the plant was monitored by electronic autoradiography of dried plant.



Fig. 1. Fresh seeds of *Zea mays* and plants transferred into culture rooms.

## RESULTS

The determination of radioactivity uptake was based on measured data presented in Tab. 1. It is hard to determine if the measured activity was from pure  $^{223}\text{Ra}^{2+}$  ions or from the studied labelled nanoparticles. Presence of  $^{223}\text{Ra}^{2+}$  is possible because of hydrolysis of hydroxyapatite nanoparticles or because of its metabolism in plants.

In Fig. 2, distribution of  $^{223}\text{Ra}$  accumulated as [ $^{223}\text{Ra}$ ]HA or  $^{223}\text{Ra}^{2+}$  is shown. As it may be seen, bigger part of accumulated activity was in the roots but a significant part is transferred into the aboveground parts of the plant, too.

The results revealed that the plants accumulated (19-47) % of applied activity. Main part of the accumulated activity was accumulated in roots (77-96) % and a significant part of activity was translocated to upper parts of the plants (4-23) % (Fig. 2., Tab. 1.)

**Tab. 1.** Uptake and translocation of both [ $^{223}\text{Ra}$ ]HA and  $^{223}\text{Ra}^{2+}$  ion in plants measured via electronic autoradiography.  $A_r$  is the activity in the root,  $A_p$  is the activity in the remaining part of the plant.

Plant No.	$A_r$ [kcpm]	$A_p$ [kcpm]	% $A_r$	% $A_p$
1	2.5	0.6	81	19
2	3.5	0.6	85	15
3	3.4	0.5	87	13
4	1.6	0.5	77	23
5	4.2	0.8	83	17
6	2.8	0.3	89	11
7	2.3	0.3	90	10
8	6.3	0.2	96	4
9	3.2	0.8	81	19
10	1.4	0.3	81	19

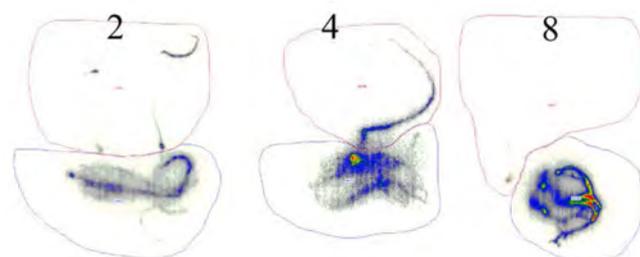


Fig. 2. Activity accumulation in chosen plant samples.

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# NANOHYDROXYAPATITE AS UNIVERSAL BIOCOMPATIBLE CARRIER FOR RADIOPHARMACY

Kozempel, J.; Vlk, M.; Mičolová, P.; Kukleva, E.; Málková, E.; Sakmár, M.; Nykl, P.; Lobaz, V.<sup>1</sup>; Hrubý, M.<sup>1</sup>; Šlouf, M.<sup>1</sup>

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## INTRODUCTION

Development of carriers for radionuclides in nuclear medicine is very important for targeted cancer treatment and high efficiency diagnostics. There are many ways to solve this problem, one of them is the use of nanomaterials based on hydroxyapatite (Fig. 1).

Hydroxyapatite is wide spread in nature; bones and enamel basically consist of hydroxyapatite. In the current medicine, artificial hydroxyapatite is used for bone reparation and replacement, as an additive to cosmetics and tooth paste because of its high biocompatibility. Also, nanohydroxyapatite has been considered for cancer treatment.

The aim of this work was to prepare hydroxyapatite nanoparticles, to modify them with organic additives and to optimize the labelling procedure with various radionuclides.

In addition, the possibility of hydroxyapatite use as diagnostic and therapeutic radiopharmaceutical was evaluated. *In vitro* stability studies were also performed.



**Fig. 1.** Scheme of nanoparticle based radiomedicine development.

## EXPERIMENTAL

Nanohydroxyapatites are intensely studied and applied in biotechnology and medicine because of their biocompatibility and easy elimination *in vivo*. Among their benefits, easy and fast production method belongs: precipitation of mixture of  $\text{Ca}(\text{NO}_3)_2$  and  $(\text{NH}_4)_2\text{HPO}_4$  under pH 11 in excess of water (Ca:P = 1.67).

Prepared hydroxyapatites were characterized via FT-IR and electronic microscopy. Labelling procedures were developed with generator radionuclides ( $^{223}\text{Ra}$ ,  $^{99\text{m}}\text{Tc}$ ,  $^{68}\text{Ga}$ ) and commercially available  $^{18}\text{F}$ . Two labelling strategies were used in this study: surface labelling (Surface) and volume incorporations (Volume).

*In vitro* stability tests were performed under room temperature in various biologically relevant media.

## RESULTS

Prepared particles, characterized via FT-IR, showed as hydroxyapatite. Microscopic analysis showed important information about size and form of the particles.

Labelling yields were determined by radiometric detection and for some samples were over 95 % (Tab. 1). Also *in vitro* stability studies showed acceptable results for further *in vivo* stability studies.

So, nanohydroxyapatites are appropriate candidates as radionuclide carriers for nuclear medicine for both therapeutic and diagnostic radionuclides. Relatively high labelling yields and appropriate *in vitro* stability prove this assumption.

Other key parameters that affect the future of studied nanoparticles in clinical practice such as size, form and *in vivo* stability will be studied in future. All these parameters could have significant impact on biodistribution and elimination mechanisms of the particles.

**Tab. 1.** Labelling yields. N – number of samples.

Nuclide	Method	Yield [%]	N
$^{99\text{m}}\text{Tc}$	Surface	$94,7 \pm 1,3$	8
$^{99\text{m}}\text{Tc}$	Volume	$94,8 \pm 0,7$	16
$^{223}\text{Ra}$	Surface	$94,7 \pm 1,6$	16
$^{223}\text{Ra}$	Volume	$98,8 \pm 1,2$	10

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# TITANIUM DIOXIDE, PERSPECTIVE CARRIER FOR THERANOSTIC RADIONUCLIDES, PREPARATION, LABELLING, STABILITY *IN VITRO*

Mičolová, P.; Sakmár, M.; Málková, E.; Kukleva, E.; Vlk, M.; Kozempel, J.

## INTRODUCTION

The main aim of this study was the preparation of a suitable nanomaterial for possible use as a carrier of theranostic radionuclides.

Titanium dioxide is an interesting material for many applications, e.g. as a pigment, part of suncreams or photocatalyst. In nuclear medicine, TiO<sub>2</sub> found its place as a sorbent in <sup>68</sup>Ge/<sup>68</sup>Ga generators. Due to its stability, surface area, and sorption and physical properties, TiO<sub>2</sub> could be also a suitable carrier for alpha emitters in targeted alpha therapy. It could enable creation of theranostic drug for nuclear medicine by combining a therapeutic radionuclide with SPECT or PET radionuclides such as e.g. <sup>99m</sup>Tc, or <sup>18</sup>F or <sup>68</sup>Ga, respectively.

## EXPERIMENTAL

TiO<sub>2</sub> was prepared by hydrolysis of tetra-*n*-butylorthotitanate in 2-propanol.

Two labelling strategies were used in this study: surface labelling and volume incorporations.

The stability of labelled nanoparticles were studied *in vitro*. Three matrices were used: physiological saline, bovine blood plasma and bovine blood serum. The process of stability experiments is shown in Fig. 1.

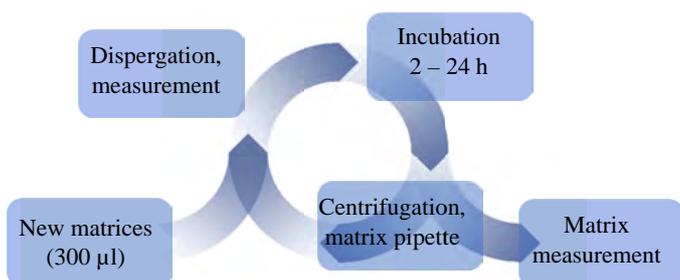


Fig. 1. *In vitro* stability studies.

The supernates were changed after 2 – 7 – 12 – 17 – 26 – 35 – 59 hours after labelling (in the case of <sup>99m</sup>Tc, the last sampling was after 31 hours) and the released activities were calculated. The average released activities for each labelling strategy are shown in Fig. 2 and 3.

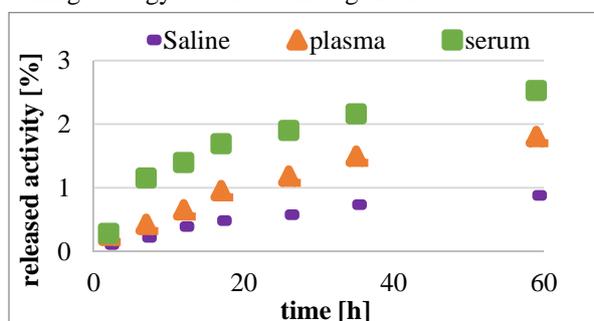


Fig. 2. <sup>223</sup>Ra-TiO<sub>2</sub> – surface labelling.

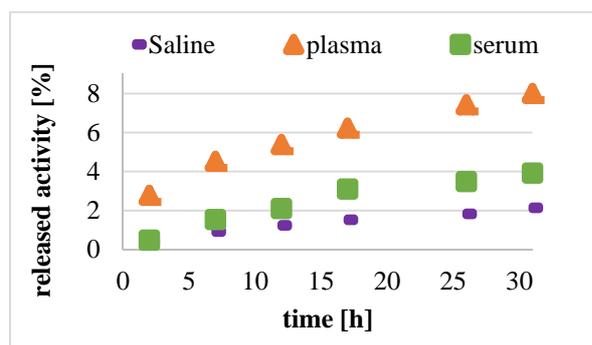


Fig. 3. <sup>99m</sup>Tc-TiO<sub>2</sub> – surface labelling.

## RESULTS

The yields of TiO<sub>2</sub> nanoparticles labelling were higher than 98 % (<sup>223</sup>Ra) and 95 % (<sup>99m</sup>Tc). The average released activities for both radionuclides and both labelling strategies are summarized in Tab. 1. All released activities were below 10 % except for stability in plasma with <sup>99m</sup>Tc-TiO<sub>2</sub> where the released activity was 65 %. This could be done due to aged plasma.

Tab. 1. *In vitro* stability in physiological saline (PS), bovine blood plasma (BP) and bovine blood serum (BS) after 59 h (<sup>223</sup>Ra) or 31 h (<sup>99m</sup>Tc).

		Surface [%]	Incorporation [%]
<sup>223</sup> Ra	PS	0,8	0,5
	BP	1,8	2,2
	BS	2,5	1,7
<sup>99m</sup> Tc	PS	2,1	1,5
	BP	8,0	65
	BS	3,9	5,8

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This research has been supported by the Technology Agency of the Czech Republic and Czech Technical University in Prague under contract No.: TA03010027 and SGS16/251/OHK4/3T/14

# ISOLATION METHOD OF Ac FROM MIXTURE OF RADIUM, ACTINIUM AND THORIUM

Kozempel, J.; Vlk, M.; Mičolová, P.; Kukleva, E.; Fialová, K.; Kománková, L.; Bajžíková, A.; Podlaha, J.

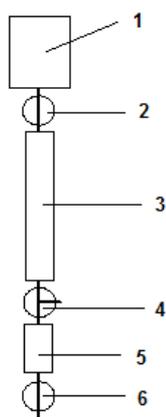
## INTRODUCTION

Submitted invention provides the isolation method of Ac, e.g. radionuclide  $^{227}\text{Ac}$ , from mixture of radium, actinium and thorium (e.g.  $^{226}\text{Ra}/^{223}\text{Ra}/^{227}\text{Ac}/^{227}\text{Th}/^{228}\text{Th}/^{229}\text{Th}$ ). The advantage of this method, among others, is the isolation of  $^{226}\text{Ra}$ , which could be recycled for repeated irradiation.

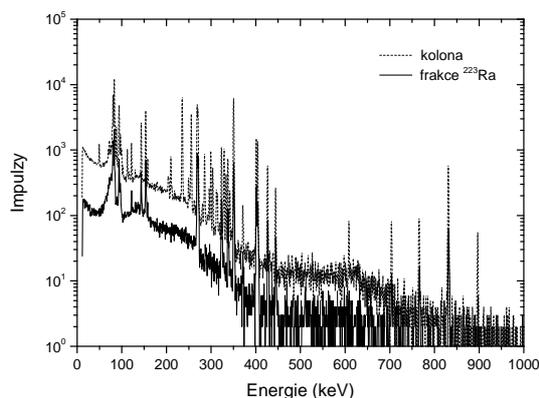
## EXPERIMENTAL

The submitted solution provides the actinium isolation method from the mixture of radium, actinium and thorium, which includes following steps:

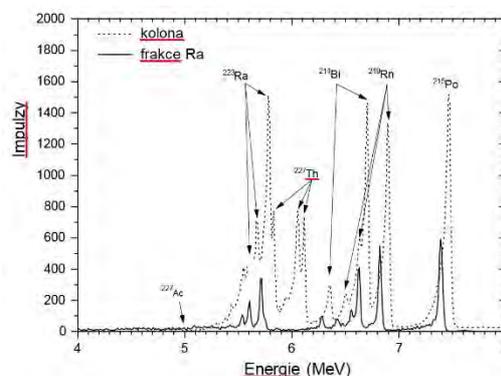
- The mixture of Ra/Ac/Th is applied on a separation column containing anion exchanger based on styrene reticulated by divinylbenzene. The content of reticulating agent is in the range from 5 to 50 %, advantageously from 8 % to 16 % (e.g. Dowex 1×8 – strong reticulated anion exchanger with 8 and more per cent of divinylbenzene) in nitrate cycle. The elution is provided by eluent consisting of the mixture of nitric acid (0,6 – 0,8 M) and methanol – volume ratio acid:methanol = from 30:70 to 10:90.
- The eluate from separation column is cleaned on another column with anion exchanger based on styrene reticulated by divinylbenzene similar to step a). The elution is similar to step a).
- The eluate (from step b)) containing  $^{226}\text{Ra}$  is isolated for its recycling and recovered for repeated irradiation.
- Ac and/or Th are eluted from the columns by solution consisting of 5-10 M mineral acid and at least one complexing agent. As mineral acid, nitric acid and/or hydrochloric acid can be used.



**Fig. 1.** Schematic arrangement of separation columns for separation of Ac, Th and Ra (1 – reservoir of eluent, 3 – separation column, 5 - cleaning column, 2, 4, 6 – valves).



**Fig. 2.** Gamma spectrum of clean  $^{223}\text{Ra}$  fraction as compared with  $^{227}\text{Ac}$  and  $^{227}\text{Th}$  mixture sorbed on separation column (kolona).



**Fig. 3.** Alpha spectrum of clean  $^{223}\text{Ra}$  fraction as compared with  $^{227}\text{Ac}$  and  $^{227}\text{Th}$  mixture.

## RESULTS

Procedure for  $^{227}\text{Ac}$  preparation and production from irradiated  $^{226}\text{Ra}$  provides actinium in satisfactory radiochemical and radionuclide purity. As possible applications of actinium-227  $^{227}\text{Ac}/^{223}\text{Ra}$  generator for nuclear medicine, Ac/Be neutron source for industry or radionuclide battery for space or military applications could be considered.

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# STUDY OF $^{223}\text{Ra}$ UPTAKE MECHANISM BY $\text{Fe}_3\text{O}_4$ NANOPARTICLES: TOWARDS NEW PROSPECTIVE THERANOSTIC SPIONS

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## INTRODUCTION

Superparamagnetic iron oxide nanoparticles (SPIONs) are being intensively studied and applied in medicine and biotechnology due to their magnetic properties, biocompatibility along with low clinical toxicity, easiness of the synthesis in nanoscale sizes and in clinically-relevant quantities [1]. Moreover, the recently developed nanoconstructs such as  $\text{Fe}_3\text{O}_4@Au@m\text{SiO}_2$  allowed to combine MRI monitoring, on-demand drug release, magnetic field targeted drug delivery and optical imaging (NIR photothermal ablation, fluorescence) [2]. Due to such unique properties of SPIONs, their great potential to be used as radionuclide-carrying agents for the targeted radiotherapy is obvious.

Radium-223 is a first-in-class alpha-emitting radionuclide approved by the FDA and EMA for the treatment of bone metastases originating from castration resistant prostate cancer. The high linear energy transfer of alpha particles ensures the enhanced ability to induce double-stranded DNA breaks and therefore the high cytotoxic effect [3].

## EXPERIMENTAL

SPIONs were prepared via coprecipitation of iron (II) and iron (III) salts in presence of ammonium hydroxide.

Weighted quantities of prepared NPs were contacted with 1-2 mL of  $^{223}\text{Ra}$  solutions in PBS ( $a_V = 1 \text{ kBq/mL}$ ) at the ratio  $V/m = 100\text{-}1000 \text{ mL/g}$  for 5-60 minutes using vial-shaker. After that, the NPs were simply separated from the reaction mixtures using permanent Nd magnet, which forced the NPs to settle-down to the bottom of vials. Labelled NPs were washed twice with fresh PBS. The radium activities in all liquid fractions removed and in the separated NPs were measured.

The prepared [ $^{223}\text{Ra}$ ] $\text{Fe}_3\text{O}_4$  NPs were shaken with PBS, 1-5% albumin solution in PBS or water (Sigma-Aldrich), the bovine serum (Sigma-Aldrich), plasma (Sigma-Aldrich), Geloplasma® solution for infusion (Fresenius Kabi, UK), and 1% poly(vinylpyrrolidone) (PVP) solution in water (Sigma-Aldrich) for 1-24 hours. After that, the solution was separated from the magnetite NPs as described above and both liquid and solid phases were analysed radiometrically.

Modelling of the radium-223 uptake by  $\text{Fe}_3\text{O}_4$  NPs was performed. The first step of modelling was the calculation of speciation diagrams of the system in question. The second step of modelling was the construction of the model and its incorporation into the calculation code, by means of which the experimental data and dependencies were described and simulated.

## RESULTS

The  $\text{Fe}_3\text{O}_4$  SPIONs were prepared and the method of their direct surface labelling with radium-223 was developed. While the TEM analyses confirmed the SPIONs structure (Fig. 1), the radiometric analyses showed good labelling

yields (Fig. 2) and stability in several biological media *in vitro*. We have found that the process of  $^{223}\text{Ra}$  uptake by  $\text{Fe}_3\text{O}_4$  NPs corresponds well with the sorption and surface complexation, rather than the precipitation mechanism. Our data also indicate that the initial and relatively fast  $^{223}\text{Ra}$  uptake on surface (edge sites) is followed by a slower process of  $^{223}\text{Ra}$  incorporation into interstitial positions of  $\text{Fe}_3\text{O}_4$  NPs (layer sites).

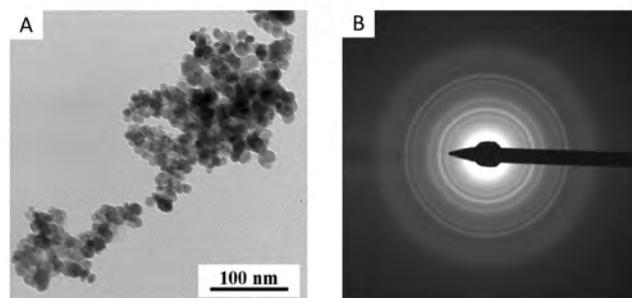


Fig. 1. TEM analysis of the SPIONs: A – TEM/BF micrograph showing the size and shape of the nanoparticles, B – TEM/SAED diffraction pattern.

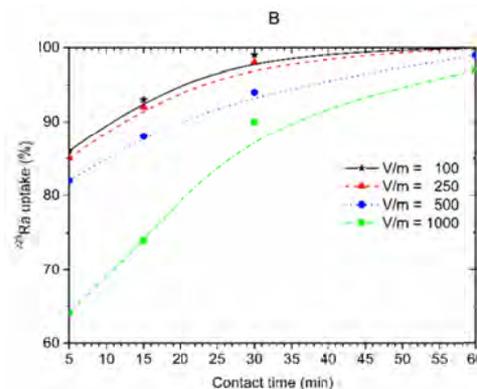


Fig. 2. Radium-223 uptake from PBS at pH=7.4 vs. contact time at various V/m ratios (mL/g).

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## PREPARATION OF STABILISED NANOPARTICLES

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### INTRODUCTION

Hydroxyapatite and titanium dioxide are commonly used in a number of medicinal applications. Hydroxyapatites serve to bone regenerations or for their substitution. Titanium dioxide is used as a pigment in food, cosmetics or in tooth paste. These carriers have amazing sorption properties for many radionuclides, however, they aggregate really fast and then sediment. For this reason, it is necessary to focus the research onto the issue of the prepared nanoparticles stabilisation. Detergents, polymers or donor ligands are suitable candidates for nanoparticles stabilisation.

### EXPERIMENTAL

Due to fast aggregation, four stabilisers were used: sodium citrate (NaCit), hexamin, dimethylsulfoxid (DMSO) and poly(*N*-(2-hydroxypropyl)metacrylamid) – HPMA.

The stabilisations of the prepared nanoparticles were done by dialysis. Firstly, TiO<sub>2</sub> was prepared then lyophilized, stabilised for 2 hours and dialysed (Fig. 1). The size of nanoparticles was studied by dynamic light scattering (DLS). The results are shown in Tab. 1.

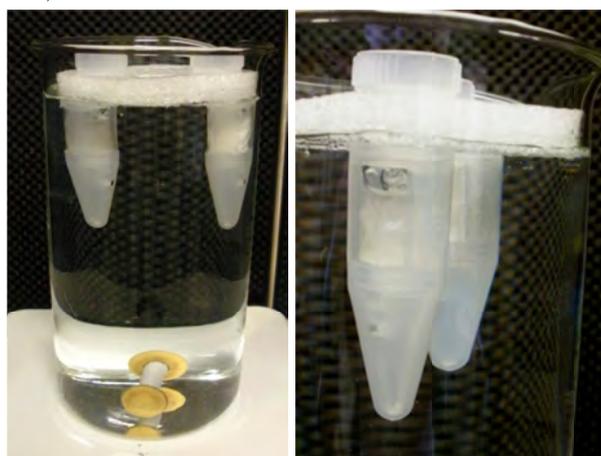


Fig. 1. Dialysis of stabilised nanoparticles.

Tab. 1. DLS results

stabiliser	d [μm]	ZP [mV]
NaCit	0,4	0,002
DMSO	0,3	0,001
Hexamin	0,3	0,001

Among other ways of stabilisation, the electrostatic stabilisation was studied. The following phosphonic acids were used as stabilisers:

- AEPA – 2-aminoethylphosphonic acid,
- AMPA – (aminomethyl)phosphonic acid,
- APPA – 3-aminopropylphosphonic acid,
- IDMPA – iminodi(methylphosphonic acid),
- NPMG – N-(phosponomethyl)glycin,
- NPMIDA – N-(phosponomethyl)iminodiacetic acid hydrate,
- PAA – phosphonoacetic acid.

The DLS results are shown in Tab. 2.

Tab. 2. DLS results – electrostatic stabilisation.

stabiliser	d [nm]	ZP [mV]
AEPA	220	-44,5
AMPA	230	-26,5
APPA	300	-33,4
IDMPA	210	-27,1
NPMG	220	-39,0
NPMIDA	190	-42,3
PAA	200	-36,5

Stabilised nanoparticles <sup>223</sup>Ra-TiO<sub>2</sub> were filtered through 0,22 μm filter. Results are shown in Tab. 3.

Tab. 3. Filtration results

stabiliser	Percentage distribution of activity [%]			
	sample	filter	vial	injection
DMSO	7	86	3	4
Hexamine	4	89	3	4
HPMA	8	82	4	6

Another filtration was done by centrifugation through a 20kDa filter (Amicon). The results are in Tab. 4.

Tab. 4. Centrifugation results

stabiliser	Sample activity [kBq]	Solution activity [Bg]	Labelling yield [%]
NPMIDA	4,8	40	99

### RESULTS

The best results were shown for particles stabilised by phosphonic acid NPMIDA. The size of particles was around 200 nm. However, for the best results it is necessary to find another way of stabilisation and prepare particle sizes below 100 nm.

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# PREPARATION OF POROUS MATERIAL FOR RADIONUCLIDE CAPTURE

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## INTRODUCTION

The main aim of this study was the preparation of porous materials possibly applicable for radionuclide capture. Possible materials which could be used are nanoporous materials (pore size of 1 to 100 nm) or polymers. This is why nanoporous metal oxides and macroporous materials based on silicagel with modified surface, e.g. styrene-divinylbenzene-N,N,N',N'-tetraoctyldiglycolamide, were prepared and characterized. Newly prepared materials were tested for radionuclide sorption in our laboratory (for <sup>223</sup>Ra and <sup>227</sup>Th) and ÚJV Řež laboratories.

## EXPERIMENTAL

The preparation of samples:

I – sorbent Al<sub>2</sub>O<sub>3</sub>:Ag was prepared from the solution of microAgNO<sub>3</sub> and the suspension of Al<sub>2</sub>O<sub>3</sub>. The mixture was heated (100 °C) and stirred for 20 minutes, then filtered, washed by water and ethanol and dried.

II – sorbent Al<sub>2</sub>O<sub>3</sub>:Ag was prepared from the suspension of nanoAgNO<sub>3</sub>, then the sodium borohydride and ethanol were added. The mixture was added to the solution of silver ions. The sorbent was filtered, washed by acetone and dried.

III – sorbent Al<sub>2</sub>O<sub>3</sub>:Ag was prepared from microAgNO<sub>3</sub>, AgNO<sub>3</sub> and sodium borohydride. The preparation was the same as in the previous case.

IV – Macroporous silicagel with modified surface: The styrene and divinylbenzene were added dropwise to silicagel in toluene. The last step was adding of 2,2'-azobis(2-methylpropionitrile). The mixture was heated (90 °C, 20 min) and dried for 24 hours. The prepared mixture in methanol was stirred for 30 minutes and then filtered. This step was repeated once more. The solution of TODGA in dichloromethane was added to the prepared washed solution and stirred for one hour. The sorbent was dried.

The prepared samples (I – III) were tested in ÚJV Řež. The sorption of Sr, Eu, Cs were tested. The sorbent was contacted with previously named ions solutions. The percentages of sorption ranged from 0.5 to 2 % for Sr, from 2 to 10 % for Cs, and from 80 to 90 % for Eu.

The sorption of <sup>223</sup>Ra was studied on column loaded with the sorbent IV at three different pH values. On the column, <sup>223</sup>Ra solution was introduced. The volume of feed solution (the activity added on column) was 1.1 ml. Then the columns were eluted with a mixture of 80 % methanol and 0.7 M nitric acid (8:2 v/v, pH 3-4) and at pH 7 and 10-11. Fractions with the volume ~ 1 BV (BV = column bed volume) were collected. The results are shown in Tab. 1.

Tab. 1. Overview of results – the measurement of <sup>223</sup>Ra on sample IV.

Measurement	Fraction activity [cps]		
	pH 3 – 4	pH 7	pH 10 – 11
Feed	10327	6896	9183
Fraction 1	166	23	21
Fraction 2	668	76	20
Fraction 3	34	87	23
Fraction 4	70	877	496
Fraction 5	92	258	-
Fraction 6	218	283	-

## RESULTS

Two types of material were prepared and tested – nanoporous Ag on Al<sub>2</sub>O<sub>3</sub> and composite SiO<sub>2</sub>-copolymer-TODGA. Samples I, II and III were tested for sorption of Sr, Cs and Eu. The results showed that the studied materials were not efficient sorbents for these ions. The uptake of Eu was similar to commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

However, the material IV turned more suitable for capture of radium. The experiments were performed at different pH values. The elution in alkali pH did not yield desired results since the alkali pH caused obstruction of the elution. At pH 3–4, <sup>223</sup>Ra remains captured on the column – less than 2 % are eluted in each successive 1 BV fraction of the eluate.

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# PROSPECTIVE CARRIERS OF $^{223}\text{Ra}$ FOR TARGETED ALPHA THERAPY

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## INTRODUCTION

Targeted alpha particle therapy (TAT) is very powerful tool against cancer, since DNA double-strand breaks caused by alpha radiation induce cells death. Main advantage of radionuclides decaying by alpha particle cascade in a short-lived chain is the deposition of high energy in very small volume (approx. 27 MeV in the case of  $^{223}\text{Ra}$ ). However, main disadvantage of such *in vivo* generator is the release of daughter hot atoms from all chemical bonds. Energy of chemical bond is just several eV compared to recoil energy of daughter atom that typically ranges to about 100 keV. We report here on basic aspects that have to be addressed in TAT systems and describe our experiments with prospective carriers of  $^{223}\text{Ra}$  intended for bone therapy based on hydroxyapatite (HA) nanoparticles (NPs).

## EXPERIMENTAL

In a typical experiment, 1.2 mol/L aqueous solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  and 0.8 mol/L aqueous solution of  $(\text{NH}_4)_2\text{HPO}_4$  were mixed together in a vial. Before addition of calcium salt solution pH was adjusted by addition of  $\text{NH}_4\text{OH}$  and was measured with pH-meter. The suspension was mixed at laboratory temperature for one hour and then the precipitate was centrifuged, supernate was removed and HA NPs were washed twice with ultrapure water and dried under reduced pressure.

Dried HA NPs were used for surface labelling by the following procedure. NPs were dispersed in physiological solution in ultrasound. Into each suspension,  $^{223}\text{Ra}$  eluate (pH adjusted with aqueous ammonia) was added and the suspensions were mixed for one hour in a vortex at laboratory temperature, then centrifuged, the supernate removed, and the  $^{223}\text{Ra}$ -sHA NPs were washed with ultrapure water and finally left in water suspension.

For volume labelling of HA NPs, the following procedure was employed: In a certain volume of fresh  $^{223}\text{Ra}$  eluate from a generator, pH was adjusted with addition of aqueous ammonia, 0.8 M aqueous solution of  $(\text{NH}_4)_2\text{HPO}_4$  was added and the solution was mixed. Into the mixture, 1.2 M aqueous solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  was added drop-wise and the suspension formed was mixed for one hour in a vortex at laboratory temperature. Then, the reaction mixture was centrifuged, the supernate removed, and the  $^{223}\text{Ra}$ -iHA NPs were washed with ultrapure water and finally left in water suspension.

**Tab. 1.** Summary of labelling experiments results with  $^{223}\text{Ra}$ . \* after 8 days. S – surface labelling, V – volume labelling

Sample	Initial activity total [kcps]	HA-NPs mass [mg]	Labelling yield [%]	Total activity washout in saline, 24 h [%]
S1.1	11	5	96	1,9
S1.2	17	3	86	1,3
S1.3	11	2	93	3,9
S2.1	11	5	98	0,7
S2.2	10	2	97	1,2
S2.3	19	1	62	10
V1.1	10	5	85	13
V1.2	11	2	97	2,2
V1.3	17	1	98	0,7
V2.0	57	5	99	0,8, 0,4*

## RESULTS

Hydroxyapatite is a good candidate for  $^{223}\text{Ra}$  labelling, since Ra/Ca analogy allows direct radium incorporation into the structure of nanoparticles or even its re-sorption together with daughter nuclei on the NPs surface. Labelling yields were high and total activity washout in model experiments was acceptable. Good correlations were found between the amount of NPs material and labelling yields in both labelling strategies. Also a correlation of total activity release with labelling yields was surprising. Further tailoring of NPs and further stability experiments are however needed.

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Procházková, L. - Čuba, V. - Ekberg, Ch. - Tietze, S. - Jakubec, I.: **Fabrication of Solid ZnCdO and ZnMgO Solutions via Gamma Radiolysis.** In: 13<sup>th</sup> Tihany Symposium on Radiation Chemistry - Program and Abstracts. 2015, p. 152.

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Rosendorf, T. - Hofmanová, E.: **Pilot in situ Diffusion Experiment on Compacted Bentonite in the Czech Republic.** In: Goldschmidt Abstracts 2015, p. 2685.

Rosendorf, T. - Hofmanová, E. - A Červinka, R.: **Effect of Rock and Cement Materials on Diffusion of Radiocontaminants in Bentonite.** In: Czech Chemical Society Symposium Series. 2016, vol. 14, no. 5. ISSN 2336-7202. (in Czech).

Rosendorf, T. - Hofmanová, E. - Vopálka, D. - Večerník, P. - Červinka, R.: **HTO Diffusion Experiment Over Folded Layers of Compacted Bentonite and Cement Pastes.** In: *Proc. seminar "Deep Underground Repository 2016"*. 2016, no. 48. (in Czech).

Sakmár, M. - Mičolová, P. - Vlček, M. - Kozempel, J.: **Preparation of TiO<sub>2</sub> Phosphonate Composites and Their Marking <sup>99m</sup>Tc and <sup>223</sup>Ra.** In: *Proc. of the Students' Sci. Conf. FNS CU Bratislava*. 2016, 1140-1145. ISBN 978-80-223-4103-5. (in Czech).

Špendlíková, I. - Němec, M. - A Prášek, T.: **Preparation of Anhydrous Uranium Tetrafluoride as a Possible Matrix Material for Accelerator Mass Spectrometry.** In: Abstracts – 9<sup>th</sup> International Conference on Nuclear and Radiochemistry – NRC9. 2016, p. 393.

Špendlíková, I. - Němec, M. - Steier, P.: **Precipitation of Titanium Dioxide with Simultaneous Uranium Sorption and its Application in Accelerator Mass Spectrometry.** In: Abstracts – 9<sup>th</sup> International Conference on Nuclear and Radiochemistry – NRC9. 2016, p. 90.

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Višňák, J. - Sobek, L.: **Quantum Chemical Calculations and Spectroscopic Measurements of Spectroscopic and thermodynamic properties of Given Uranyl Complexes in Aqueous Solution with Possible Environmental and Industrial Applications**. In: *EPJ Web of Conferences*. 2016, vol. 128. ISSN 2100-014X.

Vlk, M. - Mičolová, P. - Málková, E. - Bajžíková, A. - Kukleva, E. - Kománková, L. - Sakmár, M. - Kozempel, J.: **Radium-223 Labelled Nanocarriers for Alpha Radionuclide Therapy**. In: *Molecular and Supramolecular Carriers for Imaging and Therapy*. 2015, p. 8.

Vlk, M. - Mičolová, P. - Málková, E. - Kukleva, E. - Nykl, P. - Sakmár, M. - Kozempel, J.: **Preparation of Hydroxyapatite as Teranositic Carriers, Labeling and Stability in Vitro**. In: *Nukleární medicína*. 2015, pp. 15-16. ISSN 1805-1146.

Vlk, M. - et al.: **Magnetic Nanoparticle In Vivo Evaluation  $^{223}\text{Ra}$** . In: *Nukleární medicína*. 2016, p. 13. ISSN 1805-1146. (in Czech).

Zavadilová, A. - Vyhlídal, D. - Kubeček, V. - Šulc, J.: **Intracavity Interferometry Using Synchronously Pumped OPO**. In: *Proceedings of SPIE*. 2016, Vol. 10142. ISSN 0277-786X. ISBN 978-1-5106-0734-7.

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John, J.: **Support of Activities in the Division of Nuclear and Radiochemistry (DNRC) EuCheMS.** Prague: Ministry of Education, Youth and Sports of the Czech Republic. 2015. (in Czech).

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John, J. - Mareš, K. - Geist, A. - Bremer, A. - Stauch, C. - Ebert, E. - Modolo, G. - Bukaemskiy, A.: **Treatment of Isotopically Tailored Molybdenum.** ASGAR Deliverable D 2.1.4, Bruxelles: Euratom 7FP. 2015,.

John, J. - Němec, M. - Kořán, P. - Lehto, J. - Koivula, T. - Scully, P. - Omtvedt, J.P. - Retegan, T.: **Cooperation in education and training In Nuclear CHEMISTRY (CINCH-II) - The 2<sup>nd</sup> and the Final EC Reports.** CINCH-II Deliverable D5.5, Bruxelles: Euratom FP7. 2016.

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Štekl, I. - Hodák, R. - Přidal, P. - Smolek, K. - Burešová, H.: **Plastic scintillator based on polystyrene used as detectors**. Czech Patent. Praha. CZ 305761. 20.01.2016. (in Czech).

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Vlk, M. - Málková, E. - Kozempel, J. - Brynych, V. - Pospěchová, J.: **Composite sorbent PAN-TCF**. Functional Sample. 2015.

# THESES

Author, **Title**, Supervisor, Year

## DOCTORAL / DISSERTATION

Andris, B.

**Development of Processes for the Determination of Beta-Emitting Limited Radionuclides by LSC**

*Šebesta, F., 2015*

Bárta, J.

**Radiation- and Photo-induced Preparation of Synthetic Garnets Based on LuAG (Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>)**

*Pospíšil, M. / Čuba, V., 2015*

Fejgl, M.

**Application of C-14 Activity Determination for Monitoring of the Dose Load Received by the Public**

*Světlík, I. (NPI AS CR, Řež) / Němec, M., 2015*

Kovařík, P.

**Development of Progressive Technologies for Organic Radioactive Waste Treatment**

*John, J., 2015*

Krausová, I.

**Short-Term Products of Photonuclear Reactions on Microtron and Their Use for the Instrumental Photon Activation Analysis**

*Mizera, J. (NPI AS CR, Řež), 2015*

Pavelková, T.

**Radiation Method of Actinoid Oxides Preparation**

*Čuba, V. / Šebesta, F., 2015*

Špendlíková, I.

**Development of Sample Preparation Processes for the Determination of  $^{236}\text{U}$  by AMS**

*Němec, M. / John, J., 2015*

Šťastná, K.

**Development of Processes for the Separation of Curium from Americium**

*John, J. / Němec, M., 2015*

Toufarová, M.

**Study of Reactivity of All-Carbon Nanostructures Induced by Ionizing and Non-Ionizing Radiation**

*Juha, L. (Institute of Physics, AS CR) / Pospíšil, M., 2015*

Vlk, M.

**Synthesis and Study of Isotopically Labelled Betulinines**

*John, J. / Šarek, J. (Betulinines, Stříbrná Skalice) / Kozempel, J., 2015*

Burešová, H.

**New Scintillation Detectors Based on Polystyrene**

*Šimkovic, F. (Comenius University in Bratislava) / Štekl, I. (CTU in Prague - IEAP), 2016*

## MASTER / DIPLOMA

Kukleva, E.

**Carriers of Pt and Ra Theranostic Radionuclides for Nuclear Medicine**

*Kozempel, J., 2015*

Svobodová, T.

**Determination of  $^{210}\text{Pb}$  in Selected Materials by Gamma Spectrometry**

*John, J., 2015*

Wangle, T.

**Preparation of Simulated Spent Nuclear Fuel Containing Caesium and Iodine**

*Cologna, M. (KIT Karlsruhe, Germany), 2015*

Kuba, J.

**Single Channel Analyzer in Labview for Radiochemistry Practice**

*Němec, M., 2016*

Málková, E.

**Synthesis and Study of Nanocarriers for Nuclear Medicine**

*Vlk, M., 2016*

Popovich, K.

**Biofunctionalized Nanocomposites for Singlet Oxygen Production**

*Čuba, V., 2016*

Rosendorf, T.

**Study of Radionuclide Diffusion Through Compacted Bentonite Affected by Other Barrier Materials.**

*Hofmanová, E. (ÚJV Řež, a. s.), 2016*

Vondrášková, A.

**Luminescence and Scintillation Characteristics of Nanopowder Scintillators Based on Aluminum Garnets**

*Nikl, M. (Institute of Physics, AS CR), 2016*

## BACHELOR

Florianová, M.

### **Separation of Radionuclides from Radioactive Wastes Originating from Decommissioning of Nuclear Facilities**

*Čubová, K., 2015*

Kittnerová, J.

### **Cementitious Materials in Barriers of Radioactive Waste Repositories**

*Drtinová, B., 2015*

Kománková, L.

### **Preparation of Carbon Nanostructure-Based Sorbents for $^{227}\text{Ac}/^{223}\text{Ra}$ Separation**

*Kozempel, J., 2015*

Neužilová, B.

### **Radiation Sensitivity of Microorganisms under Various Conditions**

*Múčka, V., 2015*

Nykl, P.

### **Radiation Controlled Synthesis of Ag Nanoparticles**

*Silber, R., 2015*

Pastorek, A.

### **Plasma Infrared Emission Spectra of the Rare Gases in Excited Rydberg States**

*Civiš, S. (IPCH AS CR), 2015*

Pelikánová, I. T.

**Methods for Detection of Singlet Oxygen Generated in Luminescent Nanocomposites**

*Čuba, V., 2015*

Pokorný, M.

**Separation and Determination of Technetium**

*Čubová, K., 2015*

Slezák, T.

**Photolytic and Radiolytic Removal of Heavy Metals from Aqueous Solutions**

*Pospíšil, M., 2015*

Šimúthová, Z.

**Simulation of Reactive Transport of Radioactive Contaminants in Barriers of Waste Repositories with the Use of Geochemical Modeling Code PHREEQC**

*Vopálka, D., 2015*

## PROJECTS, GRANTS AND CONTRACTUAL RESEARCH

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

### EU PROJECTS

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

**CEBAMA - Cement-based materials, properties, evolution, barrier functions**, EC FP7 CA 662147, Euratom (Horizont 2020); Vopálka, D.

### NATIONAL PROJECTS

**Research of Ionic Liquids for Application in Separation processes**, TH01020381, Technology Agency of the CR; Čubová, K., J.

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

**Inova FOND**, TG02010033, Technology Agency of the CR; Čuba, V.

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

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

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

**Teaching laboratory of radiopharmaceuticals and labelled compounds**, C120d, Ministry of Education, Youth and Sports, Czech Republic; Kozempel, J.

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

**New multistage nanodiagnostics for cancer imaging and prediction of antiangiogenic therapy efficacy**, NV16-30544A, Ministry of Health, Czech Republic; Kozempel, J.

**Recyclable decontamination solution for decommissioning of nuclear facilities**, FV10023, Ministry of Industry and Trade, Czech Republic; Němec, M.

Development and verification of laboratory experimental courses for lifelong education and for newly prepared fields of study, MŠMT CZ, Špendlíková, I.

## CTU GRANTS

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

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

**Study of Selected Critical Radionuclides Migration in Repository Barriers**, SGS13/224/OHK4/3T/14, CTU Prague; Hofmanová, E.

**Carriers of radionuclides for targeted therapy and diagnostic**, SGS15/094/OHK4/1T/14, CTU Prague; Kozempel, J.

**Partitioning of Selected Radionuclides in Advanced Nuclear Fuel Cycles**, SGS15/216/OHK4/3T/14, CTU Prague; Distler, P.

**Preparation of Theranostic Radionuclides Carriers for Nuclear Medicine**, SGS16/251/OHK4/3T/14, CTU Prague; Mičolová, P.

**Study of Speciation, Complexation and Migration of Critical Radionuclides**, SGS16/250/OHK4/3T/14, CTU Prague; Baborová, L.

**Materials Research for InovaSEED**, CZ.1.05/3.1.00/14.0301, CTU Prague; Čuba, V.

## CONTRACTUAL RESEARCH

**Research support for Safety Assessment of Deep Geological Repository**, 14SMN319, SÚRAO CZ; ÚJV Řež, Vopálka, D.

**Safety assesment of repository Richard**, C1981-16-0, SÚRAO ČR; Amec Foster Wheeler s.r.o. Slovakia, Vopálka, D.

**Research of uncertainty assesment of safety analysis of deep geological repository of radioactive waste**, SÚRAO CZ, Vetešník, A.

**Composite ion exchangers for analytical applications**, 8301404D000 TRISKEM France, Šebesta, F.

**Composite absorber for Cs-137 determination in sea water**, 8301405D000 WHOI USA, Šebesta, F.

**KNiFC-PAN composite ion exchanger preparation**, 8301501D000 BSH Hamburg Germany, Šebesta, F.

**Production of absorbers for radiochemical analyses**, 8301510D000 TRISKEM France, Šebesta, F.

**Preparation of KNiFC-PAN composite ion exchanger for Cs-137 determination in sea water**, 8301520D000 WHOI USA, Šebesta, F.

**Development and testing of absorbers for chromatographic applications**, 8301523D000 Watrex CZ, Vlk, M.

## RESEARCH FELLOWSHIPS / VISITING SCIENTISTS

### OUTGOING:

Bláha, P.

**Radiobiological and radiation chemical aspects of chromosome instability in mammalian cell subclones irradiated with ionizing radiation of different LET (Ph.D. stay)**

*Joint Institute for Nuclear Research (JINR), Dubna, Russian Federation, January 2015 – December 2016*

Bárta, J.

**Course and training “EXAFS for beginners” at the MAX II synchrotron facility**

*Max-Lab, Lund, Sweden, April 2015*

Kondé, J.

**Gamma-ray radiolysis of CyMe<sub>4</sub>-BTBP and CyMe<sub>4</sub>-BTPPhen in their solutions in cyclohexanone-based diluents or FS-13 (experimental stay, Talisman project)**

*Chalmers University of Technology, Gothenburg, Sweden, September 2015*

Bartl, P.

**Study of actinide liquid-liquid extraction kinetics using microstructured reactors (MSR)**

*Argonne National Laboratory, Lemont, USA, November 2015 – May 2016*

Bárta, J.

**Experimental & training stay at the RD18 experiment – coincidence timing resolution, streak camera, light yield measurements**

*CERN, Geneva, Switzerland, February 2016*

Procházková, L.

**Short Term Scientific Mission (COST project TD1401): Cathodoluminescence of ZnO-based samples**

*Institute of Physics, University of Tartu, Estonia, March – April 2016*

Bárta, J.

**Spectrally resolved thermoluminescence and other optical characterization techniques (experimental stay)**

*University Milano-Bicocca, Milano, Italy, June – July 2016*

Čuba, V.; Bárta, J.; Procházková, L.; Popovich, K.

**ASCIMAT School on Advanced Scintillator Materials**

*University Milano-Bicocca, Milano, Italy, September 2016*

Baborová, L.

**Modelling radionuclide transport in soils**

*Cranfield University, United Kingdom, September – December 2016*

Procházková, L.

**Short Term Scientific Mission (COST project TD1401): Spectral-time resolved measurements of ZnO:Ga-based composites**

*CERN, Geneva, Switzerland, November 2016*

Můčka, V.

**Consultation and discussion on the progress of Ph.D. thesis of Ing. Pavel Bláha**

*Joint Institute for Nuclear Research (JINR), Dubna, Russian Federation, November 2016*

## INCOMING:

Sladkov, V.

**Study of Complex Equilibriums of Actinide Ions in Solution**

*Institut de Physique Nucléaire, Orsay, France, April 2015*

Mátel, L.

**Determination of artificial radionuclides in the environment**

*Department of Nuclear Chemistry, Comenius University, Bratislava, Slovakia, April 2015*

Mokhodoeva, O.

**Study of  $^{223}\text{Ra}$  uptake mechanism by  $\text{Fe}_3\text{O}_4$  nanoparticles: towards new prospective theranostic superparamagnetic iron oxide nanoparticles SPIONs**

*V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry (GEOKHI), Russian Academy of Sciences, Moscow, Russia, November 2015*

Gäggeler, H.

**Modern Applications of Nuclear Chemistry**

*Paul Scherrer Institute, Switzerland, March 2016*

Aksenov, N., Steinegger, P.

**Joint studies in the field of prospective radiopharmaceutical radionuclides and superheavy elements research**

*Joint Institute for Nuclear Research, Dubna, Russia, October 2016*



# DEPARTMENT SEMINAR

Below, the overview is given of invited opening lectures and the respective speakers at the Department seminar in 2015 and 2016. Since 2015 the seminar has been opened to broad nuclear chemistry community and is run in collaboration with the Nuclear Chemistry Working Group of the Czech Chemical Society (<http://osjch.csch.cz/en/home/>). The invited opening lectures are recorded, archived and openly accessible for the general public (subject to approval of the speaker) in the SlidesLive system at <http://slideslive.com/seminar-kjch/prednasky>. 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](http://www.jaderna-chemie.cz/?vv=seminar_en)

## 2015

Kalvoda, L. – Koubský, T.

**Application of ab-initio simulations for determining the chemical properties**

*Department of Solid State Engineering, FNSPE CTU Prague, February 2015*

Hanslík, E.

**Influence of the NPP Temelín on the environment**

*T. G. Masaryk Water Research Institute, Prague, March 2015*

Můčka, V.

**From the history of the department of Nuclear Chemistry**

*April 2015*

Mátel, L.

**Observations from Chernobyl**

*Department of Nuclear Chemistry, Comenius University, Bratislava, Slovakia,  
April 2015*

Bendová, M.

**Solution chemistry in mixtures containing ionic liquids**

*Institute of Chemical Process Fundamentals ASCR, May 2015*

Přeček, M.

**Preparation of ultrafast pulse radiolysis and fluorescence dosimetry at ELI Beamlines**

*ELI Beamlines, Prague, October 2015*

Popelová, E.

**Decommissioning of nuclear facilities**

*ENERGOPROJEKT Prague, Division of ÚJV Řež, November 2015*

Janda, J.

**Research directions in the field of sample preparation, extraction and separation and radionuclides measurements in the Army of the Czech Republic**

University of Defence, Vyškov, December 2015

Vokál, A.

**Research and development for the support of siting of the deep underground repository**

*Radioactive Waste Repository Authority of the Czech Republic, Prague, February 2016*

Gäggeler, H.

**$^{239/240}\text{Pu}$  and  $^{236}\text{U}$  in an ice core from Tien Shan (China) and an outline of the chapter Nuclear Dating in 'Applied Nuclear Chemistry'**

*Paul Scherrer Institute, Switzerland, March 2016*

Macková, A.

**Modification and characterisation of materials by energetic ions**

*Institute of Nuclear Physics AS CR, Řež, April 2016*

Řanda, Z.

**Overview of the history of radioanalytical methods development in the Czech Republic**

*Institute of Nuclear Physics AS CR, Řež, May 2016*

Aksenov, N. Steinegger, P.

**Advances in Chemistry of Superheavy Elements**

*Joint Institute for Nuclear Research, Dubna, Russia, October 2016*

Goliáš, V.

**Radioactive mineral waters springs in Lugicum (Bohemian Massif): Quantitative and temporal frame of activation processes**

*Faculty of Science, Charles University, Prague, November 2016*

Havránek, V.

**Analytical methods on accelerated ions beams and their application**

*Institute of Nuclear Physics AS CR, Řež, December 2016*



# 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.

doc. Ing. Mojmír Němec, Ph.D.

doc. Ing. Ferdinand Šebesta, CSc.

Ing. Irena Špendlíková, Ph.D.

Ing. Alena Zavadilová, Ph.D.

### Ph.D. students:

Ing. Pavel Bartl

Mgr. Barbara Basarabová

Mgr. Yulia Buchatskaya

RNDr. Martin Daňo

RNDr. Ing. Petr Distler

Ing. Kamil V. Mareš

Ing. Soběslav Neufuss

Mgr. Jana Kondé

Mgr. Kamila Šťastná

### Technician:

Jana Steinerová

## SPECIATION 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

Mgr. Lucie Baborová

Ing. Eva Hofmanová

Ing. Iveta Holánová

Ing. Tomáš Rosendorf

Ing. Jakub Višňák

### Part time:

Ing. Helena Filipská, Ph.D.

### Technician:

Olga Múčková

## RADIATION CHEMISTRY

### prof. Ing. Viliam Múčka, DrSc.

Ing. Jan Bárta, Ph.D.

doc. Ing. Václav Čuba, Ph.D.

prof. Ing. Milan Pospíšil, DrSc.

doc. Ing. Rostislav Silber, CSc.

### Ph.D. students:

Ing. Tereza Pavelková

Ing. Kseniya Popovich

Ing. Lenka Procházková

### Technician:

Alena Matyášová

## RADIOPHARMACEUTICAL CHEMISTRY

### RNDr. Ján Kozempel, Ph.D.

RNDr. Martin Vlk

### Ph.D. students:

Ing. Petra Mičolová

Ing. Ekaterina Kukleva

### Technician:

Ing. Šárka Hráčková

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