9 Radiochemical and elementary analysis

The scope of the INE radio-analytical group is a triad of R&D projects, third parties' collaborations and development of analytical methods and instrumentation. A pool of advanced analytical techniques for elemental and isotope analysis as well as for other routine analytical applications is available both in our radioactive controlled area as well as in cold labs. Our competences are in radio-analytical sample preparation, separation techniques, handling of radioactive material, technical skills and well-developed procedures. These capabilities enable us to cover a wide spectrum of analytical tasks and are, therefore, also requested by external clients, e.g., in the fields of decommissioning of nuclear installations, nuclear waste declaration or radiopharmaceuticals. A special focus is in mass spectrometry techniques that are adapted and improved for trace element analysis and speciation studies of actinides and fission products. The use of hyphenated techniques, like Sector Field (SF)-ICP-MS or Collision Cell Quadrupole CC-Q-ICP-MS coupled to species sensitive methods, e.g., to capillary electrophoresis (CE) or ion chromatography (IC), enables speciation of actinide, of fission product and iron redox states. Supersensitive determination of actinides below ppq levels and ^{99}Tc at the ppq levels in ground-, surface and seawater is achieved by accelerator mass spectrometry (AMS); see chapter 8.5 for further details. New separation methods are developed, e.g. for the simultaneous investigation of actinides and ^{99}Tc in groundwater samples from large-scale field experiments. Method development is also integrated in research projects, e.g. in the context of decommissioning. Furthermore, the analytical group supports the INE infrastructure, is involved in various teaching activities and is responsible for education of chemical laboratory assistants.

M. Plaschke, A. Bauer, M. Böttle, M. Brandauer, D. Fellhauer, M. Fuss, J. Gaona Martinez, C. Garcia, F.W. Geyer, S. Heck, S. Hilpp, F. Huber, A. Kaufmann, T. Kisely, M. Lagos, C.M. Marquardt, S. Moisei-Rabung, F. Quinto, F. Rinderknecht, E. Rolgejzer, T. Schäfer, J. Schepperle, D. Schild, A. Seither, W. Tobie, C. Walschburger, H. Geckeis

In co-operation with:

C.-O. Krauß[a], *A. Heneka*[a], *S. Gentes*[a], *P. Steier*[b]

[a] Department of Deconstruction and Decommissioning of Conventional and Nuclear Buildings, Institute for Technology and Management in Construction (TMB), Karlsruhe Institute of Technology (KIT); [b] VERA Laboratory, Faculty of Physics, University of Vienna, Währinger Straße 17, A-1090 Vienna, Austria

Analytics for the INE R&D projects

At INE a pool of advanced analytical techniques, well-developed procedures and competences in radio-analytical sample preparation and separation, handling and technical skills are available. This includes core competences in elemental and isotope analysis, chromatographic methods and nuclear spectroscopic techniques. Our personnel is trained in handling of nuclear samples and in the operation and maintenance of instruments adapted to glove boxes. Several analytical techniques listed in Table 1 are available both in inactive and active labs. In the reporting period over twenty thousand samples were routinely analyzed providing the data mainly for the INE R&D projects but also for commercial analytical services.

For element and isotope analysis sensitive ICP optical emission and different types of mass spectrometers are available. For the trace concentration range, our ICP-MS equipment includes two quadrupole instruments (a Perkin Elmer Elan 6100 adapted to a glove-box, and a Thermo X-Series2 equipped with reaction/collision cell technology) and a sector field SF-ICP-MS (a Thermo Element XR/2 adapted to a glove box). Our routine instrumentation is continuously improved and modernized, e.g., in 2016 our box-adapted Q-ICP-MS was subject of major maintenance. The box was opened, decontaminated and parts of the sample introduction system were replaced.

SF-ICP-MS provides detection limits (DL) for transuranium elements as low as ~10^{-14} mol/L (lower ppq range) and elevated mass resolution (up to 10.000) which is beneficial for accurate determination of elements suffering from interfering species, e.g., Fe or Se. Even lower detection limits, down to 10^4 actinide atoms per sample, can be obtained by Acceleration Mass Spectrometry (AMS). For such ultra-trace determination, i.e. of actinides (An) and ^{99}Tc, new radiochemical separation methods are developed and close co-operations with the AMS community at national and international facilities are maintained (for more details cf. chapter 8.5).

Analytics for external clients

Commercial analytical service is offered to various clients on the basis of formal contract agreements. Data are recorded, documented and quality controlled according to the requirements of the clients.

Quality Control of Radiopharmaceuticals

A ^{223}Ra containing alpha-radiopharmaceutical (Xofigo®) is regularly analyzed with regard to toxic heavy metal trace impurities. ^{223}Ra acts as a calcium mimic and is indicated for patients suffering from bone metastases. Due to the short penetration of the alpha emitter, a highly-localized tumor cell killing is achieved with minimal damage to surrounding healthy tissue. We weekly analyze routine samples of the radiopharmaceutical and additional samples from the methods development.

Nuclear Waste Treatment and Decommissioning of Nuclear Facilities (KTE-HDB)
We analyze routinely samples from the KTE-HDB (KTE since 2017 Kerntechnische Entsorgung Karlsruhe GmbH, previously Wiederaufarbeitungsanlage Karlsruhe GmbH, Hauptabteilung Dekontaminationsbetriebe, HDB). Samples are classified according to their origin as ashes (from an incineration facility), LAW liquid concentrates (from an evaporation plant), annually averaged samples (from different waste treatment facilities), samples from decommissioning of nuclear facilities (e.g., demolition waste) and others (e.g., wipe tests). Samples are processed by radioanalytical separation methods and analyzed using elemental, isotope and nuclear spectroscopic techniques in order to obtain isotope concentrations and vectors. The analyzed nuclides include neutron activation and fission products (^{55}Fe, ^{63}Ni, ^{90}Sr), as well as actinides (^{233,234,235,236,238}U, ^{238,239,240,241,242}Pu and $^{242,243+244}$Cm) as constituents of spent nuclear fuel. Starting fall 2016 Cm is determined additionally in all ash samples.

Analytics for decommissioning projects

For the deconstruction of a nuclear power plant, i.e. the reactor pressure vessel, waterjet abrasive suspension cutting technique is a promising cutting method providing intrinsic technical benefits. Accelerated by a waterjet, abrasive particles cut razor-sharp through, e.g. a steel material. During the cutting process, a mixture of abrasive particles (i.e., almandine garnet) and radioactive steel particles from the cut components is generated. However, by this process the amount of secondary waste is markedly increased compared to other cutting techniques. This is presently the major limitation for the application of this technique due to tremendous disposal costs.

Tab. 1: *Analytical techniques available at INE*

Elemental and Isotope Analysis
Quadrupole Inductively Coupled Mass Spectrometry (Q-ICP-MS)
Collision Cell Q-ICP-MS (CC-Q-ICP-MS)
Sector Field ICP-MS (SF-ICP-MS)
Inductively Coupled Optical Emission Spectrometry (ICP-OES)
Atomic Absorption Spectrometry (AAS)
Flame Atomic Emission Spectrometry (F-AES)
X-Ray Fluorescence Spectrometry (XRF)

Nuclear Spectroscopic Methods
Alphaspectrometry
Liquid Scintillation Counting (LSC, conventional/high sensitivity)
Gammaspectrometry (with auto-sampler)

Other Methods
Ion Chromatography (IC) for cations and anions
Gas Chromatography (GC)
Carbon Analysis (TOC, DOC, TIC, NPOC)
Specific Surface Area Analysis (BET)
Differential Thermal Analysis (DTA)
Dilatometry
Fusion and Microwave Digestions
Gravimetry and Titrations

The project MASK ("Magnetic Separation of granular mixtures from waterjet cutting to minimize secondary waste from the decommissioning of nuclear facilities", which is a follow-up of a previous project, as well funded by BMBF) starting in 2016 aims at the development and optimization of a separation technique of radioactive steel particles from inactive abrasive grains using a magnetic filter device, thus reducing drastically the amount of activated waste. For the quantification of the separation grade an analytical method based on inductively-coupled optical emission spectrometry (ICP-OES) was developed. Separated steel-grain fractions are leached with aqua regia and the steel content is quantified by the Ni content of the steel alloy. Using this method, the separation grade could be quantified and first conclusions for optimization of the separation process could be drawn. In the abrasive particle fraction after separation of the steel particles, a remaining contamination by tiny steel particles and steel adherence to abrasive grains and void fillings could be identified with scanning electron microscopy (cf. chapter 8.3) and subsequently quantified by elemental analysis. To further reduce the remaining steel content in the purified abrasive fraction further optimization and additional understanding of the separation process is still needed. For more details cf. chapter 7.

Analytics for large-scale field experiments

In the course of the Colloid formation and Migration experiment (CFM) a bentonite source was emplaced in the shear zone at the Grimsel Test Site (GTS) in May 2014 for better understanding of the real in-situ conditions in a bentonite-based geotechnical barrier (so-called **L**ong term **I**n situ **T**est, LIT). ^{45}Ca, ^{75}Se, ^{99}Tc, ^{137}Cs, ^{233}U, ^{237}Np, ^{241}Am and ^{242}Pu and the conservative tracer Amino-G are included in the source. Hydrogeological conditions are controlled in the CFM site via a mega-packer system and monitored constantly regarding volumetric flow velocity, pH, Eh, conductivity, bentonite swelling pressure and fluorescence of the effluent (conservative tracer). Water samples are taken from the outflow of the shear zone at the tunnel wall ("Pinkel" surface packer) and from an observation borehole close to the bentonite source (distance: ~10 cm). Effluent samples are analyzed at INE concerning colloid size and concentration (Laser Induced Breakdown Detection; LIBD), chemical (ICP-MS, IC) and radiochemical composition (ICP-MS, SF-ICP-MS, LSC, γ-spectroscopy, for the abbr. see Table 1). In parallel to the LIT experiment, a mock-up test is running at INE using the same compacted bentonite source, but instead of the natural fracture, a parallel plate Plexiglas setup with a 1 mm aperture is installed in an Ar glovebox.

Both the LIT experiment and the mock-up test reveal a release of the conservative tracer Amino-G from the radionuclide containing vials embedded in the compacted bentonite ring, clearly showing a direct contact of these vials with the water conducting feature. In the mock-up test, radionuclides included in

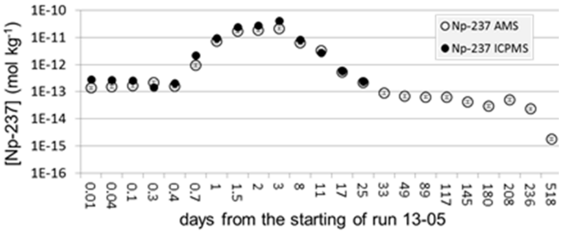

Fig. 1: *Concentrations of ^{237}Np measured with AMS (empty circles) and ICP-MS (black circles) in chosen samples of the breakthrough curve of run 13-05 until 660 days from the starting of the experiment. The last two data (at 518 and 660 days) refer to sampling at a different collection point (so-called "Pinkel").*

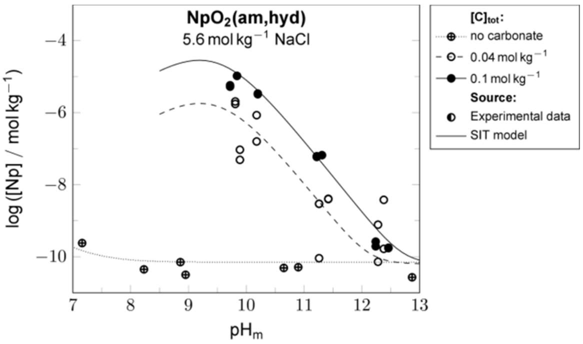

Fig. 2: *Solubility of NpO$_2$(am, hyd) in 5.6 m NaCl solutions in the absence and presence of carbonate. Solid lines calculated with thermodynamic and SIT activity models derived in the present work.*

the bentonite source with high oxidation states (^{99}Tc(VII), ^{237}Np(V),^{233}U(VI)) are released. In the LIT field experiment, a ^{99}Tc release at a very low concentration level could be assumed from SF-ICP-MS data. However, due to the isobaric interference on mass 99 from natural Ru in ICP-MS, additional accelerator mass spectrometry (AMS) measurements were necessary to quantify the exact amount of ^{99}Tc released (cf. chapter 8.5).

To test the complementarity of SF-ICP-MS and AMS for the analysis of [An] over a wide concentration range, selected samples from the previous CFM test run 13-05 (2013) have been analyzed using both techniques. While SF-ICPMS covers [An] levels from ~10 pg/g (~2×10^{10} atoms/g) and down to the DL of ~10 fg/g (~2×10^{7} atoms/g), AMS is capable to access concentration levels below 10 fg/g and down to ~10 ag/g (~2×10^{4} atoms/g). The AMS instrumental features also enabled us to develop a novel analytical method consisting in the simultaneous determination of several An without previous chemical separation from each other and with the use of non-isotopic tracers for the determination of ^{237}Np and ^{243}Am [2]. In Figure 1 a comparison of the breakthrough curve from run 13-05 of ^{237}Np determined both with SF-ICP-MS and AMS is depicted. The breakthrough curve is well-described by both analytical methods. While SF-ICP-MS provided a dense group of data limited to approx. one month from the injection, AMS allows for the long-term investigation of nearly two years. However, concentration values determined by AMS are generally lower than by SF-ICP-MS revealing an intrinsic difference in the results provided by the two analytical techniques. Possible sources of this systematic deviation will be further investigated.

Analytics for solubility studies

Carbonate minerals are ubiquitous in the natural environment, and therefore, dissolved CO_3^{2-} can be present in the groundwater horizon of a deep geological repository. Carbonate forms stable complexes with tetravalent actinides and can lead to enhanced An(IV) solubility. In a study performed in the frame of the ENTRIA project, the solubility of NpO$_2$(am, hyd) and PuO$_2$(am, hyd) is investigated in absence and presence of carbonate, in dilute to concentrated NaCl solutions with pH and [An] measured at regular time intervals until attaining equilibrium conditions. Because of the very low concentrations of Np and Pu in the absence of carbonate, and the high salt content in some of the solubility series investigated (up to 5.6 m NaCl), both LSC and SF-ICP-MS were used for the quantification of [An] in solution. Figure 2 exemplarily shows NpO$_2$(am, hyd) solubility data in 5.6 m NaCl solutions in the absence and presence of carbonate. Solid lines in the Figure 2 are calculated with the thermodynamic and activity models derived in the present work. The combination of highly sensitive analytical methods and advanced theoretical models enables us to better understand the actinide solution chemistry, further allowing to derive more reliable source terms for An(IV) under conditions relevant for nuclear waste disposal. For more details cf. chapter 4.1.

References

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[2] Quinto, F. et al., *Analytical Chemistry*, **87**, 5766, (2015).