
1. PLENARY SESSION (PLN)

Lectures

PLN.L01 (Id: 122)

RADIOCHEMICAL ANALYSIS FOR THE DETERMINATION OF RADIONUCLIDES DIFFICULT TO MEASURE FOR CHARACTERISTICS AND DECOMMISSIONING OF NUCLEAR FACILITIES

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With increasing numbers of nuclear facilities, especially nuclear power reactors, being closed in recent years and from now on, a considerable work is going to be carried out all over the world for decommissioning these nuclear facilities. For this purpose, characterization of various wastes from decommissioning is required for evaluation of the radioactivity inventory in various materials and decision making for management of the produced waste. This is carried out by quantitative determination of various radionuclides present in the materials. The neutron activation products of components and impurity in the materials used in the nuclear facilities, such as ^3H , ^{14}C , ^{36}Cl , ^{41}Ca , ^{60}Co , ^{55}Fe , ^{63}Ni , ^{133}Ba , ^{152}Eu , ^{154}Eu , and some transuranics, are the main contributors to the total radioactivity, especially in the construction materials. But some long-lived fission products, such as ^{90}Sr , ^{99}Tc , ^{129}I , and ^{137}Cs , are the major concern for materials contaminated by spent nuclear fuel. Of these radionuclides, the gamma emitting radionuclides, such as ^{60}Co , ^{133}Ba , ^{152}Eu , ^{154}Eu , or ^{137}Cs , are easily measured by gamma spectrometry. However, the determination of pure β and α emitters including ^3H , ^{14}C , ^{36}Cl , ^{41}Ca , ^{55}Fe , ^{63}Ni , ^{90}Sr , ^{99}Tc , ^{129}I and some transuranics is the major challenges, because they could not be measured without separation from the matrix of the samples and from all other radionuclides, this entitles them as the radionuclides difficult to measure. Radiochemical analysis is the only way to complete the determination of the radionuclides difficult to measure by including a complete separation of individual radionuclides from the matrix and other radionuclides before measurement by β counting, α spectrometry, or mass spectrometry. Although plenty of analytical methods have been reported for the determination of these radionuclides since the discovery of radioactivity, the suitable methods are not always available for the purpose of decommissioning. This is because a large number of samples are required to be analyzed during the decommissioning, which needs simple and rapid methods to provide a good analytical capacity. In addition, the sample matrix varies very much from concrete, graphite, exchange resin, to various metals, which requires different radiochemical methods for different sample matrix and target radionuclides. In the past few years, our laboratory developed various radiochemical analytical methods aiming at characterizati-

on of various decommissioning waste by determination of various radionuclides difficult to measure. This presentation gives an overview of these analytical methods with some examples including (1) rapid determination of tritium and ^{14}C in solid materials, such as graphite, concrete, steel, aluminium, paint, silica gel, soil, and dust; (2) determination of ^{14}C in high tritium samples, such as heavy water, waste water, and oil; (3) determination of ^{36}Cl and ^{129}I in graphite, steel, concrete, waste water, and dust; (4) determination of ^{41}Ca and ^{90}Sr in concrete; (5) determination of ^{55}Fe and ^{63}Ni in graphite, concrete, steel, aluminium, sediment, sand, waste water, seawater, and lichens.

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SPECIATION ANALYSIS OF RADIONUCLIDES IN THE ENVIRONMENT

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Naturally occurring and artificially produced radionuclides in the environment can be present in different physico-chemical forms (i. e. radionuclide species) varying in size (nominal molecular mass), charge properties and valence, oxidation state, structure and morphology, density, complexing ability etc. Low molecular mass (LMM) species are believed to be mobile and potentially bioavailable, while high molecular mass (HMM) species such as colloids, polymers, pseudocolloids and particles are considered inert. Due to time dependent transformation processes such as mobilization of radionuclide species from solid phases or interactions of mobile and reactive radionuclide species with components in soils and sediments. Therefore, the original distribution of radionuclides deposited in ecosystems will change over time and influence the ecosystem behaviour. To assess the environmental impact from radionuclide contamination, information on radionuclide species deposited, interactions within affected ecosystems and the time-dependent distribution of radionuclide species influencing mobility and biological uptake is essential. The development of speciation techniques to characterize radionuclide species in waters, soils and sediments should therefore be essential for improving the prediction power of impact and risk assessment models. The present paper will focus on analytical techniques which should be utilised for characterizing radionuclide species in the environment.

PLN.L03 (Id: 365)
**ACCELERATOR MASS SPECTROMETRY - FROM
ARCHAEOLOGY TO ASTROPHYSICS AND HUMAN
DNA****WALTER KUTSCHERA***Vienna Environmental Research Accelerator (VERA), Faculty
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The advancement of Accelerator Mass Spectrometry (AMS) some 30 years ago opened the possibility to detect long-lived radionuclides (both natural and man-made) through isotopic abundance measurements down to a level of $\sim 10^{-16}$. It thus became possible to explore our world atom by atom in almost every section of the environment at large. Worldwide there are about 80 facilities in operation covering a large range of applications. The Vienna Environmental Research Accelerator (VERA) is an AMS facility for 'all' isotopes, based on a 3 MV tandem accelerator. The principle of AMS will be described with reference to this facility, and a few selected examples will be discussed. A well-known application of AMS is radiocarbon (^{14}C) dating in archaeology and other fields, where the counting of atoms as compared to the classical way of counting beta decays increased the ^{14}C detection sensitivity by literally a factor of a million. This allowed us to date small samples of a very precious skull of the earliest humans in Europe, excavated some 100 years ago from the Mladec cave near Olomouc in the Czech Republic¹, and preserved at the Museum of Natural History in Vienna. At VERA we also started to explore areas of the nuclear landscape beyond any known isotope, such as the one around $Z = 114$, $N = 186$, where an 'island of stability' for Super Heavy Elements (SHE) has long been predicted. If there are SHE isotopes with half-lives in the hundred-million-year range, it may be possible to find traces of them in natural materials left over from the formation of the solar system. We have conducted such an AMS search and will report on recent results² and future experiments. In the previous experiment we pursued experiments to find isotopes, which have been synthesized in stars before our solar system even existed. The last example deals with events which happened during the last 50 years. Atmospheric nuclear weapons testing during the late 1950s and early 1960s led to a doubling of the ^{14}C content in the atmosphere. After the Nuclear Test Ban Treaty in 1963, the rapid distribution of the excess ^{14}C (' ^{14}C bomb peak') into the biosphere including humans allows one to study the formation of new cells in the human body after birth³. This can be accomplished by extracting DNA from millions of cell nuclei and measuring the ^{14}C content in them. Brain cells, heart cells, and fat cells have been investigated so far, leading to new insights into cell birth dates and turnover times, respectively. In addition to the biomedical application, the ^{14}C bomb peak provides an important means to study the dynamics of the CO_2 exchange between the atmosphere and the hydrosphere and biosphere, respectively. This is of utmost importance for a deeper understanding of our climate on earth.

References:

1. Wild, et al.: *Nature* 435 332 (2005).
2. Dellinger, et al.: *NIM B* (2009) on line.
3. Spalding, et al.: *Cell* 122 133 (2005).

PLN.L04 (Id: 288)
CHEMISTRY OF THE TRANSACTINIDES**JENS VOLKER KRATZ***The Johannes Gutenberg University of Mainz, Germany
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Advanced methods that have been developed and applied to study the chemical properties of the transactinide elements in comparison with their lighter homologs are presented. These include thermochromatography, and isothermal chromatography in the gas phase as well as ion-exchange and reversed-phase liquid chromatography in the aqueous phase, liquid-liquid extraction, and electrodeposition. Latest applications of these methods to studies of the chemistry of the transactinides are shown. From a systematic study of the anion-exchange behavior of Rf, it has been concluded that the properties of Rf in HCl and HNO_3 solutions are similar to those of Zr and Hf (H. Haba, et al. 2002, R. Günter, et al. 1998, H. Haba, et al. 2007). However, in HF solutions, the fluoride complex formation of Rf is significantly different to that of its homologs (E. Strub, et al. 2000, A. Kronenberg, et al. 2004, H. Haba, et al. 2004, Y. Nagame, et al., A. Toyoshima, et al. 2004). In dilute HNO_3/HF , the nitrate ion is the counter ion that removes the Rf hexafluoride di-anion more effectively from the binding sites of the anion-exchange resin than the Zr and Hf fluoride complexes. In strong HF solutions, it is the HF_2^- ion, that removes Rf much earlier from the anion-exchange resin than the much stronger fluoride complexes of Zr and Hf (H. Haba, et al. 2004, Y. Nagame, et al.). Chloride and fluoride complexation of Db has been studied in reversed-phase extraction chromatography with an aliphatic amine (W. Paulus, et al. 1999). Chelating of Db with α -hydroxyisobutyrate was shown to be much stronger than for tetravalent and trivalent metal ions (M. Schädel, et al. 1992). Sg has been eluted from a cation-exchange column as Sg oxyfluoride complex (M. Schädel, et al. 1997). In 0.1 M HNO_3 , hydrolysis of Sg is weaker than that of Mo and W (M. Schädel, et al. 1998). Successive deprotonation leads to a cationic species for Sg, while for Mo and W, neutral hydrolysed species are eluted from a cation-exchange column. In the gas phase, Sg was volatilized as SgO_2Cl_2 (A. Türler, et al. 1998) and as $\text{SgO}_2(\text{OH})_2$ (S. Hübener, et al. 2001). Elements 107 and 108 were transported in the gas phase as BhO_3Cl (R. Eichler, et al. 2000) and HsO_4 (Ch. E. Düllmann, et al. 2002). In (A. von Zweidorf, et al. 2004), the highly volatile HsO_4 was deposited on a thin layer of NaOH in the presence of water vapor, thus forming a salt in analogy to the formation of an osmate (VIII). This shows that HsO_4 , like OsO_4 , is an acid anhydride. Most recently, first chemical studies were performed with elements 112 (R. Eichler, et al. 2007) and 114 (R. Eichler, et al. 2009). Element 112 in its atomic state was shown to be very volatile, but unlike radon, reveals a metallic interaction with a Au surface (R. Eichler, et al. 2007). Preliminary results on the volatility of element 114 in its atomic state indicate that it is a very volatile element with a weaker metallic interaction with a Au surface than 112 (R. Eichler, et al. 2009). This surprising result needs to be confirmed.

PLN.L05 (Id: 366)**ELECTROCHEMICAL SEPARATION OF ACTINIDES FROM MOLTEN LiCl-KCl ON SOLID Al CATHODES****C. NOURRY, P. SOUČEK, R. MALMBECK and J.-P. GLATZ***European Commission, JRC, Institute for Transuranium Elements, P.O. Box 2340, 76125 Karlsruhe, Germany*

To comply with the sustainability goals defined for innovative reactor systems, a waste minimization through recycling of all actinides is required and can be realised using a so-called Partitioning and Transmutation (P&T) concept inherent to the reactor systems. It is obvious that the corresponding fuel cycles will play a central role because an efficient and selective recovery of the key elements is mandatory. One of the major goals is to develop and implement clean waste technologies using a global actinide management. For this purpose, advanced fuel cycle processes with full actinide fuel technologies and ultimate waste forms with a minimal content in actinides (< 0.1%) are required. This necessitates that Am and Cm can be selectively separated from lanthanide fission products, certainly the most difficult and challenging task in advanced reprocessing of spent nuclear fuel due to the very similar chemical behaviour of these elements. The separation can be derived from aqueous or pyrochemical partitioning processes. Both have advantages and disadvantages and should be applied in a complementary way. In Europe, significant progress was made for both routes in international collaborations in the frame of the European research projects PARTNEW, PYROREP, EUROPART and ACSEPT. Pyrochemical processes rely on refining techniques in high temperature (around 500 °C) molten salt (e.g. LiCl/KCl eutectic). In nuclear technology, these processes are mostly based on electrorefining or on extraction from the molten salt phase into liquid metal. In the electrorefining process the fuel is anodically dissolved, releasing actinides and lanthanides mainly as MCl_3 species into the molten salt electrolyte. The separation is based on electrodeposition of the actinides on a cathode leaving the fission products in the bulk. The choice of cathode material onto which the actinides are deposited during electrolysis is essential. Molten Cd and Bi have been widely used because they are reactive electrodes, i.e. they form stable alloys with the actinides. This alloying inhibits the re-dissolution of the electrodeposited trivalent actinides by a comproportionation reaction with not deposited An(III) in the salt melt and thus allows an efficient recovery of An metal. The redox potentials on solid cathodes show a difference in the reduction potential between actinides and lanthanides which is about 3 times higher than for liquid cathodes, improving obviously a separation of these two element groups. Solid Al cathodes unite both advantageous properties, i.e. the large difference in the electrodeposition potential and the reactivity to form alloys. Therefore we use Al electrodes for our electrochemical partitioning studies. In view of a grouped actinide recycling, foreseen in the fuel cycles of new generation reactors, electrorefining experiments using a fuel with the overall composition $U_{61}Pu_{22}Zr_{10}Am_2Ln_5$ were carried out. The metallic alloy was anodically dissolved in a LiCl-KCl eutectic and the actinides were co-deposited on Al cathodes as alloys, leaving more than 98% of the lanthanides in the salt phase. The results of a multiple-run electrorefining experiment without changing the salt bath, are very promising in view of a large-scale development of pyroreprocessing in advanced nuclear fuel cycles. They demonstrate that a grouped actinide recovery better than 99.9% are possible and therefore represent an important step towards achieving the sustainability goals of future reactor systems.

PLN.L06 (Id: 297)**RADIOACTIVE AND GASTRIN RELEASING PEPTIDE RECEPTOR SPECIFIC GOLD NANOPARTICLES IN MOLECULAR IMAGING AND THERAPY OF CANCER****KATTESH KATTI***University of Missouri, Columbia
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The most recent study involving 77,000 North American men has shown that regular prostate specific antigen (PSA) screening did not save a significant number of lives over 10 years. Development of cancer receptor specific gold nanoparticles will allow efficient targeting/optimum retention within tumors and thus provide synergistic advantages in oncology as it relates to molecular imaging and therapy of prostate cancer. Bombesin (BBN) peptides have demonstrated high affinity toward Gastrin Releasing Peptide (GRP) receptors *in vivo* that are over expressed in prostate, breast, and small cell lung carcinoma. We have synthesized a library of GRP receptor-avid nanoplateforms by conjugating gold nanoparticles (AuNPs) with Bombesin (BBN) peptides. Cellular interactions and binding affinities (IC50) of AuNP-BBN conjugates toward GRP receptors on human prostate cancer cells have been investigated in detail. *In vivo* studies using AuNP-BBN and its radiolabelled analog $^{198}AuNP-BBN$, exhibiting high binding affinity (IC50 in microgram/nano/pico molar ranges), have provided unequivocal evidence that AuNP-BBN constructs are GRP receptor specific showing accumulation with high selectivity in GRP receptor rich pancreatic acine in normal mice and also in tumors in prostate tumor bearing SCID mice. The selective uptake of AuNP-BBN peptide analogs have demonstrated realistic clinical potential in molecular imaging via X ray CT techniques as the contrast numbers in prostate tumor sites are several fold higher as compared to the pretreatment groups ($\Delta HU = 150$ units). On the therapeutic front, recent results on therapeutic efficacy and clinical translation efforts of $GA-^{198}AuNP$ (NBI-29) - a glyco protein matrix-conjugated radioactive gold nanoparticulate therapeutic agent will be discussed. Intratumoral administration of a single dose of β -emitting $GA-^{198}AuNP$ (70 Gy) resulted in clinically significant tumor regression and effective control in the growth of prostate tumors over 60 days and the overall reduction in tumor volume reached an unprecedented 82%. This presentation will include: (a) details on clinical utility of AuNP-BBN as a tumor specific molecular imaging agent for X ray CT imaging of prostate and other GRP receptor positive cancers; (b) details on clinical translation efforts of $GA-^{198}AuNP$ (NBI-29) with early Phase I clinical trial results involving therapeutic efficacy in treating prostate tumor bearing dogs. The overall oncological implications on how $GA-^{198}AuNP$ and cancer specific peptide conjugated gold nanoparticles will provide significant benefits to prostate tu, pancreatic, and breast tumor patient community will be discussed.