

9. SEPARATION METHODS, SPECIATION (SEP)

Lectures

SEP.L01 (Id: 241)

NATURAL ORGANIC MATTER (NOM) CHARACTERIZATION IN URBAN - AND NUCLEAR- WASTE IMPACTED WATERS USING MULTI- RESPONSE FLUORESCENCE

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It is well established that natural organic matter (NOM) plays an important role in metal speciation, in the transport of radioactive contaminants, in the acid-base control of natural waters, etc. NOM originates from various natural and human-impacted processes, and its constituents feature various molecular sizes, functional groups, and other properties which could be important for metal or radionuclide speciation. In this work, NOM impacted by two contrasting human impacts was analyzed using by multiresponse fluorescence, decoupled with the multi-way resolution routine PARAFAC. In the first site at Chalk River, Ontario, Canada, water downstream from a former low-level waste infiltration pit and deep groundwaters were sampled. The second site is surface water from the Grand River in Cambridge, south-central Ontario, Canada, which is impacted by urban activities and agriculture. Our analysis was done on selections of raw water, fractions isolated by ultrafiltration, and solid phase aqueous extracts (SPE). The fluorescence spectra of the NOM, resolved with PARAFAC, showed three common features: humic-like components, at excitation/emission wavelengths 325-350/450-475 nm, fulvic-like components at 325/380-420 nm and protein-like components, at 275/300 nm. Most of the NOM from the urban-impacted sites and the clean Chalk River site was submitted to ultrafiltration, with >4% of the total in the large fraction (colloidal range, larger than 5000 Da). The proportion of colloidal-sized material in the NOM was substantially higher in the Chalk River contaminated water, with ~18-26% of the total. The protein-like components in the contaminated Chalk River water were largely removed by ultrafiltration, but less so in the clean Chalk River sample and the urban-impacted waters. SPE preferentially removed the protein-like component in the contaminated Chalk River water (typically 89-95% signal decrease), but had a limited effect on humic-like and fulvic-like components. The fulvic-like and humic-like components of the urban-impacted samples and from Chalk River behaved fairly similarly, exhibiting a slight enrichment of humic-like material in the large (colloidal) fraction. Finally, addition of metals (Cu and Co) to Chalk River sample colloidal fractions changed the fluorescence signals for the humic-like and fulvic-like components, but not the protein-like components. In contrast, there was no significant change in signal with addition of Cs. In conclusion, multirespon-

se fluorescence is a promising technique to determine the origins and dynamics of NOM in field samples, with potential application to metal (Cu) and radionuclide binding (with Co, but not so for Cs). Other new applications will be discussed.

SEP.L02 (Id: 46)

EFFECT OF SHORT CHAIN CARBOXYLIC ACIDS ON U(VI) SORPTION ON SILICA AND RUTILE STUDIED BY THE USE OF CAPILLARY ZONE ELECTROPHORESIS

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Capillary zone electrophoresis (CZE) was used to study of uranyl sorption on silica and rutile in the presence of short chain carboxylic acids. These acids are chosen as they may be released into the environment by decay of plant, animal and microbial tissues¹. They can be also used as simple models of more complicated natural organic matter. First, separation and simultaneous determination of a number of short chain carboxylic acids (oxalic, formic, acetic and propionic) and U(VI) with direct UV detection is developed for analysis of solutions after the U(VI) sorption by CZE. From literature data it is known that complex formation of U(VI) with carbonate, used as a carrier electrolyte, allows U(VI) to be determined, as negatively charged species, in a single run with organic acid anions². Matrix effect of Si(IV) (possible silica dissolution products) and perchlorate (added for constant ionic strength in sorption experiments) on the separation of U(VI) and organic acids is investigated. The influence of methanol in carrier electrolyte on separation selectivity of given mixture is also studied. Under the chosen conditions calibration plots are linear in two ranges of concentration from $\sim 1 \times 10^{-5}$ to 1×10^{-3} M for oxalate, acetate, propionate, U(VI) and $\sim 1 \times 10^{-4}$ to 1×10^{-3} for formate. Accuracy of the procedure is checked by the "added-found" method in standard mixture solutions. Relative standard deviation is within the range of 2-10% and the recovery is in the range of 90-110%. This method is applied for the analysis of real solutions after U(VI) sorption on silica and rutile in the presence of short chain carboxylic acids. The sorption experiments indicate that given organic acids decrease uranium sorption either on silica or on rutile. These experiments demonstrate that short chain carboxylic acids can influence the mobility and chemistry of uranium in the environment.

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SEP.L03 (Id: 313)
HETERONUCLEAR HYDROLYSIS COMPLEX OF THORIUM(IV) AND IRON(III)

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The solubility of the Th(IV)/Fe(III) system has been studied as function of pH in the range 2.00-3.50. In the individual systems of thorium(IV) and iron(III) precipitation takes place due to formation of hydrolysis products. However, in the mixed Th(IV)/Fe(III) system precipitation of ferrihydrite takes place at low pH value, pH = 2.00, whereas at higher pH no precipitation was observed after 20 months. The mixed heteronuclear complex of composition $[\text{Th}_2\text{Fe}_2(\mu_2\text{-OH})_8(\text{H}_2\text{O})_{12}]^{10+}$ was formed in solution, with Th-Th, Th-Fe and Fe-Fe distances of 3.95 and 3.949; 3.42 and 3.4; 3.05 and 2.921 Å as determined by EXAFS and LAXS, respectively. Two and four line ferrihydrite was formed in solutions at low pH values, 2.00-2.30, as identified by X-ray diffraction (XRD). SEM analysis of these precipitates showed that some of them contained only iron, whereas the others contained both iron and thorium. Mixed Th/Fe system showed increased solubility what may affect the design of tanks for spent nuclear waste.

SEP.L04 (Id: 229)
NEW POLAR FLUORINATED DILUENTS FOR DIAMIDE LIGANDS

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Nuclear waste management is nowadays based on the usage of light hydrocarbon liquids as diluents in extraction technology. PUREX process deals with tributylphosphate solution in n paraffins; various extraction processes developed for high level waste treatment also use light hydrocarbon diluents (e.g. dodecane) to be PUREX-compatible. Heavy polar diluents that are widely studied for purposes of extraction are an alternative to light diluents. The most attractive among them are fluorinated diluents. Polar fluorinated diluents have some advantages over hydrocarbons, e.g. high chemical and radiation stability, high density, low fire risk. Fluorinated compounds of various classes (ethers, esters, nitroaromatic compounds, fluo-

rinated sulfones) have been tested as possible diluents for neutral extractants. The using of polar fluorinated diluents in solvent extraction allow to significantly increase the extraction capacity and solubility of neutral ligands. In the present work new polar fluorinated aromatic-free compounds were tested as diluents for various diamide extractants. New diluents - 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptylmethyl ether (DDFHME), 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl acetate (DDFHA) 1,1,2,2,3,3,4,4,10,10,11,11,12,12,13,13-hexadecafluoro-6,8-dioxatridecane (Formal-2) were compared with well known meta-nitrobenzotrifluoride (F-3) and trifluoromethylphenyl sulfone (FS-13). The extraction ability of diamides of dipicolinic acid, diamides of 2,2'-dipyridyl-6,6'-dicarboxylic acid, diamide of diglycolic acid in polar diluents towards some radionuclides and post-transition metals were studied. It was found that the extraction ability of diamide ligands could be highly increased while using DDFHME and Formal-2 as diluents.

SEP.L05 (Id: 18)
SOLVENT EXTRACTION STUDIES FOR THE SEPARATION OF RADIOARSENIC, RADIOGERMANIUM AND RADIOGALLIUM

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Solvent extraction techniques were developed to separate ⁷²As from bulk amounts of proton-irradiated germanium dioxide targets, ⁶⁸Ge from proton-irradiated gallium(III) oxide targets and ⁶⁸Ga from parent ⁶⁸Ge. Several methods have been reported to isolate arsenic radionuclides from irradiated Ge and germanium dioxide targets ^{1,2}. In this work the germanium dioxide target, irradiated with 17 MeV protons, was dissolved in either HCl or KOH. Then the ratio of As(III) to As(V) was determined via thin layer chromatography using ⁶⁰Si phase plate as a stationary phase and a mixture of sodium bitartrate/methanol in the ratio of 3:1 as the mobile phase. Our separation method utilizes the observation that arsenic (III) can be extracted selectively and quantitatively by cyclohexane from hydrochloric acid solution containing alkali iodide ¹. The influence of concentrations of different acids and of KI as well as the effect of various organic solvents was investigated. Optimally, the extraction of As(III) into cyclohexane occurred with 4.75M HCl and 0.5M KI, and its back-extraction into the aqueous phase with water containing 0.1% hydrogen peroxide. The overall radiochemical yield of the radioarsenic separation was about 95±2%. The method was used in the separation of high purity ⁷²As, a potentially useful positron emitter, formed via the ⁷²Ge(p,n)-reaction. An optimised method of separation of the radionuclide ⁶⁹Ge, used as a tracer in gallium/germanium separation studies, was worked out. The gallium (III) oxide target, irradiated with 17 MeV protons, was dissolved in 8M sulphuric acid and used as a stock solution. To an aliquot HCl was added

and its concentration adjusted to 0.4M in order to transfer germanium to the chloride form. With this the extraction of radiogermanium using toluene was then studied at varying concentrations of H₂SO₄. From a solution of 8M sulphuric acid and 0.4M HCl the extraction was maximum. Using the optimised separation, the radionuclide ⁶⁸Ge, formed via the ⁶⁹Ga(p,2n)-reaction, was separated from a gallium (III) oxide target irradiated with 45 MeV protons. Further on, the separation of ⁶⁸Ga from the parent ⁶⁸Ge was investigated. The method is based on anion exchange solvent extraction using Aliquat 336 in xylene from hydrochloric acid³. Aliquat 336 in xylene has been used for the first time for separations involving radiogallium and radiogermanium. Optimisation studies were related to the influence of HCl concentration and different solvents. The solvent extraction using Aliquat 336 in xylene led to a high separation yield of ⁶⁸Ga from its parent ⁶⁸Ge. The time of separation was short, about 20 min, the contamination from ⁶⁸Ge was less than 0.1 % and the final product was obtained in 0.5M KOH.

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NOVEL SOLID-PHASE EXTRACTANTS FOR RADIONUCLIDE PRECONCENTRATION

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Preconcentration of radionuclides is a necessary stage for their accurate determination in aqueous natural and technological solutions. Sorption methods are the most perspective for selective recovery and separation of radionuclides from other elements. Various sorption materials containing complexing groups have been widely applied due to their selectivity and high degree of recovery. It is especially important for radionuclide preconcentration from high salinity nitric acid solutions generated under the reprocessing of spent nuclear materials. The solid-phase extractants have gained considerable attention for preconcentration of trace elements. Special interest is given to the solid-phase extractants prepared by non-covalent immobilization of ligands on the surface of solid supports. For actinide and lanthanide preconcentration some organophosphorus and other ligands (tri-n-butylphosphate, carbamoylmethylphosphine oxide, malonamides, amines, macrocyclic compounds, eTc.) have been widely used. These reagents are usually immobilized on silica-based matrices, polystyrene and polyacrylate polymers and other supports. In the present work we used ionic liquids and various ligands as reagents for immobilization and the most perspective solid supports to prepare the novel solid-phase extractants designed for radionuclide precon-

centration. The ability of ionic liquids to be kept on solid surfaces and to reveal ion-exchange and complexing properties makes possible the synthesis of novel type solid-phase extractants. We prepared the solid-phase extractants by the non-covalent immobilization of tetraalkyl phosphonium and 1-alkyl-3-methyl imidazolium ionic liquids with different anions and studied their sorption properties. The matrices with large surface and high sorption ability were chosen as supports: multi-walled carbon nanotubes, highly cross-linked polystyrene, Amberlite XAD-7 and polyacrylonitrile fiber. The conditions of ionic liquid immobilization and radionuclide recovery were determined. The application of prepared solid-phase extractants for preconcentration of actinides, rare earth elements and radiopalladium from 1-3M nitric acid solutions was demonstrated. Special attention was being paid to the use of carbon nanotubes as a support for solid-phase extractant preparation. Carbon nanotubes have come under intense multidisciplinary study due to their unique physical and chemical properties, which make them attractive for myriad uses including radiochemistry. The features of nanostructure and large surface ensure high sorption ability of carbon nanotubes and the possibility for their modification. We prepared the solid-phase extractants on the base of multi-walled carbon nanotubes "Taunit"® (Russia) modified with ionic liquids and various ligands. Experimental data have shown high efficiency of the novel solid-phase extractants for radionuclide preconcentration from nitric acid solutions.

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SPECIATION AND THERMODYNAMICS OF LANTHANIDE AND ACTINIDE IONIC SOLUTIONS DESCRIBED USING THE MEAN SPHERICAL APPROXIMATION (MSA)

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A theoretical description of speciation and of the thermodynamic properties of lanthanide and actinide ionic solutions is proposed in the framework of the mean spherical approximation (MSA)¹⁻⁴. In this model the ions are regarded as charged hard spheres immersed in a dielectric continuum representing the solvent (water). An interesting feature of the MSA is that it yields analytic expressions. To account for complex formation, the multivalent cation (a lanthanide or an actinide ion) is assumed to possess a finite number of sites on its surface, on which anions can bind⁵. This property leads to the formation of 1:1,

1:2, 1:3,... complexes according to a stepwise complexation-equilibrium process. Explicit formulas are obtained for the speciation and the thermodynamic properties (osmotic and activity coefficients) within this model. They include the effects of complexation and electrostatic interactions. The model is applied to the case of binary and ternary aqueous solutions of divalent, trivalent and tetravalent lanthanides and actinides.

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SEP.L08 (Id: 302)

BENTONITE STABILITY AND MIGRATION BEHAVIOR OF SOME CRITICAL RADIONUCLIDES

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The contribution is focused on geotechnical, chemical, geochemical and mineralogical research of bentonite stability with the aim to determine the effect of saturation medium composition and loading by heat on bentonite stability. The main part the research is directed to the experimental results of bentonite and bentonite leachate samples obtained for the bentonite interaction under laboratory or in situ experiments. The markedly different values of Na⁺, K⁺, Ca²⁺, Mg²⁺ and SO₄²⁻ ion concentrations are caused by the mineralogical transformation and interaction of the original bentonite material with synthetic granitic water. Bentonite is included in buffer and backfill materials in most high-level waste repository concepts. Its low hydraulic conductivity, micro-porous structure, good sorption properties and plasticity make this material an effective barrier - protecting the canister and restricting the movement of radionuclides released from the waste packages after canister failure. The effect of the variable aqueous phase composition on bentonite stability using Ca-Mg and Na-Ca bentonites for the experiments was studied. The synthetic granitic waters with the higher concentration of the K⁺ and Mg²⁺ cations were applied for the study of bentonite stability. These investigations were carried out for the 12 months under the laboratory and temperature increase conditions (95 - 100 C). The mineralogical transformation and characterization of the solid phase by RTG diffraction, infrared spectroscopy and cation exchange capacity measurement were evaluated after the termination of these experiments. These mixtures were simultaneously applied for the sorption study of the selected radionuclides (¹³⁴Cs, ¹²⁵I and ⁹⁹TcO₄) with the aim to evaluate the changes of sorption behaviour as the result of bentonite with synthetic granitic water interaction. The geochemical software tool Geochemist's Wor-

kbench calculated the simple thermodynamic model of bentonite transformation during bentonite with synthetic waters interaction. It was confirmed that smectites are transformed to more stable silicates phases, such as illite/smectite mixed layers, illite. The kinetics of the smectite to illite reactions strongly depends on temperature, time and K⁺ porewater concentrations. Radionuclides of ⁹⁹Tc and ¹²⁹I may exist in the various oxidation states in the dependence of the redox conditions of the aqueous environment. Technetium exists in oxidation states from +7 to -1. In natural environments, the most stable oxidation states of technetium are +7 and +4 under oxidizing and reducing conditions, respectively. The -1, +5, and molecular I₂ [I₂⁰(aq)] oxidation states are those most relevant for iodine in environmental systems. Iodine usually exists in fresh water in the -1 oxidation state as iodide (I⁻), in alkaline and marine environments, iodine usually exists in the +5 oxidation state as iodate (IO₃⁻).

SEP.L09 (Id: 20)

SPECIATION OF CURIUM(III) AND EUROPIUM(III) IN HUMAN URINE SAMPLES

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Due to their radiation and heavy metal properties, radionuclides represent a serious health risk to humans in case of incorporation. To understand their toxicity, transport, deposition and elimination in the human organism, it is therefore crucial to elucidate their chemical behavior and properties on a molecular level. For trivalent actinides originating from nuclear power plants knowledge about their metabolism is very limited. In case of incorporation, they tend to accumulate in liver and skeleton and are excreted to maximum 10 - 20 % within the first week. Nevertheless this excretion occurs mainly through the kidneys, which are known to be particularly radiation sensitive. To address the lack of knowledge, we studied the speciation of curium (as a representative of trivalent actinides) and europium (as the lanthanide analogue) in human urine and their complexation with single constituents. Since both of these heavy metals exhibit unique fluorescence properties, time-resolved laser-induced fluorescence spectroscopy (TRLFS) is an adequate tool for this purpose. Fresh 24-hours-urine samples were collected from healthy volunteers and analyzed within few days. The inorganic composition of all samples was determined using mass spectrometry with inductive coupled plasma (ICP-MS) and ion chromatography (IC). Then all samples were spiked in vitro with curium or europium and single as well as time-resolved laser-induced fluorescence spectra were measured. We analyzed at least 10 different urine samples and were able to divide all samples into two different groups according to their fluorescence spectra. We found that all samples with pH below 5.6 and all samples with pH above 6.0 each exhibit strikingly similar spectra. Compared to each other the spectra of both groups are very different and therefore easy to distinguish.

Furthermore the lifetime of the metals in samples with higher pH is substantially longer than in samples with lower pH. ICP-MS and IC analysis revealed that the inorganic composition of samples which exhibit the same fluorescence spectra can vary broadly within magnitudes. Therefore the most important factor influencing the speciation of metals in human urine does not seem to be the composition but rather the pH value. To identify the dominating species we also recorded the fluorescence spectra of both metals in electrolyte solution containing all inorganic but no organic components of urine. Furthermore we studied the complexation of both metals with urea and citric acid as main organic urine constituents. Comparing the measured spectra and lifetimes with this reference data, we found that at lower pH a complex citric acid species dominates the speciation of both metals while at higher pH the spectra were identical to those in electrolyte solution ruling out any involvement of organic ligands. The exact nature of this inorganic metal species has yet to be clarified.

SEP.L10 (Id: 171) COMPLEXATION OF CURIUM(III) WITH PYOVERDIN-MODEL COMPOUNDS

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The aerobic groundwater bacterium *Pseudomonas fluorescens* (CCUG 32456) isolated from the aquifers at the Äspö Hard Rock Laboratory, Sweden, secretes siderophores of the pyoverdinin-type. Besides iron(III), these unique bioligands are also able to form strong complexes with actinides (e.g., U(VI), Np(V), and Cm(III))¹⁻³. For U(VI) and Np(V) we could show that mainly the catecholate and to less extent the hydroxamate functionalities of the pyoverdinin molecule are involved in the actinide coordination^{1,2}. For Cm(III) it is still not clear which functional group of the pyoverdinin molecule causes the great stability constants. In general, Cm(III) interactions with pyoverdinin-model compounds and especially with chromophore-models are poorly understood. To address this lack, we present findings regarding the speciation of Cm(III) with 2,3-dihydroxynaphthalene in aqueous solution by time-resolved laser-induced fluorescence spectroscopy (TRLFS) at trace Cm(III) concentrations (0.3 µM) over a wide pH range. TRLFS is a well established direct speciation technique for investigating the complexes formed by actinides in both geochemical and biochemical environments. Four Cm(III)-dihydroxynaphthalene species of the type MxLyHz could be identified from the spectroscopic measurements. The stability constants of these strong Cm(III)-bioligand complexes and their individual spectroscopic properties (excitation and emission spectra, lifetimes) are reported. TRLFS shows that Cm(III)-dihydroxynaphthalene species cause a strong red shift of the characteristic Cm(III) (aq) emission band at 593.8 to 614.4 nm. The findings of our Cm(III) speciation study in comparison with the literature indicate a stron-

ger affinity of Cm(III) to the catechol functionality of the pyoverdinin molecules as found for U(VI) and Np(V).

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SEP.L11 (Id: 204) THE POURBAIX DIAGRAM OF ASTATINE IN AQUEOUS MEDIUM

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Astatine (At), element 85, is below iodine in the periodic table of elements. One of its isotopes, ²¹¹At, is a promising candidate as a therapeutic agent in nuclear medicine¹. Although it is clear that much of the chemistry described for halogens is applicable to astatine, a more metallic character is expected as compared to its nearest halogen neighbor, iodine. However, At chemistry in aqueous solution remains poorly understood. There are no stable isotope of astatine, its longest-lived isotope having a half-life of 8.3 h. All investigations are thus derived from radiochemical studies at ultra-trace concentration, typically between 10⁻¹² and 10⁻¹⁵ mol/L and no spectroscopic tools can be used to identify unambiguously the formed species. The chemical forms of astatine are usually deduced from its behavior in given conditions with respect to the behavior of expected model compounds. In this work, a combined experimental and theoretical approach is used to define the potential/pH diagram of astatine (Pourbaix diagram) in non-complexing medium with the aim of answering the two main questions raised in the literature: does At(0) exist in aqueous solution and what is the chemical form of At(III), if it exists? The experimental methodology considers that a given species is characterized by its distribution coefficient (D) experimentally determined in a biphasic system. The change in speciation arising from a change in experimental conditions is observed by a change in D value². Unlike most of previous studies, we present a quantitative analysis of the experimental data based on equilibrium reactions, to identify the species formed and derive the thermodynamic parameters.

The theoretical methodology is based on quasi-relativistic quantum chemistry computations and solvation free energy calculations using polarizable continuum models. The results show that At at the oxidation state 0 cannot exist in aqueous solution. The three oxidation states present in the range of water stability are At(-I), At(I) and At(III) and exist as At^- , At^+ and AtO^+ , respectively, in the 1 to 2 pH range³. When the pH increases, AtO^+ reacts with water to form two hydrolysis species, $\text{AtO}(\text{OH})$ and $\text{AtO}(\text{OH})_2^-$.

thus enhancing the extraction capabilities and the role the side groups, in protecting the molecule against the radiolysis will be discussed.

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THE INFLUENCE OF THE SIDE GROUPS OF THE BTP AND BTBP TYPE LIGANDS ON LIQUID-LIQUID EXTRACTION OF ACTINIDES AND LANTHANIDES

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Fossil fuels are no longer a choice for energy production, both because of their diminishing availability and the by-products of their combustion processes. A possibility to replace the fossil fuels would be utilization of nuclear power. No green-house gases are produced, but as any industry, it generates wastes. A proper plan for reusing valuable nuclides, both by preparing another kind of fuel or by transmutation, which, besides transforming the long-lived nuclides into short-lived ones, generates energy, seem to be P&T (partitioning and transmutation). The partitioning is the process of separation nuclides from the rest of the waste and involves a separation process which utilize an organic solvent containing one or several molecules and a diluent for extraction purposes. Among the last extractant families developed in Europe, the 2,6-di(5,6-diethyl-1,2,4 triazin-3 yl)pyridine (BTP) and 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)-[2,2']bipyridine (BTBP) were/are the most promising molecules for an eventual industrial application. The present work focuses on several aspects insufficiently studied before and concerning the influence of the side groups attached to the "core" of the molecule, for both BTPs and BTBPs. The importance of the diluents regarding both the extraction capabilities of the formed system and the role of the diluents in protecting the molecule against radiolysis without adding a scavenging molecule will be very briefly discussed. However this part will not be further developed here. The importance of the side groups added to the molecule first to facilitate dissolution, easing the phase transfer and

Posters

SEP.P01 (Id: 306)

STUDY OF HDEHP-PAN SOLID EXTRACTANTS FOR ^{90}Sr DETERMINATION

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Application of solid extractants containing di-(2-ethylhexyl)phosphoric acid (HDEHP) in the support based on modified polycrylonitrile (PAN) has been proposed at the CTU in Prague, Department of Nuclear Chemistry, for the determination of ^{90}Sr by means of measuring the activity of its ^{90}Y daughter utilising a procedure similar to that developed by Burnett et al. in 1975 for the determination of ^{228}Ra ¹. For the introductory study, ^{152}Eu and ^{133}Ba were used as chemical homologues of ^{90}Y and ^{90}Sr . For these radionuclides, dependences of mass distribution coefficients (D_g) on the nitric acid concentration were measured for several types of HDEHP-PAN solid extractants; the results obtained were compared with the data presented by Horwitz et al. in his 1975 paper². For one of the solid extractants, similar dependence was also determined for the hydrochloric acid. The mechanism of the Eu^{3+} and Ba^{2+} ions was confirmed to follow the theoretical two-phase equation for the chelating extractants. The shifts of the curves measured for various solid extractants could be ascribed to the different amounts of HDEHP in the extractants. Further, influence of the presence of nitrates (total salinity), calcium (Sr homologue) and iron (Y major interferent) ions on the D_g values were determined. For both Eu and Ba, a decrease of D_g values with increasing nitrates concentration was observed. As expected, the $D_g(\text{Eu})$ values were suppressed already by relatively low iron concentrations. The influence of iron ions could be masked by the addition of ascorbic acid if working in hydrochloric acid. The $D_g(\text{Eu})$ values were not influenced by the presence of calcium while, as expected, uptake of barium at low acidities was strongly suppressed already by relatively low calcium concentrations. The results obtained make application of solid extractants containing HDEHP in PAN support prospective for ^{90}Sr determination.

This work was supported by grant MSM 6840770020.

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SEP.P02 (Id: 312)

INVESTIGATION OF MOBILITY OF PLUTONIUM IN ENVIRONMENTAL AND NUCLEAR WASTE SAMPLES USING SEQUENTIAL EXTRACTION

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Fractionation of plutonium isotopes (^{238}Pu , $^{239,240}\text{Pu}$) was conducted for environmental samples including soil and sediment, and bio-shielding concrete from decommissioning of nuclear reactor in this work. The fractionation were carried out by dynamically sequential extraction system using an on-line sequential injection (SI) combined with a specially designed extraction column. Plutonium in the fractions from the sequential extraction was separated by ion exchange chromatography and measured using α spectrometry. Different distributions of plutonium in environmental samples and bio-shielding concrete were observed. The analytical results show a higher mobility of plutonium in concrete sample than in environmental samples analyzed in this work, which means attention should be paid to the treatment and disposal of low level concrete waste from decommissioning of nuclear facilities.

SEP.P03 (Id: 149)

SOLVENT EXTRACTION OF AMERICIUM BY IMIDOPHOSPHATES

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Solvent extraction was described for the analytical determination of americium in the liquid samples. Arylestere of imidodiphosphoric, imidothiodiphosphoric, imidodithiodiphosphoric acids and tetraphenylimidodithiodiphosphine were used as representatives of bidentate organophosphoric chelating agents. Pentaphenyldiimidotriphosphate, from the group of tridentate agents, was used. The extraction properties of tetraphenyl imidodiphosphates and their sulphur analogues for trivalent americium in 0.1-1 mol/L HNO_3 into toluene and also in linear combination with TOPO were investigated. The dependences of equilibrium ratios of americium on analytical or equilibrium concentration of chelating agents, pH, initial concentration of nitric acid and initial concentration of TOPO were studied. The structures of the complexes in the organic phase were determined and the value of extraction constants were

calculated for all systems. The optimal extracted species were AmA_3 , $\text{AmA}_3(\text{HA})$, the addition of TOPO induced synergistic extraction of AmA_3 .TOPO. The utilization of sulphur analogues was insignificant.

SEP.P04 (Id: 308)
THE LIQUID-LIQUID EXTRACTION OF MINOR ACTINIDES WITH CyMe_4 -BTBP IN SELECTED DILUENTS

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The CyMe_4 -BTBP (6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazine-3-yl)-2,2'-bipyridine) has been demonstrated to be a prospective extractant for the liquid-liquid extraction of minor actinides. For industrial applications, its solubility in 1-octanol is low and the kinetics of extraction in this diluent is slow. Better performance has been demonstrated in cyclohexanone, however, the partial miscibility of this solvent with water makes its industrial use problematic. Therefore, the main purpose of this study was to find the most suitable diluent for the CyMe_4 -BTBP. The separation of americium(III) from europium(III) was studied. This is in particular reference to the separation of minor actinides from the high-level liquid waste issuing from the reprocessing of spent nuclear fuel. The results obtained using the diluents tested were compared with the data for cyclohexanone or 1-octanol as reference diluents. The principal diluents tested were alkylcyclohexanones. The parameters studied included the dependence of distribution ratios of americium(III) on the position of the alkyl group on the cyclohexanone ring, on the length of the alkyl substituent and on the number of alkyl groups in the ring. Extraction by the neat diluents (without CyMe_4 -BTBP extractant) was also studied as well as the dependence of the distribution ratio on the concentration of nitric acid. It has been shown that the alkylated cyclohexanones are promising diluents for the partitioning of minor actinides from lanthanides by CyMe_4 -BTBP. In particular, 3-methylcyclohexanone was found to have the optimum properties compared with the other cyclohexanones.

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SEP.P05 (Id: 307)
A TRLFS STUDY OF EUROPIUM SPECIATION WITH GLYCOLIC ACID

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Europium is often used as a model of the fission products from the lanthanides and minor actinides group. Glycolic acid is used in modern decontamination solutions and has been also proposed as a complexing agent in the reprocessing of spent nuclear fuel. The aim of this study was to carry out a more detailed study of europium complexation with glycolic acid using Time-Resolved Laser-Induced Fluorescence Spectroscopy (TRLFS), including determination of the stability constants of europium complexes with glycolic acid, and to compare the results with published data ¹. Furthermore, this work should also clarify the impact of sample preparation in air and under N_2 atmosphere, i.e. the role of hydroxo- and carbonato-complexes at $\text{pH} > 7$. Because Eu complexes with glycolic acid show good fluorescent properties, the TRLFS method was chosen for their study. The studied parameters included the influence of the concentration of CO_3^{2-} on the formation of europium carbonato-complexes, effect of pH on the formation of hydroxo-complexes of europium (solutions prepared under N_2 atmosphere), and europium complexation in solutions with glycolic acid (comparison of the samples prepared on air and under N_2 atmosphere). The fluorescence spectra of individual samples and the time of fluorescence of prepared complexes were recorded. The results obtained were compared with those published by Stumpf et al. ¹. Based on the comparison of the results obtained for samples prepared on air and under N_2 atmosphere, it can be concluded that the transfer of atmospheric CO_2 is negligible even at relatively high pH value and that the influence of carbonate complexes in europium-glycolic acid systems is negligible. The TRLFS method was further supplemented with the extraction method, which can be also used for determining the stability constants of complexes of europium with glycolic acid. In the following step, stability constants of prepared complexes will be obtained from measured data using factor analysis.

This work was supported by grant MSM 6840770020.

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SEP.P06 (Id: 206)
COMPLEXATION OF At⁺ AND AtO⁺ WITH
INORGANIC LIGANDS; A COMBINED
EXPERIMENTAL AND THEORETICAL APPROACH
TO CHARACTERIZE THE FORMED SPECIES

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Astatine (At, Z = 85: [Xe]4f145d106s26p5) is below iodine and belongs to the halogen group. One of its isotopes, ²¹¹At, is a promising candidate as a therapeutic agent in nuclear medicine ¹. It has been reported that astatine presents a metal-like behavior when existing under the oxidation states +I and +III as At⁺ and AtO⁺ species ². However, the number of studies dealing with the complexation properties of these cationic forms is limited. Low availability of astatine makes experimental work difficult (usually investigations derived from radiochemical studies at ultra-trace concentrations, typically between 10⁻¹² and 10⁻¹⁵ mol L⁻¹). In this work, we propose a combined experimental and theoretical approach to characterize the interaction between these metallic forms and simple inorganic anions (Cl⁻, Br⁻, SCN⁻). A competition method based on solid/liquid separation or liquid/liquid extraction is proposed to determine the equilibrium constants ³. To assess the reliability of the experimental results, they are compared to theoretical computations. The spin-orbit density functional theory (SO-DFT) approach, which uses two-components relativistic effective core potentials (RECPs), has been used to investigate the spectroscopic properties of At, At₂ and HAt species. In conjunction with our own built up basis sets (double and triple ζ augmented with diffuse and polarization functions), SO-B3LYP and SO-M06 functionals offer results in good agreement with that in the literature. In order to compare measured and computed equilibrium constants of the astatine reactions, aqueous solvation effects have been introduced using polarizable continuum models (PCM with UAHF and UAKS cavities). Obtained results show a good agreement between theoretical and experimental values. They also indicate that astatine species have a soft character according to the HSAB theory.

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SEP.P07 (Id: 57)
THE STUDY OF THE SPECIATION OF URANYL-
SULPHATE COMPLEXES BY UV-VIS ABSORPTION
SPECTRA DECOMPOSITION

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Uranyl-sulphate complexes are the most significant U(VI) species in acid solutions containing sulphate ions. The study of their properties is of practical significance for characterisation of solutions used in underground uranium ore leaching and following remediation of leaching sites. At low pH values, the speciation of U(VI) mainly depends on its total concentration [U^{VI}] and sulphate ions concentration [SO₄²⁻]. As absorption UV-VIS spectra of UO₂(NO₃)₂ + Na₂SO₄ solutions were found significantly dependent upon the ratio $\Phi = [\text{SO}_4^{2-}]/[\text{U}^{\text{VI}}]$, the spectrophotometric method for closer study of U(VI) - SO₄²⁻ complexes speciation was used. The solutions under study were of constant uranium concentration [U^{VI}] = 5x10⁻² mol L⁻¹. Required values of the Φ ratio were adjusted by proper additions of Na₂SO₄ solution and varied from $\Phi = 0$ up to $\Phi = 20$. Constant pH value pH = 2 was maintained by the additions of either HNO₃ or NaOH solution of negligible volume. Absorption spectra were recorded using UV/VIS spectrophotometer CARRY 100 within the wave-length range 190 - 900 nm. The following U(VI) species were considered under the given conditions: UO₂²⁺, UO₂SO₄ (aq), UO₂(SO₄)₂²⁻ and UO₂(SO₄)₃⁴⁻. As the most pronounced effects of the Φ value changes on the spectra appeared at wave-lengths between 380 and 500 nm, these parts of spectra were used as a database for the identification of individual U(VI) species and for determination of their individual spectra by deconvolution of the experimental spectrum. Proposed simple deconvolution method requires a preliminary estimation of relative amounts of individual species. Stability constants from NEA database and SIT method of activity coefficients calculation at high ionic strength were used for this purpose. The spectrum of UO₂(NO₃)₂ solution without Na₂SO₄ ($\Phi = 0$, pH = 2) was considered to be the individual spectrum of pure UO₂²⁺ species. Absorbance data following from it and calculated relative amounts of all four species for each Φ value were taken as the basic set of input data for deconvolution. The absorbance of each of the three remaining species (UO₂SO₄ (aq), UO₂(SO₄)₂²⁻, UO₂(SO₄)₃⁴⁻) at given wave length can be find by solving the system of three linear equations involving experimental data from three spectra of different Φ ratio. The disagreement of spectra calculated from different triplets of experimental spectra can be caused either by experimental errors or by incorrect estimation of relative amounts of individual species. The presented method can be helpful even for estimation of accuracy of stability constants and SIT activity coefficients used in speciation calculations.

SEP.P08 (Id: 26)
THE EFFECT OF INDUCED α -RADIOLYSIS ON THE U(IV)/U(VI) RATIO IN URANIUM ORES

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The variation of the concentration of U(IV) and U(VI) species from uranium ores due to the α -radiolysis induced by an ^{241}Am source in several deposit conditions is studied. The X-rays patterns show some differences for the studied ores before and after external α -radiolysis. The concentrations of U(IV) and U(VI) species was determined spectrophotometrically.

SEP.P09 (Id: 275)
USE OF HYDROLYSIS FOR SEPARATION AND REMOVAL OF RADIONUCLIDES FROM SOLUTION

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Behaviour of radionuclides in such processes as sorption, ion-exchange, ultrafiltration, etc., that are used for removal of radionuclides from solution, is largely determined by their speciation in solution. The hydrolysis of metal ions in solution is particularly interesting in that respect, since most of the liquid radioactive wastes are aqueous solutions. The following forms of metal ions (Me^{z+}) occur in aqueous solution as the pH increases from acidic to basic conditions: - hydrated cations ($\text{Me}(\text{H}_2\text{O})^{z+}$) - mononuclear hydroxocomplexes ($\text{Me}(\text{OH})_q^{(z-q)+}$) - polynuclear hydroxocomplexes ($\text{Me}_p(\text{OH})_q^{(pz-q)+}$) - pseudocolloids. Each of the above forms possesses specific physico-chemical properties that can be effectively used for separation of radionuclides from solution. It has been shown that using the differences in ability of various metals to form hydroxocomplexes and the differences in behaviour of the above species in sorption and ultrafiltration processes it is possible to develop highly selective methods for extraction of radionuclides from solution, including anionic species.

SEP.P010 (Id: 51)
PHOTOCATALYTIC DEGRADATION/SORPTION OF RADIOCOBALT FROM EDTA-Co COMPLEXES USING CRYPTOMELANE-TYPE MnO_2

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Manganese dioxide was synthesised from hydrometallurgical wastewater simulant and the material was identified as cryptomelane-type MnO_2 (potassium form of α - MnO_2). The material showed good trace level heavy metal uptake properties, uptake preference $\text{Co} > \text{Cd} > \text{Ni}$, from 0.1M NaNO_3 background solution. The material showed also very fast copper uptake kinetics but its powdery physical form prevented its use in typical column experiment. However, using the material in batch mode in application, such as fluidized bed-type UV-photoreactor was found to be ideal for the material. The synthesised cryptomelane-type MnO_2 was tested in UV-photoreactor for its Co-EDTA degradation properties (10 μM Co and 10 μM EDTA concentrations in 0.1 M NaNO_3 background). In these experiments cobalt uptake of 99% was observed after 1 hour of UV photon irradiation. As for comparison, a well known TiO_2 was tested as reference material that showed about 90% cobalt uptake after 6 hours of irradiation under identical experiment conditions. It was also noted that the cobalt uptake on cryptomelane without UV irradiation was very modest, only about 10%. It was concluded that synthesis of cryptomelane-type MnO_2 was successful from rather complex precursor solution (hydrometallurgical wastewater simulant) and that the material has interesting ion exchange/catalytic properties but the powdery physical form of the material prohibits its use in traditional column applications.

SEP.P11 (Id: 58)
SEQUENTIAL SEPARATION OF ^{90}Sr FROM α EMITTERS WITH MIXED SOLVENT ANION EXCHANGE AND THEIR DETERMINATION BY LSC AND A SPECTROMETRY

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Strontium, plutonium and americium are isotopes the determination of which is most often encountered in practice (from all α and pure β emitters) because of their radiotoxicity, long period of half life and potential hazardous effects on human life. It is well known that their determination, because of their radiochemical properties, requires isolation from sample and separation from other elements (active or inactive) before detection. In past many methods were developed for their separation from different kind of samples. Main characteristics of almost all this methods is that separation and determination of strontium isotopes are separated from α emitters. Therefore the main aim of this paper is the development of a method for strontium and α emitters separation in one step by mixed solvent anion exchange. It will be shown that Sr, Y and the mentioned α emitters can be isolated from complex samples and separated from great amounts of Ca and many other elements and, subsequently, separated mutually on the chromatographic column filled with strong base anion exchangers (Amberlite CG-400 or Dowex 1x8) in nitrate form combined with alcoholic solutions of nitric acid as eluent. It will be also shown how combination of the used alcohols can improve separation efficiency between mentioned isotopes. Separation of Sr and Y from

Am and Pu can be achieved on the column filled with the mentioned exchanger and alcohol (ethanol, methanol)-water mixture as eluent. Pu and Am can be easily stripped from column by water. In addition, it will be shown how this type of isolation can accelerate $^{89,90}\text{Sr}$ determination on LSC or proportional counter and determination of Pu and Am by α spectrometry.

SEP.P12 (Id: 59)
ANALYSIS OF ^{55}Fe BY COMBINATION OF CHROMATOGRAPHIC SEPARATION AND LIQUID SCINTILLATION DETECTION

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^{55}Fe is an activation product, low energetic β emitter with approximately 2.74 year half life. Therefore, its presence in natural systems is limited in time and mainly dependent on nuclear reactor operation. As a rule determination of ^{55}Fe requires chemical separation prior detection. For this purposes separation on anion exchange column in two steps is usually used which makes it time-consuming. In addition, in the last decade improvements of methodology were described in few publications but mainly for its determination in liquid radioactive waste samples. Therefore, the main aim of this paper is to show the way for iron isolation from liquid samples with a high concentration of ions that enable simple determination of ^{55}Fe . Iron binding on extraction chromatographic resins developed by Horwitz and co-workers, so called TRU and Ln resin, will be discussed. The method for concentration and separation from all interfering isotopes on extraction chromatographic column which enables rapid and simple determination will be proposed. It will be shown how Fe can be easily separated from great amounts of macro elements, α and β emitters on column filled with TRU or Ln resin by using HCl and/or HNO_3 in one step. The advantages and disadvantages of using of Ln and TRU resins will be discussed. After the isolation, activity of ^{55}Fe is determined by counting on the liquid scintillation counter by using quench correction curve. It will be described which type of quenching mainly affects the accuracy of determination. Type of the polynomial approximation for efficiency determination (and quench correction) in sense of minimization of determination error will be proposed. Budget of uncertainty of determination will be discussed.

SEP.P13 (Id: 148)
ELECTRODEPOSITION OF SELECTED α -EMITTING RADIONUCLIDES FROM OXALATE-AMMONIUM SULFATE ELECTROLYTE AND MEASURED BY MEANS OF SOLID-STATE ALPHA SPECTROMETRY

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This method describes electrodeposition of selected group of α -emitting radionuclides such as method suitable for measuring by means of solid-state α spectrometry. The effect of volume and pH of electrolyte, distance of electrodes, current and plating time versus different α -emitting radionuclides was observed in order to optimize conditions to obtain maximum yield.

SEP.P14 (Id: 184)
SORBENTS OF HEAVY METALS BASED ON COMBINATION OF LOW RANK COALS AND CHITOSAN

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The study has been aimed at development of cheap sorbents of toxic heavy metals and radionuclides based on low rank, low energetic coals in combination with chitosan for use in treatment of both waste and drinking water and construction of active geochemical barriers. Sorbents based on lignite and naturally oxidized lignite (oxihumolite, leonardite) were prepared, both raw and impregnated with chitosan from its solution in oxalic acid. The sorbents were characterized by chemical and structural analyses. Their sorption performance for Co, Cu, and Cd was tested in equilibrium sorption experiments with respect to pH. The sorption efficiencies were calculated from the amount of metal retained by the sorbent, which was determined by instrumental neutron activation analysis in the short time irradiation mode with epithermal neutrons (in Cd shielding). Although chitosan provides only surface coating of the coal sorbents, its presence has affected significantly their sorption performance. At identical pH values, the sorption efficiencies of the chitosan coated coals were higher than those of the raw coals for all three metals, and this difference increased with pH. The chitosan coating obviously stabilizes coal in basic solution and inhibits leaching of humic substances and their complexes with the metals from coal into solution. Besides fixing metal humates within the sorbents, chitosan may positively affect the sorption efficiency also by its buffering action against the hydroxide addition.

SEP.P15 (Id: 289)
DETERMINATION OF ^{59}Ni IN RADIOACTIVE WASTES

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The aim of this study was suggestion and examination of method for radioanalytical determination of ^{59}Ni in radioactive wastes using low energy photon spectrometry (LEPS). New composite material PAN-DMG, containing chelating agent dimethylglyoxime (DMG) immobilized in porous matrix of binding polymer polyacrylonitrile, was used for nickel separation and concentration. Method for preparation of ^{59}Ni sample for LEPS was developed using homogeneous precipitation of nickel with DMG. Proposed radioanalytical method was tested with two types of real radioactive wastes (boric acid concentrate from NPP evaporator and primary circuit coolant ionex resin).

SEP.P16 (Id: 309)
PREPARATION OF SAMPLES FOR α -SPECTROMETRY BY DIRECT EVAPORATION OF EXTRACTED SPECIES

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Because of the energy loss of α particles by self-absorption, α spectrometry requires thin, uniform, and nearly weightless samples. Several methods exist for sample preparation e.g., electrodeposition, or co-precipitation. Unfortunately, the methods yielding the best energy resolution are not always quantitative and are usually relatively demanding and time-consuming. This fact makes application of α -spectrometry for screening tests with radiotracers complicated. For its simplicity and fastness, the possibility to prepare samples for α spectrometry by direct evaporation was investigated in order to evaluate the efficiency of Am/Cm separation. The simple aliquots of aqueous or organic phase, aliquots in the presence of an excess of volatile organic solvent (acetone) or mixed with tensioactive (tetraethylene glycol) were deposited on stainless steel planchets, evaporated under infrared lamp and heated in flame until glowed with dull red colour. The influence of sample preparation technique on counting efficiency and energy resolution has been investigated. The results show there is not one versatile technique, but the preparation should consider the particular composition of samples to be measured.

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SEP.P17 (Id: 254)
SOLUBILITY AND SORPTION BEHAVIOR OF MONAZITE CHEMICAL COMPONENTS IN HUMIC ACID SOLUTION

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Using the method of solubility it is shown that long (15 days) exposure of monazite powder in the aqueous solutions of natural or synthetic humic acids (HA) give rise to 10 to 100 times higher solubility of heavy p-, d- and f-elements of Mendeleev periodic system in comparison with solutions without humic acids. The level and rate of the solubility is shown to depend on the initial concentration of HA in solution and pH. It has been concluded that the resistance of inorganic phosphates toward HA should be taken into consideration in the construction of phosphate matrixes for immobilization of poisonous and radioactive chemical elements. Another aspect of monazite solubility in HA natural water solutions concerns the transfer of the solubility products, the humic complexes of p-, d- and f-elements through heterogeneous porous media with ion-exchange properties. This problem is extremely complicated and manifold^{1,2}. As the first approximation the transfer (or sorption, S) of the microelements (ME) in the "gross-system", which assumed to include the water soluble and colloid HA, HA- and hydroxo-complexes of ME, the ion-exchanger, depends on the heterogeneous interaction in the sub-systems "ME-ion-exchanger", "ME-HA", "HA-ion-exchanger". Within the frame of this concept [2] the presentation summarizes experimental data on sorption behavior of La(III), Th(IV), U(VI), Sr(II) and other microelements, the soluble chemical components of monazite in HA water solutions, toward strong cation-exchanger in Na-form. Example of such a data shows that sorption of a ME is strongly dependent on the HA solubility as a function of pH. Another coexisting factor is the "ME - HA(colloid)" - "ME- ion-exchanger" competitive sorption at critical micelle concentration point (pH<4). Physico-chemical aspects of the gross-system evolution in the field of such parameters as pH, HA content, monazite solubility are discussed in the presentation.

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**UPTAKE OF ARSENIC BY MANGANESE DIOXIDE
FROM WATER**

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Arsenic contamination of drinking water has been reported from many parts of the world. The maximum permissible level of total arsenic in drinking water is $10 \mu\text{g L}^{-1}$ as recommended by WHO. Natural geochemical contamination through soil leaching is the primary contributor of dissolved arsenic in ground water around the world. The most common species present in water are the inorganic species: As(V), predominates in well oxygenated waters, and As(III), predominates in ground water. The reduced state, As(III), is more toxic, more soluble, and more labile than the oxidized As(V). Methods for removal of arsenic from water have been reviewed¹. Arsenic remediation from water using manganese dioxide has been reported in the literature². In the present work, uptake of As(III) and As(V) by manganese dioxide was studied. Manganese dioxide was chemically synthesized in laboratory by various methods. Uptake was studied by batch equilibration method using ^{76}As as radioactive tracer. The influence of various parameters such as method of preparation and storage and aging, pH, initial concentration of arsenic and contact time has been studied. Uptake of arsenic is dependent on method of preparation of MnO_2 . Also, uptake efficiency for As(III) and As(V) is different.

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