Annual Report 1996

Institute of Radiochemistry

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The overall goal of the institute is to contribute through basic and applied research to the better understanding of radionuclide transport in the environment. This goes beyond mere phenomenological observation of the processes involved. We have set out to understand the individual transport-controlling processes on a molecular level and then use this knowledge to synthesize a more comprehensive view of radionuclide transport.

We have made progress in elucidating some of the molecular processes such as the speciation of uranium in solution and the binding of uranium to inorganic and natural organic materials. We have shown that our synthetic humic acids can effectively model the functionality of natural humic acids and therefore constitute a stable standard for inter-laboratory comparison of the thermodynamic properties describing metal-humic acid interaction. First steps were made to incorporate our knowledge of the chemistry involved in radionuclide transport into existing risk assessment software that did not consider the detailed chemistry along the environmental transport path.

One of our many tools to understand the coordination of radionuclides in solution, in inorganic and organic materials, and on surfaces is X-ray Absorption Spectroscopy (XAS). The construction of the Rossendorf Beam Line (ROBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, is rapidly moving forward. ROBL will provide the ability to investigate radioactive elements beyond uranium. Due to the hard work of the team which is jointly staffed by members of the Institute of Ion-Beam Physics and Materials Research, the Institute of Radiochemistry, and the Department of Experimental Facilities and Information Technology, the project is on time and within budget. The experimental hutchs were already tested for their tightness against radiation by using the white beam of the ESRF light source. Currently, the optical components are being installed and first tests using monochromatic radiation from 5 to 35 keV are planned for the fall of 1997.

The commissioning of our new radiochemistry building, however, is less successful. Although the construction was completed in the beginning of 1996 and the building was inaugurated in March of 1996, we still have not obtained our license to handle radioactive materials. The licensing process is extremely involved and slow. The FZR has spent close to half a million DM alone for obtaining the mandated independent expertise on the suitability of the building and its installations to handle the projected levels of radioactivity. Currently, a second independent evaluation with a projected cost to the FZR of 60,000 DM has been requested by the authorities. Despite all these obstacles, we are still hopeful that the Sächsische Staatsministerium für Umwelt und Landesentwicklung will grant us the unrestricted operating license for handling radioactive material including non-fissionable actinides in the second half of 1997. This would enable us to expand our research beyond uranium and address the issues of environmental contaminations that were caused world-wide by the production of nuclear weapons and by accidents from careless operation of nuclear facilities.

During 1996, we embarked on several new projects that are not reflected in this report. We began to characterize the biosorption of radioactive contaminants by microorganisms which are isolated from a uranium mill tailing pile that we selected as a project for interdisciplinary and application-oriented research. We are currently characterizing the mineralogy, hydrology, chemistry and radiochemistry, and biochemistry and microbiology of the uranium mine tailing pile “Haberlandhalde” in Johanngeorgenstadt in Saxony. This is done as a collaboration among our Departments of Radioecology and Nuclear Waste Disposal and Organic Tracer Chemistry, the Institute of Geology and Hydrology of the Technische Universität Bergakademie Freiberg, the Umweltforschungszentrum Leipzig and our newly-founded group of Microbiology and Genetics, for which two modern molecular-biological and genetic laboratories were established. Once our current exploratory studies are successfully completed, we envision a large collaboration on an international level. Another project that was begun is the investigation of the transfer factors of uranium between soil and plants as a function of its chemical form in the environment. This is done in collaboration with the Verein für Kernverfahrenstechnik und Analytik e.V. (VKTA),
Rossendorf, and the Institute of Plant and Wood Chemistry of the Technische Universität Dresden.

Although, the research on the chemistry of the heaviest elements is not in the mainstream of the institute, I would like to mention that several members of the institute and of my radiochemistry group at the Technische Universität Dresden were involved in the international collaboration that successfully carried out the first chemistry experiments with element 106, Seaborgium. It was shown that Seaborgium chemically behaves like its lighter homologues, molybdenum, Mo, and tungsten, W.

I would also like to report that the institute's first graduate student, Dr. A. Vahle, obtained her degree with *summa cum laude* from the Technische Universität Dresden in 1996.

We would like to thank the many visitors, German and international, for their interest in our research and for their participation in the institute's seminars. We would like to also thank our scientific collaborators and the visiting scientists for coming to Rossendorf during 1996 to share their knowledge and experience with us. We continue to strongly encourage the collaborations and visits by scientists in the future.

Rossendorf, May 1997                                      Prof. Dr. Heino Nitsche
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V. ACKNOWLEDGMENTS
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Speciation and Migration of Radionuclides
TITRATION OF A URANIUM MILL TAILING WATER FROM HELMSDORF - SPECIES DETERMINATION BY TIME-RESOLVED LASER-INDUCED FLUORESCENCE SPECTROSCOPY (TRLFS)

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The distribution of U(VI) species in different tailing water samples of an uranium mining area was calculated with the speciation modeling software EQ 3/6 NR /1/ using the NEA data base /2/. To validate this calculation, a series of TRLFS measurements was carried out. The pH of the original tailing water from the tailing site Helmsdorf was changed by addition of perchloric acid. At pH values lower than pH six, fluorescence spectra found that are typical for uranylphosphate and uranysulfate solution species.

Experimental and Results

Tab. 1 lists the main chemical components of the Helmsdorf tailing water. From these data, we calculated the species distribution in this solution as a function of pH using the modeling software package EQ3/6NR /1/. The speciation diagram is shown in Fig. 1.

![Fig. 1: Species distribution as function of pH in the tailing water (concentrations see Tab. 1)](image1)

This system has a low calcium concentration and therefore the Ca$_2$UO$_2$(CO$_3$)$_2$(aq) species will not be formed in a measurable concentration. At pH values higher than six only carbonate species exist. These species do not show any fluorescence signals. Therefore it is impossible to determine these species by TRLFS. At lower pH values, complexes form between the uranyl ions and phosphate. At a pH lower than 4.5, the uranysulfate speciation becomes dominant. We obtained spectroscopic information on the tailing water using time-resolved laser-induced fluorescence spectroscopy (TRLFS). The TRLFS method and our experimental setup are described in /3,4/. The excitation wavelength used was 266 nm. The TRLFS of the original tailing water shows a spectrum that is typical for organic compounds in natural systems. No uranium fluorescence could be obtained. We increased the calcium concentration by adding a Ca(ClO$_4$)$_2$ solution with the same pH and obtained the spectrum of the Ca$_2$UO$_2$(CO$_3$)$_2$(aq) species. Fig. 2 shows the comparison of this spectrum with a spectrum that was obtained from

![Fig. 2 (left): Fluorescence spectra of original tailing water (solid); synthetic solution with 1x10$^{-2}$ M Ca$^{2+}$; 2x10$^{-5}$ M UO$_2^{2-}$ and 2x10$^{-3}$ M HCO$_3$/CO$_3^{2-}$ (dot) and tailing water after addition of 1.25x10$^{-2}$ M Ca$^{2+}$ (dash)](image2)

![Fig. 3 (right): Fluorescence spectra of the tailing water as a function of pH](image3)
In a second series of measurements, we titrated the original tailing water with perchloric acid by keeping a constant ratio (90%) of the original tailing water to the added perchloric acid. With decreasing pH, we found fluorescence spectra. Fig. 2 shows spectra which were measured at constant delay times. With decreasing pH, the spectral shape changes strongly. Starting at about pH 6, the fluorescence intensity increases and reaches a maximum at about pH 4. Analysis of the emission wavelength of the band maxima showed that these spectra can be ascribed to the formation of phosphate complexes. If the pH is lowered to below three, the spectra become typical to those for sulfate complexation of uranium(VI). This agrees with the speciation calculations. At pH values below six complex formation begins between uranium(VI) and phosphate. Because the fluorescence intensity of the phosphate complexes is very strong, we can determine them concurrently to the sulfate complexes. The formation of uranyl sulfate and phosphate complexes begins for both approximately below pH 6. The maximum concentration for the phosphate complexes was determined at pH 4.9 deconvoluting the different species using the lifetime function. At lower pH values, the more then two times higher concentration of the second sulfate complex gives an additional fluorescence signal, which results in an increase of the integral fluorescence intensity up to pH 4.3. At pH values lower than 4.3, we found fluorescence spectra of uranyl sulfate species.

The TRLFS measurements of the Helmsdorf uranium tailing water in the pH range from two to nine confirmed the speciation calculations for free uranyl, uranyl phosphate and uranyl sulfate species. This validates the thermodynamic data for these systems. This work is currently being extended to the basic pH range in order to detect the formation of uranyl hydroxo complexes such as $\text{UO}_2(\text{OH})_4^{2-}$.

References
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QUENCHING EFFECT OF CHLORIDE ION ON URANYL-SULFATE COMPLEX FLUORESCENCE

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In uranium mining related waters chloride ions can quench the fluorescence of uranyl species. Uranyl sulfate complexes are the main species on acidic uranium solutions containing sulfate ions. Therefore the quenching effect of chloride ions on the fluorescence of U(VI)-sulfate complexes was investigated in aqueous U(VI)-sulfate solutions ([U(VI)] = 1x10⁻⁵ M, [SO₄²⁻] = 2x10⁻⁵ M, [Cl⁻] = 1x10⁻⁴ to 5x10⁻⁵ M, pH = 2, ionic strength = 1 M). Time-resolved laser-induced fluorescence spectroscopy measurements were carried out to evaluate the fluorescence decay constants and the quenching coefficients for $\text{UO}_2^{2+}$, $\text{UO}_2\text{SO}_4$ and $\text{UO}_2(\text{SO}_4)_2^{2-}$. The quenching coefficients of $\text{UO}_2^{2+}$, $\text{UO}_2\text{SO}_4$ and $\text{UO}_2(\text{SO}_4)_2^{2-}$ range from 4.0×10⁻² to 6.27×10⁻³ M⁻¹s⁻¹, from 1.23×10⁻² to 1.42×10⁻³ M⁻¹s⁻¹, and from 2.48×10⁻⁷ to 3.58×10⁻⁷ M⁻¹s⁻¹, respectively.

Results and Discussion
Fig. 1 shows the influence of sulfate concentration on the fluorescence spectra of U(VI). The time delay was set to 100 ns, and the chloride concentration was 1x10⁻³ M. No marked difference in the shape of spectra was observed in the sulfate concentration range from 2x10⁻² to 2x10⁻¹ M. The four strong fluorescence emission peaks are located at 494, 515, 539 and 564 nm. Because the corresponding fluorescence emission peaks of the free $\text{UO}_2^{2+}$ without sulfate and chloride ions present are located at 485, 509, 532 and 558 nm, the peaks of the U(VI)-sulfate system are shifted to longer wavelengths.
Fig. 1: Fluorescence spectra of uranylions in sulfate media at different sulfate concentration.

Fig. 2 shows the time-resolved fluorescence spectra of U(VI) at sulfate and chloride concentrations of $2 \times 10^{-3}$ M and $1 \times 10^{-3}$ M, respectively. Assuming a short laser pulse relative to the apparent excited state lifetime, the fluorescence decay curves can be described as follows:

$$A(t) = A_0 \times c_i \times \exp(-t/t_i)$$

where $A_0$ are the initial specific fluorescence intensities of the species $i$ at $t = 0$, $c_i$ the species concentration and $t_i$ fluorescence decay constants of the fluorescent species. By fitting the time-resolved fluorescence spectra with parameters according to the above equation, we obtain the number of fluorescent species in the sample solution, and the fluorescence decay constant of each species. The initial fluorescence are mainly dependent on the absorbance of the U(VI) complexes and on the prefiltter effect /1/. The evaluated fluorescence decay constant depends on the quenching of coexisting species, namely chloride ions in the present work. From the fit we derive that the fluorescence spectrum shown in Fig. 3 is a superposition of the spectra of three species.

The dominant U(VI) species under these conditions are $\text{UO}_2^{2+}$, $\text{UO}_2\text{SO}_4$ and $\text{UO}_2(\text{SO}_4)_2^{2-}$ with the respective fluorescence decay constants of $892 \pm 42$, $2476 \pm 137$ and $5769 \pm 504$ ns. The fluorescence decay constant decreases with increasing chloride concentration. We also found that the initial fluorescence decreases with increasing chloride concentration at constant sulfate concentration. As the sulfate concentration increases at the constant chloride concentration, the initial fluorescence of $\text{UO}_2^{2+}$ decreases, but those of $\text{UO}_2\text{SO}_4$ and $\text{UO}_2(\text{SO}_4)_2^{2-}$ increase, indicating the formation of uranyl-sulfate complexes in the solutions of higher sulfate concentration.

From the fluorescence decay constants obtained in the present work, the quenching coefficient, $k_q$, of chloride ion can be calculated according to the Stern-Volmer equation /2/. Fig. 3 shows the dependence of the fluorescence decay constant of $\text{UO}_2\text{SO}_4$ on the chloride concentration at a constant sulfate concentration of $5 \times 10^{-2}$ M. The $k_q$ can be calculated from the slope of the line, and the fluorescence decay constant without chloride ion, $t_{0}$, can be obtained from the intersection at zero chloride concentration. The obtained $k_q$ values are summarized in Tab. 1. We relate for the first time $k_q$ to the species $\text{UO}_2^{2+}$, $\text{UO}_2\text{SO}_4$ and $\text{UO}_2(\text{SO}_4)_2^{2-}$.

References


Identification of a Uranium Surface Species Sorbed on a Ferrihydrite Surface Using Time-Resolved Laser-Induced Fluorescence Spectroscopy (TRLFS)

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A surface species of uranium sorbed on a ferrihydrite surface at pH 5.8 was identified by Time-Resolved Laser-induced Fluorescence Spectroscopy (TRLFS). The fluorescence maximum of this uranium surface species occurs between 600 and 700 nm. It is easily distinguishable from the fluorescence maximum at 480 to 550 nm of uranium in solution.

Results and discussion

The sorption of uranium on the iron mineral ferrihydrite was studied in the pH range of 3.5 - 9.5 in a system open to the atmosphere. The batch experiments were carried out under the following experimental conditions: total U(VI) concentration of $1 \times 10^{-5}$ M, ferrihydrite concentration of $1 \times 10^{-5}$ M (as Fe), ionic strength of 0.1 M adjusted with NaNO$_3$, and a contact time of 50 hours between the solid phase and uranium solution. The experiments showed that uranium sorbs to the ferrihydrite surface in the pH range of 4.0 to 8.5 and reaches its sorption maximum between pH 5.5 and 7.5. Similar results were found by Waite and coworkers /1/. Fig. 1 shows that at pH 5.8 95 ± 5 % of the uranium sorbs to a 1 mM suspension of the iron mineral ferrihydrite.

Waite and coworkers /1/ tried to investigate the nature of the uranium sorbed to ferrihydrite surface and conducted EXAFS measurements on samples representing sorption conditions of pH 5.0 and 5.5. They found an average U to Fe distance of 3.37 Å and concluded that the major uranium species at the ferrihydrite surface is an inner-sphere mononuclear bidentate complex.

We carried out TRLFS measurement on above described batch samples at pH 5.8 to obtain more information about the uranium surface species that are bound to the ferrihydrite. The first series of TRLFS measurements were performed with solutions containing $1 \times 10^{-5}$ M of uranium(VI) and no iron(III). Time-resolved fluorescence spectra between 480 and 550 nm are shown in Fig. 2. This fluorescence signal was also observed by Meinrath et al. /2/. At this pH mainly the uranium hydrolysis products are present in solution, in particular $\text{UO}_2(\text{OH})_2^{2-}$, $(\text{UO}_2)_2(\text{OH})_5^{2-}$ and $\text{UO}_2(\text{OH})_3^{+}$. The second series of TRLFS measurements were conducted with solutions containing 1 mM of ferrihydrite and no uranium. No fluorescence signal could be detected in these suspensions. However, in solutions containing both 1 mM Fe as ferrihydrite and $1 \times 10^{-5}$ M of uranium(VI) that were mixed for 50...
hours, it was clearly showed that the characteristic fluorescence signal of uranium in the wavelengths 480-550 nm disappeared as a function of time in the presence of ferrihydrite and a new species appeared with a fluorescence signal at wavelengths between 600 and 700 nm. The fluorescence spectrum of this new species is depicted in Fig. 3. Based on previously conducted sorption experiments /1/, this new fluorescence signal can be assigned to a uranium surface species forming on a ferrihydrite surface at pH 5.8. Using speciation calculations, this uranium surface species on the ferrihydrite surface could be due to a specific surface complex forming on the ferrihydrite surface or to surface precipitation of the solid uranium hydroxide phase schoepite, $\text{UO}_2(\text{OH})_2(\text{H}_2\text{O})_2$.

TRLFS seems to be a promising surface-sensitive technique to detect surface species in complex aqueous solutions. The results of this study could be especially helpful for identifying surface species in natural waters containing uranium and iron at weakly acidic to neutral pH.

Acknowledgment
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References

SORPTION OF URANIUM(VI) ONTO PHYLLITE

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The adsorption of U(VI) onto phylrite and onto several of individual minerals was studied in batch experiments under ambient conditions. The pH range of 3.5 - 9.5 was studied with an uranium concentration of $1 \times 10^{-5}$ M and a solid to solution ratio of 1 g/20 mL, using the 63 to 200 µm size fraction. Maximum sorption of uranium onto the various mineral surfaces occurred between pH 6.0 and 7.3. Based on the calculated uranium speciation, the sorption of uranium was attributed to a combination of precipitation of the solid uranium phase schoepite and to surface complex formation between $\text{UO}_2(\text{OH})_2$ and the individual mineral surfaces.

Experimental
The phyllite was obtained from the uranium mining site “Schlema-Alberoda” near Aue in Western Saxony. It was collected 540 m underground and represents /1/ a fairly typical light-colored phyllite of this mining site. The phyllite was crushed, ground and separated into different size fractions by sieving. The 63 to 200 µm fraction was used in batch sorption experiments. The feldspar minerals oligoclase, labradorite, orthoclase and the glimmer minerals muscovite and biotite were purchased and treated identical to the phyllite. The quartz used in these experiments was a commercially available fine-grained quartz, 0.2 - 0.8 mm, which was already washed and calcined. One gram of the solid material of the 63 to 200 µm fraction was added to 20 mL of distilled water in polypropylene centrifuge tubes. Then the pH was adjusted to the desired pH value using the appropriate amounts of HNO$_3$ and NaOH. In samples with a pH higher than 7, a calculated amount of NaHCO$_3$ was added to accelerate the equilibration process with atmospheric CO$_2$. Twenty-four hours later, uranium was added to obtain a concentration of $1 \times 10^{-5}$ M, and the pH was readjusted. The samples were shaken for about 50 hours and the final pH values were measured. The samples were centrifuged at 3000 rpm for 7 min. The supernatant was transferred to a polypropylene sample container, acidified to a pH of about 1.5, and analyzed for uranium with ICP-MS. The difference of the analyzed supernatant solution to the added $1 \times 10^{-5}$ M uranium was attributed to sorption. Furthermore, values for the specific surface area (BET) were determined for various feldspar minerals (0.3 - 0.7 m$^2$/g), quartz (0.2 m$^2$/g), muscovite (1.4 m$^2$/g), biotite (1.3 m$^2$/g), and phyllite (4.0 m$^2$/g).

Results and Discussion
The results of the batch sorption experiments are depicted in Fig. 1. The sorption maxima of
uranium onto the various minerals and phyllite surfaces takes place in the near neutral pH range of about 6.0 to 7.3, and seems to be independent of the individual surfaces.

However, there is a difference in the amount of the sorbed uranium. Quartz and oligoclase sorb less uranium (approximately 45 %) compared to orthoclase and labradorite and the glimmer minerals biotite and muscovite which sorb up to 80-90 %. Phyllite sorbed nearly 96 % of uranium in the pH range of 6.5 to 7.0. This is a surprising result considering the composition of the phyllite which consists of about 30-60 % quartz, 20-50 % glimmer, 0-20 % chlorite and 0-20 % feldspar. It was expected that the uranium sorption of the phyllite would be lower because the sorption onto the individual minerals is significantly lower. The maximum amount of uranium sorbed onto the phyllite should not be larger than the amount that is sorbed onto its strongest sorbing individual mineral. However, there may be two possible explanations for these high sorption values. First, chlorite was not yet included in this study and it may be possible that this mineral sorbs more uranium than the other minerals. Secondly, a thin film of brownish-reddish color was observed at the end of the phyllite sorption experiments. This film may possibly be the result of various dissolution and reprecipitation reactions at the phyllite surface. Because the phyllite contains about 2 % of iron, this newly formed secondary surface precipitation phase may contain more iron than the initial phyllite surface. Small amounts of iron minerals are sufficient to adsorb large quantities of uranium from solution. Various studies /2, 3/ have shown that at neutral pH, 20 mL of an 1 mM iron-suspension was responsible for sorbing almost 100 % of uranium in a 10^{-5} M uranium solution. Furthermore, Bruno et al. /4/ showed that uranium can also be removed from solution by co-precipitation with a newly formed solid phase. The reasons why the amount of the uranium sorbed onto the various minerals studied is still under investigation. It is very likely related to the different number of surface sites of each mineral, to a different affinity of these sites for uranium, and to different specific surface areas.

Conclusions
Sorption was strongest in the pH range 6.0 - 7.3 and this pH dependency applies to all the minerals studied. By comparing speciation calculations with the results from the sorption experiments, one can conclude that the sorption of uranium is possibly a combination of surface precipitation of the solid uranium hydroxide schoepite UO(\textsubscript{2})(OH)\textsubscript{2}\got{2}O and adsorption of the neutral charged complex [UO\textsubscript{2}(OH)\textsubscript{2}]\got{2} onto the mineral and phyllite surface forming surface complexes.

Acknowledgment
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SORPTION OF URANIUM (VI) ON POLYPROPYLENE SURFACES

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The sorption of uranium (VI) on polypropylene centrifuge tubes was studied as a function of pH and various uranium(VI) concentrations in a system open to the atmosphere. The sorption of uranium to polypropylene had its sorption maximum in the pH range of about 6.0 to 7.3 and reached values of up to 50 % of uranium sorbed to the centrifuge tubes when using an initial U(VI) concentration of 1\(\times\)10\(^{-5}\) M. At a starting concentration of 1\(\times\)10\(^{-6}\) M sorption was still significant. Approximately 10-20 % of the uranium in the pH range of 6.0 to 7.3 sorbed to the polypropylene.

Results and discussion
Polypropylene is a commonly used container material in batch experiments. Several authors (e.g. /1,2/) claim that the loss is negligible of uranium (VI) from solution onto polypropylene container walls during sorption experiments of uranium on various geomaterials. However, these authors do not specify pH and uranium concentration. In batch experiments, the amount of dissolved species sorbed to a solid surface is usually determined by subtracting the concentration of the dissolved element at the end of the sorption experiment from the initially added element concentration. The amount of the sorbed element could then be used to determine K\(_d\) values or surface complex formation constants with the solid surface. However, when a considerable amount of uranium is sorbed to the polypropylene these constants will be invalid.

To obtain more information about the sorption process of uranium to solid phases, the speciation of uranium in a 1\(\times\)10\(^{-5}\) M uranium solution open to the atmosphere (P\(_{\text{CO}_2}\) = -3.47) was calculated with HYDRAQL /3/ using formation constants from Grenthe et al. /4/.

In the first calculation shown in Fig. 1 the formation of solid uranium phases is allowed and in the second one, displayed in Fig. 2, their formation is excluded.

Fig. 1: Speciation calculation of uranium (1\(\times\)10\(^{-6}\) M) conducted with HYDRAQL in a system open to the atmosphere. Solid species are included in the calculation.

Fig. 1 shows that, assuming equilibrium conditions, the solid uranium phase schoepite, UO\(_2\)(OH)\(_2\)\(\cdot\)H\(_2\)O, precipitates in the pH range of 5.3 to 7.3 and thereby reduces the concentration of dissolved uranium in this pH regime. However, using an initial uranium(VI) concentration of 1\(\times\)10\(^{-6}\) M and also including the formation of all solid uranium phases no precipitation of dissolved uranium is predicted. In Fig. 2, the formation of solid uranium phases is excluded, because this should represent the scenario were the formation of solid uranium phases is kinetically hindered or where equilibrium conditions are not established. These speciation calculations are compared with the results from batch experiments in which the sorption of
uranium (VI) to centrifuge tubes made of polypropylene using three different uranium concentrations (1E-5 M, 1E-6 M, and 1E-7 M) was studied in the pH range from 3.5 to 9.5 in a system open to the atmosphere. The contact time between the dissolved uranium and the solid phase polypropylene was 50 hours. It was found for an initial uranium concentration of 1E-5 M that the sorption of uranium to the centrifuge tubes takes place in the pH range of 6.2 to 8.0. The amount of uranium sorbed to the centrifuge tubes was highest at a pH of about 7.0, with a maximum of 5 - 10%. Using an initial uranium concentration of 1E-6 M, it was shown that the sorption starts at slightly lower pH values and the maximum amount of U(VI) sorbed to the polypropylene is higher. Sorption occurs from pH 5.0 to 8.0 whereby the sorption maximum is observed between pH 6.0 to 7.3 with a maximum of about 15-20%. The highest relative amount of uranium sorbed to the polypropylene was obtained for an initial uranium concentration of 1E-7 M. Sorption was observed between pH 4.4 to 8.0 and reached its maximum in the pH range of 6.0 to 7.3 with up to 50 % of the U(VI) sorbed to the polypropylene. Results of these batch experiments are displayed in Fig. 3 and show that some data points are widely scattered around the fitted curved indicating that centrifuge tubes might show different sorption characteristics based on individual surface roughness. This study clearly shows that sorption of uranium to centrifuge tubes made out of polypropylene in the near neutral pH range can be
significant and therefore should be routinely checked. Furthermore, it appears obvious by
comparing these results with results obtained from sorption experiments conducted with
minerals and rocks /5,6/ that the area in which sorption takes place seems to be fairly independ-
ent of the solid surface. Moreover, sorption seems not to be affected by the charge of the
surface. Feldspar minerals, for example, have a point of zero charge at about pH 2 indicating
that the surface in the pH region where sorption is strongest is negatively charged, whereas
ferrihydrite has a point of zero charge of about 7.8 meaning that its surface is positively charged
in the region of maximum sorption. Comparing these results with the information obtained from
the speciation calculations shown in Fig. 1 it can be seen that the pH area in which sorption
takes place is quite similar to the area where schoepite precipitates. Conclusively, the reduction
of uranium out of solution could be attributed to surface precipitation. However, previous
sorption experiments with uranium sorbing to ferrihydrite /6/ and the results of the present study
showed that sorption is even stronger and the sorption area wider when using an starting
uranium concentration of 1@10^6 M and 1@10^7 M, both uranium concentrations where, based on
known formation constants no precipitation of a solid uranium phase occurs. If surface precipi-
tation is the only process responsible for the reduction of uranium in solution, the same amount
of uranium should precipitate on each mineral. However, this was not the case. Referring to the
speciation calculation depicted in Fig. 2, it can be seen that there is one aqueous uranium
complex, UO_{2}(OH)_{2}, dominating in the pH range with maximum sorption. The same complex is
also dominating in speciation calculations using a maximum uranium concentration of 1@10^6 M
and 1@10^7 M. At higher pH values uranium carbonate species become the dominant species and
the sorption of uranium to the various mineral surfaces is reduced. It could be possible that
this neutral charged aqueous uranium complex forms surface complexes with the solid mineral
or rock particle surface.

Conclusions
At U(VI) concentrations of 1@10^6 M and 1@10^7 M neither schoepite nor another solid uranium
phase should precipitate. However, there is a remarkable coincidence between the solubility
minimum of schoepite and the pH range where the sorption of U(VI) onto the centrifuge tubes is
maximum. This may indicate that at U(VI) concentrations of 1@10^6 M or below the formation
of a solid uranium phase, similar to schoepite, may occur on the polypropylene material.
Furthermore, the formation of surface complexes between the neutral charged UO_{2}(OH)_{2} and
the solid surface may contribute to the decrease of the uranium in solution. Based on the
results from batch experiments and speciation calculations of uranium it was concluded that the
sorption of uranium is controlled by a combination of surface precipitation of the uranium
hydroxide phase schoepite and/or an additional similar solid uranium phase and the formation
of surface complexes between the neutral charged uranium species UO_{2}(OH)_{2} and the solid
surface.

Acknowledgment
The authors would like to thank Dr. Wiesener for ICP-MS measurements.

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(1994)
INTERACTION OF URANIUM(VI) WITH SILICON SPECIES IN AQUEOUS SOLUTIONS

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The interaction between soluble species of uranium(VI) with silicic acid was studied in 0.3 M NaClO₄ solution using Time-resolved Laser-induced Fluorescence Spectroscopy (TRLFS). The stability constant of the complex UO₂OSi(OH)₃⁺ was determined at pH 3.9, an uranyl concentration of 2.1·10⁻⁵ M, and monosilicic acid concentrations up to 3.0·10⁻³ M. Fluorescence lifetimes were obtained for the free uranyl cation, the 1:1 complex and for particles which are probably the result from interactions of polymeric silicic acid with uranyl ions.

Results and discussion
The TRLFS spectra were measured with delay times ranging from 0.1 µs to 135 µs, with increments of 0.5 µs. The excitation wavelength was 266 nm. Fig. 1 depicts the influence of the ligand on the UO₂⁺-fluorescence. The measured spectra showed an increase of the fluorescence intensity with increasing ligand concentration. It exists a linear relation between the log [fluorescence intensity] vs. log [Si]total. The slope of about 0.9 indicates a predominantly 1:1 complex formation with monomeric silicic acid. The slope of smaller than one could be attributed to a second silicato-uranyl complex which may form between uranyl ions with polymeric silicic acid.

The fluorescence decay of solutions containing silicic acid is much slower than in pure uranyl solutions. The fluorescence lifetimes were determined by evaluation the time-resolved fluorescence spectra (Tab. 1).
We assume that three species are present in solutions containing 2.1·10⁻⁵ M UO₂⁺ and silicic acid concentrations from 4.0·10⁻⁵ M to 3.0·10⁻³ M at a pH of 3.9. There are no lifetimes available in the literature for the uranyl-silicate system. One species was determined with a lifetime of 1.4 ± 0.16 µs which is typical for the free uranyl ion /1/. For the 1:1 complex we determined a lifetime of 34 ± 3 µs. A third fluorescence lifetime between 90 and 200 µs suggests an interaction of uranium(VI) with polymeric silicic acid particles. About 80 % of the total silicon concentration were detected using the $-silicomo-lybdate method which shows that the solutions contained polymeric silicic acid. We assume that these particles form during the preparation of the silicic acid solution (quick neutralization of sodium metasilicate solution).

Using peak deconvolution to evaluate TRLFS spectra, it was possible to calculate the spectra of the three individual species (Fig. 2). The integrated fluorescence signal from 450 nm to 650 nm measured at different silicic acid concentrations was fitted to a sum of exponential decay functions /2/. This lifetime fitting process yielded the concentrations of the involved species, UO₂⁺-free, UO₂OSi(OH)₃⁺ and [UO₂₂⁺ polymeric silicic acid adducts; [UO₂₂⁺(SiO₂₀.₅OH)₉]²⁻]. The interaction of uranyl ions with monosilicic acid can be described by the following reaction /3/:

![Fig. 1: TRLFS-spectra as a function of monosilicic acid concentration (delay time: 2.1 µs, pH = 3.9)](image)

![Table 1: Lifetimes and fluorescence signals relative to UO₂⁺ at an ionic strength of 0.3 M and a total silicic acid concentration of 3.0·10⁻³ M](table)

<table>
<thead>
<tr>
<th>Species</th>
<th>Lifetime [µs]</th>
<th>Fluorescence signal (rel. to UO₂⁺)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂⁺</td>
<td>1.4 ± 0.16</td>
<td>1</td>
</tr>
<tr>
<td>UO₂OSi(OH)₃⁺</td>
<td>34 ± 3</td>
<td>1.4</td>
</tr>
<tr>
<td>UO₂⁺ polymeric silicic acid</td>
<td>95 - 200</td>
<td>3</td>
</tr>
</tbody>
</table>

Tab. 1: Lifetimes and fluorescence signals relative to UO₂⁺ at an ionic strength of 0.3 M and a total silicic acid concentration of 3.0·10⁻³ M

References
/1/...
/2/...
/3/...
We determined a stability constant \( \log \beta^o = -(1.60 \pm 0.36) \) for this reaction. The stability constant was extrapolated to infinite dilution using the Davies-Equation.

Conclusions
The results of this study shows that the TRLFS technique was able to investigate the complexation of U(VI) with silicic acid at low concentrations \((c_{\text{Si, total}} < 0.01 \text{ M})\). Our determined stability constant \( \log \beta^o = -(1.60 \pm 0.36) \) suggests a stronger complexation of U(VI) with silicic acid compared to the stability constant \( \log \beta^o = -(2.25 \pm 0.13) \) obtained by Porter and Weber /3/ as well as \( \log \beta^o = -(2.70 \pm 0.34) \) reported by Satoh and Choppin /4/. First TRLFS measurements were performed using tetramethylorthosilicate (TMOS) as source of silicic acid in order to minimize the formation of polymeric silicon species.

The fluorescence lifetime between 90 and 200 \( \mu s \) was not detected. Therefore, the assumption was confirmed that this fluorescence lifetime is related to the interaction of uranyl ions with adducts of polymeric silicic acid.

Acknowledgments
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References

REDOX BEHAVIOR AND SPECIATION OF HEXAVALENT URANIUM IN NON-COMPLEXING MEDIA
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The redox behavior of U(VI) in environmental relevant concentrations was studied over the pH range 4-12 by voltammetric methods. The reduction waves were correlated with speciation calculations.

Environmental radionuclide and heavy metal transport via the aquatic pathway depends mainly on the chemical species of the elements that form in natural waters and on their specific interaction with the contacting solid phases (rocks, sediments and soils).

Experimental methods, results and modeling
The U(VI) reduction in non-complexing solution was studied over a wide pH range by square-wave and cyclic voltammetry. The reduction waves were compared with species distributions which were calculated by the multi-equilibria program RAMESES (variant VIII) /1/ using U(VI) hydrolysis constants /2/ adjusted to \( I(c) = 0.1 \text{ M} \). The voltammetric measurements were carried out using the AUTOLAB Potentiostat (Eco Chemie) combined with the Metrohm polarographic cell.
The voltammetric waves of $5 \cdot 10^{-4}$ M U(VI) in 0.1 M NaClO$_4$ solution were recorded in the range of -0.2 V to -1.2 V using a static mercury drop electrode (SMDE) versus a Ag/AgCl, KCl/3M (SE) reference electrode. The pH was kept constant by addition of corresponding amounts of diluted HClO$_4$ and carbonate-free NaOH before the measurement which was carried out under nitrogen.

In addition to the well-known reversible U(VI)/U(V) reduction in mineral-acid solution at -180 mV vs. SE /3/ there are two ranges with characteristic reduction behavior.

i) pH 4-8: The voltammograms show the decrease of the cathodic wave at -180 mV vs. SE at the pH is increased from 4 to 6 and the simultaneous appearance of a wave at -650 mV vs. SE (Fig. 1a). This change is caused by the hydrolysis of the uranyl(VI) ion where coordinated water molecules are replaced by hydroxyl groups /4/.

ii) pH 8.5-12: Between pH 8 and pH 10 we find the transition of the uranyl(VI)-dihydroxo complex to the trihydroxo complex which is the only species in the pH range 10-12. Above pH 8 the voltammograms shift to more negative potentials (Fig. 1b), just at the pH where the trihydroxo complex is formed. In contrast to the second peak group we do not find a uniform wave family for the reduction of the pure U(VI)-trihydroxo complex in the pH section 10-12.

The speciation diagram (Fig. 2) shows that the concentration of the free uranyl(VI) ion decreases to zero and different hydrolyzed species are formed with increasing pH:

(a) $[\text{UO}_2(\text{OH})_2]^{2+}$ in the pH range 5-10 and $[\text{UO}_2(\text{OH})_2]^{3+}$ above 8,
(b) $[\text{UO}_3(\text{OH})]^{4+}$ and $[(\text{UO}_2)_{2}(\text{OH})_2]^{5+}$ at pH 4.5-6,
(c) $[(\text{UO}_2)_{3}(\text{OH})_2]^{6+}$ and $[(\text{UO}_2)_{4}(\text{OH})]^{7+}$ at pH 5-8 and,
(d) $[(\text{UO}_2)_{5}(\text{OH})]^{8+}$ at pH 7.5-10.

Acknowledgments

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SOFTWARE TO COMPUTE FLUORESCENCE LIFETIMES FROM TIME-RESOLVED LASER-INDUCED FLUORESCENCE SPECTROSCOPY (TRLFS) STUDIES, EXPLOITING THE FULL SPECTRUM

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Nearly all published speciation data that is based on TRLFS experiments is derived from only a part of the primary spectroscopic information. The software "POLYLIFE" was developed to improve this situation. To obtain fluorescence lifetimes, it applies a robust multi-level minimization strategy to the whole wavelength range.

Methodology

With time-resolved laser-induced fluorescence spectroscopy (TRLFS) it is possible to discriminate between species that show nearly identical fluorescence spectra, especially in environmental samples. Here the component of interest, e.g., uranium(VI), is usually present only in very small amounts, and nevertheless with a complicated speciation pattern. To obtain fluorescence lifetimes, the fluorescence is fitted as a function of time to a sum of exponential decay functions. Up to now, only a limited number of wavelengths (most often the main peaks) or the integral of the whole spectrum (or part of it) is used for the fit, see e.g., /1/.

We use the full information of the 2D-TRLFS-spectrum. The spectrum is analyzed separately and sequentially for each wavelength. Fluorescence lifetimes and signal amplitudes are obtained for all the distinguishable species together with their respective standard deviations. Then the fluorescence lifetimes are averaged over all wavelengths with their standard deviations as weighing factors. This gives a total fluorescence lifetime for each species and the standard deviation of the mean. The nonlinear fitting procedure to find the best parameter set has three steps. First, user-specified parameter guesses (or in absence of them, a guess from the program) are used to start a random search algorithm. The second minimization level feeds the results of step one into a derivative-free optimization method that is based on the simplex method. And third, these results in turn initializes a Levenberg-Marquardt search. For step one and three, modules from /2/ have been adapted, whereas step two is based on /3/.

Results

C was chosen as the programming language. The program, called POLYLIFE, runs under various UNIX operating systems; a port to MS Windows is planned. The user can analyze the whole spectrum or just a part of it by defining a wavelength and/or a time window. To smooth the signal it is possible to integrate over a fixed number of wavelength (pooling). The input for the program has to be supplied by the user either interactively or in a batch file (with each item on a separate line). Its structure is listed below and gives also an overview about the main software features available at the moment:

- Name of input file with 2-D spectrum
- Name of output file
- Number of distinguishable species
- Estimation values of the fluorescence lifetime in nanoseconds (ns) for each species. Each such value can be followed by space and any letter to indicate that this lifetime should be considered as fixed throughout the minimization procedure.
- "j" or "n" for whether or not extensive runtime output should be generated
- Start of the wavelength window in nm
- End of the wavelength window in nm
- Number of wavelengths to be pooled for internal averaging
- Start of the decay time window in ns
- End of the decay time window in ns

The program is limited to a maximum of up to four species, 500 wavelengths and 30 time steps. The spectrum to be analyzed must be in a format where the first line consists of a keyword and all the time steps (in ns). Each following line starts with the wavelength (in nm) and contains the signal for each time step. All entries in the input file have to be separated by at least one space or tab. The program output has the following column structure:
- 1st column: wavelength in nm
- 2nd column: lifetime in ns for 1st species
- 3rd column: error of lifetime in ns for 1st species
- 4th column: signal amplitude for 1st species

{ same blocks of 4 columns for 2nd, 3rd, ... species }

- last column: sum of squared deviations between measured and calculated fluorescence signal

Discussion and Conclusions
There are several advantages of the new software. The exploitation of the full spectral information allows for the detection of species contributing only to a small part of the spectrum. It is based on a very robust fitting procedure and gives more reliable parameter uncertainties. The data processing is flexible and the software can be used in batch mode for background operation. It has already been applied successfully to a variety of TRLFS spectra in systems containing uranyl complexes, e.g., in /4/.

References

COUPLING OF CHEMICAL SPECIATION MODELING WITH RISK ASSESSMENT SOFTWARE: CODE DEVELOPMENT WITH EMPHASIS ON PARAMETER SENSITIVITY ANALYSIS

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An already approved risk assessment software package (PRISM / BIOPATH) has been extended with chemical speciation code modules. This enables a better description of the physico-chemical state of environmental systems by unfolding the \(K_d\) value, which presently is the only parameter beside concentrations and pH to characterize the chemistry in PRISM / BIOPATH applications. Up to now the chemical speciation is calculated by the EQ3/6 software. It is planned to incorporate other chemical speciation codes.

Modelling Approach and Results
PRISM /1/ is a suite of three programs used for parameter sensitivity analysis. The BIOPATH /2/ code provides the risk assessment model predictions. Its mathematical method is based on compartment theory. Presently, BIOPATH utilizes the \(K_d\) concept of distribution coefficients, i.e., ratios of the sorbed (fixed, immobilized) and unsorbed (free) fraction of a component. This is, however, a consolidation of many physico-chemical processes into one parameter, creating a severe weakness of the \(K_d\) principle /3/. A much better strategy is to decompose the \(K_d\) value into its main defining processes. Thus the parameters affecting the \(K_d\) the strongest can be identified and extra measurements be designed to reduce their uncertainties.

We make \(K_d\) values available to the risk assessment code via on-line calls of external speciation programs. This will slow down the computing, but makes the model development efficacious and fast, and provides a much higher accuracy of the results. The EQ3/6 /4/ package was chosen from the variety of available speciation programs. It is available as source code, has been used for many years and was checked by a number of international validation programs. EQ3/6 covers all chemical reactions in homogeneous aqueous solutions, including redox reactions, and handles precipitation and dissolution equilibria using kinetic rate laws. A drawback is the lack of an implementation of surface complexation models. But due to the flexible software interfaces that we designed between speciation and risk assessment codes, it needs
a comparatively small effort to later substitute the present speciation modules by another, better
program. The following strategy proved to be successful, with all the non-chemical set-up steps
left out for the sake of clarity:

Step: Action (the term box is used as a synonym for compartment):
1 Define the compartment structure and create a file MODEL_BOX
2 Define the chemical model for each box, collect all the necessary chemical data and create a
file MODEL_CHEM.
3 Scan MODEL_CHEM with a separate preprocessor executable CHEM2EQ and build from it in
parallel (to guarantee consistency between all files):
   - an EQ3NR input template EQ3.TEMPLATE
   - a PRISM1 input file MODEL.PRISM
   - a further input file DIM.CHEM containing just the dimensions of the problem: number of
boxes and number of components for each box
4 Run of PRISM1: generation of all parameter set variations
5 Run of PRISM2: loop over all parameter sets, for each vector a subroutine user.for() is called:
   5.1 Build an EQ3NR input file for each box and concatenate them to one large input file
       PRISM.3i (also including the constant parameters)
   5.2 Run EQ3NR to get for all boxes: the speciation of the aqueous phase and the saturation
       indices for the minerals
   5.3 Check for mineral oversaturation, call in such cases EQ6
   5.4 Calculate K values for all boxes, using the results from the EQ3NR output file PRISM.3o
       (and the EQ6 output file PRISM.6o if necessary)
   5.5 Build the input vector for BIOPATH
   5.6 Run BIOPATH
   5.7 Update all concentrations for the next time step and go back to step 5.1 until the end of the
       time scale is reached
   5.8 Collect the final response sets together with the respective input parameter sets and write
       an output file
6 Run of PRISM3: Sensitivity analysis of the output file
7 Create graphs and reports

The file MODEL_CHEM has to be written by the user, following a well-defined, line-oriented
structure. After some general information for documentation purposes, detailed chemical data
for each compartment are specified. This includes pH and redox state information, all compo-
nents and their concentration value. To keep the chemical model as simple as possible (and
thereby speeding up the computation), the set of chemical components can differ from box to
box. Reaction constants $ can be modified depending on the actual components for each
compartment. Such reactions may include complexation, precipitation/dissolution and sorp-
tion. Another option allows to suppress certain reactions totally. Finally, every line starting
with a double-cross # is a comment, inserted to guide the user when checking the input file, and is
consequently skipped by the program.

In EQ3.TEMPLATE, for each parameter that is varied by PRISM, an appropriate tag of the form
#@##PARAi## is inserted, with iii standing for the respective three-digits number of the param-
eter (= position in the vector obtained from PRISM). All constant parameters (of the chemical
model) are not forwarded to PRISM but rather incorporated into the EQ3NR template to make
the model and thus the computing lean and fast.

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PREPARATION OF THIN-LAYER SOURCES FOR THE DIRECT MEASUREMENT OF ACTINIDES IN CONCRETE

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The determination of alpha-active nuclides in the “clearance-level” region is essential during the decommissioning of nuclear plants. The direct measurement of thin layer sources is an easy method to determine actinides in concrete without chemical separation.

For the direct measurements of actinides in concrete extremely thin and large area sources are required because the alpha-radiation has only a short range and it is absorbed in the concrete layers. Previously we prepared layers $\approx 5 \, \mu m$ with a particle size of $\approx 2 \, \mu m$ /1/. Using a two step crushing process, particle sizes with a mean diameter of 0.6 $\mu m$ were obtained. The first step involves breaking the concrete into particles with diameters between 0.02 mm (fragmentation with pulsed electrical discharge /2/) and 0.2 mm (with a jaw breaker). In the second step, the concrete is milled with special wolfram carbide milling spheres having a diameter of 1.5 $\mu m$. To prevent particle agglomeration in the suspension during the preparation of the sources this process should be carried out at a pH which is very different from the pH of the zeta potential. The zeta potential was determined by adjusting the pH of our solution accordingly we obtained layers of about 1 $\mu m$ thickness.

![GIC-spectra and peak fitting functions of concrete with 10.1 Bq/g Am. 20 h measuring time, background spectrum substracted.](image)

Fig. 1: GIC-spectra and peak fitting functions of concrete with 10.1 Bq/g $^{241}$Am. 20 h measuring time, background spectrum substracted.

Fig. 1 shows the alpha-spectra and the peak fitting functions of a concrete with an added $^{241}$Am tracer at various thickness. The spectra were measured with a grid ionization chamber (GIC). The diameter of the source was 200 mm.

The peak width of the signal is directly proportional to the layer thickness at a near-constant peak height. The peaks from the 1 $\mu m$-sources are comparable to the ones of ideal “massless” spectra. We are fitting the spectra of reference and unknown samples and compare the peak shape. By fitting and deconvoluting the unknown sample spectra, it is possible to determine different actinides and their concentration in a single sample. This direct measurement can be done within one day and does neither require thermal chemical treatment of the concrete nor chemical separation and electrochemical deposition.

Fig. 2 shows the spectra of the same concrete sample using a large-area passivated ion-implanted planar silicon detector (PIPS). The diameter of the source was 80 mm.
**Acknowledgments**

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We gratefully acknowledge the collaboration of Dr. I. Haase, TU Dresden for particle size analysis, Dr. H. Friedrich, IKTS Fraunhofer Gesellschaft for the Zeta potential measurement and B. Barz for the source preparation.

**References**


**DETERMINATION OF ACTINIDES IN FISH SAMPLES FROM THE RIVER IRTYSH AND THE KOIENOVSKOIE LAKE**

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*The fish samples from two areas which may be contaminated by irradiated nuclear fuel were measured for transuranium elements. In all samples only very low concentrations of $^{237}$Np were found.*

The direct determination of the actinides in solid samples is practically impossible due to their minuscule quantities and the short range of the "-radiation. Therefore, the transuranics were separated from the bulk mass of the samples and then separated from each other. First the samples were incinerated at 600 to 700°C in order to completely destroy all organic material present. After the incineration, masses between 0.85 and 4.54 % of the initial wet mass were obtained. The samples were leached treated with $\text{H}_2\text{O}_2$ to obtain tetravalent pluto-
Table 1: The measured total $^{137}$Cs activity of fractions 1 and 2 in comparison to the $^{137}$Cs content of the samples from the Koienovskoie Lake and the River Irtysh.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$^{137}$Cs Bq/g</th>
<th>fraction 1 Bq/g</th>
<th>$^{137}$Np Bq/g</th>
<th>fraction 2 Bq/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Koienovskoie Lake</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>441(Y)</td>
<td>14.25</td>
<td>3.26$	imes$10^{-3}</td>
<td>2.29$	imes$10^{-3}</td>
<td>1.90$	imes$10^{-3}</td>
</tr>
<tr>
<td>444</td>
<td>12.34</td>
<td>2.44$	imes$10^{-3}</td>
<td>1.15$	imes$10^{-3}</td>
<td>3.10$	imes$10^{-3}</td>
</tr>
<tr>
<td>62</td>
<td>39.32</td>
<td>1.68$	imes$10^{-3}</td>
<td>9.10$	imes$10^{-4}</td>
<td>3.30$	imes$10^{-4}</td>
</tr>
<tr>
<td>65</td>
<td>43.32</td>
<td>3.85$	imes$10^{-4}</td>
<td>2.11$	imes$10^{-4}</td>
<td>7.50$	imes$10^{-5}</td>
</tr>
<tr>
<td>625</td>
<td>43.20</td>
<td>8.47$	imes$10^{-4}</td>
<td>2.20$	imes$10^{-4}</td>
<td>1.22$	imes$10^{-4}</td>
</tr>
<tr>
<td>638</td>
<td>27.47</td>
<td>3.66$	imes$10^{-4}</td>
<td>8.0$	imes$10^{-5}</td>
<td>1.60$	imes$10^{-5}</td>
</tr>
<tr>
<td>River Irtysh</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N1-2</td>
<td>0.020</td>
<td>2.90$	imes$10^{-4}</td>
<td>1.60$	imes$10^{-4}</td>
<td>7.0$	imes$10^{-5}</td>
</tr>
<tr>
<td>N3-5</td>
<td>0.065</td>
<td>2.4$	imes$10^{-3}</td>
<td>8.0$	imes$10^{-4}</td>
<td>6.0$	imes$10^{-4}</td>
</tr>
<tr>
<td>N6-13</td>
<td>0.065</td>
<td>8.0$	imes$10^{-4}</td>
<td>2.0$	imes$10^{-4}</td>
<td>2.0$	imes$10^{-4}</td>
</tr>
<tr>
<td>441(B)</td>
<td>0.075</td>
<td>1.40$	imes$10^{-4}</td>
<td>3.0$	imes$10^{-4}</td>
<td>1.0$	imes$10^{-3}</td>
</tr>
<tr>
<td>442</td>
<td>&lt;0.005</td>
<td>1.80$	imes$10^{-4}</td>
<td>2.0$	imes$10^{-4}</td>
<td>1.0$	imes$10^{-4}</td>
</tr>
<tr>
<td>11-1</td>
<td>&lt;0.005</td>
<td>1.6$	imes$10^{-4}</td>
<td>3.0$	imes$10^{-4}</td>
<td>0</td>
</tr>
</tbody>
</table>

The cesium activity and the total $^{137}$Cs activity of both fractions are higher in the Koienovskoie Lake samples than in the Irtysh River samples. The $^{237}$Np-peak is measurable in fraction 1 of all samples. The measured $^{237}$Np activity is from about 4.0$^{-3}$ to 10$^{-4}$ Bq/g. The annual exposure limit in Germany for the ingestion of $^{237}$Np is 1.0$^{-4}$ Bq per person. This would be equivalent to a consumption of 2500 kg fish per person and year using the values from the most contaminated sample No. 65.

The $^{137}$Cs activity compared to the cesium-content is shown in Tab. 1.

In the fraction 2 of all samples no spectral lines of americium were found. Future measurements are planned with more sample masses in order to better determine the activities of the trivalent actinides.
The lateral distribution of ultra-traces of radium in natural rock material was recorded by secondary ion mass spectrometry (SIMS) in the presence of other members of the decay series.

Part of the research on the transport behaviour of radium downstream of the Königstein uranium mine /1/ was focused on the following issues:

i) the distribution of Ra on the mesoscopic level, i.e., with a resolution of about 0.1 mm, in the radioactivity-containing cenomanian sandstone strata of the aquifer no. 4 located above the granite basement and

ii) the identification of its specific mineralogic binding sites.

The radioactive equilibrium within this decay series was expected to be locally disturbed (Ra bound separately from U) because these sandstone strata are more or less affected by ground water streams and both elements are characterised by different solubility and retention properties. Sequential extraction, which was applied in parallel /2/, corroborated this assumption.

Concerning the locally resolved analysis of Ra, it should be noted that there are a number of experimental problems:

i) Ra cannot be specifically detected by autoradiography using films /3/ or luminoradiography /4/ for recording alpha tracks;

ii) the alpha and gamma lines of Ra-226 as the mostly abundant isotope suffer from more or less serious superposition effects due to the radiation of other nuclides. This prevents a direct spectrometric identification of the Ra radiation even if a local measurement would be achievable;

iii) corresponding to the average specific radioactivity of #50 kBq/kg, the mass of Ra-226 is at best in the lower ppb range.

Therefore, an extremely sensitive method would be required to measure the Ra atoms (or ions) that are distributed within the sandstone. We applied secondary ion mass spectrometry which should cover the above-mentioned concentration range because of an expected high ionisation yield for Ra. Moreover, the method has a spatial resolution of about 1 µm.

First results are reported here using a Cameca ims 5f double-focussing magnetic sector field spectrometer. At first, the usual mass resolution of M/ΔM = 300 was adjusted for positive secondary ions, combined with energy filtering. Rock samples of different strata were investigated in the as-received state and after H2SO4 leaching. A 2-nm Au film was deposited onto the polished cross sections to achieve electrical conductivity. Areas of 250x250 µm2 were scanned.

Test measurements were performed using a sample which was doped with 5x10^-10 g Ra-226 on an area of about 1 mm2. The results for three natural sandstone types showed that the energy filtering mode was not sufficient to suppress disturbing cluster species (among them also 197Au29Si+ (225.9437 Da), 206PbH16O+ (225.9872 Da) and 226Ra (226.0254 Da). However, this mode causes a disadvantageous yield drop and requires frequent mass calibration. Finally, the search for radium was successful by recording the Ba signal in an enlarged area. It was shown earlier that the radium homolog barium is bound in a similar manner in the leached rock types /2/.

This study showed that ultra-traces of Ra can be directly detected by SIMS. Its lateral/spatial distribution in natural rock material was recorded in the presence of other members of the decay series, perhaps for the first time.

Fig. 1 shows a site where Ra could be unambiguously detected.
Fig. 1: Comparison of images of a polished sandstone sample (Wechsellagerung, leached); left: radium distribution according to SIMS (area: 250 @50 µm², radium signal: relative intensities); right: photomicrograph of the same area.

Acknowledgment
The authors thank Dr. H. Wendrock, Institut für Festkörper- und Werkstofforschung Dresden e.V., for preparing the photomicrographs.

References
Organic Matter and its Interaction with Radionuclides
ISOLATION AND CHARACTERIZATION OF HUMIC ACID FROM A FLOODPLAIN OF THE RHEIN RIVER

M. Bubner, S. Pompe, A. Otto, K.H. Heise
Forschungszentrum Rossendorf e.V., Institute of Radiochemistry

We isolated humic acid as reference material from mud of the floodplain of the Rhein river. A combination of organic and inorganic extraction were devised to take into account the high content of inorganic and low molecular organic compounds, coming probably from industrial and urban products during the genesis of the humic material.

Results and discussion

In order to determine the influence of urban and industrial products during the genesis of humic acids we isolated and characterized humic acid from mud of a floodplain of the Rhein river, near Rheinstetten. The wet sample had a pH of 8. It was dried on air and analyzed.

The analytical results are summarized in Tab. 1. To isolate the humic acid the sample was dried under vacuum (13 Pa) and the low-molecular organics were separated by successively extracting them with heptane and ethanol. Non-bound humic acids were extracted with 1 M NaOH. The main humic acid fraction was separated with 2 M HCl from the alkaline earth containing soil matrix with 2 M HCl. Then the humic acid-containing precipitate was taken up in 2 M NaOH and precipitated with 2 M HCl. The results are summarized in Tab. 2. The isolated humic acid contained a high amount of inorganic materials. Therefore, the sample was further purified according Kim et al. /2/. The results of the chemical analysis of the purified humic acid are compared in Tab. 3 with two other humic acids that did not undergo further purification.

Conclusions

The results show that the alkaline earth, silicates and aluminum that are bound to humic acid cannot easily be removed. In order to remove most of these impurities the humic acid should undergo a multiple chemical treatment with NaOH and HCl. This however would significantly alter the chemical structure and perhaps also the functionality of the humic acid. In light of our results, it appears questionable if iron and aluminium can be reduced to trace levels.

We are currently devising a method to overcome this problem.

Acknowledgment

The authors thank W. Wiesener and M. Saupe for doing the element analysis, H. Görner for the determination of the elemental composition, M. Meyer and R. Ruske for the experimental work.

References

SYNTHESIS OF URANIUM(VI) AND CALCIUM COMPLEXES WITH CARBOXYLIC AND HUMIC ACIDS

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Forschungszentrum Rossendorf e.V., Institute of Radiochemistry

Uranyl complexes of organic carboxylic acids which represent structural elements of humic acids, and uranyl and calcium complexes of a natural and a synthetic humic acid were synthesized by ligand exchange starting from uranyl acetate or calcium acetate, respectively. These well-characterized substances serve as model and reference substances for structural investigations by EXAFS, ESCA and FTIR.

Experiments and discussion
Interpretation of the results from structural investigations of structures of uranyl-humic acid complexes by EXAFS, ESCA and FTIR necessitate the comparison of experimental data from substances with unknown structure with data from defined and well characterized models and reference substances /1, 2/. Therefore we synthesized uranyl complexes of organic acids with molecular structures corresponding to structural elements of humic acids, and humic acid complexes of a natural reference humic acid and a synthetic model humic acid with the maximum loading of uranyl and calcium. Solid complexes of carboxylic and humic acids were synthesized by exchanging the acetate ligand of uranyl acetate with either carboxylic or humic acid.

1. Uranyl complexes of organic carboxylic acids
Several different carboxylic acids, listed in Tab. 1, were chosen to prepare complexes with U(VI). Their carboxylate groups may simulate the carboxylate groups in humic acids.


<table>
<thead>
<tr>
<th>Functionality - functional group</th>
<th>Carboxylic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>aromatic carboxylic acid, unsubstituted</td>
<td>benzoic acid</td>
</tr>
<tr>
<td>aromatic carboxylic acid, OH- in o-position</td>
<td>salicylic acid</td>
</tr>
<tr>
<td>aromatic carboxylic acid, OH-blocked</td>
<td>o-methoxybenzoic acid</td>
</tr>
<tr>
<td>aliphatic dicarboxylic acid</td>
<td>malonic acid</td>
</tr>
<tr>
<td>aliphatic dicarboxylic acid, salt</td>
<td>malonic acid, monoammonium salt</td>
</tr>
</tbody>
</table>

Tab. 1: Carboxylic acids representing functional groups of humic acids

Due to the steric arrangement of the COOH-groups in the molecule and the low solubility of the forming complex, the reaction of stoichiometric amounts of the malonic acid led to pure uranyl malonate. Aromatic carboxylic acids give mixed complexes with three ligands as shown in Fig. 1. The desired product can only be isolated if the acetic acid can be quantitatively removed. A special case of ligand exchange is the reaction of insoluble uranyl malonate with diammonium malonate yielding diammonium uranyl dimalonate /3/.


1. Uranyl complexes of organic carboxylic acids

2. Uranyl and calcium complexes of humic acids
For the reaction of uranyl or calcium acetate with humic acids suspended in water, highly purified Aldrich humic acid, A2, and a synthetic humic acid, type M1 /4/, were used. On the
basis of the determined mval COOH per g humic acid. 4.8 meq/g for A2 and 1.0 meq/g for M1, an one-fold excess of uranyl acetate and a ten-fold excess of calcium acetate were used for the complex formation. The products were isolated by centrifugation and lyophilization.

<table>
<thead>
<tr>
<th>Humate</th>
<th>C [%]</th>
<th>H [%]</th>
<th>N [%]</th>
<th>Ca [%]</th>
<th>U [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2-Ca</td>
<td>calculated</td>
<td>49.2</td>
<td>3.9</td>
<td>0.6</td>
<td>8.7</td>
</tr>
<tr>
<td></td>
<td>experimental</td>
<td>50.5</td>
<td>3.8</td>
<td>0.7</td>
<td>8.1</td>
</tr>
<tr>
<td>M1-Ca</td>
<td>calculated</td>
<td>61.6</td>
<td>5.5</td>
<td>0.2</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>experimental</td>
<td>60.8</td>
<td>5.4</td>
<td>0.4</td>
<td>2.0</td>
</tr>
<tr>
<td>A2-UO2</td>
<td>calculated</td>
<td>32.8</td>
<td>2.6</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>experimental</td>
<td>32.3</td>
<td>2.3</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>M1-UO2</td>
<td>calculated</td>
<td>55.3</td>
<td>4.9</td>
<td>4.4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>experimental</td>
<td>49.9</td>
<td>4.6</td>
<td>3.9</td>
<td>-</td>
</tr>
</tbody>
</table>

Tab. 3: The elemental composition of the calcium and uranyl humates compared to those calculated for neutral complexes quantitatively saturated of the COOH-groups by either calcium or uranyl ions. The difference in affinity of UO22+ and Ca2+ ions to the humic acids were also examined. For this purpose, the humic acids were reacted with one-fold excess of defined mixtures of uranyl and calcium acetate having molar proportions of 1:1, 1:3 and 1:1. The exchange of the cations between solid calcium humates and a one-fold excess of dissolved uranyl acetate was examined in a subsequent experiment. In all the experiments, the molar proportion were determined of Ca to U in the resulting solid product and in the supernatant solution. The results of these experiments are summarized in Tab. 4 and 5.

Results and conclusions
The availability of defined uranyl complexes of carboxylic acids is a prerequisite for investigations characterizing parameters of COO-binding in definite molecule structures. Such model compounds may serve for comparing unknown parameters of COO-binding in uranyl humate complexes. The synthesized carboxylato uranyl complexes have a defined elemental composition and a defined structure. The synthesized calcium and uranyl humates seem to be stoichiometric neutral complexes, according to elemental analysis. They are applicable for comparative studies of the binding parameters of uranyl ions in humic acid complexes and other carboxylato-functional analogs.

The reactions of humic acids with mixtures of calcium and uranyl acetate and the exchange of uranyl between calcium humate and uranyl acetate show a greater affinity of UO22+ ions to humic acid when compared to calcium. The synthetic humic acid, M1, shows a lower solubility of its uranyl complex, due to its lower COOH-content.

Acknowledgment
The authors thank W. Wiesener for ICP-MS analysis and H. Görner for elemental analysis.

References
Thermoanalysis of a Synthetic and a Natural Humic Acid and Their Calcium- and Uranyl Compounds

G. Schuster, M. Bubner, S. Pompe, K.H. Heise, H. Nitsche
Forschungszentrum Rossendorf e.V., Institute of Radiochemistry

TG, DTG and DTA measurements were performed of the decomposition of a synthetic humic acid (R36) and a natural humic acid (A2) from Aldrich and their respective Ca and U(VI) compounds. Conclusions were done about the chemical structure and the influence of the metal cations on the thermal stability of the humic molecules. By reaction to definite compounds of the metals the content of bound metal was determined.

Experimental

We studied the thermal decomposition of a) a synthetic humic acid (R36) that was prepared from xylose, phenylalanine and glycine, b) a natural humic acid (A2) from Aldrich, and c) their respective calcium and uranium (VI) compounds. This compounds were prepared by the reaction of solutions of the humic acid and the metal acetates. Preparation and purification of the substances was described earlier /1, 2, 3/. About 5 mg were inserted in a Setaram thermoanalyzer, heated with 10°C/min up to 110°C where the temperature was held for 20 minutes. Then the temperature was increased to 1000°C and held for 10 minutes. The heating was done under a constant flow of oxygen (3 l/h). The determination varied between 0.1 and 0.6 %, depending on the substance investigated.

Results and Discussion

In a first endothermal reaction at about 80°C, 6 to 11 % moisture are evaporated (reaction 1). The main oxidation of the organic matter takes place in two exothermal reactions with peak temperatures of Tp = 285 to 340°C (reaction 2) and 370 to 450°C (reaction 3). R36 showed a fourth exothermal reaction at 530°C, and the calcium and uranyl complexes showed several small peaks above 450°C where the reaction to the final inorganic compounds occurred. The DTG thermograms of R36 and its respective Ca and U(VI) complexes are shown in Fig. 1.

Aliphatic and aromatic bonds in humic acids are broken above 350°C and 400°C, respectively, where oxidation occurs /4/. Therefore the mass loss of the exothermal reaction 2 is proportional to the aliphatic, and that of reaction 3 to the aromatic groups. According to these results, R36 should have much more aliphatic and less aromatic groups than A2. Tab. 1 summarizes the mass losses and their assignments.

After reaction 3 is completed, more than 85% of the organic matter is oxidized. The reaction temperatures for the individual compounds are summarized in Tab. 2. The shift of the temperature for reaction 3 is a measure of the thermal stability of the compound. This shifts may be due to the different metal-humic acid bond strength or to different steric proportions between the metal and humic acid groups. In the first case, a dependence should exist on the electronegativity and in the second case on the ionic radius. Neither dependencies could be found.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction-temp. [°C]</th>
<th>ΔT [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>R36</td>
<td>448</td>
<td></td>
</tr>
<tr>
<td>R36-Ca</td>
<td>403,9</td>
<td>- 44,1</td>
</tr>
<tr>
<td>R36-UO2</td>
<td>371</td>
<td>- 77</td>
</tr>
<tr>
<td>A2</td>
<td>393,9</td>
<td></td>
</tr>
<tr>
<td>A2-Ca</td>
<td>383,5</td>
<td>- 10,4</td>
</tr>
<tr>
<td>A2-UO2</td>
<td>483,5</td>
<td>+ 89,4</td>
</tr>
</tbody>
</table>

Tab. 2: Reaction temperature shift for the reaction that degrades more then 85% of the organic matter
Calculation of the content of bound metal from the oxidation
The inorganic residues of the reactions are definitely CaO, UO₂, and Na₂CO₃. From their amount the content of bonded metal could be calculated. The calcium and uranium (VI) humates were prepared by reacting them with the respective metal acetates. This divalent metals can react in two different reaction paths /2/:

\[
\begin{align*}
\text{HA} + \text{Ca(CH}_3\text{COO)}_6 & \quad \rightarrow \quad \text{HACa} + 2 \text{ CH}_3\text{COOH} & \quad \text{Me : HA} = 1 : 1 \quad (1) \\
\text{HA} + 2 \text{Ca(CH}_3\text{COO)}_6 & \quad \rightarrow \quad \text{HA}[\text{Ca(CH}_3\text{COO)}_6]_2 + 2\text{CH}_3\text{COOH} & \quad \text{Me : HA} = 2 : 1 \quad (2)
\end{align*}
\]

In both cases the two H⁺ ions of the resulting acetic acid are dissociated from the carboxylic groups of the humic acid (HA).

Based on the determined amount of carboxylic groups per gram humic acid, which is 4.8 mequ/g for the A2 and 1 mequ/g for the R36, the theoretical metal content was calculated for both reaction paths and compared with the experimental values derives from TA (thermal analysis). The results are listed in Tab. 3. Calcium reacts with R36 in a 1:1 and with A2 in a 2:1 ratio. U(VI) shows with A2 a 1:1 and with R36 a mixed 1:1 and 2:1 ratio.

References

COMPLEXATION BEHAVIOR OF A SYNTHETIC HUMIC ACID WITH URANYL IONS IN COMPARISON TO A NATURAL HUMIC ACID BY TIME-RESOLVED LASER-INDUCED FLUORESCENCE SPECTROSCOPY

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The complexation behavior of a synthetic humic acid (HA) and purified natural humic acid from Fluka with uranyl ions was investigated by time-resolved laser-induced fluorescence spectroscopy (TRLFS). The spectroscopic data were evaluated using the charge neutralization model of Kim and Czerwinski. Both humic acids show a comparable complexation behavior with uranyl ions (pH 3.90 ± 0.05; I: 0.1 M NaClO₄).

Experimental and results
The aim of this work was to compare the complexation behavior of a synthetic humic acid (type M42) prepared from glutamic acid monohydrate and xylose /1/ and of the purified HA from Fluka /2/ with U(VI) in aqueous solution. This should determine whether or not the synthetic HA can be used as a model substance to describe the complexation behavior of natural HA.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Synthetic HA (M42)</th>
<th>Fluka-HA</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA [mg/L]</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>UO₂⁺ [mol/L]</td>
<td>1.0·10⁻⁶ - 4.2·10⁻⁶</td>
<td>0.3·10⁻⁶ - 2.9·10⁻⁶</td>
</tr>
</tbody>
</table>

Tab. 1: Experimental conditions (pH: 3.90 ± 0.05; I: 0.1 M NaClO₄)

The measurements were performed at pH 3.90±0.05 and 22 ± 1 °C in 0.1 M NaClO₄. Tab. 1 shows the humic acid and uranyl concentrations of the samples investigated. The proton exchange capacities (PEC) of the HA were determined with the calcium acetate method; they are 3.23 ± 0.05 meq/g for synthetic HA and 3.8 ± 0.1 meq/g for Fluka-HA. Uranyl solutions without HA present were measured for all samples in order to determine the depend-
ence of the relative fluorescence intensity on the uranyl concentration. The measurements were carried out with a Nd:YAG laser as an excitation source with an excitation wavelength of 266 nm. The laser energies applied were 450 ± 50 µJ for synthetic HA and 700 ± 70 µJ for Fluka-HA. A more detailed description of the measuring conditions is described in /1/.

Fig. 1: Emission spectra of uranyl humate solutions (Fluka-HA) in dependence on the uranyl concentration.

The measured baseline-corrected spectra of the samples with Fluka-HA are depicted in Fig. 1. The spectra represent the sum of the fluorescence intensity of the free uranyl ion, the first hydrolytic uranyl species (UO$_2$OH$^+$) and a residue of scattered laser light (second order) at 532 nm. The spectra were deconvoluted by using spectra from earlier measurements and conventional peak deconvolution methods (non-linear least square method) to calculate the contribution of the free uranyl ion to the fluorescence signal. The spectrum of UO$_2$OH$^+$ was included in the peak deconvolution because of its strong fluorescence yield, but it was neglected in the following calculations. According to a calculation of the species distribution /1/, only a minor amount of UO$_2$OH$^+$ (< 2.2 %) is present at the applied experimental conditions. For all cases, no emission spectra of the uranyl humate complex was observed. The integrals of the relative fluorescence intensities between 465 and 600 nm were calculated from the spectra of the solutions without HA. The results were used to calibrate the fluorescence signal of the free uranyl ion in the solutions with HA.

The evaluation of the spectroscopic data was performed using the metal ion charge neutralization model of Kim and Czerwinski /4/, in which the complexation reaction of a given metal ion with humic acid is considered as a metal ion charge neutralization process. In this reaction the metal ion (M) occupies the number of proton exchange sites equal to its charge (z+) (eq. 1).

\[
M^{z+} + HA(z^-) \rightarrow MHA(z^-)
\]  

In this model the loading capacity (LC), the mole fraction of the maximum available complexing sites of the humic acid, which varies with pH, metal ion, ionic strength and HA is introduced. The resulting complexation constants derived from this model are invariant of experimental conditions. The graphically determined loading capacities of the HA with uranyl ions and the complexation constants of the HA are:

<table>
<thead>
<tr>
<th></th>
<th>LC [%]</th>
<th>log $[$µmol/L$]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic HA (M42)</td>
<td>0.23 ± 0.06 (3F)</td>
<td>6.16 ± 0.33 (3F)</td>
</tr>
<tr>
<td>Fluka-HA</td>
<td>0.24 ± 0.06 (3F)</td>
<td>6.04 ± 0.23 (3F)</td>
</tr>
</tbody>
</table>

Both HA show comparable results within the given errors. This result points to a similar complexation behavior of both HA with uranyl ions under the conditions applied.

Conclusions
Comparison of the behavior of a synthetic HA to a natural HA (Fluka) by TRLFS has shown both comparable loading capacities and complexation constants for uranyl ions. From this, we can conclude that our synthetic HA models the functionality of natural HA very well.

Acknowledgments
We thank A. Otto for help with the sample preparation and Dr. W. Wiesener, Zentralabteilung Analytik, for ICP-MS measurements.

References
INTERACTION OF Pb(II) AND Bi(III) WITH HUMIC ACID STUDIED BY TIME-RESOLVED LASER-INDUCED FLUORESCENCE SPECTROSCOPY (TRLFS)

A. Brachmann, G. Geipel, G. Bernhard, H. Nitsche  
Forschungszentrum Rossendorf e.V. Institute of Radiochemistry

To determine the stability constants of lead and bismuth complexes with humic acid (FLUKA), we applied TRLFS using a Nd:YAG laser pumped OPO system. A description of the experimental setup is given elsewhere /2/.

The residues of the former uranium mining in Saxony and Thuringia contain two sources of these elements: The radioactive decay of naturally occurring uranium isotopes and paragenetic minerals of the uranium mineralisations. Weathering processes lead to the introduction of Bi(III) and Pb(II) into seepage waters where they can interact with humic substances.

Using the concept of metal ion charge neutralization /1/, we obtained the stability constants \( \log \beta_{y,0.1 M} = 3.7 \pm 0.2(2\sigma) \) for Pb(II) - humate and \( 6.73 \pm 0.06(2\sigma) \) for Bi(OH)\(_2\) - humate.

Results and discussion

Bismuth and lead are main group elements and their aquo ions Bi\(^{3+}\) and Pb\(^{2+}\) do not show fluorescence in aqueous solution. However, humic acid is fluorescent when dissolved in water. The complex formation of humic acid with certain metal ions decreases the fluorescence signal of the ligand which can be used to determine the concentration of the free humic acid. This method has been used by several authors to characterize the complexation of metal ions with fluorescent organic ligands and is known as Fluorescence quenching titration (e.g., /3/).

The experiments were carried out under atmospheric conditions. In order to avoid metal ion hydrolysis and carbonate complexation, the pH was held constant at about 4.5 and 4.0 for the lead - humic acid and the bismuth - humic acid experiments, respectively. Under these conditions only the Pb\(^{2+}\) aquo ion exists, and Bi(OH)\(_2\)\(^+\) is the main Bi(III) species. The experiments were performed at a constant ionic strength of 0.1 M NaClO\(_4\) and a temperature of 23 ± 1°C. TRLFS allows measurements at concentration ranges relevant to environmental conditions. This is particularly the case for the humic acid concentration which was 0.645 mg/L. To obtain evaluable analytical effects, the metal concentrations had to be increased above environmental levels. The metal-to-humic-acid ratios from 40 to 3000 and from 0.3 to 4 were used to study the Pb\(^{2+}\) humate and the Bi(OH)\(_2\)\(^+\) humate complexation, respectively.

Fig. 1: Humic acid fluorescence as a function of [Bi(III)]\(_{total}\). Fig. 1 shows humic acid fluorescence spectra as function of total Bi\(^{3+}\) concentration. Fluorescence of humic acid can be seen as a broad unstructured emission band in the spectral range from about 300 nm to 600 nm. The intensity decreases with increasing metal concentration due to the fluorescence depletion effect. The spectral band at 355 nm is due to Raman emission of
the water molecule. Additionally, the second order of excitation wavelength (600 nm) and H$_2$O-
Raman band (670 nm) which are generated in the spectrograph overlap with the humic acid
fluorescence signal. Similar spectra of humic acid fluorescence were observed for Pb$^{2+}$ -
humate formation.

The influence of the complexed metal on the fluorescence intensity is not equally distributed
over the entire spectral range. The extend of fluorescence depletion is most intense for those
structural elements which are involved in the metal ion binding. Due to the complex nature of
humic acid fluorescence, reliable spectra deconvolution is not possible. A distinctive metal -
humate spectra was not observed. Therefore we used the decrease in fluorescence directly to
calculate the free ligand concentration. The most intense depletion occurs in the spectral range
from 470 nm to 500 nm for Bi(OH)$_2^{+}$ - humate complexation, and from 530 nm to 550 nm for
Pb$^{2+}$ - humate complexation. The effects of the complexed metal ion on the electronic structure
of the humic acid molecule are specific for each species. Therefore different spectral changes
of the humic acid fluorescence are obtained.

The integrated fluorescence signal over the above-mentioned wavelength ranges was used to
calculate the complex stability constants according to the method that was summarized by
Brachmann /4/. Using the model of metal ion charge neutralization, the following complexation
constants were derived:

\[
\begin{align*}
\text{Pb}^{2+} + \text{HA(II)} & \rightarrow \text{WPbHA(II)} & \log \beta_{\text{Pb}^{2+}}^{\text{HA(II)}} = 3.7 \pm 0.2 \ (2F) \\
\text{Bi(OH)}_2^{+} + \text{HA(I)} & \rightarrow \text{WBi(OH)}_2\text{HA(I)} & \log \beta_{\text{Bi}^{2+}}^{\text{HA(I)}} = 6.73 \pm 0.06 \ (2F)
\end{align*}
\]

Conclusions
We showed that complexation of Pb$^{2+}$ and Bi$^{3+}$ with humic acid occurs. Because of the relatively
strong complex stability, the humate formation of these elements can compete with metal ion
hydrolysis and complexation with other inorganic ligands. According to literature data, TRLFS
studies on the complexation behavior of metal ions with humic substances have been carried
out only using data derived from the fluorescence signal of metal ions (UO$_2^{2+}$, Am$^{3+}$, Cm$^{3+}$). This
study shows that also the ligand fluorescence can be used to characterize the complexation
reactions.

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/1/ Kim, J.I., Czerwinski, K.R.: Complexation of Metal Ions with Humic Acid, Metal Ion Charge Neutralization
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/4/ Brachmann, A.: Zeitaufgelöste laserinduzierte Fluoreszenzspektroskopie zur Charakterisierung der
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1997.

COMPLEX FORMATION OF HEXAVALENT URANIUM WITH LIGNIN DEGRADA-
TION PRODUCTS

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The complexation of U(VI) with the lignin degradation products protocatechuic acid, ferulic acid, vanillic acid and
vanillin was studied at I = 0.1 M by potentiometric pH titration. The stability constants were estimated from Bjerrum’s
formation function using (a) successive approximation and (b) Irving’s least-squares treatment. To consider U(VI)
hydrolysis, non-linear fitting of the pH titration curves was carried out with the multi-equilibria program
SCOGS(version 2).

The natural disintegration of the highly stable lignin is a very slow process because only white
rot fungi are able to start the radical depolymerisation of the phenolic matrix by their special
enzyme system. The second step is the oxidative side-chain removal followed by phenol ring
cleavage and the fast degradation of the non-aromatic fragments. In this process the oxidation
of some more stable phenolic monomers occurs. Beginning with 4-hydroxy-3-methoxyacetic
acid (ferulic acid), the sequence leads over 4-hydroxy-3-methoxybenzaldehyde (vanillin) and
4-hydroxy-3-methoxy-benzoic acid (vanillic acid) to 3,4-dihydroxy-benzoic acid (protocatechuic acid). These compounds are also found in leachates of the hydrothermal wood treatment. Their phenolic hydroxyl and carboxylic groups are able to bind metals. The complex stability constants were determined potentiometrically by measuring the hydrogen ion concentration in the system: uranyl perchlorate/complexant at constant ionic strength (I = 0.1 M, NaClO4) and temperature in dependence of the added carbonate-free strong base titrant.

The titrations were carried out with an automatic titrator (model: Schott TPC 2000) equipped with a low-drift pH electrode (type: Orion-Ross 81/03), stirrer, inert gas inlet and titrant dosage capillary.

The evaluation of the pH titration curves was carried out: (1) on the classical theory of stepwise complex formation, analyzing Bjerrum's formation function (1921) by successive approximation:

\[ \beta = \frac{n_{MA}^R}{n_{MA}} = \frac{[MA]^{-1}}{[MA]} = \frac{[MA]^n[A]}{[MA]^n[A]} \]

or linear regression, as introduced by Irving and Rossotti /1/:

\[ \beta = \frac{n_{MA}^R}{n_{MA}} = \frac{(2+\alpha)n_{MA}^R[A]}{(n+1)_{MA}} \]

and (2) by non-linear fitting of the unmodified pH titration curve with Sayce's multi-equilibria program "SCOGS" (Stability Constants of General Species) /2/ considering hydrolysis and the formation of mixed-ligand complexes.

The following hydrolysis constants of UO22+ as log Qxy values, recalculated for I = 0.1 M by log Qxy = log Kxy + a1/2/(1+112) + bm were used /3/:

<table>
<thead>
<tr>
<th>Complex</th>
<th>log Qxy Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO2(OH)2</td>
<td>-5.976</td>
</tr>
<tr>
<td>(UO2)2(OH)3</td>
<td>-10.8</td>
</tr>
<tr>
<td>UO2(OH)4</td>
<td>-20.0</td>
</tr>
<tr>
<td>UO2(OH)5</td>
<td>-33.8</td>
</tr>
</tbody>
</table>

Protocatechuic acid: 3,4-dihydroxybenzoic acid forms very stable complexes with U(VI). The evaluation of Bjerrum's formation function led to stability constants of the (1:1)- and (1:2)-complexes, which are in full agreement with the stability values, calculated by SCOGS curve fitting and given in the literature /4/, i.e., U(VI) hydrolysis is strongly suppressed in the presence of this complexant (Tab. 1).

Ferulic acid: Assuming the complex [UO2(fer)2] the introduction of the acidic [UO2H(fer)] led to constant values, which are independent on the U(VI) concentration and the fit discrepancy around pH 5 disappeared (Tab. 1). Additional consideration of [UO2H2(fer)2] (log β 16, [UO2H2(fer)2] -22) and [UO2(fer)OH] -0.05 did not contribute to a good curve simulation.

Vanillin: The interaction of U(VI) with vanillic acid results in a stepwise formation of mono-nuclear (1:1)- and (1:2)-complexes (Tab. 1). The stability constants, evaluated in the different ways, are in distinct conformity, i.e. hydrolysis plays no evident role in the pH range studied (3.6#pH#6.5).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H3(pro)</td>
<td>4.26/8.64/13.1</td>
<td>14.8 ± 0.74</td>
<td>-</td>
<td>25.9 ± 1.0</td>
<td>-</td>
</tr>
<tr>
<td>H2(fer)</td>
<td>4.45/8.81</td>
<td>6.88 ± 0.56</td>
<td>11.9 ± 0.65</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H(vac)</td>
<td>4.35/8.71</td>
<td>7.16 ± 0.82</td>
<td>-</td>
<td>13.6 ± 1.1</td>
<td>-</td>
</tr>
<tr>
<td>H(van)</td>
<td>7.18</td>
<td>4.47 ± 0.09</td>
<td>-</td>
<td>-</td>
<td>-3.95 ± 0.5</td>
</tr>
</tbody>
</table>

Tab. 1: Stability of U(VI) complexes with protocatechuic acid, ferulic acid, vanillic acid and vanillin computed by non-linear curve fitting considering hydrolysis.
[\text{UO}_3\text{(van)(OH)}_3]^- did not result in a more improved approximation. These species are therefore not as predominant as [\text{UO}_2\text{(van)}_2\text{(OH)}_2]^2^-.

Acknowledgments
This study was supported by the Sächsisches Ministerium für Wissenschaft und Kunst under contract no. 4.7541.88-FZR/402.

References
/2/ Sayce, I.G.: Talanta 15, 1397 (1968)

INTERACTION OF U(VI) WITH WOOD DEGRADATION PRODUCTS
A POTENTIOMETRIC STUDY

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Carboxylic and phenolic hydroxyl groups of wood degradation products and their complex formation with U(VI) were determined by potentiometric titration. Considering U(VI)-hydrolysis, the formation constants were computed using the multi-equilibrium program SCOGS2.

During the process of mine flooding, wood can be hydrothermally degraded and its products may have an influence on contaminant migration. The degradation process was simulated in laboratory experiments using mine wood and distilled water under nitrogen at 90 bar and 70°C (W/N-p,T) /1/. Direct titration of the solution was carried out to determine the carboxyl- and phenolic hydroxyl content. They were found to be 2.9 meq/g TOC and 5.7 meq/g TOC, respectively. The dissociation constants (pK\text{diss}) are 4.4 for the carboxylic and 9.3 for the phenolic hydroxyl groups (20°C, I = 0.1 M NaClO).

For the evaluation of formation constants, the solutions were treated as mixtures of two ligands. Different ratios of total ligand:U(VI) were titrated with carbonate-free NaOH under nitrogen. The formation constants considering hydrolysis of the U(VI) were determined using the program SCOGS2 /2/ (Tab. 1), $ being defined as the cumulative formation constant:

\[
\log \beta = \log \left( \frac{[\text{UO}]}{[\text{Ligand}][\text{OH}]} \right)
\]

(n = negative integer).

For a total ligand to U(VI) ratio of 16.4:1, no distinction between the complexes UO\text{B(OH)}_3 and UO\text{B(OH)}_4 (A = carboxylic groups, B = phenolic hydroxyl groups) was possible. Both can occur, but not at the same time. Neither the non-hydrolyzed complexes (UO\text{A, UO\text{B}}) nor complexes with two ligands (UO\text{A(OH)}_2, UO\text{B(OH)}_2, UO\text{AB(OH)}_2 (n=0,1,2) were necessary to fit the potentiometric data. A different extract obtained from the same mine wood (distilled water, 95°C, 1 bar, air (W/L-NB)) contained more carboxylic groups (7.8 meq/g TOC, pK\text{diss} = 4.4) and phenolic hydroxyl groups (6.3 meq/g TOC, pK\text{diss} = 8.5). Due to the presence of oxygen in the solution during the degradation process more functional groups were formed which are slightly more acidic than the functional groups of the degradation products.
products obtained under nitrogen. The stability constants with U(VI) show that stronger complexes were formed (Tab. 2).

In contrast to the other sample (W/N-p,T) non-hydrolyzed complexes and complexes containing two ligands were determined.

Conclusions

Mine wood degrades under hydrothermal conditions and functional groups are being formed. The higher the oxygen content in solution, the more acidic these groups are forming stabler complexes with U(VI).

Acknowledgments

This work was supported by the Sächsisches Ministerium für Wissenschaft und Kunst under contract No. 4-7541.83-FZR/402.

References


INTERACTION OF HEXAVALENT URANIUM WITH GLUCONIC ACID AND GLUCURONIC ACID

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The interaction of U(VI) with gluconic acid and glucuronic acid was studied at I = 0.1 M by potentiometric pH titration. First results for stability constants, measured under the given conditions, were calculated by means of the multi-equilibria program SCOGS(version2), taking hydrolysis into account.

A great variety of cellulose degradation compounds with its different functional groups contributes to the complexation of heavy metals in natural waters. With regard to the remediation of mining sites the interaction of U(VI) with gluconic acid and glucuronic acid was studied by pH potentiometry.

Experimental methods, evaluation and results

The determinations were carried out by titrating solutions of uranyl perchlorate (5@10^{-5} - 5@10^{-4} M) and complexant (1@10^{-3} M) with strong base at constant ionic strength (I = 0.1 M, NaClO₂) and temperature (25°C) as described in the previous article. The evaluation was done by the “SCOGS” multi-equilibria program /1/ after the determination of the complexant’s dissociation constant.

Gluconic acid: Assuming the interaction as a stepwise formation of mono-nuclear complexes, i.e. [UO₂(uco)]^{x+} with x$1, the SCOGS curve fitting leads to a set of constants (log β₃= 3.90/8.70/13.7 for x = 1-3) with a curve approximation of Fᵦ = 7.6@10^{-2}. If we consider partially hydrolyzed species the fit could be improved to Fᵦ = 1.5@10^{-2} with the result: log β₁₂ = -1.43 ± 0.95 for [UO₂(uco)(OH)]²⁺ and log β₁₃ = -9.76 ± 3.8 for [UO₂(uco)(OH)₂]³⁻ (Tab. 1). Additional introduction of other hydrolyzed species resulted in a loss of fit accuracy.

<table>
<thead>
<tr>
<th>complexant [A]</th>
<th>pK_{diss}</th>
<th>log β₁,₁ [UO₂(AOH)]</th>
<th>log β₁,₂ [UO₂A(OH)₂]</th>
<th>log β₁,₃ [UO₂A(OH)₃]²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) H(uco)</td>
<td>3.78 ± 0.028</td>
<td>-</td>
<td>-1.43 ± 0.95</td>
<td>-9.76 ± 3.8</td>
</tr>
<tr>
<td>2) H(uro)</td>
<td>3.57 ± 0.021</td>
<td>-1.41 ± 0.40</td>
<td>-5.63 ± 0.21</td>
<td>-</td>
</tr>
</tbody>
</table>

Tab. 1: Stability of U(VI) complexes with gluconic acid¹ and glucuronic acid² computed by non-linear pH curve fitting considering hydrolysis

Glucuronic acid: In this case we found a similar behavior. The interaction constants of the complexes [UO₂(uro)]^{x+} with x$1 changed evidently with the uranium-complexant ratio. Considering hydrolysis, we found the best fit assuming the species [UO₂(uro)(OH)]²⁻ with log β₁₁ = -5.61 ± 0.15 (Tab. 1). The additional introduction of the neutral complex [UO₂(uro)(OH)] led to log β₁₁ = -1.43 ± 0.4 and log β₂ = -5.64 ± 0.17 without any changes in the fit. Other
species e.g. \([\text{UO}_2\text{O}](\text{uro})\text{OH})\] and \([\text{UO}_2\text{O}](\text{uro})(\text{uro})\text{OH}\] do not exist in such solutions and the occurrence of \([\text{UO}_2\text{O}](\text{uro})\] and \([\text{UO}_2\text{O}](\text{uro})\text{OH}\] has less probability.

Conclusions
The interaction of U(VI) with gluconic acid and glucuronic acid do not lead to a series of pure complexes. Our pH curve fittings pointed out that mono-nuclear complexes with one organic ligand and two or three hydroxyl groups in the first coordination sphere are formed. Escandar et al. /2/ describe a similar situation for the formation of gluconato complexes of Cd(II), Hg(II) and Pb(II) (Tab. 2). They concluded that the complexation occurs mainly via carboxylic groups and that neighboring hydroxyl groups are involved in the coordination. The introduced species for the best fitting of the pH titration curve are assumed and their existence should be verified by independent methods such as, for example, infrared (FTIR) and laser-fluorescence spectroscopy (TRLFS) as well as X-ray absorption spectroscopy (EXAFS).

<table>
<thead>
<tr>
<th>metal ion [M(^{2+})]</th>
<th>(\log \beta_{11} [\text{MA}^+])</th>
<th>(\log \beta_{11,1} [\text{MA(OH)}])</th>
<th>(\log \beta_{11,2} [\text{MA(OH)}^+])</th>
<th>(\log \beta_{22,2} [\text{MA}_2(\text{OH})_2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(^{2+})</td>
<td>2.3</td>
<td>-</td>
<td>-15.7</td>
<td>-</td>
</tr>
<tr>
<td>Hg(^{2+})</td>
<td>-</td>
<td>-0.09</td>
<td>-4.03</td>
<td>-</td>
</tr>
<tr>
<td>Pb(^{2+})</td>
<td>2.49</td>
<td>-</td>
<td>-11.8</td>
<td>-10.7</td>
</tr>
</tbody>
</table>

Tab. 2: Gluconato complex stabilities of Cd(II), Hg(II) and Pb(II) according to Escandar et al. /2/

Acknowledgments
This study was supported by the Sächsisches Ministerium für Wissenschaft und Kunst under contract no. 4.7541.88-FZR/402.

References
/1/ Sayce, I.G.: Talanta 15, 1397 (1968)
The time dependency of the redox potential is shown in Fig. 1. After 21 days, more than 99.5% of the reactive groups were oxidized. The reducing capacity was determined to 11.5 ± 0.3 meq/g from two measurements series (series 1, 11.8 meq/g and series 2, 11.2 meq/g).

The reaction rate was estimated. The lignin oxidation by ferricyanide is a first order process (Fig. 2) with a reaction rate constant of $(1.24±0.08) \times 10^{-8}$ s$^{-1}$.

Lignin shows a much higher reducing capacity than humic acid under the same conditions. This means lignin is able to reduce higher substance amounts than humic acid in environmental processes.

Acknowledgments
We thank N. Zier and R. Schiene, Technische Universität Dresden, Institute of Plant and Wood Chemistry, Tharandt, for supplying the lignin samples.

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References

ANALYSIS OF CARBOHYDRATES DISSOLVED FROM PITWOOD UNDER MINE FLOODING CONDITIONS

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Carbohydrates were analyzed stemming from hydrothermal treatment of pitwood under acidic and neutral conditions. The composition of the hydrothermal extracts was studied as a function of time.

In the process of uranium mine flooding in Saxony and Thuringia, Germany, hemicelluloses of the pitwood may become structurally changed and degraded /1, 2/. The conditions prevalent in the mine have been simulated in our experiments on a wood sample obtained from the remediation company Wismut GmbH. They are summarized in Tab. 1.
The hydrothermal treatment as a function of time was first carried out with a system, in which water or mine water was periodically changed (W/L-NB-f-h and W/L-NBS-f-h) and second in a stationary system without any inflow and outflow of water (W/L-NB-s-h).

Hydrothermal treatment of pitwood hemicelluloses that consists mainly of O-acetylgalactoglucomannan and arabinino-4-O-methyl-glucuronoxylan leads to the extraction of oligomeric sugars. They are about 5% of the overall sugar content for sample W/N-p,T, and to a smaller extend of monomeric sugars. Fifty one percent of the oligomeric sugars are xylose and mannose. The main component of monomeric sugars is arabinose (Tab. 2). This means that (1) the largest proportion of xylose and mannose is not hydrolysed and therefore available in the extract as oligosaccharides, and (2) arabinose is preferentially subject to hydrolytic cleavage because of its side-chain position in the above-specified hemicellulose.

If the wood is treated for one year with acidic water from the Königstein mine (W/L-TS), one percent of monosaccharides were isolated relative to the total wood mass. Due to the short extraction time of only five hours, the monosaccharide content of the sample W/L-NBS is low when it is compared with the amount obtained from long-term treatment in acidic medium and in deionized water under pressure.

The time dependency of the wood degradation shows (1) that 1-2% of the wood is decomposed to monosaccharides and (2) after an extraction time of about 30 h, the total monosaccharide content in the stationary system is higher than in the systems with fresh water supply (Fig. 1).

The monosaccharide concentration increases more as a function of leaching time in the stationary than in the freshwater system. The higher concentration in the stationary system may be due to the additional penetration of the inner wood sphere by the remaining leachate. Moreover, it could be shown that for the experiments with acidic mine water influx only a minor change of the total monosaccharide content occurs in comparison with the system with deionized water (W/L-NB-f-h).

Acknowledgment
This work was supported by the Sächsische Ministerium für Wissenschaft und Kunst under contract No. 4-7541.83-FZR/402.

References
EXPPEMENTS FOR THE DISPOSAL OF CARBON-14 LABELED ORGANIC MATERIAL: 1. MINERALIZATION OF ORGANIC MODEL COMPOUNDS BY AMMONIUM PEROXYDISULFATE

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Universität Leipzig, Kontrollbereich Permoserstraße

Spent carbon-14 labeled organic compounds and their inactive surrogates were, with few exceptions, completely mineralized by wet oxidation at 90 - 100°C using acidified ammonium peroxydisulfate. The activity of the evolved \(^{14}\)CO\(_2\) was determined by a novel gas cuvette combined with a commercially available proportional counter tube.

Peroxydisulfate (S\(_2\)O\(_8^{2-}\)) is one of the strongest oxidants (standard electrode potential in acid solution \(E^{\circ}= +2.13 \text{ V} /1/\)). Acidified solutions of ammonium peroxydisulfate are stable at room temperature but become a rapid oxidant at elevated temperatures (80 - 100°C) which stimulate the generation of the free sulfate radical SO\(_4^{2-}\) (\(E^{\circ}~ + 2.6 \text{ V}\)). This radical initiates, in the presence of organics, a chain reaction including the production of OH\(^-\) and organic free radicals \(2/1\).

\[
S_2O_8^{2-} + 2 H^+ - 2e^- \text{ (organics)} \rightarrow W \quad 2 HSO_4^{2-} + (CO_2 + H_2O) \quad (1)
\]

The resulting product is harmless ammonium sulfate. Because of its properties, peroxydisulfate found a widespread use to convert the organic materials to water, carbon dioxide and inorganic materials (e.g., \(2/2\)). We have employed this process for wet combustion of our organic model substances.

Experimental
A 250 ml three-necked reaction flask was equipped with a magnetic stirrer bar, a reflux condenser and a 100 mL dropping funnel with a pressure equalizing tube. The condenser was connected to a cupric oxide filled quartz tube (catalyst) followed by a safety bottle and two gas traps. The catalyst in the quartz tube was heated at about 650°C. A 50 mL solution or dispersion of an organic compound (equating on equivalent of 4 millimole carbon) in 0.05 M sulfuric acid was placed in a reaction flask and subsequently heated and stirred for 4 hours at a temperature of 95 - 100°C. Twenty five mL of a 1.9 M solution of ammonium peroxydisulfate was slowly added (4 - 5 drops/min.). Evolving CO\(_2\) and other volatile products were swept away by a \(N_2\) gas stream and passed to the catalyst and the gas traps. Carbon dioxide was absorbed in 0.1 M sodium hydroxide and was determined by titration (only the inactive CO\(_2\)). The nitrogen gas stream (about 17 mL/min.) was circulated with a peristaltic pump. Chlorine, formed by the oxidation of any chlorides in the sample, is removed from the gas stream by a U-tube which contained crystalline stannous chloride. Additional experiments were conducted with the radioactive acetic acid [2-\(^{14}\)C] sodium salt, and 4-hydroxy-benzoic acid [ring UL-\(^{14}\)C] at low activity levels (max. 10 µCi). The radioactivity of \(^{14}\)CO\(_2\) was measured by a gas flow cuvette connected with a commercially available proportional counter tube (type LB 6280). It was positioned between the catalytic oxidation tube and the safety bottle.

### Results and Discussion
Tab. 1 shows the recovery of CO\(_2\) from the mineralization of selected organics with ammonium peroxydisulfate with or without the additional thermal catalytic oxidation.

Some substances were incompletely

<table>
<thead>
<tr>
<th>substance name</th>
<th>% CO(_2) yield</th>
<th>% CO(_2) without catal. oxidation</th>
<th>% CO(_2) with catal. oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetophenone</td>
<td>92</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>Succinic acid</td>
<td>96</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>1,2-Dibromoethane</td>
<td>13</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>4-Hydroxybenzoic acid</td>
<td>72</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>2-Nitrophenol</td>
<td>47</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>Palmitic acid (C(_{16}))</td>
<td>2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Nonanoic acid</td>
<td>93</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>83</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>Thiourea</td>
<td>95</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>Trapidil ®*</td>
<td>86</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>2-Xylene</td>
<td>25</td>
<td>39</td>
<td></td>
</tr>
</tbody>
</table>

* pharmaceutical agent

Tab. 1: Mineralization of some inactive organic substances with ammonium peroxydisulfate.
mineralized into carbon dioxide because of their insolubility in the aqueous phase and their low chemical reactivity.

Fig. 1 presents the kinetics of the mineralization for two C-14 labeled model substances by measuring the β-radiation of the produced \(^{14}\)CO\(_2\). The degradation into C-14 carbon dioxide after a short incubation period was vigorous. Complete mineralization was achieved after about 120 min. The residual solutions contained a little radioactivity (< 0.02 µCi).

Acknowledgment
This study was supported by Sächsisches Ministerium für Wissenschaft und Kunst under contract No. 4-7581. 312/20.

References

EXPERIMENTS FOR THE DISPOSAL OF CARBON-14 LABELED ORGANIC MATERIAL: 2. MINERALIZATION OF ORGANIC MODEL SUBSTANCES USING HYDROGEN PEROXIDE AND A MIXTURE OF TRANSITION METAL SALTS

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Universität Leipzig, Kontrollbereich Permoserstraße

The oxidation of non-labeled organic model compounds by hydrogen peroxide and a catalytic mixture of transition metal salts was investigated to obtain a method for the conversion of radioactive \(^{14}\)C organic compounds. The recovery (as \% CO\(_2\)) was generally > 80\%, with the exceptions of chloroacetic acid, palmitic acid, 1,2-Dibromo-ethane and 2-xylene.

Hydrogen peroxide is a cheap and relatively strong oxidant (E°= +1.78 V). However it reacts quite slowly with the most organic substrates. It may be required to activate the peroxide with UV irradiation or with transition metal ions at elevated temperature. Activation improves the reactivity toward a substrate through the formation of stronger oxidizing species such as hydroxyl (OH\(^\cdot\)) or hydroxyperoxyl (HO\(_2\)) free radicals. The Fenton-reaction e.g., uses Fe(II) salts in acidic conditions to produce OH\(^\cdot\) free radicals. The decomposition of H\(_2\)O\(_2\) is catalyzed by transition metal ions and predominates in the absence of organics in the reaction mixture:

\[ 2 \, H_2O_2 \rightarrow 2 \, H_2O + O_2 \]  

(1)

If organics are present in the reaction mixture the following reaction occurs together with reaction (1):

\[ \text{organic} + H_2O_2 \rightarrow CO_2 + H_2O + \text{(inorganics)} \]  

(2)

The Fenton-oxidation involves the formation of various refractory byproducts like acetic and oxalic acids and their homologs /1/.

Recently, Falcon and coworkers /2/ used a mixture of Fe(II), Cu(II) and Mn(II) salts to achieve
almost complete oxidation due to a possible synergistic effect. They also determined the optimal proportions of the catalytic mixture Fe:Cu:Mn. The $\text{H}_2\text{O}_2$ decomposition can be suppressed by slowly adding the hydrogen peroxide to the reaction mixture. We used the method of Falcon and coworkers to convert organic model compounds.

Experimental
In a 100-mL three-necked flask, equipped with a magnetic stirrer bar, a 10-mL dropping funnel with pressure equalizing tube, a gas inlet tube and a reflux condenser was placed a solution containing 28 mg of iron(II) sulfate heptahydrate, 25 mg of copper(II) sulfate pentahydrate, 22 mg manganese(II) sulfate tetrahydrate and the organic compound of interest (the amount is calculated for 4 mmol of carbon) in 50 mL of water. The pH was adjusted to 3.0 using 0.05 M sulfuric acid. 5.0 mL of 35% hydrogen peroxide was placed in the dropping funnel. A quartz combustion tube connected with two gas absorption traps containing 0.2 M NaOH was attached to the upper end of the condenser. The quartz tube was filled with a wire CuO catalyst and was heated to 650°C. Then the reaction mixture was stirred at 95 - 100°C and the hydrogen peroxide was added dropwise from the dropping funnel over a period of about 2 hours (1 - 2 drops per min). A N$_2$ stream (17 mL/min) was continuously circulated through the apparatus by a peristaltic pump. The CO$_2$ evolved in this process was transported by the gas stream and absorbed in 0.2 M NaOH. The absorbed CO$_2$ was determined with a titrimetric method described by Winkler /3/, which we have slightly modified.

Results and Discussion
The procedure described here illustrates a practical and convenient method especially for the mineralization of water soluble organic substances. The results are shown in Tab. 1.

The oxidation leads to low recovery rates if hydrophobic (e.g., palmitic acid) or volatile substances (e.g., 1,2-dibromoethane or 2-xylene) are used. While the reaction proceeds, the pH value of the solution may change to basic values. In this case, the catalysts may precipitate as hydroxides.

Tab. 1: Wet mineralization of some organic substances using hydrogen peroxide and the catalytic mixture of Fe-II, Mn-II and Cu-II salts

<table>
<thead>
<tr>
<th>substance name</th>
<th>% CO$_2$ recovery</th>
<th>substance name</th>
<th>% CO$_2$ recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>94.9</td>
<td>Methyl alcohol</td>
<td>95.5</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>95.6</td>
<td>2-Toluic acid</td>
<td>95.0</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>90.5</td>
<td>2-Nitrophenol</td>
<td>87.8</td>
</tr>
<tr>
<td>Chloracetic acid</td>
<td>73.9</td>
<td>Palmitic acid (C$_{16}$)</td>
<td>3.8</td>
</tr>
<tr>
<td>1,2-Dibromoethane</td>
<td>38.5</td>
<td>Phenol</td>
<td>81.2</td>
</tr>
<tr>
<td>Acetic acid, Na-salt</td>
<td>98.0</td>
<td>Trapidil®*</td>
<td>86.7</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>97.9</td>
<td>Triethylamine</td>
<td>100.1</td>
</tr>
<tr>
<td>4-Hydroxybenzoic acid</td>
<td>96.3</td>
<td>2-Xylene</td>
<td>53.6</td>
</tr>
</tbody>
</table>

* pharmaceutical agent (subst. Triazolo pyrimidine)

Acknowledgment
This study was supported by Sächsisches Ministerium für Wissenschaft und Kunst under contract No. 4-7581.312/20

References
Application of X-Ray Absorption Spectroscopy
ARSENITE AND ARSENATE CONCENTRATION RATIOS IN AQUEOUS MIXTURES BY XANES

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Forschungszentrum Rossendorf e.V., Institute of Radiochemistry
1 Institute of Bioinorganic and Radiopharmaceutical Chemistry

Relative concentrations of As(III) and As(V) present in mixtures can be determined by a least squares fit of their XANES spectrum with a linear combination of the pure component spectra.

An edge-shift greater than 3 eV is observed in As K-edge x-ray near edge structure, XANES, spectra of As(III) and As(V) compounds. This shift is great enough to allow a qualitative determination of the arsenic oxidation state in samples with unknown arsenic speciation /1/. The XANES of As(III) and As(V) compounds also exhibit pronounced white lines, WL, formally corresponding to a dipole-allowed 1s→6p transition. The prominence of these XANES features makes them useful for a quantitative determination of relative concentrations of As(III) and As(V) present in mixtures. The mixture’s XANES spectrum can be modeled as the sum of XANES spectra of the individual, pure components.

0.019 M aqueous solutions of arsenite (AsO$_3^{3-}$), arsenate (AsO$_4^{3-}$), and mixtures of the two having concentration ratios of 1:3, 1:1 and 3:1, were prepared from AsO$_3^{3-}$ and AsO$_4^{3-}$ stock solutions. Transmission As K-edge XANES spectra of these samples were recorded at the Hamburger Synchrotronstrahlungs labor, HASYLAB, beamline X1.1, using a Si(311) double-crystal monochromator detuned to about 50% of the maximum incident flux. All samples were measured in 1.3 cm diameter polyethylene cuvettes of 4 mL volume. The arsenic concentration in the samples yielded an edge-jump of less than 0.3, thereby avoiding thickness effects in the region of the spectrum’s WL /2/. The relative As(III) and As(V) concentrations in the 1:3, 1:1, and 3:1 AsO$_3^{3-}$ : AsO$_4^{3-}$ mixtures were determined by a least squares fit of their XANES with a linear combination of the pure component AsO$_3^{3-}$ and AsO$_4^{3-}$ spectra. A similar XANES fit procedure for the determination of the amount of Se(IV) and Se(VI) in samples containing selenium has been reported /3/. The XANES spectra of the mixtures, the fitted spectra and the individual AsO$_3^{3-}$ and AsO$_4^{3-}$ components are depicted in Fig. 1. The WL maxima of the AsO$_3^{3-}$ and AsO$_4^{3-}$ spectra are at 11868.3 and 11872.2 eV, respectively. These remain distinguishable in the XANES spectra of the mixtures. Fits to both absorption and first derivative spectra (not shown here) gave excellent agreement between experiment and fit. The fits, depicted as solid lines, can hardly be differentiated from the experimental spectrum, depicted as dots. Varying the energy

### Tab. 1: Relative concentrations of As(III) and As(V), expressed in percent, for solution mixtures obtained from fits of their XANES (+0.003) and first derivative spectra (+0.006), compared to results from polarographic measurements.

<table>
<thead>
<tr>
<th>SAMPLE PREPARATION*</th>
<th>EXPERIMENT</th>
<th>XANES</th>
<th>Polaroigraphy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Absorption</td>
<td>1st derivative</td>
<td></td>
</tr>
<tr>
<td>As(III)</td>
<td>As(V)</td>
<td>As(III)</td>
<td>As(V)</td>
</tr>
<tr>
<td>75</td>
<td>25</td>
<td>71.0</td>
<td>28.5</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>47.0</td>
<td>52.8</td>
</tr>
<tr>
<td>25</td>
<td>75</td>
<td>23.8</td>
<td>74.6</td>
</tr>
</tbody>
</table>

* Calculated from stoichiometry and weights of As$_2$O$_3$ and H$_2$AsO$_4$·0.5H$_2$O used for the preparation of the stock solutions.
** Calculated from the polarographic results for As(III) and the total arsenic concentration of the sample.
range for the fit did not significantly alter the goodness of the fit nor did it influence the results obtained for the As(III) : As(V) ratio.

Tab. 1 summarizes the relative concentrations of As(III) and As(V) obtained from the fits and compares them to those obtained from polarographic As(III) determination. The fits to the absorption data yielded results similar to fits to first derivative spectra. The results from the XANES curve fitting are in better agreement with the values expected, according to the sample preparation, than those from the polarographic determination. The XANES fits lead to a quantitative determination of the relative As(III) concentration to within 6%. This is better than the 10% error estimated for determinations using polarography.

The success of this method for the determination of relative concentrations of As(III) and As(V) in mixtures renders studies on other environmentally relevant samples feasible. A significant advantage of XANES analysis is that samples can be studied without prior separation of the arsenic species from the matrix.

References


DIFFERENTIATION BETWEEN MONODENTATE AND BIDENTATE CARBOXYLATE LIGANDS COORDINATED TO URANYL IONS USING EXAFS

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The possibility is explored of detecting the carbon atoms in bidentate and monodentate coordinated carboxylate ligands in uranyl complexes by EXAFS analysis, including multiple-scattering pathways. The EXAFS results are compared to XRD data reported in the literature.

We have investigated the U L-III-edge EXAFS of two carboxylato uranyl complexes of known structure: sodium triacetatodioxouranium(VI), Na[UO₂(C₆H₃O₂)₃] (I) /1/ and dibenzoatodioxouranium(VI), UO₂(C₆H₅O₂)₂ (II) /2/. This study was aimed at exploring the possibility of differentiating between bidentate (bi) and monodentate (mono) coordinated carboxylate ions. The UO₂²⁺ cation in I is surrounded by three carboxylate ligands, stemming from three acetate ions, coordinated exclusively in a bi fashion. The benzoate carboxylate group in II bridges two neighboring UO₂²⁺ units; each O atom exhibits mono coordination to uranium.

The fact that bi-coordinated carboxylate groups generally exhibit longer metal-oxygen bond distances than their mono counterparts /3/ can be used for interpreting EXAFS data from UO₂²⁺-complexes based on fits of the first two oxygen coordination shells (U-O₁ and U-O₂). However, interpretation of data based solely on U-O₁ distances cannot be inconclusive; information from further-distant shells is often needed. Obtaining this information from the analysis of EXAFS data can be complicated by the presence of multiple scattering (MS) pathways along the O=U=O unit and along atoms in the coordinating carboxylate groups. For example, the near-collinear arrangement of carbon atoms in the bi configuration can cause amplitude enhancement of scattering on the distal carbon atom. Detecting a carbonyl carbon atom, C, in mono coordination may be difficult due to overlap of single scattering (SS) with MS oscillations.

In order to evaluate the possibility of detecting the carbon atoms in bi and mono complexes, the MS pathways were calculated using FEFF6 /4/ and used in the analysis of EXAFS data for compounds I and II. These results were compared to XRD data reported in the literature.

U L-III-edge EXAFS transmission spectra of I and II were measured at the Stanford Synchrotron
Radiation Laboratory, SSRL, (beamline 2.3) using a Si(220) double-crystal monochromator detuned to 50% of the maximum incident flux. The samples were dispersed in Teflon and pressed as 1.3 cm diameter pellets. The \( k^2 \)-weighted U \( L_{III} \) EXAFS for \( I \) and \( II \) and their corresponding Fourier transforms (FT) are shown in Fig. 1. The FT for \( II \) exhibits no peaks distinctly above the background noise at distances greater than \( R_{U-Oax} \) and \( R_{U-Oeq} \). \( R_{U-Oax} \) in \( I \) is significantly longer than in \( II \) and the FT shows more distant coordinations shells. Also noticeable is, although \( I \) has no atoms between 2.85 and 3.98 Å away from uranium, its FT spectrum exhibits intensity around \( R_+ \) ~3 Å.

![Fig. 1: \( k^2 \)-weighted U \( L_{III} \)-edge EXAFS spectra and their corresponding Fourier transform for \( I \) (above) and \( II \) (below). The solid line is the experimental data; the dashed line is the result of the fit described in the text.](image)

The dashed lines in Fig. 1 depict the results from fits of the spectra using SS and the following MS paths: MS, the four-legged MS path involving both axial oxygen atoms (U\(^{\text{ii}}\) O\(_{ax1}\) U\(^{\text{ii}}\) O\(_{ax2}\) U); MS-C, the three-legged path between U-O-C atoms; MS-E/A, MS pathways between O\(_{ax}\)-U-O\(_{eq}\) and the MS path leading to the focussing effect along the linear U-C-C' in the bi-ligated compound \( I \), MS-C'. The fit results for the interatomic distances to uranium (R) coordination numbers (N), and Debye-Waller factors (F\(^2\)) in both compounds are shown in Tab. 1 and compared to XRD results.

<table>
<thead>
<tr>
<th>Shell</th>
<th>N</th>
<th>( R ) [Å]</th>
<th>F(^2) [Å(^2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( I )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(_{ax})</td>
<td>2' (2)</td>
<td>1.78 (1.76)</td>
<td>0.002</td>
</tr>
<tr>
<td>O(_{eq})</td>
<td>4.3 (6)</td>
<td>2.49 (2.47)</td>
<td>0.005</td>
</tr>
<tr>
<td>C</td>
<td>2.5 (3)</td>
<td>2.89 (2.85)</td>
<td>0.002</td>
</tr>
<tr>
<td>Na</td>
<td>3' (3)</td>
<td>3.98 (3.93)</td>
<td>0.016</td>
</tr>
<tr>
<td>C'</td>
<td>5 (3)</td>
<td>4.40 (4.35)</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>( II )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(_{ax})</td>
<td>2' (2)</td>
<td>1.76 (1.75)</td>
<td>0.002</td>
</tr>
<tr>
<td>O(_{eq})</td>
<td>4.1 (4)</td>
<td>2.29 (2.28)</td>
<td>0.004</td>
</tr>
<tr>
<td>C</td>
<td>5.3 (4)</td>
<td>3.42 (3.46)</td>
<td>0.010</td>
</tr>
</tbody>
</table>

Held constant during fit.

Tab. 1: EXAFS structural parameters for \( I \) and \( II \) compared to XRD values /1/, /2/ (in parentheses).

obtain physically meaningful results. F\(^2\) for the MS paths was assumed to be the sum of F\(^2\) from the SS paths for the atoms involved and the O\(_{eq}\)-C bond distance was taken to be 1.26 Å. In this way the MS paths could be included in the fit without increasing the number of variable parameters by linking their parameters with the corresponding SS values. \( N_{O_{eq}} \) was kept constant at 2 and \( N_{Na} \) was held constant at 3, the value obtained from an initial fit to filtered data. The edge shift (\( \Delta E_0 \)) was held constant at the value obtained from a fit to the first two shell filtered data. In the case of \( II \), detecting atoms further distant than the first two bond distances is not possible; if the existence of the carboxyl C atom were not known, it would not have been included in the fit. The oscillations from the SS path of this C atom and the MS-E/A, MS-C, and MS paths in \( II \) tend to cancel each other out leaving only a weak signal. There is also no evidence for more distant atoms in the spectrum; these weak backscatterers are too far away to be observed. In contrast, although the U-C' bond distance in \( I \) is 4.35 Å, this atom shows up with a rather large intensity due to the MS-C' path. Moreover, the MS-C' path must be included in the fit to obtain physically meaningful results. The peaks near 3 Å in the FT spectrum of \( I \) can only be accounted for by including MS-E/A and MS paths into the fit.

These results show that identifying bi-carboxylate ligands coordinated to a uranyl unit based on their usually relatively long \( R_{U-Oeq} \) bond lengths can be substantiated by detecting the carboxyl
C and distal C’ atoms in the analysis of U L_3^-edge EXAFS spectra. MS paths involving these atoms and the first two shells O_{ax} and O_{eq} must be included in the analysis. Only the O_{ax} and O_{eq} bond distances are evident in the EXAFS of the compound having mono bridging carboxylate ligands, II. Substantiating the mode of coordination by detecting further distant C atoms is not possible in this case.

Acknowledgments
Measurements were made at SSRL, which is operated by the U.S. Department of Energy, Office of Basic Energy Sciences, Divisions of Chemical Sciences and Materials Science.

References

STRUCTURAL ANALYSIS OF URANIUM(VI) COMPLEXES WITH SIMPLE CARBOXYLIC ACIDS IN AQUEOUS SOLUTION USING EXAFS
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¹ Lawrence Berkeley National Laboratory, Berkeley, CA, USA

Structural analysis of eight aqueous uranyl carboxylates by EXAFS reveals three basic types of near-neighbor environments.

Aqueous solutions of uranyl acetate (1), phthalate (2), maleate (3), malonate (4), succinate (5), malate (6), citrate (7), and tartrate (8) were prepared by dissolving uranyl nitrate hexahydrate and the corresponding acid in bidistilled water. Prior to sample preparation, the uranium and ligand concentrations and the pH value of the solutions were calculated to yield only one uranyl species. For the speciation calculations, we used published complexation constants and acid dissociation constants and included the hydrolysis equilibria of the uranyl ion. According to these calculations, more than 95% of the uranium in solution was present as the desired uranyl complex with a specific uranium to ligand ratio, U(VI):L (see Tab. 1).

Structural parameters for the aqueous uranyl complexes 1-8 were determined by uranium L_3^-edge EXAFS analysis (see Tab. 2).

Table 1: Sample composition and calculated U(VI) speciation using published complex formation constants.

<table>
<thead>
<tr>
<th>No.</th>
<th>Acid</th>
<th>U(VI) mol/L</th>
<th>pH</th>
<th>U(VI) : L ratio (of the complex)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>acetic</td>
<td>1.10</td>
<td>3.7</td>
<td>1:3</td>
</tr>
<tr>
<td>2</td>
<td>phthalic</td>
<td>0.06</td>
<td>4.6</td>
<td>1:1</td>
</tr>
<tr>
<td>3</td>
<td>maleic</td>
<td>0.01</td>
<td>4.2</td>
<td>1:1</td>
</tr>
<tr>
<td>4</td>
<td>malonic</td>
<td>0.20</td>
<td>3.9</td>
<td>1:2</td>
</tr>
<tr>
<td>5</td>
<td>succinic</td>
<td>0.50</td>
<td>4.0</td>
<td>1:1</td>
</tr>
<tr>
<td>6</td>
<td>malic</td>
<td>0.10</td>
<td>3.2</td>
<td>2:2</td>
</tr>
<tr>
<td>7</td>
<td>citric</td>
<td>0.10</td>
<td>3.9</td>
<td>2:2</td>
</tr>
<tr>
<td>8</td>
<td>tartaric</td>
<td>0.10</td>
<td>3.4</td>
<td>2:2</td>
</tr>
</tbody>
</table>

Table 2: EXAFS structural parameters of aqueous uranyl complexes.

<table>
<thead>
<tr>
<th>No.</th>
<th>Uranyl complex</th>
<th>U-O_{ax}</th>
<th>U-O_{eq}</th>
<th>U-X</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>acetate</td>
<td>2.44</td>
<td>0.008</td>
<td>C</td>
</tr>
<tr>
<td>2</td>
<td>phthalate</td>
<td>2.37</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>maleate</td>
<td>2.37</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>malonate</td>
<td>2.36</td>
<td>0.007</td>
<td>U</td>
</tr>
<tr>
<td>5</td>
<td>succinate</td>
<td>2.48</td>
<td>0.008</td>
<td>C</td>
</tr>
<tr>
<td>6</td>
<td>malate</td>
<td>2.37</td>
<td>0.005</td>
<td>U</td>
</tr>
<tr>
<td>7</td>
<td>citrate</td>
<td>2.38</td>
<td>0.007</td>
<td>U</td>
</tr>
<tr>
<td>8</td>
<td>tartrate</td>
<td>2.36</td>
<td>0.006</td>
<td>U</td>
</tr>
</tbody>
</table>

Structural parameters for the aqueous uranyl complexes 1-8 were determined by uranium L_3^-edge EXAFS analysis (see Tab. 2).

Although a variety of aliphatic and aromatic uranyl carboxylates were studied, the near-neighbor environment of uranium in these aqueous complexes can be grouped into three basic types, i.e., A, B, and C. The Fourier transforms of the uranium L_3^-edge EXAFS for one representative of each type (A-C) are shown in Fig. 1. Uranyl acetate (1) and succinate (5) belong to type A coordination and are characterized by bidentate ligation of the COO-group with a U-O_{ax} bond.
distance larger than 2.42 Å. The assignment of bidentate coordination is supported by the detection of an additional carbon coordination shell at 4.3 Å due to multiple-scattering enhancement along a linear U-C₃-C₂ arrangement. A structural model for the uranyl acetate solution (1), where three acetate ligands adopt a bidentate geometry, is shown in Fig. 2.

Coordination of types B and C is characterized by monodentate ligation of the COO⁻-group with a typical U-Oeq distance of 2.37 Å. Aqueous uranyl carboxylates of type C differ from type B by the detection of an additional coordination shell due to single-scattering U-U interaction at 3.9 Å C. Such a U-U coordination shell is not observed for type B complexes (samples 2 and 3). In malic, citric, and tartaric acids, both the "-hydroxyl group and the COO⁻-groups play a key role in the formation of 2:2 dimers in solution. A detailed account of the EXAFS analysis and the structural model derived for complexes 6-8 was published recently /1/.

The structural parameters obtained for different coordination modes may be used to guide the EXAFS analysis of interaction products of uranium(VI) with naturally occurring organic macromolecules such as humic and fulvic acids and lignin which posses many carboxylic and hydroxyl groups.

Acknowledgments
The help of G. Grambole and A. Otto and the advice of E. Förster during sample preparation are gratefully acknowledged. EXAFS measurements were made at Beamline 2-3 at SSRL, which is operated by the US Department of Energy.

References

STRUCTURAL INVESTIGATIONS OF TECHNETIUM AND RHENIUM COMPLEXES BY EXAFS. 2. STUDIES OF Tc AND Re OLGIGLYCINE COMPLEXES

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Structural parameters for the first three coordination shells of several aqueous Tc(V) and Re(V) oligoglycine complexes were measured by EXAFS spectroscopy. A more detailed account of these studies can be found in /1/.

Experimental
Starting from a solution of ⁹⁰TcO₄⁻ in water, aqueous technetium complexes with the oligoglycine ligands Gly₄, Gly₅, and Gly₆, where Gly stands for the glycyl residue, were prepared by an upscaled synthesis as described in /2/. Due to the thermal instability of these complexes at room temperature, samples were kept at -10°C after partial lyophilization. The rhenium complexes with Gly₄ and Gly₅ were prepared immediately before measurements without further
lyophilization by mixing ReO$_4$$^-$, Sn$^{2+}$, and tartrate solutions and adding the corresponding oligoglycine ligand. Technetium K-edge and rhenium L$_{III}$-edge x-ray absorption spectra were collected at room temperature in transmission and fluorescence modes, respectively. The Tc samples were measured at Hamburger Synchrotronstrahlungslabor, HASYLAB. The Re complexes were measured at Stanford Synchrotron Radiation Laboratory, SSRL.

Results
The extended x-ray absorption fine structure (EXAFS) of the Tc and Re spectra was analyzed according to the standard procedure described in /3/. The EXAFS structural parameters obtained are given in Tab. 1. The first coordination shell of the Tc and Re complexes consists of one oxygen atom at a distance of ca. 1.69 Å from the central atom. This is a typical value for the monooxotechnetium species in Tc(V) complexes. The same Tc(V) oxidation state was determined by analysis of Tc K-edge energies and is described in more detail elsewhere /1/. In all Tc complexes, approximately four light atoms like nitrogen or oxygen were detected at an average distance of 2.05 Å. If all four atoms are nitrogen, they could represent three amide and one amine nitrogen atoms of the oligoglycine ligand. This would mean that the NH$_2$ group of the peptide is involved in the technetium complexation. In the Re(V) complexes, the average Re-N distance is 1.97 Å, i.e., slightly shorter than in the corresponding Tc(V) complexes.

The third coordination shell of the Tc(V) and Re(V) complexes could only be fit if a heavy backscatterer is included, i.e., technetium and rhenium at 2.85 Å and 2.91 Å, respectively. This was an unexpected result. A plausible explanation for the presence of Tc-Tc and Re-Re interactions at ca. 2.9 Å remains to be found. Also, the presence of an additional coordination shell at ca. 4 Å in the Fourier transforms of the Tc complexes needs to be analyzed in future studies including analysis of multiple-scattering paths along the peptide backbone carbonyl oxygen atoms.

Tab. 1: EXAFS structural parameters for the Me-X coordination shells, where Me is Tc or Re.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Near-neighbor atom, X</th>
<th>Coordination number, $N_x$</th>
<th>Distance, Me-X (Å)</th>
<th>$F^2$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc-Gly$_4$</td>
<td>O</td>
<td>0.8</td>
<td>1.67</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>3.8</td>
<td>2.03</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td>Tc</td>
<td>1.1</td>
<td>2.86</td>
<td>0.009</td>
</tr>
<tr>
<td>Tc-Gly$_5$</td>
<td>O</td>
<td>0.8</td>
<td>1.69</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>4.3</td>
<td>2.07</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>Tc</td>
<td>0.9</td>
<td>2.85</td>
<td>0.008</td>
</tr>
<tr>
<td>Tc-Gly$_6$</td>
<td>O</td>
<td>0.7</td>
<td>1.68</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>3.6</td>
<td>2.06</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>Tc</td>
<td>1.1</td>
<td>2.82</td>
<td>0.009</td>
</tr>
<tr>
<td>Re-Gly$_4$</td>
<td>O</td>
<td>1.4</td>
<td>1.70</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>4.4</td>
<td>1.96</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>Re</td>
<td>1.4</td>
<td>2.91</td>
<td>0.008</td>
</tr>
<tr>
<td>Re-Gly$_5$</td>
<td>O</td>
<td>1.4</td>
<td>1.70</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>4.4</td>
<td>1.98</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>Re</td>
<td>1.4</td>
<td>2.92</td>
<td>0.009</td>
</tr>
</tbody>
</table>

Experimental uncertainties of $N_x$ and distance Me-X are ±30% and ±0.02 Å, respectively.

In summary, EXAFS analysis confirmed that the oxidation state of Tc and Re in aqueous oligoglycine complexes is +5. All Tc(V) and Re(V) oligoglycine complexes studied have similar structural parameters for their first three coordination shells. The peptide nitrogen atoms seem to be involved in a complicated complexation with the Tc and Re atoms. The observed metal-metal interaction at distances below 3 Å indicates the formation of binuclear complexes in solution.

References
X-RAY ABSORPTION SPECTROSCOPIC AND MöSSBAUER STUDIES OF REDOX AND CATION-ORDERING PROCESSES IN MANGANESE FERRITE *

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X-ray absorption spectra of manganese ferrites were recorded at the Mn K-edge to determine the manganese valences of differently prepared samples from the energy shift of their x-ray absorption edges relative to the Mn K-edge position of the reference samples MnO, Mn3O4 and Mn2O3. The site occupation ratio of Fe2+ cations on tetrahedral (A) and octahedral (B) sites of the spinel structure was determined from Mössbauer spectra taken at 4.2 K in an external magnetic field of 6 Tesla.

The manganese ferrite samples were prepared by the decomposition of a freeze-dried Mn-Fe2-formate precursor. Decomposition in an oxidizing atmosphere (air) at 400°C yielded a spinel phase similar to the defect spinel (−(Fe,Mn)3O4). From the x-ray absorption spectra shown in the figure below, a value of 2.8 was obtained for the Mn valence of this phase.

![X-ray absorption spectra](image)

Fig. 1: Mn K-edge x-ray absorption of manganese compounds indicated.

Through decomposition of the Mn-Fe2-formate in a nitrogen atmosphere at 600°C for 30 minutes, a manganowuestite phase was formed in addition to a spinel phase. The oxidation of this decomposition product at temperatures of 500, 600, 850 and 1000°C in an atmosphere with defined oxygen pressure led to the formation of manganese ferrites with different manganese valences and cation distributions. For the sample treated at 500°C, a Mn valence of 2.7 was found from the x-ray absorption spectrum. Treatment at 600°C and higher temperatures resulted in a Mn valence of 2.0. With decreasing Mn valence a decrease of the fraction of Fe cations on tetrahedral (A) sites was observed in the Mössbauer spectra.

Excluding any cation vacancies, the following cation distribution was deduced from this: (Mn0.34Fe0.66)Al(Mn0.66Fe0.34)3O4. Assuming that Mn3+ ions occupy exclusively octahedral sites and Mn2+ ions only tetrahedral sites, this cation distribution corresponds to a Mn valence of 2.67, which is in accord with the value of 2.7 obtained from the x-ray absorption spectra. In the manganese ferrite treated at 1000°C an absence of Mn3+ cations was found and only 16% Fe cations have been observed to occupy tetrahedral sites.


POLARIZED X-RAY-ABSORPTION SPECTROSCOPY OF THE URANYL ION: COMPARISON OF EXPERIMENT AND THEORY *

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The x-ray linear dichroism of the uranyl ion (UO22+) in the uranium L3-edge extended x-ray absorption fine structure (EXAFS), and L1- and L2-edge x-ray absorption near edge structure (XANES), has been investigated both by experiment and theory. A striking polarization depend-
ence is observed in the experimental XANES and EXAFS for an oriented single crystal of uranyl acetate dihydrate \([\text{UO}_2(\text{CH}_3\text{CO}_2)_2\text{H}_2\text{O}]\), with the x-ray polarization vector aligned either parallel or perpendicular to the bond axis of the linear uranyl cation (O-U-O). Single-crystal results are compared to experimental spectra for a polycrystalline uranyl acetate sample and to calculations using the \textit{ab initio} multiple-scattering (MS) code \textsc{FEFF} 6. Theoretical XANES spectra for uranyl fluoride \((\text{UO}_2\text{F}_2)\) reproduce all the features of the measured uranyl acetate spectra. By identifying scattering paths which contribute to individual features in the calculated spectrum, a detailed understanding of the L\(_1\)-edge XANES is obtained. MS paths within the uranyl cation have a notable influence upon the XANES. The measured L\(_3\)-edge EXAFS is also influenced by MS, specifically when the x-ray polarization is parallel to the uranyl species. These MS contributions are extracted from the total EXAFS and compared to calculations. The best agreement with the isolated MS signal is obtained by using nonoverlapped muffin-tin spheres in the \textsc{FEFF} 6 calculation. This contrasts the L\(_1\)-edge XANES calculations, in which overlapping was required for the best agreement with experiment.

Behavior of Colloids and Aerosols
Several methods of determining submicron particle size distributions were tested on an artificial model colloid (silica particles) and on a real environmental sample. The susceptibilities of the different methods to artifacts are discussed and a strategy for particle sizing is developed.

A puzzling problem in colloid research is that experimental results can dramatically depend on the experimental technique used to investigate a colloid. This is due to the tendency of colloidal suspensions to change when ambient conditions are altered, i.e., due to the thermodynamic instability of colloids. Two techniques of colloid research of entirely different physical principles were first tested on a ‘model colloid’: the relatively invasive technique of filtration and the almost non-invasive technique of PCS.

A sample of suspended silica particles was prepared by acidifying a 0.1 molar solution of sodium silicate with HClO₄ to a pH value of 3.92 ± 0.05. Particles were grown during a period of 8 days. Eight PCS measurements were taken on day 8 of the experiment. PCS results showed that the vast majority of the particles was in the size range below 80 nm with the main peak being in the 50 to 80 nm region.

Fig. 1 gives an autocorrelation function and the corresponding light-intensity-weighted size distribution. Fig. 2 shows the filtration scheme we applied first. Nuclepore filters of 47 mm diameter were used. With this filtration scheme a classification of the submicron particles into 4 size classes should be reached. The lower size limits of these classes should differ by factors of 2.5, 8 and 3.3 from that of the corresponding neighbor class. All the filtrates were analyzed for their silicon concentrations by ICP-MS. The results are given in Fig. 2. The figure indicates that most of the particles had been removed by the 400 nm Filter. This is in sharp contrast to the PCS results (Fig. 1). Alternatively, we used the filtration scheme depicted in Fig. 3. This scheme avoided filtration to complete dryness (dead-end filtration) and the experiments were done parallel to each other and not in sequence. The ICP-MS results of the filtrates from the filtration according to this second scheme are given in Fig. 3. These results are striking: when using this filtration regime, there is good agreement between the filtration experiment and the PCS measurements.

Our experiment shows that dead-end filtration was not suited to characterize the particles under study. Finding 50 to 80 nm and smaller particles primarily on the 400 nm filter results in a misinterpretation of the true particle size by almost one order of magnitude. The main reason of this failure is obviously ‘self-coagulation’ during the process of filtration /1,2/. Filtration according to Scheme 2 (Fig. 3) reduced the filtration artifacts considerably. Further steps toward artifact reduction could be made using a stirring cell or performing a cross-flow filtration. Filtration, however, is generally not a reliable technique of particle size determination in the submicron size range and particle sizes determined by filtration should always be viewed with caution. Our experiment also demonstrates the need for applying more than one method for particle-sizing in the submicron size range. Using several (at least two) techniques validates the results and increases the probability for recognizing artifacts.
The experience gained from these tests on artificial 'model particles' was applied to study colloids in environmental samples. Submicron particles from backwater of a sanitary landfill that is located on top of a uranium mine tailing were investigated using two independent methods of particle separation (filtration and centrifugation) and two independent sizing methods (PCS and SEM) /3/. The PCS measurements (after the appropriate separation steps) revealed submicron particles from 30 to 300 nm. This was in good agreement with the SEM micrograph shown in Fig. 4 where individual particles of this size range can be identified. The large agglomerate in the picture also consists of these small particles and is likely a result of the filtration process. One can therefore assume that the particles of 30 to 300 nm move freely through the backwater and not as larger agglomerates as the one that is shown in the center of the micrograph.

References


DETERMINATION OF THE PARTICLE DIAMETER OF INDUSTRIAL TiO$_2$ IN AQUEOUS SUSPENSION IN THE PRESENCE OF A DETERGENT

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The particle size of TiO$_2$ in aqueous suspension was measured by filtration and photon correlation spectroscopy. The results showed agglomerated particles of 110±50 nm diameter. The particles were stable to both sonication and the addition of surfactants.

A UV-activated oxidation of C-14-labeled organic substances in a colloidal suspension of TiO$_2$ was developed by Förster et al. /1/. The particle size of the TiO$_2$ in the suspension is one important parameter for this process. We tested two different TiO$_2$ Powders (P25 (DEGUSSA) /2/ and Hombikat UV100 (Sachtleben Chemie GmbH, Duisburg)). According to the producers, the size of the primary particles was about 21 nm and <10 nm for the P25 and UV100 powder, respectively. We measured the size of the TiO$_2$ particles with the photon correlation spectroscopy BI-90 (Brookhaven Instruments Corp.). The powders were suspended in water together with the surfactant Präwozell®-N9 (Buna AG Schkopau) which is a non-ionogenic tenside based on nonylphenole and ethenoxide. The laser power was 400 mW, the laser wavelength 514.5 nm, and the temperature 25°C.

Prior to the measurements on the TiO$_2$ suspensions, we tested the solvent (Milli-Q water) and the surfactant solution. The Milli-Q water, showing a photomultiplier count rate of only 1 to 2 kcps, was virtually free of scatterers. However, the tenside solution showed a remarkable count rate (124 kcps) at a dilution of 1:500. The deconvolution of the autocorrelation function obtained from this tenside solution yielded a particle size of 6±3 nm. This suggests that tenside micelles had formed. After a dilution of this solution to 1:25000, the count rate decreased to 6 kcps, a value low enough to allow an unperturbed sizing of the TiO$_2$ particles.

This dilute tenside solution was used to make a 100 ppm TiO$_2$ suspension. Following a ultrasound sonication of 5 min, the TiO$_2$ particle size was measured with the BI-90. Because the powder type UV100 sedimented within minutes, we will report only the measurements on the P25 titanium dioxide in the following. From the 100 ppm stock solution, dilutions as low as 0.1 ppm were made and measured with the BI-90. Fig.1 shows the dependence of the count rate on the TiO$_2$ concentration. The most favorable concentration range for photon correlation spectroscopy (PCS) lies between 1 and 10 ppm. Tab. 1 gives the results of PCS. The size of the suspended TiO$_2$ particles was found to be 110±50 nm.

<table>
<thead>
<tr>
<th>Concentration [ppm]</th>
<th>Count rate [kcps]</th>
<th>Particle size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>5258</td>
<td>152±50</td>
</tr>
<tr>
<td>1</td>
<td>519</td>
<td>65±30</td>
</tr>
<tr>
<td>0.1</td>
<td>189.5</td>
<td>100±50</td>
</tr>
</tbody>
</table>

Fig. 2 shows a transmission electron micrograph of the TiO$_2$ powder (provided by the manufacturer). Comparing the micrograph and the PCS results for the particle size of the powder, one can assume that PCS detects relatively stable agglomerates that are also visible in Fig. 2 and that are not sufficiently separated in the aqueous suspension, despite the detergent. The application of a more concentrated tenside solution as well as a longer ultrasound sonication did not result in a reduction of the particle size of the TiO$_2$ suspension.
The PCS results do not, however, exclude the presence of particles in the size range of about 20 nm reported in /2/. Because of the $r^6$-dependence of the scattered light intensity on the radius $r$ of a particle, small particles are often masked by larger ones in light scattering experiments. The small particles become only 'visible' by PCS then if the larger ones are removed from the suspension. We removed larger particles by filtration through a 100 nm and a 50 nm Nuclepore filter (Costar GmbH). Fig. 3 shows a scanning electron micrograph of the deposits on the 100 nm filter which confirms the existence of the 100 nm agglomerates found by PCS. The PCS results obtained from the filtrates are given in Tab. 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Count Rate [kcps]</th>
<th>Particle size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>unfiltered</td>
<td>594</td>
<td>160±50</td>
</tr>
<tr>
<td>Filtrate 100nm</td>
<td>357</td>
<td>100±20</td>
</tr>
<tr>
<td>Filtrate 50nm</td>
<td>5.5</td>
<td>7±4; 30±10</td>
</tr>
</tbody>
</table>

It is obvious from this table that a large proportion of the particles are removed by the two filters and that these removable particles emit most of the scattered light. In particular, the 50 nm filtration causes a strong count rate decrease. The count rate after this filtration lies in the range that should, according to our experience, be regarded as the lower detection limit of our photon correlation spectroscope /3/. The results of particle sizing for this filtrate, however, make physical sense if one takes into consideration that the accuracy of the particle sizing with PCS on such very dilute colloidal suspensions is only within a factor of two. These results confirm that there is a small amount of particles of the size range given by the producer of the TiO$_2$ powder.

The conclusion can be drawn from our experiment that most of the suspended particles were in the size range of 110±50 nm. A comparison with a TEM micrograph suggests that these particles were agglomerates which cannot be split into smaller particles by mild methods of dispersion such as adding a detergent or us sonication. However, the measurements also show that a small portion of the particles was in the size range indicated by the producer of the TiO$_2$ powder. These small particles should presumably be regarded as the 'primary particles' that form the agglomerates.

References
/2/ Hochdisperse Metalloxide nach dem Aerosil®-Verfahren. Schriftenreihe Pigmente Nr. 56, Degussa AG, 1989
DETECTION OF AEROSOL LOSSES IN GLASS VESSELS

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Several electrostatic depletion effects were determined using polydisperse aerosols under defined flow, geometry, and aerosol diameter and concentration conditions.

The electrostatic deposition of particles in sampling lines and aerosol vessels of non-conductive materials is difficult to characterize. In experiments with monodisperse aerosols, McMurry and Rader /1/ as well as Liu et al. /2/ observed high particle losses in electrostatically-charged Teflon film bags and in plastic tubes, which were charged by bending and flexing. Liu et al. minimized the losses by wrapping the external surface of the plastic tubing with an aluminum foil. Crump, Flagan, and Seinfeld /3/ determined the particle loss rate of monodisperse aerosols in a glass vessel and could explain their experimental results by only considering diffusional and gravitational losses. However, they suspected that the scatter of their data was an indication of an uncontrolled electrical charge effect.

Our method directly determines the loss of electrical charged particles from polydisperse aerosols in vessels of non-conductive materials. The experimental conditions (18 L/h flow, 300 mL volume, 15 - 300 nm particle diameter, < 2\times10^{19}/cm^3 particle concentration) offer the advantage of minimizing the influence of effects such as gravitational settling, impaction or diffusion loss to the wall, charge redistribution, and population decrease due to coagulation. We have studied the electrostatic aerosol loss in different glass vessels (of quartz (QG), borosilicate glass (BG), and silicate glass (SG)) in comparison to that in Teflon (T) and steel (S) vessels. All glass vessels were pre-treated with distilled water, heated to 250 °C and equilibrated with laboratory air of 30% humidity. Before and during the aerosol loss measurements the outside of the glass vessels was exposed to one of the following conditions:

1. in laboratory atmosphere surrounded by a grounded Faraday cage,
2. slightly wiped with a cloth before the experiment, and
3. totally immersed in an electrolytic bath containing 3% sodium chloride in water.

The aerosols were generated in an atomizer (2g/L NaCl), passed through a diffusion dryer, diluted with dry air (5% humidity), neutralized in a TSI 3077 neutralizer and then passed through the appropriate experimental vessel (SG, BG, QG, T, S) or a simple steel tube connector (C) which served as an arbitrary reference with negligible particle loss. The emerging aerosol was then classified (in mobility equivalent particle diameter $D_m$ classes) in a TSI 3934 Scanning Mobility Particle Sizer (SMPS). We removed the neutralizer from the SMPS and determined only the positively charged particles. A defined and constant fraction of all particles in each mobility class were measured with the unmodified SMPS. The particle loss fraction ($LF$) is calculated from the particle concentration in the experimental vessel and the steel tube reference ($C$). Examples for the $LF$'s from neutralized and solely atomized aerosols (without the TSI 3077 neutralizer upstream from the vessel) are given in Fig. 1, and those of the positively charged particles from neutralized aerosols are given in Fig. 2.
All singly and multiply-positive and negative charged particles with diameters less than 150 nm are totally removed in the Teflon vessel. Fig. 1 shows the experimental particle loss from neutralized aerosols compared to all particles present, excluding neutral particles for equilibrium conditions that were calculated according to Wiedensohler /4/. A smaller fraction of all charged particles with diameters greater than a certain value are removed in BG vessels under experimental condition (1), as described above (Fig. 1). Electric fields arise from the contact-electric or tribo-electric charging of the outside surface by wiping and create a high LF (Fig. 2). This is due to the electric field lines passing through the space inside the vessel and terminating at locally different charges outside the vessel. Assuming the appropriate geometry, we can fit the experimental LF with the formula for electrostatic precipitation (Fig. 1 and 2). From this, the electric field strength (E) is calculated. Removing the outside surface charging by immersing the vessels into an electric conducting liquid instantly reduces the particle losses in SG vessels to the level of the steel vessel S (Fig. 2). However, in BG and especially in QG vessels, long times are necessary for LF reduction. A build-up of charged particles at some sites of the inner surface during the action of the outer charge may have occurred. The charge of the particles vanishes slowly due to capturing opposite charged particles and due to electrolytic conduction on the inner surface of the vessels. The conductivity is high in the thick alkali and alkaline-earths-containing swelling layers of the SG, lower in the thinner layers of the BG vessels, and negligible on the QG surfaces. We found equal transmissions of steel, borosilicate, and silicate tubes as well as of flexible pipes of polyvinylchloride for aerosols when the outside was electrolytically shielded with the salt bath.

References

TRANSPORT OF RADON DAUGHTERS BY SALT AEROSOLS

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The adsorption of radon decay products on sodium chloride and ammonium sulphate aerosols under laboratory conditions was investigated. The salt aerosols were produced using an atomizer. Adsorption has been measured by "^s-spectrometry after filtering the aerosol.

An important indoor radiation exposure to the public is due to the inhalation of radon decay products. The estimated health risk associated with this is much higher than those due to other environmental carcinogens /1/. Radon decay products are chemically active, unlike their inert gaseous parent. They can attach to surfaces, such as aerosols, walls or other indoor surfaces and can also deposit on lung tissue. Potential health hazards depend, in part, on the concentration of the daughter isotopes and on its mobility. Thus, the fraction of decay products attached to aerosols is an important determinant of radon progeny behavior.
Laboratory experiments were conducted to determine the effect of the nature and the concentration of aerosols on its ability to attach radon decay products. Salt aerosols were produced by atomizing aqueous solutions and drying the aerosol using a modified commercially available generator (TOPAS, model SLG 270). Aerosol concentration and size distribution were measured using a scanning mobility particle sizer (TSI, model 3934). Typical results are shown in Fig. 1.

The aerosol was mixed with radon-containing air (typical 750 Bq) in a 0.5 L glass vessel. Ten minutes after mixing, the whole gas volume was pumped off from the vessel to a filter sampler. To determine the number of radon daughter atoms attached to aerosol particles, the Po-214 decays on the filter were measured on-line by a PIPS-silicon detector for 4 hours. After this time nearly all short-lived decay products have decayed. The measured total counts were normalized to the expected number of counts calculated from the radon activity and the decay time in the mixing vessel (10 min). The resulting attachment efficiencies were determined for aerosol volume concentrations ranging over two and four orders of magnitude for NaCl and \((\text{NH}_4)_2\text{SO}_4\), respectively (Fig. 2).

According to Fig. 2, the attachment of radon daughters to ammonium sulphate seems to be higher than to sodium chloride, especially at low aerosol surface concentration. A substantial scattering of data points at higher concentrations was observed. We are currently improving the experimental setup in order to decrease the scattering at high aerosol concentration.

References

DIFFERENT SHAPES OF AEROSOLS GENERATED BY ATOMIZATION

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The aerosols of sodium chloride and ammonium sulfate used in adsorption and transport experiments of radon decay products /1/ have been characterized by the particle size distribution, the total particle mass concentration and the shape of the aerosol particles. Hollow ammonium sulfate spheres and crystalline sodium chloride particles were observed.

The polydisperse aerosols of sodium chloride and ammonium sulfate are produced by spraying solutions of both salts of the same mass concentration with a Collison atomizer and drying the droplets and particles with a diffusion dryer as described in /2/.

For the determination of the particle size distribution, the aerosols are diluted and passed through the scanning mobility particle sizer (SMPS) /2/. For an independent determination of the mass concentrations, the aerosol substances are sampled on fibrous glass filters, extracted in water, and examined by chemical analysis (CA) for \(\text{SO}_4^{2-}\) or \(\text{Cl}\), respectively.

Fig.1 depicts the total volume concentration of the aerosols from CA (after conversion of the mass to the volume concentration by the theoretical density) and that from the SMPS measurements (assuming spheres and summation over all particles) as a function of the salt mass concentration in the atomizer.

To observe their shapes, the particles from a small part (1 L in 4.5 min) of the total aerosol flow (250 L/h) were separated on microporous polyester membrane filters. The SEM images of the sodium chloride particles always showed cubic shapes with more or less rounded corners and edges (Fig. 2). The ammonium sulfate particles are spheres (Fig. 3). Only with mechanical pressure were we able to crack greater aggregates of the spheres.
and to find that the spheres were hollow (Fig. 4). The weakest parts of the sphere walls are in the region where single spheres are grown together. There, they seem to sink into each other and break more easily.

According to Raabe /3/, the type of particles produced will depend upon the conditions of drying as well as the chemical nature of the materials. If droplets are dried rapidly, essentially shells may be formed by the encrustation of the surfaces. We see from the SEM micrographs that drying by free evaporation of the water into the surrounding gas is hindered where neighboring spheres attach to each other. The re-dissolution into the inner liquid competes with the evaporation, thereby weakening the crust at these areas. Despite these differences in particle shape between the two salts, we did not see any characteristic differences in the particle spectra, in the total aerosol number, or in the volume concentrations outside the range of experimental error (F=9%, Fig. 1). (The SMPS results may have some systematic losses in comparison with the CA). Therefore, we assume that coagulation processes superpose the extremely short droplet drying process, thereby compensating the initial differences in the aerodynamic or mobility properties of the aerosols. What is true for the similarity of the aerodynamic properties may not be true for the inner structure of the primary particles. Differences in these properties may significantly influence the adsorption of the individual particles. Therefore, we are planning to further investigate the crystalline or non-crystalline properties of the particles.

References

Chemistry of the Heaviest Elements
REACTION GAS CHROMATOGRAPHY OF OXIDE AND HYDROXIDE SPECIES OF MOLYBDENUM - SIMULATION AND EXPERIMENT

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The reaction gas chromatography of oxide and hydroxide species of molybdenum in thermochromatographic columns was simulated with a microscopic model. Calculated thermochromatograms were compared to experimental results.

In the O_2-H_2O/SiO_2 system all group 6 elements are transported via reaction gas chromatography, governed by the surface reactions dissociative chemisorption and associative desorption (M = Cr, Mo, W) /1/.

\[
\text{MO}_x(\text{OH})_y(\text{g}) \xrightleftharpoons{\text{diss. chemisorption}} \text{MO}_x(\text{ads}) + \text{H}_2\text{O}_{(g)} \quad (1)
\]

To describe reaction gas chromatography the microscopic model proposed by Zvara /2/ has been extended /3/.

Simulations of gas chromatography can be done with a Monte Carlo procedure based on this model. The method has been applied to thermochromatographic surface reaction studies with oxide and hydroxide species of molybdenum in open tubular quartz columns. Positions and shapes of thermochromatographic zones were calculated in dependence of reaction type, humidity of the carrier gas, and exposure time and were compared to experimental results. The reaction gas chromatographic transport of molybdenum via reaction (1) through a thermochromatographic column has been studied already and is summarized in /1/. For all simulations, the thermodynamic state functions evaluated by conventional methods or estimated from literature data in /1/ were used. Thermochromatograms were calculated assuming the real experimental conditions described in /1/.

As can be seen from Fig. 1, both simulated peak positions and shapes correspond very well
with the experimental results under the assumption that molybdenum is transported according to reaction (1). This holds also at different water vapour pressures of the carrier gas /3/. The best correspondence between simulation and experiment was obtained with a value of \( \Delta H_{\text{diss,ads}} = -50 \text{ kJ/mol} \). The same enthalpy was evaluated from experiments by conventional methods /1/.

As an example for potential applications, thermochromatograms for different basic reactions and exposure times were calculated by Monte Carlo simulations based on the model of Zvara and the extended model and are compared in Fig. 2. The simulation shows that the invariable species \( \text{MoO}_3(\text{OH})_2 \) transported via simple reversible adsorption would quickly reach the region of its deposition temperature and then move very slowly. In contrast, chromatography according to reaction (1) via dissociative adsorption - associative desorption with \( \Delta H_{\text{diss,ads}} = -35.4 \text{ kJ/mol} /1/ is characterized by a slow but steady migration. The peak shapes of the deposition zones also depend significantly on the basic reaction. Narrow peaks are obtained if the chromatography is governed by simple reversible adsorption, whereas broader peaks are obtained for chromatography according to reaction (1). All simple reversible adsorption processes are characterized by similar values of \( \Delta S_{\text{ads}} \), which has no effect on position or shape of the peak. In contrast, \( \Delta S_{\text{diss,ads}} \) affects the migration velocity of the deposition zone as well as its shape. As demonstrated here the Monte Carlo simulation of reaction gas chromatography on the base of the extended model /3/ is an essential and reliable tool to model, evaluate, and interpret gas-solid chromatography experiments. Contrary to all other evaluation methods it allows to calculate the shape of thermochromatographic deposition zones.

Acknowledgments
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References

ON-LINE ISOThERMAL GAS CHROMATOGRAPHY WITH SHORT-LIVED MOLYBDENUM AND TECHNETIUM ISOTOPES IN THE \( \text{O}_2-\text{H}_2\text{O}_{(g)}/\text{SiO}_{2(s)} \)-SYSTEM

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In preparation for an experiment to study the chemical properties of element 106 (seaborgium, Sg), model studies were performed with short-lived molybdenum isotopes. The behavior of technetium as a homologue of element 107 (nielsbohrium, Ns) was also studied.

In order to study the reaction

\[
\text{MO}_3(\text{OH})_2(\text{g}) \xrightleftharpoons[\text{ass. desorption}]{\text{diss. chemisorption}} \text{MO}_3(\text{ads}) + \text{H}_2\text{O}_{(g)}
\]

which is assumed to be valid for all group 6 elements (including Sg) in the \( \text{O}_2-\text{H}_2\text{O}_{(g)}/\text{SiO}_{2(s)} \)-system /1/, on-line isothermal gas chromatography experiments were performed using short-lived molybdenum isotopes as model nuclides.

Among other fission products, short-lived Mo and Tc isotopes were produced from the \( ^{235}\text{U} \) fission target of the radiochemistry gas-jet /2/ at the U-120 cyclotron of the Forschungszentrum Rossendorf with neutrons produced in the reaction \( ^{9}\text{Be} (\text{d}, \text{n})^{10}\text{B} \). For the rapid transport of the fission products, the He/MoO\(_3\)-version (1.0 l/min) of the radiochemistry gas-jet was used.

A quartz wool plug for destroying the aerosol particles was placed in the first section of the furnace which was kept at 1100 °C. The temperature of the 40-cm-long isothermal part of the
column was varied between 500 EC and 1000 EC. The recluster unit was operated with an Ar/KCl aerosol. The KCl clusters loaded with volatile species were collected on a glass fibre filter and measured on-line with a HPGe detector. Moist oxygen with a partial pressure of water of about 12 kPa was used as reactive gas at a flow rate of 0.5 l/min.

Fig. 1 shows elution yields of the isotope $^{104}$Mo as a function of the isothermal temperature in the chromatographic column. The given yields are relative to a direct catch measurement using an empty quartz glass tube at room temperature. The isotopes $^{103}$Mo and $^{105}$Mo were also measured and gave similar yield curves.

The elution yield depends significantly on the temperature of the isothermal part of the column. With increasing temperature, a flat increase was obtained as typically for reaction gas chromatography /3/. The yield plateau was reached at a temperature of 900EC.

In case of longer lived $^{101}$Mo ($t_{1/2} = 14.6$ min), the yield plateau is already reached at temperatures above 500EC. However, the yield was expected to be higher than measured in the experiments for both the short-lived isotopes $^{103-105}$Mo and the longer lived isotope $^{101}$Mo. Only a small part of the losses results from the radioactive decay in the chromatographic column. In the temperature range studied, the retention time in the chromatographic column is in the order of a few seconds to minutes. Heavy losses are caused by the interaction between volatile species and the surface of the recluster chamber before the species are reattached to aerosol particles. High temperatures have a negative effect on the recluster yield. In case of short-lived isotopes, additional considerable losses are a result of the radioactive decay in the recluster chamber due to the dwell time of about one minute.

With respect to possible future experiments with element 107 preliminary investigations to the behavior of short-lived Tc isotopes were performed.

For all Tc isotopes, the short-lived $^{105}$Tc ($t_{1/2} = 54.2$ s) as well as the longer lived $^{101}$Tc ($t_{2} = 14.2$ min), $^{104}$Tc ($t_{1/2} = 18.2$ min) and $^{105}$Tc ($t_{1/2} = 7.6$ min), yield plateaus were obtained in the temperature range 400 EC - 1000EC. The elution yield was $50 \pm 10\%$ compared to the direct catch. At temperatures of $\#600$ EC a slight increase of the yield was measured as a result of the higher recluster yield at decreasing temperature.

As expected, due to higher volatilities /4/, oxides and hydroxides of Tc pass the chromatographic system under study at temperatures below 1000 EC faster and with higher yields than the corresponding Mo species. Therefore, the O$_2$-H$_2$O$_2$(g)/SiO$_2$(s)-system should be better suited to investigate group 7 than group 6 elements.

Acknowledgments
This work was supported by the BMBF, contract 06 DR 666 I (4)/1, and was performed in cooperation with the GSI Darmstadt.

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/4/ Steffen, A., Bächmann, K.: Gas Chromatographic Study of Volatile Oxides and Hydroxides of Re, Tc, Os, Ru and Ir-II. Talanta 25, 677 (1978)
Fig. 1: Calculation of sublimation enthalpies of Es and Fm based on the proportionality between adsorption and sublimation enthalpies.

Fig. 2: Calculated sublimation enthalpies of Es and Fm.

THERMOCHROMATOGRAPHY OF HEAVY ACTINIDES - DETERMINATION OF THE SUBLIMATION ENTHALPY OF ES

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The adsorption of Cf, Es, and Fm on several metals was studied thermochromatographically. Based on the adsorption data and the correlation between adsorption and sublimation heats, we calculated the Es sublimation enthalpy of 167±15 kJ/mol (95 %). This is significantly higher than the value obtained by direct vapor pressure measurements (133 kJ/mol /1/). However, our value fits better to the theory.

Theoretical calculations using different approaches /2, 3, 4/ indicate that the sublimation enthalpies decrease smoothly from Cf to No. This is in contrast to the opposite trend of the experimental values for Es (133 kJ/mol /1/) and Fm (143 kJ/mol /5/). Therefore, we checked these values based on the correlation between the sublimation and adsorption enthalpies, experimentally well established for metallic adsorbate bonding /6/, especially in case of the lanthanides /7/.

Our experimental setup, the procedure, and the data analysis is described elsewhere /8/. The actinides were produced at the UNILAC (GSI) in the 246Cm + 22Ne reaction and at the U-400 (FLNR) and the Philips cyclotron (PSI) in the 246Cm + 18O reaction.

In all experiments a separation was observed on the chromatographic column in the order Cf, Es, and Fm. This is supported by the EICHLER-MIEDEMA model /9/, developed for understanding the adsorption enthalpy at zero coverage which predicts this position of Es between Cf and Fm.

Obviously, the magnitude of the metallic properties of Es determining the adsorption behavior must be between those of Cf and Fm and one has to expect that the sublimation enthalpy of Es is between those of Cf and Fm. Based on the proportionality mentioned above, one can calculate the sublimation enthalpies of Fm and Es from the measured adsorption heats. Fig. 1 illustrates the procedure for the case of sublimation on Mo.

If the sublimation enthalpies of Cf, Es, and Fm are correct, the adsorption sublimation enthalpy pairs should yield a straight line in the diagram. This is not the case. Because Cf has been well investigated, one may assume that its sublimation enthalpy /10/ is correct and there exist two possibilities: If the reported Es sublimation value is correct, then the Fm sublimation enthalpy would be about 79 kJ/mol, or if the Fm value is correct, then the Es sublimation enthalpy would be about 167 kJ/mol.

The results of these calculations for all experiments are shown in Fig. 2. For Es a sublimation heat of 167±15 kJ/mol (95 %) results, which is typical for a metallic divalent element. The sublimation enthalpy of Fm would be 74±52 kJ/mol (95 %), far too small for the metallic divalent Fm.

The sublimation enthalpy of Es calculated here agrees well with the expected value based on theoretical calculations using different approaches /2, 3, 4/.
and experimentally obtained sublimation enthalpies of Cf, Es and Fm. The similar trends of the desorption and sublimation enthalpies emphasize the possibility to derive sublimation enthalpies from adsorption experiments even for the actinides beyond Fm.

Acknowledgments
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References

THERMOCHROMATOGRAPHY OF NO-259

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For the first time the adsorption of No on several metals was studied by thermochromatography.

In continuation of thermochromatographic adsorption studies of the heaviest actinides /1, 2/ the adsorption of No on several metals was studied. The experimental setup used in this work was similar to the one described in /2/. We chose a temperature of 1480 K at the starting position in the column and a quartz support tube for the thermochromatographic columns. These columns, made from metallic Ti, V, Nb, Ta and Mo foils, were wrapped in a Ta lining to protect them from oxygen emitted from the quartz tube. Helium was used as carrier gas with a flow rate of 230 cm³ per minute. It was purified from water and oxygen with molecular sieve and a Ti getter, respectively. No-259 was produced both at the U-400 cyclotron (FLNR) and at the Philips cyclotron (PSI) in the reaction

\[ ^{248}\text{Cm} ^{(18}\text{O, } ^{3}n)^{259}\text{No}. \]

The reaction products were collected in Ti catcher foils. After irradiating the target for 4 hours they were used as thermochromatographic samples without further preparation.
After the thermochromatography the nuclide distributions along the columns were measured off-line by alpha spectroscopy. Fig. 1 shows the activity distribution of $^{259}$No and other actinide nuclides on a Nb column.

![Thermochromatogram of $^{259}$No on a Nb Column](image)

<table>
<thead>
<tr>
<th>Actinide</th>
<th>Column</th>
<th>Deposition Temp. [K]</th>
<th>Adsorption Enthalpy [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cf</td>
<td>Ti</td>
<td>810</td>
<td>-201</td>
</tr>
<tr>
<td></td>
<td>V</td>
<td>1250</td>
<td>-303</td>
</tr>
<tr>
<td></td>
<td>Nb</td>
<td>1173</td>
<td>-290</td>
</tr>
<tr>
<td></td>
<td>Ta</td>
<td>1250</td>
<td>-309</td>
</tr>
<tr>
<td></td>
<td>Mo</td>
<td>1260</td>
<td>-305</td>
</tr>
<tr>
<td>Es</td>
<td>Ti</td>
<td>760</td>
<td>-189</td>
</tr>
<tr>
<td></td>
<td>V</td>
<td>1140</td>
<td>-277</td>
</tr>
<tr>
<td></td>
<td>Nb</td>
<td>1083</td>
<td>-268</td>
</tr>
<tr>
<td></td>
<td>Ta</td>
<td>1150</td>
<td>-284</td>
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<tr>
<td></td>
<td>Mo</td>
<td>1200</td>
<td>-291</td>
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<tr>
<td>Fm</td>
<td>Ti</td>
<td>730</td>
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<tr>
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<td>-241</td>
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<td></td>
<td>Ta</td>
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<td>-267</td>
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<tr>
<td></td>
<td>Mo</td>
<td>1150</td>
<td>-279</td>
</tr>
<tr>
<td>No</td>
<td>Ti</td>
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<td>-177</td>
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<td></td>
<td>V</td>
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<td>Nb</td>
<td>973</td>
<td>-241</td>
</tr>
<tr>
<td></td>
<td>Ta*</td>
<td>1040</td>
<td>-258</td>
</tr>
<tr>
<td></td>
<td>Mo*</td>
<td>1140</td>
<td>-277</td>
</tr>
</tbody>
</table>

*only one event registered*

Tab. 1: Deposition Temperatures and Adsorption Enthalpies of Actinides

The program TECRAD /3/ was used to derive adsorption enthalpies from the deposition temperatures. Tab. 1 summarizes our experimental deposition temperatures and the calculated adsorption enthalpies.

The different adsorption enthalpies of Cf, Es and Fm reflect the tendency from metallic tri- to divalency in the second part of the actinide series.

Nobelium is always adsorbed at the position of Fm. This allows the conclusion, that at Fm the metallic divalency is fully developed. This is in agreement with previous investigations of Md /4/.

Acknowledgments

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CALCULATION OF RATE CONSTANTS OF THE BASIC REACTIONS OF REACTION GAS CHROMATOGRAPHY - TRACE AMOUNT COMPONENTS IN LAMINAR GAS FLOW

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Trace amount components in gas phase follow other statistical rules than main components of the carrier gas. These statistical rules are based on dilution effects. Instructions for the calculation of the rate constant of adsorption and the rate constant of streamline flow in a laminar gas flow for trace amount components are set out.

Any component in the gas phase that has an extremely small concentration - # 10^6 volume percent - is called a trace amount component, abbreviated in the following tac. The transport of tac is governed by collisions with the carrier gas. The mean free path $\xi$ of a species x is the natural parameter to discontinue the tube. In the suggested problem the tube radius is much greater than the mean free path. As laminar flow is considered, the radial velocity profile is parabolic and is discreted in this work by:

$$v_{r(x)} = v_0 \left[1 - j \left(j + \frac{1}{2}\right)^2\right] \quad (1)$$

where $(j_{m,x} + \frac{1}{2})$ is the ratio $(r_{max} \xi_{x}^{-1})$, $r_{max}$ the tube radius, and 0 # j # $j_{m,x}$ is an integer number that discontinue the tube into a sum of hollow cylinders with volume flow $V_t = 2j \xi_x^2 v_{r(x)}$. $v_0$ is the maximum flow velocity in the tube.

Let a tac be just desorbed from the tube wall, so at first one has to consider the chance of tac to become a free particle in the gas flow in respect to recollision with the wall. This means, that we separate the zone of transport over macroscopic distances along the tube from a radial oriented zone in the gas phase, in that the tac is in a standby position. Geometric factors set up a power series in $4B$ scattering, which yields for the total collision probability with the wall within the approximation that only molecules in the first 8 zone hit the wall and that the hypotenuse of a molecule located in this zone next to the wall is of constant length $8$:

$$0_{ads,h} = (dS/4B)^3 \sum_{p=0}^4 \sum_{l=0}^4 (dS/4B)^{2p+1} \left[1 - 2(dS/4B)^{2p+1}\right] = 0.2327 \quad (2)$$

with h as average scattering angle of the unit sphere $(dS/4B)_h = \frac{1}{2} I_0^{B/2} d2(1 - \cos 2)$, l is the number of collisions inside the first 8 zone and p the probability of rediffusion into the first 8 zone from inner hollow cylinders. The chance of collision with the wall is for the first (l = 1) and the first three collisions (1 # (p + l) # 3) 87.9% and 99.995% of the total collision probability with the wall respectively. The same considerations lead to the same results for tac to get into the inner zones of the tube. Therefore molecules that are three mean free paths or more away from the wall of the tube can be handled as free particles in respect to the existence of the tube wall /1/. The quantitative analysis of this problem in kinetic gas theory is new.

The transport of tac along the tube is done by collisions with the carrier gas. The slow velocity of laminar flow $[v_0 \# 16 \text{ m s}^{-1}]$ is a small disturbance of molecular movement given by Maxwell distribution and its average velocity $v_M = 730 \text{ m s}^{-1}$; Ar, 1000 K and therefore separable. This is valid especially in the region next to the tube wall, where the laminar flow is vanishing small. The tac distribute according to equation (2): 23% of the desorbed particles will hit the wall without becoming free particles. Other 23% will be free particles in the laminar gas flow. The rest of 54% will stay inside the standby zone.

For small Knudsen numbers adsorption of free particles is related to a probability of collision with the wall instead of drifting through the surfaces of the inner hollow cylinders. The "collisions" with surfaces of inner cylinders are a measure of collisions with other molecules in gas phase. When $6_{x,cg}$ is the probability factor of collision with the wall, the rate constant of collision with the wall of the carrier gas is given by:

$$k_{w,cg} = 6_{w,cg} v_{M,cg} 8_{cg}^{-1} = (j_{m,cg} + \frac{1}{2}) 2^{-1} \left[(j_{m,cg} + \frac{1}{2})^2 + (j_{m,cg} - \frac{1}{2})^2\right]^{-1} v_{M,cg} 8_{cg}^{-1} \quad (3)$$

The calculation of the probability factor of collisions with the wall for tac - as a free particle - is more difficult, since the lack of interchange effects has to be taken into consideration. In short it is the difference between a particle and any particle. The interchange effects are characteristic for components of the carrier gas, because it's the pressure dominating substance and the particles are indistinguishable. Also, the pressure forces the carrier gas into regions of less
laminar flow velocity. The probability of a radial place of tac in a carrier gas is given then by averaging over possible location, the laminar flow velocity of the carrier gas at that place and the time of residence of tac there! The probability factor of collision with the wall for tac as free particle can be calculated by:

\[
6_{w,\text{tac, free}} = \frac{1}{1 + \left[1 - j_{m,\text{tac}} \left( j_{m,\text{tac}} + \frac{1}{2}\right)^2\right] \left( j_{m,\text{tac}} + \frac{1}{2}\right) \left( j_{m,\text{tac}} - 1\right)^{-1}}
\]

The rate constant of collision with the wall as an upper limit for adsorption for tac is given by:

\[
k_{w,\text{tac, tot}} = 0_{w, h} \left(1 + 6_{w,\text{tac, free}}\right) v_{m,\text{tac}} \delta_{\text{tac}}^{-1}
\]

Where \(n_x\) is the particle density in the gas phase of species \(x\). This definition means, that two tac do not interact with another in a macroscopic paraboloid given by the tube radius, \(v_0\), and the average time of tac spent in the gas phase.

Streamline flow of desorbed tac as a free particle in a laminar flow of carrier gas is a function of velocity averaged over the transported volume and secondly of momentum transfer from carrier gas to tac. The average value of \(v_{r, \text{tac}}\) is found at the half value of the normed generating function of the averaging integral and the rate constant of streamline flow is:

\[
k_{r,\text{tac, free}} = 0.800(227) v_0 \delta_{\text{cg}}^{-1} m_{\text{cg}} m_{\text{tac}}^{-1}
\]

The transport of tac as free particle in the gas phase by streamline flow is faster as the average laminar flow velocity of a carrier gas of equal mass. This effect is again a consequence of interchange effects of the molecules of the carrier gas. The rate constant is a product of averaging. Therefore tac and carrier gas follow the same physical interactions but not the same statistics. The error of about 28% is calculated from the normed slope \([V_{(r)} v_{(r)}]\) versus \(j_{m, r} + \frac{1}{2}\) by averaging with a 2:1:1 weighting of maximal value and the half values. As laminar flow is considered, there is no experimental parameter to influence this error.

The distribution of immediate collision with the wall, residence inside the standby zone and free particle gives a total streamline flow rate constant of:

\[
Y k_{r,\text{tac, tot}} = \left\{(1 - 2 \ 0_{w, h}) \left(2 j_{m, \text{tac}} + 1\right)^{-1} + 0.8 \ 0_{w, h}\right\} v_0 \delta_{\text{cg}}^{-1} m_{\text{cg}} m_{\text{tac}}^{-1}
\]

Acknowledgments
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**OLGA EXPERIMENTS WITH 261-104 UNDER CHLORINATING AND BROMINATING CONDITIONS**

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With the On-Line Gas Chromatography Apparatus OLGA III the retention times of element 104 chloride and bromide were measured in a quartz column using the isotope 261-104 with a half-life of 78 s. With HCl as chlorinating agent element 104 was found to pass through the column at 150°C, whereas with HBr this temperature shifted to about 300°C. Under both halogenating conditions, the homologous element Hf passed through the column at higher temperatures than element 104, in agreement with expectations.

A target (diameter 8 mm) containing 1.01 ± 0.06 mg/cm² 247Gd, covered by about 200 Fm/cm² Gd (30 % enriched in 152Gd) on a 10 Fm Be foil was bombarded with 0.5 - 0.7 pA of a 99 MeV 18O beam at the vertical beam line of the 4m cyclotron at FLNR Dubna. From the target recoil-
ing products were thermalized in the heavy-ion gas-jet chamber from PSI /1/ and transported with a He/C gas-jet through a 2 mm polyethylene capillary of about 5 m length to the OLGA system. Here, the graphite particles were collected on a quartz wool plug kept at about 950 to 1000 EC. To that position about 300 ml/min of HCl or HBr gas were added to form volatile halides which were then transported along a 2 m 1.0 mm i.d. quartz column kept at an isothermal but variable temperature. Behind the column the molecules were reattached to KCl particles and transported through a 5 m long 2 mm i.d. capillary to the PSI tape system for counting (45 s steps).

A typical "γ"-spectrum collected during a two hour OLGA run with HBr gas at 300 EC from all 6 detectors is depicted in Fig. 1. Besides small lines at 6.6 and 7.7 MeV, from $^{214}$Bi and $^{214}$Po (decay product of $^{214}$Bi), a group of 5 counts is found between 8.3 and 8.4 MeV. We assign this event group to $^{261}$104 and its daughter $^{257}$No. This assignment is corroborated by the decay of this event group (insert in Fig. 1).

In Fig. 2 the measured yields of the event group between 8.3 to 8.4 MeV is shown as a function of the OLGA temperature for HCl and HBr. We observe that element 104 forms volatile molecules with HCl above about 150 EC. With HBr the retention temperature at which maximum yield is found is shifted to about 300 EC.

This shift is indicative of a lower volatility of element 104 bromide if compared to element 104 chloride. Most likely, the compounds formed in the OLGA systems under our experimental conditions are $^{104}$Cl and $^{104}$Br, respectively. Simultaneously measured Hf produced in the reaction with Gd indicated a lower volatility of both the chloride and the bromide if compared to the corresponding 104 chloride and bromide, respectively. Having in mind that $^{91}$ZrCl and $^{91}$ZrBr are slightly less volatile than the corresponding Hf compounds we have the volatility sequence element 104 > Hf $>$ Zr, for both the chlorides and the bromides, respectively.

The high volatility of element 104 chloride is in line with estimates using relativistic models /2/.

Acknowledgments
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References
FIRST THERMOCHEMICAL PROPERTY OF SEABORGIUM DETERMINED

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LBNL Berkeley - University Bern - FLNR Dubna - GSI Darmstadt - TU Dresden - Chalmers University of
Technology Göteborg - GH Kassel - ITS and LLNL Livermore - University Mainz - University Oslo - FZ
Rossendorf - JAERI Tokai - PSI Villigen collaboration

Using the PSI On-Line Gas Chromatography Apparatus OLGA III the nuclides $^{265}$Sg and $^{266}$Sg were unambiguously identified and their half-lives determined. As predicted by relativistic calculations and by extrapolations of chemical properties, it was demonstrated that Sg oxychlorides are indeed less volatile than their lighter homologue Mo- and equally or less volatile than W-oxychlorides.

After a first successful experiment /1/, in which we chemically separated Sg in the form of volatile oxychlorides and unambiguously identified the nuclides $^{265}$Sg and $^{266}$Sg using OLGA III, a second series of experiments was performed. It was our goal to confirm the results of the first experiment and to determine the volatility of Sg-oxychlorides in respect to their lighter homologue group 6 oxychlorides.

In relativistic calculations /2/ it was shown that SgOCl$_2$ should be the most stable oxychloride compound of Sg, and the least volatile MoOCl$_2$ compound. From extrapolations of thermochemical properties it was concluded that SgOCl$_2$, as a macroscopic compound, has a higher sublimation enthalpy than WOCl$_2$ or MoOCl$_2$ and also SgOCl$_4$. With the aid of an empirical correlation between sublimation enthalpy and adsorption enthalpy on quartz surfaces $^0_1\text{H}(\text{SgOCl}_2) = -106 \text{ kJ/mol}$ was predicted /3/.

First, the volatility of WO$_2$Cl$_2$ was carefully measured under conditions which were identical to the actual Sg experiment. Short-lived W-isotopes were produced in the 119 MeV $^{22}$Ne on $^{152}$Gd reaction at the GSI UNILAC accelerator.

The yield curve measured for WOCl$_2$ is shown in Fig. 1. With the Monte Carlo method an adsorption enthalpy $^0_1\text{H}(\text{WOCl}_2) = 96 \text{ kJ/mol}$ was determined in good agreement with a previous measurement /1/. In addition, the shape of the calculated yield curve corresponds very well to the experimental data.

At 350°C isothermal temperature and with a beam dose of $2.31 \times 10^{17}$ two decay chains attributed to $^{265}$Sg and one decay chain attributed to $^{266}$Sg were observed, confirming earlier results where...
Sg decays were observed at 300°C and 400°C isothermal temperature. At the lower isothermal temperature of 250°C a beam dose of 5.22\(^{17}\) was accumulated without observing decays of \(^{265,266}\)Sg. Nevertheless, \(^{168}\)W was still detected at about 75\% of its yield at 350°C and was used to monitor system performance.

Tab. 1: \(^{265,266}\)Sg events observed in the 1996 experiments.

<table>
<thead>
<tr>
<th>(E_1 [\text{MeV}])</th>
<th>(t_1 [\text{s}])</th>
<th>(E_2 [\text{MeV}])</th>
<th>(t_2 [\text{s}])</th>
<th>Mode</th>
<th>Decay Assignment</th>
<th>Isothermal Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.87</td>
<td>7.0</td>
<td>8.20</td>
<td>15.2</td>
<td>MD</td>
<td>(^{265})Sg 6 (^{261})Rf or (^{257})No</td>
<td>350°C</td>
</tr>
<tr>
<td>8.68</td>
<td>1.4</td>
<td>8.35</td>
<td>150.2</td>
<td>MD</td>
<td>(^{265})Sg 6 (^{261})Rf or (^{257})No</td>
<td>350°C</td>
</tr>
<tr>
<td>8.74</td>
<td>15.1</td>
<td>SF</td>
<td>1.7</td>
<td>SF</td>
<td>(^{266})Sg 6 (^{262})Rf</td>
<td>350°C</td>
</tr>
<tr>
<td>8.65</td>
<td>3.5</td>
<td>SF</td>
<td>2.4</td>
<td>SF</td>
<td>(^{266})Sg 6 (^{262})Rf</td>
<td>119 MeV, direct catch, tape system</td>
</tr>
</tbody>
</table>

In Tab. 1 all event chains attributed to the decay of \(^{265}\)Sg and \(^{266}\)Sg are summarized. Together with the decay chains observed in the 1995 experiments /1/, new more accurate half-lives and production cross sections can be calculated for \(^{265}\)Sg and \(^{266}\)Sg (122 ± 2 MeV, 68\% c.i.):

\[
^{265}\text{Sg}: \quad t_{1/2} = 5.4 (+4.4/-1.7) \text{ s} \quad \text{and} \quad F = 395 (+250/-180) \text{ pb}, \quad \text{and for} \quad ^{266}\text{Sg}: \quad t_{1/2} = 15.6 (+21.3/-5.7) \text{ s} \quad \text{and} \quad F = 22 (+20/-13) \text{ pb}.
\]

In Fig. 1 all seven Sg events which were measured at 300°C to 400°C isothermal temperature were summarized to one data point. Furthermore, the right hand scale of Fig. 1 was chosen in such a manner that the mean number of detected Sg events per \(10^{17}\) beam particles corresponded to 100\% relative yield. The error limits on the Sg data point in relative yield correspond to the 68\% error of 7 detected events. At 250°C isothermal temperature 0 events were observed. The upper error limit of 0 events at a 68\% confidence level corresponds to 1.84 events /4/. Also shown are the expected yield curve intervals for \(^{265}\)SgO\(_2\)Cl\(_2\) and \(^{266}\)SgO\(_2\)Cl\(_2\) calculated for \(h_a^{0(T)}(\text{SgO}_2\text{Cl}_2) = -106 \text{ kJ/mol}\) and half-lives (including error limits) from this report. The predicted volatility of SgO\(_2\)Cl\(_2\) is in full agreement with the available experimental data. In order to compare the volatility of SgO\(_2\)Cl\(_2\) with its lighter homologues the limits of possible adsorption enthalpies have to be determined. They are given by a relative yield #32\% at 250°C and a lower half-life limit of 3.7 s and a relative yield of $62\%$ and an upper half-life limit of 36.9 s. The corresponding interval of adsorption enthalpy is:

- 95 kJ/mol #) \(h_a^{0(T)}(\text{SgO}_2\text{Cl}_2) \) # - 130 kJ/mol.

Therefore, the relative volatility of group 6 oxychlorides is MoO\(_2\)Cl\(_2\) > WO\(_2\)Cl\(_2\) > SgO\(_2\)Cl\(_2\). The error limits on the adsorption enthalpy depend not only on the statistics of the experimental data but also on the error limits of the half-lives. More accurate half-life measurements will significantly reduce the current interval of possible adsorption enthalpy values. Nevertheless, we have determined the first thermochemical property of a compound of the heaviest element currently accessible by chemical means.

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Taut, St., S. Hübener, B. Eichler, H.W. Gäggeler, M. Schädel, S. Timokhin, I. Zvara, H. Nitsche
Thermochromatography of Heavy Actinides on Metal Surfaces at High Temperature
4th International Conference on Nuclear and Radiochemistry
Saint Malo, France, 08.-13.09.1996

X-ray Photoelectron Study of the Interaction of $\text{UO}_2(\text{ClO}_4)_2$ with Calcite and Diabase Minerals in Water Solutions
1st Russian-German Seminar on X-ray Photoelectron Spectroscopy and X-ray Spectroscopy
Voronezh, Russia, 27.05.-01.06.1996

Gas Chromatography Studies of Group 6 Elements in the $\text{O}_2$-$\text{H}_2\text{O}^+/\text{SiO}_2$-System
4th International Conference on Nuclear and Radiochemistry
Saint Malo, France, 08.-13.09.1996

OLGA experiments with $^{261}104$ under chlorinating and brominating conditions
4th International Conference on Nuclear and Radiochemistry
Saint Malo, France, 08.-13.09.1996

Yarzhemsky, V.G., T. Reich, P. Streubel, R. Szargan
Lineshape Asymmetry Parameters in X-ray Photoelectron Spectra
17th International Conference X-ray and Inner-Shell Processes
Hamburg, Germany, 09.-13.09.1996
III. SEMINARS
INSTITUTE SEMINARS

Dr. Norman Edelstein
Lawrence Berkeley National Laboratory, Berkeley (USA)
Speciation of Radionuclides by X-ray Absorption Spectroscopy
09.04.1996

Dipl. Min. Stephan Krämer
California Institute of Technology, Environmental Engineering Science, Pasadena, (USA)
Kinetik der ligandenkontrollierten Auflösung von Oxidphasen
16.04.1996

Dr. Barbara Hard
Umwelt-Forschungszentrum Leipzig GmbH, Sektion "Umweltmikrobiologie"
Entwicklung eines mikrobiologischen Verfahrens zur Reinigung radioaktiv belasteter Uranbergwerkswässer aus Ronneburg/Thüringen
10.05.1996

Dr. Thomas Fanghänel
Forschungszentrum Karlsruhe, Institut für Nukleare Entsorgungstechnik
Aquatische Chemie von Actiniden in konzentrierten Salzlösungen
21.05.1996

Prof. Dr. Vladimir Balek
Nuclear Research Institute Rez, Czech Republic
Radiometrische Emaniermethode zur Charakterisierung von Festkörperoberflächen
11.06.1996

Dr. Sonja Selenska-Pobell
Universität Bayreuth, Lehrstuhl für Genetik / TU Dresden, Institut für Mikrobiologie
Die Rolle von Bakterien in Uran-Abfallhalden
12.06.1996

Priv. Doz. Dr. Klaus Albert
Universität Tübingen
Grundlagen und Anwendungen der Festkörper-NMR-Spektroskopie zur Untersuchung umweltrelevanter Proben
19.06.1996

Dr. Alexej A. Bessonov
Russian Academy of Science, Institute of Physical Chemistry; Moscow, Russia
Electron Absorption Spectra and Structure Peculiarities of Solid Neptunium(V) Compounds
27.06.1996

Prof. Dr. Hans Bergmann
Friedrich-Schiller-Universität Jena, Institut für Ernährung und Umwelt
Spurenelementstatus ökochemischer Reaktionen in Pflanzen in Abhängigkeit von biochemischen Faktoren und der Bodenfeuchte
02.07.1996

Dr. Alexej A. Bessonov
Russian Academy of Science, Institute of Physical Chemistry; Moscow, Russia
On Hydration Number of Actinide Dioxo Cations
10.07.1996

Prof. Dr. Shinya Nagasaki
University of Tokyo, Japan
Colloid Chemistry and Migration in Geologic Formation - Recent Research Activities in the University of Tokyo
13.08.1996

Dr. Evgeni Kalinin
St. Petersburg State University, Dept. of Radiochemistry; St. Petersburg, Russia
Tritium and Chemistry of Intermediate Reactive Particles
21.08.1996
Dr. Patrick G. Allen  
Glenn T. Seaborg Institute for Transactinium Science, LLNL Livermore, USA  
XAFS Speciation Studies of Radionuclides  
02.09.1996

Prof. Dr. Gregory R. Choppin  
The Florida State University, Department of Chemistry, Tallahassee, USA  
Present and Future Technologies for Actinide Separation  
19.09.1996

Prof. Dr. Gregory R. Choppin  
The Florida State University, Department of Chemistry, Tallahassee, USA  
100th Anniversary of the Discovery of Radioactivity  
20.09.1996 (FZR Center Seminar)

Prof. Dr. Carolyn J. Anderson  
Washington University, Med.Center, Mallinckrodt Institute of Radiology, St. Louis, USA  
Copper-64-labeled Proteins and Peptides for PET Imaging and Therapy  
09.10.1996

Prof. Dr. Vala Ragnarsdottir  
University of Bristol, Department of Geology; Bristol, Great Britain  
The Structure and Coordination of Aqueous and Mineral Surface Complexes  
15.10.1996

BS Chris Muskett  
University of Bristol, Department of Geology; Bristol, Great Britain  
Adsorption of Uranium onto Ironhydroxides and Phylllosilicates  
15.10.1996

Prof. Dr. Alexander S. Shulakow  
St. Petersburg State University, Institute of Physics; St. Petersburg, Russia  
XUV Emission Spectroscopy as a Tool for the Study of Chemical Phase Composition of Thin Layers  
17.10.1996

Prof. Dr. Hansruedi von Gunten  
Labor für Radio- und Umweltchemie der Universität Bern und des Paul-Scherrer-Instituts, Villigen, Schweiz  
Ungleichgewichte in den natürlichzerfallsreihen - Anwendungen in der Geochemie  
22.10.1996

Prof. Dr. Hansruedi von Gunten  
Labor für Radio- und Umweltchemie der Universität Bern und des Paul-Scherrer-Instituts, Villigen, Schweiz  
Altersbestimmung mit nuklearen Methoden - Ein Überblick und neuere Anwendungen  
24.10.1996 (FZR Center Seminar)

Prof. Dr. Svetlana Tretjakova  
VIK Dubna, Russia  
Solid State Nuclear Detectors for Radiochemistry  
21.11.1996

Dr. Andrey V. Legin  
St. Petersburg State University, Dept. of Radiochemistry; St. Petersburg, Russia  
Solid State Chemical Sensors and Sensor Systems for Analysis of Complex Liquid Media  
04.12.1996

**INTERNAL SEMINARS** (open to the public)

Dr. Harald Zänker  
Einführung in die Photonenkorrelationsspektroskopie  
30.04.1996
Dr. Harald Zänker  
Kolloidchemische Untersuchungen an Kieselsäure und Uran-Silikat-Komplex in saurer Lösung (I)  
18.06.1996  
Dr. Harald Zänker  
Kolloidchemische Untersuchungen an Kieselsäure und Uran-Silikat-Komplex in saurer Lösung (II)  
27.06.1996  
Dipl.-Chem. A. Roßberg  
Untersuchungen zur Charakterisierung von titan- und chromhaltigen Ni/Al₂O₃-Katalysatoren  
(Diplomarbeit TH Merseburg)  
30.09.1996  
Dr. Eckhart Förster  
Das C-14-Konvertierungsprojekt - bisherige Ergebnisse und Ausblick  
15.10.1996  
Dr. Melissa A. Denecke  
EXAFS-Ergebnisse von festen Uranylcarboxylaten  
04.11.1996  
Dipl.-Chem. R. Jankowsky (FWB)  
Strukturuntersuchungen an Aminosäure- und Oligopeptiden von Rhenium und Technetium  
04.11.1996  
Dipl.-Chem. A. Roßberg  
EXAFS-Ergebnisse zur Sorption von U(VI) an Kohlen  
05.12.1996  
Dr. G. Bonsdorf (TU Dresden)  
XANES- und Mößbauer-Spektroskopie zur Untersuchung von Redox- und Kationenordnungszuständen in Manganferrit  
05.12.1996  
Dr. Tobias Reich  
EXAFS-Ergebnisse zur Uranabsorption an Calcit, Diabas und Silicagel  
17.12.1996  

WORKSHOPS

Tagung Arbeitskreis “Freimessung von Anlagenteilen und Bauschutt aus dem Abbau kerntechnischer Anlagen des Brennstoffkreislaufs”

FZR, Institut für Radiochemie; VKTA Rossendorf  
TU München, Institut für Radiochemie  
FZ Karlsruhe (INR, PTE, HDB, KGV, HS-US)  
WAK-LA Karlsruhe  
BFS-Salzgitter  
GRS Köln  
LfU Baden-Württemberg  
Bayrisches Landesamt für Umweltschutz  
Wismut GmbH, Chemnitz  
Rossendorf, 06.11.1996  
C. Nebelung (FZR)  
Direktmessung alpha-aktiver Nuklide  
K. Fleischer (VKTA)  
Eindringverhalten radioaktiver Kontamination in ungeschützte Betonoberflächen  
S. Niese, B. Gleisberg, W. Boden (VKTA)  
Low-level Aktivitätsbestimmung von Leitnukliden im Eindampfrückstand im KKW Lubmin
R. Berg (WAK)
Stand der Anlagencharakterisierung der WAK

C. Schultheiss (FZK/ INR)
Verfahren zur direkten Beschichtung von Probenträgern für die Alpha-Spektrometrie

S. Nikles, U. Gerstmann (TU München)
Stand der Arbeiten zur Freimessung

Methods and Applications of Low-Level Radioactivity Measurements

Forschungszentrum Rossendorf (FZR)
Verein für Kernverfahrenstechnik und Analytik Rossendorf (VTKA)
Rossendorf, 07.-08.11.1996

Einfluß von Huminsäuren auf das Migrationsverhalten radioaktiver und nichtradioaktiver Stoffe

Forschungszentrum Rossendorf, Institut für Radiochemie
Universität Mainz, Institut für Kernchemie
Universität des Saarlandes, Institut für Anorg. u. Analyt. Chemie und Radiochemie
Forschungszentrum Karlsruhe, Institut für Nukleare Entsorgung
Rossendorf, 14.-15.11.1996

S. Pompe (Rossendorf)
Darstellung und Charakterisierung von synthetischen Huminsäuren als Funktionalitätsmodelle natürlicher Huminsäuren

A. Brachmann (Rossendorf)
Bestimmung von Komplexierungskonstanten des Urans mit Funktionalitätsmodellen und natürlichen Huminsäuren mittels TRLFS

T. Reich (Rossendorf)
EXAFS-Messungen an Komplexen von Uranyl mit Funktionalitätsmodellen und natürlichen Huminsäuren

A. Mansel (Mainz)
Komplexierung von La(III), Sm(III) und Am(III) in Huminsäurelösungen

A. Seibert (Mainz)
Komplexierung von Np(V) in geringer Konzentration mit Huminsäure

U. Keuth (Saarbrücken)
Fraktionierung von Huminsäuren durch Isotachophorese und Kapillar-Zonenelektrophorese

H. Schank (Saarbrücken)
Bestimmung von Schwermetallen in Gegenwart von Huminsäuren mit Hilfe elektrochemischer Verfahren

Chr. Marquard (Karlsruhe)
Komplexierung von Np(V) mit Huminsäuren

R. Artinger (Karlsruhe)
Stand der experimentellen Arbeiten zur Migration von Aktiniden in Säulenexperimenten

H. Geckeis (Karlsruhe)
Einfluß von Huminsäuren auf die Sorption von Aktinidionen an Mineraloberflächen
IV. PERSONNEL
PERSONNEL

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DP M. Grantz  DC S. Pompe  DC A. Vahle
DC B. Mack  DC A. Roßberg  DC T. Zorn

* post doc
* term contract
V. ACKNOWLEDGMENTS
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Three projects were supported by the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (BMBF):

- Stillegung und Rückbau: Direktmessung "-aktiver Nuklide in Bauschutt zur Freigabeent-scheidung.
  Contract No. BMBF 02 S 7655 A8

- Chemistry of element 106.
  Contract No. BMBF 06 DR 666 I (4)/1

- Influence of humic acids on migration behavior of radioactive and non-radioactive heavy elements under natural conditions.
  Contract No. BMBF 02 E 88150

Three projects were supported by Commission of the European Communities:

- Effects of Humic Substances on the Migration of Radionuclides: Complexation and Transport of Actinides.
  Contract No. F14W-CT96-0027

- Joint European Thermodynamic Database for Environmental Modeling (JETDEM).
  In collaboration with:
  FZK Karlsruhe, Germany; RCM Environmental Ltd., United Kingdom; Kungliga Tekniska Hogskolan, Department of Chemistry, Sweden; University of Aberdeen, Department of Chemistry, United Kingdom; Quantisci, Spain; Uppsala University, Institute of Earth Sciences, Sweden
  Contract No. F14W-CT96-0029

  In collaboration with:
  SCK-CEN Mol, Belgium; Studsvik Ecosafe AB, Sweden; Riso National Laboratory, Denmark; Westlakes Research Institutes, Great Britain
  Contract No. F14P-CT95-0021

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- Mine-water Induced Wood Decomposition and Influence of the Degradation Products on Radionuclide Speciation, Sorption and Migration.
  Contract No. SMWK 4.7541.83-FZR/402

- Influence of Natural Water-borne Organic Substances on the Valency of Radionuclides and Toxic Heavy Metals.
  Contract No. SMWK 4.7541.88-FZR/512

- Soil-Plant Transfer Factors for Uranium.
  Contract No. SMWK 4.7531.50-03-VKTA/601

- Chemical conversion of $^{14}$C-labeled products to $[^{14}$C]Barium carbonate for long-time disposal.
  Contract No. SMWK 4.7581.312/20
- Förderung von Maßnahmen und Projekten der Entwicklungshilfe für die Staaten Mittel-, Ost- und Südeuropas sowie die neuen unabhängigen Staaten (NUS).
  Contract No. SMWK 26-3551.10/96-85 Reg. Präsidium

One project was supported by Deutsche Forschungsgemeinschaft (DFG):

- Properties of heavy actinides.
  Contract No. DFG Hu 642/1-1

Five projects were supported by the following sponsors:

- Migration of $^{226}$Ra in sediments of the Königstein uranium mine.
  was supported in part by a contract with the WISMUT GmbH.

- INTAS: Gas-phase chemistry studies of elements 104 and 106.
  In collaboration with:
  University of Berne, Switzerland,
  Joint Institute of Nuclear Research, Russia
  Contract No. INTAS 94-424.

- Development of experimental arrangements and methods for on-line high temperature gas chromatography of the heaviest elements.
  In cooperation with GSI.
  GSI DRINK.

- EXAFS-Untersuchungen umweltrelevanter Uranylkomplexverbindungen und deren Sorbate.
  Hamburger Synchrotronstrahlungslabor HASYLAB am Deutschen Elektronen-Synchrotron DESY;
  Contract No. II-94-06

- Complexation and Sorption Phenomena of Uranium in Environmentally-Relevant Systems.
  Stanford Synchrotron Radiation Laboratory SSRL; U.S. Department of Energy
  Contract No. 2362 MP