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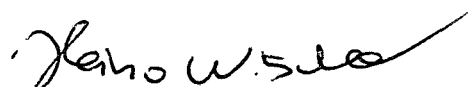
Institute of Radiochemistry

Preface

The Institute of Radiochemistry is one of five institutes of the Forschungszentrum Rossendorf e.V. that was founded in 1992.

Since the founding of the Institute, a reorientation of the scientific direction was initiated: From the production and application of radioisotopes during the period before 1992 toward the new focus of radioecological research for risk assessment and remediation of radionuclide contaminations. The research relates to contamination problems from uranium mining in the German states of Saxony and Thuringia and in the neighboring Czech Republic, and from nuclear weapons production, testing, and accidents in the former Soviet Union. The new research direction of the Institute covers the essential aspects of radionuclide transport in the geo- and biosphere. It includes the distribution of radioactivity in ground- and surface waters and in air. We are studying the interaction of radioactive materials (a) at the interface between aqueous phase and rocks, minerals and soils, (b) the formation and distribution of colloids and aerosols, and (c) the mobilization and retardation of radionuclides through the interaction with organic contaminants and biological decay products. Our studies are essential for the successful development of environmental decontamination and remediation strategies.

This report reflects the scientific transition of the Institute. The contributions to the section on "Ecological Research" are already focused toward the new challenge. The research that is summarized as "General Research" and "Chemistry of the Heavy Elements" clearly bear the elements of aerosol science.

The Institute has made significant progress in achieving the new research profile since 1992, and I expect that we will have completed this process by the end of 1994.

I would like very much to thank Dr. G. Bernhard for having assembled and led a competent and devoted scientific team during his tenure as acting director until my arrival in September 1993.

Rossendorf, June 1994   Prof. Dr. Heino Nitsche

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I. SCIENTIFIC CONTRIBUTIONS

1. ECOLOGICAL RESEARCH

RADIONUCLIDE CONCENTRATIONS IN ROCK MATERIALS - A FUNCTION OF THE GRAIN SIZE ?

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In earlier reports /1/ we have described, that in the mill tailing piles were found increasing activity ratios for some radionuclides related to the U-238 (Th-234) content with the depth. For the radionuclides Th-230 and Ra-226 this behavior can't depend on the migration of the uranium nuclides U-234 and U-238 respectively. The half lifes of the named nuclides (Th-230 and Ra-226) are too long, so that the increase of the activity ratios cannot be a consequence of the decay of U-234. On the other hand the migration of Th-230 and Ra-226 in an ionic form cannot occur in such high concentration consisting their chemical behavior at the given conditions of the mill tailing piles.

There must exist other mechanisms generating these increasing activity ratios.

A first explanation, that the Uranium-238 is washed from the mill tailing pile would require that nearly one fourth of the originally available uranium in the mill tailing pile must be leached. The second possibility their was produce these high ratios is, that in the deeper layers of the mill tailing pile higher amounts must be washed out than in the upper levels. This is only possible if weathering - especially of sulfide minerals - inside the mill tailing pile would be very high and the produced sulfuric acid has leached the uranium. A second explanation for the increased activity ratios could be, that the radionuclides were transported bonded to small particles or as colloids.

An earlier determination of the distribution of grain sizes in the rock material is given in Fig. 1.

The specific surface of the particles increases with decreasing grain size, shown in Fig 2. This means that relatively more ions could be sorbed on the smaller particles. The smaller particles are also products of the weathering process, including minerals like montmorillonite, a good natural sorbens that adsorbs uranium and radium, too / 2, 3, 4, 5 /.
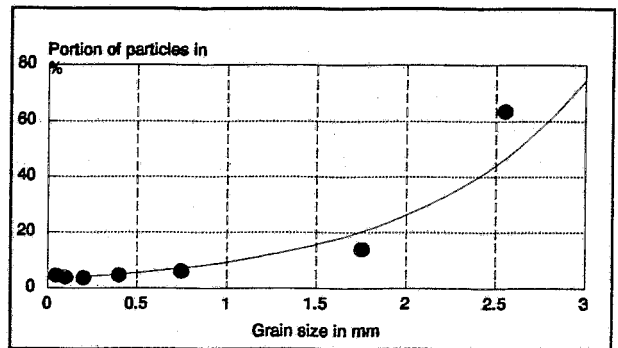
Fig. 1: Portion of grain sizes on the particles of rockmaterial
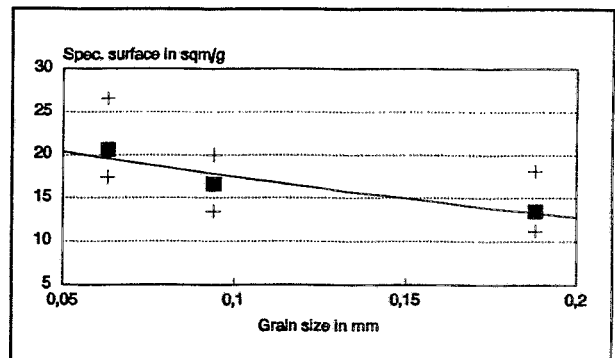
Fig. 2: Dependence of the specific surface on the grain size

We have determined the activity concentration for the radionuclides of the U-238 series in dependence on the grain size. In Fig. 3 the increase of these radionuclide concentrations with decreasing grain size is shown for U-238, Th-230 and Ra-226. The largest increase occurs for Ra-226. Its activity concentration increases about six times with a grain size decrease from 2.2 mm to smaller than 0.1 mm. For Th-230 is this increase smaller, but about twice the amount for Th-234 and U-238, respectively. This means, the smallest particles have the highest activity concentrations for the daughter nuclides Th-230 and Ra-226.
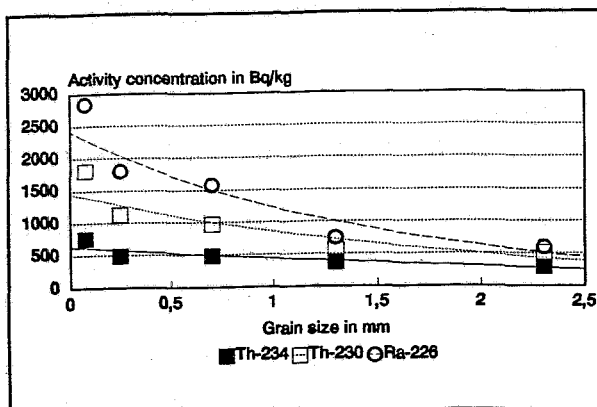
Fig. 3: Dependence of the activity concentration on the grain size

These small particles can be transported to deeper layers of the mill tailing pile by rain water, flowing through the pile.

The transport effect of small rock materials and weathered minerals may explain the increase of the activity ratios in the deeper layers of the mill tailing pile.

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LEACHING EXPERIMENTS WITH LABORATORY COLUMS AND OUTDOOR LYSIMETERS - A FIRST COMPARISON

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During the past, we used for our leaching experients only glass columns that were fillled with several natural rock materials. These experiments were carried out with synthetic leaching solutions, which had a chemical composition similar to the rain water from the Schlema region (pH ~ 4.5; sulfuric acid).

For a better comparison between these column experiments and the natural behavior, we used outdoor lysimeters. The dimensions of these lysimeters were 30 cm in height and 20 cm in diameter. Two of these lysimeters were filled with rockmaterial from the Schlema mining region. In the first lysimeter, we leached material from the mill tailing pile no. 250 and in the other lysimeter material from the pile named "Hammerberghalde" was used. The lysimeters were filled with about 12 kg of the rockmaterial, giving a height inside the lysimeter of about 25 cm. The radioactive content of this material was determined using gamma spectrometry.

In a second experiment that was conducted in the laboratory we used a glass colunm of 100 cm height and a diameter of 10 cm. This colunm was also filled with rock material from the mill tailing pile no. 250 in Schlema. The distribution of the natural radioactive nuclides for this colunm was measured before beginning the experiment.

Over a period of one-half of a year, we sampled the rain water which had passed the lysimeters. Each 450 ml of this rain water were measured using gamma spectrometry. In the same manner we leached the material in the glass column, using a synthetic "rain water" containing 1E-4 Mol/L sulfuric acid.

Fig. 1: Dependence of the activity concentration of U-238, Th-230, Ra-226 and Bi-214 on the eluating time in the lysimeter experiment

In Fig. 1 and 2 are shown the concentrations for U-238 (calculated by using the U-235 isotopes), Th-230, Ra-226 and Bi-214 for the two eluates. In both cases we found for the Bi-214 concentrations very small values of about 2-3 Bq/l. We obtained similar results also for the isotopes Pb-214 and Pb-210.

For the Ra-226 concentrations we found, after the first 4 weeks for the glass column experiment, values of up to 5 Bq/L. Ra-226 and Th-230, showed nearly the same time

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dependence, however, the Ra-226 activity concentrations were smaller than the ones for thorium.

At the first view there are greater differencies for the dependence of the uranium concentration on the eluating time. For the lysimeter experiment, the uranium concentration in the first 15 weeks was between 5 Bq/L and 18 Bq/L. From weeks 16 to 25, we could not take samples because there was no rainfall. From week 30 upwards the uranium concentration decreased. The concentration was below 5 Bq/L.
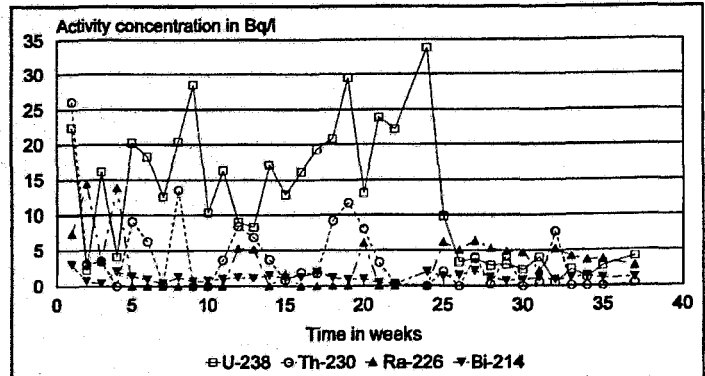
Fig. 2: Dependence of the actvity concentration of U-238, Th-230, Ra-226 and Bi-214 on the eluating time in the glassy column experiment

The glassy colunm experiment showed up to week 25 a uranium activity concentration between 10 Bq/L and 35 Bq/L. Later the uranium concentration was lower then 5 Bq/L. If we assume that the leached uranium comes from the uranium which is sorbed on the rock material, then this sharp decrease in concentration could be explained that all sorbed uranium, which is soluble under the experimental conditions, is desorbed. This could also take place in the lysimeter experiment. The used amount of rock material was smaller and the filling height in the lysimeter was lower. Therefore the time of contact between the rain water and the rock material was shorter and the found uranium concentrations in the solutions were lower.

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SORPTION EXPERIMENTS WITH URANIUM - EXPERIENCES WITH ROCK MATERIAL

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There are two possibilities to determine distribution ratios on rockmaterials - batch and column experiments. Using both methods, we investigated distribution ratios of uranium on rock materials. The rock materials used in the experiments were granodiorite from the Lausitz region, which has a low uranium content and material from the mill tailing pile no. 250 in Schlema.

The batch experiments were carried out with rock material which was washed with 0.1 N HNO_3 and distilled water. For each experiment, we used 2 g of the rock material. The rock material was contacted with uranium solutions, containing 0.01g/L, 0.1g/L, 0.8g/L and 8.0 g/L uranium. The pH was adjusted to 3.5. During the 24 h sorption phase, the pH was adjusted within one-half of a pH unit. After the sorption time, the solution was separated and the uranium concentration was determined using the spectrophotometric method described by Florence [1]. The rock material was washed with distilled water and the sorbed uranium was desorbed with 0.1 N HNO_3. This uranium was also determined by spectrophotometry. The uranium concentrations were used to calculate the distribution ratios of uranium on the rock materials. In Fig. 1, the distribution ratios are shown in dependence on the uranium concentration in the respective solution. With decreasing uranium concentration, the distirbution ratios increases. The distribution ratios on the rock material from Schlema are somewhat higher than on granodiorite. This effect is caused by the mineral composition of the Schlema rock material, which contains carbonate-containing minerals, like calcite and dolomite, and also the weathering mineral montmorillonite [2, 3, 4].

Fig. 1: Distribution ratios of Uranium in dependence of the Uranium concentration

In the column experiments, a glass column with a diameter of 6 mm and a length of 150 mm was filled with 10 g of sieved and washed material. The air in the column was replaced by distilled water. Then the column was leached with 50 ml of a uranium solution (100 mg/l U, pH = 3.5). Each 5 ml of the column leachate was sampled and the uranium concentration was measured. After covering the column with the uranium solution, the material was washed with 50 ml of distilled water. Then

the sorbed uranium was desorbed using nitric acid. Each consecutive 50 ml of nitric acid had a higher hydrogen ion concentration as the previous one, beginning with 1E-5 mol/L and ending at 1E-2 mol/L.

Fig. 2 shows the uranium concentration in the eluates as a function of the elution volume. There is a difference in the sorption behavior of both minerals. The granodiorite sorbs only little uranium and the most uranium passes through the column. The concentration of sorbed uranium reaches a maximum value of about 50 µg/g.

The rock material sorbs uranium is sorbed. The concentration on the rock material reaches about 350 µg/g.
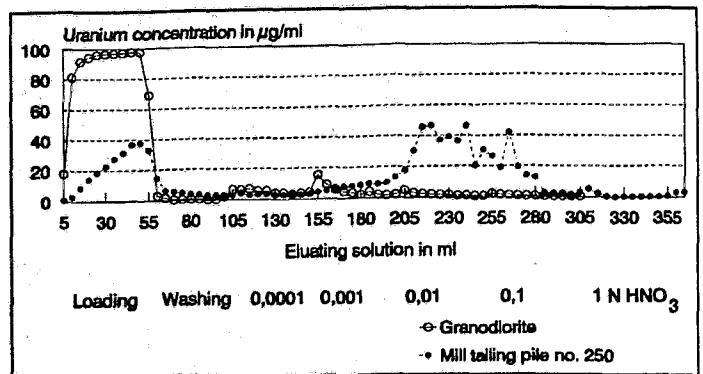
Fig. 2: Concentration of Uranium in eluates of sorption column experiments

The desorbing steps are dependent on the pH of the solution. For granodiorite, the desorption begun with the lowest hydrogen ion concentration of 1E-4 Mol/L and all uranium was desorbed if the hydrogen ion concentration reached 1E-2 Mol/L. For the rock material, the desorption started at higher hydrogen ion concentrations (1E-3 Mol/L). Most of the sorbed uranium was soluble between hydrogen ion concentrations of 1E-2 and 0.1 Mol/L.

From the results of the "dynamic" colunm experiments, we calculated the distributuion ratio of uranium during the leaching period. Depending on the hydrogen ion concentration, distribution ratios up to about 100 were found. With increasing pH, the distribution ratios increases and the values for the rock materials are also higher then those for the granodiorite.
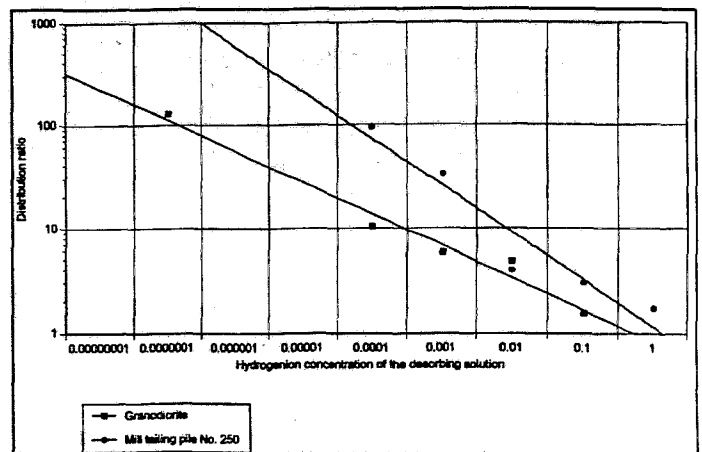
Fig. 3: Distribution ratios of Uranium depending on Hydrogen ion concentration in desorption column experiments

The values for the distribution ratios in the column experiments and in the batch experiments at lower concentrations are in the same order.

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COMPARATIVE DETERMINATION OF URANIUM IN SEEPAGE WATERS OF URANIUM-MINING ROCK PILES

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The rock piles, stemming from the former uranium mining in the Erzgebirge region, have been exposed to rain and air for many years. The numerous geo(bio)chemical reactions due to this exposure are reflected in the composition of the seepage water draining from the bottom of the piles. Radioactive and toxic elements, such as U and its decay daughters, As and several other heavy metals can be released in this way. Transport of these pollutants depends not only on the concentration in the seepage water, but also on their speciation, which is a result of many chemical interactions inside the pile. For the determination of total elemental concentrations, several independent analytical techniques should be used in order to obtain accurate and reliable results.

Considering the uranium content in seepage and mining waters, this paper presents data obtained by several different methods. They are gamma-spectrometry (GS), spectrophotometry (SP), square-wave polarography (SWP) and, in some cases, mass spectrometry with inductively coupled plasma (ICP-MS). Some of the features of the methods are outlined below:

- GS: high-purity Ge detector (GMX 20185) and 92X spectrum master (EG&G Ortec, München); Marinelli beaker; γ lines of U-235 at 143, 163 and 205 keV; calibration curve; total concentrations of U from activity concentration of U-235 according to $c(U) = 1.805\ a(U\text{-}235)$ mg Bq^{-1};
- SP: HP 8452 diode-array spectrophotometer (Hewlett-Packard, Waldbronn); 2-(5-Bromo-2-pyridylazo)-5-(diethylamino)phenol (Merck), masking and buffering reagents; pH = 7.85; no extraction separation; absorbance at 578 nm against reagent blank /1/; calibration curve;
- SWP: AUTOLAB (Ecochemie, Utrecht) and 663 VA stand (Metrohm, Herisau); HMDE; pH adjusted to 1.8 - 2.0 by HNO_3 addition; peak at about -0.15 V corresponding to U(VI)/U(V) reduction; twofold standard addition; repeated determinations;
- ICP-MS: ELAN 5000 (Perkin Elmer, Überlingen) with Ar plasma and quadrupol mass spectrometer.

The samples were original seepage waters from a number of rock piles of the Schlema region as well as waters from mining pits. In order to maintain their speciation, the waters were collected in polyethylene containers without acidification, which is normally applied for sample preservation. Most of the samples have characterised by a neutral pH, high conductivities and high sulphate and arsenic concentrations, in addition to their radioactive constituents.

Figure 1 gives a survey of the uranium concentrations in mining waters as determined by GS, SP, SWP and ICP-MS. The data vary within one order of magnitude. The different techniques have resulted in a principal agreement and they all appear to be

appropriate for determining total uranium concentrations in the lower ppm range. However, GS needs a considerably greater expenditure of time, whereas ICP-MS, which is originally designed for determining lower trace contents, is the most expensive of the techniques used.

The discrepancies in the results may point to systematic deviations that are superimposed to the random errors. Gamma-spectrometry gave the highest concentrations. This might be due to imperfections in the calibration or, contrarily, to incomplete coverage of the total uranium in the case of the other techniques (wall adsorption effects in the vessels?).

Fig. 1: Plot of uranium concentrations in mining waters of different origin as determined by means of various techniques

For SP and SWP, the dissolved uranium(VI) must be analytically accessible. In the original seepage water, uranium is bound in a complex, as indicated by polarography. However, the quantification failed, because the "chemical" conditions in the solution were not stable on adding the uranium standard having a high acidity. Calculations based on thermo-dynamic equilibrium data /2/ and inputs of the concentrations of total sulphate and TIC, suggested that the presence of carbonato complexes must be expected for the region near pH = 8 (Fig. 2). It should be noted that gaseous CO_2 was disregarded in the carbonate balance. Independently of this detail, for pH < 4 the calculations pointed to the predomi-nance of uranyl sulphate. Obviously, this does not disturb the polarographic determination.

Fig. 2: Distribution of uranium(VI) species as calculated for complexation by hydroxide, carbonate and sulphate ions
total concentrations (in mol dm⁻³): U(VI) 5E-6, CO₃ 3E-3, SO₄ 2E-2

Some additional data of the measurements shall be reported in order to illustrate the reliability of the methods. The uncertainty of the data obtained by GS and ICP-MS is about 5 - 10%. With SWP, the correlation coefficient calculated for the standard addition procedure (peak current vs. cell concentration of analyte) was better than 0.999 as a rule. Hence, random errors have a low influence in dosage. The duplicate SWP measurements showed relative ranges $\Delta c_i/c$ with the median at 8.6%. $\Delta c_i/c$

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increased up to 24% determined at the lowest concentrations of ca. 0.5 mg dm^{-3}. This is due to the higher degree of scattering in the current signal, which could not be compensated for by smoothing the polarograms in the case of peak currents <10 nA. An improvement can be expected using cathodic adsorptive stripping voltammetry, which has a higher sensitity.

In the spectrophotometric measurements, the molar absorption coefficient was averaged to 7.2 * 10^4 dm^3 cm^{-1} mol^{-1} in agreement with the literature /3/.

Acknowledgements

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DISTRIBUTION OF STABLE ISOTOPES OF HYDROGEN, CARBON, AND OXYGEN IN URANIUM-MINING ROCK PILE MATERIAL AND IN SEEPAGE LIQUID

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The distribution of the stable isotopes of the natural elements undergo changes within thermodynamic equilibria (chemical equilibria, phase transformations), but also in reactions governed by different kinetics of the reacting species. These effects are of growing importance with decreasing atomic weight and temperature /1/.

This work examines the downward transport of water through mining rock piles which contain carbonate minerals /2/. The isotopic compositions of hydrogen, carbon and oxygen were measured in the solid and liquid phases, respectively, selecting an appropriate rock sample of the pile no. 66 and seepage liquid from the rock pile base. The latter was found to contain bicarbonate (2 mmol dm^{-3}) and sulphate (20 mmol dm^{-3}).

The isotopic compositions of hydrogen, carbon, and oxygen are compiled in Table 1. They are reported in the δ-notation according to the international standards PDB (Peedee Belemnite) and SMOW (Standard Mean Ocean Water). The errors due to sample preparation and mass spectrometry amount to ±2‰ (H), ±0.2‰ (C) and ±0.4‰ (O).

Table 1: Results of Isotopic Measurements (in ‰)

Water of seepage liquid	δD = -66.2	$\delta^{18}O$ = -9.1
Carbonate contained in the rock	$\delta^{13}C$ = -5.1	$\delta^{18}O$ = +19.2
Total inorganic carbon (TIC) contained in the seepage liquid	$\delta^{13}C$ = -5.9	$\delta^{18}O$ = +20.0

The values of δD and $\delta^{18}O$ for H_2O follow the relationship $\delta D = 8 * \delta^{18}O + 10‰$ /3/ within the experimental error. That means this water is of meteoric origin (The term "meteoric" applies to water that was recently involved in atmospheric circulation). The O-18 content was found to be slightly higher than the mean value for rainwater in the Erzgebirge region (-10.2‰). This fact may point to evaporation effects occurring on the surface of the rock pile.

The C-13 and O-18 variations in carbonate minerals are dependent on their specific way of generation and metamorphic alteration. The carbonate of the rock under investigation should be of inorganic-metamorphic origin corresponding to the petrographic findings /2/. Moreover, the findings are in good agreement with former investigations on calcites and dolomites of the Schneeberg district /4/.

The TIC of the seepage liquid may be the result of the following reaction:

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca^{2+} + 2\,HCO_3^- \tag{1}$$
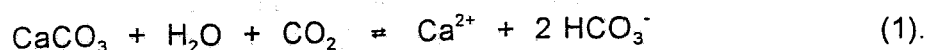
Frequent $\delta^{13}C$ values for TIC in ground waters are in the range of about -15‰ due to the contribution of isotopically light soil CO_2 ($\approx$ -25‰) generated by degradation of organic matter in the soil. The distinctly more positive value (Table 1) reflects another source of CO_2. The first possibility to be considered is atmospheric CO_2 ($\approx$ -7‰). Another source may be the carbonate of the rock pile reacting with sulphuric acid which in turn is produced from atmospheric SO_2 or from sulphide minerals deposited:

$$2\,CaCO_3 + H_2SO_4 \rightleftharpoons 2\,Ca^{2+} + 2\,HCO_3^- + SO_4^{2-} \tag{2}$$
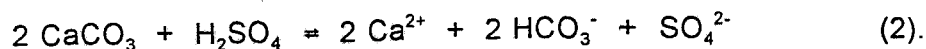
Concerning the $\delta^{18}O$ values, an equilibrium between meteoric water and the disseminated carbonates in paleocoic rocks cannot be assumed. However, the oxygen of TIC and of the water in the seepage liquid will have equilibrated. Based on the experimental values and, hence, $\Delta\delta(HCO_3^- - H_2O) = (29.1\pm0.8)$‰, equation (3)

$$10^3 \ln\alpha(HCO_3^- - H_2O) = (2.92\pm0.07)*10^6\,T^{-2} - (2.66\pm0.18) \tag{3}$$

gives a range for the equilibrium temperature of (295 - 312) K. This seems too high for a surface process in nature. A possible explanation is an experimental imperfection during the treatment of the liquid sample, where mixing with water-free phosphoric acid may have caused a rise in temperature.

Summarising, it can be concluded from chemical and isotopic data that the seepage liquid penetrated through the interior of the rockpile. The TIC content and its isotopic composition indicate a partial dissolution of the carbonates contained in the rock pile, with sulphuric acid being involved.

Further isotopic distribution measurements are planned concerning the origin of the sulphate content of the seepage. Measurements of residence times of water were performed also in field using non-sorbing radionuclides /6/ or fluorescein salts /7/.

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BATCH-TESTING WITH INTEGRATED ANALYSIS

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Within the present investigations of the ecological impacts caused by the former uranium-mining activities in western Saxony, it is of interest to study different aspects of the migration of harmful elements from the numerous rockpiles. In a first contribution to this subject /1/ an apparatus has been presented that allows for the combination of retention experiments performed as batch-testing, and electroanalysis. Preliminary results have been reported as an illustration.

This contribution presents a more comprehensive overview using the systems granodiorite/Pb(II) (abbr. gr/Pb) and, for a less part, rockpile material/U(VI) (abbr. ro/U). The retention experiments were divided in loading and elution sections (abbr. lo and el, resp.).
Loading started under the following conditions:
- $c_{lo,0}$ = 100 - 1 mg Pb dm^{-3}, pH$_{lo,0}$ = 4 (or 2) in unbuffered 0.05 M KNO$_3$ medium and two sorts of buffer solutions, respectively, volume-to-mass ratio 50 cm^3 : 3.33 g and
- $c_{lo,0}$ = 10 mg U dm^{-3}, pH$_{lo,0}$ = 2, unbuffered, 30 cm^3 : 3 g.
Elution was done using
- nitrate solution, pH$_{el,0}$ = 2 (or 4) in the case of Pb-loaded granodiorite and
- 0.1 M HNO$_3$ for original rockpile material.
Electroanalysis involved pH measurements and fast square-wave voltammetric scans for t > 0.5 min.
The distribution ratios were calculated according to eqs. (1) and (2), whereas the percentages of loading and elution were defined by eqs. (3) and (4).

$$R_{d,lo} = \left(\frac{c_{lo,0}}{c_{lo}} - 1 \right) \frac{V}{m} \quad (1) \qquad R_{d,el} = \left(\frac{c_{lo,0} - c_{lo,end}}{c_{el}} - 1 \right) \frac{V}{m} \quad (2)$$

$$P_{lo} = 1 - \frac{c_{lo}}{c_{lo,0}} \quad (3) \qquad P_{el} = \frac{c_{el}}{(c_{lo,0} - c_{lo,end})} \quad (4)$$

The in situ measurements during the experiments gave the following results and conclusions for both the retention and speciation processes:
- The pH was found to undergo a distinct rise in unbuffered systems. Its speed increased with increasing starting pH, with decreasing starting metal ion concentrations (e.g.: gr without Pb^{2+}: pH = 4 → ca. 9!) and with decreasing grain size of the solid. Moreover, the use of rock pile material gave a faster pH rise than that of granodiorite.
According to the literature /2,3/ the pH changes may be caused by
i) competitive reactions of surface (S-OH) protonation and formation of surface complexes

$$\text{S-OH} + \text{H}_3\text{O}_{aq}^+ \rightleftharpoons \text{S-OH}_2^+ + \text{H}_2\text{O} \quad (5)$$
$$\text{S-OH} + \text{Me}^{2+} \rightleftharpoons \text{S-OMe}^+ + \text{H}^+ \quad (6)$$

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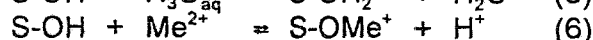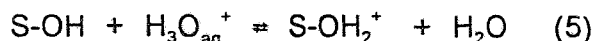
ii) competitive ion exchange reactions involving alkali and alkaline earth cations loosely bound in interlayers of certain silicate structures,

iii) proton-assisted transformation of silicates, e.g. biotite, and

iv) decomposition of carbonates, e.g. calcite or dolomite, in the case of rockpile material.

- The actual height of the pH_{lo} has enormous consequences for both speciation of the metal components and their fixation to the rock material.

- With increasing pH_{lo} the voltammetric curves showed at first that the peaks decreased for the Pb^{2+}/Pb^0 and UO_2^{2+}/UO_2^+ reductions. Besides, the curves revealed the occurrence of new peaks shifted cathodically (ΔE_p). This points to the formation of complex species. It is assumed that other than hydroxo complexes will be present, as the simulation of the processes using NaOH addition did not give identical peak patterns. Calculations based on thermodynamic equilibrium data /4/ suggest the formation of carbonato complexes for the systems with rockpile material.

- The distribution ratios of loading were found to grow with time and with rising pH_{lo}. Figure 1 shows the findings for
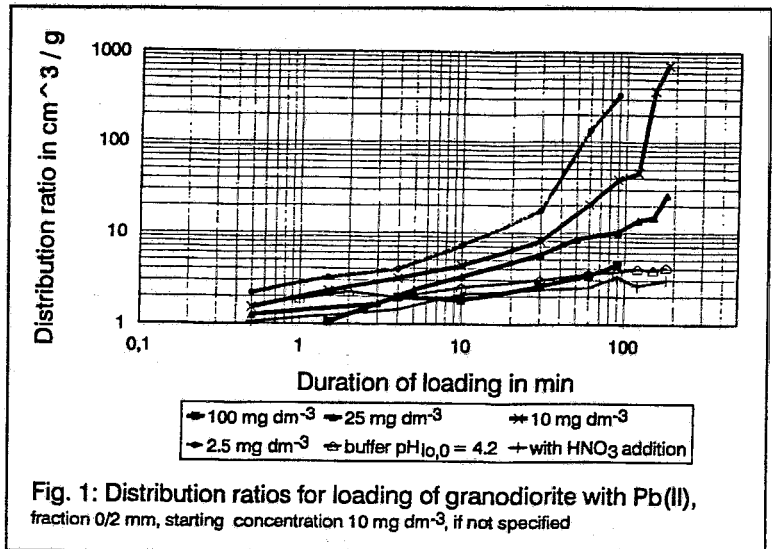
Fig. 1: Distribution ratios for loading of granodiorite with Pb(II), fraction 0/2 mm, starting concentration 10 mg dm⁻³, if not specified

Fig. 2: pH dependences of the percentages of loading for the systems granodiorite (0/2 mm) / Pb(II) and rockpile material / U(VI) (start. concn. 10 mg dm⁻³)

the gr/Pb system. Maximum R_d values are in the order of 10^3 cm³ g⁻¹. When the acidity was kept constant at pH_{lo} = 4 and 2, only weak fixation or no noticeable loading effects were observed, respectively.

For the ro/U system, the distribution ratios were in the range 50 - 100 cm³ g⁻¹ even after one day. The relation between both metals confirms the findings of Bode /5/ obtained on triassic rocks from the Asse region.

The fixation is characterised by system-specific groups of curves, as is shown in

Figure 2. This means, the fixation of U(VI) to rockpile material occurs at significantly lower pH than that of Pb(II) to granodiorite, although the fixation was found to be less complete for the ro/U system. This may be caused by carbonato complexation.

- Linear log R_d - log t plots at constant pH indicate that the kinetics of fixation and release appeared to be uniform for the time studied.

- In view of remediation efforts, the fixation of metal species to rock materials cannot be regarded as being irreversible, but is considered to be labile, as this process can be reversed depending on the actual pH. Rain water in the upper Erzgebirge was found to have an acidity in the range pH = 4.2 - 4.5 /6/. Thus it may affect the fixation even of uranium.

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SYNTHETIC HUMIC ACIDS FOR STUDIES OF METAL COMPLEXING BEHAVIOUR

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Humic acids, the alkali soluble share of natural humic substances, are polyelectrolytical biopolymers. Under different conditions humic acids gives chemical reactions, especially with metal ions under formation of complex compounds. However, the chemical structures of humic acids are further unknown and never will be totally clear, because their origin and the conditions of formation in nature never are the same. Varying nature of organic precursors, different physical conditions in formation processes of humic substances and accidental presence of xenobiotics leads inevitable to changeable humic acids with different properties. The unknown relationships of macromolecular structure of natural humic acids hampers the reliability of results from interaction studies between humic acids and metal ions. Therefore interpretations of results are often unsatisfactory, because different results of similar experiments are often interpreted as experimental error.
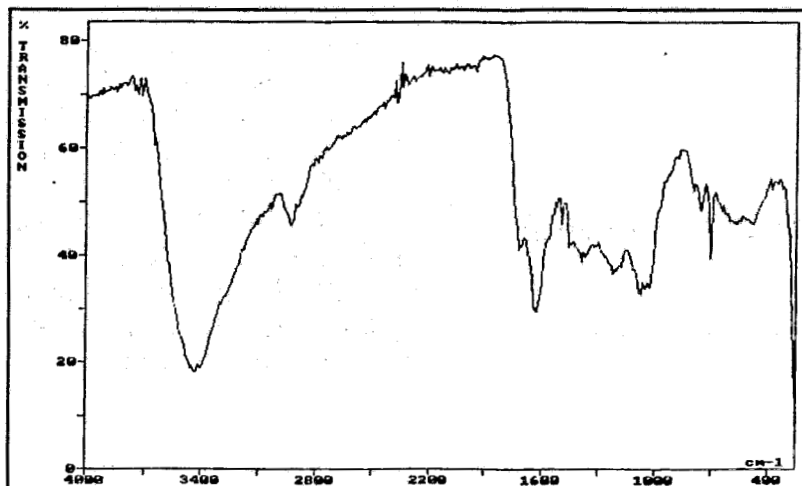
We have synthesized model humic acids by condensation of reducing sugars and amino acids /1/ and a following dialysis step. The synthetically produced humic acids have a more defined structure and better pronounced characteristic features, than natural humic acids, e.g., extracted from soils or brown coals.

Fig. 1: IR-spectrum of a synthetic humic acid from glucose and phenylalanine (above), in comparsion with purified FLUKA-humic acid (below).

In addition, the light accessibility of the simple precursors as carbon 14-labelled compounds is excellent for synthesis of labelled humic acids. C-14

labelled humic acids are very useful for studying their complexation behavior for heavy metals.

More details for the preparation of "artifical" humic acids will be published soon /2/. The prepared, non-labelled humic acids have been characterized by IR-spectroscopy and capillary electrophoresis; investigations with other methods are in preparation. However, all synthesized humic acids shows differences when compared to the natural humic acids. Figure 1 shows the IR-spectrum of the humic acid, prepared from glucose and phenylalanine, in comparsion with the IR-spectrum of a natural humic acid from brown coal (FLUKA), purified by repeated precipitations with hydrochloric acid /3/. The well-known characteristic bands of humic acids /4, 5, 6/ are also present in the IR-spectra of the synthetic humic acid, e.g., the bands in the regions of 3400 cm^{-1} (H-bonded -OH); 1720 cm^{-1}, 1210 cm^{-1} (carboxylic acid groups); 1050 cm^{-1} (C-O-streching); 1650 - 1670 cm^{-1} (N-H-streching, C=C, C=O); 2920 and 2860 cm^{-1} (aliphatic C-H-absorption); and 1020 - 1050 cm^{-1} (C-O of alcohols and carbohydrates).
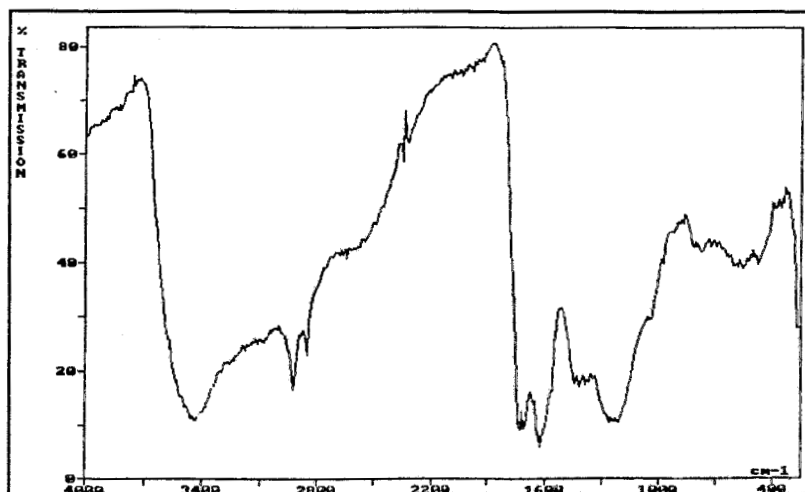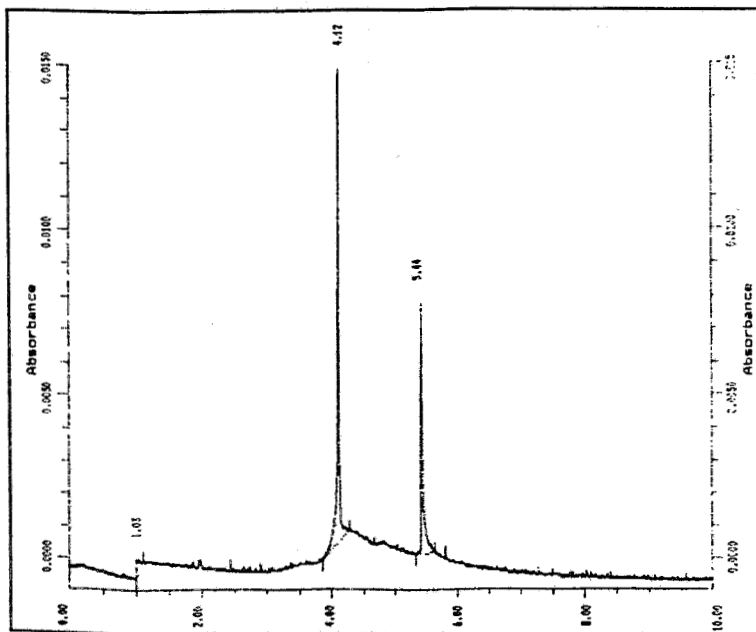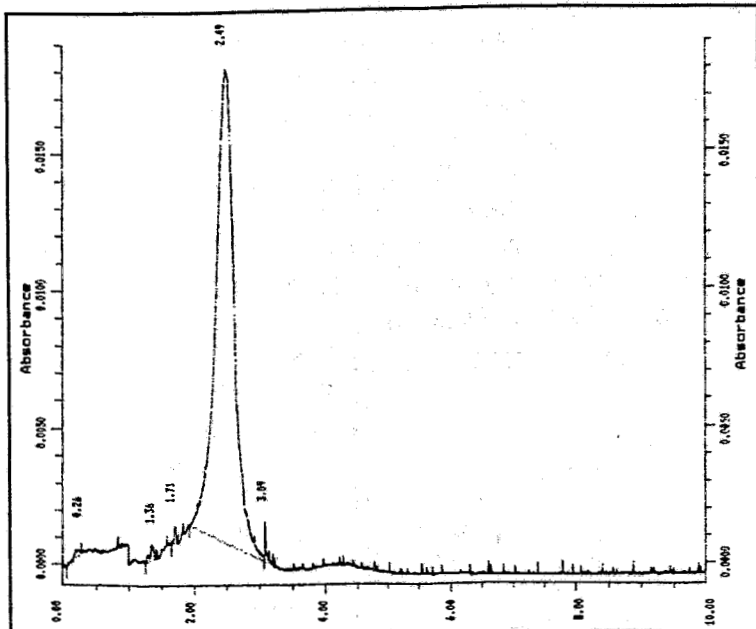

Fig. 2: Capillar-Electropherogram of a synthetic humic acid from glucose and phenylalanine (above) in comparsion with purified FLUKA-humic acid (below).

The conditions of electrophoresis with the BECKMAN P/ACE System 2050:
Buffer: KH_2PO_4-$Na_2B_4O_7$, pH = 8,57;
Capillary: fused silica 0,75 µm i.d, length 47 cm (eff. 40 cm);
Power: 30 KV;
Temperature 30° C ;
UV-detection: 214 nm

The synthetically produced humic acid from glucose and phenylalanine has additionally aromatic bands at 700 cm^{-1} and 755 cm^{-1}. This difference, and also the observed differences in intensities of some bands, are due to the chemical properties of the precursors of the synthesized humic acids.

The behaviour of the synthetic humic acids in capillary electro-phoresis is comparable with the behaviour of natural humic acids. The capillary electrophoresis demonstrated the differences of molecule size and with them the differences of charge between synthesized and natural humic acid.

Figure 2 shows the electropherogram of the humic acid from glucose and phenylalanine in comparision with the electropherogram of the purified FLUKA humic acid. The natural humic acid from FLUKA has two separate noticable sharp peaks, rising from a broad background peak. A specific feature for the synthesized humic acid is one relatively broad peak, and a second background peak in the position of the naturally humic acid. It is to assume, that the synthesized humic acid has a relatively wide size distribution of molecules, whereas the purified FLUKA humic acid has mainly two fractions of sizes close together. This thesis is supported by thermoanalytical investigations /7/. An other expected result of these investigations is, that the synthetic humic acid probably consist of smaller molecules than the natural acids. It is recognizable by the significant shorter migration time during the electrophoresis experiments. Further investigations are currently being performed.

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CHARACTERIZATION OF HUMIC ACIDS

I. ISOLATION OF HUMIC ACIDS FROM SOILS AND OTHER NATURAL MATERIALS

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The literature of the last twenty years shows the importance of humic substances on the migration and retardation behaviour of heavy metals and other xenobiotics. Our research is directed toward finding answers to the following questions:

- to what extend does the complexation ability of humic acids depend on their shape, especially their form , number and position of functional groups,
- how do other factors influence the system, such as pH, salt concentration or presence of other organics, the complexing behaviour of humic acids.

Experiments with isolated or specially modified humic acids are helpful in solving these questions.

Due to the diversity and changeability of humic acids it is impossible up to now to verify, that the chemical and physical properties of isolated humic acid fully represent the characteristics of natural humic systems. The isolation process may have altered important characteristics.

Knowledge about these changes of the elemental composition and structure and the nature and number of functional groups can be obtained by multiple repetition of the isolation procedure and subsequent comparison of the results of the individual chemical and physico-chemical analyses.

Humic acid from FLUKA and a podsol from district Rosenthal - Halle have been used for such a comparision.

The pre-treatment of the soil matter included the following steps: drying at 70 and 105°C, crushing and screening in sieve fractions from 2 to 0,063 mm. The soil pre-treated was kept in a refrigerator at 6 to 10°C. Equivalents of the appropriate sieve fractions were recombined for the extraction procedure described below.

The isolation of humic acids was carried out by two different methods: extraction with alkaline solution and extraction with organic solvents. All extractions were carried out under inert-gas atmosphere or in vacuum,respectively, to avoid uncontrolled oxidation reactions.

The isolation of humic acids from soil material involves the following steps: extraction of cationic impurities with 2% HCl and subsequent lyophilization; extraction of humic acids with 2M NaOH; precipitation of humic acids with 2M HCl; dissolution in 2,5% Na_2CO_3; precipitation with 2M HCl; dialysis against distilled water and lyophilization. The extraction and precipitation steps have been repeated up to 3 times with the objective to obtain knowledge about the chemical and physical changes of the humic acid molecule structure during the isolation process.

The isolation of humic acids from the soil material by organic solubilizers involves the following steps: extraction of cationic impurities with 2% HCl and following

lyophilization; extraction of humic acid precursors and other organic substances with the solvent sequence ether, benzene, acetone, ethanole, and dioxane; extraction of humic acid with dimethylformamide and pyridine; lyophilization of the dimethylform-amide extract; dialysis against distilled water and lyophilization of the humic acid suspension (133 Pa, 20°C). Table 1 shows the results of the elemental analyses of humic acids produced by the above described isolation methods.

Tab. 1: Results of the elemental analysis of isolated humic acids

No.	origin and pretreatment of humic acid	C	H	N	S	O
1	orig. FLUKA humic acid /1-1093 dried in vakuum (133Pa, 20°C)	48,0	3,8	0,6	1,4	46,2
2	FLUKA humic acid, alkal. extr., dialyzis	55,7	3,4	0,8	2,0	38,1
3	FLUKA humic acid, alkal. extr., dialyzis	56,0	3,6	0,8	2,0	37,6
4	FLUKA humic acid, 2x alkal. extr., dialyzis	56,5	3,8	0,8	2,0	36,9
5	FLUKA humic acid, 3x alkal. extr., dialyzis	58,8	3,8	0,9	1,7	34,7
6	FLUKA humic acid, DMF extr., dialyzis	53,7	4,9	2,5	1,7	37,2
7	humic acid, alkal. extr. from podsol, dialyzis	52,15	5,3	2,7	0,35	39,5

The increasing carbon content during multiple repetition of the alkaline isolation procedure for humic acids indicated a decrease of oxygen-containing functional groups (No.1 to 5). Higher nitrogen content of the humic acid produced by dimethylform-amide extraction (No.6) shows evident the fitting of nitrogen containing groups from the solvent into the humic acid matrix.

Summarizing can be stated: Humic acids isolated from natural material under well-defined reaction conditions by alkaline extraction are representative and may be used as models in chemical and physical experiments, if the decrease of oxygen containing functional groups can be tolerated or taken into the consideration.
Humic acids isolated by extraction with organic solvents seems to be less suitable in model experiments. Fitting of reactive groups from the solvents as acetone, dioxane, dimethylformamide and pyridine in the humic acid matrix can not be excluded.

CHARACTERIZATION OF HUMIC ACIDS

II. CHARACTERIZATION BY RADIOREAGENT - DERIVATIZATION WITH [^{14}C]DIAZOMETHANE

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The derivatization of humic acids with IR and NMR spectroscopy is a well-established method for characterization and determination of functional groups /1/. Classification of humic acids may be achieved by comparison of the type and number of functional groups.

Using [^{14}C]diazomethane it is possible to introduce [^{14}C]methyl groups in the humic acid molecule by transforming -COOH to -COO^{14}CH$_3$ and phenolic -OH to -O^{14}CH$_3$. If [^{14}C]diazomethane of a known specific radioactivity is used, it is possible very precisely to determine the number of methylated groups in the humic acid molecule by measuring the specific activity of the reaction product. Therefore the precision of the result depends only on the accuracy of radioactivity measurement. The condition of the methylation reaction can carried out reproducibly.

The determination and the differentiation between -COOH and phenolic -OH groups is based on the hydrolysis of carboxylic esters and the resistance of phenolic ethers against alkali.

The derivatization of humic acids with diazomethane or ^{14}C-labelling one respectively and following hydrolysis of the carboxylic esters may be used also for modification of humic acids, that means for blocking the phenolic -OH or its ^{14}C-labelling. But the simultaneous hydrolysis of original esters in the humic acid molecule can occur also. After the hydrolysis reaction, a higher number of carboxylic groups in the humic acid molecule must be expected.

Using the ^{14}C-methylation method the increase of carboxylic groups corresponding to the original ester groups may be calculated. Fig. 1 shows these connections.

Using [^{14}C]diazomethane of known specific radioactivity the following results concerning the number of functionally groups in humic acids were obtained:

- the spec. radioactivity of <u>2</u> is representative for the total amount of groups suitable for methylating with diazomethane,
- the specific radioactivity of <u>3</u> is representative for phenolic -OH groups,
- the difference of specific radioactivity between <u>2</u> und <u>3</u> is representative for free COOH-groups,
- the spec. radioactivity of <u>6</u> is representative for the total amount of carboxylic components in the humic acid molecule (esters and free carboxylic groups),
- the difference in spec. radioactivity between <u>6</u> and the calculated one for <u>X</u> gives the content of originally ester groups at <u>1</u> in the humic acid molecule.

Uncertainities in the preparation of chemically variable macromolecules such as humic acids arise from the unapproachability of sterically hindered functional groups and the insolubility of these substances in organic solvents, and from chemical changes during the long reaction times of alkaline hydrolysis at higher temperatures.

Although the experimentally achieved and calculated results of the determination of functional groups with [^{14}C]diazomethane not can be considered as absolute, it is possible to distinguish humic acids of different origin from each other. The results of the experimental work are well reproducible (Tab.1).

Fig. 1 Derivatization of humic acids with [^{14}C]diazomethane
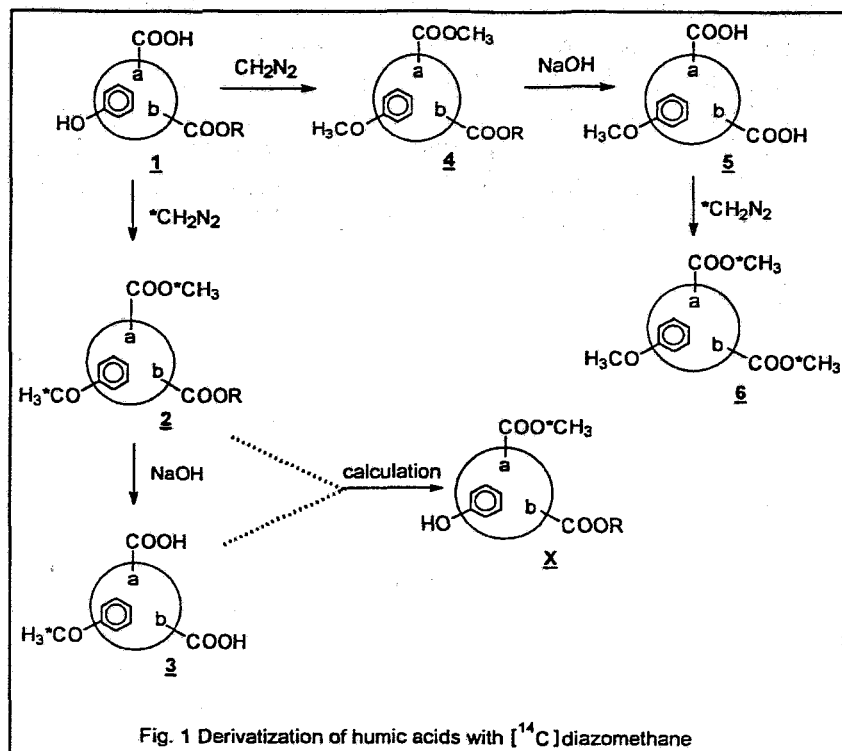
Tab. 1 Derivatization of humic acids with [^{14}C]diazomethane.

No.	origin and pretreatment of humic acid	fitted [^{14}C]methyl-groups [mmol/g]	
1	FLUKA humic acid, original	4,7	
2	FLUKA humic acid, alk. extr., dialyzed, 8 h methylated	8,1	
3	the same as 2, but 2,5 h methylated		7,8
4	the same as 2, but 1 h methylated	7,7	
5	ICN humic acid, original		5,1
6	podsol, alkal. extr., dialyzed	5,2	
7	podsol, DMF extr., dialyzed	7,3	
8	copolymerisat from podsol-humic and acid-hydrochinone		6,9
9	synthetic humic acid from glycine - glucose		5,6
10	synthetic humic acid from phenylalanine - glucose	4,3	

In the experiments [^{14}C]diazomethane (spec. activity 5 - 10 kBq/mmol) has been generated from commercially [N-^{14}CH$_3$]diazald or from synthesised nitroso-[^{14}C]methyl-urea using especially modified vacuum equipment /2/. The same device was used for the preparation of unmodified diazomethane and for the methylation procedure.
Humic acids or other humic materials have been pretreated by dispersion in distilled water and subsequent lyophilization. The methylation reaction was done in methanol

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suspension with refluxing diazomethane at temperatures below 10°C under inert gas atmosphere and slight reduced pressure.

Ester hydrolysis was carried out using 1M NaOH at 40 to 50°C under vacuum. Modified humic acids were precipitated with 1M HCl and dialyzed.

Specific radioactivity of humic substances was determined by liquid scintillation counting (Beckman mod. 6000 LL) after combustion of the substances with a sample oxidizer (Canberra-Packard mod. P 307)

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THERMOANALYTICAL INVESTIGATIONS ON HUMIC COMPOUNDS

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The humic compounds like humic- and fulvic acid and lignin, contained in the groundwater of uranium mining plants, are able to form soluble complexes with radionuclides of the decay series of uranium. Therefore they are to consider in the formulation of models for the restoration of uranium mining plants and its environment. The humic compounds are characterized by an enormous structural variety. Eliminating the troubles caused by this fact it is usual in the present work in this field to assume a principial similar complex formation mechanism for all the different species by the carboxylic groups without attention to the complicated structure of the makromolecules [1]. I is impossible up to now, to derivate generally relevant models basing on exact thermodynamic data. It is obvious now, that such models are only to get with data, which are determined individually from the humic compounds occuring in each mine. That is the reason why the research on humic compounds has won an appreciable significance in the last years.

Since many years the thermoanalysis is a successfully applicated method for the research on humic compounds [2,3]. It is also a constituent of a actual monograph on the chemistry of humic compounds [4].

For the works on the chemistry on humic compounds in the Institut of Radiochemistry of the Research Center Rossendorf a DTA/TG/DTG device STA 92 from Setaram (France) is used in combination with the carbon - water determinator RC 412 from Leco (USA). With this arrangement are to measure the thermic effects, the mass change and the amounts of carbondioxide and water, which are developed in the oxidation- and pyrolysis reaction in dependence on temperature. The topics of this works are at first qualitative informations about the following facts:
- Identification and comparison of the humic compounds (fingerprints)
- Control of purity
- Detection of chemical and structural changes
- Testing the reproducibility of chemical reactions with the humic compounds
- Search for characteristic thermoanalytical signals for the complex formation

In further works the following quantitativ values are to measure:
- Determination of carbon containing groups according to its reactivity
- Determination of hydrogen, water and structural OH groups from thermoanalytic diagrams
- Determination of the reaction enthalpy and activation energy of the decomposition reaction

This informations should be completed and verified by the combination of these results with those of mass spectrometry, elementary analysis, chemical derivation and marking with radioactive isotopes. With this combination of investigation methods we see a chance to promote the investigations on the solubility and complex formation, sorption behaviour and long term stability, which are the essential basis for the description of the migration behaviour of the complexes of humic compounds with the radionuclides.

Investigations on the Experimental Methods

A. Interpretation of oxidation and thermal destruction curves

The DTA/TG curves shown in Fig. 1 represent the oxidative destruction of the humic acid ICN which is spread over a temperature region from 190 to 730°C. There are sharp peaks at 302 and 710°C. This shape of diagram enables to a differentiated evaluation of the peaks and a coordination to decomposed groups of the molecule.
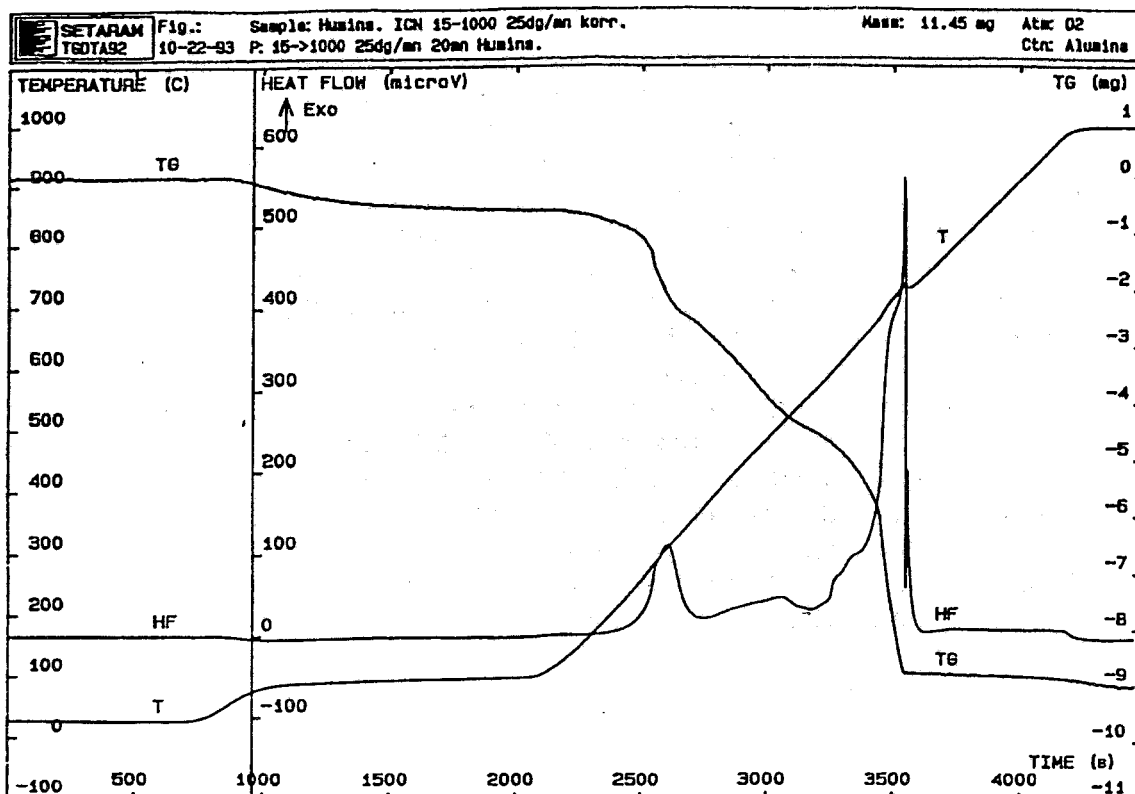
Fig. 1: Thermoanalytical diagram of thermal gravimetry (TG) and differential thermoanalysis (DTA = HF in the diagram) of the humic acid ICN (20°C/min, oxygen)

The reproducibility was proved by two measurements under constant conditions as mass of sample, particle diameter, heating rate, gas flow, material and shape of the crucible. Like to be seen in Fig. 2 the result are prompt congruent curves, demonstrating a high degree of reproducibility.

As mentioned above in the same thermal program the carbon dioxide and water developed in the oxidation process was quantitatively determined a function of temperature. The results are shown in Fig. 3. From these curves it is possible to account the C:H ratios for the single peaks and to get information about the kind of the oxidized groups of the macromolecule (Table 1).
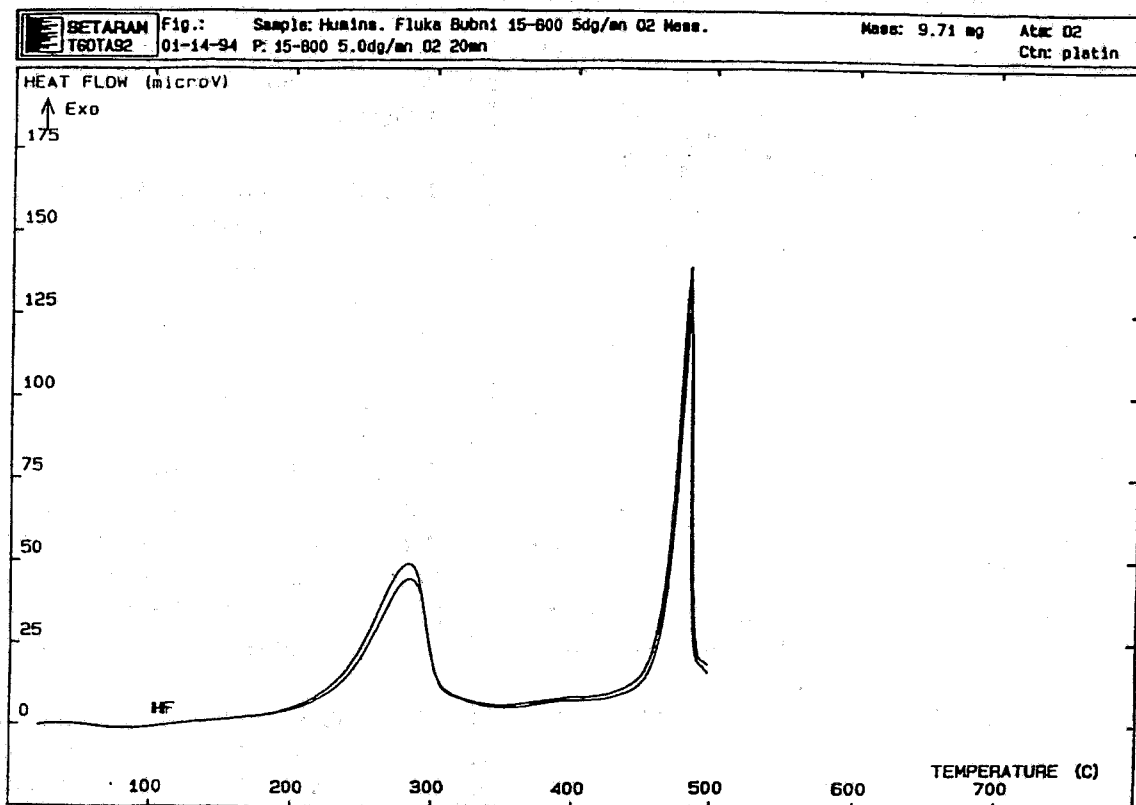
Fig. 2: Test of reproducibility of the thermal analytic measurements (humic acid FLUKA, 5°C/min, oxygen).

$T_p[°C]$	Analysenwerte [M%]		Molzahlen		Molzahlen (C = 1)		Molverh C : H
	C	H	C	H	C	H	
236	0,62	1,20	0,051	1,20	1	23,53	0,043
435	12,8	1,59	1,07	1,59	1	1,49	0,67
559	8,61	1,09	0,72	1,09	1	1,53	0,66
682	41,53	1,87	3,46	1,87	1	0,54	1,85

Tab. 1: Molar ratios C:H derived from the peaks of the oxidation reactions in Fig. 3
CH_3 - Group: C:H = 1:3 = 0,33; COOH - Group: C:H = 1:1 = 1
1 CH_3 - Group + 2 COOH - Group: C:H = 3:5 = 0,6

Fig. 3: CO_2 and H_2O development at the oxidation of humic acid as a function of temperature (25°C/min, oxygen)

This information can be extended by measurements carried out in inert gas atmosphere in the same thermal program (Fig. 4). The comparison of the destruction by oxidation and by thermic dissociation gives further results of the structure of the humic acid.

A possible explanation of the course of the oxidation of the humic acid ICN using this measurements is, that in the first phase up to 235°C moisture was determined and water formed from
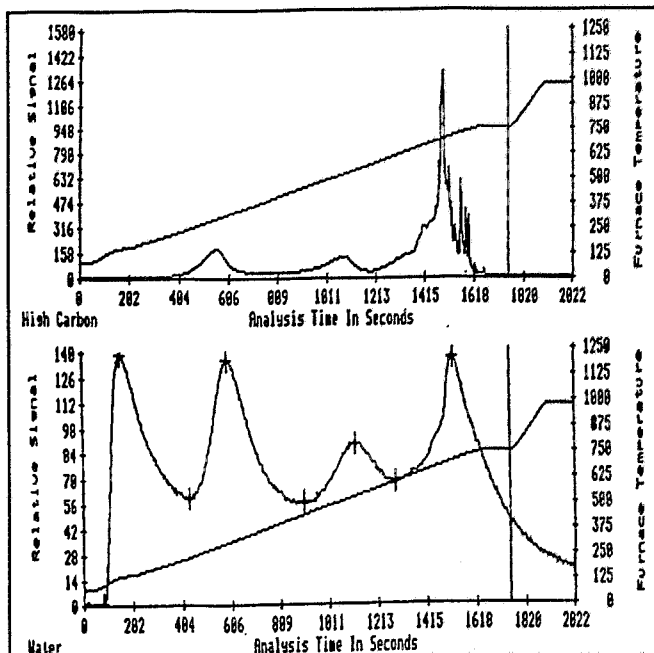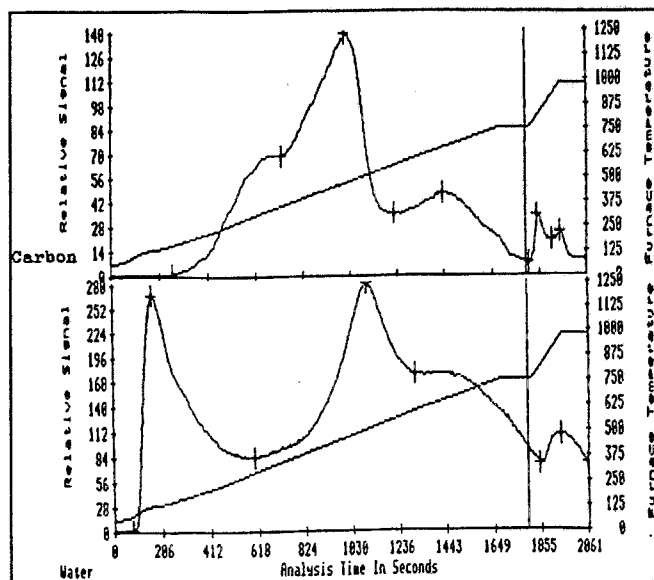

Fig. 4: CO_2 and H_2O development at the dissoziation of the humic acid ICN as a function of temperatur (25°C/min, nitrogen)

aliphatic OH groups. In the second section up to 435°C mainly methyl groups and carboxylic groups react to CO_2 and H_2O. Only at the high temperatures of 560°C the phenolic OH groups and some resistent C-H bondings are oxidized and till 680°C the residual phenolic OH groups and the carbon frame of the polymer. This interpretation is in agreement with infrared spectrometric investigations in the literature [5].

B. Qualitative Identification of Humic Compounds, Fingerprints

In Fig. 5 such an attempt is made on the basis of the oxidation reaction of four substances.. The two humic acids Fluka and ICN are easily recognized as one class of compounds, though individual characteristics are to be mentioned. But the lignin NAD is quite different from them and is surprisingly similar to the humic acid made from peat.

Fig. 5: Comparision of humic compounds according the DTA curves
(sample mass = 15+2mg, heating rate = 2,5°C/min, oxygen, alumina crucible)

In a second run in Fig. 6 the deviations are shown of the curves measured at a sample with which was performed a chemical reaction. The fine structured oxidation dia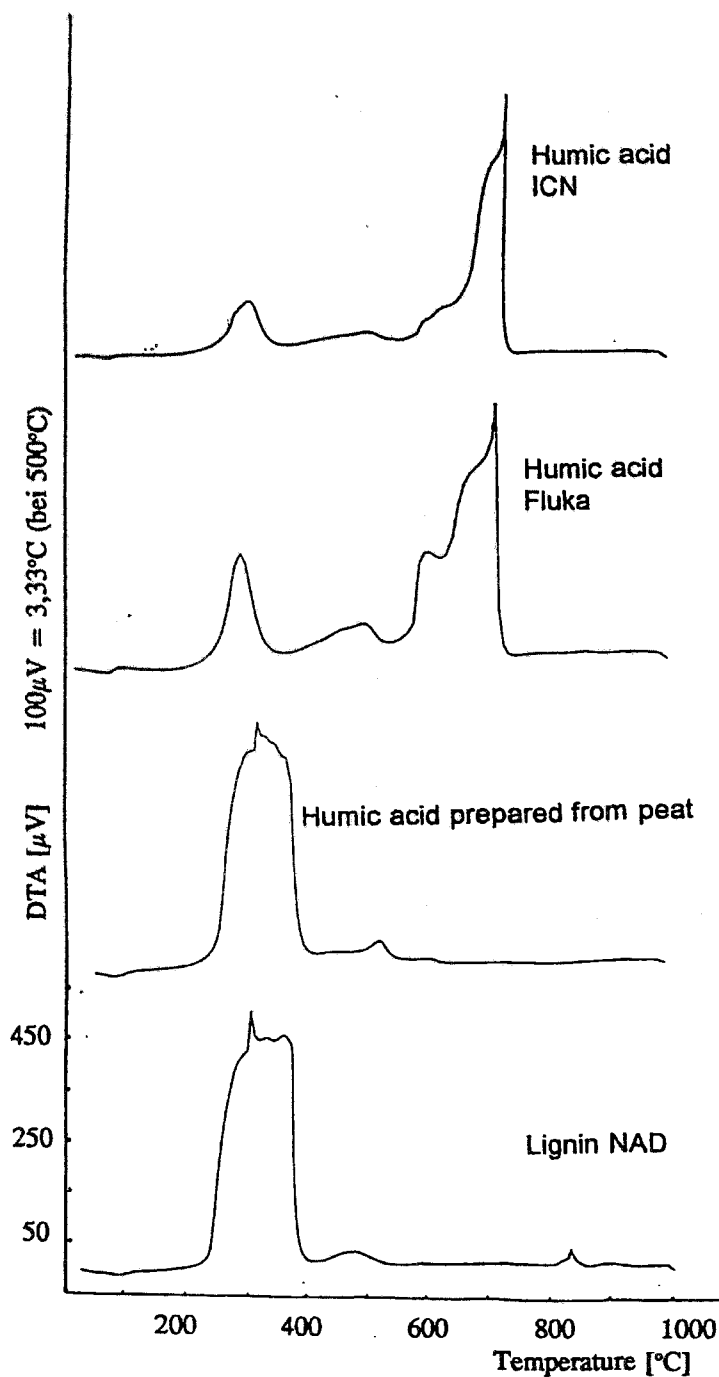gram of the untreated humic acid FLUKA is spread over a wide temperature region. Chemical treatment results in a diagram, which only shows one needle shaped peak. That is the case, if the humic acid is dissolved in sodium hydroxide to the sodium salt and precipitated again with hydrochloric acid. The curves do not change essentially after following dialysis and methylation. This needle shaped peak is typically for a very vigorous oxidation, nearly a detonation. That can be caused by chemical or morphological facts. In the first case, the reaction displaces the relative inactive carbon-rich parts of the macromolecule, which remain in the unsoluble waste. The hydrogen-rich smaller molecules oxidize at much lower temperature and with a high reaction rate. The big reaction enthalpy additionally raises the temperature and accelerates the reaction. In the second case, the enormous reactivity results from the fact, that the precipitation with hydrochloric acid produces a very fine powder with a high specific surface area, that is able to a very fast reaction with oxygen. Which of them is in action must be decided in further investgations. The decrease of the heating rate down to 2.5°C/min did´nt spread the needle sheaped peak, but as a result of this attempt a lot of small

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peaks became visible in the high temperature region of the untreated humic acid Fluka.
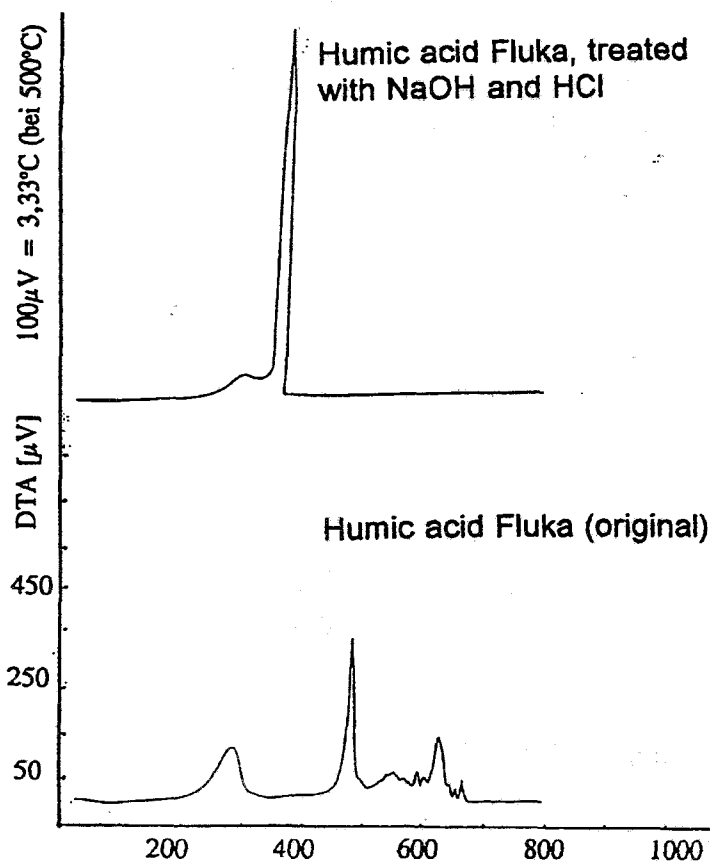
Fig. 6: Comparision of original humic acid FLUKA with a chemical treated one (sample mass: 10+0,05mg, heating rate: 2.5°C/min, Pt crucible)

In summary the investigations on the methodical possibilities have shown, that the Thermal Analysis in combination with the quantitative determination of the reaction products CO_2 and H_2O in a thermal program are sufficient to give reliable informations of the structure, the chemical constitution and the chemical behaviour of the humic compounds.

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A SPECTROPHOTOMETRIC EXAMINATION OF THE INTERACTION OF HUMIC ACID WITH NEODYMIUM

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Complexation of radionuclides and heavy metals in natural water with organic degradation products from the biosphere plays an important role in their mobilization and distribution into the environment. The investigation of these processes, especially an exact identification of the chemical species and their interaction with different geomedia contributes to the adjustment of the models used in risk assessment for areas with heavy impact, e.g. mining and milling facilities, smelteries, waste disposal sites.

In order to look how the strong UV-absorption behaviour of the organic matter can be used for complexation measurements, the influence of free transition metals, in our case Nd (III), on the broad absorption band near its maximum has been studied (Fig.1). The considerable difference in the absorption coefficients between the free humic acid (ICN - Fine Chemicals; H^+ - exchange capacity: 5.62 ± 0.15 meq / g) and the saturated complex, $\varepsilon(HA) = (0.2481 \pm 0.005) * E + 05$ L / Mol * cm and $\varepsilon(NdA) = (0.1652 \pm 0.004) * E + 05$ L / Mol * cm, respectively, and the negligible absorption of the metal ion, enables us to follow the changes in the equilibrium by addition of increasing amounts of Nd (III) (1 - 20 µMol/L) to a constant level of humic acid in the solution (60 µMol / L corresponding to 20 µeq / L tridentate ligand).
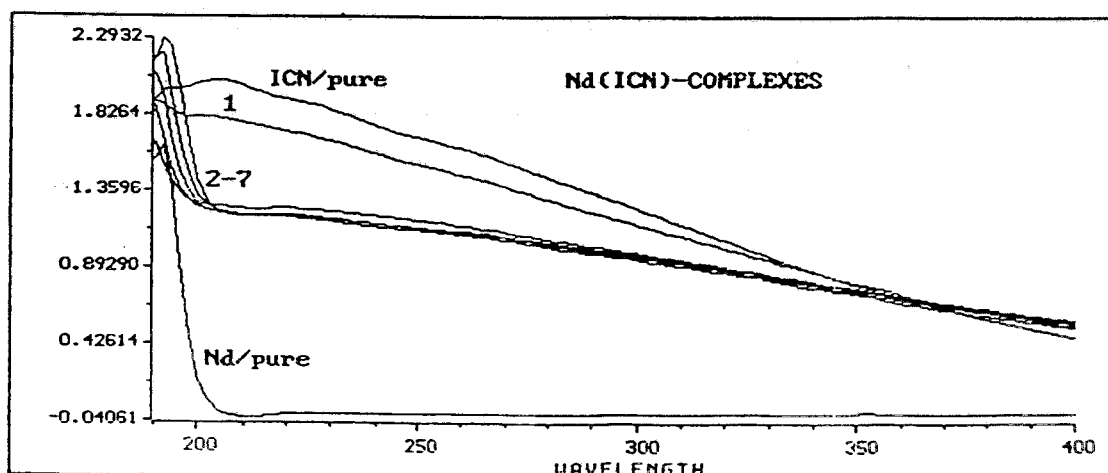
Fig. 1: Changes in the humic acid aborption band by adding Nd (III) in 0.1 M NaCl solution

Starting with $\beta_1 = [NdA] / ([Nd] [HA])$ (Eq.1) and $[HA] = [HA]_0 - [NdA]$ respectively $[Nd] = [Nd]_0 - [NdA]$ the equilibrium's complex concentration was determined from the absorbance $A^* = A / d = \varepsilon (HA) * [HA] + \varepsilon (NdA) * [NdA]$ using $Q = [NdA] = (A^* - \varepsilon (HA) * [HA]_0) / (\varepsilon (NdA) - \varepsilon (HA))$ and the interaction constant could be computed by $\beta_1 = Q / (([Nd]_0 - Q) ([HA]_0 - Q))$.

Nd-Concentration [µMol/L]	Absorbance at 214 nm	Complex Stability $\log \beta_1$ [L/Mol]
0	$(0.4944 \pm 0.008)_{n=6}$	
1.255	0.48606	6.3067
2.51	0.47597	6.3022
5.02	0.45594	6.2921
7.53	0.43609	6.3083
10.04	0.41682	6.2957
12.55	0.39810	6.3067
15.06	0.37929	6.3975
17.57	0.36100	6.5486
20.08	0.33959	7.1587
25.1-100.4	$(0.3304 \pm 0.008)_{n=18}$	

Table 1: Mean Value of Absorbance and Calculated Complex Stability

The mean values of triple measurements at each Nd addition proved to be constant up to 12 µMol / L [Tab.1], with the result $\log \beta_1$ = (6.30 ± 0.06) L / Mol (ionic strength 0.1, NaCl, pH = 6.3 ± 0.3).

The examination of Eq.1 by plotting $\log$ ([NdA] / [Nd]) against $\log$ [HA] reveals a straight line with the slope 0.994 (correlation coefficient 0.960) (Fig. 2), corroborating Kim's assumption /1/ that three functional groups are involved in the complexation of one metal ion. It is remarkable that the maximum Nd amount bound to the humic acid is much lower (only 85%) than the H^+-exchange capacity.

A comparison with recent data, measured in weak acidic media, shows that our result is close to the complex stability of Am (6.39 / 6.44 /1/; 6.27 / 6.36 /2/; 6.4 /3/) and Eu (7.38 /2/; 7.3 - 8 /I=0.01/ /3/), confirming a stronger similarity of Nd than Eu (4f-series) to Am of the actinide series.
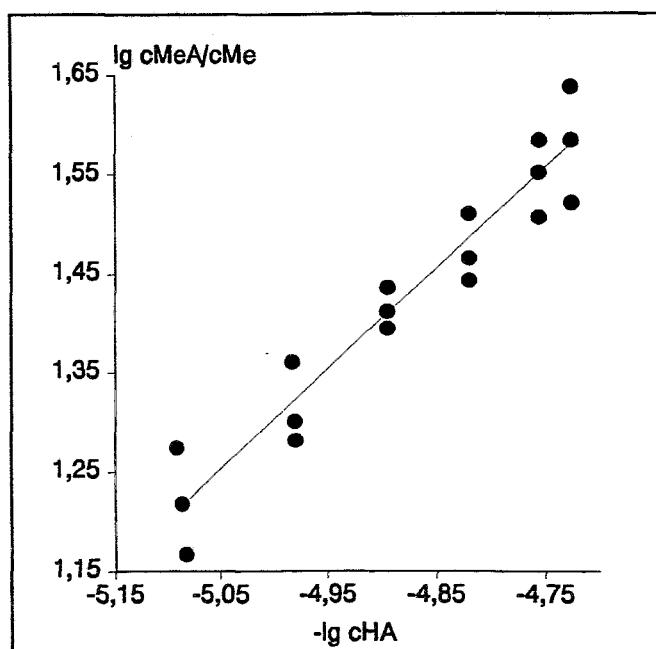
Fig. 2: Plot of log[NdA]/[Nd] against log[HA]

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ANION-CHROMATOGRAPHIC DETERMINATION OF ARSENIC IN ENVIRONMENTAL MEDIA

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Arsenic in the form of arsenite and arsenate in environmental samples as for example natural waters and soils can be determined by HPIC using different stationary phases and eluents.

Beside the well known IC-separation by means of an agglomerated ion-exchange resin (Dionex® IonPac AS-3 column), bicarbonate eluent (pH 9.56) and conductivity detection /1/, mainly ion-pair chromatographic processes on liophilic C_{18}-stationary phases (e.g. LiChrosorb® RP-18 or Waters® µBondapak C_{18}) with methanolic tetraalkylammonium salts solutions as eluents and graphite-furnace AAS detection dominate the determination of arsenic-species, even including dimethylarsinic acid and methylarsonic acid /2/. An example of non-suppressed chromatographic determination using a strongly basic ion-exchange resin with quarternary ammonium functionality (Wescan® Anion/R), alkaline-tartrate eluent and conductivity detection is given in /3/.

To determine the total amount of arsenic in waste water, especially in rock pile seapage water and mine water we used a hp® Anion Chromatography System /4/, consisting of a microparticulate polystyrene divinylbenzene copolymer as column packing and a phthalate buffer (pH 8.6) in water-acetonitrile as eluent which contained a liophilic quarternary ammonium salt for dynamic coating the stationary phase. In the separation arsenate competes with phthalate for the attachment to the ammonium ions on the solid phase. Because of the high UV-absorbance of phthalate the arsenate and all the other anions are detected by negative UV-signals.

For the calibration an arsenate standard was prepared according to /5/ from freshly sublimed As_2O_3 by dissolution in NaOH, oxidation with aqua regia, repeated careful evaporation to dryness with small amounts of concentrated HCl (removal of NO_3^-) and an appropriate dilution with water.

The separations were carried out in a 125x4.0 mm-i.d. column at 40 °C with an eluent flow rate of 1.5 ml/min, and the peaks were detected in the UV- range at 266 nm. The chromatogram (Fig.1) in comparison to the hp® Anion Checkout Sample shows the arsenate to be eluted nearly at the same position as the phosphate. The mean retention time of the arsenate is 5.621±0.055 min in comparison to 1.965, 4.377 and 9.817 min for chloride, nitrate and sulfate, respectively. A simultaneous determination of arsenate and phosphate is impossible due to the only small difference in retention time (5.621/5.499). The factors for the separation of arsenate from chloride, nitrate, phosphate and sulfate amount to 3.619±0.05, 1.327, 1.025 and 0.5468, respectively. The small relative standard deviation of 1.4% is an expression for the high precision of the separations.

Regarding the dependence of the peak height on the concentration, we found a direct proportionality over two orders of magnitude, in the range of 1 - 100 ppm arsenate. A linear regression for about 30 measurements in between 5 and 50 ppm revealed
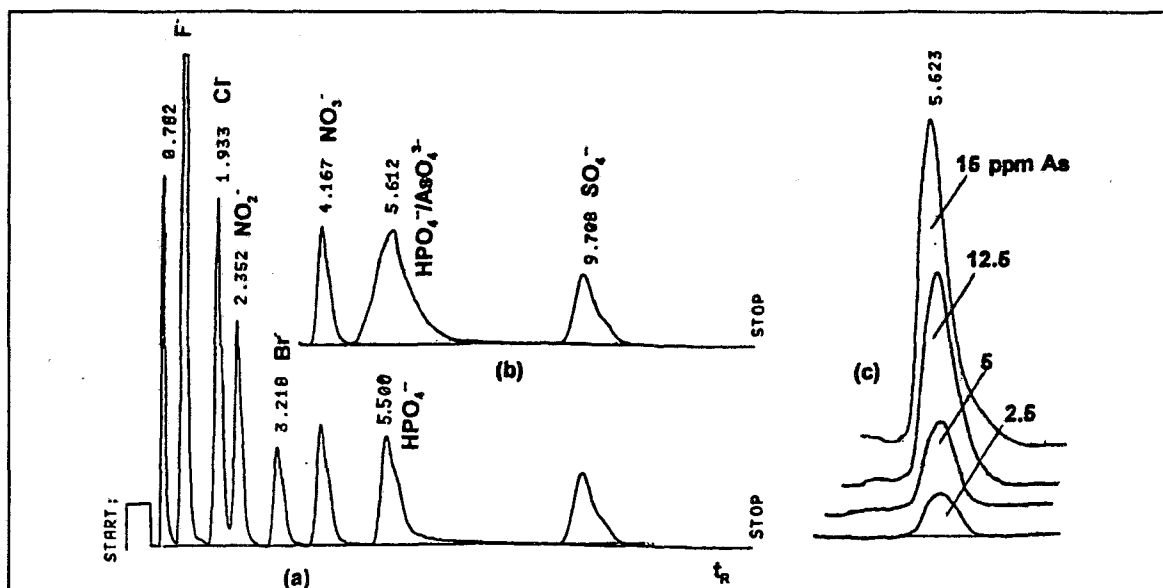
Fig. 1: Separation of chloride, nitrite, bromide, nitrate, phosphate and sulfate
(a) in the absence and (b) in the presence of arsenate as well as
(c) arsenate peak at different concentrations

the relationship c(As) [ppm] = 0.216 H [mm] + 0.296 with a correlation coefficient of
0.9994. The detection limit as the threefold blanc's standard deviation (6 mm) devided
by the sensitivity (34.2 mm/ppm) is 0.18 ppm arsenate. At low concentrations, pre-
cision decreases strongly and we find an increasing overlapping with the rear edge of
the preceding peak caused by trace amounts of nitrate. Arsenate determinations, the-
refore, should not be carried out below 1 ppm by this method.

The total amount of arsenic in original uranium-mine water from western ore mountain
sites was determinened after the above mentioned oxidation treatment. In the pre-
sence of chloride and sulfate as the main constituents as well as some silicate and ni-
trate we found total arsenic contents around 6 ppm with an error of about 4%.

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SYNTHESIS OF SOME ECOLOGICAL RELEVANT CARBON-14 LABELLED PCB CONGENERS

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Polychlorinated biphenyls (PCB´s) had many industrial applications in the past. Since the toxicity of these compounds became known, they were the focus of much public attention. The high chemical inertness of most of all 209 PCB-congeners is one of the reason for their omnipresence in the biosphere today, although in low concentrations. However, via the food chain toxic PCB´s can accumulate in animals and, at least, strains the humans.

Probably the microbiological PCB destruction has the best chances of success for a global application in environmental rehabilitation. But the mechanisms of these biological methods are mostly unknown and it can not be excluded, that in these processes products may be generated of higher toxicity than the original PCB´s. For this reason worldwide efforts are being made to explore the mechanism of microbiological attacks on the PCB´s and to identify the residual products of the PCB destruction.

Fundamental studies on the biological and chemical behaviour of PCB in very complex systems often demand tracer experiments using carbon-14 labelled compounds /1/. Known suitable synthetic procedures to obtain ^{14}C-labelled PCB such as the Gomberg-Hey- and the Ullman reaction permit only labelling of one of the benzene rings in PCB. Fol-lowing tracer studies with such labelled molecules only allow knowledge about the labelled part in the molecule. In this communication we report the synthesis of uniformly labelled PCB´s.

An approach to get such compounds are synthetic pathways starting from [U-^{14}C]benzene and [U-^{14}C]nitrobenzene via [U-^{14}C]benzidine as a key product, shown in Figure 1. A variation of the classic reduction method for [^{14}C]nitrobenzene with zinc in an alkaline medium leads to [U-^{14}C]hydrazobenzene and its immediate transformation to [U-^{14}C]benzidinedihydrochloride with 70% of yield.

The acetylation of [U-^{14}C]benzidine avoiding the isolation of the very radiolytic instable, free [U-^{14}C]benzidine base in a sodiumacetate buffer leads to N,N´-diacetylbenzidine and N-mono-acetylbenzidine respectively (fig. 2 and 3). The first compound is obtained by acylation of [U-^{14}C]benzidine with acetic anhydride
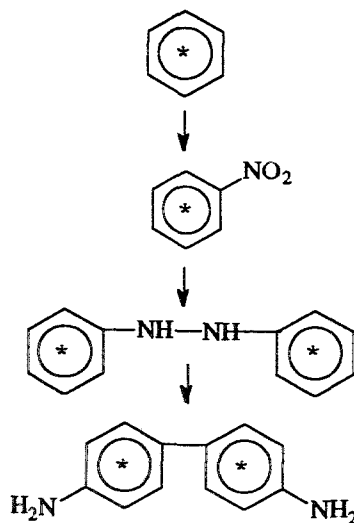

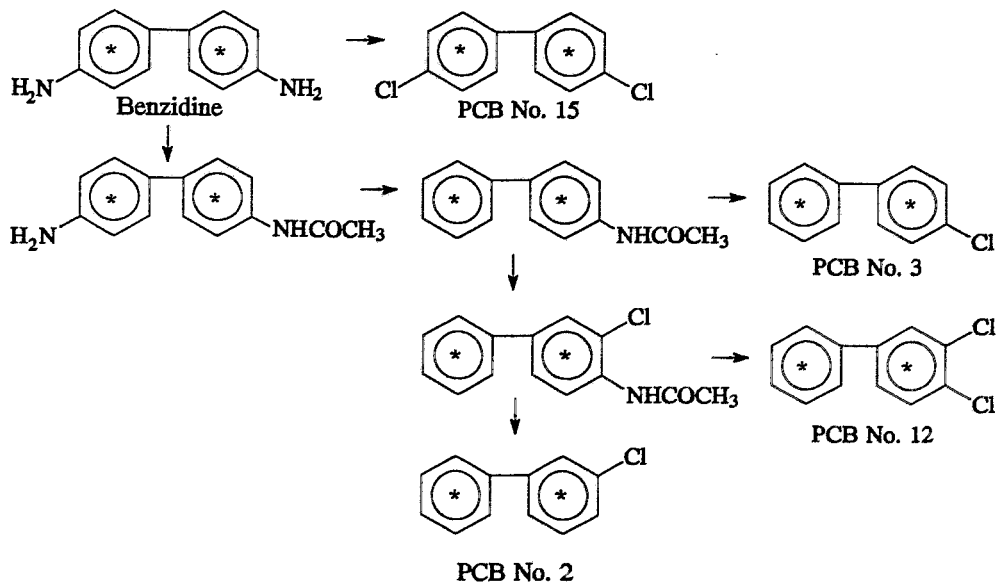Fig. 1: Scheme of [U-C14]Benzidine Synthesis

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Fig. 2: Scheme of [C-14]PCB Synthesis via Monoacetyl-[U-C14]benzidine
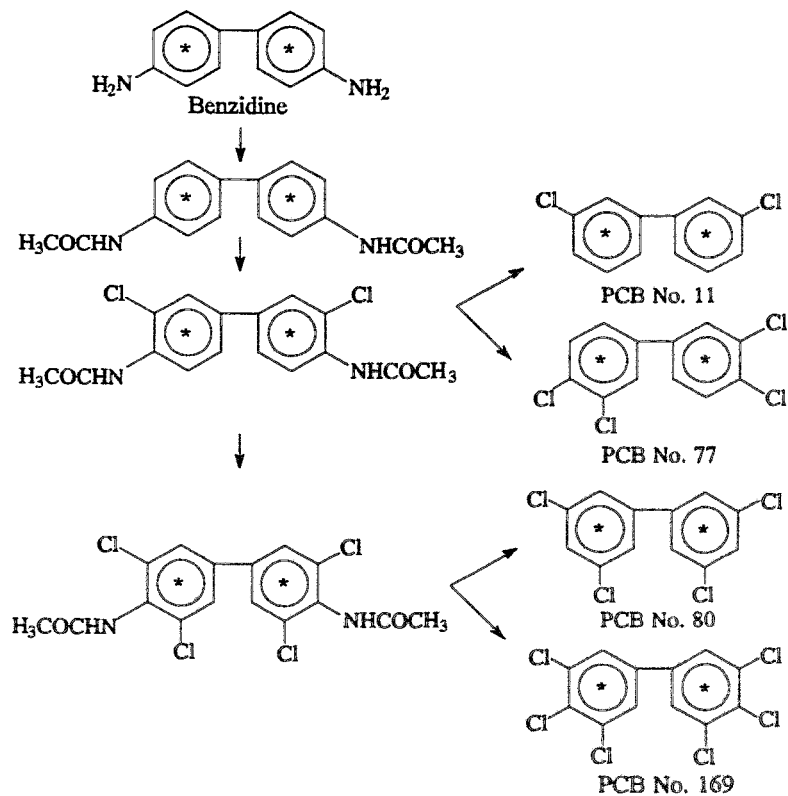

Fig. 3: Scheme of [C-14]PCB Synthesis via Diacetyl-[U-C14]benzidine

in ethanole in practically quantitative yield. The reaction to get the secound one must be carried out under conditions where the product precipitate before its further reaction /3/ with the acylating reagent. The yield of N-monoacetylbenzidine was near 70 %.

The deamination reaction of N-monoacetyl[U-^{14}C]benzidine leads to 4-acetyl-amino-bi-phenyle serving as key a product for PCB congeners with exclusive chlorosubstitution in one of the benzene rings as shown in figure 2.

The following reactions to get the PCB´s starting from N,N´-diacetylbenzidine or 4-acetylaminobiphenyl respectively are

- the chlorination with variable amounts of chlorosuccinimide or elemental chlorine /2/, called as reaction "A" ;
- the deacylation of the N-acetylaminogrup with concentrated hydrochloric acid in ethanole /2/, called as reaction "B" ;
- the Sandmeyer reaction /1/, called as reaction "C", and
- the deamination /1/, called as reaction "D".

In such manner the following eight [U-^{14}C]PCB-congeners, Ballschmiter No. 2, 3, 11, 12, 15, 77, 80 and 169, have been obtained, as summarized in tab.1:

Tab.1: Synthesis of some ^{14}C-labelled PCB congeres

PCB[x)] No.	position of chloro-sub-stituion	starting substances	types of synthesis reactions
2	3	4-acetamino-[U-^{14}C]biphenyle	A(1), B, D
3	4	4-acetamino-[U-^{14}C]biphenyle	B, C
11	3,3'	N,N'-diacetyl-[U-^{14}C]benzidine	A(2), B, D
12	3,4	4-acetamino-[U-^{14}C]biphenyle	A(1), B, C
15	4,4'	[U-^{14}C]benzidine	C
77	3,3',4,4'	N,N'-diacetamino-[U-^{14}C]benzidine	A(2), B, C
80	3,3',5,5'	N,N'-diacetamino-[U-^{14}C]benzidine	A(4), B, D
169	3,3',4,4',5,5'	N,N'-diacetamino-[U-^{14}C]benzidine	A(4), B, C

[x)] Ballschmiters number

In this table the index by the reactions on type of "A" gives the millimole of Chloro-succinimide per millimole of the each starting substance.

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2. GENERAL RESEARCH

FISSION-PRODUCT VAPOUR REACTIONS IN THE PRIMARY COOLANT SYSTEM OF LIGHT-WATER REACTORS UNDER SEVERE ACCIDENT CONDITIONS

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A state-of-the-art report on vapour reactions in the Primary Coolant System (PCS) of Light Water Reactors (LWR) /1/ has been written. The report forms a part of the Reinforced Concerted Action (RCA) on the source term of radioactive elements to the environment following a severe accident at a LWR. The RCA is part of a programme of work on nuclear reactor safety, which has been initiated by the Commission of the European Communities (CEC).

The aim of the report is to identify the uncertainties of chemical vapour reactions of fission products which have to be clarified for a better modelling of the source term by means of mechanistic codes. The conditions under consideration are restricted to those prevailing in the different accident sequences in the PCS during the in-vessel melt progression period. Precursory processes of fission-product release from the degrading core and subsequent processes of the fission-product retention in the containment are beyond the scope of the review.

The temperature range at the surfaces is between 600 and 1073K, the total pressure is between 0.2 and 17 MPa and the hydrogen-to-steam partial pressure ratio is of the magnitude of 0.001 to 1. The volatile fission products, Cs, I and Te, and their compounds, which have been shown to have the most important impact on the source term, reach partial vapour pressures in the range between $6*10^{-5}$ and 0.15 MPa. Further the wall materials of the PCS and the presence of vapours and aerosols from all the other core and reactor construction materials have to be considered as reaction partners. Due to the configuration of the system, to the timing of the thermal and hydraulic conditions, and to the possible chemical reactions, the processes are extremely complex. However, these are important processes which directly influence the magnitude and timing of the fission-product release from the PCS to the containment building.

According to the European Strategy an iterative circular process, which involves computer based code development and evaluation, associated database acquisition and large- and small-scale experiments, have to be carried out to gain a sound understanding and assessment of the source term in an economic way. This review is based on recent reviews and assessments on fission product effects but is directed mainly to experimental methods and chemical analytical techniques which are necessary to gain valuable results in small scale separate effects tests.

A brief summary of the conclusions is given below:

1. Thermodynamics

The thermochemical database of the gaseous and pure condensed state fission product and structure material species and their compounds is good. Nevertheless,

thermochemical data are needed for dimeric or polymeric gaseous species, for nonstoichiometric compounds, for steam-volatile hydroxides (gaseous solutions in steam) at high water partial pressures.

There are indications of a high degree of caesium speciation in hydrogen containing high pressure steam. Up to now the thermochemical data are available only for the dimeric (besides the monomeric) caesium hydroxide. Fig. 1 gives an example of the calculation of the vapour pressures (or mole fractions n in the actual phase) of the different species under the conditions of the containment bypassing V-sequence. Evidently, the dimeric caesium hydroxide pressure reaches higher pressures than the monomeric just under condensation and revaporization conditions. Thus, this species may be important also for kinetic considerations. - The calculation was made with the MTDATA code and the SGTE and AEA databases.

2. Vapour-Vapour Reactions

Vapour-vapour chemical reactions alter the transport behaviour of Cs, I and Te. The chemical compounds of the radionuclides formed in the PCS determine their condensation behaviour with steam in the containment (e.g., I or HI or CsI). However, the question arises whether thermochemical equlibria are established or not. Thermochemical equlibrium is supposed to be immediately established at least at temperatures of 2000 °C or higher after the escape of reaction products from the melting core (a part of I, HI and Cs exists in the free gaseous state). For high effluent flow rates, environmental conditions (temperature drop, concentration lowering) may change before the thermochemical equlibrium is achieved.

The shift of the hydrolysis of CsI

$$CsI + H_2O = CsOH + HI$$

by CsOH consuming reactions can lead to volatile iodine compounds.

One of the possible processes to convert CsI to HI is the indirect or direct reaction of CsOH or CsI with boric acid.

$$H_3BO_3 + CsI = CsBO_2 + HI + H_2O$$

More complex particles (borates, polymeric or in steam dissolved hydroxides) have to be considered in the real PCS during deposition and revaporization. Selected separate effect studies are necessary that can identify the complex chemical entities. The best detection method for this experiments is high-pressure mass spectrometry.

3. Vapour-Surface Reactions

The overall process of the deposition of vapours on structural surfaces consists of the consecutive steps
- gas phase mass transport to the surface
- adsorption and/or condensation at the surface
- chemical reaction at the surface
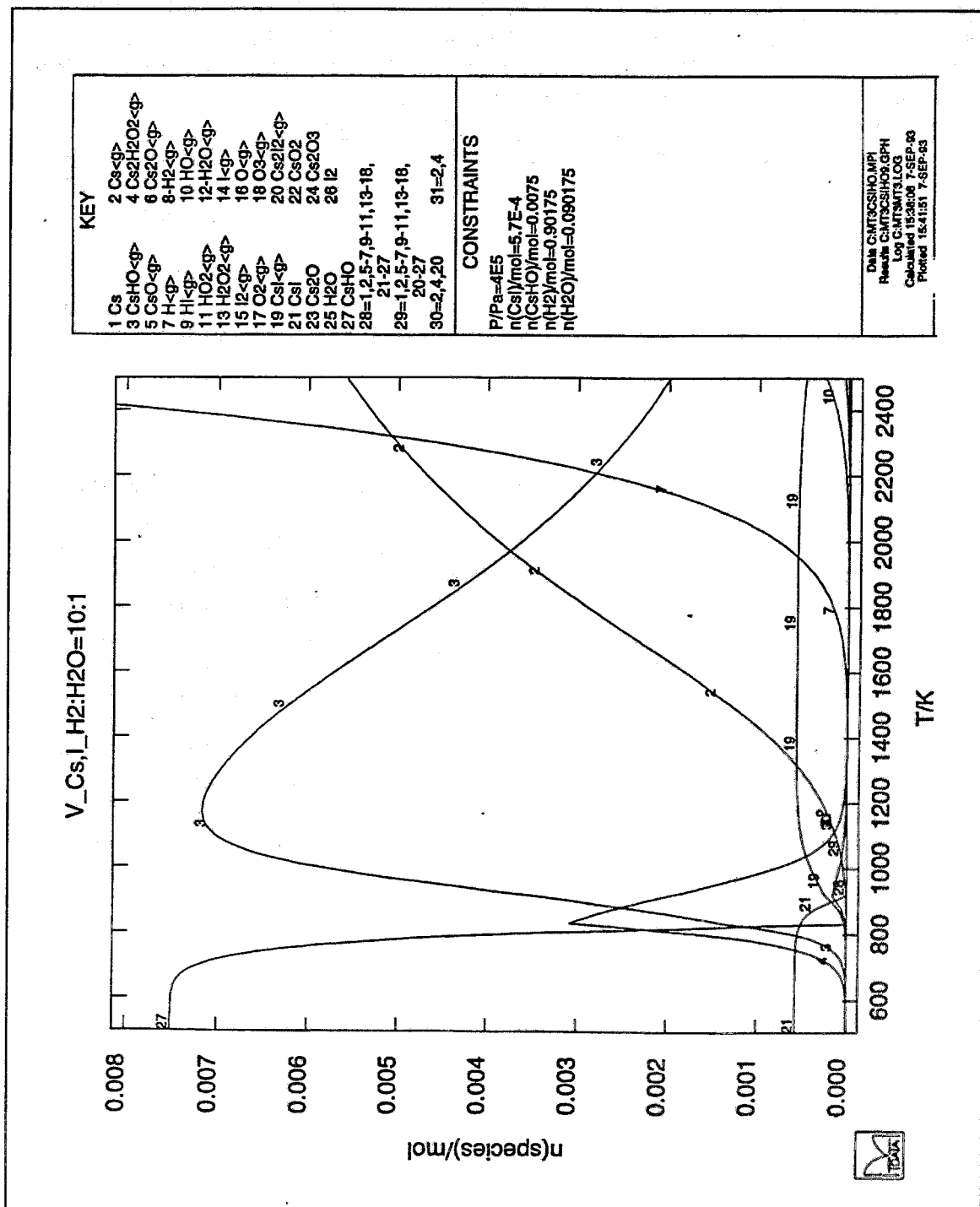- mass transport within the surface layer

Fig. 1: Calculation of the vapour pressures of the different species under the conditions of the containment bypassing V-sequence

Each step mentioned above may be rate-determining. Whereas for high temperatures (>1000 K) gas-phase mass transport is the rate-determining step, at low temperatures adsorption and/or chemical kinetics or solid state mass transport may be rate-determining due to their high activation enthalpies. The latter reactions depend sensitively also on the redox potential and other gaseous partial pressures at the surface (the passivation, activation, scaling and tarnishing state).

In codes empirical deposition laws are introduced for caesium and tellurium. Redox-potentials and in some cases temperature conditions are not taken into account up to now. To examine these processes, experiments under well-defined conditions should be carried out.

The only on-line method to follow the deposition, adsorption, and compound forming processes is γ-spectrometry in small scale experiments. For post-test analysis a high variety of sophisticated photon and particle beam induced methods have been applied for the Phebus-FP and Falcon programmes.

4. Vapour-Aerosol Reactions

Aerosol deposition may enhance fission product retention in the PCS. However, aerosol deposition on surfaces within the nuclear reactor building, could be revaporized as a consequence of fission-product decay heat, convective heating of the structures or changes in the chemical environment. The partitioning of depositing vapours between structural surfaces and aerosol surfaces is an important question. This is why fission products bound to surfaces may be retained in their position under conditions where aerosols are reentrained in the gas flow.

There is a lack of data as to the chemical thermodynamics and, in particular, the kinetics of the reactions between fission product vapours and structural material aerosols. Currently only gas transport kinetics and condensation onto aerosols are the processes modelled in reactor accident calculations. Reactions between gases and aerosol particles are invastigated only with the the particles in the deposited state. The characterization methods for deposited nuclear aerosol particles are similar to those for the surface characterization. Invasive and non-invasive in-situ chemical characterization methods are under development for atmospherical or industrial aerosols. However, there is reasonable doubt that these methods can be of much value for nuclear aerosols, because the obstacles which have to be overcome to establish such methods under radioactive and high-pressure conditions, are too big.

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    ST(93)-P 53, FZR, Dresden, January 1994

IN LINE MEASUREMENT OF THE STEAM-TO-HYDROGEN RATIO IN REACTOR PRIMARY CIRCUIT EXPERIMENTS

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Mixtures of steam and hydrogen are formed due to the reaction of the water coolant with zirconium base type cladding materials and with the uranium fuel during the in-vessel phase of a severe light water reactor accident /1/:

$$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2 \tag{1}$$

$$3UO_2 + H_2O \rightarrow U_3O_7 + H_2 \ . \tag{2}$$
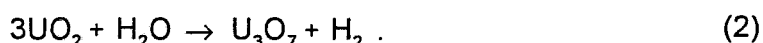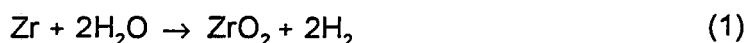
To study the kinetics of these reactions the fast responding in-line-measurement of the steam-to-hydrogen ratio would be useful in small and medium scale experiments. Moreover the transport and retention behaviour of the radiotoxic fission products, iodine and tellurium, will be decisively influenced by the reaction with hydrogen and steam /2/

$$2HI \rightleftharpoons I_2 + H_2 \tag{3}$$

$$H_2Te + 2H_2O \rightleftharpoons TeO_2 + 3H_2 \ . \tag{4}$$
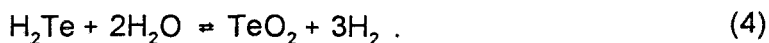
The ratio (p_{H_2O}/p_{H_2}) of the steam and hydrogen partial pressures can be measured with potentiometric high temperature solid electrolyte (SE) cells /3/. The potential at the measuring electrode

$$H_2 + O^{--}(in\ SE) \rightleftharpoons H_2O + 2e^- \tag{5}$$
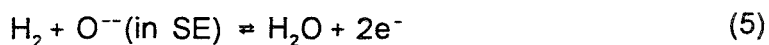
is measured against an oxygen reference electrode (usually with an oxygen partial pressure p_{O_2} = 0.21 atm of the surrounding air)

$$2e^- + \frac{1}{2}O_2 \rightleftharpoons O^{--}(in\ SE), \tag{6}$$
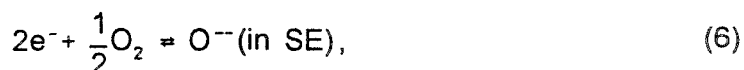
thus leading to a relation for the cell voltage (U):

$$U = \frac{\Delta G^o}{2F} + \frac{RT}{2F}\ln\frac{p_{H_2O}}{p_{H_2}} - \frac{RT}{4F}\ln p_{O_2}, \tag{7}$$
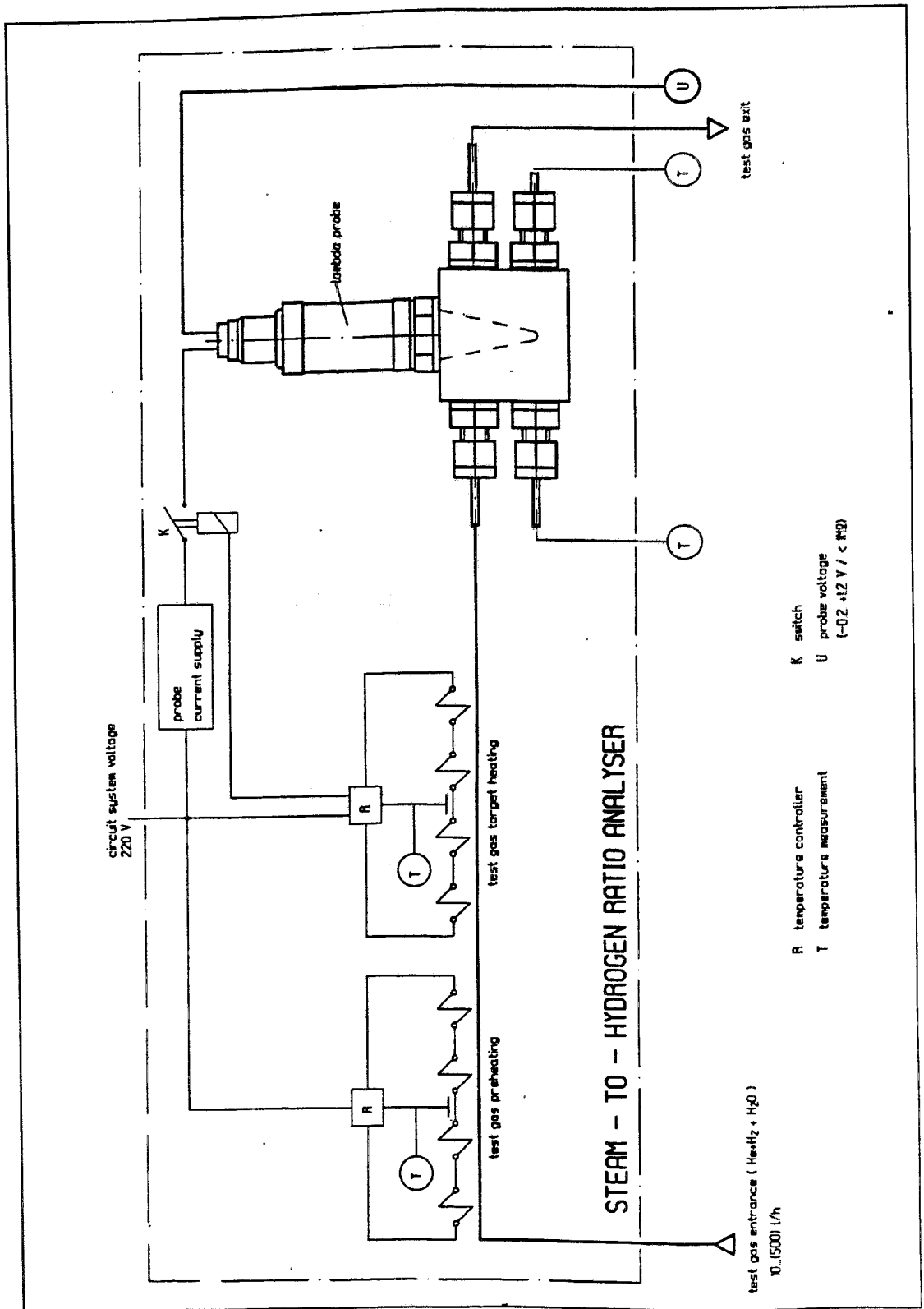
Fig. 1: Device for measuring the steam-to-hydrogen ratio with a Lambda probe in a test gas.

with $\Delta G°$ free energy of water formation
       F   FARADAYs constant
       R   gas constant
       T   cell temperature.

The frequently used yttrium-doped or calcium-stabilized zirconium dioxide oxygen-ion-conducting solid electrolytes are prone to fracture under thermal and mechanical shock conditions. Therefore a conventional Lambda probe /4/ was tested for this purpose. Lambda probes have been developed to indicate the fuel-to-oxygen ratio in automotive exhaust gases.

In a test the primary circuit gas was simulated by a hydrogen and steam mixture that was diluted with helium to a high degree.

The hydrogen content was prepared by mixing of pure helium and a helium with 1% hydrogen by flow controllers between $p_{H_2} = 5{,}95 \times 10^{-5}$ and $1{,}52 \times 10^{-3}$ atm. The water content in the helium-hydrogen-gas flow was adjusted by saturation of the gas at various temperatures between 0 and 20°C ($p_{O_2} = 6{,}03 \times 10^{-3}$ and $2{,}31 \times 10^{-2}$ atm).

The nuclear and thermochemical heating of the gas were simulated by electrical heating in two steps (Fig. 1). The Lambda probe was screwed into a metal block.

Fig. 2 shows the dependence of the steam-to-hydrogen ratio from the voltage of the cell at 700°C. The theoretical curve was calculated by relation (7).
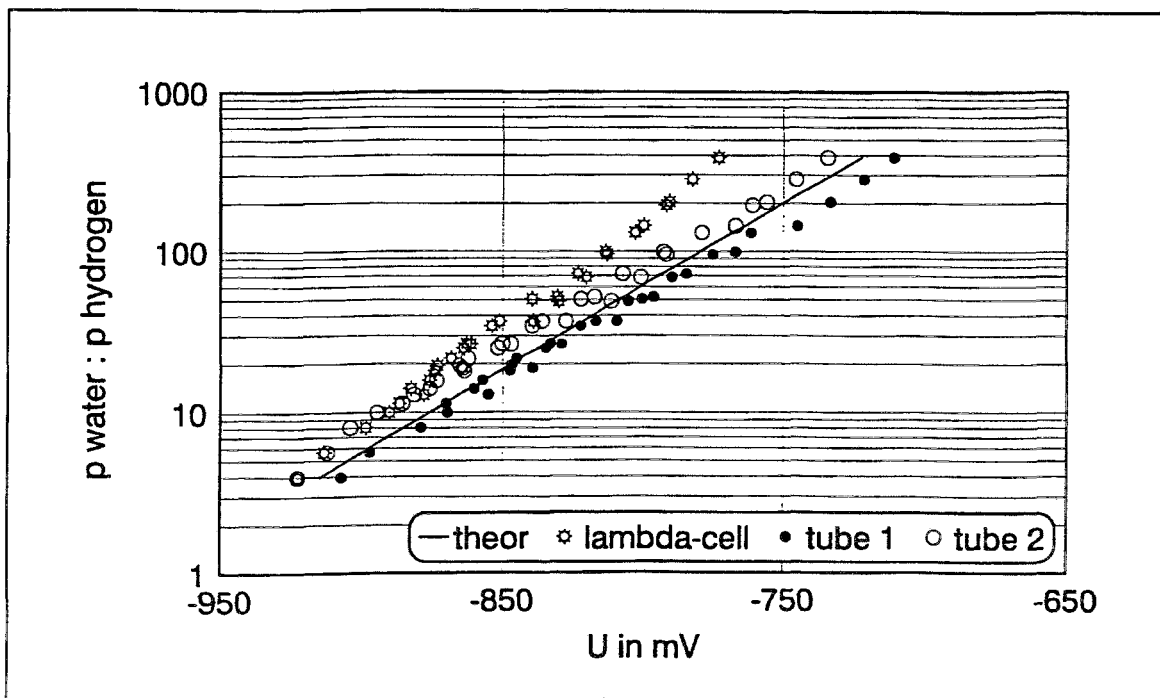

Fig. 2:   Water-to-hydrogen ratio against cell voltage

In addition to the Lambda cell measurement, the voltage was measured in two tube type calcium-stabilized zirconium dioxide cells described in /5/. In comparison to these cells, the Lambda probe shows a systematic but reproducible deviation from the calculated curvature. But in the range of p_{H_2O}/p_{H_2} from 3 to 300 the Lambda probe is practicably useful under the high pressure coolant circuit conditions. The cell responds to changes of the water or hydrogen content in the diluted gas after 0.2sec.

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POTENTIAL [211]AT- RADIOPHARMACEUTICALS- SYNTHESIS BY ISOTOPE EXCHANGE AND BIODISTRIBUTION

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Abstract: A simple procedure for labelling of At-radiopharmaceuticals based on the nucleophilic exchange in presence of Cu(I) and an excess of reducing agents is describted. Radiochemical yields >90 % are obtained at 100 °C within 30 minutes for aromatic amines. The in-vivo distribution of the labelling compound [p-At-isopropylamphetamine] can be illustrated by the high brain to blood radioactivity ratio measured in wistar rats.

Introduction: The α- emitter [211]At appears as one of the most suitable representatives for endoradiotherapy of malignancies /1a/.
Two possibilities to achieve astatine enrichment in tumor tissue are:
  - i.v. injection and radionuclide uptake by tumor metabolism /1b/   and
  - depositing of particles in tumour tissue via tumour supplying vessel.
At present, the second way seems to be more successfull /2,3/. But, the application of this method is restricted and only accessible if the tumour localisation allows the necessary surgical procedures. On the other hand, only a few astatine labelled compounds are stable in-vivo to obtain satisfying intratumoral concentration, e.g. [At-methylene blue] /4/. The testing of further compounds should be promoted. We carried out experiments to find out, if astatine compounds could be prepared analogous to the widespread applicated iodine radiopharmaceuticals. Because of the better metabolic stability, halogene labelling aromatic compounds should be preferred.Various substituted aromatic compounds or phenyl fatty acids were labelled by iodine echange. One successful attempt to catalyze the nucleophilic exchange of iodine was the application of metallic Cu or copper salts by MERTENS /5/.
The present paper deals with the modification of this simple and rapid method for labelling compounds p-iodoisopropylamphetamine [IMP], benzylamine [BA] and m-iodbenzyl-guanidine [MIBG] with astatine to high yields.

Experimental: Highly purified [211]At ([210]At < 10^{-5}%) was obtained by the (α,2n)- reaction of 28 MeV α- particles from natural bismuth at the Rossendorf Cyclotron U-120. The astatine was separeted by thermochromatography from the target materials as "At°x H_2O" in water /6/. Into a sterile septum closed glass vial containing water dissolved 2mg substrate (IMP, 100µl) were added a surplus of ascorbic acid, 0.15 mg $CuSO_4xH_2O$ (50 µl), 0.5 mg $SnSO_4$ (100 µl) and 50- 200 µl "At°x H_2O". After boiling for 30 minutes and cooling down an injectable isotonic solution of pH 4 is obtained by adding a sterile fresh prepared, oxygene free solution containing sodium citrat. The estimation of the labelling yields were performed by means of TLC (SILICAGEL MERK) and the detection system (COBRA PACKARD). The chromatografic separation were carried out by appropriated conditions, table 1.

Resultats and discussion: Table 1 is shown that various compounds will be astatized by rapid procedure under mild conditions.

compounds	catalyst	yield	temp.(°C)	eluate
[At-CH$_3$COOH]	-	95	40	[1]
[At-C$_{16}$H$_{32}$COOH]	-	90	105	[2]
[At-aniline]	Cu^{2+}	80-85	160	[1]
[p-At-IMP]	Cu^{2+}	90	150	[3]
[p-At-IMP]	Cu^{2+}/Sn^{2+}	95	100	[3]
[m-At-BA]	Cu^{2+}/Sn^{2+}	93	100	[1]
[At-MIBG]	Cu^{2+}/Sn^{2+}	96	100	[4]

Tab. 1: Synthesis of astatized compounds via halogen exchange, labelling yields by TLC, mobile phases:
[1] C$_2$H$_5$OH / NH$_3$ (conc) / H$_2$O = 80/4/16   [2] C$_7$H$_{16}$ / (C$_2$H$_5$)$_2$O / CH$_3$COOH (conc) = 70/40/2
[3] CHCl$_3$ / C$_2$H$_5$OH / NH$_3$ (conc.) = 80/15/5   [4] Ethylacetat / C$_2$H$_5$OH   = 50/50

The labelling yields of aromatic compounds (no amines) by the Cu(I)- methods were compared with the results gained by Cu(II)-method without additional reductant. The labelling method allows quantitativly radiochemical yield within 30 min at 100°C for aromatic At-compounds of radiopharmaceutical interest.

Further, it can be shown that lower radiochemical yields are obtained for aromatic amines with Cu(II). An excess of reducing agents avoids the formation of Cu(II) which otherwise could evoke side reaction and longer reaction times.

The quality of the radiopharmaceuticals can be illustrated by the brain to blood ratio for [At-IMP] and [I-IMP] measured by biodistibution after i.v. injection in wistar rats.

	time [min]	brain	blood	liver	stomach	thyroid
1	30	2.3	0.14	2.3	1.5	0.4
2	90	2.0	0.29	5.8	5.1	0.7
3	180	1.5	0.19	1.0	4.7	0.8
4	5	2.0	0.07	1.5	0.5	1.8
5	60	1.8	0.10	2.0	1.1	0.8
6	180	1.7	0.15	1.3	1.3	1.4
7	300	1.6	0.13	1.2	1.9	2.4

Tab. 2: Retention of [At-/I-IMP] after i.v. application in healthy wistar rats, values in selected organs in % of the radioactivity /g tissue (thyroid: total organ), time corrected
[1-3] [p-^{211}At-IMP]   [4-7] [p-^{123}I-IMP]

Table 2 indicated that the ratio [brain/blood] is simulare to At-IMP in comparison with I-IMP, based of the higher retention of [At-IMP] in the blood, stomach, thyroid of [At-IMP] and caused by the small distinguished in-vivo dehalogenization of At-compounds.

The paper shows that a simple chemistry applicable on astatized aryl compounds allows a high radiochemical yield in real kit conditions. The astatized compounds can be used as a radiopharmaceutical directly [At-IMP] or as an intermediate for labelling of proteins and other biomolecules (At- amines).

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THE INFLUENCE OF CHEMICAL INTERACTIONS BETWEEN FISSION PRODUCTS AND WALL MATERIAL ON THE AEROSOL BEHAVIOUR IN A THERMAL GRADIENT TUBE

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After a hypothetical severe accident in a nuclear power reactor, radionuclides are transported through the Reactor Coolant System (RCS) into the containment. In radionuclide source term calculations, which are used to predict the behaviour of radioactive fission products in the RCS, the chemical interactions between the gaseous species on one hand and the wall material on the other hand are often neglected. This fact has partly arisen as a consequence of the complexity of chemistry-based phenomena. Thus aerosol growth- and deposition processes depend on the chemical constituents of the gas phase and consequently also on the gas-wall interactions. The relevance of this effects to the release of radioactive aerosols into the containment is not well understood. We performed improved calculations of the influence of chemical reactions between gaseous fission products and solid wall structures on the aerosol formation.

In this investigation, the FALCON experiment FAL-ISP1 is analyzed by means of model calculations. The experiment was carried out at 4 June 1992 in the FALCON facility at Winfrith Technology Centre. In the experiment, the fission product and aerosol behaviour in a silica thermal gradient tube was investigated. In such a silica tube, gas-wall interactions do not exist. Therefore, two model calculations were carried out on the basis of this experiment:

- Calculation by using the orginal silica thermal gradient tube
- Calculation after replacing the silica tube by a hypothetical tube made of SS 304 stainless steel.

GEOMETRY OF THE TUBE:
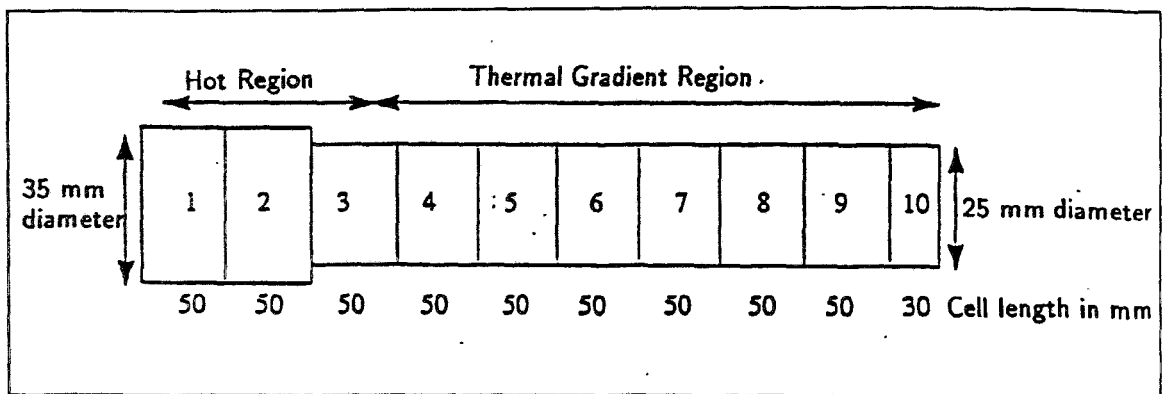
THERMALHYDRAULIC and CHEMICAL CONDITIONS:

Time-scale [sec]	P [bar]	ΔT [K]	Δv [m/sec]	Carrier Gas	H_2O	B	Contr. Rod	Fiss. Prod.
0 - 30	1	1070-450	0.48-0.26	He	yes	yes	yes	no
30 - 450	1	1200-500	0.50-0.30	He	yes	yes	yes	yes
450 -1200	1	1000-400	0.35-0.15	He	no	no	yes	yes

The VICTORIA code /3/ contain best estimate models for aerosol physics and chemistry as well as for transport of fission products and aerosols in the tubes of a RCS. For the calculations two different version of VICTORIA were used:

- The Ester version, which consists of the coupled codes ICARE2/VICTORIA
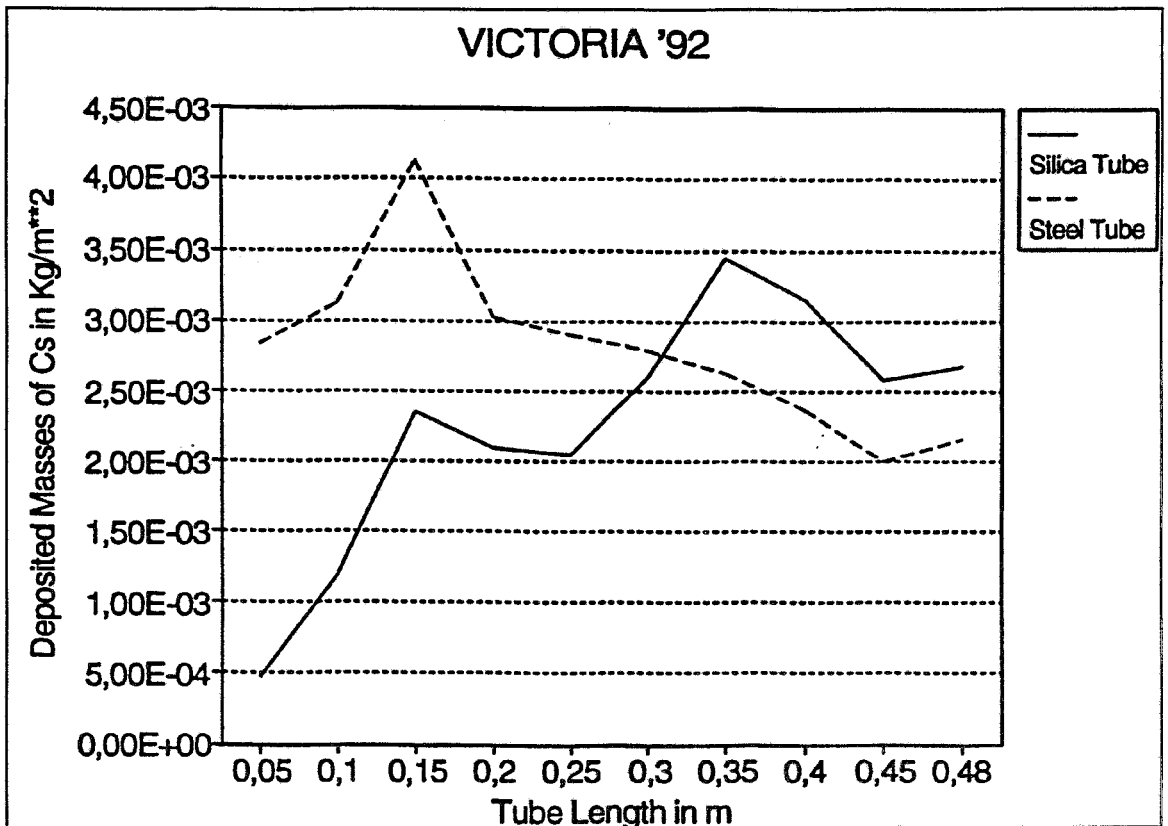- The improved VICTORIA92 standalone version

Fig. 1: As an example is shown the deposited masses of Cesium in a silica- and a steel tube, calculated with the VICTORIA 92 version.

DISCUSSION AND CONCLUSIONS

The deposition rates of the two most important fission products (FP) Cs and I in a silica- and a steel tube, respectively, shows a quite different behaviour. Following our calculations, the transport of FP into the Containment is reduced or at least delayed because of interactions with the steel tube. To clarify the situation much more experimental investigations with steel tubes seems necessary, especially on-line measurements of deposition and resuspension rates of FP.

In comparison with the former version, calculation with VICTORIA92 shows much more realistic result and agrees better with the experimental data (not shown here). We assume that the calculated deposition in the steel tube using VICTORIA92 is much closer to expected interactions. The amendment of improved models and data within existing codes seems important for the correct treatment of aerosol chemistry effects.

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Report NUREG/CR-5545, SAND 90-0756, R3, R4, Rev. 1 (1992)

3. CHEMISTRY OF HEAVY ELEMENTS

CONTRIBUTION TO THE EVALUATION OF THERMOCHROMATOGRAPHIC EXPERIMENTS

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The starting point of the evaluation of carrier-free thermochromatographic experiments, i.e. the determination of the adsorption enthalpy, is the transport-equation

$$\frac{dz}{dt} = \frac{u(T)}{1 + q(T)},\tag{1}$$

derived under weak assumptions in /1/. The temperature-dependent function $u(T) = u_o \cdot T/T_o$ means the velocity and $q(T)$ the corrected partition coefficient /2/ including the more complex dissociative adsorption reactions /3/: [1]

$$q(T) = a\frac{c_{ads}^0}{c_{gas}}\exp(\frac{\Delta S_{diss.ads}^0}{R})\exp(\frac{-\Delta H_{ads}^0}{RT}).\tag{2}$$

A solution of eqn. (1) needs the temperature-profile of the tube $T(z)$. The inverse function $z = f(T)$ exists because it is monotonous in the relevant region.

In the standard approach /2/ the mean approximation for a solution of eqn. (1) was the assumption of a linear temperature profile: $T = T_s + gz$ with $g = const. < 0$. Those an approximative evaluation of eqn. (1) was possible in order to get the enthalpy ΔH_a^0 using a modified Ei^* function with the asymptotics $\exp(x)/x$. In Refs. /3,4/ the evalution is also performed within the standard approach.

The aim of this investigation is to avoid the assumption of a linear temperature profile. Equation (1) can be rewritten without any approximations to:

$$t_{exp} + \int_{T_A}^{T_s} \frac{1 + q(T)}{u(T)}\frac{dz(T)}{dT}\, dT = 0,\tag{3}$$

and the enthalpy can be determined from the zero of this equation. We realize from eqn. (3) that for each enthalpy the adsorption temperature depends on the "temperature history" during the transport through the tube.

The zero of eqn. (3) was calculated with the FORTRAN programm TECRAD. The function $dz(T)/dT$ is assigned with high accuracy in a direct way from the measured profil by means of a spline-procedure.

Test calculations show the influence of the temperature profile of the tube on the determination of the enthalpy for various (hypothetical) adsorption temperatures. The temperature gradient tube and the data from the experiments described in /4/ have been used. Fig.1 shows the temperature profiles in the relevant part of the tube, i.e. the interval between the starting temperature (1410 K) and the lowest resumable adsorption temperature. The four profiles are: 1. the measured profile (bold straight line), 2. the equivalent linear profile (dotted line), 3. a modelled tanh profile (dashed line) and 4. a modelled 1/x profile (dash-dotted line).

[1] The meaning of the symbols are: z-length coordinate of the tube, t-time, T-temperature, $\Delta S_{diss.ads}^0$-dissociative adsorption-entropy, ΔH_{ads}^0-adsorption-enthalpy, t_{exp}-time of the experiment, T_S-starting temperature, T_A-adsorption temperature, a-surface area per unit of column length, u_0-initial velocity, T_o-standard temperature, g-temperature gradient, c_i-concentration of species i.

The results are plotted in Fig. 2. The differences of the enthalpy depending on the choosen profiles are in the order of 10 kJ/mol. From this follows that by consideration of real temperature profiles the amendment of the evaluated data is in the same order.

The next step is the application of the profile-depending procedure to the experiments presented in /4/.
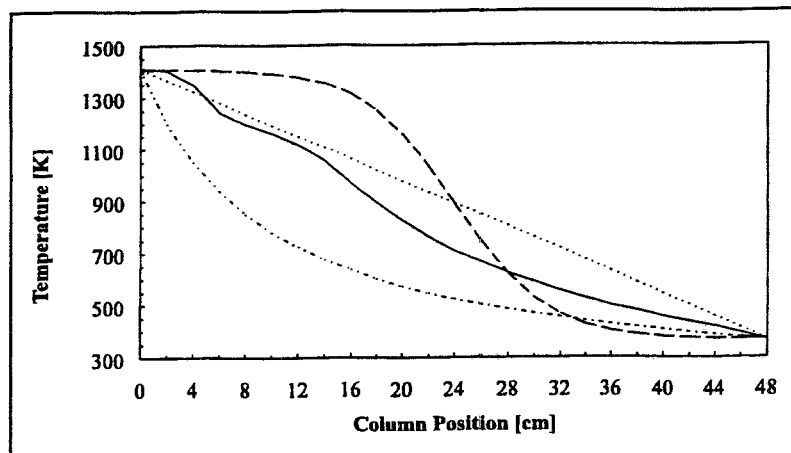

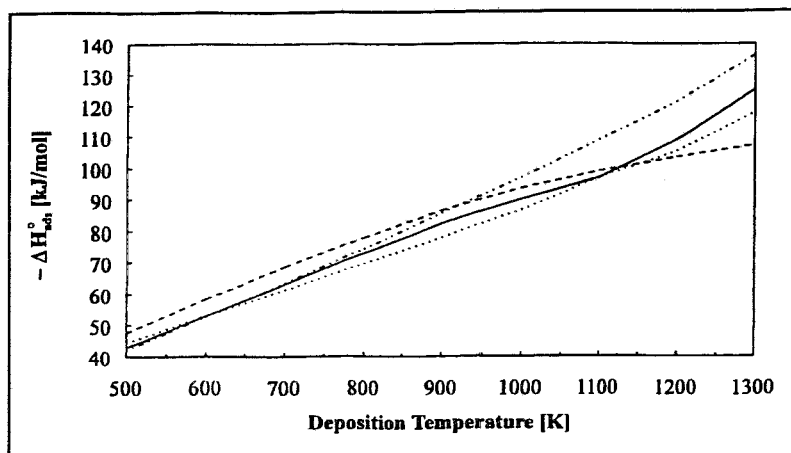**Fig. 1:** Real, linear and model-temperature profiles (s.Text)

Fig. 2: Dependence of the deposition temperature on ΔH_{ads} for the temperature profiles from Fig.1

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DESIGN AND CHARACTERISTICS OF THE RADIOCHEMISTRY GAS - JET

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Gas-jet systems have found widespread application in studies of and with short-lived nuclides. In this technique nuclear reaction products recoiling out of a solid target are stopped in a flowing gas that contains aerosol particles. The thermalized recoil atoms are attached onto the aerosol particles and then transported through capillaries to experimental arrangements located far away from the irradiation position.

Gas-jet systems installed at nuclear reactors delivering a complex mixture of fission products have been used for experimental studies as the development of fast chemical separations /1/, the measurement of decay properties of short-lived isotopes /2/ and the study of chemical reactions on the surface of aerosol particles /3/.

For the transportation of products from heavy ion induced reactions to the set-up for nuclear chemical studies, the gas-jet technique has been applied, too.

Typical recoil ranges of fission products and products from heavy ion induced reactions in air at 1 bar are in the order of several centimeters. In principle, the gas-jet technique can be applied also for the transport of reaction products from proton, deuteron or α-particle induced fusion reactions, but the very low recoil energy requires the use of very thin targets. In order to achieve production yields of practical use complicated multi-stack target arrangements have to be applied /4/.

The low beam energy of the U-120 cyclotron does not allow to produce a broad spectrum of short-lived nuclides in fusion reactions. For this reason we have designed a gas-jet system based on the neutron induced fission of uranium. At the U-120 cyclotron neutrons can be produced in the reaction ^{9}Be (d,n) ^{10}B. For years a neutron beam line based on this reaction has been used for tumor therapy /5/.

As seen from Fig. 1 the neutron yield maximum is at a neutron energy of 5 MeV /5/. This is close to the cross section minimum of the ^{235}U (n,f) reaction at 6 MeV. However, in order to take advantage of the high cross section at neutron energies of about 7 MeV the neutrons are used without moderation.

The set-up of the radiochemistry gas-jet is shown schematically in Fig. 2.

^{235}U with an abundance of 89.8 % is used as the target material. The target of 50 mm diameter and an average thickness of 275 µg/cm^2. U was prepared by electroplating from a $(NH_4)_2SO_4$ solution on 25 µm thick titanium and installed in a chamber made of titanium. Titanium was chosen to keep the neutron induced radioactivity as low as possible. The design is almost the same as that of the SAPHIR gas-jet chamber of the Paul Scherrer Institute Villigen /1/. At the U-120 cyclotron the uranium target is positioned 8 cm behind the beryllium target of the neutron beam line inside a
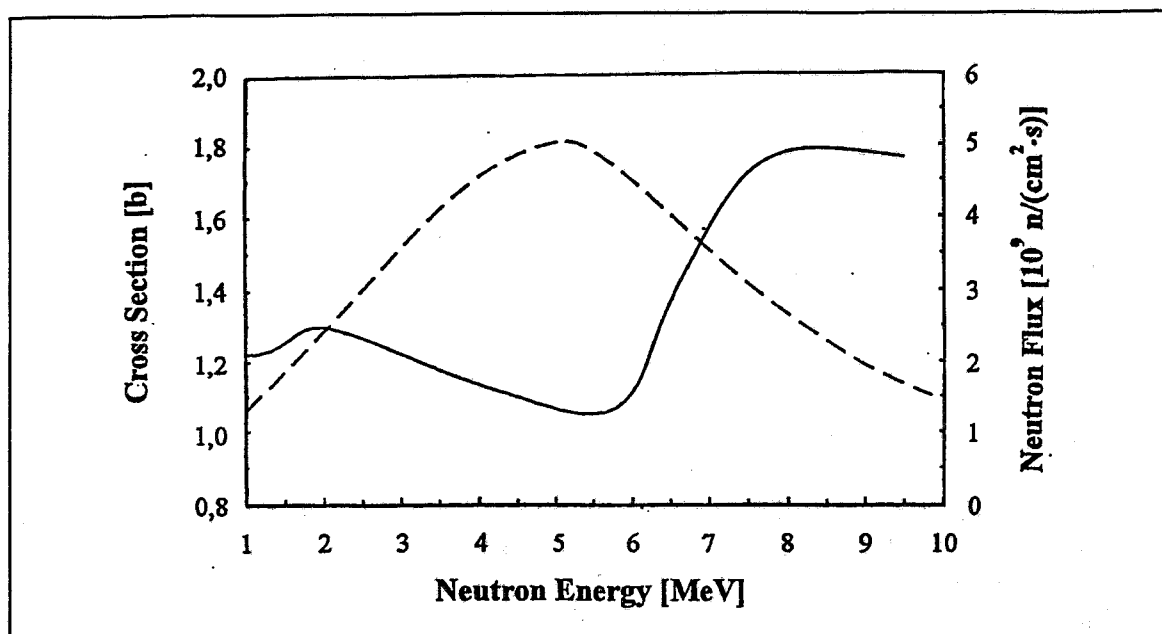
cylindrical polyethylene box.

Fig. 1: Yield depending energy spectrum of neutrons produced at the U-120 cyclotron in the ^{9}Be (d,n) ^{10}B reaction at a deuteron energy of 13.5 MeV (- -) /5/ and cross section of the ^{235}U (n,f) reaction in dependence on neutron energy (—) /6/.

Ar/MoO$_3$-aerosol has been used to test the gas-jet. The aerosol is generated by flowing argon (1 l/min) over MoO$_3$ which is heated to at least 890 K. Leaving the generator, the aerosol flows through a cooling loop made of a 5 m long stainless steel tube (4 mm i.d.) and then through a 20 m long polyethylene tube of the same inner diameter into the target chamber.

To transport the radionuclides attached onto the aerosol particles to the experimental arrangements a 20 m long polyethylene capillary of 2 mm i.d. is used. Glass fibre filters are being used for collecting the radionuclides. The carrier gas argon passing the aerosol filter is released into a delaying tube for the decay of short-lived gaseous nuclides. After having passed a charcoal trap the gas is released into the ventilation system of the cyclotron building. The transport capillary is placed in an outer tube in order to protect the capillary mechanically and to retain any possible leakage. The outer tube is connected to the target chamber housing. A permanent air stream ventilating the housing and the outer tube is pumped through a glass fibre filter. The radioactivity of this aerosol filter is measured continuously in order to indicate a leak. The transportation time through the 20 m long capillary was measured to be 6 s at a chamber pressure of 1.24 bar and an argon carrier gas flow of 1 l/min (at normal temperature and pressure).

The transportation yield was determined by γ-spectroscopic measurements of the collecting filters. In separate irradiations under the same beam conditions the uranium target was covered by a 34 µm thick aluminium foil in order to catch the recoiling fission products completely. ^{91}Sr and ^{143}Ce were taken as representative radionuclides

of the light and heavy mass peak of the ^{235}U fission, respectively.

At an oven temperature of the aerosol generator of 900 K, a chamber pressure of 2.25 bar and an argon flow of 1 l/min, the transportation yield was 45 % for ^{91}Sr and 55 % for ^{143}Ce. These values are comparable to the 40 % for non-volatile fission products of the SAPHIR gas-jet at PSI with a 130 m long capillary /1/ and the 60 % of the TRIGA gas-jet at Mainz having a transportation distance of about 5 m and using alkali halide aerosols /7/.
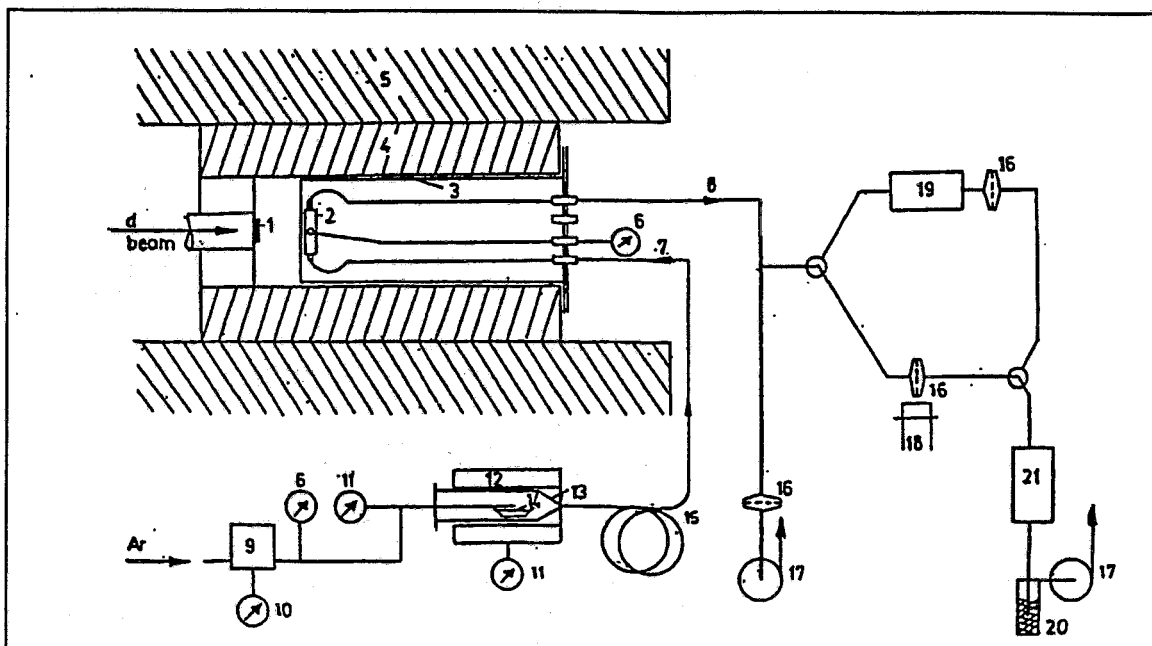
Fig. 2: Set-up of the radiochemistry gas-jet at the U-120 cyclotron.
1) Be-target, 2) ^{235}U-target chamber, 3) polyethylene box, 4) shielding (steel), 5) shielding (paraffin), 6) pressure gauge, 7) polyethylene tube, 8) transportation capillary, 9) gas flow controller, 10) flow meter, 11) thermometer, 12) furnace, 13) aerosol generator, 14) MoO$_3$, 15) cooling loop, 16) collecting filter, 17) pump, 18) HPGe or Ge(Li) detector, 19) experimental arrangement (to be installed), 20) charcoal trap, 21) delaying tube.

At a chamber pressure of 1.24 bar the ^{91}Sr/^{143}Ce-ratio on the collecting filter was only 0.6 indicating that the light fission products are thermalized uncompletely. For a complete thermalization the chamber depth (25 mm) is to low. However, in this way the light fission products can be suppressed. A suppression of the heavy fission products can be achieved by covering the target with an aluminium layer of about 10 µm.

The summary radioactivity of isotopes with half-lives between 10 min and 33 h collected during one hour amounts to about 100 kBq.

Fig. 3 shows the low energy part of a γ-spectrum of an 1 h on-line measurement of a collecting filter. The spectrum covers the half-life range between 10 s and 1 h. In order to collect radionuclides with shorter half-lives the carrier gas flow has to be increased.
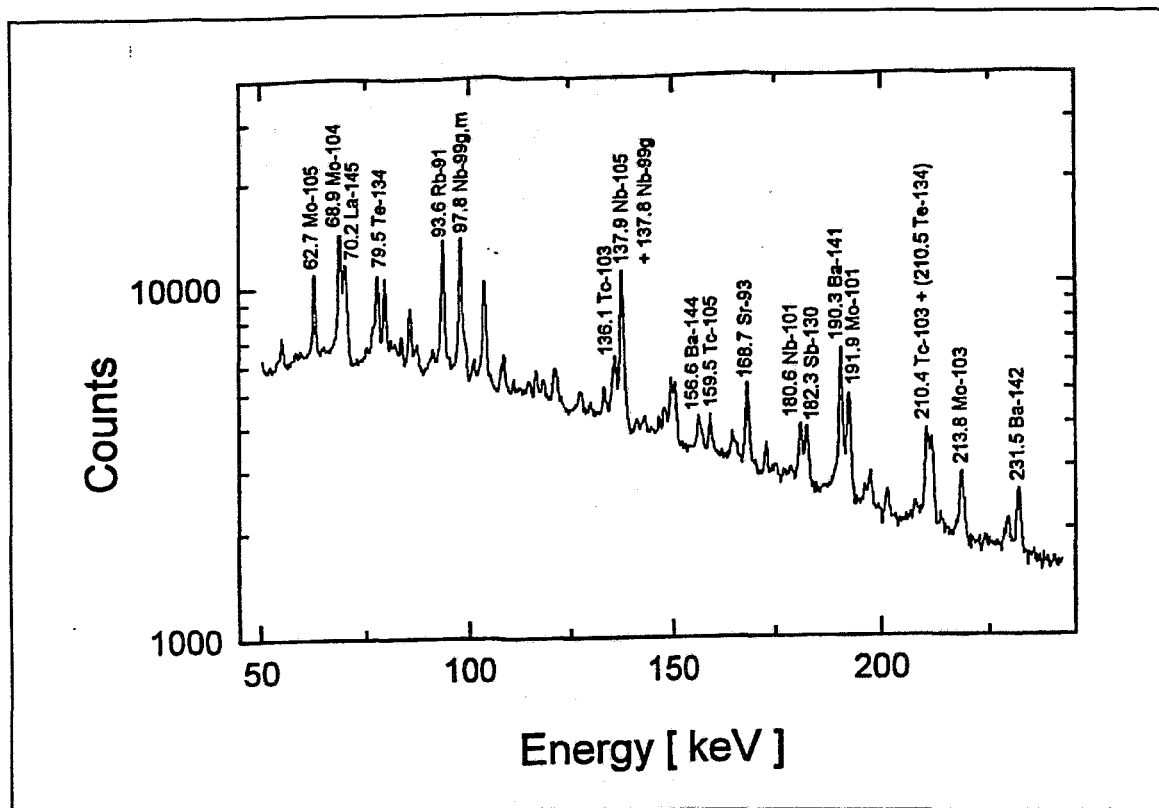
Fig. 3: γ-spectrum of a collecting filter, measured on-line during 1 h collecting time
(HPGe detector, resolution at 122 keV: 0.49 keV, temperature of the aerosolgenerator
furnace: 895 K, carrier gas: Ar, gas flow: 0.8 l/min at 1.24 bar)

The whole system has to be tested further in order to find out the optimum conditions
for a stable and efficient transportation of radionuclides. However, already now the
radiochemistry gas-jet can be used as a continuous source of short-lived isotopes or
for collecting longer-lived fission products for experimental studies.

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GAS CHROMATOGRAPHIC STUDIES OF TUNGSTEN IN HUMID OXYGEN

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Extending previous investigations of the lighter homologues of element 106 to tungsten its volatilization and adsorption behaviour in the presence of humid oxygen was studied by thermochromatography. The carrier-free tungsten isotope [177]W was produced in the [nat]Hf (α, xn) reaction. Collection of the tungsten activity, experimental set-up and measurement correspond to those described for molybdenum /1/.
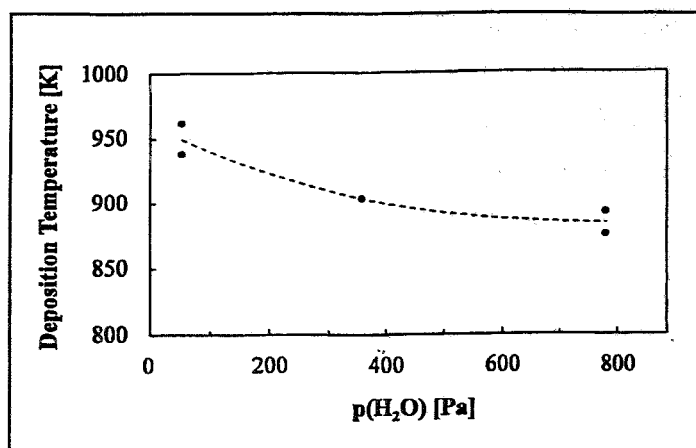

Fig. 1: Deposition temperature of carrier-free tungsten as a function of the partial pressure of water, $v_0(Ar) = 1.0$ l/min, $v_0(O_2) = 0.5$ l/min

As known from literature there are only minor differences in the chemical properties of molybdenum and tungsten because their atom radii are very similar /2/. Tungsten behaves similar to molybdenum in the O_2/H_2O-system, i.e. its deposition temperature depends on the humidity of the carrier gas as depicted in Fig. 1. Therefore a complex transport reaction can be assumed whereby in the end WO_3 is adsorbed on the quartz surface according to (1).

$$WO_2(OH)_{2(g)} \quad \leftrightarrow \quad WO_{3(ads)} + H_2O_{(g)} \qquad (1)$$

However, the deposition temperatures are higher than those of molybdenum. ΔH°_{ads} was calculated with equation (2) to be $(-69.8 \pm 6,9)$ kJ/mol assuming that equilibrium (1) has reached /3/.

$$f(E_i^{\cdot}) = E_i^{\cdot} \left(\frac{-\Delta H^{\circ}_{ads}}{R \cdot T_D}\right) - E_i^{\cdot} \left(\frac{-\Delta H^{\circ}_{ads}}{R \cdot T_S}\right) \qquad (2)$$

with
$$f(E_i^*) = \cfrac{t_r \cdot v_0 \cdot g \cdot c_{gas}(H_2O)}{a \cdot T_0 \cdot c^{\circ}_{ads}(MO_3) \cdot e^{\frac{\Delta S^{\bullet}_{diss,ads}}{R}}}$$

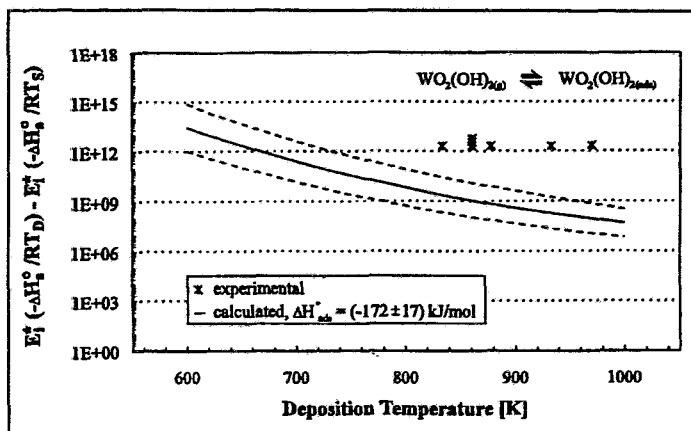$$\Delta H^{\circ}_{ads} = (16.9 \pm 8.2) + (0.690 \pm 0.042)\, \Delta H^{\circ}_{298,\,subl} \qquad (3)$$

Fig. 2: Comparison of theoretically calculated and experimentally determined $f(E_i^*)$ values for direct adsorption of $WO_2(OH)_2$
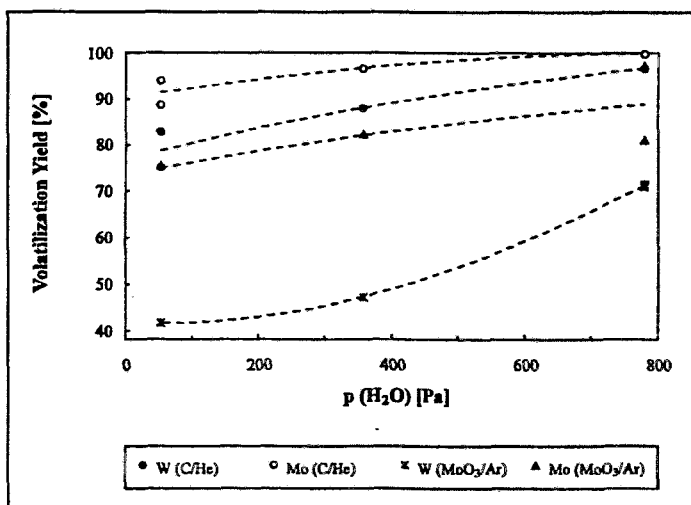

Fig.3: Volatilization yield of molybdenum and tungsten in off-line experiments as a function of the partial pressure of water

A second way for confirming the complex transport reaction is the comparison of $f(E_i^*)$ values determined from theoretical and experimental values. The knowledge of a compound's sublimation enthalpy allows an estimate of its adsorption enthalpy by means of the empirical relation (3) /4/. Inserting the ΔH°_{ads} value in equation (2) one get $f(E_i^*)$. In case of a direct adsorption of the transported compound the experimental values for $f(E_i^*)$ should lie within the margins of error of the theoretical calculated $f(E_i^*)$ values. As depicted in Fig. 2, the experimental values deviate considerably from the theoretical curves. This is taken as a further evidence for a dissociative adsorption according to (1).

WO_3 is not only stronger adsorbed on quartz than MoO_3 but also its volatility in humid oxygen was found to be lower (Fig. 3). Remarkable in Fig. 3 is the high volatilization yield under the condition that the carrier-free isotopes of molybdenum and tungsten were collected on C aerosol particles. The influence of the MoO_3 carrier on the volatilization yield has to be studied further.

From kinetic volatilization studies with the short-lived tungsten isotope ^{165}W ($t_{1/2}$ = 5.1 s) the overall transportation time was evaluated. With regard to the study of element 106 the resulting 11 - 20 s are promising. However, isothermal gas chromatographic

experiments have to follow.

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GAS CHROMATOGRAPHIC STUDIES OF MOLYBDENUM IN HUMID OXYGEN

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In previous experiments molybdenum as a homologue of element 106 was volatilized completely at 1400 K if argon with admixtures of humid oxygen was used as the carrier gas /1/. In a thermochromatographic quartz column the molybdenum was transported down to 400 K and deposited in a wide temperature range. Without admixtures of $H_2O_{(g)}$ the molybdenum was deposited at 1400 K. The volatility of molybdenum in humid oxygen may be interpreted with the formation of a rather volatile hydroxide, $MoO_2(OH)_{2(g)}$, which either is chemically stable and remains unchanged during its transport in the temperature gradient tube /2/ or dissociates according to the chemical transport reaction (1).
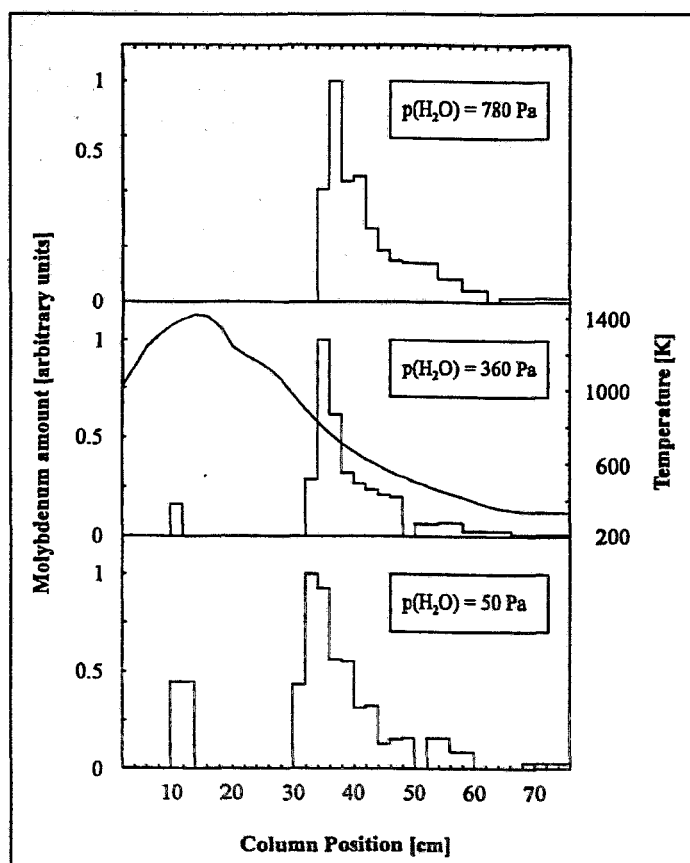
$$MoO_2(OH)_{2(g)} \quad \leftrightarrow \quad MoO_{3(ads)} + H_2O_{(g)} \qquad (1)$$

Fig. 1: Thermochromatographic distribution of molybdenum in trace amounts at different water partial pressures $v_0(Ar) = 1.0$ l/min, $v_0(O_2) = 0.5$ l/min

Further thermochromatographic studies have been carried out to identify the elementary transport processes. In off-line experiments the influence of water vapour on the chromatographic behaviour of trace amounts of molybdenum has been studied.

Isotopes of molybdenum were produced by thermal neutron induced fission of ^{235}U ($\rightarrow^{99}Mo$) or in the bombardment of natural zirconium with α-particles ($\rightarrow^{93m}Mo$), respectively, and transported out of the target chamber by means of a gas jet system. MoO_3 or C were used as aerosol particles, Ar or He as the carrier gas. The aerosol particles were collected on a paper filter. It was positioned in the quartz column in front of a quartz wool plug and burned carefully. In some cases molybdenum was released from thick zirconium foils (20 μm) by heating up the zirconium to

1470 K in humid air /3/. The experimental set-up was almost the same as described earlier /1/. A mixture of argon and humid oxygen in a ratio of 2:1 was used as the carrier gas in the thermochromatographic experiments. The distribution of molybdenum in the columns was measured off-line in 2 cm sections by γ-spectrometry. As seen from Fig. 1 the position of the peak maximum depends on the partial pressure of water. Therefore we conclude that the transport in the temperature gradient tube is governed by the complex transport reaction.
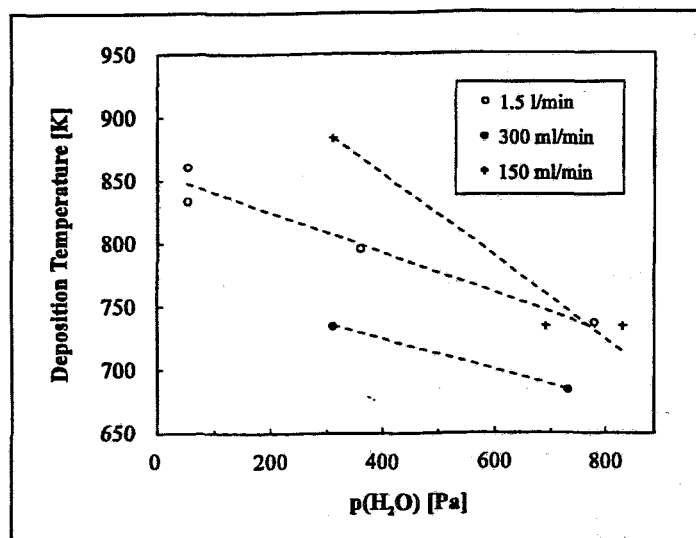

Fig. 2: Deposition temperatures of molybdenum in trace amounts as a function of the partial pressure of water at different gas throughputs.
The temperature profiles were differently at various flow rates.

As depicted in Fig. 2, the deposition temperature depends on both the gas flow rate and the humidity of the carrier gas. For calculating $\Delta H°_{ads}$ a formalism was used which was published recently for transport reactions like (1) /4/. As resulting adsorption enthalpies we got $\Delta H°_{ads}$ = (-65.7 ± 5.2) kJ/mol at v_0 = 1.5 l/min and $\Delta H°_{ads}$ = (-55.9 ± 1.8) kJ/mol at the lower flow rates. The given uncertainty is the standard deviation. The difference between the enthalpy values may be due to the high uncertainty of the deposition temperature (± 50 K). Considering this value in the calculation of $\Delta H°_{ads}$ the margins of error overlap. Further a constant temperature gradient is assumed in the calculation but couldn't realized experimentally. Non-equilibrium conditions at the phase border at high flow rates and the modification of the quartz surface by impurities or weighable molybdenum amounts could be other reasons for these deviations.

The use of MoO_3 instead of C as cluster material is an addition of an inactive carrier to the molybdenum isotopes. The molybdenum quantity varied from carrier-free to 0.7 µg as determined by neutron activation analysis at the SAPHIR reactor. In this concentration range no essential difference in the chromatographic transport behaviour was observed. Systematic studies in a broader concentration range have to be continued.

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