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M. Lochny[a]; B. Bisplinghoff[a]
[a] Institute for Safety Research and Reactor Technology, Jülich, Germany

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HPLC FOR FAST CHARACTERIZATION OF CONTAMINANTS IN STRUCTURAL MATERIALS OF A PEBBLE-BED REACTOR

M. Lochny* and B. Bisplinghoff

Institute for Safety Research and Reactor Technology,
Forschungszentrum Jülich GmbH,
D-52428 Jülich, Germany

ABSTRACT

As part of the preparations for waste disposal from the Jülich Experimental Nuclear Power Plant high-temperature reactor, an analysis system was developed at the Institute for Safety Research and Reactor Technology of Forschungszentrum Jülich GmbH with the aim of identifying and quantifying 47 nuclides from both metallic and ceramic materials. In addition to the conventional wet-chemical separation schemes, high-performance liquid chromatography was used on an analytical scale for the determination of most β-emitters and of those nuclides that decay via electron capture. The associated advantages and drawbacks, as well as the problems encountered and their solutions, are explained with the aid of selected chromatograms.

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*Corresponding author. Fax: 02461 61 2450; E-mail: m.lochny@fz-juelich.de

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INTRODUCTION

In 1987 the 15 MW_{el} AVR reactor (AVR: Experimental Nuclear Power Plant) at the Research Center Jülich was put into its postoperational phase. Up to then, the reactor had been operated for 21 years for completion of various experiments. In the course of this time, approximately 300,000 spent-fuel elements were produced, have been transferred from the reactor well into 115 Castor casks, and interim-stored on the premises of Forschungszentrum Jülich GmbH. A decision on the disposal strategy is still pending. Meanwhile, the exact nuclide inventory of the structural materials is being planned.

Due to numerous out-of-specification experiments and because no samples were retained in the construction phase of the reactor, the nuclide inventory cannot be exactly determined through calculations. A precise chemical and radiochemical analysis of various structural materials in different locations was necessary. In the last months of 1998, a hole was drilled from outside into the core for visual inspection and sampling in the order of 1) inner reactor vessel (steel), 2) thermal shield (steel), 3) reactor shuttering (steel), 4) carbon brick, and f) graphite (see Fig. 1). The 50-cm-thick carbon brick layer assumed the function of shielding and thermal insulation; the graphite layer, also 50 cm in thickness, represented the reflector.

Accordingly, the investigation of the drilling samples comprises 3 different matrices: steel, carbon brick, and graphite. Their different conditions and compositions governed the procedure for analysis presented in this study. We first present the separation scheme developed and conclude with a description of the high-performance liquid chromatography (HPLC) results.

With respect to the nuclides formed in the course of the operating phase, we assumed beforehand that graphite internals, having absorbed a high neutron dose over a long period, are relatively strongly contaminated with fission and activation products. The level of nuclides depends on the purity of the structural

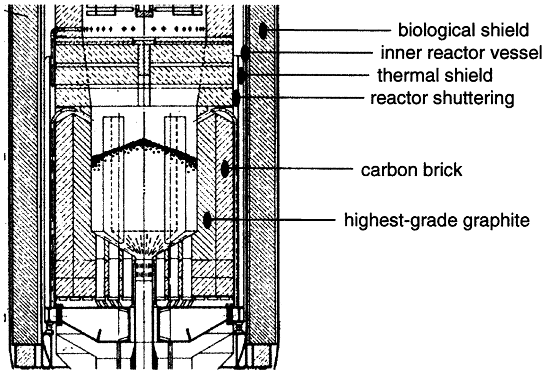

Figure 1. Longitudinal section of the core of the AVR reactor and its surrounding structures (12).

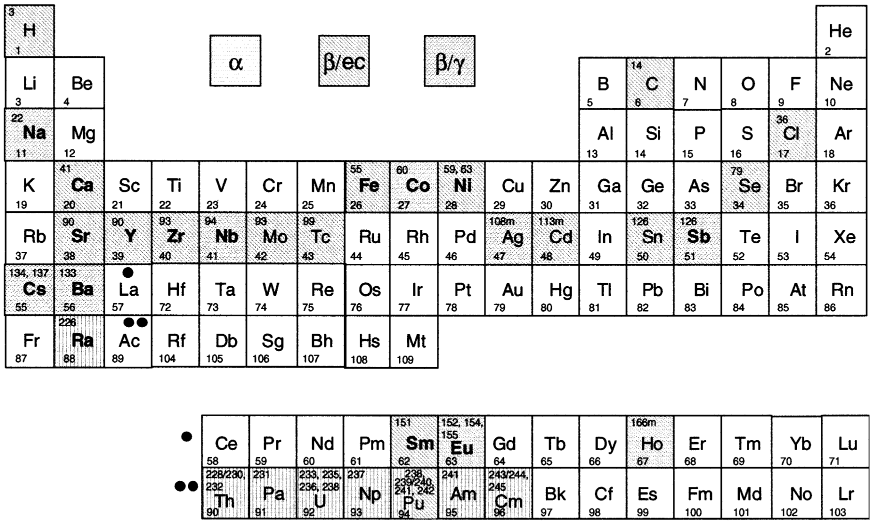

Figure 2. Spectrum of nuclides of the AVR analysis system (shaded-line fields with mass numbers of nuclides to be determined). All elements determined by HPLC are in bold face, ^{55}Fe and ^{60}Co to be determined only in graphite and carbon brick but not in metal samples.

material and its position in the reaction zone. Fission product migration is probably enhanced by the high temperatures prevailing in the reactor. All steel internals should exhibit a lower degree of contamination because they were shielded by graphite materials.

The AVR GmbH contractor defined a total analysis scope of 47 nuclides to be determined. The scope is based on the list of nuclides that would need to be declared in the event of decommissioning the reactor. In addition, the list serves to confirm experimental conditions and allows for adjustment of the nuclide vector to real conditions. For the sake of clarity, the nuclides are shown in the periodic table of elements in Fig. 2. They are divided according to their type of radiation into α-emitters, β-emitters and those with electron capture (ec), and γ- and β/γ-emitters.

Analyses of radioactive digestion solutions with a high matrix content, also with preconcentration of the solutes, have been performed by HPLC with respect to many metals and metalloids (Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg, Pb, Se, and Te) (1,2). The simultaneous separation of alkaline earth metals, even in combination with 9 other metal elements, with high-resolution in less than 1 hour through the use of different HPLC systems is described elsewhere (3,4,5). The coupling of HPLC and on-line scintillation counting for the analysis of non-gamma-emitting radionuclides has been proposed (6,7). Our challenge in the present work was to deal with the 3 different matrices of steel, carbon brick, and graphite and to analyze a total of 47 nuclides. HPLC was identified as an ideal method for completely separating 18 of the 47 nuclides. None of the above-mentioned methods could fulfill the requirements for this analytical task.

EXPERIMENTAL

Technical Equipment and Chemicals

The HPLC system used consisted of S1020 and S1100 solvent delivery systems with analytical 2-piston pumps and a column oven with S4010 control unit (Sykam GmbH, Gilching, Germany), which kept the column constantly at 70°C. The samples were introduced into the system from a 250-μL loop through a manual Rheodyne injection valve (model 9125, Rheodyne L.P., Cotati, Calif, USA) and separated on the Aminex® A9 cation exchanger (Biorad Laboratories, Hercules, Calif, USA) in a 250 × 4.6 mm column of polyether ether ketone at flow rates of 0.5 and 1.0 mL/min.

For on-line detection, an LB 506 C-1 radioactivity monitor (Berthold GmbH & Co KG, Bad Wildbad, Germany) equipped with a solid scintillator measuring cell of the WUW SL type (Forschungszentrum Jülich GmbH, Germany, vol $\approx$ 350 μL) (8) and a UV/VIS detector model 200 (Linear Instruments Corporation, Reno, Nev, USA) were connected in series. The latter detected inactive components in the μg/g range at a wavelength of 648 nm after postcolumn derivatization with arsenazo III (Aldrich-Chemie, Steinheim, Germany). The energy window of the radioactive monitor was completely opened to detect the largest possible number of decay events.

For exact quantification, the effluent was fractionated and measured off-line by liquid scintillation counting (LSC). The fraction collector, Cygnet™, was from Isco Inc (Lincoln, Neb, USA); the off-line LS counter TriCarb® 2200 and the liquid scintillation cocktail Ultima Gold™ AB were from Packard Instrument Co (Meriden, Conn, USA).

Mixtures of citric and ascorbic acids with differing small amounts of ethylenediamine (EDA) of puriss. p.a. purity from Fluka Chemie AG (Buchs, Switzerland) were used as the mobile phase. The elution solutions were prepared with ultrapure water ($R > 18$ MΩ, Elgastat-Maxima-HPLC, Elga Ltd, Bucks, UK). The Dowex® 1X8 anion exchanger involved in sample preparation was obtained from Dow Deutschland Inc (Rheinmünster, Germany).

Separation Scheme

A total α-analysis was performed for each of the samples, and if required, a single determination was made with the α-spectrometer. All γ-emitters were identified and quantified by high-resolution γ-spectrometry. As a rule, the lowest detection limits of β/ec-emitters are achieved with liquid scintillation counting (LSC) in off-line operation but only for spectra of a pure nuclide. If a mixture of several β/ec-emitters is present, interferences occur in the spectrum that impede or make impossible an evaluation. The mixture must be separated into its single components. The application of HPLC is an efficient method for this purpose.

Figure 3 schematically shows the AVR analysis system. The HPLC located at the bottom of the scheme was used for the fine separation of the nuclides specified. The nuclides in brackets were simultaneously determined through other methods.

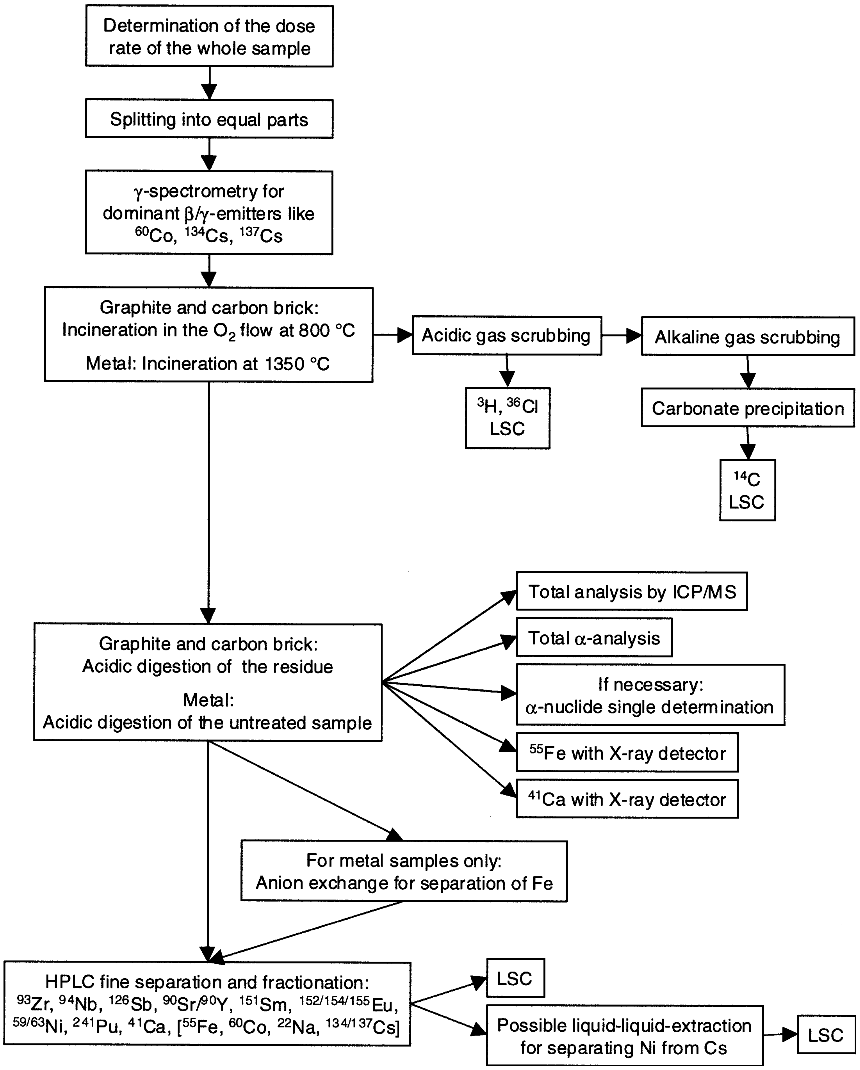

Figure 3. Simplified scheme of the AVR analysis system.

Sample Preparation/Pretreatment

Graphite and Carbon Brick

Because the ceramic materials could not be wet-chemically digested, they were thermally converted with oxygen at 800°C in quantities between 0.4 and 1.2 g. The combustion apparatus specifically developed for this purpose, which is described in detail in (9), was designed so that it could be set up in a glovebox and minimize the discharge of highly volatile elements. Only the elements H, C, Se, and Tc were passed from the combustion chamber into the connected washing bottles in the form of oxygen compounds. The remaining ashes were brought into solution in a mixture of HNO_3, H_2O_2, and HBF_4 in a microwave pressure digestion apparatus, evaporated to dryness, and taken up in approximately 10–20 mL of 0.15 mol/L HNO_3.

Metal

The nuclides ^{3}H and ^{14}C were quantified after combustion in a normal tube furnace at approximately 1350°C. For the determination of all the other nuclides, between 0.4 and 1.2 g of the starting material was dissolved in boiling concentrated subboiled HCl, converted with H_2O_2 into the most stable oxidation stages ($Fe(II) \rightarrow Fe(III)$), evaporated to dryness, and taken up in approximately 15 mL subboiled 9 mol/L HCl.

Because steel samples contain large amounts of iron, the capacity of the HPLC cation-exchanger column would be exhausted; therefore, iron must be separated in a prior step. Fe separation was effected via a precleaned Dowex® 1X8 anion exchanger column. After feeding the 9 mol/L hydrochloric sample solution, the column was washed with 9 mol/L HCl. The resin, which contained Fe, Co, U, Pu, B, Cd, Mo, Cu, Mn, and Ag, was rejected. Together with the iron, ^{60}Co was also quantitatively fixed on the column as a main activity source. A disadvantage of this method was the subsequent exclusion of ^{55}Fe and ^{60}Co determinations in the metal samples by HPLC. The eluate collected was evaporated to dryness and taken up in 5–10 mL 0.1 mol/L HCl.

RESULTS AND DISCUSSION

HPLC Separation Methods and Application

In the preparation phase, separation methods were developed on the basis of the high-capacity Aminex® A9 cation exchanger, which had already proven efficient in actinoid and lanthanoid partitioning (10). In numerous preliminary tests, the retention times of the individual elements were determined through the use of pure HPLC standard solutions. Because problems were expected with the different matrices, the samples were inactively supported with a mix of all the elements to be separated by HPLC. Approximately 10 μg/g of each support material was injected into the column.

Three separations and 1 flushing method are presented in which the following elements were identified: Zr, Nb, Sb, Na, Cs, Y, Eu, Ni, Sm, Co, Fe, Ca, Sr, and (Ba, Ra).

Zr, Nb, and Sb always eluted near the dead time of roughly 2 minutes. For the samples for which a quantification of the nuclides ^{93}Zr, ^{94}Nb, and ^{126}Sb was required, only a detection limit was specified. The detection limit ranged from 20 to 330 Bq/g of metal or carbon material and depended on the concentration of other radionuclides with the same retention time. For a more precise determination of the 3 nuclides, a special treatment of this fraction would have been necessary.

Ni and Cs were found in the same fraction by some of the methods. Ba and Ra could have been partitioned without any problem, but their resolution was unnecessary.

All the samples examined by HPLC contained so low volume-specific α-activities that they did not disturb the LSC determination of the other emitters. If this had not been the case, we would have partitioned them beforehand by solid-phase extraction on the Actinide Resin™ from Eichrom (Eichrom Europe, Paris, France).

Separation of Sr and Y

^{90}Sr and ^{90}Y were present in secular equilibrium. For this reason, one of their nuclides is sufficient for their quantification. Sr was selected because it is much more strongly bound by the ion exchange resin than is Y and most of the other nuclides considered. Thus the easiest way for Sr partitioning was to find a separation method that results in a late elution of Sr and an early rinse of all the other metallic elements. The eluent composition for which interferences with other nuclides can be completely ruled out and the Sr is eluted with an acceptable retention time was 0.1 mol/L citric acid, 0.02 mol/L ascorbic acid, and 5.0 mL/L EDA at pH = 4.01 and 1 mL/min. Figure 4 shows the separation of Sr from a carbon brick sample as an example.

Figure 4 shows that even Ca, with a comparatively very strong affinity for the cation exchanger, eluted after approximately 18 minutes, whereas Sr had almost double the amount of retention time. The other elements examined, Zr, Nb, Sb, Y, Eu, Ni, Sm, Co, and Fe, eluted near the dead volume together with a fraction designated "rest." Apart from the alkaline earth metals, only the alkali metals, of which Na is specified for the standard solution and Cs for the carbon brick sample, showed a slightly stronger bond to the ion exchange resin than the other

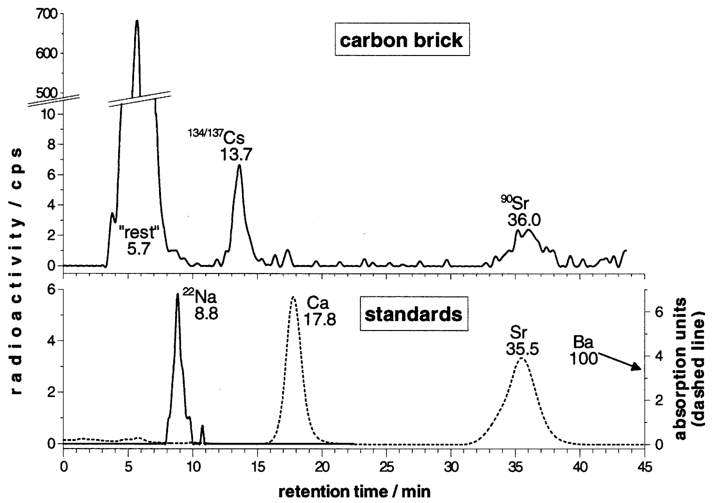

Figure 4. Separation of Sr from a carbon brick sample with 0.1 mol/L citric acid, 0.02 mol/L ascorbic acid, 5.0 mL/L EDA. pH ≈ 4.01 at 1 mL/min. The peak named "rest" includes the elements Zr, Nb, Sb, Y, Eu, Ni, Sm, Co, and Fe; thus it is much higher than the other 2 peaks in this chromatogram.

metals of the peak "rest". For the Ba shown in the chromatogram, which eluted much later and in a wide interval of 80–105 minutes, an even higher concentration of EDA or the gradient technique is recommended. The same techniques should be applied to Ra, which leaves the column long after Ba. Its exact retention time was therefore not determined. The retention times of the metals considered are summarized in Table 1.

Table 1. Summary of the Retention Times Determined for the Sr, Y Separation

Element(s)	Rounded Retention Time (min)	Interference
Zr, Nb, Sb, Y, Eu, Ni, Sm, Co, Fe	6	no separation
Na	9	—
Cs	14	—
Ca	18	—
Sr	36	—
Ba	100	—

Separated with 0.1 mol/L citric acid, 0.02 mol/L ascorbic acid, 5.0 mL/L EDA, pH = 4.01, at 1 mL/min.
— No interference.

Separation of Y, Eu, and Sm

The separation of Eu and Sm through the use of 0.1 mol/L citric acid with EDA was not successful. Although it was possible to shift the retention times at different EDA concentrations, this did not affect the excessively small selectivity difference for these 2 metals. A significant difference in the selectivity for Eu and Sm, described in (10), is based on an eluent of 0.4 mol/L citric acid and 0.02 mol/L ascorbic acid with pH = 2.90. In comparison, the pH value was further lowered to 2.82 and the flow rate reduced to 0.5 mL/min to point out the difference more clearly.

Measurements were made with a UV/VIS detector, as required, following a postcolumn derivatization. Because most transition metals (not Y) form color complexes with the PAR azo dye, we stained the lanthanoid metals with arsenazo III. In contrast to PAR, this dyeing process has the advantage that in low concentrations (0.1 mmol/L metal at 0.05–0.1 mL/min versus 1.0 mL/min of the eluent) it only influences the subsequent LSC measurement marginally through a color quench; that is, the LSC spectrum is shifted to lower energies. A correction of the measured activity is not necessary because the number of counts remains unmodified. Support with corresponding inactive metal solutions of the order 10 μg/g per element is considered a prerequisite for this type of detection. In the case of radioactivity concentrations below the detection limit, inactive support is necessary if the measurement is to be pursued on-line via a UV/VIS detector. Slight changes in the system (aged eluent solution, aged column material, matrix effects, etc.) can then be detected on-line, and one can immediately respond to them and cleanly cut the desired fractions.

The task was to separate Sm so that ^{151}Sm could be determined in addition to the 3 relevant Eu isotopes: ^{152}Eu, ^{154}Eu, and ^{155}Eu. As can be seen from Fig. 5 and Table 2, this method is also suited for the quantification of ^{90}Y because the interval of approximately 35 to 70 minutes in which it elutes remains free from interferences by other fission and activation products.

The elements that eluted before Y, such as Zr, Nb, Sb, Na, and Cs, are below the respective detection limits; the data representing those that eluted after Sm, such as Ni, Co, Fe, and the alkaline earth metals are cut off in the chromatogram.

The differences in the peak heights of the inactive signal (broken line) are due to different flow rates of the dye fed. The slight shift in retention times is due to the aged elution solution.

Zr, Nb, Sb; Na, Cs, Y, Eu, Ni; and Sm, Co, Fe in Metal, Carbon Brick, and Graphite Samples

A higher concentration of the EDA pusher in the eluent not only led to shorter retention times but simultaneously causes a sharpening of the peak in the

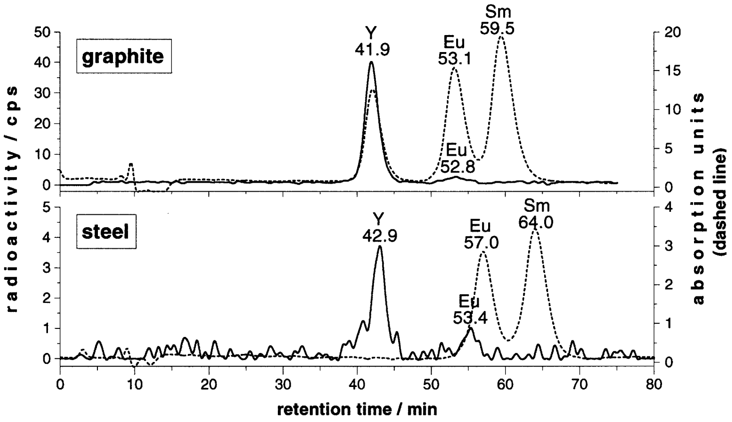

Figure 5. Fine separation of Eu and Sm from a graphite and a steel sample. The UV/VIS signal is possibly due to Y, Eu, and Sm inactive traces (μg/g scale). Elements eluting before Y, such as Zr, Nb, Sb, Na, and Cs, are below the limit of detection; those eluting after Sm, such as Ni, Co, Fe, and the alkaline earth metals are cut.

chromatogram. The metal ions eluted earlier and the cut fractions were smaller. For the metal samples, the eluent consisted of 0.1 mol/L citric acid, 0.02 mol/L ascorbic acid, and 1.8 mL/L EDA at pH ≈ 2.95. An associated characteristic chromatogram is shown in Fig. 6, and the corresponding data are presented in Table 3.

The total maximum α-activity was determined to be 100 Bq/g for all metal samples. All the actinoids were eluted in the range up to Na (not specified here) under the conditions selected.

Only the activity of ^{90}Y caused a visible peak. Apart from Sm, Y and Eu were determined according to a different method (see Separation of Y, Eu, and Sm), which made the overlapping of their peaks in the chromatogram meaning-

Table 2. Retention Times and Interferences for the Y, Eu, and Sm Separation

Element(s)	Rounded Retention Time (min)	Interference
Zr, Nb, Sb, Na, Cs	<40	strong interference
Y	42	—
Eu	53	slight interference
Sm	60	slight interference
Ni, Co, Fe, etc	>70	meaningless

Separation with 0.4 mol/L citric acid and 0.02 mol/L ascorbic acid, pH = 2.90, at 0.5 mL/min.
— No interference.

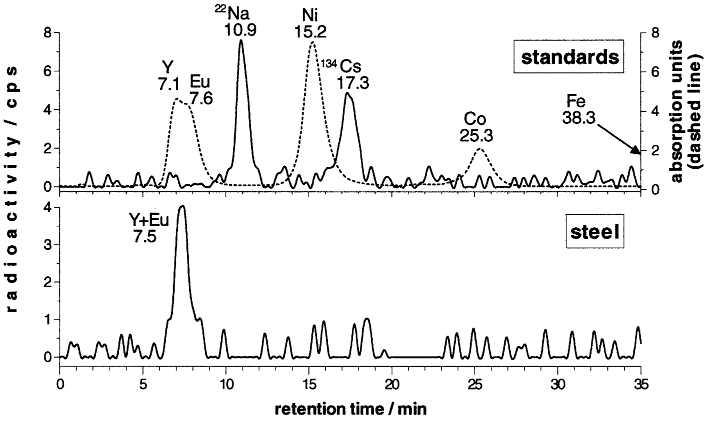

Figure 6. Partitioning of the nuclide inventory of a steel sample after an anion exchange process. Apart from Y and Eu, the concentrations of radionuclides are below the limit of on-line detection.

less. The other metals had concentrations below their on-line detection limits. Their position in the chromatogram can be read from the elution of the standards.

The accelerated partitioning of the entire nuclide inventory by the higher concentration of EDA caused Ni to elute in a fraction with Cs (Fig. 6). This fraction was subjected to a liquid-liquid extraction with Cyanex® 301. The large fraction of approximately 7 mL from the HPLC was evaporated to 2 mL for this purpose and extracted with 2 mL 0.5 mol/L Cyanex® 301 in dodecane. The organic Cyanex phase contained ^{63}Ni and the aqueous phase contained the ^{134}Cs and ^{137}Cs isotopes. The recovery rate was 91%.

Table 3. Retention Times and Interferences for the Complete Separation of Metallic Samples

Element	Rounded Retention Time (min)	Interference
Y	7	strong interference
Eu	8	strong interference
Na	11	—
Ni	15	—
Cs	17	—
Co	25	—
Fe	38	—

Separation with 0.1 mol/L citric acid, 0.02 mol/L ascorbic acid, 1.8 mL/L EDA at pH ≈ 2.95 and 1 mL/min after anion exchange.
— No interference

For the carbon brick and graphite samples, due to the partially much greater nuclide inventory, the chromatograms were stretched. For this purpose, the concentration of EDA was lowered to 1.0 mL/L. The eluent consisted of 0.1 mol/L citric acid, 0.02 mol/L ascorbic acid, 1.0 mL/L EDA at pH ≈ 2.63.

As can be seen from the chromatograms in Figs. 7 and 8, the samples essentially contain the fission products Cs, Y, Eu, and Co, and even the graphite samples differed greatly from each other both with respect to total activity and activity distribution.

Possible actinides left the column before the Fe fraction, and Pu eluted after its lighter homologues in the region of the Co (see Table 4).

A peak for Sr is neither present in Fig. 6 nor in Fig. 7. Sr remained on the column much longer than did the double-retention time of the last relevant nuclide (^{55}Fe) and was only eluted under drastic conditions (flushing of the ion exchange resin). Quantification can only be performed with the aid of the Y peak.

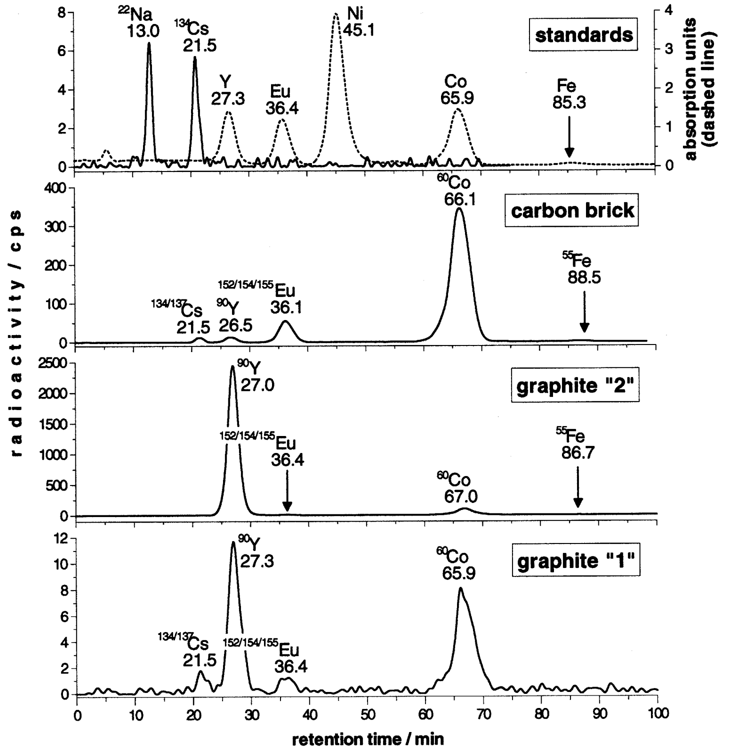

Figure 7. Partitioning of the nuclide inventory of a carbon brick sample and of 2 different graphite samples.

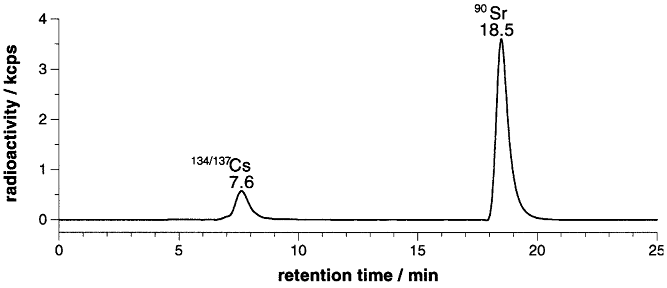

Figure 8. Typical chromatogram of a scrubbing elution. Residual quantities of dragged-along Cs are easily recognized.

Nuclides eluting very late, such as ^{90}Sr or ^{133}Ba, are so strongly bound by the ion exchange resin under the conditions selected that they were only eluted from the first sample feed after elution of the last relevant element (Fe) of the second run. This means that a cleaning step was not necessary after each measurement but only after every second measurement.

Flushing the Ionic Exchange Resin

Prior to each measurement, the column was checked to ensure that it was free of residues from previous separations and thus cross-contamination was deterred. For this purpose, the resin was cleaned after each or after every second

Table 4. Retention Times and Interferences for the Complete Separation of Carbon Samples

Element	Rounded Retention Time (min)	Interference
Na	13	—
Cs	22	—
Y	27	—
Eu	36	—
Ni	45	—
Co	66	—
Fe	85	—

Separation with 0.1 mol/L citric acid, 0.02 mol/L ascorbic acid, and 1.0 mL/L EDA at pH ≈ 2.63 and 1 mL/min.

measurement with a scrubbing eluent as described in the previous paragraph. The eluent should not differ too much from the separation eluent so that the subsequent equilibration time is not unnecessarily prolonged. Therefore, a mixture of citric acid, ascorbic acid, and EDA was also used in concentrations of 0.4 mol/L, 0.02 mol/L, and 20 mL/L. The solution reached a pH value of approximately 3.9.

After flushing the ion exchanging medium, it must be rinsed by the separation eluent until the system is equilibrated and a reproducible retention time can be obtained in the next run. The flushing and equilibration of the ion exchange resin required approximately 90 minutes to completion, but this process is the only way spreads can be prevented.

As can be seen from Fig. 8, part of the Cs is only removed from the resin by the scrubbing eluent. This indicates that Cs possibly assumes 2 different bonding states on the resin caused by the matrix, which leads to 2 peaks. In addition, ^{134}Cs and ^{137}Cs were jointly eluted and could only be determined separately with insufficient accuracy by off-line LSC, which is dependent on the share of the isotopes in the total Cs activity. After running HPLC analysis, we chose therefore not to quantify Cs by LSC, and completed only the γ-spectrometry analysis.

In accordance with the dimensions of the analytical HPLC column and the feed quantities expected, the feed volume was limited to 250 μL. As a rule, digestion solutions that contained between 0.4 and 1.2 g substance in a 10–20 mL acid solution were used. The absolute activity concentrations fed into the column only amounted to 1.25–2.5% of the total activity of a sample aliquot and the absolute quantities varied between 5 and 30 mg. This amount provides relatively high detection limits, which were determined as 5–500 Bq/g of metal or carbon material as determined by AVR analysis.

Sample Posttreatment

The fractions collected from the HPLC exhibited volumes greater than 2 mL. Volumes of this size cannot be directly used for the off-line LSC measurement because of the danger that they will not be mixed homogeneously or as single phases with the LSC cocktail. Therefore, the volume of such fractions was previously reduced to approximately 2 mL under an ebullator supported by a heating plate (approximately 80°C). All LSC samples were stored in a cool, dark place for approximately 2 hours prior to the measurement and after mixing with about 15 mL LSC cocktail to rule out luminescence, which might suggest a falsely high activity. For short-lived nuclides, such as ^{90}Y (β^-, 64.1 hour), the time between fraction sampling and LSC measurement must also be taken into account. However, if the ^{90}Y activity is determined with the aid of the activity of its much longer-lived parent nuclide ^{90}Sr (β^-, 28.5 years), this period can be neglected.

Problems Accompanying the Sample Posttreatment and Evaluation and Analysis

The evaluation of the LSC spectra was performed according to the method of Weise and Filss (11). In some cases, the mixed spectra of several nuclides were involved because no 100% separations were achieved through the HPLC for the following reasons:

1. In the case of great concentration differences between 2 elements eluting immediately one after the other, the minor component is found in the chromatogram as the shoulder of the principal component. In this case, the LSC spectra of the 2 emitters should significantly differ from each other.
2. By selecting the above method, we deliberately accepted that 2 elements were eluted simultaneously because the separation was satisfactory with respect to all the other components. In this case, too, the LSC spectra of the 2 emitters should significantly differ from each other or a further separation step was done, as was the case after the elution of Ni and Cs in metal samples (see also problems in HPLC separations).

Quantitative Data of Activities

Because of the existing contractual situation, no precise data can be published at this time, but the variations from the HPLC measurements can be specified: Due to the different location of sampling for each matrix, the samples showed great activity concentration differences. Thus, for example, the ^{63}Ni activity of the metal samples varied between the detection limit of 20 Bq/g and 14 kBq/g, but the highest value was determined as 136 kBq/g for a graphite sample. Whereas in carbon brick ^{55}Fe contents of 1–3 MBq/g were found, the values in graphite were lower by 1 to 2 orders of magnitude. As has already been mentioned in the Introduction, carbon brick is, due to its fabrication process, generally much more contaminated with transition metals than is graphite. Thus the carbon brick generates higher activities of radioactive isotopes, increasing with operating time of the reactor. Apart from this, the activation of the core-surrounding materials is a function of neutron flux, which is a square function of the distance from the fuel. Furthermore, built-in graphite structures in the core, so-called graphite noses, diminish the neutron flux and the activation immediately behind these noses. The diffusion of activation products into the first layers of the contaminated material, which is a function of the temperature, also must be considered during analysis. All the evidence presented suggests that the radioactivity levels are sensitive to the location where the samples were taken. Therefore, we were not surprised to find extreme differences (2 orders of magnitude for the ^{90}Sr and ^{90}Y content) of the graphite samples, ranging between 10 kBq/g and 1 MBq/g.

CONCLUSION

The use of HPLC in the radioanalysis of structural materials from a pebble-bed reactor provides advantages in the fine separation range of single elements. This concerns, in particular, β-emitters that should be quantified separately by the usual LSC method. The main characteristic of a β-spectrum is its continuity. A mixture of several β-emitters will lead to a sum spectrum, in which case the single components of the mixture cannot be assigned and defined precisely.

In this work, the pretreatment of drilled samples from a graphite-moderated reactor was reduced more through the use of HPLC than it had been in wet chemical procedures. This is due to the fact that HPLC is a multielement separation technique. However, the methods are restricted on an analytical scale because of the limited feed volume of less than 1 mL, which implies high detection limits in some cases.

If the HPLC separation method selected is designed so that the effluent contains a mixture of 2 elements, its combination with liquid-liquid extraction (see Ni and Cs separation) represents an ideal, efficient supplementation.

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