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The application of ICP-MS to direct actinide analysis

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ABSTRACT

The ICP-MS technique has been applied to the analysis of the actinide contents of corrodant solutions from experiments performed to study the corrosion of spent nuclear fuel in simulated groundwaters. Analysis was performed directly on the solutions, without employing separation or isotope dilution techniques. The results from two analytical campaigns using natural indium and thorium internal standards are compared.

Under both oxic and anoxic conditions, the U contents can be determined with good accuracy and precision. The same applies to Np and Pu under oxic conditions, where the solution concentrations range down to about 0.1 ppb. Under anoxic conditions, where solution concentrations are lower by one or two orders of magnitude, reasonable results for these two actinides can be obtained, but with much lower precision. Direct analysis of Am and Cm, however, gave unsatisfactory results, since the technique is limited by poor measurement statistics and background uncertainty.

SAMMANFATTNING

ICP-MS teknik har tillämpats på analysen av aktinidinnehållet i korrosions-
lösningar från experiment utförda för att studera korrosionen av utbränt
kärnbränsle i simulerade grundvatten. Analys utfördes direkt på lösningarna,
utan att använda separation- eller isotoputspädningsteknik. Resultaten jämförs
från två analyskampanjer där naturligt indium och torium använts som
internstandarder.

Under både aeroba och anaeroba förhållanden kan U innehållet bestämmas
med god noggrannhet och precision. Detta gäller också Np och Pu under
aeroba förhållanden, då koncentrationerna i lösningen stäcker sig ner till om-
kring 0,1 ppb. Under anaeroba förhållanden, då koncentrationerna i lösning-
en är en eller två storleksordningar lägre, kan hyggliga resultat erhållas för
dessa två aktinider, fastän med lägre precision. Direkt analys av Am och Cm
gav emellertid otillfredsställande resultat, eftersom tekniken begränsades av
dålig mätstatistik och osäkerheter i bakgrundsnivån.

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1 INTRODUCTION

Studies on the corrosion of spent nuclear fuel in natural groundwaters are being performed in several countries, including Sweden, as part of large programmes to demonstrate the feasibility of safe, permanent disposal in deep-rock repositories. The Swedish programme is managed by the Swedish Nuclear Fuel and Waste Management Co (SKB), a daughter company to the nuclear utilities, and most of the experimental work on spent fuel corrosion is performed in the Hot Cell Laboratory of Studsvik Nuclear at Studsvik. The fuel corrosion data is included in the safety analysis performed and periodically updated by SKB, and which is subjected to stringent review by independent authorities. Although the corrosion tests are performed over a period of years, a safety analysis must span a timescale of perhaps 10^6 years. Clearly, against this chronological background, the extrapolation of experimental results from corrosion tests alone is an inadequate basis for safety analysis, which must be based firmly on the identification and quantification of the corrosion processes involved.

In the experimental programme in the hot-cells, which has been in progress since 1982, short (20mm long) specimens of spent fuel and clad are exposed to corrosion under both oxic and anoxic conditions in a synthetic groundwater (123 ppm HCO_3^-; pH 8.0-8.2). Deionized water and a saline groundwater are also used as corrodants. A sequential corrosion scheme is usually employed such that the corrodant is replaced with fresh solution after predetermined contact periods. Several 10 ml aliquots of the leachant are centrifuged through membrane filters with nominal apertures of 1.2 - 2.0 nm (Amicon Corp., USA) The empty leaching vessels are stripped of possible adsorbed material by exposure for a few days to 5M HNO_3/0.5M HF. All specimens have hitherto been subjected to an analytical programme including laser fluorescence (U), alpha spectrometry (Pu, Cm), gamma spectrometry (gamma-emitting fission products) and radiochemical separation and beta-counting (Sr, Tc). A review of the status of the Swedish programme as of late 1991 has been published recently /1-1/.

2 APPLICATION OF THE ICP-MS TECHNIQUE TO RADIOACTIVE MATERIALS

The accumulated results obtained over the past 10 years using the analytical programme mentioned above,have given a good understanding of the corrosion of spent fuel /1-1/. However, there is still some uncertainty in distinguishing between chronologically overlapping processes, and their quantification. It was recognized that the opportunities for multi-elemental analysis offered by the ICP-MS technique could appreciably extend the analytical menu and provide data on the corrosion behaviour of elements of little or no radiological significance, but which could help to elucidate the processes involved. Further, it was thought that the analytical workload possible with the ICP-MS technique would replace all other methods used previously. Accordingly, a VG Elemental PlasmaQuad (Fisons Instruments) was ordered in 1991, and, after a non-radioactive test-run period, installed in a glovebox with a ventilation system for radiological use. The instrument was commissioned for radioactive use in June 1992. Figure 2-1 shows the instrument and sample-changer as installed in the Hot Cell Laboratory.
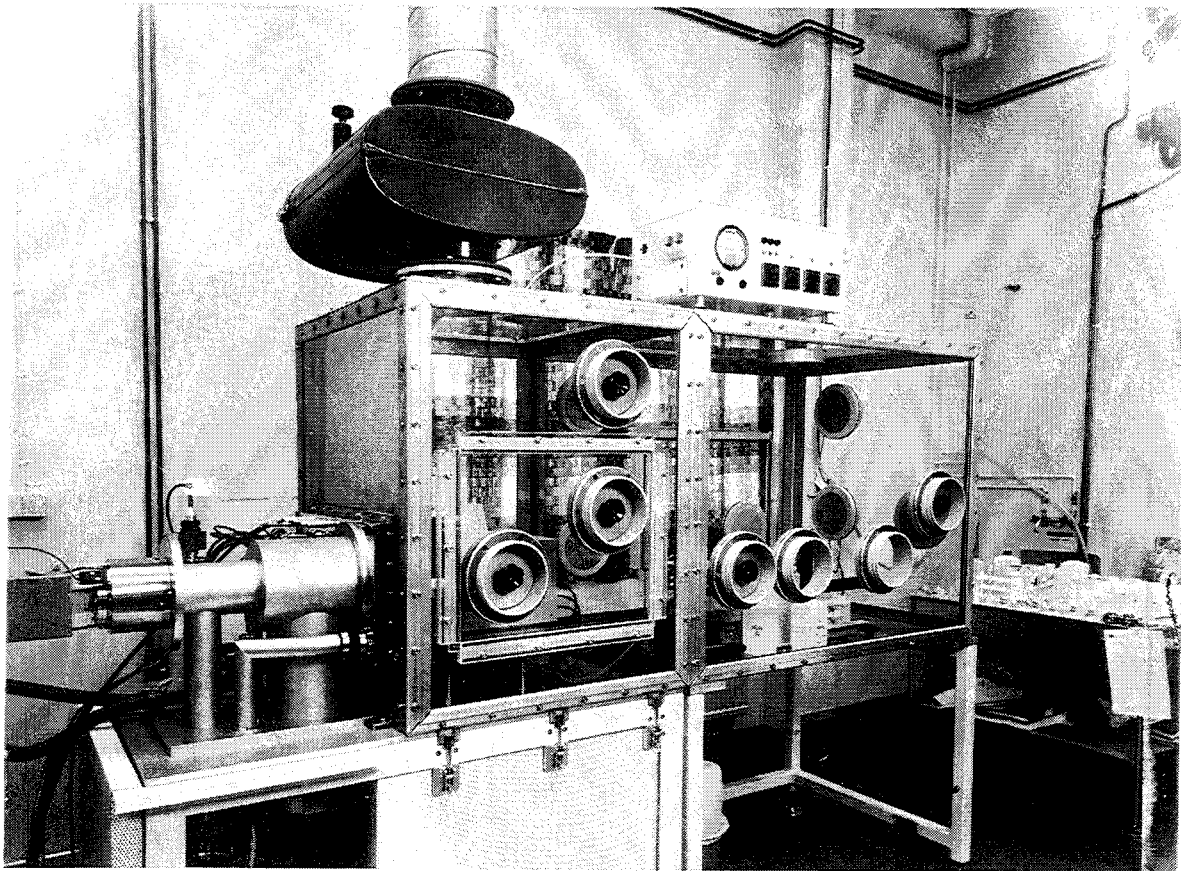

Figure 2-1. The VG PlasmaQuad installed in its glovebox.

The VG PlasmaQuad is delivered with software for both automatic instrument operation and full data treatment up to reporting of elemental concentrations in the samples examined. This latter software, however, is based on a library of isotopic compositions relevant to the lithosphere, and is, therefore, unsuitable for application to samples containing fission products (FP) and actinides, where the isotopic compositions depart significantly from those in the lithosphere. Further, the isotopic compositions of radioactive specimens can vary from sample to sample depending on the enrichment of the original fuel, the irradiation conditions, burnup and decay time.

As a consequence of these factors, the pattern of isobaric interferences in FP/actinide samples will differ from those in lithospheric materials, and will not be predictable other than by calculations performed external to the instrument. Thus, it was decided that data treatment should be performed on an individual sample basis using PC spread-sheets, where sample-related variables could be better accommodated.

At the current time, two PC-based spreadsheets have been developed for data treatment and background correction, but are subject to periodic modification and extension as experience with their application to routine analysis accumulates.

The first of these, the General Spreadsheet (GSS), concentrates mainly on the fission products but scans peaks over much of the mass range 82 to 244. The main aim of the spreadsheet is the automatic correction for Kr and Xe in the argon used, and for isobaric interferences, although these are presently restricted to the fission products, as their interferences are more amenable to accurate calculation. Such calculation can, in practice, only be performed with the help of fuel irradiation codes. The code used here is ORIGEN-2 (benchmarked by destructive analysis of reference fuel specimens; see below) which was used to generate inventories of fission products and actinides in fuel irradiated to a range of burnups (21.2 to 49.0 MWd/kgU) and different decay times. The fuel and irradiation parametersused for the calculations were those for the bottom stringer rod from Ringhals-1 BWR, which is described in more detail below, and, which served as the spent fuel source for the analytical programme described here.

The calculations showed that, for the fission products, the effect of burnup on both total inventory and isotopic composition, and hence the problem of isobaric interference, was most pronounced for nuclides on the high mass side of the low mass fission yield peak as the plutonium/uranium fission ratio increased.Correction for isobaric interference, however, was found relatively straightforward,and as a first step, two basic versions of the general spreadsheet with correction terms for two burnup levels, 25.0 and 49.0 MWd/kgU, were developed. Details of the isobaric correction method for fission products, (which is based on selection of key nuclides and isotopic ratios calculated by means of the ORIGEN code), together with background subtraction methodology, will be reported elsewhere.

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For the actinides, however, total inventories and isotopic compositions are strongly dependent on both irradiation conditions (particularly the neutron spectrum), the fuel burnup and radioactive decay, and their accurate calculation with the ORIGEN code is difficult. Hence,corrections for isobaric interferences, which will be described below, are applied later to the spreadsheet.

The second spreadsheet, the Actinide Spreadsheet (ActSS), is restricted to a peak scan only over the mass range 220 to 255, thus saving instrument time, and has been directed more towards an attempt to determine Am and Cm nuclides directly on the samples, and for this purpose isotopic compositions of the actinides in the inventory specimens (see below) have been determined by ICP-MS after ion exchange separations.

3 EXPERIMENTAL

3.1 SPENT FUEL CORROSION TESTS

The Swedish spent fuel corrosion programme consist of a series of experimental sub-programmes using several reference fuels of different types and irradiation characteristics, and different patterns of corrosion tests. This paper descibes the application of the ICP-MS technique to analysis of samples from the Variable burnup / variable linear heat rating experiment, where the dependence of fuel composition on burnup is particularly marked. The spent fuel used in the tests was from a bottom stringer rod which had been irradiated during 8 cycles in the Ringhals-1 BWR.

Figure 3-1 presents a gamma scan of the rod together with a cutting plan which shows the position of the fuel specimens relevant to this paper. An extensive post-irradiation examination programme was also performed on the rod. The local fuel bulk burnup along the higher enriched section of the fuel column varied from 21.2 to 49.0 MWd/kg U. Since the local linear heat-rating was proportional to the burnup, the rod was well-suited to the main aim of this test, which was to investigate the effects on corrosion of migrational effects and structural changes in the fuel during reactor operation. Sixteen sections of fuel/clad were used for the corrosion tests and two shorter sections (L, H) for burnup and inventory determination.

The results of the actinide determinations on the inventory specimens, which were performed by means of a combination of ICP-MS analysis of the dissolved specimens and isotopic analysis of separated Pu using a Varian solid source instrument,are also shown in Figure 3-1. The build-up of higher mass number nuclides with burnup is clearly seen. The burnups of the 16 corrosion test specimens were calculated from the burnup values on the 2 inventory specimens and Cs-137 determination (NDE) on individual fuel pellets. Specimen actinide contents and isotopic compositions were derived by interpolation between the values given in Figure 3-1 using composition/burnup relations calculated in a series of ORIGEN runs.

The corrosion tests,which were started in March 1990, have so far consisted of 8 completed contact periods of varying length; the 9th is still in progress. The direct actinide analysis described here was applied to centrifugate specimens from the 8th contact period. Ten of the sixteen fuel specimens were corroded in the synthetic bicarbonate groundwater (see above) under oxic conditions (50 cm^3 of static air above the solution), while the remaining 6 were corroded in the same groundwater under nominally anoxic conditions produced by flowing 5%H$_2$ /Ar over the solution surface. Details of experimental parameters are given in Table 3-1.

ACTINIDE INVENTORIES

Micrograms/g U

INV-L 25.0 MWd/kgU	NUCLIDE	INV-H 49.0 MWd/kgU
236.1	Np-237	502.9
3943.7	Pu-239	3911.0
1821.6	Pu-240	3136.3
522.8	Pu-241	914.2
241.9	Pu-242	1233.7
216.8	Am-241	324.0
25.7	Am-243	254.2
2.00	Cm-244	90.70

| L | 11-1 | 11-2 | 11-3 | 11-4 | 11-5 | 11-6 | 11-7 | 11-8 | 11-9 | 11-10 | 11-11 | 11-12 | 11-13 | 11-14 | 11-15 | 11-16 | H | FUEL SPECIMENS

| 1 | | | | 5 | | | | 10 | | | | 15 | | | | 20 | | | | 25 | | | | 30 | | | | 35 | | | | 40 | | | | 45 | | | 48 | FUEL PELLET No.

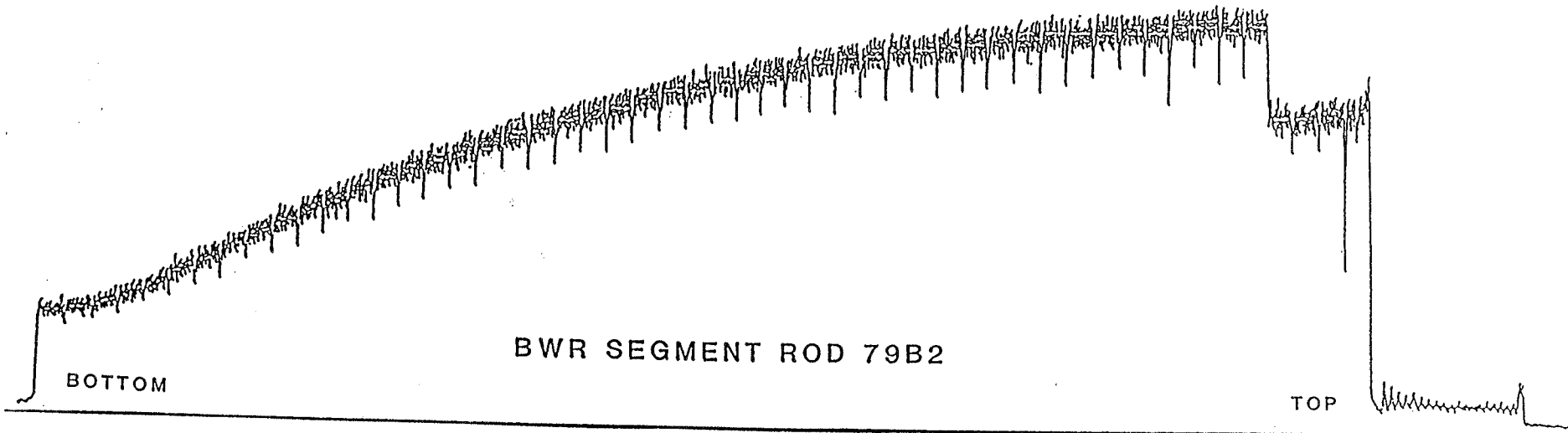BWR SEGMENT ROD 79B2

BOTTOM

TOP

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Figure 2-1. *Gamma scan of the stringer rod showing positions of corrosion test specimens, and positions and actinide compositions of inventory specimens.*

As mentioned above, each corrodant, on completion of the contact period, yields duplicate samples of 3 fractions; centrifugate, membrane filter and vessel strip solution. Only analysis of the centrifugate samples is considered here.

Table 3-1. Experimental parameters for the eighth contact period.

Specimen	Corrodant	Time (d)	pH		Specimen	Corrodant	Time (d)	pH
11-1	GW-OX	301	8.43		11-6	GW-ANOX	328	9.65
11-2		301	8.44		11-7		328	9.51
11-3		301	8.41		11-9		328	9.27
11-4		301	8.51		11-13		328	9.01
11-5		301	8.49		11-14		328	9.04
11-8		300	8.38		11-15		328	8.72
11-10		300	8.47					
11-11		300	8.51					
11-12		300	8.49					
11-16		300	8.52					

3.2 ANALYTICAL METHODOLOGY

All samples in the Series 11 corrosion tests analysed according to the General Spreadsheet procedure were prepared with a 100 ppb natural Indium reference standard. (More recently,diluted samples with 10 ppb are often used.) The collected counts for mass peaks over the whole range (82 to 244), after automatic correction for background Kr and Xe, and for isobaric interferences, were then related to the In-115 signal, yielding a series of ratios. Sensitivity factors relative to In were determined using a range of multicomponent standards of elements with natural isotopic composition,including uranium, and some radioactive standards for Tc-99, and plutonium. Standards were analysed between every group of 4 centrifugate samples. All centrifugate specimens from the 8th contact period (those mainly considered here) were analyzed in duplicate in separate campaigns.

Since the corrosion tests were performed in Pyrex vessels, and it is possible that small quantities of impurities are extracted during the tests,the determination of background levels was performed on samples of groundwater in Pyrex vessels under both oxic and anoxic conditions placed in the hot-cell, such that the gamma field was similar to that experienced during the corrosion tests. Samples of these groundwaters were withdrawn from the hot-cell and subjected to the standard analytical procedure during each analysis campaign.

The background levels of minor constituents in the chemicals used in preparation of the bicarbonate groundwater are of significance in the determination of some fission products, particularly at later stages in the corrosion process

when dissolution/release rates have decreased, but, in general, the accuracy and detection limits are determined by the measured concentrations and the degree of success in correcting for isobaric interferences.

The surface area of the spent fuel is usually unknown due to measurement difficulties, and, further,varies with radial position. Hence, it is customary to express the solubilization of those species which are not solubility-limited, and therefore represent selective attack or matrix dissolution, as fractional release values, i.e., as fractions of the total specimen inventory released. It is at the fractional release level of evaluation that the quality of the data correction procedures for isobaric interference and background subtraction can be assessed for multi-isotope species.

As an illustration of this, the values of fractional release rates for cesium and technetium obtained in the corrosion tests to date are plotted against corrosion time in Figure 3-2. In each case, the curves for oxic groundwater (GW-OX) represent the mean values +/- one standard deviation for all 10 fuel specimens corroded under such conditions,while individual plots are presented for the 3 specimens tested under anoxic conditions. (In the future Swedish deep-rock depository much lower E_H values are anticipated.) The mean values of the release fractions for Cs-133 and -135 have been used for cesium release; Tc-99 is monoisotopic.

Both Cs and Tc are selectively released to the corrodant under oxic conditions, at least during the first years of water contact, and as a result, the measured concentrations were mostly in the 1-100 ppb range, although the in the first phase of corrosion,values for Cs of several hundred ppb were measured. After the Cs "fission product" mass peaks (133, 134, 135 and 137) were corrected for both natural Cs and Ba backgrounds and for isobaric interference from Ba fission product peaks, excellent agreement was found between the release fractions calculated for the mass 133, 135 and 137 isotopes.

Such comparison is, of course,impossible for the monoisotopic Tc-99, but the 99 mass peak is subject to no isobaric interference, and general background levels are low, so that good accuracy for the data is assumed. Thus, the spread in the GW-OX data in Figure 3-2 is attributed to differences in corrosion behaviour of the 10 fuel specimens which were of different burnups. Also, the corrosion mechanisms for Cs and Tc are clearly different.

Under anox conditions, the measured Cs concentrations were still at about the ppb level, while for Tc-99, concentrations decreased down to the 0.05 ppb level. In spite of this, the data quality in Figure 3-2 appears to be satisfactory and the corrosion behaviour of the 3 fuel specimens, with different burnups and inventories, is seen to be very similar. Specimen 15 shows some divergence from the trend, but this specimen was last in the flowing gas train, and similar divergences were seen with other species, suggesting that atmospheric control had been incompletely maintained.
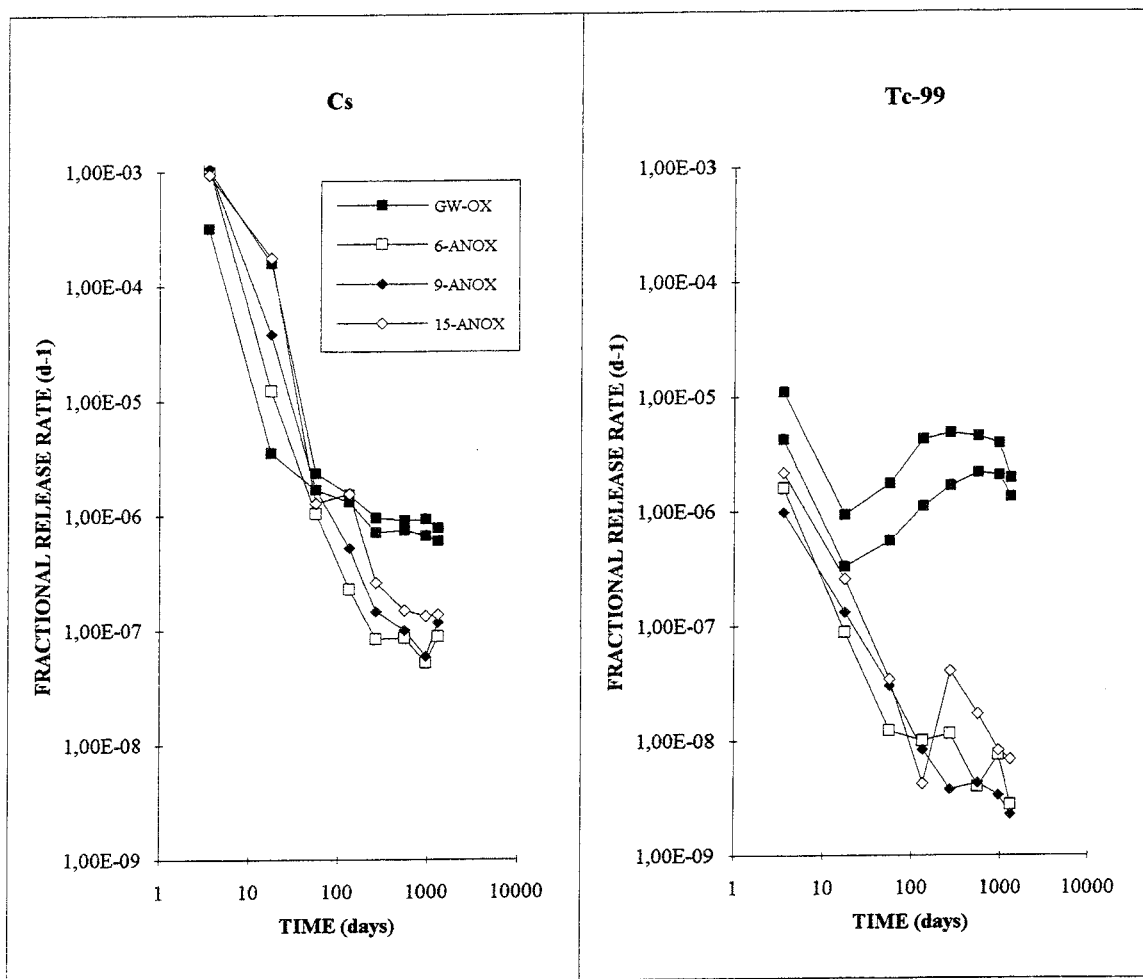
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Figure 3-2. Fission product results: fractional release rates of cesium and technetium-99 under oxic and anoxic conditions.

The determination of **uranium** in centrifugates from tests performed in bicarbonate groundwater under oxic conditions presents few problems since usually concentrations of the order of several mg/L are found. In groundwater under anoxic or reducing conditions, however, uranium solubility decreases sharply to the ppb level. The ICP-MS technique offers three mass peaks for the determination of U-238; masses 119, 238 and 254, from U-238^{2+}, U-238^{+} and U-238-O^{+} respectively. The 3 methods have been applied to the analysis of the centrifugates from the 8th contact period (119 and 238 in the GSS; 254 in the ActSS), and the results obtained are compared in Table 3-2. Note that 2 GW-ANOX specimens show unusually high uranium contents;the cause of this effect is that DIW-OX was the corrodant used in the previous contact period,and some of the uranium deposited on the fuel surface at that time has been redissolved and held in solution by carbonate complexing.

The values obtained by the 3 methods (single analysis) on several of the specimens show significant scatter, but when the results for the 238 and 254

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mass peaks are normalized to the corresponding values for the 119 peak, only fairly small relative bias effects are observed; -2.4% for the 254 peak and +5.9% for the 238 peak.

For the low level GW-ANOX samples, it can be seen that the combined effect of poor counting statistics for both peak and background has resulted in negative values for the 119 peak, while the other methods show satisfactory agreement.

All samples were also analyzed by the laser fluorescence (LF) method used during the earlier analytical campaigns. When the LF results were normalized to the ICP-MS 119 peak results, they gave the same relative bias as was found for the 254 peak method (-2.4%), which corresponds to a bias of about -1.5%, when the ICP-MS results are corrected for the U-235 and U-236 contents. Since the LF method has a detection limit of about 50 ppb in this type of sample, he U contents in the GW-ANOX samples were not detected.

Table 3-2. Uranium determination: Method comparison.

| Spec. | Corrodant | ppb | | | Normalized to $U238^{2+}$ | |
		UO^+	$U238^{2+}$	$U238^+$	UO^+	$U238^+$
11-1	GW-OX	1296.3.	1457.5	1429.2	88.9	98.1
11-2		1459.8	1587.6	1570.0	92.0	98.9
11-3		1634.9	1698.0	1709.1	96.3	100.6
11-4		1802.3	1853.3	2010.5	97.2	108.5
11-5		2076.8	2120.6	2421.8	97.9	114.2
11-8		2073.7	2046.7	2262.4	101.3	110.5
11-10		1570.2	1611.8	1716.3	97.4	106.5
11-11		NA	1792.2	1949.4	NA	108.8
11-12		1716.0	1697.4	1841.9	101.1	108.5
11-16		1635.0	1637.2	1805.0	99.9	110.7
11-7	GW-ANOX	661.5	649.5	659.8	101.8	101.6
11-14		765.1	981.1	801.7	(78.0)	(81.7)
				Mean	97.4	105.9
11-9	GW-ANOX	15.6	-100.8	14.2		
11-13		31.9	-77.0	28.4		
11-14		18.2	-23.7	15.7		
11-15		60.1	-35.1	50.7		

For the **transuranic actinides, Np, Pu, Am and Cm**, the concentrations in solution are dependent on both the dissolution of the UO_2 fuel matrix in which they are in solid solution.and on their own solubilities. In the bicarbonate groundwater used in the corrosion test discussed in this paper, the concentrations of Am and Cm are always low, while Np and Pu are usually at the level of a few tenths of a ppb under oxic conditions. Under anoxic conditions, their concentrations decrease by about two orders of magnitude.

As mentioned above, the determination of plutonium and americium is further complicated by the large changes in their isotopic compositions with fuel burnup and with irradiation conditions, and these effects are particularly evident in the fuel specimens used in the corrosion test.

Figure 3-3 presents the mass spectra of the actinides in fuel specimens from the top (high burnup) end of the fuel rod. The upper spectrum is of the dissolved inventory fuel specimen (INV-H; See Fig.2). The 238 peak.which was measured in the analogue mode, has been inserted into the spectrum measured by pulse counting, and, in the fuel specimens used in the test, is of the order of 100 times larger than the U-235 and U-236 peaks. It can be noted here that even the U isotopic composition varies along the rod, being dependent on both the initial enrichment and the local burnup.

The lower spectrum is of the centrifugate from the 8th contact period of fuel specimen 11-16, which had a burnup of 48.8 MWd/kg U, close to the inventory specimen burnup of 49.0 MWd/kg U, and therefore with very similar actinide inventories and isotopic compositions. The U-235 and U-236 peak heights as plotted are comparable in the two spectra which readily demonstrates the relative concentrations of the other actinides.

Since the decay time from reactor shut-down to ICP-MS measurement was about 5 years, it is assumed in the following that only the 241 peak is of mixed composition (Pu-241 and Am-241). The 238 peak, however, contains a negligible Pu-238 component and the 239 peak (Pu) contains a small correctable component due to U-238-H$^+$ formed in the plasma.

The actinide mass assignment is, therefore; Np; 237: Pu; 239, 240, (241), 242: Am; (241), 243: and Cm;244.The corresponding spectra from the low burnup end of the rod are, of course, very different from those shown in Figure 3-3, as can be seen on inspection of the inventory values given in Figure 3-1.

Comparison of the 2 spectra in the figure shows clearly that in the bicarbonate groundwater under oxic conditions the concentrations of the transuranic actinides relative to the U concentration have decreased by about an order of magnitude compared with the ratios in the fuel matrix. These effects will not be discussed further in this paper, which is directed only towards actinide analysis; a detailed discussion has been published recently /1-1/.

The **neptunium** 237 peak is, in principle.subject to interference by U-236-H$^+$ formed in the plasma, but this effect is extremely small with spent fuel.and can be neglected. In Table 3-3 is presented a comparison of the Np concentrations in the centrifugates determined in two separate analytical campaigns using the 2 spreadsheets for evaluation. As mentioned above, 100 ppb of natural indium was used as the internal standard in the GSS analytical campaign, while a 10 ppb natural thorium standard was used for the ActSS.

The results for groundwater centrifugates under oxic conditions show fairly satisfactory agreement, although the average difference between the 2 spreadsheets is 10%. However.it is uncertain to what degree this difference is
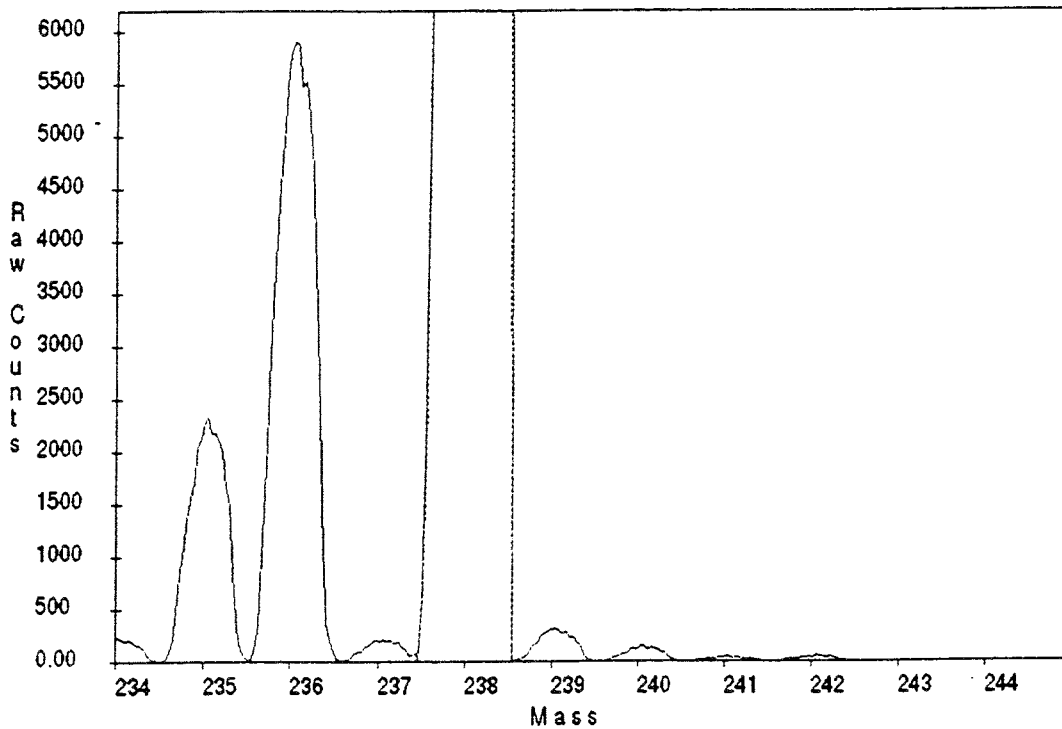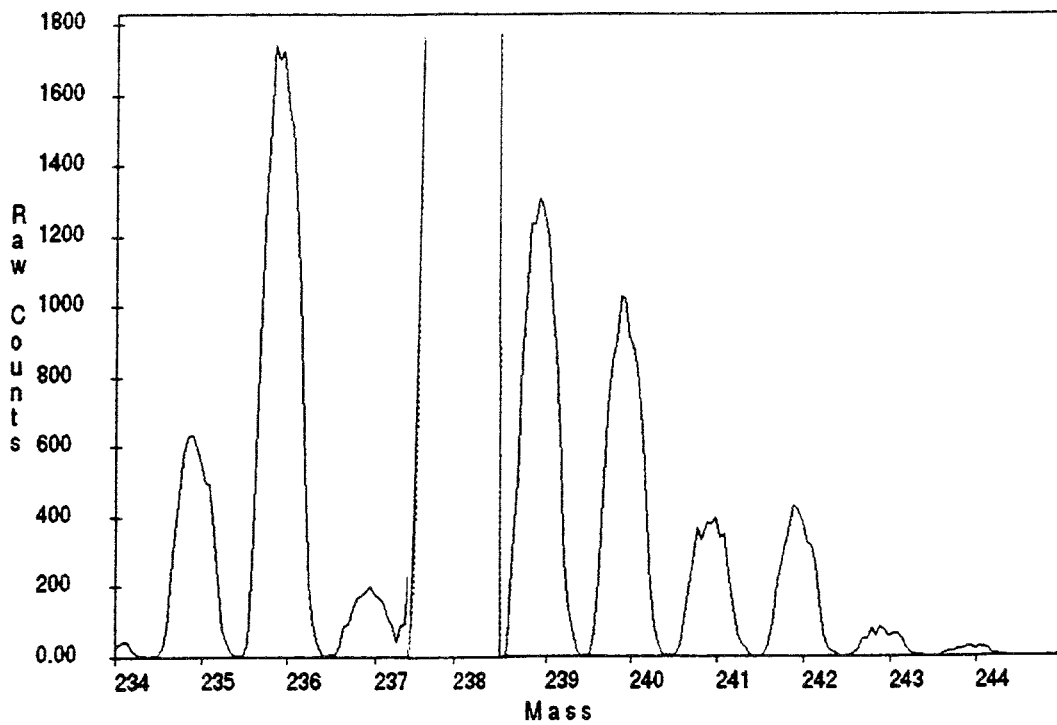
Figure 3-3. Actinide spectra from specimens from the high burnup end of the rod.

Upper; Dissolved fuel from inventory specimen INV-H.

Lower; Centrifugate from 8th contact period of fuel specimen 11-16.

due to the different concentrations of internal standards used in the 2 campaigns or to statistical uncertainty in background subtraction. It can also be seen that the concentrations increase with ascending specimen number, and

therefore inventory, indicating that equilibrium solubility has not been attained.

Currently the accuracy of the determination has not been established.since the radiometric determination of Np-237 was not included in the earlier analytical programme. However.it has been observed that the release fraction results for U, Pu and Np obtained on a few experiments in the corrosion progamme which were performed at low pH, where congruent dissolution would be expected, were very similar.and this can be considered as an indirect confirmation of reasonable accuracy.

The Np concentrations for anoxic conditions presented in Table 3-3 show that at these levels the results are subject to large statistical and background subtraction uncertainties.and that the measured concentrations have a scatter of about an order of magnitude.

Table 3-3. Neptunium determination: Comparison of results from the 2 spread sheets.

Spec.	ppb				Spec.	ppb		
	ActSS	GSS	Mean			ActSS	GSS	Mean
GW-OX					GW-ANOX			
11-1	0.1332	0.1472	0.1402		11-6	0.0007	0.0014	0.0010
11-2	0.0869	0.0955	0.0912		11-7	0.0021	0.0131	0.0021
11-3	0.1512	0.1619	0.1566		11-9	0.0016	0.0025	0.0021
11-4	0.1278	0.1560	0.1419		11-13	0.0038	0.0041	0.0039
11-5	0.1878	0.2137	0.2008		11-14	0.0092	0.0229	0.0092
11-8	0.2301	0.2571	0.2436		11-15	0.0050	0.0058	0.0054
11-10	0.2453	0.2640	0.2547					
11-11	NA	0.2556	0.2556					
11-12	0.2462	0.2536	0.2499					
11-16	0.2534	0.2717	0.2626					

The aim of the work described in this paper was to study the possibility and limitations of **direct** analysis of the actinides, and since the Pu-241 peak also contains a significant and variable Am-241 component, it is clear that the determination of **plutonium** concentrations must be based partly on calculation.Further, the U/Pu ratios in the centrifugates are so large that the U-238-H^+ contribution to the 239 peak becomes significant. Although the value of the required correction factor is determined daily (using the 254 UO^+ peak in the ActSS), variations during the sample analyses may adversely affect the accuracy of the Pu-239 determination. Since the UH^+ factor was determined less frequently during the ICP-MS actinide analysis of the earlier specimens in the Series 11 tests, it was decided that for all samples, the Pu-239 should be calculated from the Pu-240 peak.

The correction factors used are based on the isotopic ratios in the inventories of each specimen, which were derived by an ORIGEN-based interpolation between the measured values in the two inventory specimens. Particularly for

the higher mass numbers 242, 243 and 244, the interpolation is non-linear, the contents increasing steeply with burnup (See the table in Figure 3-1). This is obviously a complicated and probably inexact procedure to be used until such time when the corrosion specimen inventories can be measured directly by dissolution and analysis after the corrosion tests are completed.

The Pu-241 content can be calculated by 3 methods; directly from the inventory ratios to the measured Pu-240 and Pu-242 contents, and indirectly from the Am-241 inventory ratio to the measured Am-243 content. The results of the application of these methods to the 10 GW-OX samples in one of the GSS campaigns are presented in Table 3-4, together with the calculated Am-241 contents which are obtained at the same time.

Table 3-4. Concentrations (ppb) of Pu-241 and Am-241 calculated from inventory isotopic ratios and the measured Pu-240, Pu-24 and Am-243 concentrations.

Spec	ppb Pu-241 (calculated)			ppb Am-241 (calculated)		
	Pu241/ Pu240	Pu241/ Pu242	Am241 /Am243	Pu241/ Pu240	Pu241/ Pu242	Am241/ Am243
11-1	0.0232	0.0262	0.0092	0.0001	-0.0029	0.0140
11-2	0.0194	0.0159	0.0099	-0.0025	0.0010	0.0070
11-3	0.1294	0.1095	0.1042	0.0039	0.0238	0.0290
11-4	0.0171	0.0182	0.0076	0.0007	-0.0005	0.0102
11-5	0.0254	0.0212	0.0186	-0.0028	0.0014	0.0040
11-8	0.0243	0.0248	0.0188	-0.0019	-0.0023	0.0036
11-10	0.0325	0.0334	0.0278	0.0008	-0.0002	0.0055
11-11	0.0367	0.0386	0.0305	0.0004	-0.0015	0.0066
11-12	0.0389	0.0408	0.0360	0.0004	-0.0015	0.0033
11-16	0.0620	0.0600	0.0638	0.0033	0.0053	0.0015

The Pu-241 contents calculated from the Pu-240 and Pu-242 peaks show satisfactory agreement over the whole sample series.considering the variation with burnup of the correction factors applied.while use of the Am-241/Am-243 ratio yields consistently lower values. This is most marked for the lower burnup specimens where the correction factors are high and the Am-243 contents are very low. It can be seen, however, that agreement between the 3 methods is better for specimen 11-3, which had a relatively high Pu content, probably due to centrifugate contamination with fuel fines, since the contents of other species also showed abnormally high values.

Inspection of the calculated Am-241 results in Table 3-4 shows that the values obtained by means of the plutonium isotopic ratios (subtraction of the calculated Pu-241 contents from the measured 241 peaks) are very low or negative, suggesting that in the bicarbonate groundwater the 241 peak is due predominantly to Pu-241. This is supported by earlier alpha spectrometric results on the centrifugates which showed consistently lower release values for americium and curium than for plutonium.

The Am-241 results, of course, demonstrate the difficulty and inaccuracy involved in the background correction procedure in these samples, where the total pulse counts are low, and particularly in the case of americium and curium are of about the same order of magnitude as the background.

For **plutonium,** as for the other actinides and the rare earths, evaluation of the corrosion experiment results is performed using the release fractions for individual nuclides for comparison with other species as a test of congruent dissolution, and using total element concentrations in order to study approach to saturation. Thus, the total plutonium concentrations in each sample was determined by the summation of the measured concentrations of Pu-240 and -242, and the concentrations of Pu-239 and -241 as calculated by the procedure discussed above.

The same method was used for **americium,** using the measured Am-243 concentrations and the calculated Am-241, while for **curium** the Cm-244 concentrations were used directly. Negative values were obtained occasionally for these two elements as a result of the background subtraction procedure, and these were included in the summation in order to reflect the poor measurement statistics.

The results are presented in Table 3-5 below. The ActSS values are the results of single measurements.while the GSS values are the arithmetic mean of duplicate analyses. Different batches of centrifugate were used for the two spreadsheet series.

Table 3-5. Summary of Pu, Am and Cm results using the two spreadsheets.

Spec.	Corrodant	Total Pu (ppb)		Total Am (ppb)		Total Cm (ppb)	
		ActSS	GSS	ActSS	GSS	ActSS	GSS
11-1	GW-OX	0.2598	0.2753	-0.0056	0.0009	-0.0004	0.0004
11-2		0.1690	0.2056	0.0041	0.0008	-0.0001	-0.0008
11-3		1.2319	1.2986	0.0217	0.0216	0.0020	0.0015
11-4		0.1656	0.1688	0.0018	0.0024	-0.0002	0.0014
11-5		0.2062	0.2372	0.0011	0.0010	0.0009	-0.0002
11-8		0.2215	0.2365	0.0017	-0.0001	0.0007	0.0012
11-10		0.2921	0.3212	0.0026	0.0039	0.0013	0.0013
11-11		NA	0.3664	NA	0.0039	NA	0.0013
11-12		0.3757	0.3892	0.0010	0.0018	-0.0001	0.0008
11-16		0.5707	0.6193	0.0002	0.0054	0.0001	0.0023
11-6	GW-ANOX	0.0043	0.0024	-0.0001	-0.0004	0.0000	0.0004
11-7		0.0113	0.0021	0.0001	0.0012	0.0007	0.0008
11-9		0.0093	0.0015	0.0002	0.0002	0.0005	0.0003
11-13		0.0124	0.0088	-0.0001	0.0006	-0.0001	0.0008
11-14		0.0131	0.0194	0.0024	0.0022	0.0004	0.0012
11-15		0.0191	0.0082	0.0039	0.0019	0.0011	0.0013

In groundwater under oxic conditions, all centrifugates, with the exception of 11-3, which was discussed above.gave plutonium concentrations of a few tenths of a ppb. As for the U and Np results presented earlier, the Pu concen-

trations determined with the ActSS are in general about 6% lower than those from the GSS. Although this apparent bias may be due only to fluctuations in the instrument operational characteristics, or to the different batches of centrifugate, it is thought probable that the amounts of internal standard, 10 ppb thorium and 100 ppb indium respectively in the two procedures.are mainly responsible.

When the plutonium concentrations in the GW-OX samples were compared with those calculated from the results of alpha spectrometric measurements, it was found that the ICP-MS values were on average about 12% higher. The routine alpha spectrometric method is based on measurement of the 5.15 MeV alpha peak due to Pu-239/Pu-240 in aliquots of centrifugate mounted on planchets and allowed to air-dry. The 5.15 MeV peak is located in the low-energy tail of the much larger 5.50 MeV peak (from Pu-238 and Am-241) which causes appreciable uncertainty in background correction.and tends to give low values. Thus, it is probable that the concentration values from the ActSS procedure are more accurate.

In groundwater under anoxic conditions, the centrifugate plutonium concentrations decrease by between 1 and 2 orders of magnitude.resulting in a severe loss of accuracy and precision. However, the concentrations can be estimated to within a factor of 5 or so, which is an improvement on the alpha spectrometric method, which, with the background problem mentioned above, is unable to detect these levels.

From the results in Table 3-5, it can be seen that the direct determination of the low levels of **americium** and **curium** in centrifugates, under both oxic and anoxic conditions, is infeasible.at least with the current instrumental set-up using a pneumatic nebulizer. It can be noted, however, that certainly americium, and possibly curium, were measurable in the centrifugate from specimen 11-3, which is believed to be contaminated with a small quantity of fuel fines.

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4 CONCLUSIONS

The possibilities have been studied of using the ICP-MS technique for the direct, routine determination of the actinides in solutions arising from a series of corrosion tests on spent nuclear fuel of different burnups, and, hence, different inventories and isotopic compositions.

Uranium can be determined by means of 3 mass peaks at concentrations from the ppm to the ppb level. The accuracy and precision are comparable to that attained by the laser fluorescence method.which.however, has a higher detection limit of about 50 ppb.

Under oxic conditions, concentrations of both neptunium and plutonium at the 0.1-1 ppb level can be measured with satisfactory accuracy and precision if multiple analyses are performed. Under anoxic conditions, their concentrations decrease to about 0.01 ppb or lower, but it is considered that values of concentration can be estimated to within about one order of magnitude.

In all groundwater centrifugates (pH about 8), the americium and curium contents are at about or below the detection limit. The pulse counts need to be increased by a factor of 10 or more to permit measurement and it is hoped that this will be attained on installation of a Mistral nebulizer.

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