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Analysis of radioactive corrosion test specimens by means of ICP-MS Comparison with earlier methods

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ANALYSIS OF RADIOACTIVE CORROSION TEST SPECIMENS BY MEANS OF ICP-MS

COMPARISON WITH EARLIER METHODS

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

Information on SKB technical reports from 1977-1978 (TR 121), 1979 (TR 79-28), 1980 (TR 80-26), 1981 (TR 81-17), 1982 (TR 82-28), 1983 (TR 83-77), 1984 (TR 85-01), 1985 (TR 85-20), 1986 (TR 86-31), 1987 (TR 87-33), 1988 (TR 88-32), 1989 (TR 89-40), 1990 (TR 90-46), 1991 (TR 91-64), 1992 (TR 92-46), 1993 (TR 93-34), 1994 (TR 94-33), 1995 (TR 95-37) and 1996 (TR 96-25) is available through SKB.

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ABSTRACT

In June 1992, an ICP-MS instrument (Inductively Coupled Plasma- Mass Spectrometry) was commissioned for use with radioactive sample solutions at Studsvik Nuclear's Hot Cell Laboratory. For conventional environmental samples, the instrument permits the simultaneous analysis of many trace elements, but the software used in evaluation of the mass spectra is based on a library of isotopic compositions relevant only for elements in the lithosphere. Fission products and actinides, however, have isotopic compositions which are significantly different from the natural elements, and which also vary with the burnup of the nuclear fuel specimen. Consequently, a spreadsheet had to be developed which could evaluate the mass spectra with these isotopic compositions. Further, procedures were developed for the correction of background levels of certain natural elements, introduced in the chemicals used in the corrosion experiments, which affect the measurement accuracy for the fission products.

Following these preparations, a large number of samples (about 200) from SKB's experimental programme for the study of spent fuel corrosion have been analyzed by the ICP-MS technique. Many of these samples were archive solutions of samples which had been taken earlier in the programme. This report presents a comparison of the analytical results for uranium, plutonium, cesium, strontium and technetium by both the ICP-MS technique, and the previously used analytical methods.

For the three fission products, a satisfactory agreement between the results from the various methods was obtained, but for uranium and plutonium the ICP-MS method gave results which were 10-20 % higher than the conventional methods.

The comparison programme has also shown, not unexpectedly, that significant losses of plutonium from solution had occurred, by precipitation and/or adsorption, in the archive solutions during storage. It can be expected that such losses also occur for the other actinides, and consequently, all the analytical results for actinides in older archive solutions must be treated with great caution.

SAMMANFATTNING

I juni 1992 togs ett ICP-MS instrument (Inductively Coupled Plasma- Mass Spectrometry) i bruk för analys av radioaktiva provlösningar vid Studsvik Nuclear Hot Cell Laboratoriet. Vid analys av vanliga miljöprov möjliggör instrumentet analys av många spårämnen samtidigt, men mjukvaran som används för utvärdering av masspektra är baserad på data på isotopiska sammansättningar som är giltiga endast för grundämnena i jordens litosfär. Eftersom fissionsprodukter och aktinider har isotopiska sammansättningar som skiljer sig från de naturliga ämnena och dessutom varierar med kärnbränslets utbränning, måste ett kalkylblad utvecklas som korregerar det uppmätta masspektra för dessa sammansättningar. Dessutom har procedurer utvecklats som beräknar bakgrundsnivåerna av vissa naturliga ämnen (p.g.a. de använda kemikalierna) som påverkar mätnoggrannheten för fissionsprodukterna.

Efter dessa förberedelser har ett stort antal prov (cirka 200) från SKBs experimentprogram för studier av använt bränslekorrosion analyserats medelst ICP-MS tekniken, av vilka många var arkivlösningar från tidigare provtagningar. I denna rapport jämförs resultaten av ICP-MS mätningarna (för uran, plutonium, cesium, strontium och technetium) på dessa prov med motsvarande resultaten från de tidigare använda analysmetoderna.

För de tre fissionsprodukterna erhöles en tillfredsställande överensstämmelse mellan metoderna, men för uran och plutonium gav ICP-MS analysmetoden 10-20% högre värden än de konventionella analysmetoderna.

Detta jämförelseprogram har också visat, inte helt oväntat, att plutonium förlust från lösning, (genom utfällning och/eller adsorption) hade inträffat i arkivlösningarna under förvaring. Det kan väntas att sådana förluster inträffar även av de övriga aktinider, och följaktligen borde samtliga analysresultat för aktinider i äldre arkivlösningar behandlas med stor försiktighet.

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SUMMARY AND CONCLUSIONS

This report presents the results of a comparison of the analytical results on a large number of corrosion test specimens, where analysis has been performed both by direct ICP-MS analysis, i.e., without prior chemical separation, and by the corresponding conventional analytical methods employed during the first 10 years of the programme. The decision, taken in 1991, to purchase and commission an ICP-MS instrument for the analysis of radioactive samples in the corrosion programme, was motivated by:

- a) the aim of broadening the data base available for the evaluation of fuel corrosion experiments by using the multi-nuclide analytical potential of the instrument.
- b) the possibility of replacing the conventional analytical methods used up to that time by the ICP-MS technique.

The sample solutions used in the comparison programme were from corrosion tests on specimens from three of the reference fuels used in the SKB experimental programme on spent fuel corrosion. The inventories of selected fission products and actinides in these reference fuels had been determined by the conventional analytical methods at the beginning of their respective corrosion test programmes.

For the ICP-MS technique, however, inventory values are required for a larger number of nuclides. These were determined by ICP-MS analysis on new inventory specimens for the Series 3 and 7 corrosion tests, since the original specimens were judged to be too old, while for the Series 11 corrosion tests, the original inventory specimens were re-analyzed by the ICP-MS technique, due to unavailability of suitable new fuel. Perhaps due to this, the two sets of inventory values showed significant differences, and these have been taken into consideration in the comparison of methods.

Most of the samples included in this method comparison were centrifugate samples, since they contain most of the material released during corrosion of the fuel. Samples of corrosion vessel strip solutions were also included, but difficulties have been experienced with evaluation of the ICP-MS results on some of these samples, partly because they consist largely of dissolved fuel fines, and partly because of the presence of dissolved Zircaloy clad.

The samples from the Series 3 and 7 corrosion tests (BWR and PWR reference fuels) were included in the method comparison in order to provide an analytical overlap between the ICP-MS and conventional methods. Most of the samples, however, were from the Series 11 corrosion tests, and the comparison has been extended to include the ICP-MS analysis of samples (archive solutions) from all the corrosion tests performed in this series prior

to commissioning of the instrument. One of the main aims of the comparison programme is to explore the possibility of using the results of these retro-active analyses to extend the broader data base to the initial stages of fuel/water contact.

Only 5 elements, uranium, plutonium, cesium, strontium and technetium, have been analyzed for by both the ICP-MS technique and conventional methods. For each element, the ICP-MS analytical results have been compared with the results from corresponding conventional analytical method. In the case of uranium, the comparison is made between the measured solution concentrations, while for the other elements, the comparison has been made at the release fraction level, partly because different isotopes have been used for the analyses, and partly to allow a comparison to be made of the release behaviour of the measured elements.

For all 5 elements, a good linear correspondence between the results over 2-3 orders of magnitude of concentration was observed, extending down to release fractions of E-05 or less. Normally the corrosion tests in the SKB programme are performed with water contact periods of a few hundred days, and, therefore, fractional release rates of the order of E-07/day can be measured with satisfactory precision.

The average ratios of the results obtained by the ICP-MS technique to those from the corresponding conventional method, however, diverge significantly from unity, even when they are adjusted for the differences in inventory values mentioned above. The ratio values for the Series 11 specimens, which are more numerous, are presented in the table below. The values are only approximate since there is appreciable scatter in the data, probably due to the fact that many of the ICP-MS results are from single analyses performed shortly after commissioning of the instrument.

Average values of the ratios of ICP-MS results to those from conventional methods. (Series 11 tests only)

Based on independent specimen inventory values

U	Cs	Sr	Tc	Pu
1.09	1.07	1.13	1.02	1.39

Adjusted to common specimen inventory values

U	Cs	Sr	Tc	Pu
1.09	0.96	0.96	0.96	1.22

A number of conclusions can be drawn on inspection of the table;

- a) Differences in the inventory values determined by ICP-MS and the conventional methods respectively account for a part of the apparent biases between the methods.

- b) Even when the method comparison is made on the basis of common inventory values, significant bias remains for the analysis of plutonium, and, to lesser extent, uranium. Possible reasons for this are discussed in the report.
- c) For the three fission products, the observed bias between the methods was only 4%, which must be regarded as good agreement at these low concentration levels.

Many of the ICP-MS analyses were performed considerably later, often years later, than the corresponding conventional analyses, and were carried out on archive solutions from early corrosion tests. During comparison of the analytical results for plutonium, it was observed that there was a much larger scatter in the data than for the other elements. Evaluation of the results showed that this could be attributed to loss of plutonium from solution, by precipitation and/or adsorption, in the archive solutions which had been stored for longer than about 6 months, even though the solutions had been acidified prior to storage. Since similar behaviour can be expected for other actinides, and, for example, the rare earth elements, the results from older archive solutions must be treated with caution before use.

1. INTRODUCTION

During June 1992, an ICP-MS instrument, (Inductively Coupled Plasma-Mass Spectrometry), a VG PlasmaQuad supplied by Fisons Instruments, which had been purchased by SKB, was commissioned for operation with radioactive specimens in Studsvik Nuclear's Hot Cell Laboratory. At that time, SKB's experimental programme for the study of the corrosion of spent fuel had been in progress at the laboratory for ten years, and a large amount of analytical data had been collected by the application of an analytical programme based on standard radiochemical and radiometric methods.

Prior to commissioning of the ICP-MS instrument, a spread-sheet had been developed /1-1/ for treatment of the basic measurement data collected in the machine during specimen analysis, in order to correct the spectral peaks for isobaric interferences. Since at that time, and in fact until quite recently, no routine methods had been developed for the chemical separation or enrichment of selected elements prior to ICP-MS analysis, it was necessary to explore the possibility of performing ICP-MS analysis **directly** on the specimens arising in the corrosion programme, i.e., in principle, **with all fission products and actinides present**. Further, both the concentration levels, and the concentration ratios of these numerous components of the corrosion test samples, were expected to show very large variations, depending on the experimental parameters of the individual corrosion tests, and the type of specimen examined; centrifugate, membrane filter or vessel strip solution. /1-2/

The software supplied with the instrument for the correction of isobaric interferences was based on a library of elemental isotopic compositions only relevant for the lithosphere. Since the isotopic compositions of the fission product elements are usually significantly different from those of the natural elements, and, together with those of the actinides, are also often dependent on the fuel burnup and irradiation history, two versions of the spread-sheet, based on burnups of 25.0 and 49.0 MWd/kg U respectively, were developed. These burnup levels were those of the two inventory specimens from the 79B2 fuel rod (see below) and their fission product and actinide inventories had been calculated by the ORIGEN-2 code, as parts of a series of ORIGEN calculations on fuel from that rod which covered burnups from 21.2 to 73.4 MWd/kg U, and a number of decay periods of different lengths.

It can be noted here that the basing of the corrections for isobaric interferences in the spread-sheets on ORIGEN calculations for only one specific fuel irradiation, and at only two burnup levels, is a simplification which can be justified by the considerable difficulties associated with the alternative of having to develop spread-sheet correction procedures for each fuel type analysed in the instrument. Further, since there is a radial burnup gradient in

all irradiated fuel pellets, which is particularly marked at the pellet rim, /1-3/, the burnup of the sample analysed will only correspond with the bulk burnup determined by destructive analysis, /1-4/, on whole fuel cross-sections (and which is used as input to ORIGEN calculations) if corrosive dissolution has occurred uniformly over the pellet. Clearly, it will almost always be extremely difficult to assign "correct" burnup and inventory values to a given specimen, and some form of simplification of the correction procedures is essential.

These comments have relevance only for fission product elements, since, as will be seen below, the correction procedures for the actinides are based primarily on isotopic compositions determined experimentally by solid source mass-spectrometric analysis of chemically separated specimens.

The performance of the spread-sheet for isobaric interference correction was tested by application to the ICP-MS mass peak data from the direct analysis of a number of radioactive centrifugate specimens which had previously been analysed by the conventional analytical methods. In this limited test, spread-sheet performance was judged to be satisfactory, and it appeared to be feasible to obtain concentration values for about 15 fission product elements. However, of the actinides, only the analysis of uranium, and in favourable conditions, neptunium and plutonium, appeared to be possible. At this time the spread-sheet, which had been developed originally as a Lotus Symphony file, was converted to Excel, and a number of minor changes in correction procedures were made.

This test, of course, was mainly of the operational function of the isobaric corrections applied in the spread-sheet. A more complete test of the accuracy of the concentrations of specific nuclides thus obtained is to compare the results from several isotopes of the same element at the release fraction level; good agreement at this level would indicate satisfactory analytical accuracy.

For this purpose, it was necessary to compare ICP-MS analytical results from corrosion test specimens from a number of different fuel specimens together with the corresponding fuel inventory values. Such a comparison programme could have been performed on corrosion test specimens generated in the on-going experimental programme, if the specimens were analysed in parallel by means of the previously used analytical programme. However, there appeared to be substantial advantages if the comparison programme also included the retroactive analysis by the ICP-MS technique of all the specimens from the early samplings performed in the Series 11 corrosion tests, which started in March 1990, so that multinuclide release data would be available even from the first stages of spent fuel corrosion.

This report, therefore, presents a comparison of experimental corrosion test data, obtained by the ICP-MS technique and by use of the earlier analytical programme, from corrosion tests performed on the 3 reference spent fuels used in the SKB programme. Most of the results refer to the Series 11 tests, with fuel of a wide range of burnups, and one of the aims of the report is to

examine the quality of the data collected during the retroactive ICP-MS analytical campaign in order to facilitate evaluation and reporting.

2. SPECIMENS

The experimental test conditions and durations, and values of the final pH and carbonate concentrations of the corrosion test solutions included in the comparison programme are shown in boxes with bold borders in Tables 2-1, 2-2, 2-3 and 2-4, together with corresponding data for all the other individual tests in these experimental series.

The Series 3 corrosion tests, (Table 2-1), which consists of 3 fuel/clad segments of the original BWR reference fuel, /2-1/, started in February 1982 and have now been subjected to over 15 years of aqueous corrosion. However, on a few occasions during this long period, there occurred inadvertent in-cell cross-contamination of corrodant solutions with acidic vessel strip solution, /2-2/, with periods of low pH contact as a consequence, and this has reduced somewhat the value of the data. These tests, however, are still of great interest, particularly for the determination of corrosion rates after such long total corrosion times, and for later post-corrosion fuel examination. Only specimens from the two latest contact periods are included in the comparison programme in order to link the ICP-MS results with those from the analytical programme used earlier.

The Series 32326 corrosion tests, (Table 2-2), were designed for the study of the corrosion of selected fragments of the same reference fuel that was used in the Series 3 corrosion tests /2-3/. Four tests were performed using as corrodant deionized water and simulated groundwater with 3 different levels of bicarbonate concentration. The fragments were initially exposed to very long static contact periods, but in 2 experiments the tests were concluded by short contact periods in the standard bicarbonate groundwater under both oxic and anoxic conditions in order to measure release rates. These latter specimens were analyzed in the ICP-MS instrument shortly after sampling, but the long static test specimens were only available as stored archive solutions.

The Series 7 corrosion tests, (Table 2-3), which were commenced in 1986, consisted originally of 14 fuel/clad segments of the SKB reference PWR fuel, /2-4/, but at the time of the commissioning of the ICP-MS instrument 6 of the tests had been concluded. Thus, only specimens from the latest contact periods of the remaining 8 tests were included in the comparison programme for linkage with the earlier analytical results.

CONTACT PERIOD																	
SPECIMEN	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
3-1	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX
3-2	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX
3-3	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX

CONTACT TIME (days)																	
SPECIMEN	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
3-1	7	7	14	63	91	182 *	182	159	218	174	367	479	238	399	1366	337	
3-2	7	7	14	63	91	182 *	182	159	218	174	367	479	238	399	1366	337	
3-3	7	7	14	63	91	182	182	159	218	174	367	479	238	399	1366	337	

* The 6th period was divided into 2 periods.

pH (CENTRIFUGATE)																	
SPECIMEN	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
3-1	NM	NM	7,30	7,00	3,90	7,50/7,00	5,70	6,50	3,85	5,20	8,15	8,25	6,80	7,00	7,90	6,8/7,5	
3-2	NM	NM	8,10	8,20	2,30	8,20/8,25	8,05	8,00	4,25	6,60	8,15	8,20	8,20	8,30	8,43	8,30	
3-3	NM	NM	8,10	8,20	4,75	8,20	8,05	8,00	4,20	5,10	8,15	8,35	8,40	8,30	8,50	8,30	

[CARBONATE] (ppm)																	
SPECIMEN	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
3-1	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	9	3	< 6	< 6	
3-2	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	125	146	110	103	
3-3	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	154	151	123	120	

Table 2-1. Series 3 Corrosion test programme. Specimens included in the comparison programme are shown with bold borders.

CONTACT PERIOD					
SPECIMEN	1	2	3	4	5
3-23	DW-OX	DW-OX	DW-OX	DW-ANOX	
3-24	DW-OX	DW-OX	DW-OX	DW-ANOX	DW-ANOX
3-25	DW-OX	DW-OX			
3-26	DW-OX	DW-OX			

CONTACT TIME (days)					
SPECIMEN	1	2	3	4	5
3-23	501	1842	118	78	
3-24	501	1842	118	78	83
3-25	501	926			
3-26	501	1020			

pH (CENTRIFUGATE)					
SPECIMEN	1	2	3	4	5
3-23	NM	8,2	8,48	9,75	
3-24	NM	8,7	8,5	9,9	9,9
3-25	NM	8,8			
3-26	NM	6,300			

[CARBONATE] (ppm)					
SPECIMEN	1	2	3	4	5
3-23	70	60	118	58	
3-24	179	119	130	78	65
3-25	257	279			
3-26	9	< 10			

Table 2-2. Series 3.2326 Corrosion test programme

CONTACT PERIOD						
SPECIMEN	1	2	3	4	5	6
7.1	GW-OX	GW-OX	DW-OX			
7.2	GW-OX	GW-OX	DW-OX	DW-OX	DW-OX	
7.3	GW-OX	GW-OX	GW-OX			
7.4	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX
7.5	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	
7.6	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	
7.7	GW-REDRK	GW-REDRK	GW-REDRK			
7.8	GW-REDRK	GW-REDRK	GW-REDRK			
7.9	GW-REDRK	GW-REDRK	GW-REDRK			
7.10	GW-REDRK	GW-REDRK	GW-REDRK			
7.11	GW-REDRK	GW-REDRK	GW-REDRK	GW-ANOX		
7.12	GW-REDRK	GW-REDRK	GW-REDRK	GW-ANOX		
7.13	GW-REDH2	GW-REDH2	GW-REDH2	GW-REDH2	GW-REDH2	GW-REDH2
7.14	GW-REDH2	GW-REDH2	GW-REDH2	GW-REDH2	GW-REDH2	

CONTACT TIME (days)						
SPECIMEN	1	2	3	4	5	6
7.1	82d	170d	436d			
7.2	82d	170d	1079d	1629d	940427	
7.3	82d	170d	436d			
7.4	82d	170d	686d	866d	1156d	940427
7.5	82d	170d	1079d	1629d	940427	
7.6	82d	170d	1217d	1492d	940427	
7.7	82d	170d	436d			
7.8	82d	170d	686d			
7.9	82d	170d	686d			
7.10	82d	170d	1555d			
7.11	82d	170d	2722d	940510		
7.12	82d	170d	2722d	940510		
7.13	82d	170d	686d	868d	1174d	940518
7.14	82d	170d	1173d	1556d	940518	

pH (CENTRIFUGATE)						
SPECIMEN	1	2	3	4	5	6
7.1	8,50	8,50	6,90			
7.2	8,50	8,50	6,43	7,93/7,70		
7.3	8,50	8,50	8,50			
7.4	8,45	8,50	8,30	8,42	8,61	
7.5	8,50	8,50	8,60	8,59		
7.6	8,55	8,50	8,49	8,60		
7.7	8,20	8,35	8,50			
7.8	8,00	8,25	7,80			
7.9	8,15	8,20	8,20			
7.10	8,10	7,60	7,93			
7.11	7,95	7,30	7,87			
7.12	8,10	7,70	7,76			
7.13	9,10	7,60	7,90	7,87	8,46	
7.14	8,80	7,30	8,13	8,32		

[CARBONATE] (ppm)						
SPECIMEN	1	2	3	4	5	6
7.1	NM	NM	20			
7.2	NM	NM	< 14	< 6		
7.3	NM	NM	163			
7.4	NM	NM	129	140	125	
7.5	NM	NM	156	131		
7.6	NM	NM	143	125		
7.7	NM	NM	NM			
7.8	NM	NM	122			
7.9	NM	NM	116			
7.10	NM	NM	146			
7.11	NM	NM	115			
7.12	NM	NM	132			
7.13	NM	NM	116	138	118	
7.14	NM	NM	170	117		

Table 2-3. Series 7 Corrosion test programme

As has been mentioned in the Introduction, the **Series 11 corrosion tests**, (Table 2-4), are of particular interest in the comparison programme. If it can be demonstrated that there is good or reasonable agreement between the results from the retroactive ICP-MS analysis of stored archive specimens from the contact periods performed early in the programme with the results obtained by conventional analysis, the release behaviour of many fission product and actinide nuclides can be followed from the first water contact with the fuel.

The 16 fuel/clad specimens studied in the experiment, /2-5/, were all from the same BWR fuel rod, a lower stringer rod segment denoted 79B2, from Ringhals 1, but had different burnups varying continuously over the range 27.0 to 48.8 MWd/kg U. Thus, the specimens had also experienced a wide range of linear heat ratings, and with roughly parallel power/time variations during the irradiation. Further, extensive fuel characterization work had been performed on the fuel.

Most of the samples considered in this comparison programme are centrifugate samples, /1-2/, since, in an attempt to limit the extremely high workload involved in performing the retroactive ICP-MS analysis programme concurrently with the normal experimental and analytical activities, it was necessary to restrict the number of vessel strip solutions, and, in particular, membrane filter specimens, examined.

SPECIMEN	BURNUP MWd/kgU	CONTACT PERIOD									CONTACT TIME (days)								
		1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
11-01	27,0	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	7	21	63	91	182	371	413	301	413
11-02	30,1	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	7	21	63	91	182	371	413	301	413
11-03	32,7	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	7	21	63	91	182	371	413	301	413
11-04	34,9	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	7	21	63	91	182	371	413	301	413
11-05	40,1	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	7	22	62	91	182	371	413	301	413
11-06	41,4	GW-ANOX	GW-ANOX	GW-ANOX	GW-ANOX	GW-ANOX	GW-ANOX	GW-ANOX	GW-ANOX	GW-ANOX	7	21	63	91	181	370	414	328	420
11-07	42,7	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-ANOX	GW-ANOX	7	22	62	91	182	372	414	328	420
11-08	43,8	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	7	21	63	91	182	371	413	300	413
11-09	44,9	GW-ANOX	GW-ANOX	GW-ANOX	GW-ANOX	GW-ANOX	GW-ANOX	GW-ANOX	GW-ANOX	GW-ANOX	7	21	63	91	181	370	414	328	421
11-10	45,8	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	7	22	62	91	182	371	413	300	413
11-11	46,5	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	7	22	62	92	181	371	413	300	413
11-12	47,0	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	7	21	63	92	181	371	413	300	413
11-13	47,6	DW-ANOX	DW-ANOX	DW-ANOX	DW-ANOX	DW-ANOX	DW-ANOX	DW-ANOX	DW-ANOX	GW-ANOX	7	21	63	91	181	370	414	328	420
11-14	48,1	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-OX	DW-ANOX	GW-ANOX	7	22	62	92	181	372	414	328	420
11-15	48,4	GW-ANOX	GW-ANOX	GW-ANOX	GW-ANOX	GW-ANOX	GW-ANOX	GW-ANOX	GW-ANOX	GW-ANOX	7	21	63	91	181	370	414	328	422
11-16	48,8	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	GW-OX	7	22	62	92	181	371	413	300	413

8

SPECIMEN	pH (CENTRIFUGATE)								
	1	2	3	4	5	6	7	8	9
11-01	8,45	8,43	8,36	7,81	8,43	8,28	8,55	8,43	8,56
11-02	8,37	8,33	8,42	8,38	8,49	8,21	8,56	8,44	8,53
11-03	8,32	8,32	8,40	8,35	8,49	8,29	8,58	8,41	8,52
11-04	8,30	8,45	8,45	8,35	8,45	8,34	8,57	8,51	8,53
11-05	8,45	8,45	8,45	8,40	8,40	8,33	8,60	8,49	8,55
11-06	9,80	9,80	9,83	9,85	9,84	9,40	9,92	9,65	9,47
11-07	6,84	6,68	8,40	3,80	6,67	7,58	9,76	9,51	9,41
11-08	8,39	8,29	8,36	8,52	8,45	8,33	8,59	8,38	8,39
11-09	9,72	9,80	9,82	9,87	9,78	9,33	9,62	9,27	9,13
11-10	8,36	8,40	8,36	8,45	8,45	8,31	8,65	8,47	8,44
11-11	8,41	8,32	8,42	8,48	8,48	8,34	8,62	8,51	8,43
11-12	8,35	8,45	8,43	8,36	8,46	8,41	8,61	8,49	8,47
11-13	5,90	6,79	5,92	4,67	4,04	3,94	9,71	9,01	9,22
11-14	6,72	6,70	6,33	3,64	6,10	5,90	9,66	9,04	9,21
11-15	9,56	9,64	9,63	9,15	9,60	9,29	9,57	8,72	9,10
11-16	8,38	8,31	8,42	8,47	8,46	8,35	8,60	8,52	8,49

SPECIMEN	[CARBONATE] (ppm)								
	1	2	3	4	5	6	7	8	9
115	115	106	139	149	148	150	122	123	
128	120	112	143	136	118	145	122	126	
136	128	108	136	125	121	145	123	118	
150	115	112	136	143	120	149	123	127	
125	138	115	134	140	120	145	131	121	
65	64	56	55	58	44	57	56	69	
< 14	< 14	101	< 14	< 14	< 10	56	56	73	
125	121	102	120	137	120	134	121	125	
61	63	45	57	58	48	62	56	63	
157	132	104	131	138	120	137	125	124	
164	130	109	150	136	120	137	120	127	
164	123	115	143	137	120	138	121	126	
< 14	< 14	< 14	< 14	< 14	< 10	67	59	54	
< 14	< 14	< 14	< 14	< 14	< 10	74	61	62	
67	65	50	56	64	51	68	61	81	
157	128	98	125	138	118	134	119	129	

Table 2-4. Series 11 Corrosion test programme.

3 BACKGROUND CORRECTIONS

3.1 SOURCES OF BACKGROUND

Although the spreadsheet has behaved satisfactorily as a routine procedure for the correction of isobaric interferences, as more corrected results became available, there were clear indications, not unexpected, that further correction routines for the correction for background levels of elements with natural isotopic composition would be necessary in order to achieve a satisfactory level of analytical accuracy and precision for nuclides over the whole spreadsheet.

There are several sources of background including:

- impurities in chemicals and water used for the preparation of leachant solutions.
- impurities in vessel materials, membrane filters, acids etc.
- in-cell contamination with materials of both natural and "active" isotopic composition.
- contamination during out-of-cell handling, particularly by calibration standards of natural isotopic composition.
- contamination and memory effects in the instrument itself.
- plasma effects such as the enhancement of the Pu-239 mass peak by U-238-H⁺.

3.2 BACKGROUND CORRECTION PROCEDURES.

The various sources of background affect the mass spectrum in different mass ranges and to different degrees, and require different correction methods. For example, the U-238-H⁺ contribution to the Pu-239 mass peak can be readily corrected for by means of U standards, and the measured U concentration in the sample, or, as is used here, the total Pu concentration can be calculated from the Pu-240 measurement and the previously measured isotopic composition of the Pu in the sample.

In SKB-type bicarbonate groundwaters, even with careful selection of chemicals, there are background levels of Rb, Sr, Cs and Ba of natural isotopic composition which are significant with respect to low-level fission product contents. These must be subtracted from the measured nuclide concentrations either by use of separate measurements on blank solutions of corrodant solutions, or by calculation of the natural backgrounds by means of isotopic ratios observed in the sample solutions.

Corrections for natural background levels for other nuclides, or for contamination effects in the instrument itself, can only be applied by means of the regular analysis of blank test solutions. For most of the samples in the large retroactive analysis campaign reported here, this was not possible, since the corrosion tests had been performed long before use of the ICP-MS technique had been considered. It has been necessary, therefore, to use the results of the background measurements performed later in the campaign for correction even of the measurements on the early archive specimens. This correction procedure is unavoidably associated with uncertainty, particularly for the results for minor constituents in the specimens, and must be taken into consideration during later evaluation. For the analyses discussed in this report, these comments only apply to the comparison of plutonium measurements, since, as mentioned above, the ICP-MS method used here for the determination of specimen Pu concentrations is based on determination of the Pu-240 content, and this is usually fairly low in bicarbonate groundwater specimens.

Details of the specific background correction procedures applied will be given in the following section where the results of the analytical method comparison programme are presented.

4 METHOD COMPARISON

4.1 URANIUM

4.1.1 Conventional method

Although neutron activation analysis was used for the first few years, the determination of uranium in most of the specimens in the spent fuel corrosion programme, has been performed by laser fluorescence analysis. /1-2/.

4.1.2 ICP-MS method

Determination of the U-238 nuclide concentration in the specimens can be effected by the measurement of three mass peaks; the **119 mass peak**, corresponding to $U-238^{2+}$, has been used for the majority of the specimens in this programme. Since the U concentration in the specimens is usually very high relative to the other elements, use of the **238 mass peak** is associated with problems due to the high counting rate, and has been restricted to specimens with low U contents, for example from tests performed under anoxic conditions, or in vessel strip solutions. A further alternative, the **254 mass peak**, corresponding to UO^+ , was only measured in a few of the specimens, and is not considered further here.

In all the measured samples, background correction has involved subtraction of standardized general backgrounds. Three standardized backgrounds have been used, representing the average results of a number of ICP-MS analyses of blank specimens of the bicarbonate groundwater under both oxic and anoxic conditions, and deionized water. As discussed above, these backgrounds have been used even for the correction of the ICP-MS results from corrosion test specimens measured retroactively.

4.1.3 Comparison of results

The results of uranium concentration measurements (expressed as ppb) by the two methods on centrifugate and vessel strip specimens are compared in Figure 4-1. Only a few membrane filter specimens have been analyzed for U by both methods, and are not considered here. Results for about 140 and 80 of the centrifugate and vessel strip solution specimens respectively are plotted in the figure. More specimens were analyzed by both methods, but had U concentrations lower than the detection level by the laser fluorescence technique, which explains the relatively few centrifugate results at low uranium concentrations.

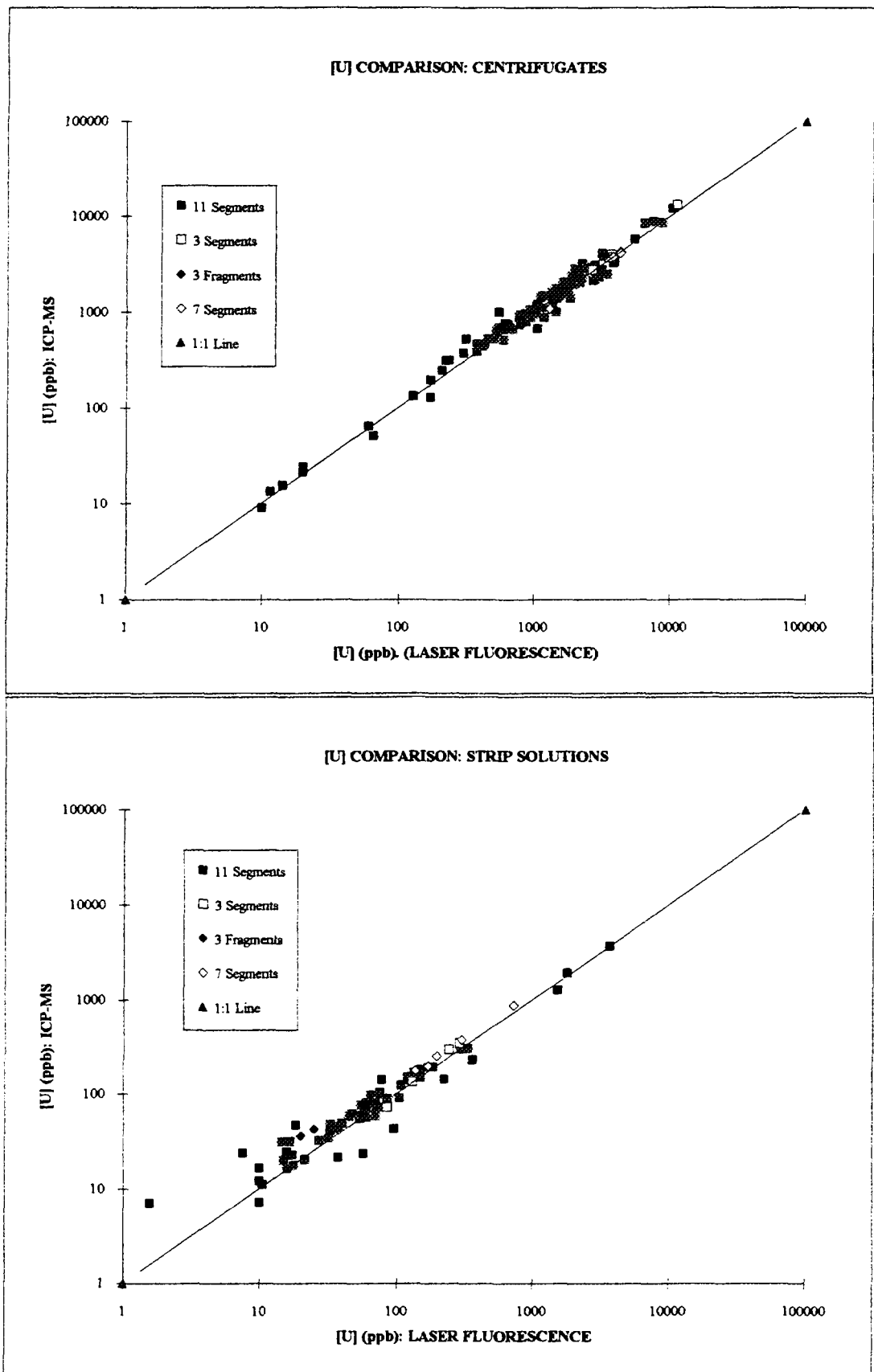


Figure 4-1. Comparison of uranium concentrations in centrifugates (above) and vessel strip solutions (below) determined by laser fluorescence analysis and by ICP-MS.

Inspection of Figure 4-1 shows that the results determined by the two methods show generally good agreement over a concentration range of about three orders of magnitude. For centrifugates specimens, the ICP-MS results tend to show higher concentrations than those obtained by the laser fluorescence method, with an average ratio of 1.09 for all specimens. A similar trend is also seen for vessel strip solutions, with an average ratio of 1.24 for the plotted results. This higher ratio, however, is largely due to results from 6 specimens with very low U concentrations; if these results are excluded from the comparison, the average ratio is reduced to 1.10.

4.2 CESIUM

4.2.1 Conventional method

All types of specimen, centrifugate, membrane filter and vessel strip solution, in the spent fuel corrosion programme, have been subjected to quantitative gamma spectrometric analysis. /1-2/, using suitable standards. Two cesium isotopes, Cs-134 and Cs-137, are normally analyzed for, since their ratio is also a useful aid to specimen identification, because of its correlation with the fuel specimen's burnup. The measured specimen activities of the two nuclides, expressed as Becquerel, are corrected for radioactive decay back to a reference date, and compared with the corresponding total specimen activity at the same date.

In this comparison programme, only results for Cs-137, which is always the more abundant of the two gamma emitters, are considered.

4.2.2 ICP-MS method

After direct analysis of radioactive solutions, the spreadsheet calculates the concentrations of 3 cesium isotopes, mass 133, 135 and 137, which are potentially suitable for the determination of specimen fission product cesium concentrations, and hence, the release from the fuel during corrosion. In this comparison programme, Cs-133 and Cs-135 have been selected for the ICP-MS method instead of Cs-137 for the reasons discussed later in this section. As a consequence of this, a direct comparison of the Cs-137 concentrations determined by the two methods is not made here, and the comparison is performed at the release fraction level, i.e., for each sample, the measured concentrations of fission product Cs-133 and Cs-135, after correction for natural backgrounds, are expressed as fractions of their respective inventories in the corroded fuel specimen. These fractions generally show very good agreement, which is a test of the efficacy of the applied spreadsheet and background corrections. The results presented here are the average of the release fractions for the two isotopes, and these values are compared with the corresponding release fractions calculated from the Cs-137 determinations described in section 4.2.1.

The decision to use only Cs-133 and Cs-135 for the ICP-MS method is based partly on consideration of the background correction procedures used, and partly on effects due to selective corrosion and radioactive decay. Natural cesium consists entirely of the 133 isotope, and, therefore, the correction for its background is only applied to the measured mass 133 peak. The background levels in the corrodant solutions used in the programme are very low and are corrected for by subtraction of the appropriate standardized backgrounds discussed above.

Both the 135 and 137 mass peaks must be corrected for contributions due to natural barium, which can be present at significant levels in the corrodants and chemicals used. The natural Ba background has been calculated for all specimens by means of their measured Ba-136/Ba-138 ratios. This ratio is significantly different for barium of natural isotopic composition and for mixtures of fission product isotopes as calculated by ORIGEN. (See the Introduction). Unfortunately, the ratios are very small, and are also sensitive to the fuel specimen burnup, and the accuracy of the calculated natural barium background is, therefore, subject to some uncertainty, particularly for low concentration samples. However, in general, the correction procedure appears to be sufficiently accurate, since, as stated above, good agreement was obtained between the release fraction results for Cs-133 and Cs-135, the latter having been corrected for natural Ba-135 background.

Hence, the release fractions for Cs-137, corrected for natural Ba-137, would also be expected to show similar good agreement, and in most cases this is also obtained. However, it has been observed that when large fission product barium concentrations are present in the analyzed samples, for example after redissolution of precipitates on the fuel surface, and when Ba concentrations are often higher than the Cs concentrations, the enhanced Ba-137 component of the 137 mass peak perturbs the isobaric correction procedure, and Cs-137 release fractions are obtained which are somewhat low compared with the Cs-133 and Cs-135 results.

It has, therefore, been found preferable to use the Cs-133 and Cs-135 isotopes for **all** samples.

4.2.3 Comparison of results

The cesium release fraction values determined by the ICP-MS and gamma spectrometric methods, for both centrifugates and vessel strip solutions, are compared in Figure 4-2. It can be seen that reasonable agreement between the two methods has been obtained over about three orders of magnitude, from E-05 to E-02, although at the high end of the range there is appreciable scatter. These points refer to some of the very high release centrifugates from the first contact period of the Series 11 corrosion tests, where only single analyses were performed on archive solutions at a time shortly after commissioning of the ICP-MS instrument. The cesium concentrations were very high in these samples, corresponding to concentrations of Cs-133 and Cs-135 at the ppm level.

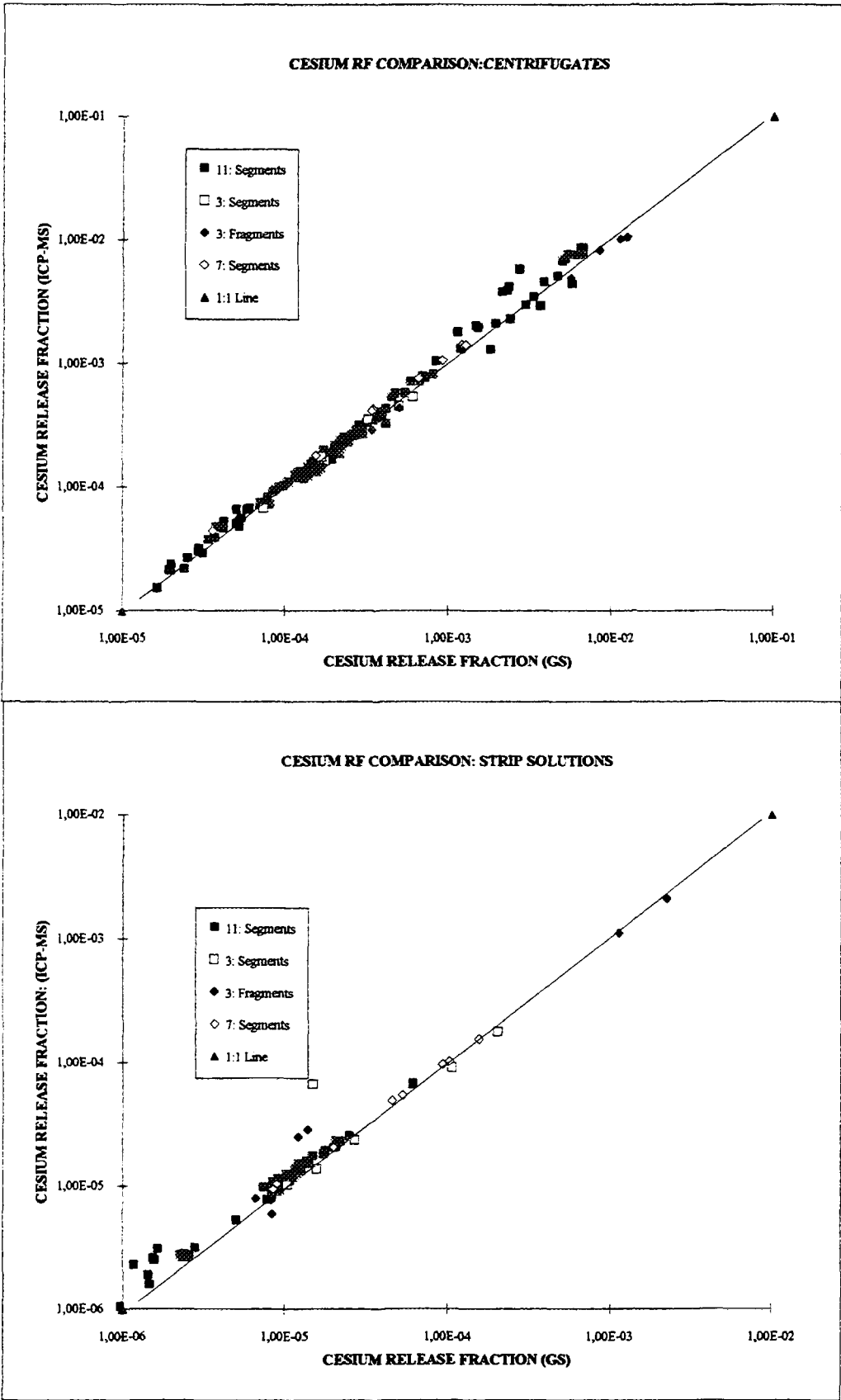


Figure 4-2. Comparison of cesium release fractions determined by gamma spectrometric analysis and ICP-MS in centrifugates (above) and vessel strip solutions (below)

For each of the three fuel types used in the corrosion programme, the average ratio of the ICP-MS release fractions to the corresponding gamma spectrometric value has been calculated. A ratio of 1.07 was found for the Series 11 samples, and for the appreciably fewer samples from the Series 3 and 7 corrosion tests, values of 0.91 and 1.18 respectively.

Here, the reader is reminded that the release fractions for cesium which are compared in this section, are derived from the solution concentrations (or activities) of the selected isotopes and the corresponding total inventory of the isotope in the spent fuel specimen used in the corrosion test.

The inventory values used for the gamma spectrometric method, and the other conventional analytical methods considered in this report, were those determined (by the same methods) on selected specimens of the three fuel types at the start of the corrosion tests, and are documented in the appropriate references listed in this report.

ICP-MS analysis, of course, requires a much more extensive inventory of nuclides than conventional analysis. Such inventories have been determined for the three reference fuels using the same spreadsheet and background correction procedures as for the sample analyses presented in this report.

For the Series 11 corrosion tests, the two inventory specimens used for the original inventory analyses were re-analyzed by the ICP-MS technique, and then individual inventories for each of the 16 corrosion test specimens were calculated by interpolation between the 2 inventory specimens. The stored solutions used for the original inventory determinations on the Series 3 and 7 reference fuels, however, were considered too old (10 and 6 years respectively) for ICP-MS inventory determination, and new fuel specimens from each fuel rod were taken, dissolved, and analyzed by ICP-MS. The new specimens were taken from locations as near as possible to the respective corrosion test specimens.

Not surprisingly, small but significant differences were found between the inventories of nuclides which could be determined by both techniques, particularly for the Series 11 specimens, where a somewhat different interpolation method had been used for the ICP-MS results. Thus, the differences between the release fractions obtained by the two methods is partly due to differences in inventory values. When these differences are corrected for, the average ratios of the ICP-MS values to the gamma spectrometric values, are 0.96 for the Series 11 specimens, and 0.95 and 1.18 for the Series 3 and 7 specimens respectively.

4.3 STRONTIUM

4.3.1 Conventional method

The earlier results are based on a standard radiochemical method /1-2/ for the determination of Sr-90. For all samples, the measured Sr-90 activity is corrected for radioactive decay to the appropriate reference date.

4.3.2 ICP-MS method

The solution concentrations of two strontium isotopes, Sr-88 and Sr-90, are calculated by means of the spreadsheet, corrected for background, and used for calculation of their respective release fractions. As in the case of cesium in the preceding section, comparison of the two results represents an internal check on the accuracy of the measurements. The solution concentrations of the two fission product isotopes are similar, but their mass peaks are affected by natural backgrounds in different ways, and require different correction procedures.

The bicarbonate groundwaters used in the SKB corrosion programme contain traces of natural strontium at the ppb level, and the natural Sr-88 content (82.6%) represents a significant component of the measured 88 mass peak. Since, as mentioned above, ICP-MS background results on the groundwaters used in the early corrosion tests are not available, the Sr-88 natural background component for each sample analyzed is calculated in the spreadsheet by means of the 86 mass peak which is assumed to represent natural Sr-86.

In most centrifugate samples, the measured 90 mass peak represents Sr-90, with perhaps a small Y-90 component formed by radioactive decay during storage prior to analysis. During some corrosion tests, however, for example those performed at low pH, and in many vessel strip and membrane filter samples, where dissolution of the Zircaloy clad has occurred, traces of natural Zr-90 can be a significant component of the measured 90 mass peak. The natural zirconium level can be calculated by a type of internal isotopic dilution analysis, but the procedure is complicated and probably inaccurate.

For most centrifugate samples, the correction procedures appear to function satisfactorily, since good agreement between the release fractions calculated for the two isotopes has been obtained.

4.3.3 Comparison of results

As in the case of cesium, the results obtained by the radiochemical and ICP-MS methods are compared at the release fraction level, and the available results for centrifugate samples are presented in Figure 4-3. The ICP-MS results plotted are the averages of the values obtained with both isotopes. For the reasons discussed above, only a few reliable values for vessel strip solutions were available, and these will not be presented here in this report.

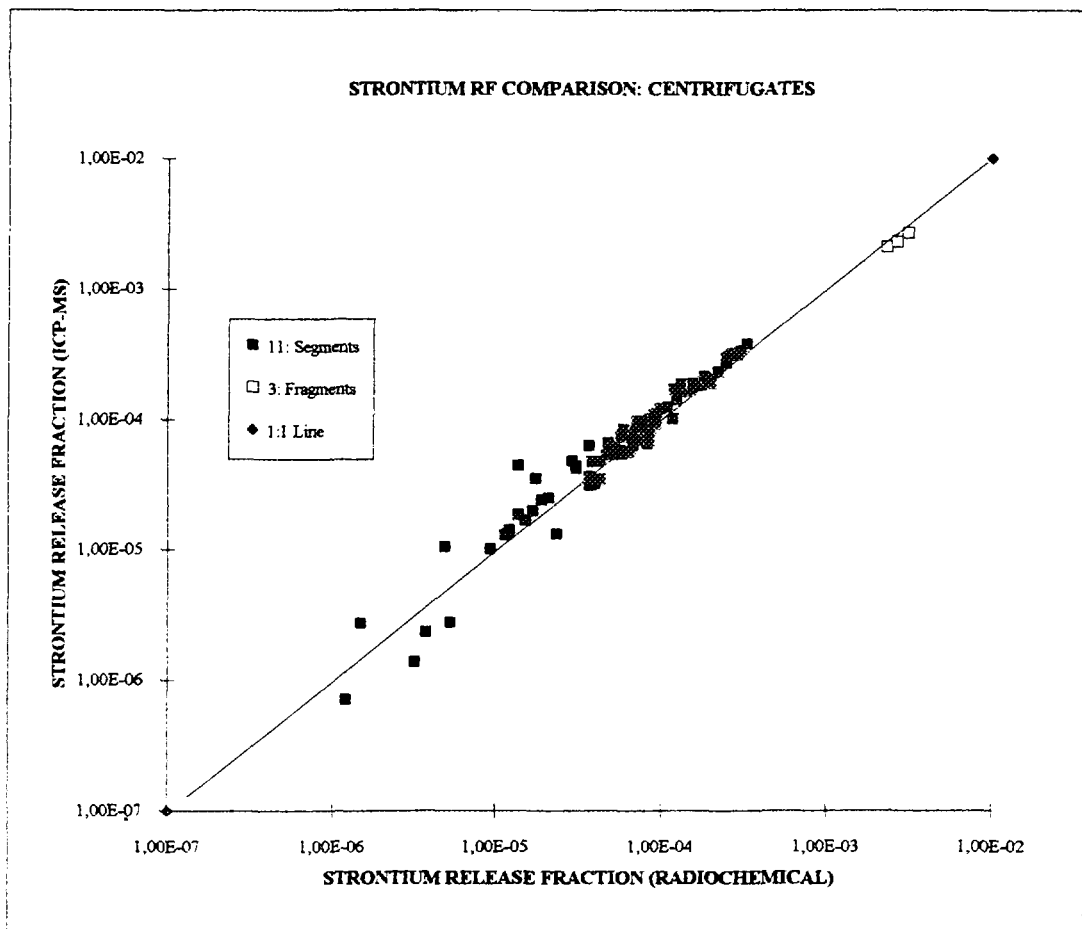


Figure 4-3. Comparison of strontium release fractions determined by radiochemical analysis and ICP-MS in centrifugates.

In such samples, and for solutions with low fission product strontium contents, it is probable that the radiochemical method is to be preferred.

Inspection of the figure shows that reasonable agreement was attained between the values obtained by the two methods over about 2 orders of magnitude, but that at release fractions below E-05, more scatter is observed, as in the case of the cesium results. For Sr-88 and -90, this level corresponds to solution concentrations of about 0.26 and 0.36 ppb respectively.

Most of the available results were from Series 11 specimens, and, for these, the average ratio to the radiometric results was 1.13, which, after correction for inventory differences, was adjusted to 0.96. For the few results available from the Series 3 fuel fragment tests, the corresponding ratios were 0.87 and 0.94.

4.4 TECHNETIUM

4.4.1 Conventional method

The details of the radiochemical separation and beta counting procedures for the determination of Tc-99 have been documented previously /1-2/. In the method used at Studsvik, stages for iodine removal were included in the separation procedure after it was found that I-129 was a possible interference. The method, therefore, has high specificity, but the measured activities in many samples have been lower than the detection limit.

4.4.2 ICP-MS method

Technetium is monoisotopic, so the ICP-MS analytical method is restricted to the use of the 99 mass peak. In the spreadsheet for the correction for isobaric interferences, the assumption is made that, in the type of sample arising in the corrosion programme, such interference is negligible, and background correction is performed, therefore, by subtraction of the appropriate standardized background as described above.

4.4.3 Comparison of results

The technetium release fractions for samples of centrifugates and vessel strip solutions determined by the radiochemical and ICP-MS methods are compared in Figure 4-4. Only samples from the Series 11 corrosion tests have been analyzed by both methods.

As in the case of cesium and strontium, it can be seen that there is a close correspondance between the results from the two methods over a range of about three orders of magnitude of sample concentrations. There is, however, a marked increase in scatter in the results at release fraction levels of about E-06, which corresponds to Tc-99 sample concentrations of about 0.06 ppb, which is close to the detection limit for the standard radiochemical method. The average ratio between the centrifugate release fraction values for the ICP-MS method and the radiochemical method was 1.02. After correction for inventory differences, a ratio of 0.96 was obtained.

4.5 PLUTONIUM

4.5.1 Conventional method

The standard method, /1-2/, used for the determination of plutonium in the corrosion test samples prior to commissioning of the ICP-MS instrument was alpha spectrometry of aliquots of sample, without chemical separation of the plutonium.

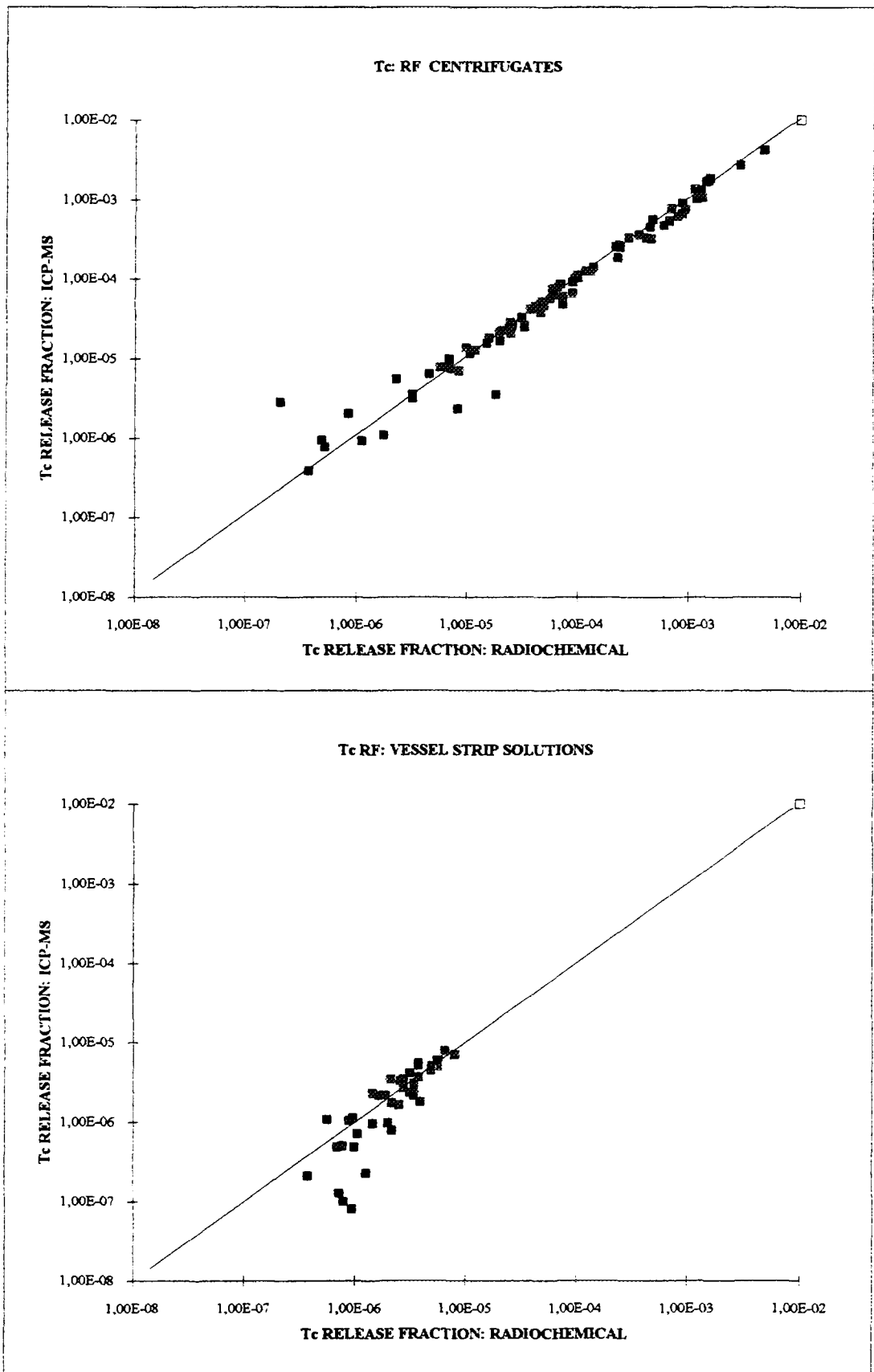


Figure 4-4. Comparison of technetium release fractions determined by radiochemical analysis and ICP-MS in centrifugates (above) and vessel strip solutions (below)

The samples were mounted directly on stainless steel discs and allowed to air dry. The alpha spectra can consist of 4 energy peaks as shown in Table 4-1. Minor components are shown in parentheses. The 6.12 MeV peak is only measurable during the first few years after the end of the fuel irradiation, due to the relatively short half-life of Cm-242.

Table 4-1. Alpha energy peaks and their nuclide components.

5.15 MeV	5.50 MeV	5.82 MeV	6.12 MeV
Pu-239, Pu-240	Pu-238, Am-241	Cm-244, (Cm-243)	Cm-242, (Cm-243)

As seen in the table, only one alpha peak, that at 5.15 MeV, is attributed to plutonium alone, but consists of two isotopes, Pu-239 and Pu-240, with half-lives of 24080 and 6542 years respectively, and the specific 5.15 MeV alpha activity of a plutonium sample, therefore, depends on its isotopic composition. In the case of the Series 3 and 7 corrosion tests, where the corrosion test specimens have nominally the same burnup as their respective inventory specimens, the relationship between the 5.15 MeV alpha peak activity and the total plutonium concentration was established by the determination of the isotopic composition of chemically separated plutonium from the inventory specimens. However, the analytical results are usually collected in the form of release fractions, expressed as the total 5.15 MeV activity in the analyzed sample, divided by the total fuel specimen inventory of the same peak, as calculated from the specimen weight and the inventory specimen analysis.

For the 16 Series 11 fuel specimens, where the inventory specimens were taken from the top and bottom of the fuel pellet stack, the 5.15 MeV alpha inventory of each specimen was calculated by interpolation between the values for the 2 inventory specimens, assuming linearity with burnup.

The absolute counting rates of the 4 measured alpha peaks, and their ratios, of the samples measured in the analytical programme, depend, of course, on the experimental parameters of the individual corrosion test. Whereas, vessel strip solution samples, which usually consist of fuel fines, contain all the components in about the same ratios as their respective inventories, centrifugate samples normally are relatively depleted in curium, and the ratio of the 5.50 MeV peak to the 5.15 MeV peak is also altered because of a lower Am-241 component.

The method used for sample preparation for alpha spectrometric analysis, air-drying of the counting discs, causes some alpha particle self-absorption in the residual salts, and the alpha peaks normally display some low energy side peak tailing which complicates the background correction procedure. Further, particularly in samples from corrosion tests performed under reducing or anoxic conditions, the 5.15 MeV peak activity is very low, with associated poor counting statistics.

4.5.2 ICP-MS method

As mentioned earlier in this report, the method chosen for the direct ICP-MS analysis of plutonium is based on the assumption that the measured 240 mass peak is subjected to negligible isobaric interference, and can be assigned to Pu-240. Thus, after subtraction of the appropriate standardized background, (groundwater under oxic, or anoxic conditions, and deionized water), the total Pu-240 content of the sample can be used together with the corresponding specimen inventory to calculate the release fraction. The plutonium **concentration** can be calculated from the Pu-240 release fraction, and the ratios of the other plutonium isotopes to Pu-240, which have been determined or derived from solid source mass spectrometric analysis of separated plutonium from the respective inventory specimens.

In this analysis comparison programme, the use of Pu-240 as the monitoring nuclide for fractional release and total concentration is clearly subject to inaccuracy with regard to the arbitrary background subtraction procedure which must be used. However, it has been preferred to the alternative of using the measured mass 239 peak, since in almost all samples, correction of the peak for the component due to U-H⁺ formed in the plasma is substantial because of the high U/Pu ratio, and is probably a larger source of error than uncertainty in the standardized backgrounds used for Pu-240.

4.5.3 Comparison of results

In the result comparisons above for U, Cs, Sr and Tc, the ratios of the results from the ICP-MS and conventional analytical methods have always been fairly close to unity both before and after adjustments for the two inventory versions. During comparison of the plutonium results, however, it was observed that there was a much larger scatter in the ratios than found in the earlier comparisons. This appeared to be due to loss of plutonium, by precipitation and/or adsorption, from the older archive solutions, although all archive samples had been acidified prior to storage.

The effect is illustrated in Figure 4-5, in which the ICP-MS plutonium release fractions for centrifugates are plotted against the corresponding results from the alpha spectrometric method. In the upper part of the figure, only the ICP-MS results from samples analyzed within a few weeks of termination of the corrosion test are plotted, while in the lower part, the results are from archive solutions which had been stored for six months or more prior to ICP-MS analysis. For the Series 11 corrosion tests, all centrifugate samples from the first six contact periods of the fuel specimens with aqueous corrodant are therefore considered as archive solutions

However, no clear correlation between the storage time of the archive solutions and the apparent loss of plutonium from solution was found, although there was a tendency for older solutions to show larger losses.

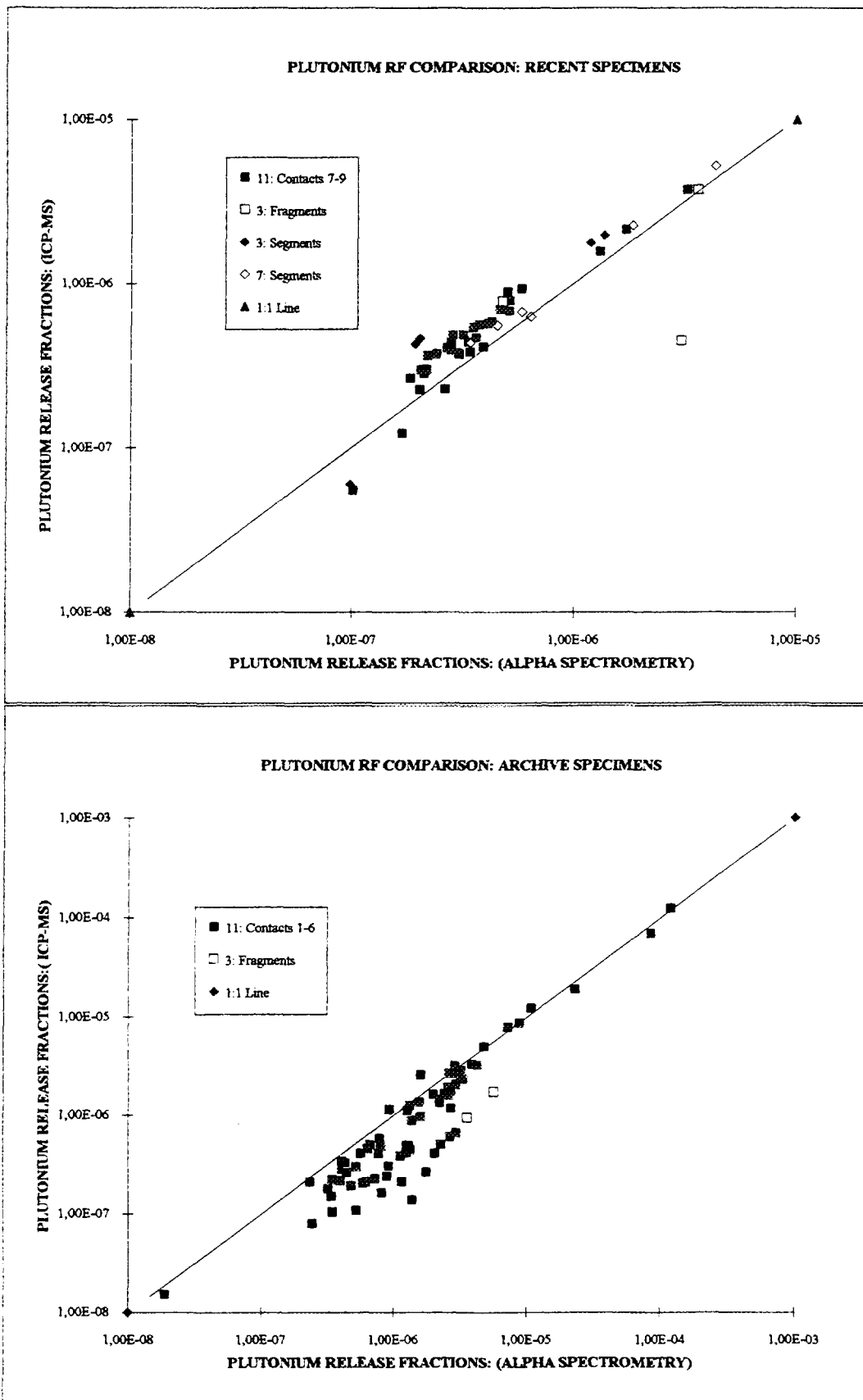


Figure 4-5. Comparison of plutonium release fractions determined by alpha spectrometric analysis and ICP-MS in centrifugate samples: recent specimens (above) and archive solutions (below)

Apart from one obvious analytical flier, and a few results at release fractions of about E-07, the ratios of most of the ICP-MS results to those by alpha spectrometric analysis in recently analyzed specimens, are significantly larger than unity. This is regarded here as the "true" analytical bias, even though many of the results from the archive solutions lie on or near the 1:1 ratio line.

There are not so many "recent analysis" results available for comparison of the analytical methods, since plutonium release to the corrodant decreases as the corrosion process proceeds, and these samples have significantly lower release fractions than those in the archive solutions. (Note that the two parts of the figure have different log-log scales). However, for the Series 11 corrosion test samples, the average ratio of the ICP-MS results to the alpha spectrometric results was 1.39. After adjustment for differences in the inventory values used, a ratio of 1.22 was obtained.

One of the main reasons for performing this comparison of analytical methods was to qualitatively assess the reliability of the results from retroactive direct ICP-MS analysis of archive solutions. The observed loss of plutonium from archive solutions discussed here, obviously means restrictions on the intended use of the ICP-MS data for other actinides and rare earth elements during experiment evaluation.

5 DISCUSSION

The main comments and conclusions which can be drawn after the method comparison presented in section 4 of this report are the following:

- a) For all the 5 elements for which a comparison can be made between the ICP-MS technique and the analytical methods used earlier in the spent fuel corrosion programme, there is a satisfactory linear correspondence between the results, (in practice, solution concentration), over 2-3 orders of magnitude.
- b) Before considering the degree of quantitative agreement between the results, it should be recalled that the comparison programme was not a stringent test of the ICP-MS technique itself. All of the retroactive ICP-MS analyses on archive solutions from earlier stages in the corrosion tests were performed shortly after commissioning of the instrument for work with radioactive samples, when experience of stable operation of the instrument was still being gathered. Further, in order to limit the analytical workload, only single analyses were performed on most of these samples, which weakens the statistical base for a comparison.
- c) Particularly for uranium and technetium, the results of the conventional analysis for low sample concentrations have often been reported as lower than the method's detection limit. Hence, the method comparison is somewhat biased towards samples with higher concentrations.
- d) The average values of the ratios between the analytical results obtained by the ICP-MS technique and the conventional methods given in section 4 are, therefore, only approximate, and have validity only for the Series 11 tests where more results are available for comparison.
- e) The values of the ratios for the Series 11 corrosion tests, both before and after adjustment for differences in the determined inventories, are presented in Table 5-1.

Table 5-1. Average values of the ratios of ICP-MS results to those from conventional methods. (Series 11 tests only)

Based on independent specimen inventory values				
U	Cs	Sr	Tc	Pu
1.09	1.07	1.13	1.02	1.39

Adjusted to common specimen inventory values				
U	Cs	Sr	Tc	Pu
1.09	0.96	0.96	0.96	1.22

The ratios most relevant for assessment of the performance of the direct analysis of corrosion test samples by ICP-MS are those which have been adjusted to take account of the differences in inventory values determined experimentally by the ICP-MS and conventional methods. It can be seen from Table 5-1, that the differences are fairly large, particularly for strontium and plutonium. Although, as mentioned above, the differences can be partly explained by the fact that the ICP-MS inventories were determined on new fuel specimens (Series 3 and 7), or on archive solutions (Series 11), it cannot be excluded that other effects specific to the ICP-MS methodology (concentration in the plasma, or the calibration technique) used at that time, contribute to the observed differences.

Inspection of the ratios adjusted for inventory differences shows that the results for the fission products Cs, Sr and Tc display a small (4%) negative bias with respect to the corresponding conventional methods, while the U and Pu results have apparently significant positive biases. For the latter elements, this may be due to the inadequacy of the standardized background subtraction procedure for taking account of variations of the instrumental component of the background during the intensive analytical campaigns. However, these questions will not be addressed further here, but will be considered later during final evaluation.

- f) For the fission products, the good agreement between the results from the various methods, - a 4% difference must be regarded as satisfactory at these low concentration levels in multi-component solutions -, suggests that the ICP-MS results for other fission products, such as rubidium and barium, which have not been included in the method comparison programme, can be used in the evaluation of corrosion test results. This extension in the number of elements analysed will facilitate result interpretation, for example for confirmation of congruent dissolution.
- g) The observed loss of plutonium from the stored archive solutions, though not unexpected, restricts the use of the ICP-MS results even for other elements, (the rare earths), where similar precipitation and/or adsorption effects can be expected. Thus, during evaluation of the analytical results for the actinides in stored solutions, the results from the alpha spectrometric method, which were performed shortly after termination of the corrosion tests, will be favoured.

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