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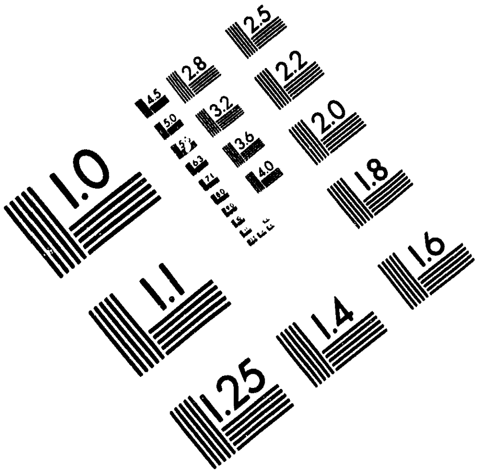

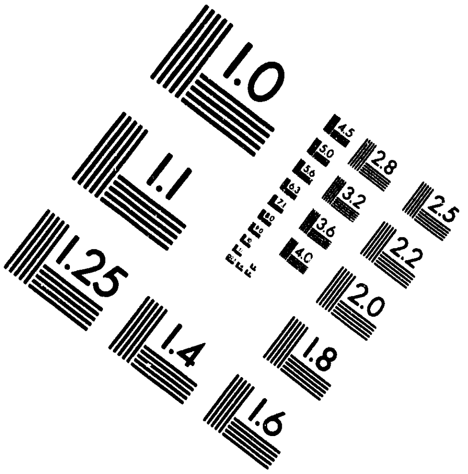

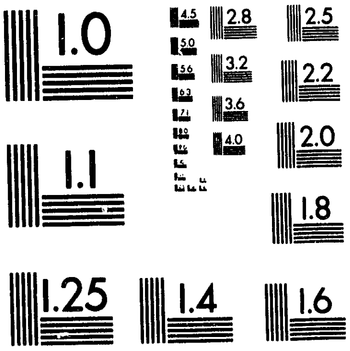

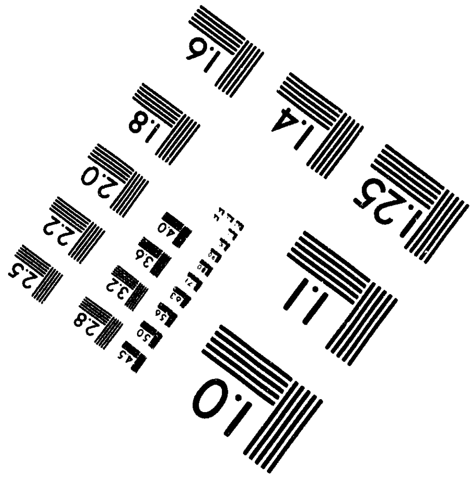

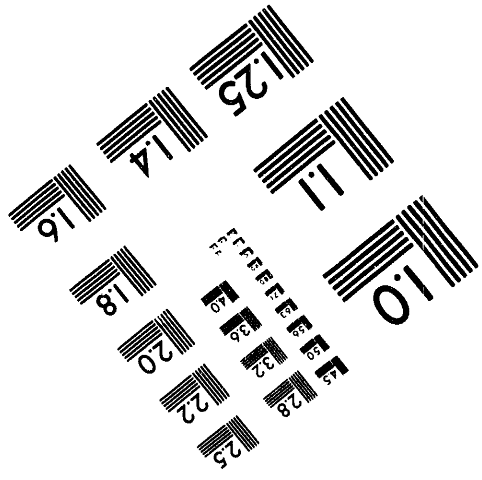

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DETERMINATION OF LONG-LIVED ACTINIDES IN SOIL LEACHATES BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

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Inductively coupled plasma - mass spectrometry (ICP-MS) was used to concurrently determine multiple long-lived ($t_{½} > 10^4$ y) actinide isotopes in soil samples. Ultrasonic nebulization was found to maximize instrument sensitivity. Instrument detection limits for actinides in solution ranged from 50 mBq L^{-1} (^{239}Pu) to 2 μBq L^{-1} (^{235}U). Hydride adducts of ^{232}Th and ^{238}U interfered with the determinations of ^{233}U and ^{239}Pu; thus, extraction chromatography was used to eliminate the sample matrix, concentrate the analytes, and separate uranium from the other actinides. Alpha spectrometric determinations of ^{230}Th, ^{239}Pu, and the ^{234}U/^{238}U activity ratio in soil leachates compared well with ICP-MS determinations; however, there were some small systematic differences (*ca*. 10%) between ICP-MS and α-spectrometric determinations of ^{234}U and ^{238}U activities.

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Introduction

For more than 50 years, the United States Department of Energy (DOE) and its predecessors have been responsible for production of the nuclear materials used in the nation's defense. The production and handling of these materials have left a legacy of radioactive contamination at various sites throughout the United States. Recent estimates[1] suggest that more than one million radiochemical analyses *per annum* will be required to support ongoing surveillance and cleanup activities at contaminated DOE facilities. There is significant concern within the DOE that analytical laboratories will be unable to process and analyze the anticipated number of incoming samples with sufficient speed to meet regulatory and programmatic milestones.

Inductively coupled plasma - mass spectrometry (ICP-MS) has been extolled elsewhere[2,3] as a very rapid technique for the determination of long-lived radionuclides. Quadrupole ICP-MS has been used to determine ^{99}Tc,[2-4] ^{129}I,[5] and actinide isotopes[6-8] in environmental samples; however, most investigators have employed ICP-MS solely for the detection of a single radioisotope or radioactive element. This approach fails to take advantage of the mass spectrometer's capability for rapid sequential analysis. As such, in this work, we examine the utility of ICP-MS for the concurrent determination of multiple long-lived ($t_{½} > 10^4$ y) actinide isotopes in soil samples.

The isotopes determined in this study were selected on the basis of the evaluation published by Smith *et al.*[9] Soil samples were selected for this study because of the difficulties inherent in their preparation for analysis. We employed ultrasonic nebulization to enhance the sensitivity of the ICP-MS instrument,[10] and extraction chromatography was used to eliminate the sample matrix, concentrate the analytes, and separate uranium from the other actinides (to minimize spectral interferences) prior to instrumental analysis. The analytes were quantitated by isotope dilution using spike concentrations compatible with α-spectrometry (< 0.1 Bq per spike). We believe that the techniques used in this work may be applied with equal success to water and biota samples.

Experimental

Equipment. A Fisons (Winsford, Cheshire, UK) PlasmaQuad II ICP-mass spectrometer was used to measure the analytes of interest. Solutions were introduced into the plasma with a CETAC (Omaha, NE, USA) U5000-AT ultrasonic nebulizer (USN); a V-groove pneumatic nebulizer (PN) and a water-cooled Scott double-pass spray chamber (both provided by Fisons) were also used to obtain some comparative performance data. Solutions were delivered to the nebulizers using a Gilson (Middleton, WI, USA) Minipuls 3 peristaltic pump. Typical instrument operating parameters are presented elsewhere.[11]

Analysis of Standards. Standards were analyzed to establish instrumental limits of detection and assess interferences. Standard solutions were prepared by volumetric dilution of 1 mg L^{-1} solutions of ^{232}Th and depleted uranium. The diluent was 5 volume % nitric acid (Optima grade, Fisher Scientific, Pittsburgh, PA, USA) in 18 MΩ-cm deionized water (Nanopure System, Barnstead Thermolyne, Dubuque, IA, USA). The isotopic composition of our uranium standard solution is listed elsewhere.[11]

Ten consecutive 30-second integrations were averaged to obtain each ICP-MS measurement of the standards. Multiple, consecutive quadrupole scans were added to obtain each integration. Except as specified, multiple ion monitoring (MIM) was used to acquire all data. The MIM dwell times per quadrupole scan were greater for minor isotopes (^{230}Th, ^{233,234,236}U, ^{237}Np, and ^{239}Pu) than those used for major isotopes (^{232}Th and ^{235,238}U).

Analysis of Soil Samples. Samples of Standard Reference Materials (SRMs) 4350B, 4353, and 4354 (National Institute of Standards and Technology, Gaithersburg, MD, USA) and Quality Assurance Program samples (QAPs) 37, 38, and 39 (DOE Environmental Measurements Laboratory, New York, NY, USA) were acid-leached, and known amounts of ^{229}Th, ^{232,233}U, and ^{242}Pu (*ca*. 80 mBq each) were added to the leachates. The spiked leachates were prepared for ICP-MS and α-spectrometric analysis using extraction chromatography. Spectral interferences were minimized by separating the leachates into uranium and thorium/transuranic (Th/TRU) fractions prior to ICP-MS analysis. The soil preparation procedure and α-spectrometric analyses are described in detail elsewhere.[12]

Using the 5% HNO_3/deionized water diluent described above, the Th/TRU fractions of the leachates were diluted two-fold prior to quantitative analysis. The uranium fractions were diluted 10-fold prior to determination of $^{234-236}$U and 100-fold prior to determination of ^{238}U. A procedure blank, diluted to the appropriate degree, was analyzed in advance of the samples. Four consecutive 30-second integrations were averaged to obtain an ICP-MS analysis of each sample. Multiple ion monitoring was used for quantitation. Dwell times were essentially the same as those used for the standard analyses; however, ^{229}Th and ^{242}Pu were added to the quadrupole scans.

The following ratios were calculated using the net isotope intensities from the diluted samples: $^{230}Th/^{229}Th$, $^{234}U/^{233}U$, $^{235}U/^{234}U$, $^{236}U/^{235}U$, $^{238}U/^{235}U$, $^{237}Np/^{239}Pu$, and $^{239}Pu/^{242}Pu$. ^{232}Th was not determined due to the poor accuracy of analog signals measured with our ICP-mass spectrometer. The uranium isotope ratios were corrected for mass bias[13] using Certified Reference Material U010 (New Brunswick Laboratory, Argonne, IL, USA). Isotope dilution with ^{229}Th, ^{233}U, and ^{242}Pu was used to determine the concentrations of the other isotopes; this approach eliminated the need to correct the concentrations for dilution and chemical yield.

Results and Discussion

Instrumental Limits of Detection. Table 1 shows solution limits of detection for various actinide isotopes measured by ICP-MS. Data are presented for two types of nebulization (pneumatic and ultrasonic) and two types of spectral acquisition (scanning and multiple ion monitoring). These data show that multiple ion monitoring with ultrasonic nebulization has the lowest limits of detection. The reductions in detection limit were due to the high efficiency of the ultrasonic nebulizer[10] and the higher precision of the background when measured by multiple ion monitoring.

Figure 1 shows the effect of integration time per replicate on limits of detection for three actinide isotopes. The figure shows that, as integration time was increased, detection limits decreased linearly with the square root of the integration time. This result is expected from consideration of counting statistics and their influence on detection limits.[10] However, longer integration times also increase sample consumption. As such, integration times must also be chosen with consideration for the available sample volume and the desired number of replicate measurements.

Interferences. Non-spectroscopic interferences in ICP-MS have been described elsewhere.[14] Spectral overlap interferences can exist in two forms: atomic ion overlap (e.g., ^{238}U on ^{238}Pu) or polyatomic ion overlap (e.g., $^{232}Th^{16}O^+$ on $^{248}Cm^+$). Figure 2 shows some polyatomic ion interferences that can be encountered in actinide determinations. Figure 2b (soil leachate, uranium fraction) shows $^{238}UH^+$ at *m/z* 239. Figure 2a (soil leachate, Th/TRU fraction) shows $^{232}ThH^+$ at *m/z* 233, $^{232}Th^{16}O^+$ at *m/z* 248, and $^{232}Th^{16}OH^+$ at *m/z* 249. Radiometric analysis of the Th/TRU fraction suggested that the mass spectral peak at *m/z* 246 in Figure 2a was due to $^{232}Th^{14}N^+$. To our knowledge, this is the first observation of metal-nitrogen polyatomic ions in an ICP-mass spectrum.

The relative intensities of the actinide hydride, oxide, and hydroxide ions have been reported elsewhere.[11,15] These polyatomic species are significant because they are likely to interfere with the determination of ^{233}U, ^{239}Pu, and ^{248,250}Cm in natural samples. Note that relative intensities of polyatomic ions can be influenced by changes in the ICP-MS operating parameters; thus, analysts should carefully examine potential interferences using the appropriate instrument operating conditions before performing any analyses. When possible, qualitative analysis of the sample (i.e., spectral interpretation) is also advisable.

Comparison of ICP-MS Results. Table 2 shows the results from soil leachate analyses performed by ICP-MS and α-spectrometry. These results are not compared to certified (or consensus) values because the soil samples were leached rather than dissolved. Because ^{233}U is a radiometric interferent upon ^{234}U, radiometric determinations for ^{234}U were obtained from unspiked leachate aliquots. The isotopes ^{235,236}U and ^{237}Np were not determined by α-spectrometry; thus, no comparison is provided.

The uncertainties presented in Table 2 for the ICP-MS measurements are based on propagation of experimental uncertainty,[16] i.e., the squared coefficients of variation (CVs) for each term in the activity calculation were added to obtain the squared CV for the calculated activity. Even with the added uncertainty due to error propagation, the CVs for the activities determined by ICP-MS are generally within 10% of the mean activity, except in the case of ^{239}Pu, where the activities are close to the detection limit. Precision can be improved by longer integration times, more replicates, or increased spike concentrations; however, we consider the precision demonstrated herein to be satisfactory for environmental surveillance.

Paired, two-tailed *t*-tests indicated no statistically significant difference between ICP-MS and α-spectrometric determinations of ^{239}Pu and ^{230}Th at the 95% confidence interval. These tests also indicated that there were small, but statistically significant differences in the ICP-MS and α-spectrometric determinations of ^{234}U and ^{238}U. Averaged over all the samples, the relative differences in the ^{234,238}U activities were approximately 10% of the α-spectrometric results. Based on examination of spiked and unspiked leachate spectra, this difference was not due to interference of ^{232}ThH^{+} upon ^{233}U^{+} in the ICP-MS measurements, nor was it due to the presence of ^{233}U in the samples. Further *t*-tests showed no significant difference between ICP-MS and α-spectrometric determination of the ^{234}U/^{238}U activity ratio. Based on these observations, we conclude that the systematic differences in the absolute activities of ^{234}U and ^{238}U were caused by the use of different isotope dilution spikes (i.e., ^{232}U for α-spectrometry *versus* ^{233}U for mass spectrometry).

As indicated in Table 2, the ICP-MS detection limits decreased as sample size was increased (compare ^{239}Pu in QAP 39 to that in SRM 4350B). This observation is significant in that required detection limits for anthropogenic isotopes in soil (e.g., ^{239}Pu + ^{240}Pu) are less than 1 Bq kg^{-1}.[17] This work suggests that such activities could be determined by ICP-MS using larger soil samples; total dissolution might also increase the mass of analyte available for measurement. We are evaluating these approaches as this work continues in our laboratory.

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Table 1. Instrumental limits of detection for actinide isotopes in solution.

	Limit of Detection/mBq L^{-1} [a]			
	scanning		multiple ion monitoring	
isotope	PN [b]	USN [c]	PN [b]	USN [c]
^{230}Th	2000	50	500	8
^{232}Th	0.04	4×10^{-3}	0.04	4×10^{-3}
^{233}U	2000	40	200	4
^{234}U	900	20	200	5
^{235}U	0.4	8×10^{-3}	0.06	2×10^{-3}
^{236}U	10	0.2	2	0.05
^{238}U	0.1	0.01	0.1	9×10^{-3}
^{237}Np	100	3	20	0.5
^{239}Pu	1×10^{4}	200	2000	50

[a] Limit of detection based on 3σ of the background equivalent concentration, pooled over 3 days.

[b] Limit of detection using pneumatic nebulization (PN) and the specified spectral acquisition technique.

[c] Limit of detection using ultrasonic nebulization (USN) and the specified spectral acquisition technique.

Table 2. Comparison of soil leachate analyses using ICP-MS and α-spectrometry

		^{230}Th/Bq kg^{-1} [a]		^{239}Pu/Bq kg^{-1} [a]	
sample	mass/g	ICP-MS	α-spec.	ICP-MS	α-spec. [b]
SRM 4350B	2.02	18 ± 2	18.1 ± 0.7	< 4 [c]	0.7 ± 0.1
	1.9	17 ± 2 [d]	19.6 ± 0.7	< 3	0.7 ± 0.1
SRM 4353	2.05	26 ± 2	32 ± 1	6 ± 1	6.8 ± 0.4
	1.84	30 ± 2 [d]	27 ± 1	7.2 ± 0.4	7.2 ± 0.4
SRM 4354	1.43	12 ± 1	11.8 ± 0.7	5 ± 1	4.0 ± 0.4
	1.49	11 ± 2 [d]	13.3 ± 0.7	3.9 ± 0.6	3.3 ± 0.4
QAP 37	3.397	10.6 ± 0.7	10.7 ± 0.6	7 ± 1	6.1 ± 0.3
QAP 38	2.89	33 ± 5	34.4 ± 0.7	8 ± 2	9.6 ± 0.6
QAP 39	3.08	9 ± 1	9.3 ± 0.6	2.0 ± 0.4	1.1 ± 0.1

[a] Mean and uncertainty of the determination. The uncertainty in the ICP-MS results are expressed as one standard deviation, derived from propagation of experimental uncertainty.[16] The uncertainty in the α-spectrometry results are expressed as one standard deviation, derived from counting statistics.

[b] Results for ^{239}Pu + ^{240}Pu.

[c] The "<" values represent the limit of detection, which is defined as three times the uncertainty in the blank equivalent concentration.

[d] Duplicate results obtained by preparation and analysis of a second leachate aliquot.

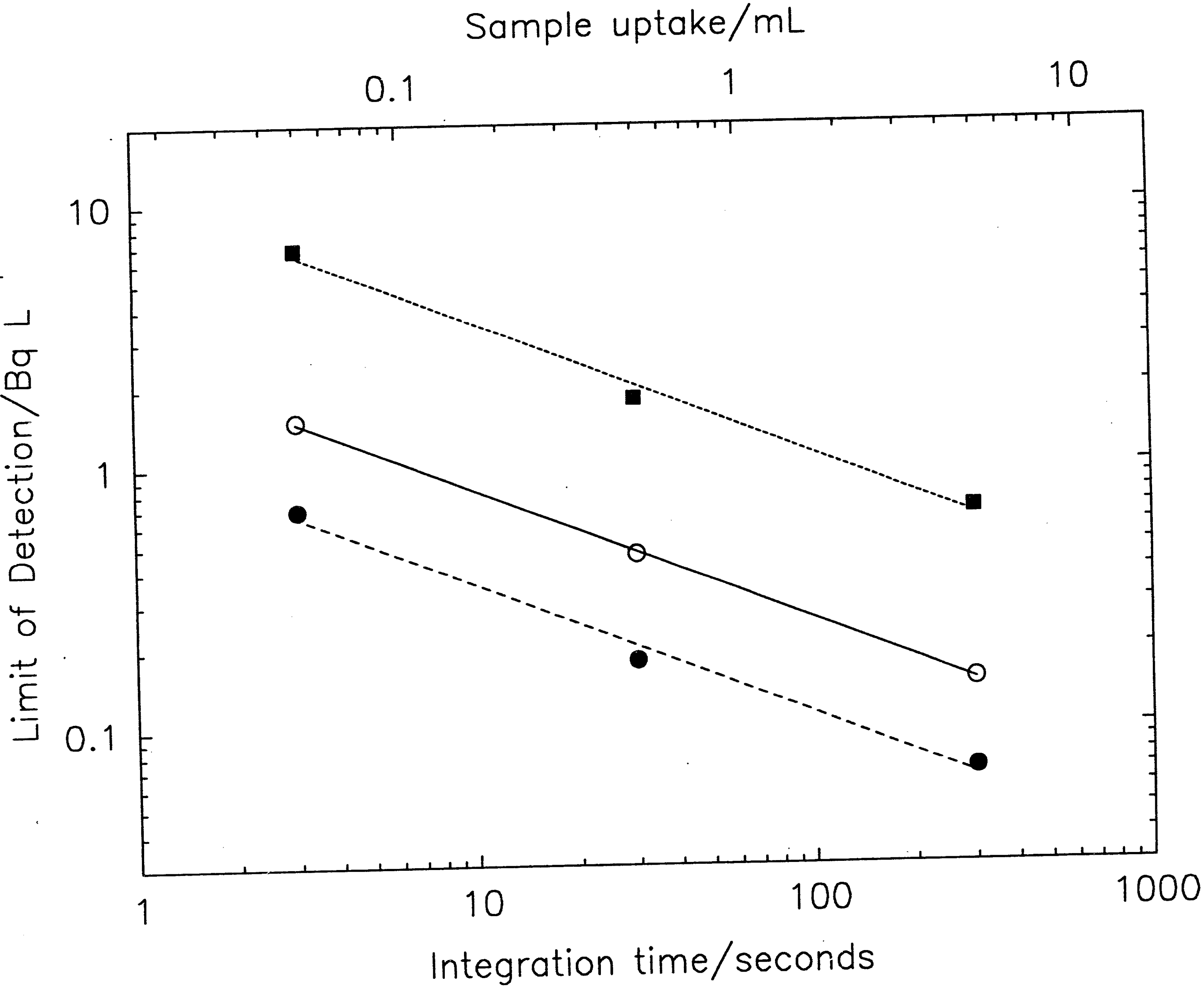
Table 2. Comparison of soil leachate analyses using ICP-MS and α-spectrometry (concluded)

		^{234}U/Bq kg^{-1} [a]		^{238}U/Bq kg^{-1} [a]	
sample	mass/g	ICP-MS	α-spec. [e]	ICP-MS	α-spec.
SRM 4350B	2.02	16 ± 1	18 ± 1	13 ± 1	14.2 ± 0.9
	1.9	16 ± 1 [d]	19 ± 1	13 ± 1	14.8 ± 0.8
SRM 4353	2.05	20 ± 3	20 ± 1	18 ± 3	20 ± 1
	1.84	19 ± 1 [d]	22 ± 1	18 ± 2	22 ± 1
SRM 4354	1.43	14 ± 1	13.6 ± 0.6	14 ± 2	13.1 ± 0.6
	1.49	14 ± 1 [d]	14.4 ± 0.8	14 ± 1	14.2 ± 0.8
QAP 37	3.397	12.1 ± 0.7	13.8 ± 0.4	11.0 ± 0.9	12.9 ± 0.4
QAP 38	2.89	15.8 ± 0.9	17.9 ± 0.8	16 ± 1	17.0 ± 0.8
QAP 39	3.08	8.5 ± 0.6	9.4 ± 0.5	8.1 ± 0.8	9.4 ± 0.5

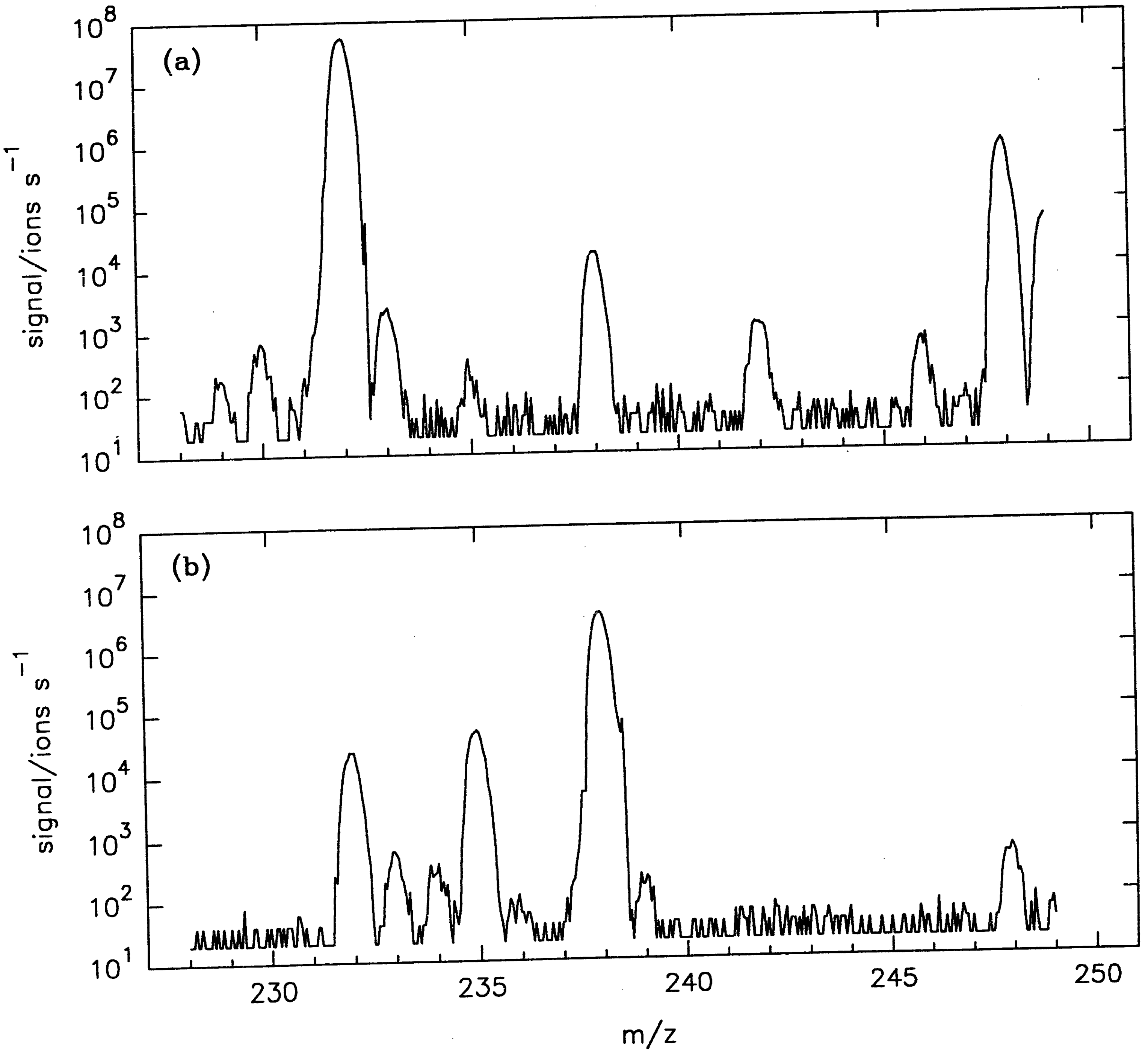
[e] Results for ^{233}U + ^{234}U.

Figure 1. Variation in instrumental limit of detection with integration time per replicate for ^{230}Th (○), ^{234}U (●), and ^{239}Pu (■) using pneumatic nebulization. Note that sample uptake per replicate (top axis) increases linearly with integration time.

Figure 2. ICP-mass spectra for the (a) Th/transuranic fraction and (b) U fraction of a soil leachate. The Th/transuranic fraction was diluted 10-fold prior to this analysis.


Sample uptake/mL
0.1
1
10
10
1
0.1
Limit of Detection/Bq L^{-1}
1
10
100
1000
Integration time/seconds

Crain fig. 1


(a)
(b)
signal/ions s^{-1}
10^1
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10^3
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230
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240
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250
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Crain fig. 2

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