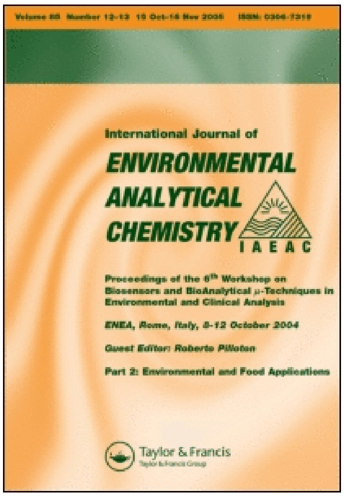

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Carter, J. A. , Walker, R. L. , Smith, D. H. and Christie, W. H.(1980) 'Isotope Dilution Resin Bead Mass Spectrometry—An Ultra Trace Technique for Measuring Nuclides in Three-Mile Island Water', International Journal of Environmental Analytical Chemistry, 8: 4, 241 — 248

To link to this Article: DOI: 10.1080/03067318008071893

URL: http://dx.doi.org/10.1080/03067318008071893

Intern. J. Environ. Anal. Chem., 1980, Vol. 8, pp. 241-248
0306-7319/80/0804-0241 $6.50/0

Printed in Great Britain

Isotope Dilution Resin Bead Mass Spectrometry— An Ultra Trace Technique for Measuring Nuclides in Three-Mile Island Water†

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(*Received May 30, 1980*)

From the onset of the Three-Mile Island reactor incident (March 28, 1979), the distinct possibility existed that actinide and fission product pollutants could escape into the surrounding environment. Experienced analytical chemists in command of techniques which achieve the highest sensitivity were called upon for assistance in performing analyses. Cooling water was analyzed for uranium and plutonium, certain fission products, additives, and possible corrosion products by isotope dilution mass spectrometry. In particular, the thermal emission isotope dilution technique, in which an anion exchange resin bead was used to concentrate the uranium and plutonium, provided technical information on samples orders of magnitude smaller than those necessary for conventional counting techniques. The resin-bead-loaded sample acts as a point source in a pulse counting two-stage high abundance sensitivity mass spectrometer, enhancing the sensitivity so that levels as low as $10^{-13} M$ plutonium and $10^{-11} M$ uranium concentrations have been detected in one ml of water; a full description of the methodology involved will be presented. The methodology employed for this exercise also provided isotopic information which was informative with respect to material source, location, and condition. Sample chronology and trace element data will also be presented on water from the Three-Mile Island site. Other potential applications of the technique will be discussed.

KEY WORDS: Mass spectrometry, resin bead, isotope dilution, ultra trace actinides, spark source, Three-Mile Island, SIMS

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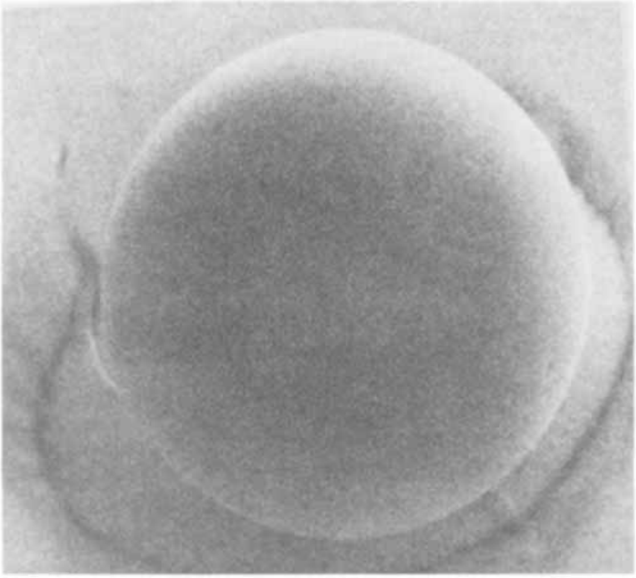
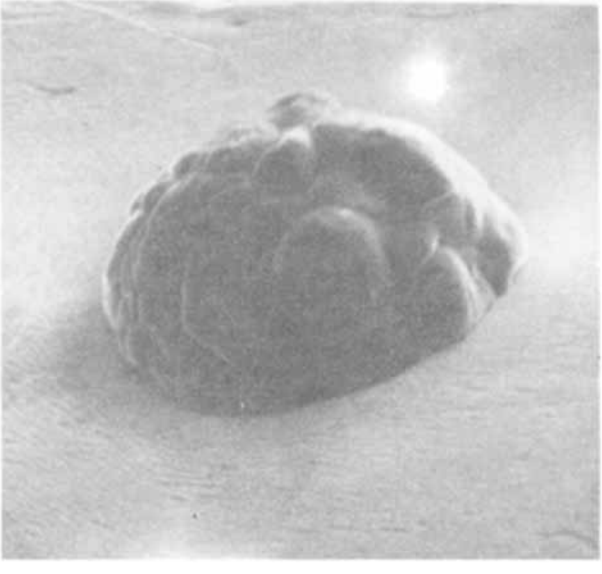
†Research sponsored by the U.S. Department of Energy, Division of Basic Energy Sciences, under contract W-7405-eng-26, with the Union Carbide Corporation.

Presented at the 10th Annual Symposium on the Analytical Chemistry of pollutants, Dortmund DFR May 28–30, 1980



1a Diameter of 0.15 mm loaded with 10^{-9} g of uranium.



1b Carbon shell of resin bead on a rhenium filament after 30 min @ 1700°C.

FIGURE 1 Anion resin beads before and after analysis.

INTRODUCTION

The technique of loading samples on resin beads for isotopic mass spectrometric analysis was first suggested by Freeman *et al.*[1] We have adapted the technique to use single anion resin beads both as chemical separation devices for plutonium and uranium and as vehicles for introducing such samples into the mass spectrometer.[2,3] This technique is particularly applicable to safeguards[4] and low-level environmental analysis problems.

This technique uses Dowex 1, 2% cross-linked anion resin beads in the nitrate form. An aliquot of the sample is adjusted at 8 *M* in HNO_3. Under these conditions, only plutonium and uranium absorb appreciably, and essentially complete separation from fission products and other actinides is achieved. Optimal adsorption of plutonium and uranium from solutions containing both elements is achieved when the uranium concentration is adjusted to about 1 μg U per bead. The samples under consideration in this work were too dilute to allow this desideratum to be met, but satisfactory adsorption was still obtained. After standing in contact with the solution for 16–24 hours, the beads are extracted and washed; they will have adsorbed a maximum of 3 ng of Pu and U per bead, the exact amount being a function of the concentration of the solution and the exposure time. Exposure times can be reduced to 30 minutes or less by agitating the beads with the solution. Samples this small have so little radioactivity ($<10^{-10}$ Ci) that they are readily transportable—no bulky (and costly) shielding is required.

Each bead serves as a sample for mass spectrometric analysis, and Pu and U are analyzed sequentially from it.[1] Plutonium ionizes from the single Re filament at about 1450°C and U at about 1700°C. The bead serves as a good approximation to a point source for the ion optics of the instrument, and the carbon matrix left from the bead seems to act as a reservoir for the sample from which it is slowly fed to the ionizing region.[5] Both of these factors serve to improve the ion collection efficiency. Figure 1 contains scanning electron micrographs showing a virgin bead and one that has been heated for 30 min at 1700°C. A substantial carbon matrix of the bead remains that contains virtually all of the U sample, which does not migrate along the Re filament.[5]

The mass spectrometers used in this work are multi-staged, pulse counting instruments with high abundance sensitivity and possess the ability to analyze very small samples.[6,7] The technique does not inherently demand such sophisticated instruments and can readily be used on single-stage mass spectrometers.[8]

Analyses of samples loaded on resin beads show no degradation of results in comparison to those loaded in the conventional manner as solutions. Table I contains results of replicate analyses of NBS isotopic standards that illustrate the reliability of the technique.

The intrinsic selectivity and sensitivity of this technique make it ideally suited for environmental studies, where only low levels of Pu and U can be expected. The incident at Three-Mile Island required just such a technique to answer some crucial questions. It was vital for engineers at the site to know if the primary cooling water had been in contact with the reactor core; and, if it had, it was imperative to know the actinide element concentration, and what fission and corrosion products were present. Isotope-dilution spark-source mass spectrometry[9] was used to measure concentrations and isotopic compositions of many elements of concern, and secondary ion mass spectrometry to measure the isotopic composition of Li. The resin bead technique described above was used to analyze Pu and U.

TABLE I

Comparison of isotopic results from resin beads to certified NBS values

SRM-015, Uranium			SRM-947, Plutonium[a]		
	Atom percent			Atom percent	
Nuclide	Resin bead[b]	NBS	Nuclide	Resin bead[b]	NBS
234	0.00854	0.00850	238	0.297	0.296
235	1.538	1.532	239	75.647	75.696
236	0.0164	0.0164	240	18.328	18.288
238	98.437	98.443	241	4.544	4.540
			242	1.184	1.180

[a] Pu values corrected to NBS data of 10/13/71.
[b] $\sim 1 \times 10^{-9}$ g each of U and Pu per sample; N = 4, with precision of 0.2 %.

RESULTS AND DISCUSSION

The Analytical Chemistry Division of Oak Ridge National Laboratory received a sample of about 3 cm^3 of primary cooling water on which to perform all required analyses. Of this, 0.1 cm^3 was used for resin bead analyses of Pu and U. Samples of other solutions of concern were received later.

Parameters describing the operation of the Three-Mile Island reactor at the time of the incident[10] (28 March 1979) were used as input for the ORIGEN computer code, which then calculated predicted isotopic compositions for Pu and U. These predicted values should not be expected to agree exactly with measured ones since the latter will vary with the position of the sample in the reactor core, the exact flux it has been exposed to, etc. Table II contains the isotopic compositions of Pu and U predicted by the ORIGEN code and those measured by our laboratory. The close agreement of the two sets of values shows unequivocally that the core had been breached and exposed to the cooling water. The Pu analysis was obtained from an estimated 10–20 pg.

TABLE II
TMI primary cooling water measurements

Uranium—Concentration: 110 ng ml^{-1}

Isotopic Composition, Atom Percent

Nuclide	ORIGEN Code	Mass Analysis
234	0.02	0.021
235	2.16	2.22
236	0.07	0.072
238	97.74	97.69
Plutonium—Concentration:		0.24 ng ml^{-1}
238	0.04	<0.1
239	90.68	90.3
240	7.86	7.8
241	1.38	1.8
242	0.04	0.1
U/Pu—Concentration Ratio		
	448	458

Table III lists concentrations and isotopic compositions for Pu and U for samples taken from three storage tanks. Pu concentrations below 10^{-11} molar gave insufficient ion signals for reliable measurement of isotopic composition.

Boron was added to the primary cooling water by engineers at the scene. The large cross-section of ^{10}B for neutron capture makes this element a good means of controlling and measuring nuclear reactivity. It is therefore important to be able to monitor and verify the concentration of ^{10}B in solution. Isotope-dilution spark-source mass spectrometry[9] was used to determine the levels of boron and other elements such as ^{135}Cs and ^{137}Cs in the primary cooling water. These results are presented in Table IV. Secondary ion mass spectrometry was used to determine the isotopic composition of both boron and lithium in these solutions. A compound containing enriched ^{7}Li had been added to the solution at the site for pH control. The need for accurate knowledge of the isotopic composition of B and Li was partially responsible for the development of a secondary ion mass spectrometric method for performing such measurements.[11]

TABLE III

Uranium and plutonium concentration by isotope dilution thermal emission mass spectrometry

	Concentration X 10^{-10} Molar	
Sample	U	Pu
A-1	25	0.0088
A-2	655	0.19
A-3	71	0.0025

U and Pu isotopic measurement in atom percent

Sample	234	235	236	238	239	240	241	242
A-1	<0.01	0.6	<0.01	99.4	†			
A-2	0.0075	0.84	0.026	99.126	82.42	12.10	4.67	0.81
A-3	<0.01	0.6	<0.01	99.4	†			

†Ultra low Pu concentration; insufficient sample for isotopic analysis.

The low levels of Ag, Cd, and In indicate that little, if any, dissolution of the control rods had taken place.

TABLE IV

Elemental composition measurements on TMI primary cooling water

Element	Concentration (μg ml^{-1})	Method[a]
B	3440	SSMS
$^{10}B = 20\%$		SIMS
$^{11}B = 80\%$		
Ag	$\leqq 0.2$	SSMS
Al	10	SSMS
Cs	8	SSMS
$^{133}Cs = 45\%$		
$^{135}Cs = 13\%$		
$^{137}Cs = 42\%$		
Cd	$\leqq 0.3$	SSMS
Li	4.6	SIMS
$^{6}Li = 0.02\%$		
$^{7}Li = 99.98\%$		
Fe	$\leqq 1$	SSMS
^{131}I	0.9	SSMS
In	$\leqq 0.5$	SSMS
K	0.4	SSMS
Na	960	FES
P	0.1	SSMS
S	20	SSMS
Si	5	SSMS
^{89}Sr, Y	1	SSMS

[a] Spark-Source Mass Spectrometry (SSMS); Flame Emission Spectrometry (FES); and Secondary Ion Mass Spectrometry (SIMS)

Note: Approximately 20 other elements also measured by SSMS.

CONCLUSIONS

The combination of the resin bead technique and extremely sensitive mass spectrometers allowed us to be of assistance in solving the problems at Three-Mile Island. For the limited sample sizes the levels of actinide concentrations reported are orders of magnitude lower than those obtained by conventional alpha counting techniques.

We received the first sample (primary cooling water) on 8 April 1979 and returned the results summarized in Tables II and IV on 10 April. This rapid response enabled scientists at the site to proceed as expeditiously as possible in attacking the problem. It should be pointed out that it is the level of ^{29}Pu (48 ppm) in our ^{242}Pu spike which limits our sensitivity in determining Pu concentrations. With ^{239}Pu at the 1 ppm level, we could measure Pu concentrations two orders of magnitude (10^{15} *M*) lower than the lowest value reported here. Unfortunately, such a spike is not presently available, however, efforts are underway to secure such a high purity ^{242}Pu spike.

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