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Radiochemical Analysis Using Empore^{TM} Rad Disks*

Lesa L. Smith[1], and Kent A. Orlandini[2]
[1]Analytical Chemistry Laboratory
Chemical Technology Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

[2]Environmental Research Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

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DISCLAIMER

RADIOCHEMICAL ANALYSIS USING EMPORE™ RAD DISKS

Lesa L. Smith
Argonne National Laboratory
Chemical Technology Division
9700 South Cass Avenue
Argonne, IL 60439
(630) 252-1890

Kent Orlandini
Argonne National Laboratory
Environmental Research Division
9700 South Cass Avenue
Argonne, IL 60439
(630) 252-4236

ABSTRACT

A solid-phase extraction technique that isolates specific radionuclides (i.e., $^{89/90}$Sr, $^{226/228}$Ra, ^{99}Tc) from surface, ground, and drinking waters is described. The analyte is isolated by pulling a sample through an appropriate Empore™ Rad Disk with a vacuum, and the disk is subsequently assayed by a suitable counting technique. The method has both laboratory and field applications. Interferences are discussed.

I. INTRODUCTION

The costs associated with environmental restoration and waste management activities at both government and private facilities are burdensome and continue to grow. However, the development and implementation of new technologies can significantly reduce these high costs.

Through a long-standing collaboration, Argonne National Laboratory and the 3M Company have developed a disk solid-phase extraction technology to improve sample preparation and recovery of radionuclides from aqueous samples (i.e., surface, ground, and drinking waters). Disks have been developed with high selectivity and great affinity for important radionuclides,[1-3] including $^{89/90}$Sr, $^{226/228}$Ra, and ^{99}Tc. Additionally, the Argonne-3M team has been successful in adapting the disks for use in the field.

The application of selective membrane technology to environmental radioanalytical chemistry offers dramatic improvements over many current laboratory techniques. Membrane technology significantly improves sample throughput, since the laboratory operations of sample processing and source preparation are compressed into a single step. Samples are acidified, as necessary, processed through the appropriate rad disk to isolate the analyte under nominal flow rates of 50 mL/min, and then assayed by a suitable counting technique. Samples are easily batched, and a 1-L sample can be processed in less than twenty minutes. Secondary wastes and associated costs are reduced because this technique eliminates many of the hazardous reagents associated with the conventional approaches to sample preparation.

II. LABORATORY APPLICATIONS

A. Strontium

Empore™ Strontium Rad Disks are used to efficiently isolate strontium from samples acidified to 2-4 M HNO_3. The disk is subsequently assayed for ^{90}Sr beta activity, or alternatively, ^{90}Y can be stripped and counted after sufficient ingrowth. As shown in Table 1, strontium retention is greater than 97% for 1 L samples that contain less than 3 mg total strontium and do not contain large amounts of certain interfering cations (e.g., 10,000 ppm of ammonium, potassium, or calcium). However, at levels typical of environmental samples, these interferences are minimal. Also, barium, radium, and lead have been shown to be retained by the disk.

Table 1. Cation interference on strontium retention

Interfering Cation[a]	Sr Retention, % (± 2%)	
	2 M HNO_3[b]	4 M HNO_3[b]
10,000 ppm Li^+		99
10,000 ppm NH_4^+	6	10
10,000 ppm Na^+	76	83
10,000 ppm Mg^{2+}		97
10,000 ppm K^+	1	3
10,000 ppm Ca^{2+}	33	24
100 ppm K^+	53	89
100 ppm Ca^{2+}	99	97
100 ppm NH_4^+	96	97
10 ppm Pb^{2+}	22	17
1 ppm Pb^{2+}	97	99
0.1 ppm Ba^{2+}	101	97
	Stable Strontium Effect	
$[Sr^{2+}]$		4 M HNO_3
1.60 mg		98
3.20 mg		97
6.40 mg		63
8.00 mg		52

[a] Solutions were prepared from the chloride salts of the listed cations, except for Sr solutions, which were from the nitrate salt.

[b] Samples contained 1.60 mg strontium per liter of nitric acid solutions.

B. Radium

Empore™ Radium Rad Disks exhibit a large capacity for radium. Over 2000 pCi of ^{226}Ra has been loaded onto a 25-mm disk. Quantitative recoveries of radium have been attained for sample volumes up to 3 L with a 47-mm disk. Additionally, these disks appear to function well over a wide range of pH. No change in the performance of these disks occurred when the matrix acid concentration was varied from deionized water through 6 M HNO_3. Experiments indicated that high levels of potassium, ammonium, and sodium interfere with the uptake of radium, as shown in Table 2. However, similar to the behavior exhibited by the strontium rad disks, these interferences are not a problem at levels typical to environmental samples. Barium also is retained by the radium disks.

C. Technetium

Empore™ Technetium Rad Disks are used to selectively extract the pertechnetate ion (TcO_4^-) from aqueous solutions. However, laboratory evidence also suggests that Tc(IV) is retained by the disk, although the mechanism is unclear. Quantitative recoveries of technetium have been achieved over a wide range of pH for sample volumes up to 12 L on a 47-mm disk. The technetium uptake efficiency remains high (>98%) from aqueous samples having aggregate anion contents above 30,000 µg/mL. Except for nitrate, perchlorate, and iodide ions, no significant interferences have been found, as shown in Table 3. The nitrate interference is important to note since many samples are acidified at the point of sampling. Therefore, for samples requiring technetium analyses, hydrochloric acid should be used for acidification.

Table 2. Cation interference on radium retention

Interfering Cation[a]	Ra Retention[b], % (± 2%)	
	0.1 M HNO_3	2 M HNO_3
10,000 ppm Li^+	98	
10,000 ppm NH_4^+	15	49
10,000 ppm Na^+	87	97
10,000 ppm Mg^{2+}	100	
10,000 ppm K^+	7	45
10,000 ppm Ca^{2+}	99	
1000 ppm NH_4^+		93
1000 ppm K^+		97
100 ppm NH_4^+	99	
100 ppm Na^+	100	
100 ppm K^+	98	
100 ppm Fe^{2+}		92
100 ppm Sr^{2+}	98	
100 ppm Ba^{2+}		45
10 ppm Ba^{2+}	84	97
10 ppm Pb^{2+}	99	
1 ppm Ba^{2+}	100	

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[a] Solutions were prepared from the chloride salts of the listed cations.

[b] Samples contained 294 pCi ^{226}Ra per liter of nitric acid solutions.

III. FIELD APPLICATIONS

The Argonne-3M team evaluated the field deployability of the Empore™ Rad disks during testing at two Department of Energy sites. Six ground-water monitoring wells and two surface water sites were sampled, with a total of 67 samples collected on Empore™ Technetium Rad Disks. Technetium-99 concentrations in these water samples ranged from 2 to 4000 pCi/L. Sample volumes ranged from 1.0 to 14.0 liters and were collected at flow rates from 150 to 440 mL/min, the latter a more than eight-fold increase over the conventional laboratory method for these disks. Off-site analysis of the membranes for ^{99}Tc was performed by liquid scintillation (LSC) and solid scintillation counting (SSC). Water samples were also analyzed for ^{99}Tc by standard methods, and general agreement to the Empore™ membrane results was exhibited (13 of 15 data sets for the LSC samples were shown to be statistically equivalent at the 95% confidence level to the standard method data). Table 4 rives the results for five sampling sites. Several sample pre-filters and effluents were also selected for analysis, and only trace amounts of residual ^{99}Tc were detected.

Table 3. Anion interference on technetium retention

Potential Interference (1000 ppm)	Tc Retention, % Acidic Soln. pH 4.5 - 6.5 (± 2%)	Neutral Soln. pH 7.0 (± 2%)	Basic Soln. pH 7.5 - 9.5 (± 2%)
Deionized Water		> 99	
PO_4^{3-}	> 99	> 99	> 99
SO_4^{2-}	99	99	99
F^-	> 99	99	99
B (H_3BO_3)	> 99	> 99	99
B ($Na_2B_4O_7$)	99	99	> 99
CO_3^{2-}		> 99	> 99
OH^- pH 9-14			> 99
OCl^- (NaOCl)			99
I^- (KI)			70
Mo^{6+} $(Mo_7O_{24})^{6-}$		85	
Mo^{6+} $(Mo_7O_{24})^{6-}$ in 3 M NaOH			98
ClO_4^- ($NaClO_4$)		12	
HSO_3^- ($NaHSO_3$)	98[a]	98[a]	98[a]

Nitrate Effect

$[NO_3^-]$	Retention, %
1.0 M (62000 ppm)	10
0.1 M (6200 ppm)	70
0.03 M (1860 ppm)	> 99

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[a] Reduced species, Tc (IV).

Table 4. Comparison of Field Sampling Results to Standard Methods for ^{99}Tc

	^{99}Tc Conc. pCi/L				
	Standard Method		Membrane Determinations		
Sampling Site	ICP-MS[a]	DOE RP550[b]	LSC[c] (ANL)	LSC (3M)	SSC[d] (ANL)
A	2069 ± 29	1901 ± 46 (N=3)	1838 ± 80 (N=4)	1979 ± 36 (N=3)	1995 ± 20 (N=2)
B	652 ± 12	656 ± 3 (N=3)	627 ± 26 (N=4)	657 ± 13 (N=3)	666 ± 3 (N=3)
C	72 ± 2	80 ± 12 (N=5)	58 ± 3 (N=2)	64 ± 4 (N=2)	N/A
D	4340 ± 60	3873 ± 116 (N=3)	3649 ± 27 (N=2)	3843 ± 73 (N=2)	3789 ± 75 (N=2)
E	11 ± 1	6 ±2 (N=3)	N/A	3.6 ± 0.1 (N=2)	N/A

[a] Inductively coupled plasma-mass spectrometry; [b] DOE Methods Compendium procedure; [c] LSC= liquid scintillation counting; [d] SSC= solid scintillation counting.

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