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Development of Field Portable Sampling and Analysis Systems

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A portable, field rugged, sampling and analysis system has been developed for the rapid screening of aqueous samples during scoping and remediation studies. Using field portable equipment, water is pumped through ion selective solid phase extraction (SPE) disks, at a flow rate of 150-250 mL/minute, and counted for the radionuclide of interest in the field using portable detectors. SPE disks are currently available for the analysis of ^{99}Tc, ^{90}Sr, radiocesium (^{134}Cs and ^{137}Cs) and radium isotopes. The

radiocesium concentration is determined by gamma spectrometry; ^{90}Sr and ^{99}Tc are determined by beta counting. A one-liter sample can be processed and ready for counting within ten minutes, with a detection limit of <50 pCi/L for ^{99}Tc or ^{90}Sr and a detection limit ~50 pCi/L for a 5-minute count for ^{137}Cs. Up to 10 liters of water have been processed for the analysis of ^{99}Tc and ^{137}Cs when lower limits of detection were required.

The sampling and analysis system has been field tested at the Savannah River Site (SRS), Aiken SC, and the Hanford Site, Richland WA. The SRS H-area tank farm storm water runoff system was analyzed for ^{90}Sr and ^{137}Cs. Groundwater from the SX tank farm at the Hanford Site was analyzed for ^{137}Cs and ^{99}Tc. Groundwater from seeps below the 100H area at Hanford was analyzed for ^{90}Sr and ^{99}Tc. The rapid analysis capability has already resulted in a significant cost savings at the Hanford SX tank farm.

Introduction

Many US Department of Energy (DOE) sites, previously associated with nuclear weapons production, are now primarily focused on restoration and remediation of the local environment. Millions of dollars are being spent each year on sample collection and analysis for radionuclide determination. The results are often used to determine the extent of movement of contaminated groundwater, or to confirm the effectiveness of remediation efforts. In many cases rigorous, expensive, laboratory based analyses are performed because there is no alternative analysis method. During remediation efforts, expedited results are often needed, at a significant additional cost. A novel field portable sample and analysis system has been developed and tested to fill this need for rapid, in the field, screening analyses of radionuclides in aqueous samples.

3M Empore™ (3M Company, St. Paul, MN) solid phase extraction (SPE) disks are composed of small particles (typically 10-30µm) enmeshed in a network of PTFE fibrils to form a strong porous sheet, or membrane. The chemical properties of the membrane are determined by the sorptive or reactive properties of the chosen particle. Empore™: Rad Disks are currently available for the analysis of ^{99}Tc, ^{90}Sr, radiocesium (^{134}Cs and ^{137}Cs) and radium. The first three elements are of concern at DOE facilities thus are the focus of the field analysis system development.

In the lab, samples are processed through the Empore™ Rad Disks by placing the appropriate SPE disk on a filter flask and drawing the filtered aqueous sample through the disk under vacuum[1]. The effective pore size of the Empore™ membrane is 0.1-0.2µm thus samples are pre-filtered through a 0.45µm particle filter to avoid physical clogging of the disk. The extraction efficiency of the SPE disks for the analyte of interest from a 1-liter sample is typically greater than 97%[2,3]. The flow rate of de-ionized (DI) water through the Technetium or Cesium disks under vacuum is often 150-200 mL/minute and 100-150 mL/minute for the Strontium disks. Higher flow rates may be achieved by pushing water through the disks with a peristaltic pump. Laboratory studies have shown that the quantitative extraction capability holds up to flow rates of 300 mL/minute or greater[4] (Figure 1).

Sample volumes of several liters of surface water have been processed through the Empore™ Rad Disks in the lab. Quantitative extractions (>95% recovery) of ^{99}Tc and ^{137}Cs were obtained for water from the Savannah River[2] in the southeast US, the Peconic River[5] on Long Island, NY, and the Columbia River[5] in Washington, at sample volumes up to 10 liters. Due to strontium in surface water, however, the capacity of the Strontium SPE disk is limited to a few liters[2] or about 3 mg of total strontium.

The Technetium and Strontium Rad Disks are counted by either gas flow beta proportional counting

(GPC) or by liquid scintillation counting (LSC). GPC is the preferred method of counting if there is any possibility of color on the SPE disk due to dissolved humic acids as color will significantly decrease the LSC counting efficiency[2]. Due to the non-selective counting method, the selectivity of the SPE disk is of paramount importance. Studies performed have shown that the Technetium disk is highly selective for Tc; only Sb has been found to be consistently retained by the SPE disk[6], U may be slightly retained under some conditions. Nitrates, at greater than 0.05M (~3000 ppm), may reduce the extraction efficiency of ^{99}Tc to less than quantitative.

The Strontium Rad Disk may also extract Ca, Ba, Ra and Pb, however Sr is preferentially extracted over these other elements. Radium and Pb have beta emitting species that will interfere with the counting of the ^{90}Sr. A check can be made for Ra interference by observing the alpha count rate, if the disk is counted on an alpha/beta proportional counter. Any alpha counts observed above background, after correcting for alpha/beta crosstalk, are usually attributable to Ra[7].

The Cesium disk may be counted by GPC, however there is a significant background due to the ^{40}K in the disk (the extractant is potassium cobalt ferrocyanide, KCFC). Also, the KCFC is not as selective as the extractants used in the other Empore™ disks. The Cesium disk will co-extract most transition metals[8]; radio-cobalt, -ruthenium and thorium can bias the beta counting result if present in the sample, and no differentiation is possible between ^{134}Cs and ^{137}Cs. Therefore, the Cesium disk is usually counted by gamma spectrometry, which is able to resolve and quantify the various isotopes that may be present.

Experimental

The knowledge gained using the Empore™ Rad Disks in the laboratory was applied to performing rapid screening analyses in the field. A battery operated Masterflex peristaltic pump was used to push collected water samples through a 0.45µm Gelman high volume groundwater sampling capsule and then through the Empore™ disks packaged in the Rapid Liquid Sampler (RLS) housing. The RLS housings have luer-lok fittings so they may be chained together if desired. Two similar disks may be placed in series to monitor breakthrough of the desired analyte, or different disks may be placed in series if more than one analyte is desired. Based on laboratory and field studies, the Strontium disk is placed first, followed by the Cesium disk and the Technetium disk placed last[7]. The processed water is collected and the volume measured in the field using either plastic volumetric equipment or battery operated balances.

Once the sample has been processed, excess water in the RLS housing is expelled using a 20-mL syringe coupled to the luer-lok fitting. The RLS housing is then opened and the disk sealed in light-duty aluminum foil or Saran® Wrap. Once sealed, the disk may be handled without risk of contamination to the detector faces.

The detectors used for the field study were a Bicron Surveyor 2000, end-window beta proportional counter, and a 3x3" NaI(Tl) detector coupled to a Quantrad Sensor PHA portable multichannel analyzer. Samples were counted by placing the wrapped disk on a flat surface and placing the detector on top of the disk. The gamma spectrometer was calibrated in the laboratory using NIST traceable sources and the calibration confirmed in the field using a thorium lantern mantle. Each spectrum was recorded in the field and saved for further analysis later, if needed.

The counting efficiency for the Bicron detector was determined in the lab by stippling a known amount of ^{90}Sr, in equilibrium with ^{90}Y, on to a Strontium disk. The disk was dried and packaged in foil. The

counting efficiency was calculated by dividing the net count rate by the known activity of ^{90}Sr/Y added. The sample activity was calculated in the field by dividing the net sample count rate by this counting efficiency and the volume processed. The beta count was often performed several times and an average result obtained.

Results

SRS H Area Tank Farm At the Savannah River Site (SRS) in South Carolina, high level waste is stored in large tanks in two "tank farms." The storm water drain system at the tank farm may contain low levels of ^{90}Sr and ^{137}Cs. Approximately 50 liters of water were collected from the 6H and 7H storm water monitor drains using permanently installed peristaltic pumps. In the field, 1 or 2 liter sub-samples were pumped through a particle filter, followed by a Strontium disk and then a Cesium disk. Several replicates at each volume were processed, although the same particle filter was used for the entire sample. These disks were returned to the lab for counting.

In the lab, the RLS housings were opened and all of the SPE disks sealed in a foil pouch. Counting of the samples resulted in 'less than detection limit' results. The foil was then opened and the disks dried as per routine laboratory analysis protocols. The Cesium disks were then counted in the SRS Underground Counting Facility (UCF)[9]. The Strontium disks were allowed to ingrow to achieve equilibrium between the ^{90}Sr and ^{90}Y and then counted on a low level alpha/beta proportional counter located in the SRS Environmental Monitoring Section (EMS) counting room. The results of the recounting of the SPE disks are shown in Table 1.

Raw water samples of the filtered water and unfiltered water were also collected for comparative analyses in the laboratory. The ^{137}Cs was determined by counting 100 mL of the water by gamma spectrometry in the UCF. The ^{90}Sr was determined by the EMS using their routine wet chemical procedures. The results of the laboratory analyses of the water are also shown in Table 1.

The results of the field analyses agree quite well with the lab analyses. However, for the ^{137}Cs, the RLS result is much more precise due to being able to process a larger sample (1-2 liters processed in the field versus 100 mL direct count) and a more optimum counting geometry (a 47mm RLS filter versus 100 mL of water in a bottle). The ^{90}Sr results from the 6H location agree between both methods; the ^{90}Sr from the 7H location was at the detection limit of both methods. Obviously, these sample activities were well below the detection limit of the field analysis method. The field sample processing method was able to produce equivalent results to the routine laboratory method.

Hanford SX Tank Farm Similarly to the SRS, the Hanford site stores its waste in large tanks, located in a number of tank farms. At the SX tank farm, one of the storage tanks had leaked in the past, releasing waste containing ^{90}Sr, ^{99}Tc and ^{137}Cs, among other isotopes, into the underlying soil. Some of this waste has migrated down into the groundwater. A 20-liter sample was collected from well number W22-46, known to be in the plume of the contaminated groundwater, using the permanent pump installed in the well. The well is known to contain elevated ^{99}Tc but ^{137}Cs has not been detected in past sampling campaigns.

Two 1-liter samples (test #1,2) and two 5-liter samples (test #3,4) were processed through Cesium and Technetium disks in series using the field portable pumping system. A single 10-liter sample (test #5) was processed through two Cesium disks in series. The large volume was processed to obtain the lowest possible detection limit; the disks were placed in series to monitor any breakthrough. Also, one of the 5-

liter samples (#4) had two Technetium disks and two Cesium disks in series to monitor breakthrough. The particle filter was changed with each set of disks; the same pump tubing was used for all the samples. The flow rate for the disks in series was nominally 175-200 mL/minute.

Once completed, excess water was pushed out of the RLS housing using a syringe and then the housing was opened. The disks were sealed in foil and counted immediately in the field. The counting equipment was set up in the back of a panel truck. The Cesium disks were all counted using the NaI detector; no observable peak due to ^{137}Cs was found in any of the samples. All the disks, Technetium and Cesium, were counted using the proportional counter. The recorded counts per minute (cpm) and calculated activity (pCi/L) for the various samples are shown in Table 2. Beta activity, above background, was measured on the Cesium disks, equating to about 50-100 pCi/L.

A second well, 299-W23-19, was drilled and pumped only a day prior to our analysis. Within one hour, a 1-liter (#6) and 5-liter (#7) sample were processed and counted demonstrating that this new well was significantly higher in ^{99}Tc activity than the old well. Additionally, a 10-liter sample (#8), another 1-liter sample (#9) and a 0.5-liter (#10) sample were also processed in the field. The new well, 299-W23-19, was scheduled to be backfilled within a few days of drilling. These rapid screening ^{99}Tc results were used to delay the backfilling of the well thus resulting in a significant cost savings by not having to re-drill the well after the laboratory results were reported. The laboratory results were not completed until a few weeks after the well had been scheduled to be backfilled.

All of these disks, from both wells, were returned to the SRS for counting in the laboratory. Only a few of the Cesium disks were counted in the UCF. The calculated concentration of ^{137}Cs in well W22-46 was <0.047 pCi/L for the 10-liter sample; in well W23-19 it was <0.10 pCi/L and <0.049 pCi/L, for the 5-liter and the 10-liter samples, respectively. The results of the laboratory counts of the Technetium disks are shown in Table 3. The correlation coefficient, r^2, for the lab GPC and field cpm is 0.965. However, there is an obvious bias in the calculated activity. The Bicron detector counting efficiency was determined in the lab to be 15% using a disk spiked with $^{90}Sr/Y$, which was dried before counting. The detector efficiency for ^{99}Tc on a wet disk would be 13% based on these results.

There is a decrease in calculated ^{99}Tc activity with volume sampled from well 299-W23-19. However, no ^{99}Tc was detected on the back up Technetium disk for sample #7. This groundwater contains elevated nitrate levels due to the leak from the waste tank; nitrate is known to compete with Tc on the disk. Studies have shown that in DI water, ^{99}Tc is retained on the top surface of the disk and is detectable by beta proportional counting methods. In high nitrate solutions, it is believed that some of the ^{99}Tc is extracted in the deeper layers of the disk thus may not be detected by the proportional counter due to shielding from the disk itself. Recounting of the disks by LSC, which is able to measure all the ^{99}Tc on the disk, supports this conclusion (Table 3). Water was submitted for ICP-MS analysis of the ^{99}Tc at the PNNL; the LSC results agree very well with the ICP-MS results. Beta counting of the disks in the field is a useful screening tool, however in high nitrate groundwater LSC appears to be the better quantitation method.

Another new well was sampled at the SX tank farm during another demonstration. Again, ^{99}Tc and ^{137}Cs were the desired analytes. A 1-L, 2-L and 4-L sample were processed and counted in the field. The sample processing and counting were completed within 1¼ hours for the three aliquots. The Cesium disks did not have any measurable beta or gamma activity. In the lab, the disks were counted to have < 0.5 pCi/L of ^{137}Cs. The results of the field and of the laboratory recounts of the Technetium disks are

shown in Table 4. Again, there was a low bias in the GPC results versus the LSC results.

Additional water was collected from well 299-W23-19 after the permanent casing was put in place. Further studies were completed on this water in the laboratory. Several 500-mL replicates were analyzed for ^{99}Tc to determine the reproducibility of the method. A 2.6% RSD is calculated for the four replicates (Table 5). Additionally, a larger volume sample (18.6 liters) was processed for ^{137}Cs to obtain a significant result. The ^{137}Cs activity was found to be 0.010 ± 0.003 pCi/L.

Also, the water was analyzed for ^{90}Sr by passing various volumes through Strontium disks. The GPC cpm of all the Strontium disks were similar even though volumes of 0.5, 1 and 2 liters were processed. When analyzed by LSC a significant portion of the activity was noted to be ^{99}Tc. Typically, by weight, about ¾ mL of solution is left on the disk after expelling the excess water with the 20-mL syringe. The ^{99}Tc in this residual water obviously biased the ^{90}Sr counting results.

100-N Groundwater Seeps During the late summer when the Columbia River level drops, groundwater seeps are exposed along the bank of the river. Groundwater below the 100-N area at the Hanford site has been contaminated with low levels of ^{99}Tc and ^{90}Sr. When the river level is low, seeps from this groundwater plume are exposed. Two 10-liter cubitainers of water were collected from a seep below the 100-N area. The river level had dropped a few hours prior to sampling to expose the seep. The measured conductivity of the river was 119.3 µS while the conductivity of the groundwater in this area averages near 280 µS. The measured conductivity of the sample collected was 175.5 µS indicating the water was a mixture of groundwater and bank stored river water.

The water was analyzed for ^{99}Tc and ^{90}Sr by passing 2-2.5 liter aliquots through the RLS disks in series, switching the order of the disks, and by passing 5 liters through either two Strontium disks or two Technetium disks. The disks were opened and counted immediately after processing using the Bicron detector. No significant activity was measured on the back up Strontium or Technetium disks for the five-liter samples. No difference in the calculated result was found whether the Strontium disk was placed first or the Technetium disk. The average calculated activity of the five samples (four 2-L and one 5-L) was 120 ± 37 pCi/L for ^{90}Sr and 38 ± 13 pCi/L for ^{99}Tc. The disks were recounted after about one hour; the average calculated activity had decreased to 61 ± 8 pCi/L for ^{90}Sr and 23 ± 9 pCi/L for ^{99}Tc. The next day, about 20 hours later, the calculated activity had decreased to 4 ± 7 and 3 ± 7 pCi/L for ^{90}Sr and ^{99}Tc, respectively. The disks were recounted in the lab several days later resulting in calculated activities of 3.4 ± 1.0 and 0.60 ± 0.09 pCi/L, respectively.

The short lived beta emitter has not been identified, however it is suspected to be the ^{222}Rn daughters of ^{214}Pb ($t_{½}$ = 27 minutes) and ^{214}Bi ($t_{½}$ = 20 minutes). Excess Rn is often found in groundwater, the Strontium disk can retain Pb, and the half-life fits the observed decay rate of the recounted disks. The bias on the ^{99}Tc was less than that of the ^{90}Sr due to lower retention of Pb by the Technetium disk versus the Strontium disk. Recounting of the disks after a few hours is practical solution to this problem. As a practice, all low level results should be recounted to confirm the calculated activities.

Conclusions

A rapid field portable sample and analysis system has been demonstrated at the Savannah River Site and the Hanford Site. Samples can be analyzed for ^{99}Tc, ^{90}Sr and/or ^{137}Cs by processing aqueous samples through ion selective membranes and counting the membranes in the field using portable detectors.

Sample volumes of several liters can be processed for ^{99}Tc and ^{137}Cs when low detection limits are required. Flow rates through the membrane can be as high as 150-200 mL/minute or more, allowing a one-liter sample to be processed and counted within 30 minutes. The portable system can be used when rapid decisions are needed in the field during scoping or remediation activities, or when it is impractical to bring large volumes of water to the lab for analysis. The entire system could be deployed for $10,000-15,000, including the pump and beta and gamma detectors (a gamma spectrometer, as used in this study, would be slightly more expensive but not necessary in most cases). The system has already resulted in significant cost savings at the Hanford Site.

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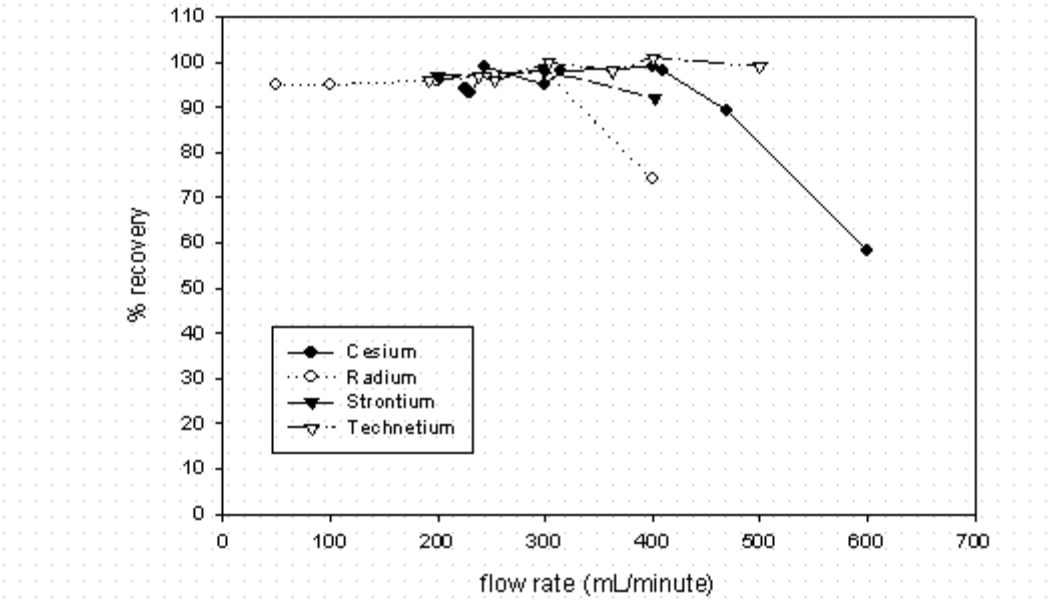
Figure 1. Flow Rate versus % Recovery for RLS Disks



location	field processed			lab processed		
	volume (L)	Cs-137	Sr-90		Cs-137	Sr-90
6H	1.86	14.4±0.2	11.2±2.9	filtered	21.1±4.5	11.8±1.5
6H	1.95	13.0+0.3	10.4+2.7	filtered		
6H				unfiltered	18.8±4.2	
7H	1.93	0.25+0.03	0.12+0.12	filtered	<2.9	1.23+0.90
7H	1.94		0.16±0.14	filtered		
7H				unfiltered	<5.2	

Table 1. Results (in pCi/L) from the SRS Tank Farm

well & test #	volume	Technetium disk			Cesium disk		
	mL	disk #	cpm	pCi/L	disk #	cpm	pCi/L
W22-46							
1	1012	231	500	1501	117-11	80	45
2	1028	30	500	1501	117-04	100	90
3	5012	267	1700	1021	117-10	180	54
4	5012	23	1900	1142	117-14	200	63
		286	0	0	117-02	100	18
5	10200				113-18	500	99
					113-09	120	13
W23-19							
6	1024	30173	4000	12012	113-12	60	0
7	5068	247	8000	4805	117-20	60	0
		329	60	36	117-07	80	9
8	10000	309	14000	4204	117-13	60	0
9	952	92	4000	12012	117-15	60	0
10	412	253	2400	14414			
blank					117-12	80	

Table 2. Field Results from the Hanford SX Tank Farm

well & test #	volume	Technetium	GPC		LSC		ICP-MS
	mL	disk #	pCi/L	error (1s)	pCi/L	error (1s)	pCi/L
W22-46							2403
							2340
1	1012	231	1607	9	2341	9	
2	1028	30	1406	9	2295	20	
3	5012	267	1363	2	1970	24	
4	5012	23	1201	2	1947	51	
		286	0.07	0.24	1.8	0.3	
W23-19							34496
							33850
6	1024	30173	12484	9	35363	365	
7	5068	247	11556	2	31788	379	
		329	39	2	92	3	
8	10000	309	9286	1	24123	119	
9	952	92	16335	10	37054	69	
10	412	253	19723	23	45724	103	

Table 3. Laboratory Recounts of SX Tank Farm Technetium RLS Disks

B8812/299-W22-48					
volume		field result		lab recount (pCi/L)	
liters	disk #	cpm Tc	pCi/L Tc	GPC	LSC
1.02	2462	20	68	38.9	80.4
2.05	2316	30	51	40.9	86.5
4.01	2456	50	43	38.5	79.2
average			54 ± 13	39.4 ± 1.3	82.0 ± 3.9

Table 4. Field and Lab Recount Results from Well B8812/299-W22-48

disk #		GPC RLS disk		LSC RLS disk		contract lab	
		pCi/L	error	pCi/L	error	pCi/L	error
30049	~0.5	11164	111	41633	255	47500	3500
30033	0.672	13327	120	49767	424	48600	3300
30140	0.488	13293	128	51538	135		
30063	0.528	14047	133	54179	195		
30084	0.558	13607	127	48177	261		
	average (4)	13569	348	50915	2573	48050	778

Table 5. Additional Results from Well 299-W23-19