

Extension of Studies with 3M Empore™ and Selentec MAG *SEPSM Technologies for Improved Radionuclide Field Sampling

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Extension of Studies with 3M Empore™ and Selentec MAG*SEPSM Technologies for Improved Radionuclide Field Sampling

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ABSTRACT

The Savannah River Technology Center is evaluating new field sampling methodologies to more easily determine concentrations of radionuclides in aqueous systems. One methodology studied makes use of 3M Empore™ disks. The disks are composed of selective resins embedded in a Teflon support. The disks remove the ion of interest from aqueous solutions when the solution is passed through the disk. The disk can then be counted directly to quantify the isotope of interest. Four types of disks were studied during this work: for the extraction of technetium (two types), cesium, plutonium, and strontium. A sampler has been developed for automated, unattended, in situ use of the Empore™ disks.

Another new methodology evaluated makes use of the process developed by Selective Environmental Technologies (Selentec) whereby selective ligands are attached to particles with a magnetite core (MAG*SEPSM). The particles retain the properties of the ligand and are also attracted to a magnet. By appropriately choosing the ligand on the particles, only the analyte of interest will be extracted when using the developed field sampler. The particles are separated from the aqueous sample using a specially designed magnet. The particles with attached analyte can then be returned to the lab for quantification.

Tests have been completed characterizing two sets of prepared particles, and begun on two additional types of particles. Particles were prepared to extract technetium, cesium, plutonium and iodine from aqueous systems. Initial tests were performed on spiked samples in the lab, with later tests demonstrating the applicability to field sampling. Field sampling procedures have been developed for a sample size of one liter or for 20 liters. Field samples were collected from around the Savannah River Site (Cs and Tc), from the Atchafalaya River near New Orleans (Tc), and from the Ob River in Russia (Tc). A distinct advantage of this sampling technique is the lack of interference caused by high suspended particulate loads.

INTRODUCTION

Monitoring for radionuclides in surface waters is required around nuclear facilities to fulfill regulatory compliance and to ensure the public safety. However, most radionuclides are present in extremely low concentrations requiring extensive processing of the water

sample prior to analysis. Current environmental sampling and analysis procedures used at the Savannah River Site (SRS), a Department of Energy nuclear production facility located in Aiken SC (currently in standby), and other nuclear facilities, require the collection of large volume water samples. Depending on the analysis required samples may require preservation, often by refrigeration or acidification. The samples must then be transported to the lab for analysis, with all their associated costs and regulations regarding shipping of hazardous materials (potentially radioactive or acidified samples). In the lab, samples are often processed by evaporation, selective precipitation, and/or chemical separation in order to achieve the required detection limits and specificity for reporting to regulatory agencies. New procedures for field sampling of five elements with radioactive isotopes are discussed in this paper.

Technetium has no stable isotopes; it is formed only through nuclear reactions. In an oxidizing environment, technetium exists as the pertechnetate ion, TcO_4^- , which is very mobile in aqueous systems (Turcotte, 1982). Technetium behaves as a nutrient analog in biological systems and may be concentrated by plants (Matsuoka, et al., 1990); in humans and animals technetium localizes in the gastrointestinal tract and thyroid gland (Till, et al., 1979). Technetium-99, a weak beta emitting radioisotope with a half life of 213,000 years, is produced by the fission of uranium and plutonium, with a fairly high fission yield of 6%. The other long lived isotopes of technetium are not produced by fission. During the reprocessing of prepared nuclear material Tc-99 may be released to the environment in small quantities via atmospheric deposition or, as at the SRS, may have been released to seepage basins with other low level radioactive waste. Monitoring of Tc-99 in aqueous systems around the SRS and other nuclear facilities is thus required in order to provide data on the possible radioactive dose received from this element.

Current analysis methods for Tc-99 in aqueous samples require the collection of at least one liter of water. At the SRS samples are then analyzed by isotope dilution/inductively coupled plasma-mass spectrometry (ID/ICP-MS; Beals, 1996) to achieve the required detection limit of 1 pCi/L (0.06 nanogram per liter). One nanogram (1.4 pCi) of Tc-97 is added to the aqueous sample as a tracer, the technetium is extracted from the aqueous sample by passing through an extraction chromatography column. Interfering elements are washed through the column with dilute acid. Finally, the technetium is eluted from the column and the eluant analyzed by ICP-MS for quantification. This process takes a few days with most of the time required for the liter of water to pass through the column.

Cesium has one stable isotope, ^{133}Cs , and is an essential nutrient element for humans. The three isotopes of cesium, collectively called radiocesium, which have half lives of greater than a few weeks are ^{134}Cs (2 years), ^{135}Cs (2.3 million years) and ^{137}Cs (30 years). Of these, ^{134}Cs and ^{137}Cs are produced by activation and fission processes, respectively, and can be released to the environment from nuclear activities. Both ^{134}Cs and ^{137}Cs are gamma emitting radionuclides. Current analysis methods for the determination of radiocesium at the SRS require the collection of one liter of water, which is counted in a Merrinelli beaker on a high purity germanium detector (HPGe) for 10,000 seconds to achieve a detection limit of 8-10 pCi/L, or the collection of a 10 liter sample, which is passed

through an ion exchange column, the resin being counted for 10,000 seconds on a HPGe detector, to achieve a detection limit of a few pCi/L. This is sufficient sensitivity to meet regulatory requirements, however, at the SRS most of the Cs-134 and Cs-137 has decayed to levels less than the reported procedural detection limits.

Strontium has several stable isotopes, as well as one radioisotope with an half life of greater than a few months. Strontium-90 is a fission product, decaying by beta emission with a half life of 29.1 years. Strontium, similarly to cesium, is an essential nutrient element. Strontium-89 (half life 50.5 days) and Sr-90 have been released to the SRS environment via low level aqueous releases; the Sr-89 has decayed completely thus is not currently measured at the SRS. Current analysis methods for Sr-90 make use of a selective chromatographic extraction resin; water samples are passed through a column containing the resin. Strontium is eluted from the resin and evaporated onto a stainless steel planchet. The chemical yield is determined gravimetrically, based on the strontium concentration of the water sample. The samples are then counted by gas flow beta proportional counting. As for the isotopic analyses discussed above, most of the time required for the analysis is for the one liter sample to pass through the resin column.

Plutonium was processed at the SRS and has been released to the environment via atmospheric and aqueous releases. The primary isotopes of concern are Pu-238 (half life 87.7 years), Pu-239 (half life 24,100 years) and Pu-240 (half life 6560 years). All are alpha emitting radioisotopes. Plutonium can exist in one of several oxidation states, and may be complexed with many common anions in solution thus making its extraction from solution difficult. Plutonium, if ingested or inhaled, may concentrate in the bone of mammals. Current analysis methods required the evaporation of a one to several liter sample, dissolution of the residue in acid, followed by a redox adjustment and two step ion exchange/chromatographic exchange column procedure prior to deposition for alpha spectrometry analysis.

Iodine is also an essential nutrient element. Several radioisotopes of iodine are produced by fission and may be released to the environment via atmospheric or aqueous releases. The only long lived radioisotope of iodine still of concern at the SRS is I-129 (half life 15.7 million years). Atmospheric releases of radioiodine may be monitored by passing a stream of air through a treated charcoal canister, followed by gamma spectrometry. Aqueous concentrations of radioiodine, however, are much more difficult to make. Iodine may exist in several oxidation states in ground or surface water, and due to the long half life of I-129, tens of liters of water would need to be processed to determine its concentration by counting methods. The SRTC has developed a technique to extract iodine from a one liter sample, concentrate it by passing through an ion exchange column, followed by ICP-MS analysis for its concentration determination (Beals, 1992; Beals and Hayes, 1995). The ICP-MS determination requires measurement of the iodine concentration in the original sample as well as the I-129/I-127 isotope ratio in the processed sample. Limited samples are analyzed at the SRS for I-129 due to the high cost of this analysis.

The Savannah River Technology Center, part of the Westinghouse Savannah River Company, which operates the Savannah River Site for the Department of Energy, is evaluating new field sampling methods which will eliminate much of the time and cost of the current protocols discussed above. The new sampling method should be able to concentrate large volume samples in the field to reduce shipping costs (and improve detection limits), should serve as the preservation medium for the sample, and should provide the initial chemical separation thereby reducing handling and processing in the lab. Two new commercial technologies were evaluated for use at the SRS, 3M Empore™ and MAG*SEPSM by Selentec. Each technology will be discussed separately below.

METHODS

The extraction of technetium from DI water, filtered and unfiltered river water, and filtered seawater was studied. Standard solutions of Tc-99 were used to spike test solutions. Spiked test solutions containing Tc-99 were counted by liquid scintillation spectrometry to determine solution activity. For this, five milliliters of solution was placed into a plastic liquid scintillation vial along with 15 milliliters of Opti-fluor® liquid scintillation cocktail from Packard. Samples were then counted three times, for 30 minutes each time, in a Packard Tri-Carb™ 2050A liquid scintillation spectrometer. An energy window of 4.0-300.0 KeV was used. The Empore™ disk or Selentec particles were also counted for adsorbed Tc-99 by placing the disk or particles in a liquid scintillation vial with 5 mL of DI water and 15 mL of cocktail, counting as above.

The concentration of Tc-99 in unspiked environmental samples was measured by either ID/ICP-MS or, when additional precision or lower detection limits were desired, by isotope dilution/positive thermal ionization-mass spectrometry (PTI-MS; Pochkowski and Beals, 1993). Technetium-97, another long-lived isotope of technetium, was used as the tracer for the isotope dilution work. The ICP-MS used was a Turner Spectrometry SOLA (now marketed by Finnigan MAT, Ltd.). The PTI-MS is a modified NIST designed, 30.5 cm, 90° deflection, single sector mass spectrometer, modifications having been made by the Environmental Technology Section of the SRTC. For both mass spectrometers, the masses monitored were 95, 97, 99 and 101. Corrections were made on the Tc-97 for any Mo-97, based on the Mo-95 count rate, and on the Tc-99 for any Ru-99, based on the Ru-101 count rate.

Solutions (DI water, river water and seawater) for testing the Cs-particles or disks were spiked with Cs-137. The Cs-137 concentration of the solution, particle or disk was measured by gamma spectrometry or by beta proportional counting (solutions or disks only). Spiked test samples containing Cs-137 were counted on 30% efficient HPGe detectors while unspiked environmental samples were counted on either the 90% or 164% efficient HPGe detectors located in the Underground Counting Facility of the Environmental Technology Section, Savannah River Technology Center (Beals, et al., 1995). Samples were typically counted 1200-1400 minutes. For the gamma spectrometry analysis, the 661.6 KeV gamma ray of Cs-137 and the 604.7 and 795.8 KeV gamma rays of Cs-134 were used for calculation of the sample activity. Some spiked test solutions

and some of the disks were counted by beta proportional counting on a Gamma Products Quad G542 low level alpha/beta proportional counter. For the beta proportional counting test solutions were dried onto one inch stainless steel dishes and counted overnight (1000 minutes), with count rates averaged over 100 minute intervals.

To study the uptake of plutonium by the two technologies DI water, river water or seawater was spiked with a known amount of Pu-238. After exposure to the disk or particles, Pu-242 was added as a tracer to the treated solution. The solution was evaporated to dryness and the Pu purified by ion exchange chromatography (Buessler and Halverson, 1987). The purified Pu was electroplated onto Pt disks for alpha spectrometry analysis. A few samples were loaded onto resin beads for thermal ionization mass spectrometry analysis (Buessler and Halverson, 1987) when lower detection limits were required, or when the Pu-239/Pu-240 ratio was required. Samples, for alpha spectrometry analysis, were counted for 3000 minutes on low background silicon surface barrier alpha detectors. The Pu-242 was used to make yield corrections to the Pu-238 activity. For some samples the sorbed Pu-238 was eluted from the Empore™ disk or the Selentec particles. Again, Pu-242 was added as a tracer to the eluant. The purification and counting were as above.

Uptake of iodine from solution was studied by spiking DI water or river water with I-129. Spiked test solutions or the particles were counted by low energy photon spectrometry. The 30 and 40 keV gamma rays of I-129 were measured; samples were counted for 300-900 minutes. The counting efficiency was determined by counting samples of similar geometry and ratioing the count rate to that obtained from the standard.

Uptake of strontium from solution was studied by spiking DI water or river water with a known amount of Sr-90. Strontium-90 decays very rapidly to Y-90. Empore™ disks that had been exposed to test solutions containing Sr-90 were counted as soon as practical after the experiment was complete. Disks were then counted again after one week, at which time the Y-90 had grown into complete equilibrium with the Sr-90. Both counts of the disks were performed by gas flow beta proportional counting. Samples were counted for 30 minutes each time.

MAG*SEPSM

One of the field sampling methods evaluated to overcome the laboratory procedural shortfalls described above makes use of selectively coated MAG*SEPSM particles. MAG*SEPSM particles are made of a magnetite core. The particles are coated with a selective ligand giving the particle the chelating properties of the chosen ligand. The MAG*SEPSM process was developed as a field clean up tool, and thus is fairly rugged. For clean up applications, coated particles are simply put in contact with the solution containing the analyte to be extracted. The particles and solution are kept well mixed for a set contact time, after which the particles are removed from the solution using a magnet. The waste solution is then discarded, the contaminant extracted off the particles, and the regenerated particles put in contact with additional solution. The MAG*SEPSM process is

being demonstrated at the Savannah River Site for the clean up of groundwater contaminated with trace metals (Bibler, et al., 1994).

For this study we hoped to use the particles as an analytical tool rather than a clean up technology. Working with the researchers at Selentec, we have prepared four batches of particles that should be selective for extracting technetium, cesium, plutonium and other actinides, and iodine from aqueous systems. To convert this to an analytical tool the following parameters were evaluated: completeness of extraction of the analyte of interest including contact time required and weight of particles per volume, and the ability to detect the analyte of interest at the required detection limits.

Particles used in these studies were prepared by Selentec according to their proprietary procedures. Four sets of particles were prepared: one coated with Aliquat®-336, a tricaprilymethylammonium chloride which has been used to extract technetium from dilute aqueous systems (Beals, 1996); one coated with a resorcinol-formaldehyde resin known to extract cesium from aqueous systems (Bibler, 1994); one coated with manganese oxide which has been used extensively for the adsorption of radium, lead, thorium, americium and plutonium from river and seawater (Bacon and Anderson, 1982; Noshkin and Gatrousis, 1974); one coated with cetylpyridinium chloride for the extraction of iodine from solution (Bors, et al., 1994). These different particle types will be referred to as Tc-particles, Cs-particles, Pu-particles and I-particles, respectively, in the following discussions.

Laboratory Studies

Tc-Particle Tests

The distribution coefficient for Tc-99 onto TEVA extraction chromatography resin (EiChroM, Industries, Inc., Darien IL) from aqueous solution is shown in Figure 1, taken from Horwitz, et al. (1995). The complexing ligand on the TEVA resin is the same as that used on the Tc-particles prepared by Selentec, thus we would expect to achieve similar distribution coefficients for the Tc-particles. As seen in Table 1, the Tc-particles do have a very high affinity for extracting Tc-99 from solution. The distribution coefficient calculated from the data in Table 1 for adsorption of Tc-99 onto the Tc-particles is about 2×10^4 . The expected distribution coefficient from Figure 1 is approximately 10^4 .

Using the MAG*SEPSM particles is more similar to performing a batch extraction than the traditional column extractions performed in a laboratory setting. In batch extractions the kinetics of adsorption are very important in determining the length of time the particles need to be in contact with the analyte in solution. We performed a series of experiments in which the uptake rate of Tc-99 onto the Tc-particles was determined. One liter of either deionized water or seawater was spiked with Tc-99 and mixed well. A five milliliter aliquot was taken prior to the addition of the MAG*SEPSM particles to serve as the time equal zero starting point. One gram of Tc-particles was then added to the solution and kept well mixed for the duration of the experiment. At specific time intervals five milliliter

aliquots of solution were taken and filtered to remove any suspended particles. All aliquots were prepared for liquid scintillation spectrometry as described in the previous section.

For analysis of Tc-99 by ID/ICP-MS we must be able to get the Tc back off the particles for introduction to the mass spectrometer. Again, we would be doing this by a batch extraction mode and we would like to know the kinetics of the desorption reaction. At the end of the above adsorption experiment, the particles were removed from solution and placed into a clean 4M nitric acid solution. The Tc-99 concentration of the acid solution at time equal zero was zero. Aliquots of the acid solution were taken over time as before and the Tc-99 concentration in solution measured by liquid scintillation spectrometry.

The results of the adsorption and desorption rate studies are shown in Figure 2A and 2B. The adsorption and desorption rates were both very rapid from DI water and seawater. The insert in Figure 2A shows an enlargement of the first 45 minutes. The adsorption of Tc-99 from DI water was nearly complete by the time the first sample was taken at five minutes. More than 90% of the Tc-99 was removed from the seawater by five minutes, with greater than 95% extraction by 10 minutes. The desorption reaction was nearly instantaneous as seen in Figure 2B.

There does appear to be a slight increase in acid solution activity over extended time periods in Figure 2B. In some studies, after the Tc-particles had been exposed to the acid stripping solution, the particles themselves were put into a liquid scintillation counting vial with cocktail and counted. We did find that only about 95% of the Tc-99 was being removed by the acid strip. This would suggest that the particles cannot be reused for different samples due to the possibility of cross contamination of one sample to the next. However, if the Tc-particles are to be used for a clean up application, we did find that we could load the Tc-particles, strip them in acid and reload them without a loss in uptake efficiency. This cycling of use and regeneration was repeated up to ten times with no noticeable loss in extraction efficiency.

Often samples are collected at a field site and then stored for an extended period of time prior to analysis. In the lab this storage period may be due to waiting for enough samples to be collected to form a batch for more efficient processing, or other time limitations in the chemical preparation labs or counting facilities. Therefore we chose to examine the effect of loading Tc-99 on the Tc-particles and then storing them prior to back extraction and analysis. Six one gram aliquots of Tc-particles were placed in a solution with Tc-99 and allowed to absorb the Tc. After a few hours, sufficient time for the particles to reach equilibrium, the particles were removed from solution. One batch of particles was back extracted with nitric acid within a few hours of loading. The elution acid and the particles were both counted by liquid scintillation spectrometry to complete a mass balance. As seen in Table 2, 94% of the Tc-99 was extracted from the particles when the back extraction was completed on the same day as the loading. One batch of particles was then back extracted each week for the next five weeks, and the mass balance completed. Over the first four weeks there may have been a slight decrease in the amount of Tc-99

recovered from the particles (Table 2), but these recoveries are similar within the counting errors, and are acceptable recoveries in terms of performing the analytical analysis. By the fifth week, there was a significant decrease in Tc-99 recovery. The lack of any additional samples prevented us from determining if this was a trend or just an outlier. To avoid any difficulty, however, all field samples were back extracted usually within a week, but not greater than 3-4 weeks, of collection.

The technique used for quantification of the Tc-99 in environmental aqueous samples is isotope dilution. The isotope used at the SRS for this is Tc-97 which is also radioactive, with a half life of 2.6 million years. Regulations prohibit the transfer and use of radioactive materials outside of a laboratory at the SRS. We know, based on the above studies, that the extraction of Tc-99 from aqueous solutions is nearly quantitative, however the back extraction may not be. To accurately correct for the chemical yield of the analytical procedure we need to introduce the Tc-97 tracer as soon as possible to the sample. In the laboratory, this can be done prior to the initial adsorption of the technetium by the Tc-particles. In the field, however, we cannot add the tracer to the sample at the time of extraction, we must assume that the extraction is quantitative. Once the Tc-particles are returned to the lab, we can add the Tc-97 tracer and monitor the chemical recovery from that point on. A study was therefore designed to determine if the Tc-97 added after the initial sample collection truly reflected the behavior of the Tc-99 we were trying to measure.

Six batches of Tc-particles were used in this study. Three one gram aliquots of the Tc-particles were placed in a solution that contained both Tc-99 and Tc-97 (simultaneous exposure). Three other one gram aliquots were placed in a solution that had only Tc-99 (sequential exposure). The technetium was allowed to adsorb onto the particles for approximately one hour. At the end of the hour, the Tc-99&97 exposed particles were removed from solution and the technetium extracted from the particles with nitric acid. The Tc-99 only exposed particles were removed from the first solution and placed into a solution that now only contained Tc-97. Again, the technetium was allowed to adsorb on to the Tc-particles for about one hour. At the end of the hour, the solution was poured off and the technetium extracted from the particles by nitric acid. We then measured the Tc-99/97 ratio in the extract of all six samples. Table 3 shows the determined ratios for the six samples (sample 6 was lost in processing thus no result is available). Samples 1-3 had been placed in the solution containing both Tc-99 and Tc-97; samples 4-6 had been placed in the Tc-99, then Tc-97, solutions separately. The ratios are nearly the same indicating that the introduction of the Tc-97 tracer after return of the sample particles to the lab is an acceptable alternative to introducing the tracer prior to introduction of the particles to the original sample.

Cs-Particle Tests

Resorcinol-formaldehyde resin had been well characterized at the SRS for the extraction of radioactive cesium from high pH solution (Bibler, 1994). In previous tests, we were able to achieve greater than 95% extraction of Cs-137 from one liter of deionized water

with one gram of resin, and achieve about 80% extraction of Cs-137 from 20 liters of seawater using six grams of resin. Using the Cs-particles prepared by Selentec with the resorcinol-formaldehyde resin attached, we were able to achieve 97% extraction of Cs-137 from one liter of water with one gram of the Cs-particles, and 80% extraction of Cs-137 from one liter of seawater with one gram of Cs-particles.

Often natural streams may exhibit slightly acidic conditions; the resorcinol-formaldehyde resin was designed to remove cesium from alkaline solutions. Thus, we studied the extraction efficiency of the Cs-particles versus pH. Not unexpectedly, the distribution coefficient for the extraction of Cs-137 from low pH solutions was fairly low (Table 4). This means that the Cs-particles will only be able to be used in streams where the pH is greater than about 5.

As for the Tc-particles, we performed a series of timed adsorption experiments to determine the kinetics of the uptake rate of Cs-137 onto the Cs-particles. Figure 3 shows the extraction rate of Cs-137 from river water that had been collected from one of the streams on the SRS. For this test, one gram of Cs-particles were used to extract Cs-137 from one liter of river water. The adsorption of Cs onto the Cs-particles was not as rapid as found for the adsorption of Tc-99 onto the Tc-particles but an equilibrium had been reached by about 45 minutes, which is not an unacceptable length of time to extract an analyte from solution.

When using MAG*SEPSM to quantify radioactive cesium in aqueous solutions the particles can be counted directly by HPGe for Cs-134 and Cs-137. For most applications, the only cesium radioisotopes of concern are Cs-134 and Cs-137; the production of Cs-135 in nuclear reactors is very low and with its longer half life it is an insignificant radiological health concern. Thus, except for reusing the Cs-particles, extraction of the cesium off the particles is not necessary as it was for the Tc-99 determinations. We did want to determine if we could regenerate the Cs-particles for reuse and so examined methods to extract adsorbed Cs-137 off the Cs-particles. Figure 4 shows that solutions of nitric acid as dilute as 0.25M can be used to remove Cs-137 from the Cs-particles. After contact with acid and rinsing with water the distribution coefficient for the extraction of Cs by the Cs-particles was unacceptably low. The potential exists that the Cs-particles could be regenerated by exposing them to a solution of NaOH, but this was not tested. For the field analyses, we therefore chose to count the Cs-particles directly without eluting the radiocesium from them, and then archive the particles.

Pu-particle Tests

Manganese oxide has been used to extract actinides from river and seawater for isotope ratio analyses, however the extraction efficiency for Pu or other elements has not been rigorously determined. Initial test of the Pu-particles were performed by spiking four aliquots of DI water with Pu-238. One gram of Pu-particles was added to three of the

four 250 mL aliquots, the fourth was kept as a control. The particles were kept well mixed in solution for one hour. At the end of that time the treated solution was poured off. A second one gram of Pu-particles was added to one bottle only, followed by mixing for an additional hour. The Pu-242 tracer was added to all four solutions and the concentration of Pu-238 remaining in solution was determined. As seen in Table 5 approximately 60% of the Pu-238 in solution was removed onto the Pu-particles. In a separate test approximately 50% of the added Pu-238 was extracted from 250 mL of river water by one gram of Pu-particles in one hour.

In order to quantify the plutonium in solution, the plutonium must be extracted off the Pu-particles and purified for alpha or mass spectrometry. A study was therefore designed to determine the most appropriate method of extracting the plutonium from the Pu-particles that would lend itself to our traditional purification procedure. For this study 250 mL aliquots of river water were spiked with Pu-238. One gram of Pu-particles were added to each aliquot for one hour. The particles, with adsorbed Pu-238, were separated from the spiked solution. The particles were then exposed to different acid types and strengths to determine the best method for the back extraction of the adsorbed Pu. The acids used are listed in Table 6. The particles with adsorbed Pu were placed in 50 mL of the acid solution for one hour. The acid solutions and the original spiked river water (to complete the mass balance) were then spiked with Pu-242 and purified as above for alpha spectrometry analysis. Apparently all dilutions of acid were sufficient to extract the Pu-238 from the Pu-particles, however we did note that the back extractions performed with hydrochloric acid resulted in a much dirtier solution, requiring additional cleanup prior to electroplating for alpha spectrometry. (The excess Pu-238 found above the spike amount is probably due to the Pu-238 in solution in the Fourmile Creek on the SRS.)

Additional tests are planned to determine if the 60% extraction efficiency is a kinetic limitation (contact time of greater than one hour is required) or a capacity limitation (greater than one gram per 250 mL is required). We also plan to examine what effect changing the oxidation state of the plutonium in solution will have on the extraction efficiency. Using this technique it would be possible to adjust the water quality conditions in the field prior to introduction of the Pu-particles to the sample.

I-particle Tests

An I-129 spike was added to 250 mL aliquots of DI water and 250 mL aliquots of river water. One gram of the I-particles were added to the solutions and kept well mixed for one hour. At the end of the contact time, the treated solutions were poured off. Both the treated solution and I-particles were counted by LEPS. Unfortunately, almost no I-129 was extracted onto the I-particles from either solution.

We next tried adjusting the oxidation state of the iodine prior to contact with the I-particles. The standard procedure used for the ICP-MS determination of I-129 uses sodium hypochlorite, followed by hydroxyl amine hydrochloride, and finally sodium bisulfite, to ensure that the iodine is reduced prior to concentration on the ion exchange

resin. Solutions were spiked with I-129 and then prepared with various combinations of these reagents prior to the introduction of the I-particles. Solutions that were treated with the sodium hypochlorite and hydroxylamine hydrochloride prior to the I-particles being added did show a 10-25% extraction efficiency. Additional tests are planned to try to improve this extraction efficiency further.

Field Studies

Sampling Equipment and Procedures

Two types of field sampling equipment have been used during this study. The first was designed for a sample size of one to two liters and can be performed with no power supplies or mechanical equipment. A Teflon or other inert plastic bottle is filled with water from the water body to be analyzed. The volume of water collected is noted (we pre-labeled the bottles as to the one liter level and filled them to that level). We used this sampler only for the analysis of Tc-99 in solution; a one liter sample is sufficient for the detection of Tc-99 by PTI-MS at environmental levels, but is not enough sample to measure radiocesium. (The other two particle types are not yet well enough characterized to attempt field sampling.) One gram of MAG*SEPSM Tc-particles are then added (the particles had been preweighed and stored in a small plastic vial, which was then poured into the sample to be analyzed) and the bottle hand shaken for an hour or more. The bottle does not require continuous agitation as it takes several minutes for the particles to settle to the bottom. In some instances we did use a small battery powered overhead mixer.

After an hour or more of mixing, a two by two inch rare earth (Nd) magnet is held on the bottom of the bottle. Within a few minutes or less all the particles settle to the bottom of the bottle such that the overlying solution can then be decanted without losing any of the Tc-particles. The magnet is removed from the bottle and Tc-particles transferred to a small (30 mL) plastic bottle with a small amount of deionized water. Only the small bottle with the particles is returned to the lab for analysis. Once back at the lab, the Tc-97 tracer is added, if not done earlier. The particles are then washed with 50 mL of 1M nitric acid, to remove any extracted molybdenum (Mo-97 would interfere with the Tc-97 tracer measurement), which is discarded. The technetium is then eluted with 4M nitric acid. Some of the samples collected were analyzed by ICP-MS (Beals, 1996) while others went immediately to the microdistillation and loading required for PTI-MS analysis (Pochkowski and Beals, 1993).

The other sampler we have used was designed by Selentec and is suitable for processing a 20 liter sample. Both the Tc-particles and the Cs-particles have been tested in this sampler. A line drawing of the sampler is shown in Figure 5 and a picture is shown in Photo 1. This sampler is portable, it can be easily moved by two people, however it does require a power source, such as a small generator. We are investigating the possibility of using 12V battery operated pumps which would eliminate the power source requirements. To operate the 20 liter sampler, water is pumped from the water body to be sampled into

the left bucket, T1. The mixer paddle is started and then the MAG*SEPSM particles are added. The solution is kept well mixed for 30 minutes for the Tc-particles, 60 minutes for the Cs-particles. Photo 2 shows the solution-particle slurry.

At the end of the extraction period the slurry is pumped through the peristaltic pump, past the enclosed magnet, into the right bucket, T2 (Photo 3). The water is pumped at a rate of about one liter per minute. The mixer paddle is left on to keep the particles from settling to the bottom of bucket T1 during the transfer step. As the water moves past the magnet, the particles are retained in the magnet housing (Photo 4), and the treated water is collected in bucket T2. After ensuring that no particles are getting past the magnet into bucket T2, the excess water may be discarded. There is a small hose in the bottom of bucket T2 that serves as the outlet for the excess water; this was used to rinse down the sides of bucket T1 to make sure all the particles were pumped past the magnet. Once the water transfer step is complete, the magnet housing may be disassembled (Photo 5) and the particles transferred to a small plastic bottle with deionized water (Photo 6). The Tc-particles are returned to the lab for processing as above. The Cs-particles can be sent directly to the counting room for the determination of the Cs-134 and Cs-137 activities.

Because there is no chemical separation required for the Cs-134 or Cs-137 analysis other than the extraction no yield monitor has been used for the sample analyses. As for the Tc-99, we have assumed nearly quantitative extraction of the cesium from the aqueous sample by the Cs-particles. A method that could be used to monitor the uptake of the cesium from solution would be to use the stable Cs-133 as a yield monitor. A small sample of the unprocessed water would need to be collected at the time of sampling. After counting the Cs-particles, the cesium could be stripped using dilute nitric acid. The Cs-133 concentration of the unprocessed water and the Cs-133 concentration of the Cs-particle strip solution could then be measured by ICP-MS or another suitable method. The concentration in the Cs-particle strip solution compared to the unprocessed water would then give an indication of the effective volume sampled by the Cs-particles. Another method to monitor the uptake would be to perform a second extraction of the excess solution collected in bucket T2. The ratio of Cs-137 on the first set of particles compared to the second set would allow the collection efficiency to be calculated. This second method would also be applicable to the Tc-particles. Based on the laboratory results, however, we felt the extraction was nearly quantitative thus did not warrant the extra effort described here.

Sample Results

One liter samples were collected for the analysis of Tc-99 from the Atchafalaya River, a tributary of the Mississippi River near New Orleans, as a dry run exercise, and then several one liter samples were collected at different locations on the Ob River in Russia. For each sample location a grab water sample was processed, with no attempt made to eliminate suspended particulate material. A second sample was filtered through a series of filters down to the 10,000 dalton level. The MAG*SEPSM extraction performed on the research vessel is shown in Photo 7. By comparing the results we hoped to determine the total

Tc-99 in the river and what fraction of the Tc-99 was truly dissolved versus what could be filtered out.

The suspended sediment concentration in the Atchafalaya River at the time of collection was 150 mg/L. Even though the suspended sediment load in the river was very high the chemical recovery of the Tc-97 tracer was similar in both fractions, indicating that the high sediment load had no effect on the uptake efficiency of the technetium from solution. The Atchafalaya River samples have been analyzed by ICP-MS. The total sample was calculated to have less than 0.693 pCi/L of Tc-99, while the dissolved sample was calculated to have less than 0.849 pCi/L of Tc-99. We would not expect to find any measurable Tc-99 in the Atchafalaya River thus these results are consistent with expected. These samples have been prepared for PTI-MS analysis but have not been completed. All the samples from the Ob River were prepared only for the PTI-MS analysis and are awaiting instrument time.

Archived Pacific Ocean samples were also processed by the MAG*SEPSM procedure. Samples were collected during a research cruise in October 1980 and acidified at the time of collection to a pH of 2. Sample sizes varied from one to two liters. As these were done in the lab, we added the Tc-97 tracer prior to introduction of the Tc-particles. Samples were shaken for one hour and then the solution poured off. The technetium was back extracted from the particles and processed for PTI-MS. They are currently awaiting instrument run time.

We used the 20 liter sampler at a few locations around the SRS for both Tc-99 and Cs-134, -137. As above the Tc-99 samples are awaiting instrument run time. The Cs samples have been counted and the results are shown in Table 7. The Savannah River forms one border of the SRS. On the Savannah River, above the influence of any SRS activities the Cs-137 concentration was determined to be <7.5 pCi/L by standard SRS methods; Cs-134 was also below detection limit. The result of the MAG*SEPSM analysis for Cs-137 was 0.022 pCi/L ($\pm 30\%$). The Environmental Technology Section has another sampler on the Savannah River, at the same location above the SRS, which is also under development. It concentrates cesium from tens of liters of water over a two week period by ion exchange. The calculated Cs-137 concentration for the same time period as the MAG*SEPSM sample was collected was 0.032 pCi/L ($\pm 31\%$), in very good agreement with our MAG*SEPSM result. The Lower Three Runs Creek is located on the SRS and receives drainage from Par Pond which is known to have Cs-137 in its sediment. Our MAG*SEPSM sample collected at this same location had a calculated activity of 1.21 pCi/L ($\pm 1.7\%$). Another sampler under development, located at the same sampling point, gave Cs-137 concentration results over time of 0.60 ± 0.42 to 2.35 ± 0.90 pCi/L. The difference in the reported error of the sample analyses is the amount of sample processed for counting and the final counting geometry of the sample.

Summary of MAG*SEPSM Technology

An analytical method has been developed making use of MAG*SEPSM technology for the analysis of radionuclides in aqueous systems. This method is applicable to field use, concentrating aqueous samples in the field such that transport of large volumes of water is avoided and no additional preservation of the sample is required if final analysis in the lab is delayed. By correctly choosing the ligand on the particles only the analyte of interest can be extracted from the sample, thus reducing the chemical purification required prior to final activity determination.

Two sets of particles have been tested in the surface waters on and near the Savannah River Site for the determination of Tc-99 and for Cs-134, -137. The Tc-particles have also been used in river systems off the SRS. The radiocesium results obtained using the MAG*SEPSM procedure are comparable to the established standard methods used at the SRS, but due to the ability to use larger samples the detection limit for radiocesium of the MAG*SEPSM method is much lower than standard procedures. Only a few of the Tc-99 analyses are completed but the initial results appear similar to expected values. If the samples collected on the Atchafalaya and Ob rivers for the analysis of Tc-99 had been analyzed by established procedures, the suspended sediment load would have plugged the extraction chromatography column making completion of the analysis very difficult. Using this new method the suspended sediment was poured off with the waste solution after the extraction of the Tc-99 onto the Tc-particles. The Tc-99 extraction was completed within a few hours using the MAG*SEPSM method as opposed to a few days for standard procedures. We have begun testing on two new batches of particles to test the applicability of this technology to the determination of other radionuclides in aqueous systems.

3M EMPORETM

EmporeTM RAD disks are a combination of 3M EmporeTM Membrane technology and selective adsorption resin technology. EmporeTM disks contain chromatographic particles enmeshed in a network of PTFE fibrils to form a strong porous sheet, or membrane. The properties of the membrane are determined by the sorptive or reactive properties of the chosen particle. Initially, membranes were prepared containing hydrophobic octyl- and octadecyl-bonded silica particles for reversed-phase extractions of environmental pollutants (Hagen, et al., 1990) and used to replace liquid-liquid extractions. This technology was then expanded to include membranes that were selective for the extraction of radionuclides from solution. The testing of the developed RAD disks is discussed below.

We tested two commercially available EmporeTM RAD disks as well as three other specially prepared materials. The Sr RAD disk makes use of IBC Advanced Technologies, Inc. AnaLigTM Molecular Recognition Technology such that the AnaLig adsorbent particles in the disk allow selective adsorption of strontium. The Tc RAD disks contain GD-1 sorbent for the selective adsorption of technetium. Both of these are commercially available. 3M prepared a membrane containing the EIChroM Industries, Inc. (Darien IL) TEVA resin, which has been well characterized for the extraction of technetium from aqueous solution (Beals, 1996). These are called the TEVA disks in the

following discussions. We also evaluated a disk for the extraction of plutonium from solution; this disk had sodium titanate incorporated in the Empore™ membrane. These are called the Pu disks in the following discussions. 3M is also prepared a "Cs RAD disk" containing the sodium form of resorcinol-formaldehyde resin, which is discussed below. 3M is currently preparing another disk which should also be selective for cesium which will contain potassium cobalt ferrocyanide (KCFC RAD disk). The KCFC RAD disk will be evaluated similarly to the other disk evaluations discussed below.

The end goal of the testing with the Empore™ technology was to place the disks in an automated sampler which would sit alongside a stream to be monitored for radionuclide concentrations. The sampler would take a small sample at predetermined intervals and pass the water through the Empore™ disks. We plan to stack several disks such that multiple radionuclides can be extracted for analysis from the same aliquot of water. The samples will be collected once a week for return to the lab for counting and quantification of the isotope of interest. The commercially modified samplers are to be installed at several locations around the SRS and collect data for the period of one quarter (three months). At the end of the field evaluation the Empore™ results will be compared to the routine sample collection and analysis results to determine the applicability of the new technology for continuous monitoring of radionuclides in aqueous systems. Many of the tests described below were designed with this end goal in mind.

Laboratory Studies

TEVA Disk Tests

Initial tests of the TEVA disk demonstrated that greater than 95% of added Tc-99 was removed from DI water, filtered river water or filtered seawater when passed through the disk. The effect of flow rate was evaluated by pumping spiked DI water through the TEVA disk using a peristaltic pump. The 95%+ extraction efficiency was consistent at flow rates up to 100 mL per minute (Figure 6).

The next series of studies examined the effect of pumping unfiltered water through the disks. Unfiltered river water was collected from Steel Creek on the SRS. For these initial studies a 25 mm diameter disk was used. With no prefiltration only 350-500 mL of river water was able to pass through the disk prior to flow stopping completely, even when pushing the water through the disk with a peristaltic pump. Using a graded Whatman filter, with nominal pore size of 10 to 1 micron we were able to pump 650-900 mL of coarsely filtered water past the disk prior to clogging. 3M recommends filtering water through a 0.1 micron filter prior to passing through the Empore™ disks as the effective pore size of the disks is about 0.1-0.2 micron.

A study was designed whereby the Steel Creek water was passed through filters of different pore size prior to passing through the TEVA disk. Gelman Supror filters with pore sizes of 0.1, 0.2, 0.45 and 0.8 micron were used for this test. The unfiltered creek water was first passed through a graded Whatman filter, then a Gelman filter, then through

the TEVA disk. We were only able to get 350 mL of water through the 0.1 μ Gelman filter, similarly to the test above. We were able to pass 800 mL of water through the 0.2 μ /TEVA disk combination, and a full liter of water through the 0.45 and 0.8 μ filters. In all cases the extraction efficiency of Tc-99 from solution was greater than 95%. The particle filters were counted by liquid scintillation spectrometry. For the smaller particle sizes, 0.1 and 0.2 μ , approximately 55% and 20%, respectively, of the Tc-99 activity was found on the particle filters rather than the TEVA disk. This was reduced to about 15% of the Tc-99 on the 0.45 and 0.8 μ particle filters, with the remaining 85% on the TEVA disk.

When the unfiltered water was heated in the presence of hydrogen peroxide to destroy the organic material prior to passing through the filters, all the Tc-99 activity was removed only on the TEVA disk, none was retained by the particle filter. We believe the dissolved organic material in solution might be coating the particle filter, reducing its effective pore size, and then removing colloidal Tc-99 from solution. Destroying the organics eliminated this effect. The field sampler will use a high volume groundwater 0.45 μ prefilter. By using this type of filter, clogging of the filter by colloids should not be a problem, and we do not expect to see retention of Tc-99 by the particle filter. However, this will have to be evaluated once the field sampling begins.

Tc RAD Disk Tests

The commercial Tc disks will be used in the field study. These commercial disks are 47mm in diameter as opposed to the 25mm disks used above. As with the TEVA disk, greater than 95% of the Tc-99 was removed by passing through the Tc disk from spiked DI water or spiked unfiltered river water (collected from L Lake, which is part of the Steel Creek system). The flow rate tested was about 30 mL/minute. We were able to pass one liter of unfiltered river water through the larger diameter disks with no apparent clogging of the Empore™ disk.

The TEVA material has been well characterized in terms of its decontamination efficiency for other radionuclides. As we are not as familiar with the GD-1 resin characteristics, we designed a study to look at the discrimination of the Tc disk for other beta emitting radionuclides. Deionized water (one liter) was spiked with either 330 pCi of Cs-137, 1400 pCi of C-14 or 400 pCi of Sr-90. The water was passed through the Tc disk at a flow rate of 30 mL/minute. The disks were then counted by beta proportional counting; any beta counts above the detector background would be attributable to the contaminant added. The decontamination factor for the C-14 and Cs-137 was greater than 99.9%. A small number of counts above background was observed for the solution containing the Sr-90, implying a greater than 98.5% decontamination of Sr from Tc by the Tc disk.

Another test completed was evaluating the best counting method of the Tc-99 collected on the Tc disk. The 3M technical data sheet on the Tc RAD Disks suggests either gas flow beta proportional counting or liquid scintillation spectrometry are suitable for activity determinations. Several disks were prepared by passing spiked DI water or spiked

unfiltered river water through Tc disks. Half of the disks were counted by beta proportional while the other half were counted by liquid scintillation. The counting efficiency for the DI water disks by liquid scintillation was 68-70%, however the counting efficiency of the river water samples by liquid scintillation was only 6-9%. The unfiltered river water disks did have significant color due to particles removed on the disk, possibly quenching the beta counting efficiency. All disks, DI or river water, counted by beta proportional counting averaged $43.6 \pm 3.1\%$ counting efficiency. In a separate study several days later an average counting efficiency of $45.0 \pm 10.3\%$ was calculated for DI and unfiltered river water samples. The larger error in the second set of data was due to the spike activity being less than 4.5 pCi in all cases, which is nearing the detection limit of the detectors.

Based on previous work we know that we can elute technetium from the TEVA resin, and thus the TEVA disks, for ICP-MS confirmation of activity. We wanted to test this for the Tc RAD disks. Several Tc disk were loaded with Tc-99 by passing spiked river water or DI water through the disks. The disks were counted to determine the initial disk activity. The disks were then loaded onto a filter flask and 30 mL of 1M nitric acid was pulled through the disk, followed by 30 mL of 4M nitric acid. Using the TEVA material, the 1M acid washes the Mo off the disk, while the 4M acid elutes the Tc. Each wash was collected separately, and will be analyzed by ICP-MS for Ru, Mo, and Tc. The disks were dried after the acid wash and recounted by beta proportional counting to determine how much activity remained on the disks. Less than 5% of the Tc-99 was still on the disks that had been loaded from DI water, however only 70-80% of the Tc-99 was eluted from the disks that had been loaded from the river water. Further tests are planned to improve this back extraction efficiency, such that we will be able to confirm any unusual count rates by ICP-MS.

Cs RAD Disk Tests

Laboratory tests of the Cs RAD disk used mostly seawater spiked with Cs-137. Two 25 mm disks were placed in series, and the Cs spiked seawater pumped through the disks at a flow rate of 5 mL/minute. Aliquots of the treated water were collected and counted by gamma spectrometry by the Analytical Development Section of the SRTC for one hour each. Both disks were also counted by gamma spectrometry. The results show breakthrough of the spiked Cs-137 after only a few hundred milliliters of the spiked seawater had passed through the disks.

Two possible explanations for this low extraction efficiency are offered. In previous laboratory tests it was noted that six grams of RF resin were required for an 80% efficient extraction of Cs from 20 liters of seawater, due to competition from other ions in the seawater matrix. There is very little RF resin able to be incorporated into a 25 mm Empore™ disk thus there may not have been sufficient capacity to hold up the Cs in the above described experiment. There was also a concern that in grinding the RF resin to a particle size that could be incorporated into the Empore™ mesh, the fresh surfaces were available for oxidation, thus reducing its extraction capability. Additional tests confirmed

the low extraction efficiency of the disk incorporating the RF resin, thus further testing of this material was not pursued.

Pu RAD Disk Tests

In the first test of the Pu disks, 10 liters of filtered seawater was passed through two stacked 25 mm disks. Cold concentrated sulfuric acid was then passed through the disks to elute the extracted Pu, and finally the disks were washed with DI water. The acid solution, DI water and disks were processed for mass spectrometry analysis. A Pu-242 tracer was added to the solutions and the disks; the disks were then leached with hot nitric acid and hydrogen peroxide. The resulting solutions were processed as above for alpha spectrometry, up to the deposition stage. The Pu was then loaded onto resin beads for PTI-MS analysis (Beals, et al., 1995). The cold acid was only able to elute 60 and 88% of the Pu off the disks. As no spike was added for this study, the extraction efficiency of the Pu disk could not be determined, however it was noted that there appeared to be more Pu on the top disk than the bottom. This was sufficient information to warrant further testing of this material.

The next study focused on the best method to elute Pu from the Pu disk. Several Pu disks were loaded with Pu-238 by passing spiked DI water through the disk. The disks were then eluted with hot and cold sulfuric acid, hot and cold nitric acid, with and without hydrogen peroxide, and with DI water as a control. Using nitric acid to leach the Pu disk resulted in a significant amount of white residue in the sample beakers (Ti?), whereas the sulfuric acid leaches resulted in a fairly clean extract. The hot (approximately 60-80°C) sulfuric was able to quantitatively extract the Pu from the disk. This was the extraction method chosen for further tests.

Next, approximately 10 liters of filtered seawater was spiked with about 27 pCi of Pu-238 and passed through two stacked Pu disks. The disks were eluted by soaking in hot concentrated sulfuric acid. In this study, the Pu-242 tracer was added to the extract and the samples analyzed by alpha spectrometry. Approximately equal amounts of Pu-238 was found on each disk, top and bottom, suggesting complete breakthrough of Pu at this sample volume. Approximately 95% of the Pu-238 was extracted from the Pu disk by the hot sulfuric acid treatment.

The next test used DI water spiked with Pu-238. Approximately one liter of water was passed through the Pu disk at a flow rate of 5 mL/minute, the effluent was collected in 100 mL aliquots. The Pu-242 tracer was added to all aliquots and all were processed for alpha spectrometry analysis. As seen in Figure 7 only 30-40% of the added Pu-238 was extracted by the Pu disk, up to about 900 mL; the last aliquot suggested only a 20% extraction efficiency. It is possible that by adjusting the oxidation state of the Pu in solution, or other water quality parameters we could improve the extraction efficiency of Pu from aqueous samples. However, for the field sampling application we will not be able to treat the water prior to passing through the Empore™ disks, thus this disk was deemed not suitable for the final application.

Sr RAD Disk Tests

The other commercially available Empore™ RAD disk we evaluated was the Sr disk. The 3M product literature recommends treating the Sr disk with methanol, then 2M nitric acid, prior to passing the sample through the disk. They recommend that the sample be acidified to 2M with nitric acid prior to extraction with the Sr disk. It is also recommended that the disk not be allowed to go dry after the initial methanol and nitric washes, nor during the sample extraction. For the field applications this will not be practicable thus the spiked DI water or river water was passed through the Sr disk without pretreatment of the disk and no acid added to the sample.

The first study used spiked DI water. One liter of water was spiked with 0.1, 0.5 and 1.0 mL of Sr-90. The solutions were passed through a Sr disk using a Millipore filter housing assembly. After the one liter sample was passed through the disk, it was washed with 20 mL of 2M nitric acid as recommended by 3M. The disks were then dried at 70°C for 15 minutes prior to counting. The net beta proportional count rate (after background subtraction) was 2.20, 6.15 and 97.50 counts per minute (cpm), respectively, for the 0.1, 0.5 and 1.0 mL spike additions. We would have expected the count rate to be 110 cpm for the 1.0 mL spike addition, with the 0.1 and 0.5 mL additions giving count rates of 11 and 55 cpm, respectively. Possibly due to the lack of any Sr carrier in the DI solution the Sr-90 was not effectively extracted from the DI water solutions.

The next test used spiked unfiltered river water. Sample sizes were varied as shown in Table 8, with all receiving 0.5 mL of the Sr-90 spike. The one liter sample clogged after only 700 mL of solution had passed. The two liter sample finished overnight, thus had air pulled through the disk for an undetermined amount of time prior to the acid rinse and counting. As shown in Table 8, the count rates were much closer to the expected 55 cpm. The only anomaly is the two liter sample counting at 35 cpm. The four liter sample also seems a bit lower than the other samples, however not significantly.

We then repeated the DI water test, with Sr carrier added as well as Sr-90. One liter of water had no added Sr carrier as a control, with 2 mg, 4 mg and 6 mg of Sr added to the other solutions. All four had 0.5 mL of the Sr-90 tracer added. The Empore™ product literature suggests a maximum loading of 3 mg Sr per disk. In this study, the solution with no added Sr carrier counted at the expected rate of 54.9 cpm, while the other three disks that had Sr carrier added counted at about 5 cpm. We would have expected the count rate for the lower Sr carrier concentration to be high with a tapering off at the highest carrier addition.

After obtaining these inconsistent results, we tried to see if wetting the disk with methanol and acid prior to the sample would improve the recovery of the spike from solution. We prepared solutions of DI water and unfiltered river water. All were spiked with 0.5 mL the Sr-90. One set of each matrix was passed through the Sr disk as in the previous

studies, with no pretreatment of the disk. The others were passed through the Sr disk after treatment with 2 mL of methanol and 20 mL of 2M nitric acid. After the solution had passed through the disk, they were all treated identically, with a 20 mL 2 M nitric acid wash and drying at 70°C for 15 minutes. The count rate of the two samples passed through the untreated disks was 57.95 and 58.70 cpm, as opposed to 49.20 and 53.90 cpm for the treated disks. In both cases the DI result is reported first. The untreated disks gave a slightly higher count rate than the treated disks; the difference between the DI and river water is not significant.

In speaking with 3M technical support, they said they have also noticed a problem in obtaining consistent count rates. They feel the most critical step is actually the drying step and recommend using 30 minutes rather than the 15 we have been using. This will be evaluated further.

Summary of Empore™ Technology

We have evaluated several Empore™ materials for the extraction of radionuclides from solution. Some of the materials are commercially available products while others were designed for testing only at the SRS. The modified field samplers will be deployed during the fourth quarter of the fiscal year, July-September. We will be testing the commercial Tc RAD disk and Sr RAD disks as well as the newly prepared KCFC disk for the extraction of radiocesium. Results from the field trail will be the final determining factor as to the performance of the Empore™ disks for field analytical sampling.

GENERAL CONCLUSIONS

Two new commercial technologies have been studied for the determination of radionuclide concentrations in aqueous systems. The Selentec MAG*SEPSM process has been shown to work in the lab as well as in the field. It is a technique that can be used for grab water sample analysis. The system is fairly portable, rugged, and uncomplicated. Much of the sample processing is performed in the field limiting the handling that must be done in the lab prior to quantification of the radionuclide of interest in the lab. The Empore™ technology has been studied in the laboratory only at this point but will be placed in the field in the near future. When used in the modified field deployable sampler, unattended continuous monitoring can be achieved by programming the sampler to take small aliquots of water, at regular intervals, and passing it through the disks. Both technologies evaluated have potential for improving field sampling for radionuclides. Continued field sampling will further demonstrate the applicability of these techniques to further improved radionuclide monitoring at the SRS and other facilities.

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Figure 1: Distribution Coefficient for the Uptake of Tc-99 by TEVA resin (from Horwitz, et al., 1995)

Figure 2: (A) Adsorption Rate for the Uptake of Tc-99 by Tc-particles

(B) Desorption Rate for the Extraction of Tc-99 from Tc-particles

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Figure 1

Distribution Coefficient for the Uptake of Tc-99 on TEVA Resin

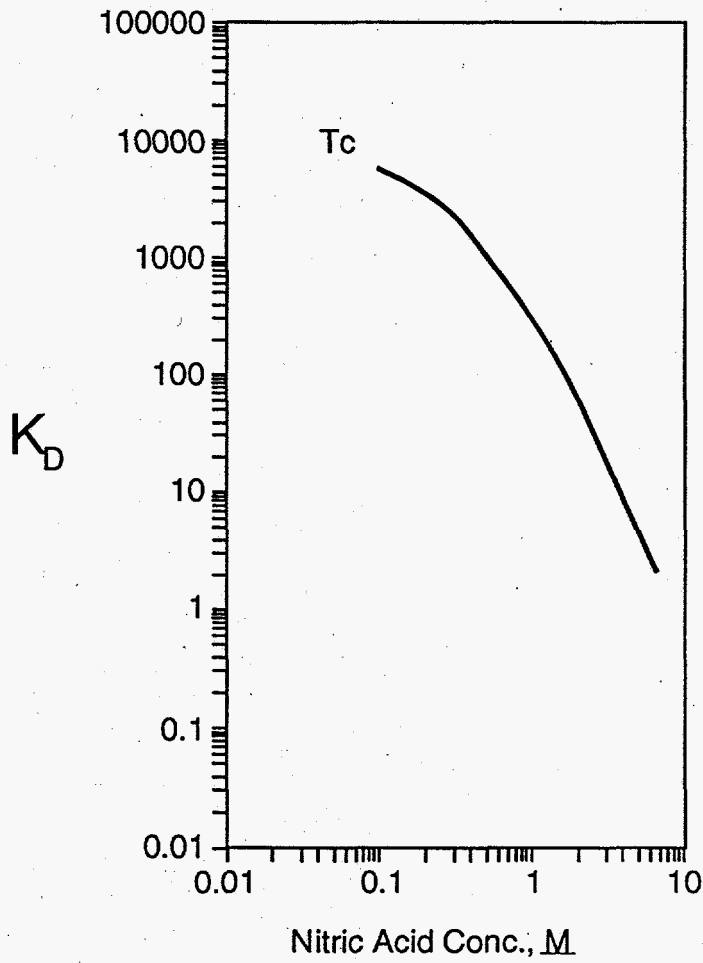


Figure 2A

Adsorption Rate for the Uptake of Tc-99 by Tc-particles

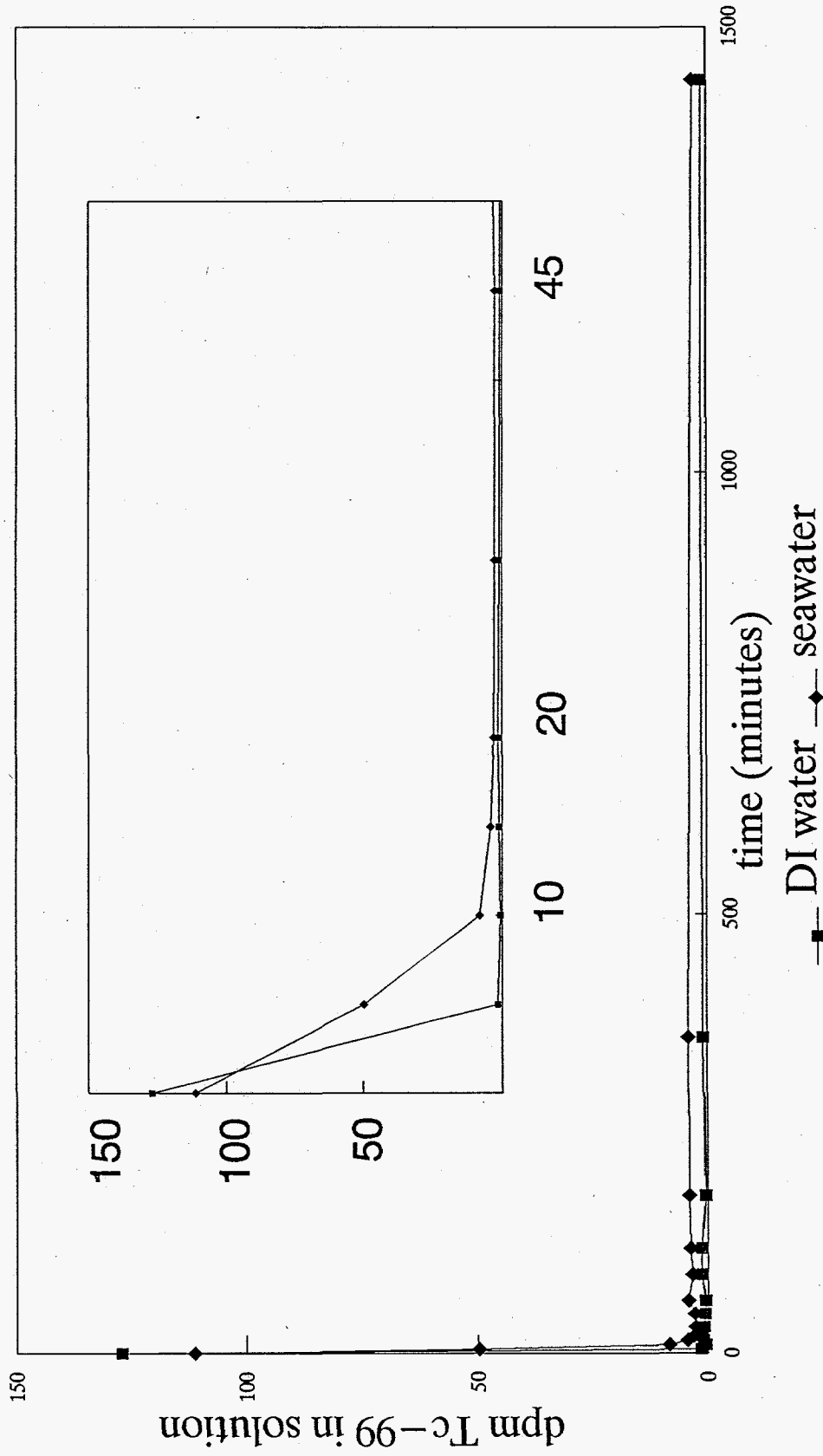


Figure 2B

Desorption Rate the Extraction of Tc-99 from Tc-particles

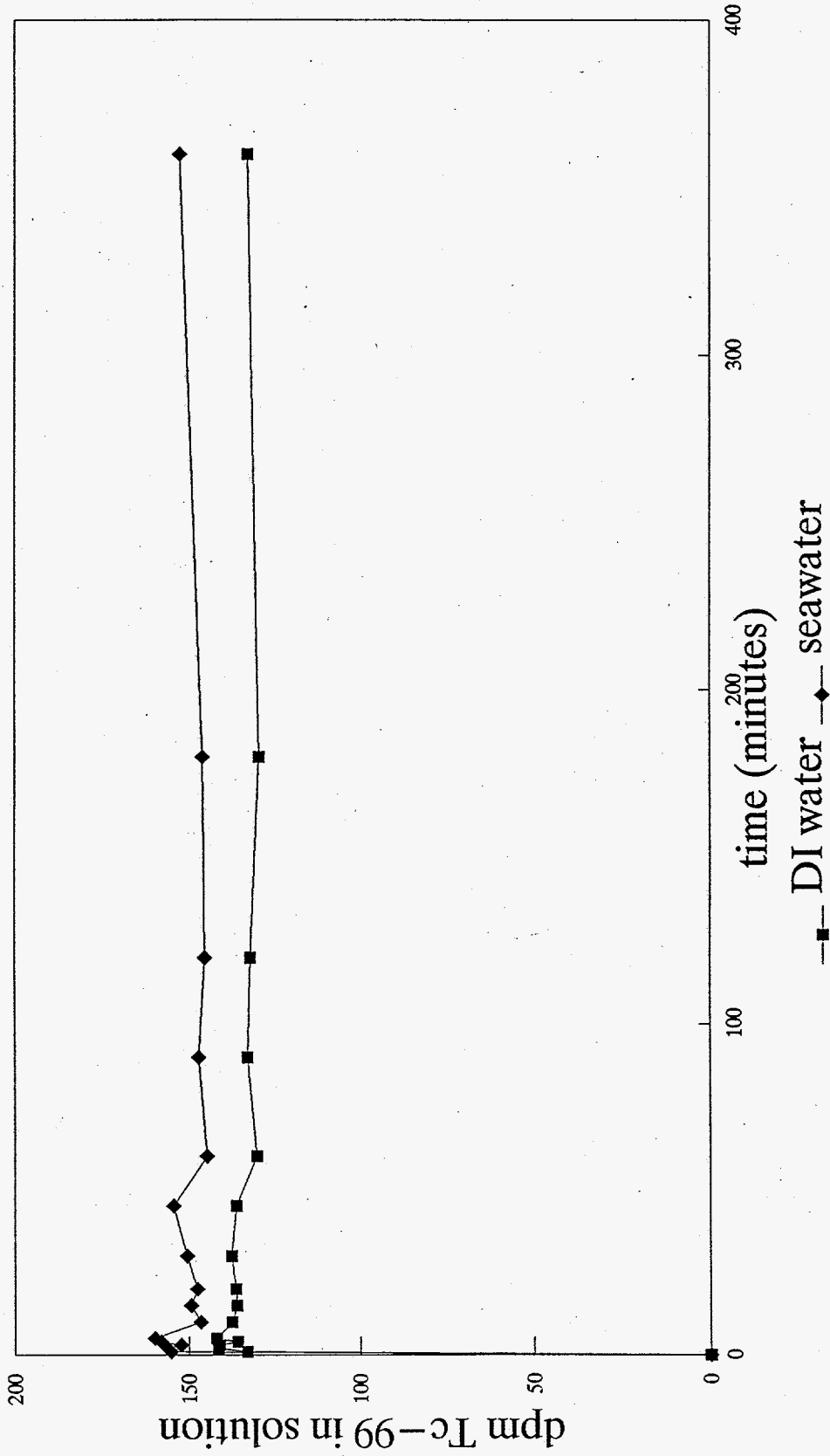


Figure 3

Adsorption Rate for the Uptake of Cs-137 by Cs-particles

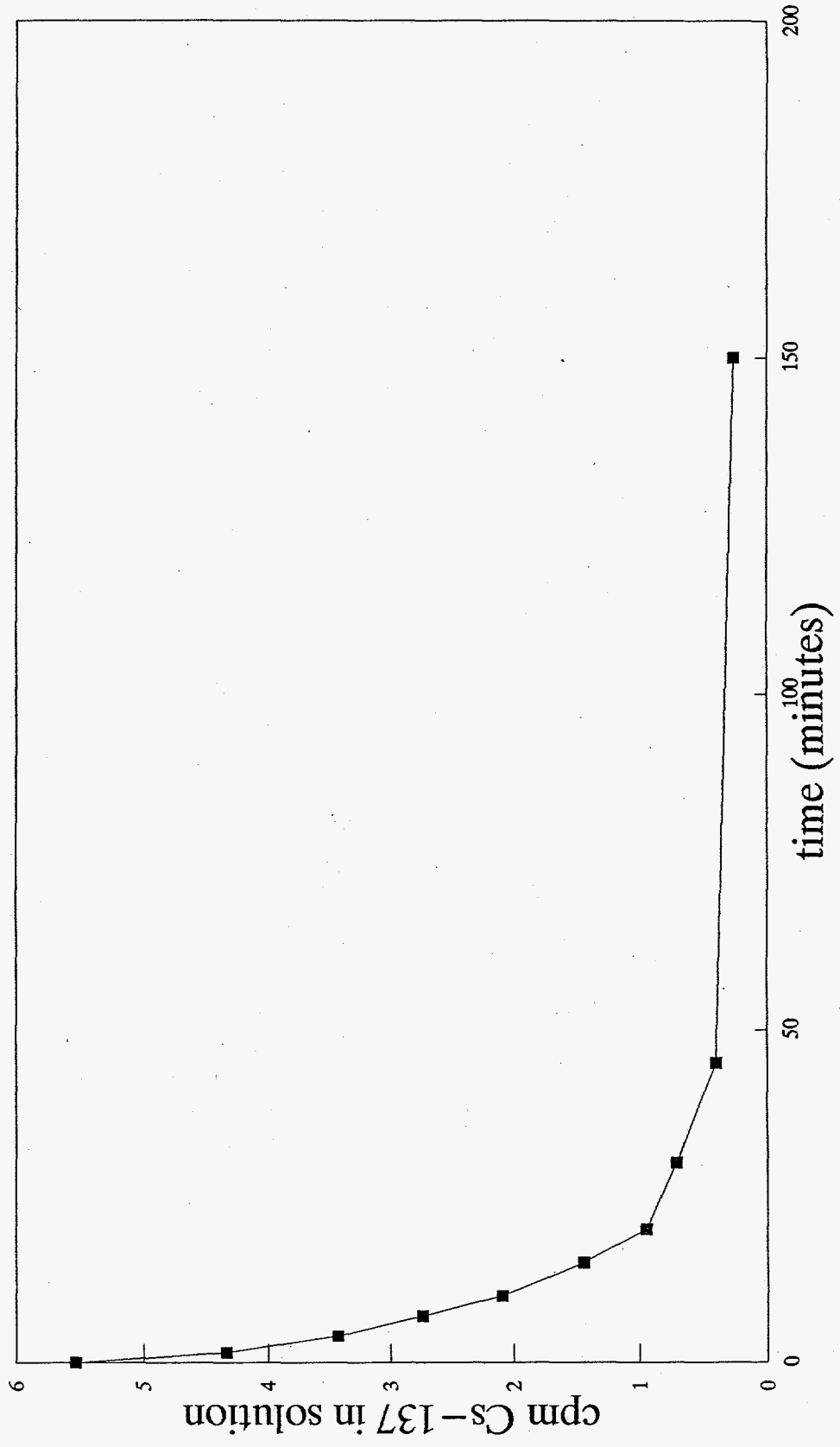
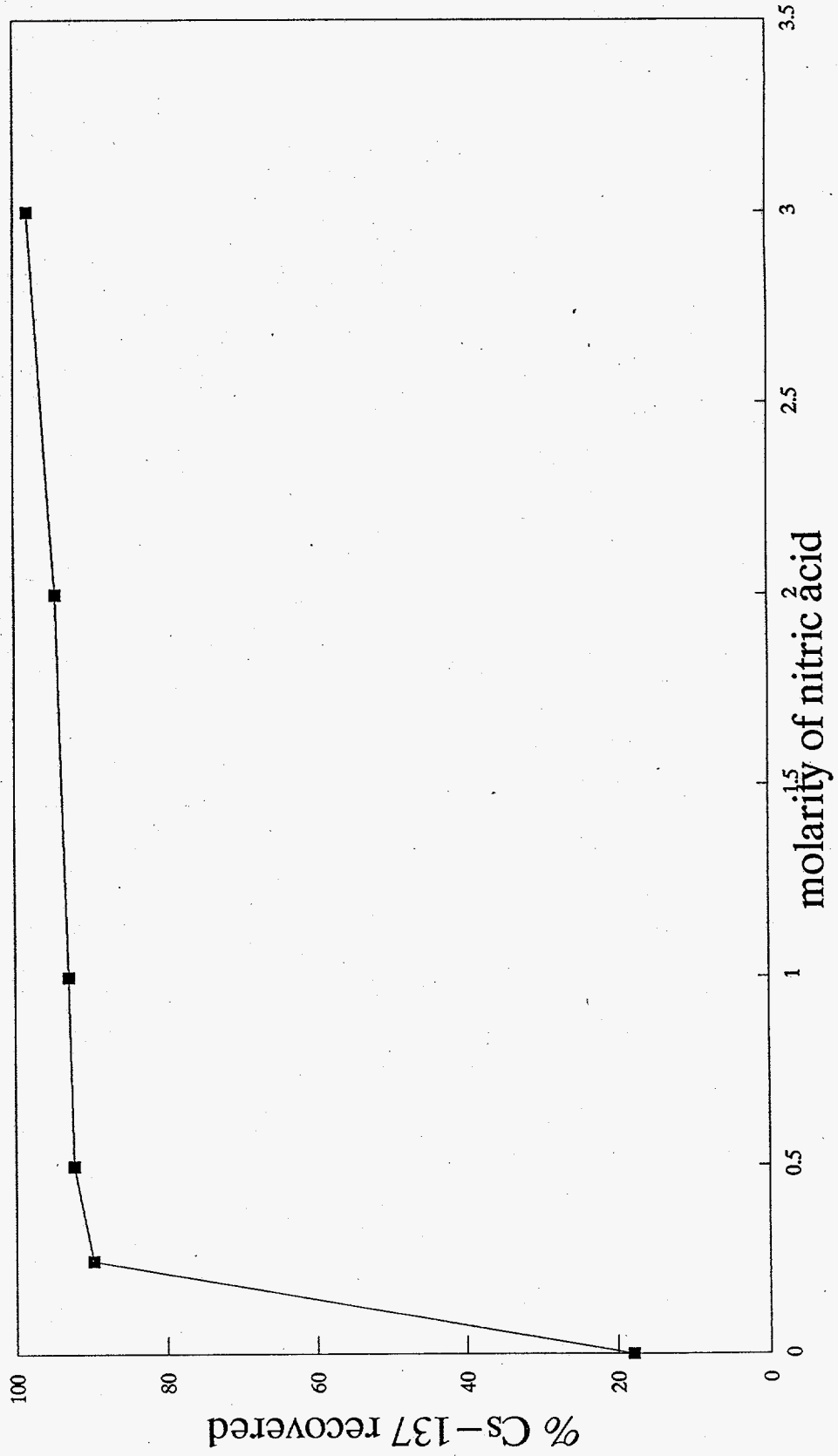
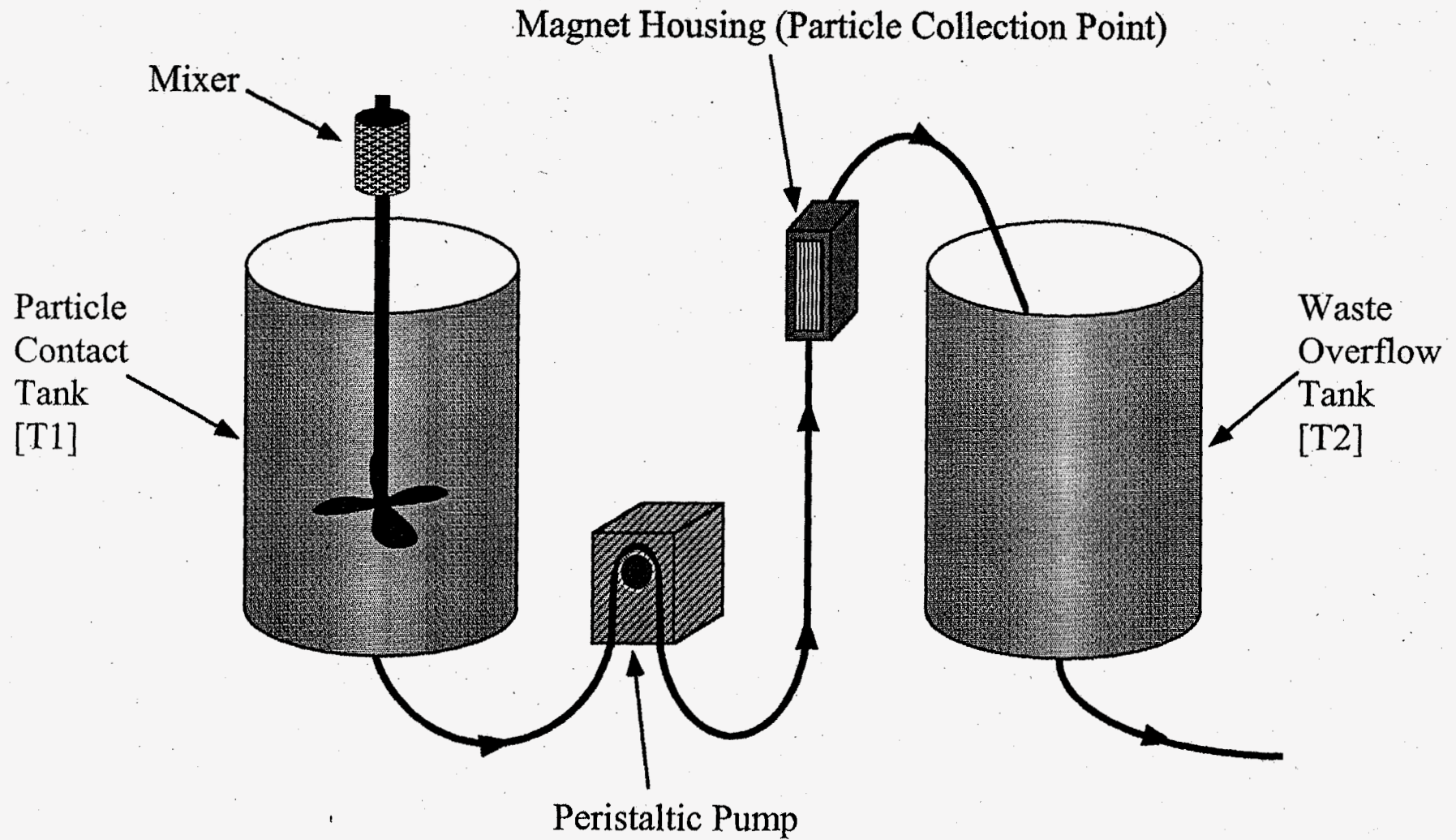


Figure 4

Extraction of Cs-137 from Cs-particles by Dilute Nitric Acid

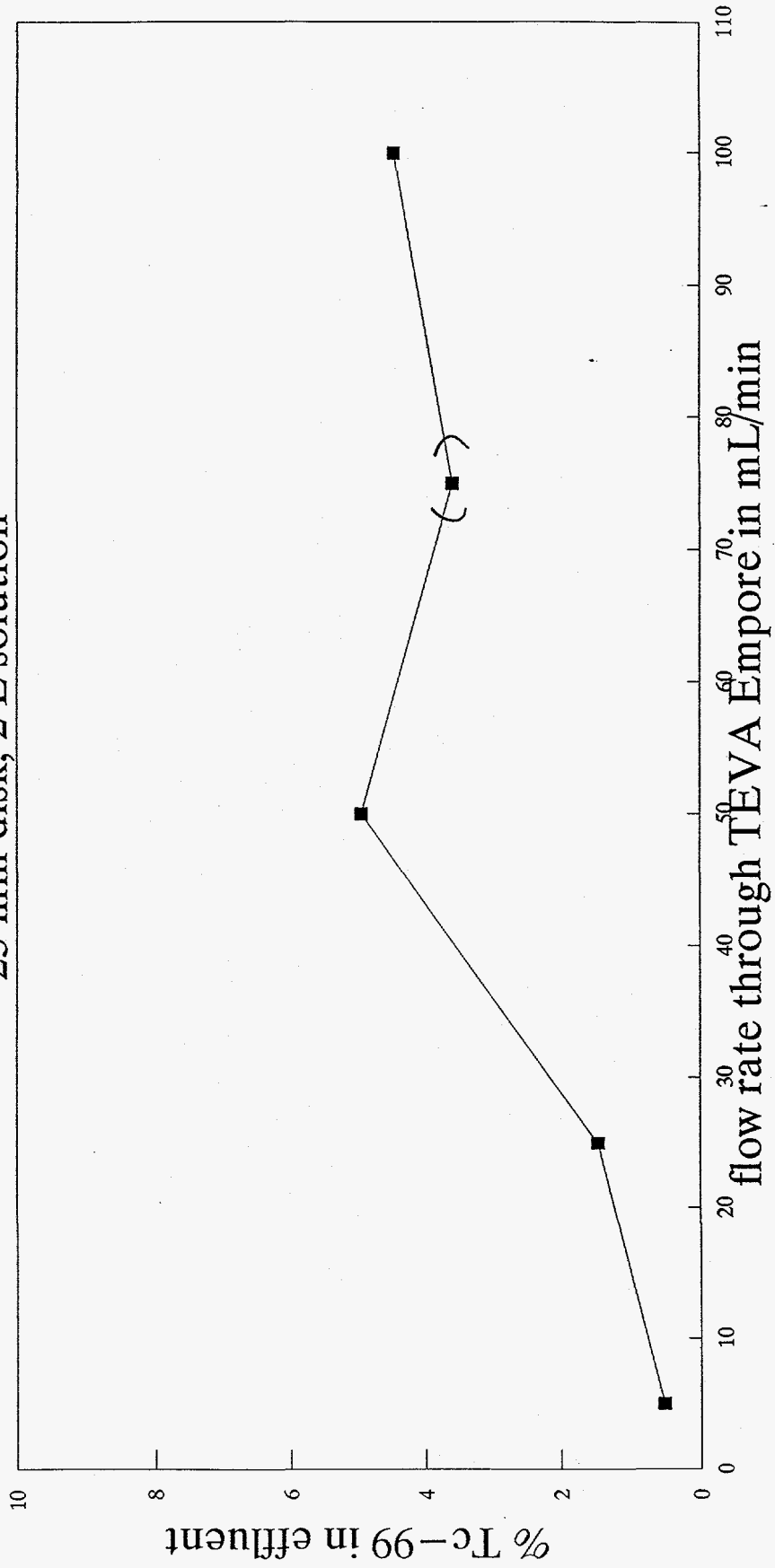


Mag*SepSM Sample Flow



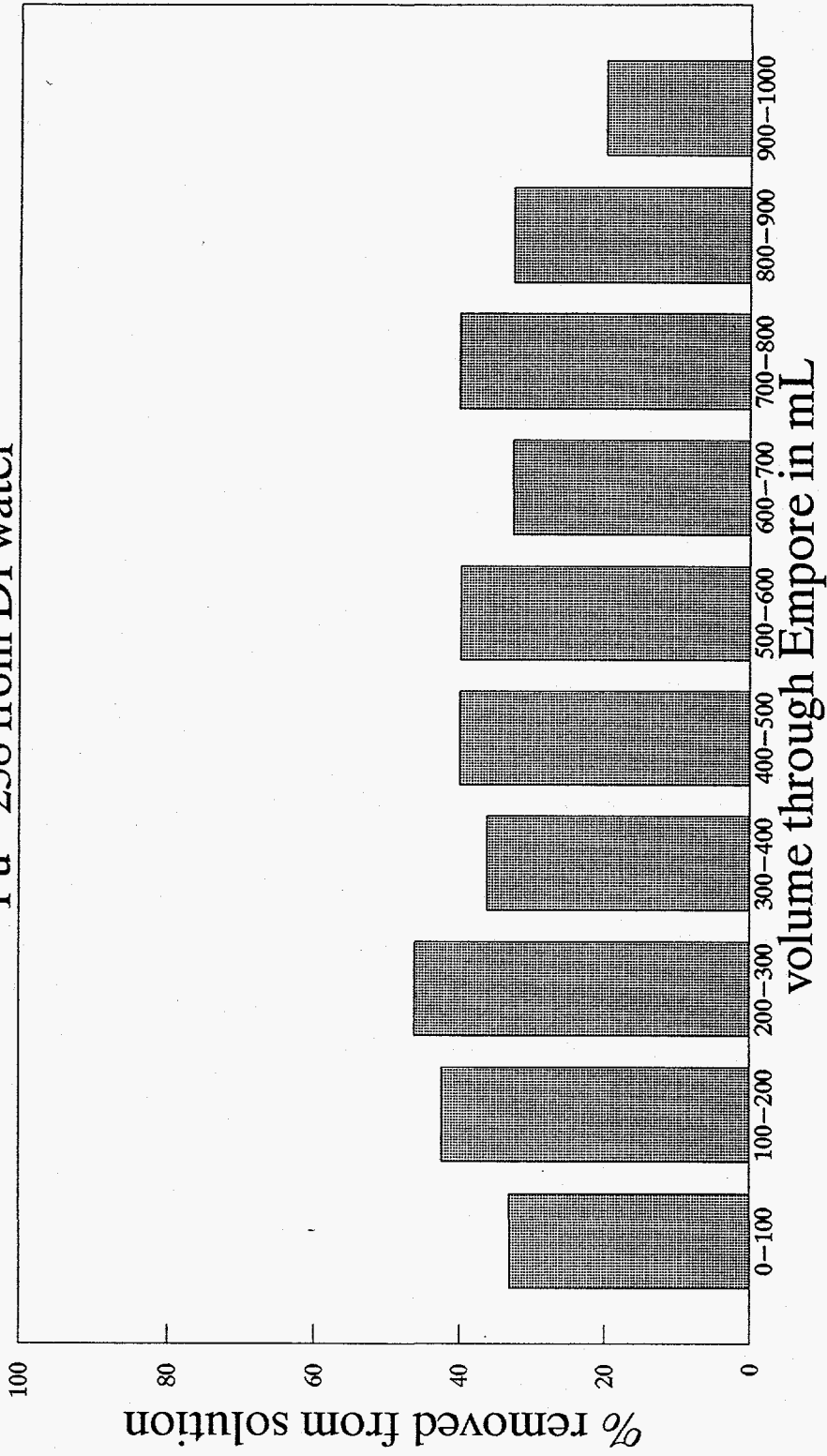
Flow Rate vs Tc-99 Retention

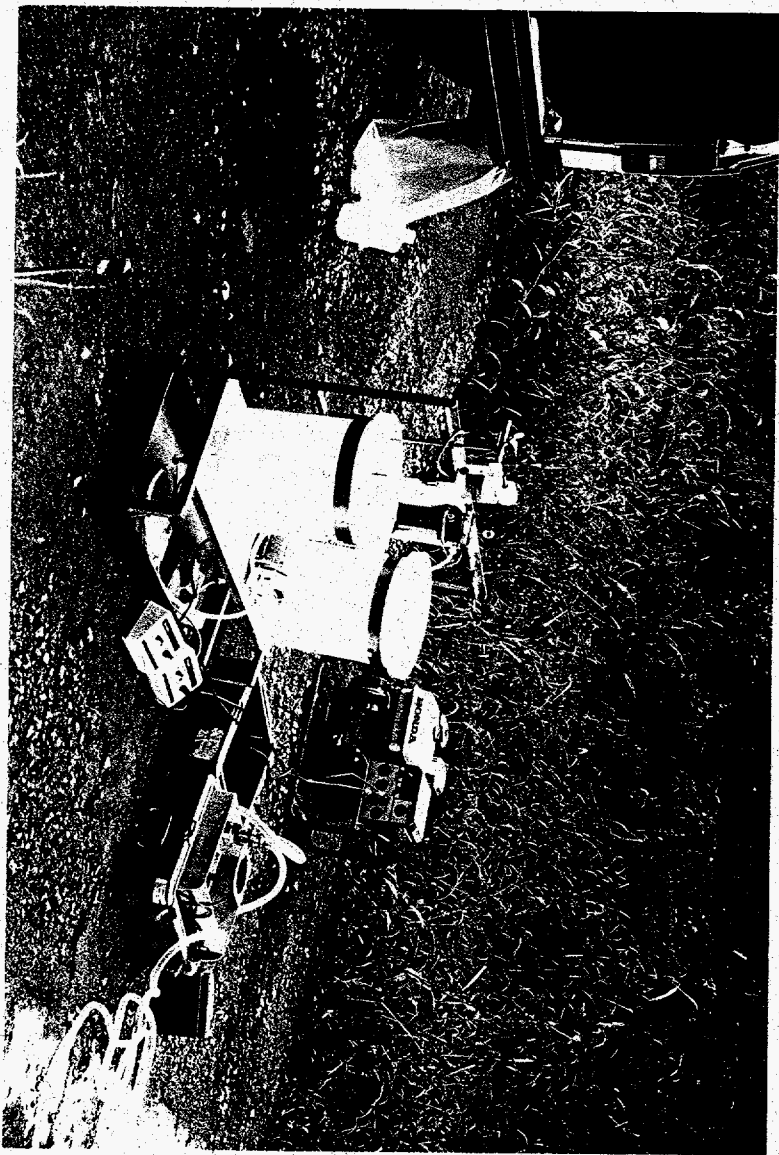
25 mm disk, 2 L solution



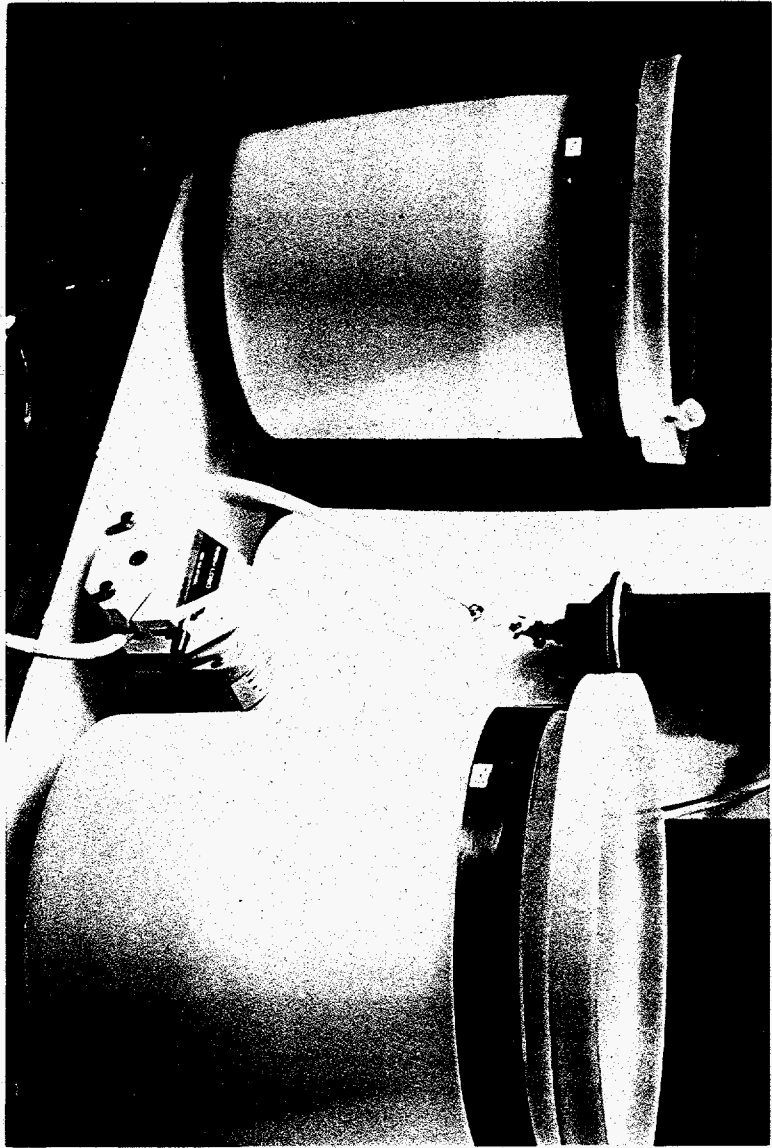
Extraction by NaTiO₄ Empore

Pu-238 from DI water











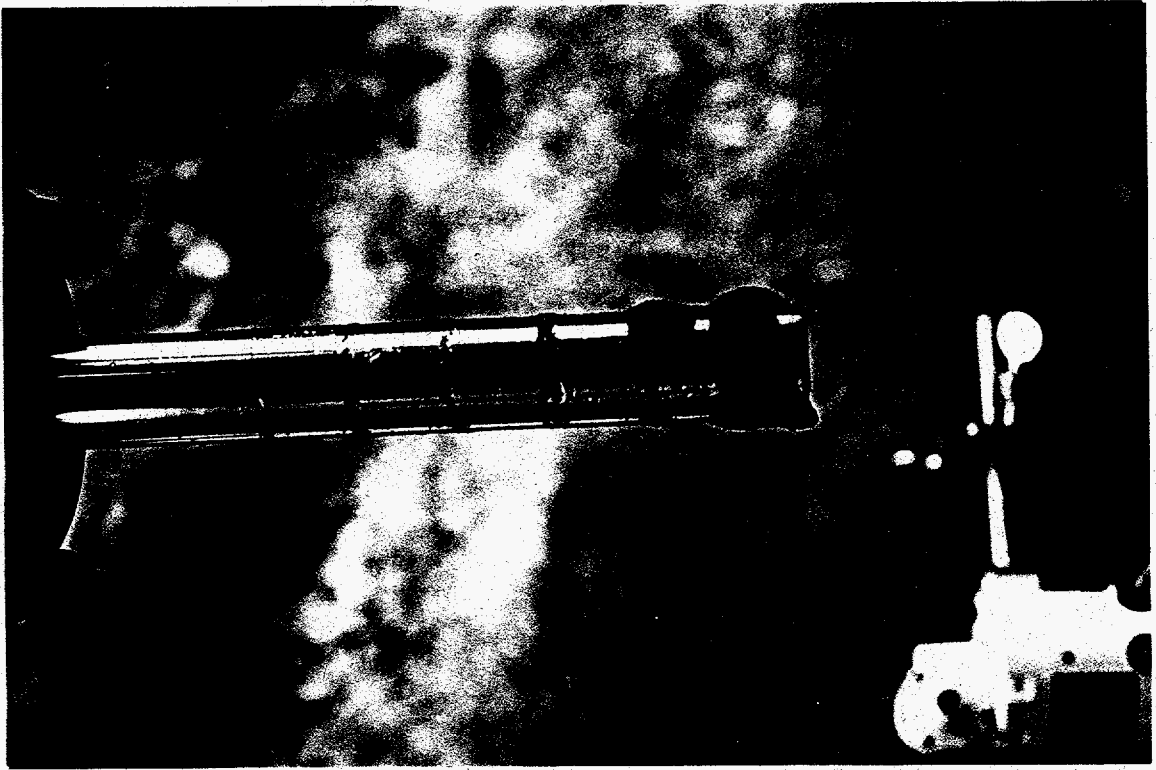




Table 1

Distribution Coefficient for the Uptake of Tc-99
by Tc-particles

<u>particle wt</u> <u>gram</u>	<u>starting sol'n</u> <u>pCi/mL</u>	<u>treated sol'n</u> <u>pCi/mL</u>	<u>percent Tc-99</u> <u>remaining</u>	<u>Distribution</u> <u>Coefficient</u>
5	1022	10.6	1.0	1.91E4
4	864	8.2	0.9	2.61E4
3	852	9.4	1.1	2.99E4
2	1974	23.6	1.2	4.13E4
1	762	35	4.6	2.08E4
0.5	868	59.2	6.8	2.74E4
0.1	1016	344	33	2.03E4
1	25	1	1.0	

Table 2

Back Extraction of Tc-99 from Tc-particles
Over Time

<u>Time of Extraction</u>	<u>% Recovered in Extract</u>
same day	94
1 week	93
2 weeks	89
3 weeks	92
4 weeks	90
5 weeks	79

Table 3

Technetium 99/97 Ratios
of Differently Exposed Tc-particles

<u>Sample #</u>	<u>Exposure</u>	<u>99/97</u>
1	simultaneous	1.14
2	simultaneous	1.18
3	simultaneous	1.35
4	sequential	1.41
5	sequential	1.10
6	sequential	lost

Table 4

Distribution Coefficient for the Uptake
of Cs-137 by Cs-particles

<u>pH</u>	<u>Dist. Coeff.</u>
2	75
4	63
6	2200
8	2056
10	4900

Table 5

Extraction of Pu-238 by Pu-particles

<u>solution</u>	<u>Pu-238 (pCi)</u>	<u>% extracted</u>
control	6.702	--
single contact	2.558	62
single contact	2.771	59
double contact	0.862	87

Table 6

Back Extraction of Pu-238 from Pu-particles

<u>acid used</u>	<u>pCi left in DI</u>	<u>pCi extracted from particles</u>	<u>% extract from DI</u>	<u>% back extract from particles</u>
1M nitric acid	2.468	6.285	72	100
8M nitric acid	2.544	3.68	59	100
1M hydrochloric acid	2.149	4.123	66	100
8M hydrochloric acid	2.736	4.369	61	100

Table 7

Radiocesium Results from Aqueous Samples
Collected on and near the SRS

<u>Location</u>	MAG*SEP			Current Method		Other Methods	
	Cs-134 <u>pCi/L</u>	Cs-137 <u>pCi/L</u>	<u>RSD</u>	Cs-134 <u>pCi/L</u>	Cs-137 <u>pCi/L</u>	Cs-137 <u>pCi/L</u>	<u>RSD</u>
Savannah River above the SRS	<0.012	0.022	30%	ND	<7.5	0.032	31%
Lower Three Run Creek on the SRS	<0.008	1.21	1.7%	ND		0.60-2.35	

Table 8

Sample Volume versus Count Rate for Sr-90 Extracted by Sr RAD Disks

<u>sample volume</u>	<u>cpm</u>
50 mL	55.90
100 mL	58.75
250 mL	60.25
500 mL	58.15
1 L (700 mL)	$46.15/0.7=65.93$
2 L	35.05
4 L	49.20