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Use of Selectively Coated MAG*SEP^{SM} Particles for Improved Radionuclide Field Sampling

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Abstract

The Savannah River Technology Center is evaluating a new field sampling methodology to more easily determine concentrations of radionuclides in aqueous systems. The new methodology makes use of the process developed by Selective Environmental Technologies (Selentec) whereby selective ligands are attached to particles with a ferrous metallic core (MAG*SEP^{SM}). 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 by pumping the water past 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. One set was prepared to extract technetium from aqueous systems, the other to extract cesium. 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, from the Atchafalaya River near New Orleans, and from the Ob River in Russia. A distinct advantage of this new 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, 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. The Savannah River Technology Center, part of the Westinghouse Savannah River Company, which operates the Savannah River Site for the Department of Energy, is therefore evaluating new field sampling methods which will eliminate much of the time and cost of the current protocols. The new sampling method should be able to concentrate large volume samples in the field to reduce shipping costs, should serve as the preservation medium for the sample, and should provide the initial chemical separation thereby reducing handling and processing in the lab.

The field sampling method evaluated for this study makes use of selectively coated MAG*SEP^{SM} particles. MAG*SEP^{SM} 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*SEP^{SM} process is being demonstrated at the Savannah River Site (SRS) for the clean up of groundwater contaminated with trace metals (Bibler, et al., 1994). Working with the researchers at Selentec, we have prepared two batches of particles that should be selective for extracting technetium and extracting cesium from aqueous systems. For this study we hoped to use the particles as an analytical tool rather than a clean up technology.

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, 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 (2 years), 135 (2.3 million years) and 137 (30 years). Of these, 134 and 137 are produced by activation and fission processes, respectively, and can be released to the environment from nuclear activities. Both Cs-134 and -137 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.

In this study we chose to examine the possibility of using MAG*SEP^{SM} technology as an analytical tool to overcome the laboratory procedural shortfalls described above. The MAG*SEP^{SM} 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. 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.

Methods

Particles used in these studies were prepared by Selentec according to their proprietary procedures. Two sets of particles were prepared, one coated with Aliquat®-336, a tricaprylymethylammonium chloride which has been used to extract technetium from dilute aqueous systems (Beals, 1996) and the other coated with a resorcinol-formaldehyde resin known to extract cesium from aqueous systems (Bibler, 1994).

These different particle types will be referred to as Tc-particles and Cs-particles, respectively, in the following discussions.

The extraction of technetium and cesium from DI water, filtered and unfiltered river water, and filtered seawater was studied. Standard solutions of Tc-99 or Cs-137 were used to spike test solutions with the desired analyte of interest. 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 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 NIST designed, in house modified, 30.5 cm, 90° deflection, single sector mass spectrometer. 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.

Samples testing the Cs-particles were measured by gamma spectrometry or by beta proportional counting. 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. Subsamples of the treated water or the Cs-particles themselves were counted on the detectors. Some spiked test samples 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, with count rates averaged over 100 minute intervals.

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. 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*SEP^{SM} 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*SEP^{SM} 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 thus 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 each of the figures shows an enlargement of the first 90 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. Three other one gram aliquots were placed in a solution that had only Tc-99. 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 contained both Tc-99 and Tc-97 at the same time; 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 (Beals, unpublished results). 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, however 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*SEP^{SM} 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, however, the contact with acid destroys the particle surface and lowers the distribution coefficient for the extraction of Cs from another solution to unacceptable levels. For the field analyses, we therefore chose to count the Cs-particles directly without eluting the radiocesium from them, and then archive the particles.

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. 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. 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 prelabeled the bottles as to the one liter level and filled them to that level). One gram of MAG*SEP^{SM} 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 poured out 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, 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. 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*SEP^{SM} particles are added. The solution is kept well mixed for 30 minutes for the Tc-particles, 60 minutes for the Cs-particles.

At the end of the extraction period the solution is pumped through the peristaltic pump, past the enclosed magnet, into the right bucket, T2. 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, and the stripped 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 and the particles transferred to a small plastic bottle with deionized water. 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. 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.

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 5. 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*SEP^{SM} analysis for Cs-137 was 0.022 pCi/L(± 30%). 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. The SRS Environmental Monitoring Report lists the activity of the Lower Three Runs Creek below the Par Pond dam as less than 15 to less than 23 pCi/L (Arnett, et al., 1994). Our sample collected at the same location had a calculated activity of 1.21 pCi/L (±1.7%). The difference in the standard SRS procedure versus the MAG*SEP^{SM} procedure is the amount of sample processed for counting and the final counting geometry. 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*SEP^{SM} sample was collected was 0.032 pCi/L (±31%), in very good agreement with our MAG*SEP^{SM} result.

SUMMARY

An analytical method has been developed making use of MAG*SEP^{SM} 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*SEP^{SM} 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*SEP^{SM} 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*SEP^{SM} method as opposed to a few days for standard procedures. We have prepared two new batches of particles to test the applicability to the determination of other radionuclides in aqueous systems.

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List of Tables and Figures

Table 1

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

particle wt gram	starting sol'n pCi/mL	treated sol'n pCi/mL	percent Tc−99 remaining	Distribution Coefficient
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

Time of Extraction	% Recovered in Extract
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

Sample #	Exposure	99/97
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

pH	Dist. Coeff.
2	75
4	63
6	2200
8	2056
10	4900

Table 5

Radiocesium Results from Aquoeus Samples Collected on and near the SRS

	MAG*SEP			Current Method	
	Cs−134	Cs−137		Cs−134	Cs−137
location	pCi/L	pCi/L	RSD	pCi/L	pCi/L
Savannah River above the SRS	<0.012	0.022	30%	nd	<7.5
Lower Three Run Creek on the SRS	<0.008	1.21	1.7%	nd	<15

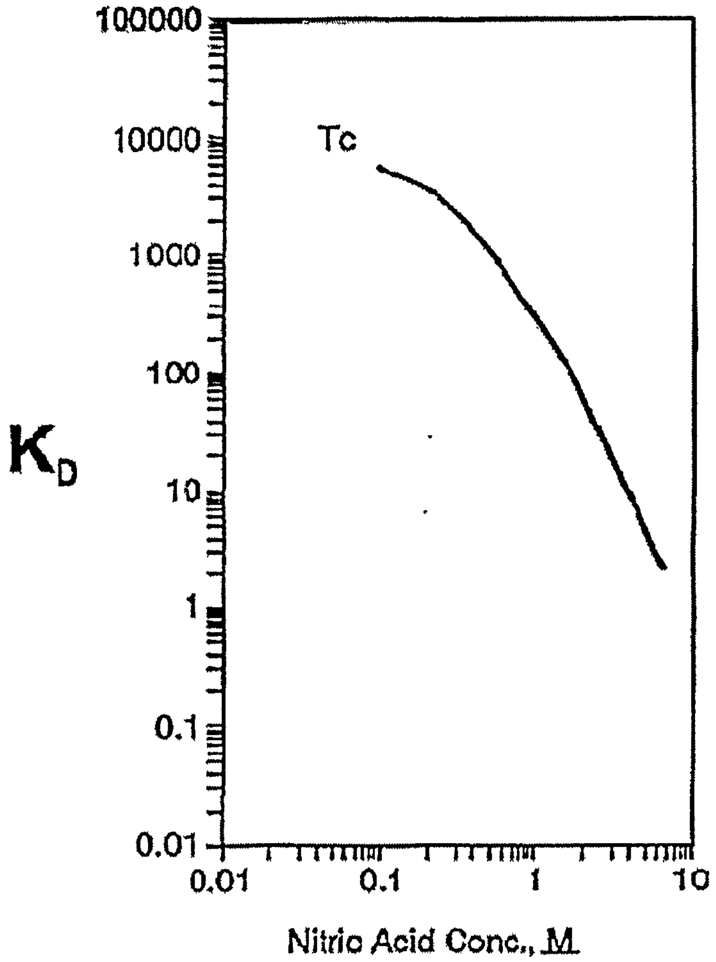
100000
10000
1000
100
10
1
0.1
0.01
K_D
Tc
0.01
0.1
1
10
Nitric Acid Conc., M

Figure 1

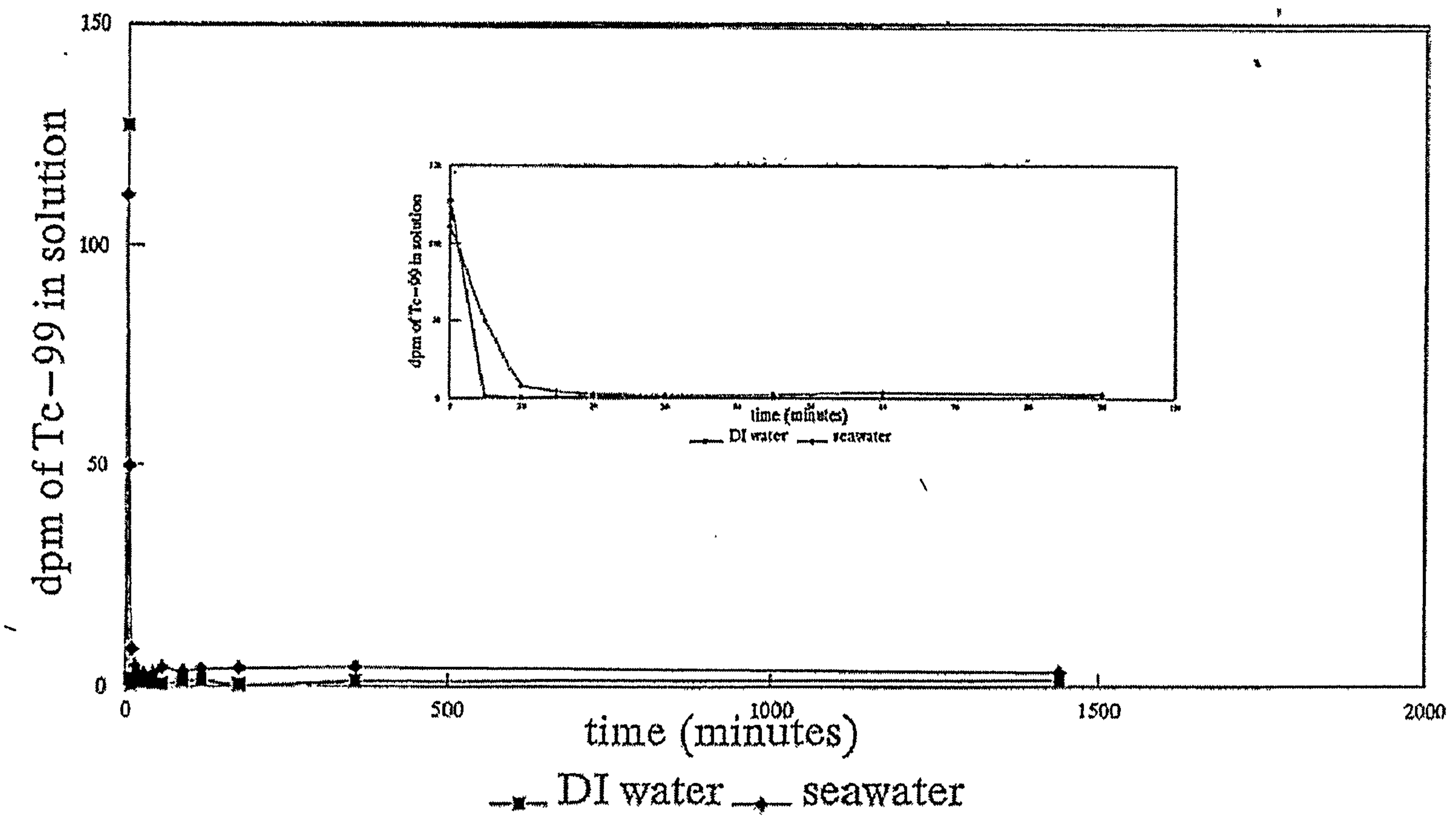
150
100
50
0
dpm of Tc−99 in solution
0
500
1000
1500
2000
time (minutes)
DI water
seawater
dpm of Tc−99 in solution
time (minutes)
DI water
seawater

Figure 2~~b~~d

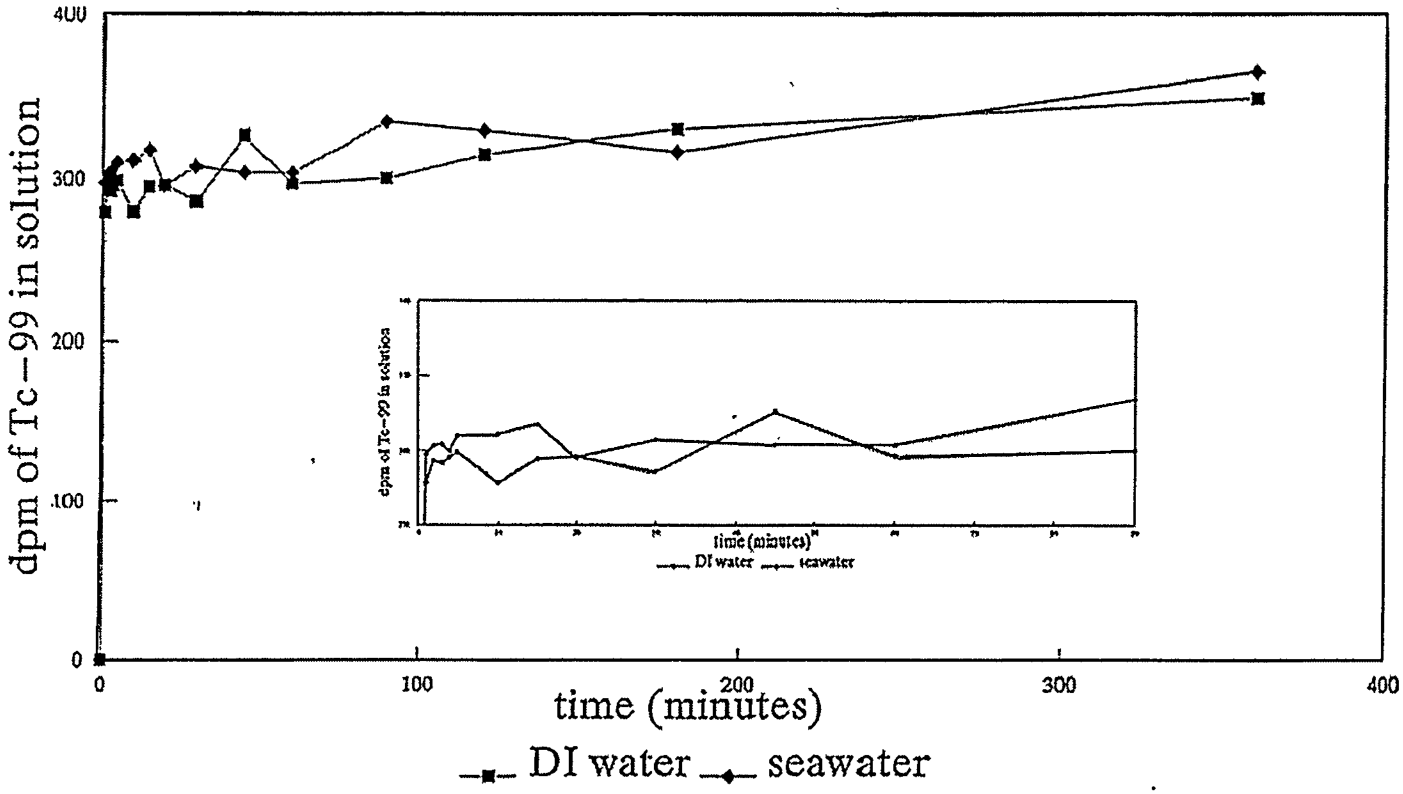
dpm of Tc−99 in solution
400
300
200
100
0
0
100
200
300
400
time (minutes)
DI water
seawater
dpm of Tc−99 in solution
time (minutes)
DI water
seawater

Figure 2b

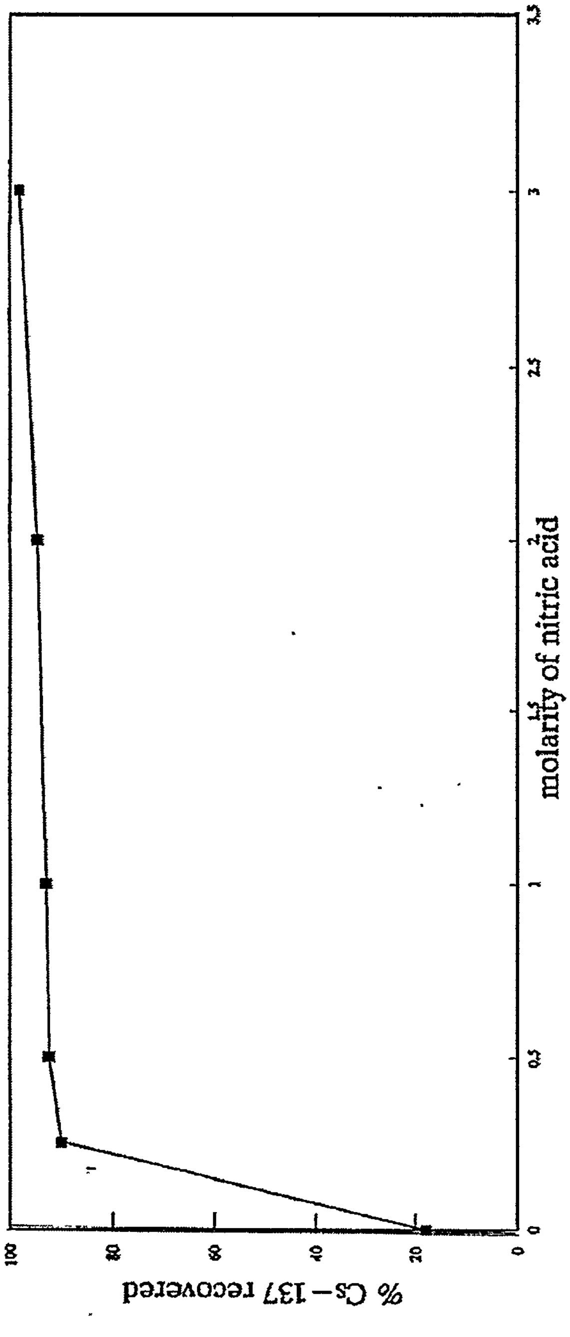
% Cs−137 recovered
0
20
40
60
80
100
0
0.5
1
1.5
2
2.5
3
3.5
molarity of nitric acid

Figure 3

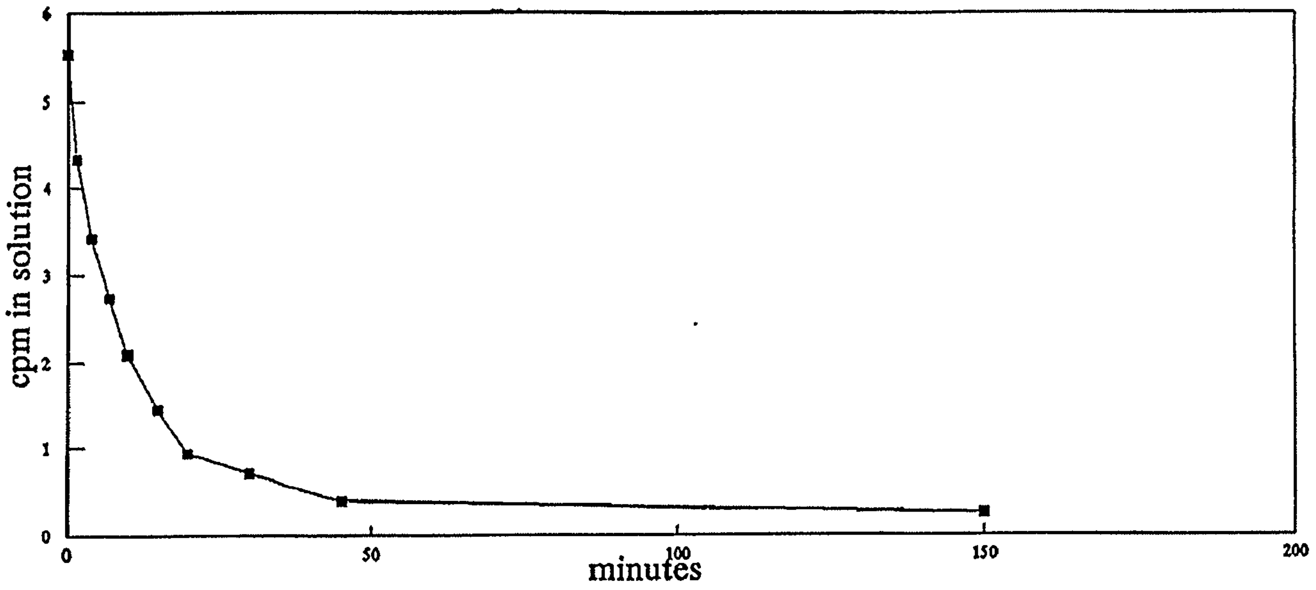

Figure 4

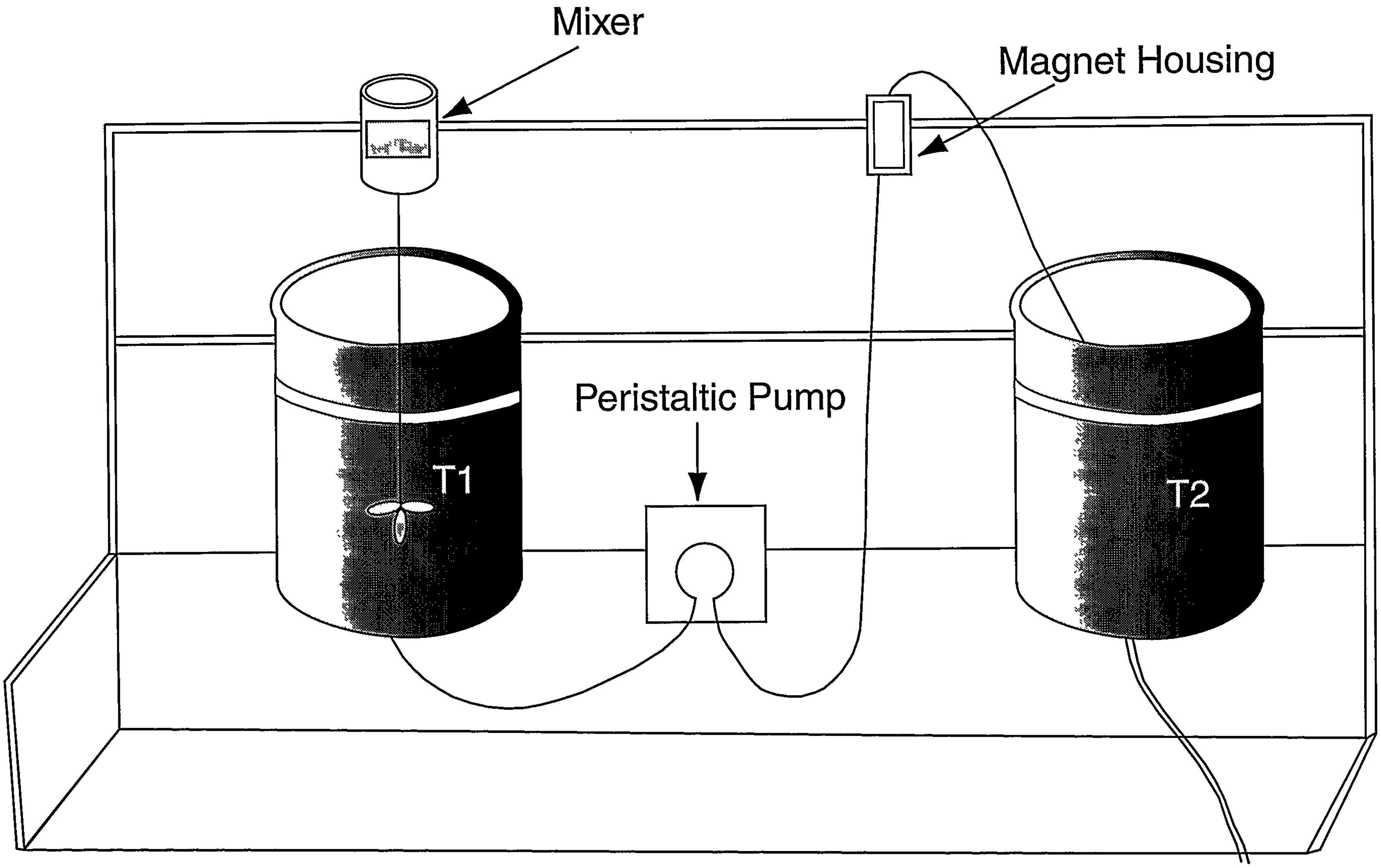

Figure 5

96X01573.AIL