ORNL/TM–13154

ornl

OAK RIDGE
NATIONAL
LABORATORY

LOCKHEED MARTIN

An Investigation of Groundwater Organics, Soil Minerals, and Activated Carbon on the Complexation, Adsorption, and Separation of Technetium-99

Baohua Gu
Kathryn E. Dowlen

Environmental Sciences Division
Publication No. 4502

MANAGED BY
LOCKHEED MARTIN ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

UCN-13673 (36 6-95)

MASTER

al

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ORNL/TM-13154

An Investigation of Groundwater Organics, Soil Minerals, and Activated Carbon on the Complexation, Adsorption, and Separation of Technetium-99

Baohua Gu[1]
Kathryn E. Dowlen[2]

---

[1] Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
[2] Oak Ridge Associated Universities, Oak Ridge, Tennessee.

Environmental Sciences Division
Publication No. 4502

Date Published: January 1996

Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6285
managed by
LOCKHEED MARTIN ENERGY RESEARCH CORP.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-96OR22464

EXECUTIVE SUMMARY

This report summarizes studies on the interactions of technetium-99 (Tc) with different organic compounds and soil minerals under both oxidizing and reducing conditions. The report is divided into four parts and includes (1) effect of natural organic matter (NOM) on the complexation and solubility of Tc, (2) complexation between Tc and trichloroethylene (TCE) in aqueous solutions, (3) adsorption of Tc on soil samples from Paducah Gaseous Diffusion Plant (PGDP), and (4) adsorption and separation of Tc on activated carbon. Various experimental techniques were applied to characterize and identify Tc complexation with organic compounds and TCE, including liquid-liquid extraction, membrane filtration, size exclusion, and gel chromatography. Results indicate, within the experimental error, Tc (as pertechnetate, TcO_4^-) did not appear to form complexes with groundwater or natural organic matter under both atmospheric and reducing conditions. However, Tc can form complexes with certain organic compounds or specific functional groups such as salicylate. Tc did not appear to form complexes with TCE in aqueous solution. Both liquid-liquid extraction and high performance liquid chromatography (HPLC) gave no indication Tc was complexed with TCE. The correlations between Tc and TCE concentrations in monitoring wells at PGDP may be a coincidence because TCE was commonly used as a decontamination reagent. Once TCE and Tc entered the groundwater, they behaved similarly because both TcO_4^- and TCE are poorly adsorbed by soils.

No significant adsorption of TcO_4^- was observed by soils from PGDP. Even when soils and reagent solutions were purged with H_2/N_2, Tc adsorption on these soils remained very low, probably because a true reducing environment was not attained in these systems. Only when soils were added with 5 mg/L Na_2S, a relatively high amount of Tc was removed by the PGDP soil. A removal of Tc under reducing conditions was attributed to both adsorption and precipitation processes. Although, a complexation between natural organic matter and Tc was not observed using membrane filtration, size exclusion and gel chromatography techniques, the addition of the organic compounds in Tc solution reduced the precipitation loss of Tc when a relatively high concentration of Na_2S was added. Results of these studies suggest Tc is present in PGDP groundwater primarily as TcO_4^-, given the relatively high DO concentration and a relatively low organic matter content in PGDP groundwater. An effective remediation technique to remove TcO_4^- from PGDP contaminated groundwater is needed. One possibility is the use of an activated carbon adsorption technique developed in this study.

During separation of groundwater organics from TcO_4^-, it was surprisingly observed that TcO_4^- was effectively and selectively removed by activated carbon. Subsequent batch adsorption and column leaching studies confirmed that activated carbon efficiently removed TcO_4^- over a wide range of pH values and various dilute electrolyte solutions (<0.01 M). The partitioning coefficient (Kd) of TcO_4^- exceeded 27,000 when actual groundwater was used, and exceeded 12,000 mL/g when background solutions of 0.01 M CaCl2 and Na_2SO_4 were used. TcO_4^- removal efficiency was >99% under these conditions, except in a 0.01 M $NaNO_3$ background solution. Column studies indicated a high adsorption capacity and selectivity of activated carbon for TcO_4^-. No Tc breakthrough was observed when more than 14,000 pore volumes of contaminated groundwater (containing ~3000 pCi Tc/L) were passed through a small column (6.6 x 30 mm) with 0.5 g activated carbon. Various chemical reagents were also studied for the recovery of TcO_4^- on activated carbon. It was found that salicylate was the most effective in desorbing and recovering the adsorbed TcO_4^-. Therefore, the use of activated carbon to remediate Tc-contaminated groundwater appears to be a promising technology, which is cost-effective and requires minimal installation and maintenance. In addition, the adsorbed TcO_4^- can be recovered for possible reuse and to minimize secondary waste operations.

TABLE OF CONTENTS

LIST OF TABLES

Table Page

LIST OF FIGURES

ABBREVIATIONS

DO	dissolved oxygen
DOE	Department of Energy
EDTA	ethylenediaminetetraacetic acid
FTIR	Fourier transform infrared
HPLC	high performance liquid chromatography
HU	hydrologic unit
MW	monitoring well
NOM	natural organic matter
NTU	Nephelometric turbidity unit
PGDP	Paducah Gaseous Diffusion Plant
Tc	technetium-99
TCE	trichloroethylene
UV	ultra-violet

ACKNOWLEDGMENTS

This research was supported by the Environmental Management Facilities at the Paducah Gaseous Diffusion Plant, Paducah, Kentucky for the U.S. Department of Energy, under contract DE-AC05-84OR21400 with Lockheed Martin Energy Systems, Inc..

1. COMPLEXATION STUDIES OF NATURAL ORGANIC MATTER WITH TECHNETIUM-99

1.1 INTRODUCTION

Technetium-99 (Tc) is a β-emitting radionuclide with a long half-life (2.13×10^5 years) and posses a long-term radiation risk to mankind. The most stable chemical species of Tc in aqueous solution under aerobic conditions is the pertechnetate anion, TcO_4^-, which is highly soluble and mobile in soil. The amount of Tc released to the environment has been increasing through fallout from nuclear weapons tests and discharges from nuclear processing plants, power plants, and other facilities (Schulte and Scoppa 1987). For example, groundwater contaminated with Tc has been identified at many U.S. Department of Energy (DOE) complexes, including PGDP, Portsmouth Gaseous Diffusion Plant, and the Hanford nuclear waste storage facilities (Brown 1967; Clausen et al., 1995). In 1988, the discovery of off-site contamination in groundwater north of PGDP resulted in DOE and the U.S. Environmental Protection Agency issuing an Administrative Consent Order to determine the nature and extent of off-site contamination. Subsequent investigations identified a Tc plume extending from the northwest corner of PGDP northward toward the Ohio River (Clausen et al., 1995).

The possibility that some of the observed transport of Technetium (Tc) at the Paducah Gaseous Diffusion Plant (PGDP) may involve the cotransport of Tc sorbed or complexed with natural organic matter (NOM) in groundwater. Review of literature suggests NOM may form complexes with Tc and enhance the solubility and transport of Tc in the subsurface soil environment (Colombo et al., 1990; Hashimoto et al., 1993; Pilkington 1990; Wildung et al., 1986; Wolfrum and Bunzl 1986). In 1993, a preliminary field experiment was performed to assess the role of groundwater organic and inorganic colloids on the migration of Tc at the PGDP site, Paducah, KY. The study revealed mineral colloids do not play a significant role in the transport of Tc at the PGDP site. The role of organic matter on Tc transport was inconclusive because both Tc and the organic matter were passed through a membrane filter with a molecular weight cut-off at 3000 dalton (nominal molecular weight). The objective of this study was to determine if Tc is complexed with natural organic matter and, if so, under what conditions the complexes form.

1.2 MATERIALS AND METHODS

1.2.1 Organic Compounds

Groundwater samples were obtained from two monitoring wells (MWs), namely MW 66 and MW 106, at PGDP site, Paducah, KY. The total organic carbon content of the groundwater samples are 0.23 and 0.27 mg C/L, respectively. Because of the low organic carbon concentrations in these samples, they had to be concentrated ~3 - 10 times on a Speedvac. The concentration process does not significantly change the nature of the organic matter because the process uses a low temperature and high vacuum. Detailed physical and chemical properties of these groundwater samples are listed in Table 1.1.

A surface water organic sample, named as GT-NOM, was used as reference, initially, to test its complexation with Tc. This organic sample originated from a wetland pond in Georgetown, SC. Detailed characterization and properties of this GT-NOM sample are presented elsewhere (Gu et al., 1994, 1995). In addition, two model organic compounds with known molecular structure, namely salicylic and phthalic acids, were used for their complexation with Tc in order to elucidate the mechanisms and functional groups possibly involved in the interactions. These organic compounds were selected because they are known to contain similar functional groups as found in NOM.

1.2.2 Chromatographic Separations and Identification

The complexation of Tc was studied by reacting Tc with different organic materials, collecting samples, and analyzing them over time. Different preparative and analytical HPLC columns were prepared in order to separate the organic compounds complexed with Tc from those associated with free organic molecules. An ISCO HPLC pump (model 2350) was used to feed the mobile phase into the column, and an UV (Linear UV/VIS 200) detector followed by a

Table 1.1 Chemical properties of groundwater obtained from monitoring wells (MW) 66 and 106 at Paducah site, Kentucky

Element	MW 66	MW 106
Cl^- (mg/L)	32.9	25.2
NO_3^- (as N) (mg/L)	5.1	1.87
SO_4^{2-} (mg/L)	11.1	10.2
PO_4^{3-} (mg/L)	0.03	-
Si (mg/L)	28.0	19.3
Fe (mg/L)	0.35	5.4
Al (mg/L)	0.34	4.0
Ca (mg/L)	33.2	15.5
Mg (mg/L)	8.6	6.6
Ba (mg/L)	0.16	0.14
Na (mg/L)	20.8	27.3
K (mg/L)	2.8	4.5
Mn (mg/L)	0.02	0.12
pH	6.2	6.1
Alkalinity (mg/L)	95.1	86.3
Conductivity (µmhos/cm)	358	287
Total Organic C (mg/L)	0.23	0.27
Dissolved Oxygen (mg/L)	5.8	5.5
Turbidity (NTU[a])	4.8	34.7
Depth to Water (ft)	42.0	41.6
Temperature (°F)	59.6	58.8

[a] NTU = Nephelometric turbidity unit.

Radiomatic 500TR flow scintillation detector were used to simultaneously measure the organic compounds and Tc activity in the eluent.

An iterative testing of columns and mobile phases were conducted to determine the optimal condition to separate the free organic compounds or Tc in solution from the Tc-organic complexes (if any). However, this report only describe those systems that worked best to separate and identify Tc and the organic compounds. For example, size-exclusion columns (Polysep-GFC-P1000, Phenomenex, CA) failed to separate Tc from some organic compounds such as phthalic and salicylic acids under various conditions. The two preparative columns used the most were a PDX-Gel-25 (Sigma Chemical Co.) and a Sephadex LH-20 (Pharmacia Fine Chemical Co., Piscataway, NJ) column packed in 6.6 x 115 mm glass columns. The mobile phase compositions and experimental conditions varied with each individual experiment and are described in detail in the "results and discussion" section. A relatively high concentration of organic matter and Tc was used in the experiment because of the detection limit of the Radiomatic detector.

1.3 RESULTS

1.3.1 Groundwater Organic Matter Characterization

Groundwater from MW 66 and MW 106 contains very low amounts of dissolved organic matter, about 0.23 mg C/L and 0.27 mg C/L, respectively. To characterize the groundwater organic compounds, the groundwater was concentrated on a Speed-Vac approximately 3-10 fold. The fourier transform infrared (FTIR) spectrum (Fig. 1.1) was acquired for the concentrated NOM from MW 106 groundwater (uncontaminated). An FTIR spectrum of groundwater from MW 66 (contaminated with Tc) was not performed because of complications associated with analyses of a radiological sample in a non-radiological laboratory. However, since both groundwater samples were from a similar geographic area and depth within the aquifer at the PGDP site, it may be generally assumed that the physical and chemical properties of NOM from the two different wells are similar in nature. This assumption is based on comparison at the

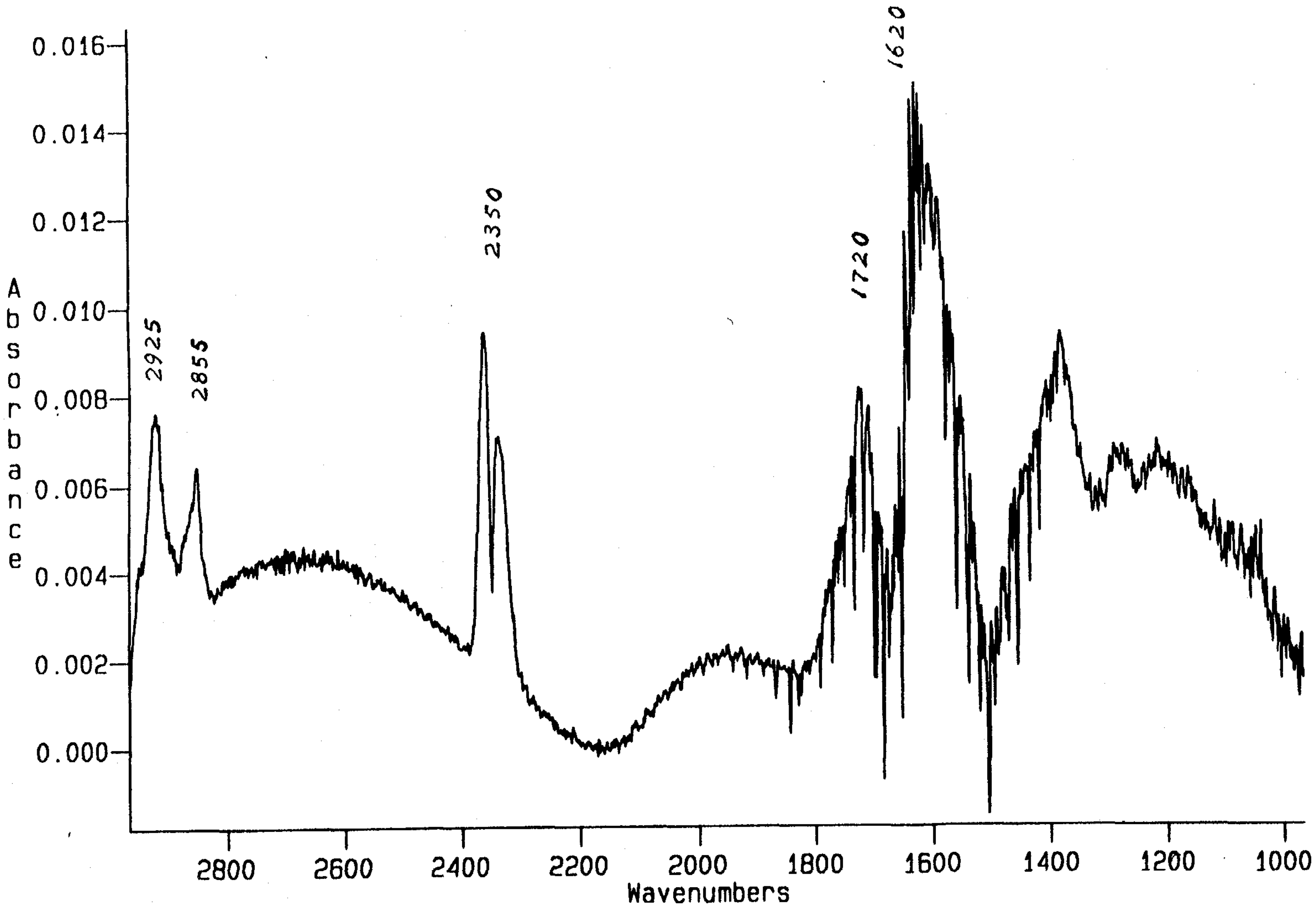


Fig. 1.1 FTIR spectra of groundwater organics from monitoring well 106, Paducah, Kentucky.

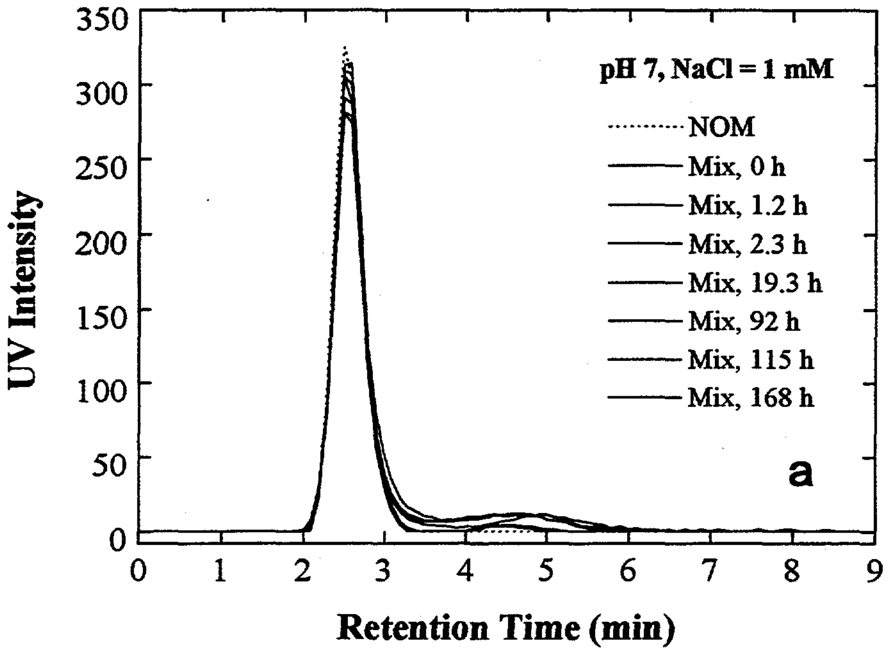
chemical properties of water samples from MW 66 and MW 106 which are very similar (Table 1.1).

The FTIR spectra in Fig. 1.1 was the difference spectra between MW 106 groundwater organics and pure water. The base line appeared somewhat noisy largely because of the relatively low organic concentration and high salt concentration in the concentrated MW 106 groundwater sample. Nevertheless, the spectra shows the groundwater organic matter contains oxygen functional groups such as –COOH or $–COO^-$ at ~1720 and 1620 cm^{-1}, and C-O and C-OH functional groups between 1200 - 1400 cm^{-1}. Absorption bands at ~2925 and 2855 cm^{-1} are due to stretching of $–CH_3$ and $–CH_2$ functional groups. The double bands at ~2350 cm^{-1} are due to the presence of CO_2. Information regarding the physical and chemical properties of NOM from Georgetown, SC was given previously (Gu et al., 1994, 1995).

1.3.2 Tc Complexation Studies with NOM

Under Atmospheric Conditions

Tc complexation with NOM was first studied in a 1 mM NaCl background solution with a pH of 7 (Fig. 1.2). Separations of Tc, NOM, or Tc-NOM complexes were accomplished using a PDX Gel-25 preparative column. After mixing Tc reference solution with NOM (10 mg/L), a 100 μL Tc-NOM mixture solution was injected into the column using a Rheodyne injector. Samples were taken at different time intervals for a total length of approximately 1 week. The retention time for NOM alone (without Tc) was ~2.5 min, and only a single UV-absorbance peak was observed (dashed line, Fig. 1.2a). On the other hand, the retention time for Tc alone (without NOM) was approximately 5 min (dashed line, Fig. 1.2b). Compared with the UV absorbance peak in Fig. 1.2a, the relatively broad peak was observed for Tc (Fig. 1.2b) is due to a much larger detector cell being used for the Radiomatic detector so a relatively high sensitivity (counts per minute, cpm) can be achieved. A large detector cell was also necessary for the mixing of eluent and the scintillation cocktail. When a mixture of Tc and NOM was injected, an UV-absorbance peak occurred exactly at the same position with the same peak height (solid lines,



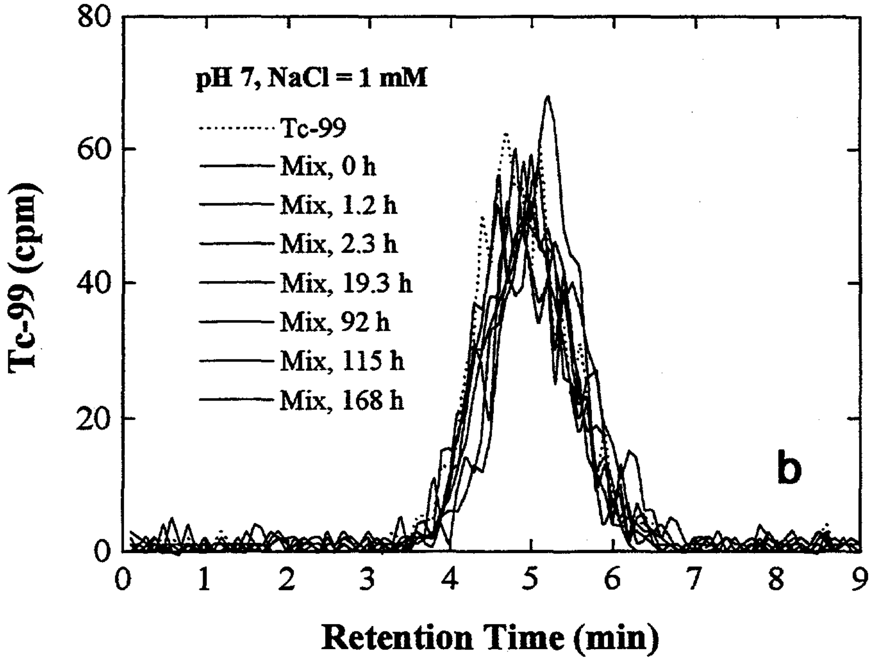


Fig. 1.2. Chromatographs of (a) NOM (by UV absorbance) and (b) Tc (by Radiomatic liquid scintillation counting) for NOM or Tc alone (dashed lines) and NOM-Tc mixtures (solid lines) at different reaction times.

Fig. 1a) as the NOM peak when it was injected alone (dashed line). A low UV-absorbance peak was also observed between 4 and 6 min (Fig. 1a) which is due to TcO_4^- which absorbs UV. Additionally, the Tc and NOM in the mixture was eluted at exactly the same position with the same peak height (solid lines, Fig. 1b) as Tc when it was injected alone (dashed line). No other elution peaks were observed even when the initial experiment was run longer than 30 min. When the mixture was injected at different times (up to 7 days), the same observations were obtained. The results indicate Tc and NOM were unlikely to be complexed under the given experimental conditions. If Tc and NOM were complexed, additional elution peaks would be expected due to the Tc-NOM complexes and the elution peaks for the Tc and NOM should coincide.

Similar experiments were repeated using a relatively high Tc concentration and a longer equilibration time (more than 3 weeks, Fig. 1.3). No significant complexation reactions between Tc and NOM were observed.

One may argue, however, that Tc-NOM complexes may dissociate when their mixture were injected into the column because of the reactions between Tc or NOM with the surfaces of bed materials. Further experiments were conducted using a size-exclusion analytical column (Polysep-GFC-P1000, Phenomenex, CA). Separation of Tc and NOM on this column is based primarily on the size of the molecules. No interactions or only weak interactions may be expected between Tc or NOM and the column packing materials (silica). Larger molecules will be eluted earlier because they travel only through large size pores within the column whereas smaller molecules are able to enter micropores, so their travel time (or retention time) will be longer. Results (Fig. 1.4) indicate the retention time for Tc alone or Tc in NOM mixture occurred at ~7.8 min whereas retention time for NOM or NOM in Tc mixture was ~9.3 min. Again, there is no indication that Tc was complexed with NOM under these conditions.

Similarly, the experiment was conducted using a Sephadex LH-20 preparative column. The retention times of Tc and NOM on this column (data not shown) are ~2.3 and 1.4 min respectively, and no apparent complexation reactions between Tc and NOM were observed.

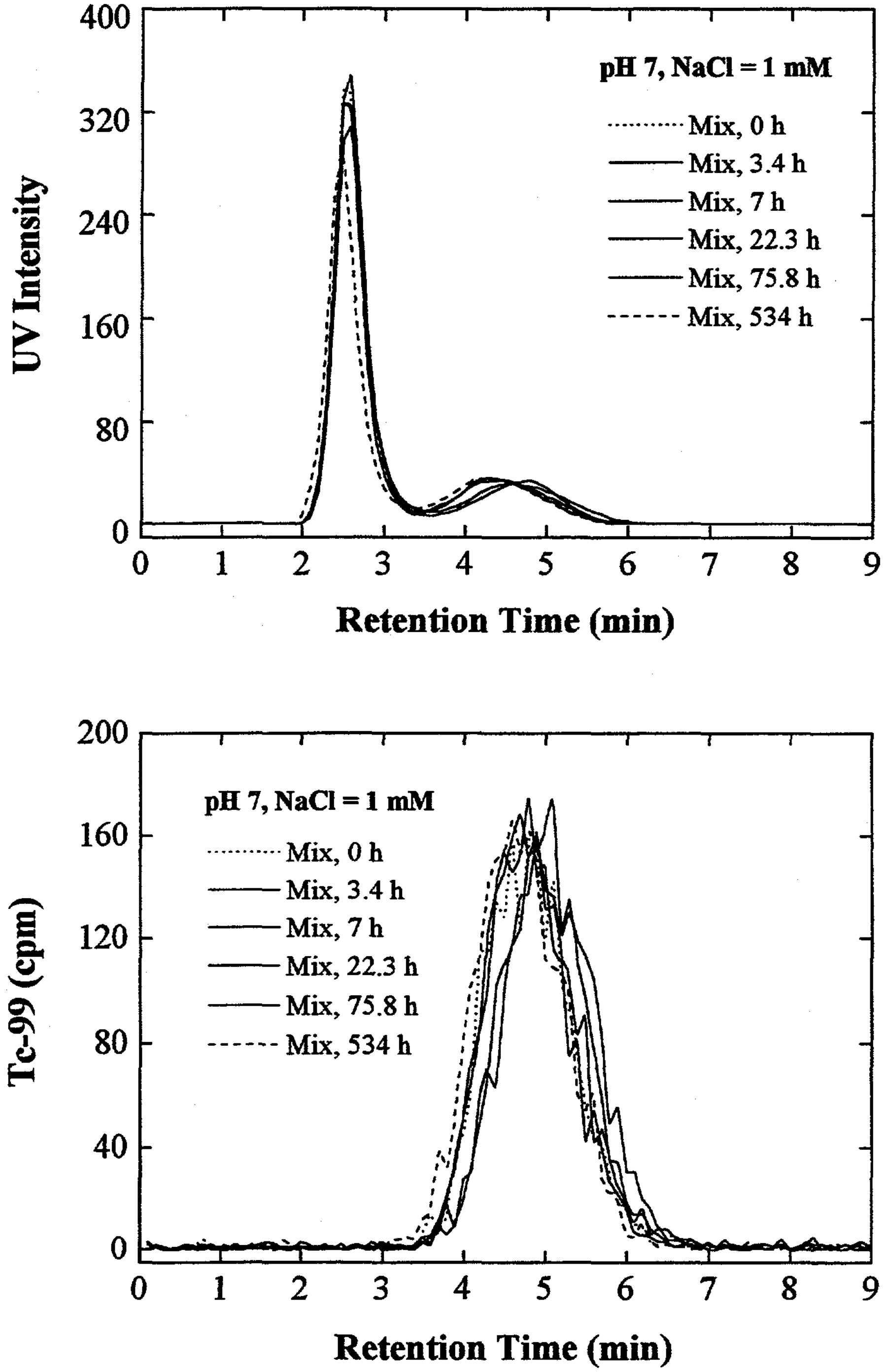


Fig. 1.3. Chromatographs of (a) NOM (by UV absorbance) and (b) Tc (by Radiomatic liquid scintillation counting) at different reaction times.

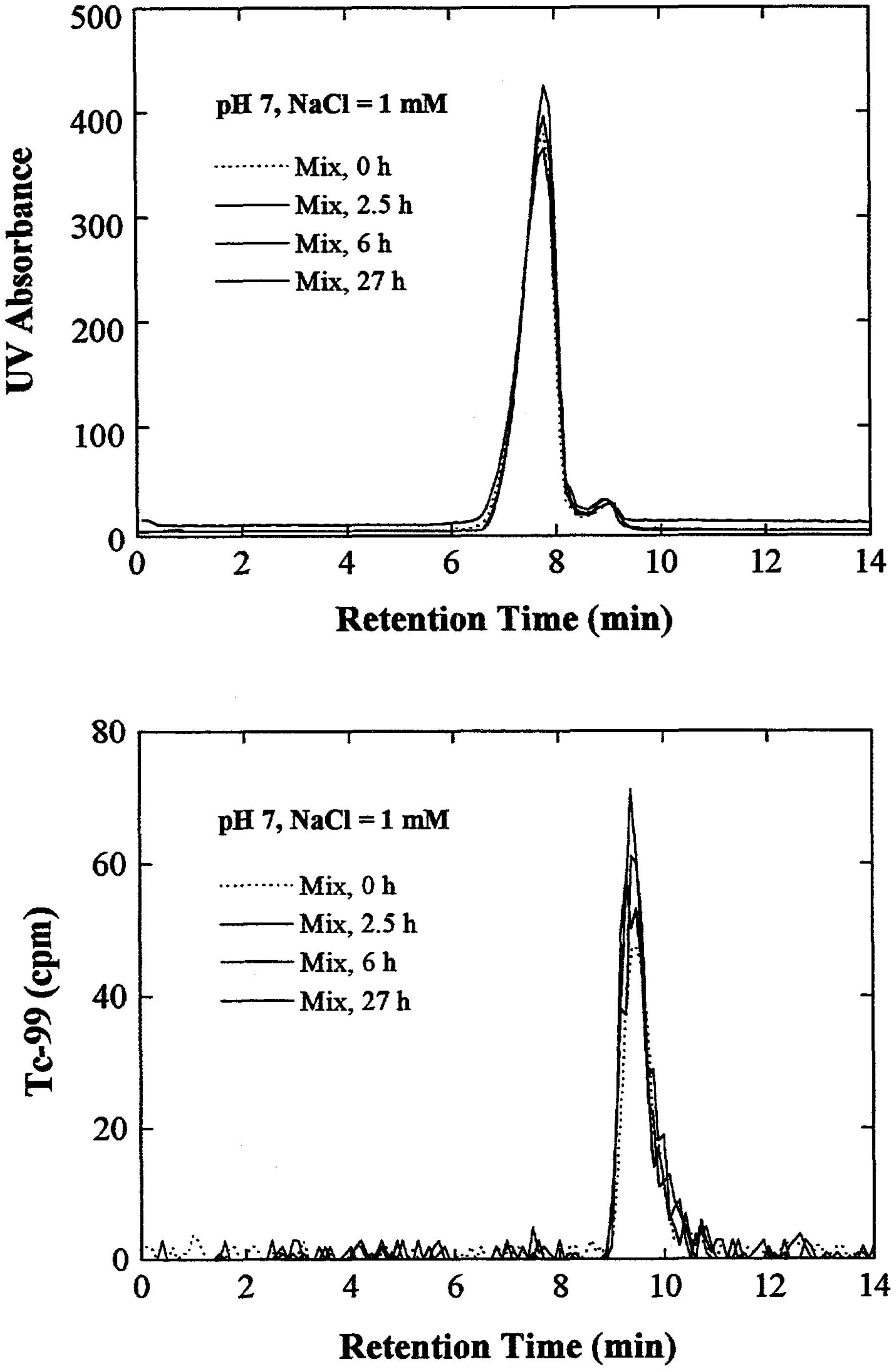


Fig. 1.4. Chromatographs of (a) NOM (by UV absorbance) and (b) Tc (by Radiomatic liquid scintillation counting) at different reaction times using a Polysep-GFC-P1000 column.

Additionally, the above experiments were evaluated at pH 5 and 4 (Figs. 1.5 and 1.6) using the Sephadex LH-20 column while maintaining the experimental conditions of the previous column tests. At pH 5, the results (Fig. 1.5) were essentially identical to that observed in Fig. 1.2.

Under Reducing Conditions

Previous studies (Colombo et al., 1990; Hashimoto et al., 1993) suggest some organic ligands such as EDTA and α-hydroxy-carboxyls (Colombo et al., 1990) form Tc complexes under reducing conditions. This is because the reduced TcO_2 has a higher tendency to form complexes with other ligands. In this study, the complexation reactions between NOM and Tc were evaluated under reducing conditions by adding appropriate amounts of Na_2S.

First, we evaluated the retention time and elution peaks of Tc and NOM independently with time in a Na_2S solution (Fig. 1.7) because of the concerns that the physical-chemical properties of NOM may change with time under reducing conditions. The concentration of Na_2S varied from 0.04 to 0.12 mM in order to maintain the solution Eh below -200 MVP. The experiment was conducted using the PDX Gel-25 column. Results indicate elution peaks of Tc or NOM under reducing conditions are about the same as those under atmospheric conditions. The peak retention time and intensity did not change significantly over time up to ~11 days. This experiment indicates the separation and identification of Tc and NOM on this column was valid even under reducing conditions and over an extended period of time. The experiment was then conducted with a Tc and NOM mixture in 0.1 mM Na_2S. Results (Fig. 1.8), however, gave no indication of Tc and NOM complexation within the experimental error. With a lower Na_2S concentration (0.01 mM) and Eh ~ −150 mV, similar results were obtained (Fig. 1.9). Complexation of Tc with natural organics (concentrated from a surface water) can not be confirmed from these studies.

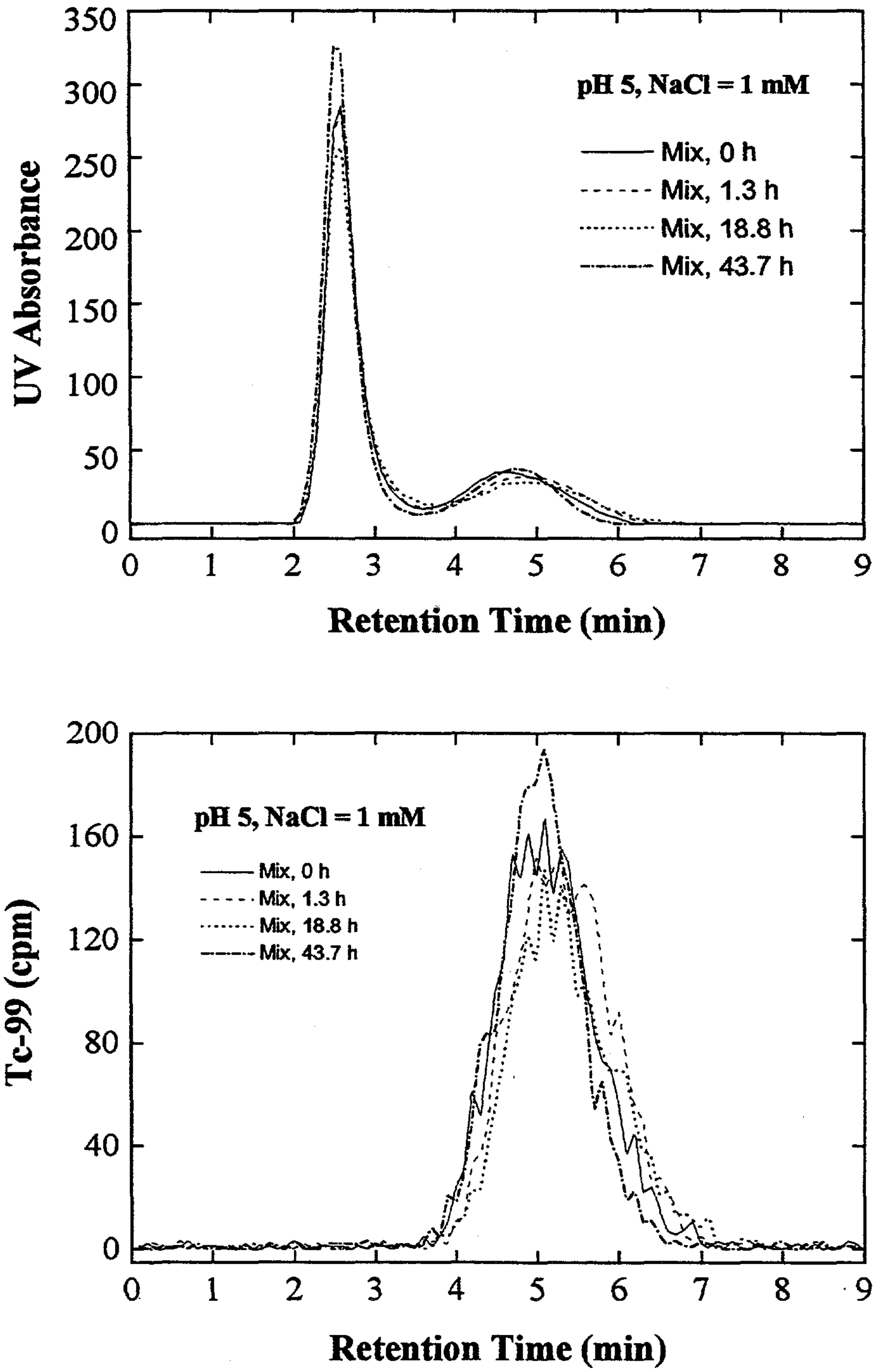


Fig. 1.5. Chromatographs of (a) NOM (by UV absorbance) and (b) Tc (by Radiomatic liquid scintillation counting) at different reaction times using a PDX Gel-25 column.

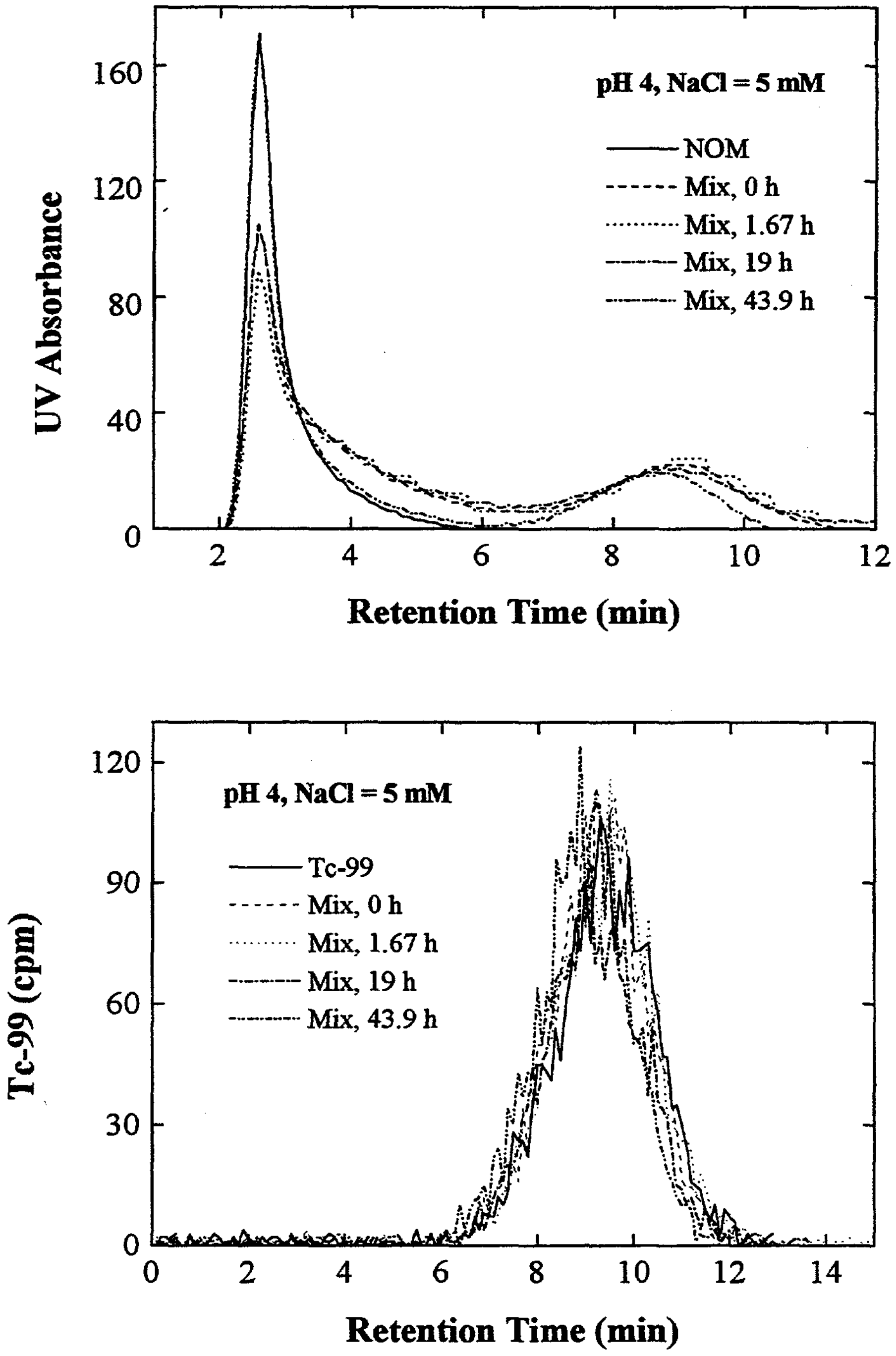


Fig. 1.6. Chromatographs of (a) NOM (by UV absorbance) and (b) Tc (by Radiomatic liquid scintillation counting) at different reaction times using a PDX Gel-25 column.

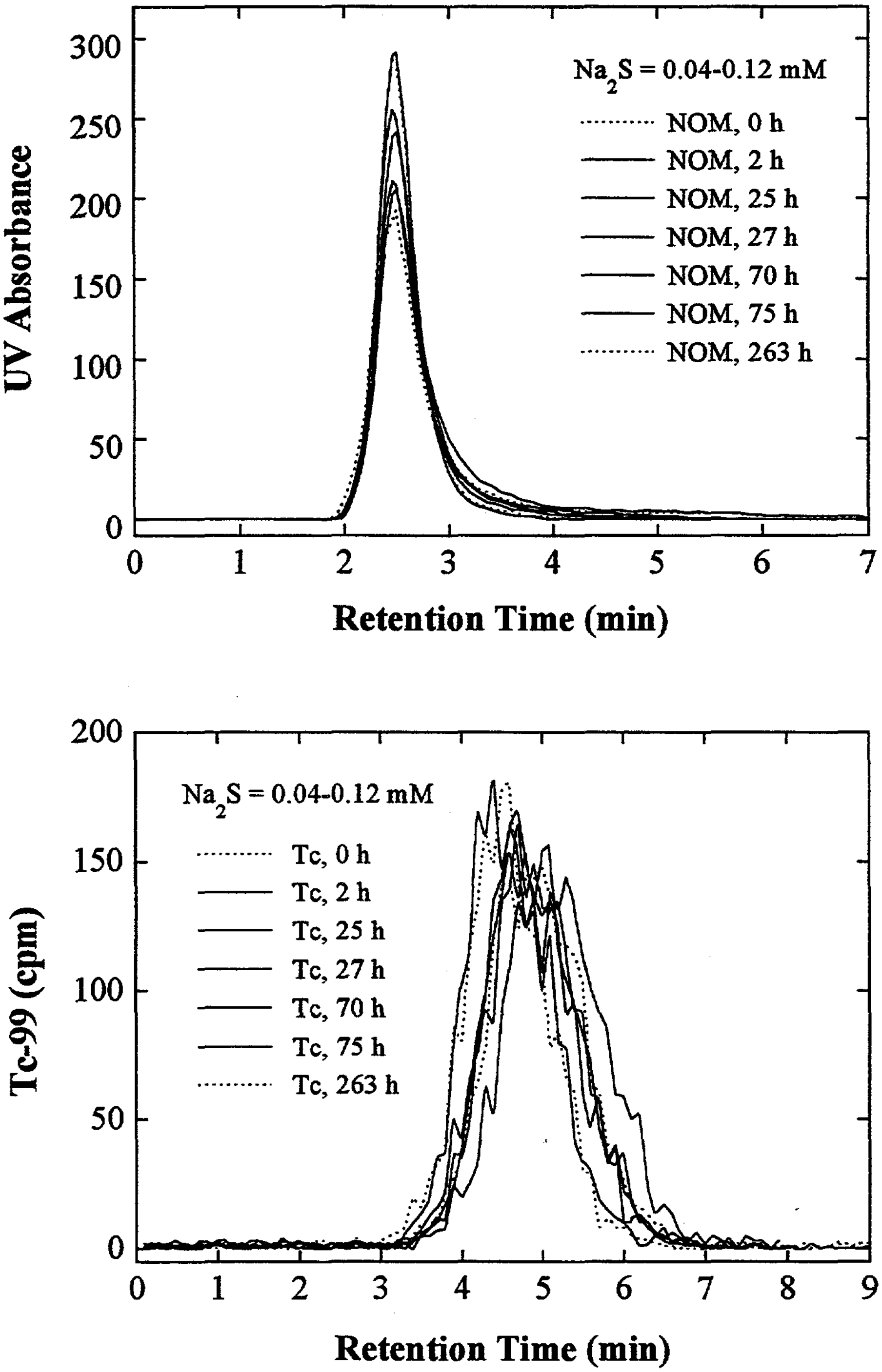


Fig. 1.7. Chromatographs of (a) NOM (by UV absorbance) and (b) Tc (by Radiomatic liquid scintillation counting) under a reducing conditions using a PDX Gel-25 column.

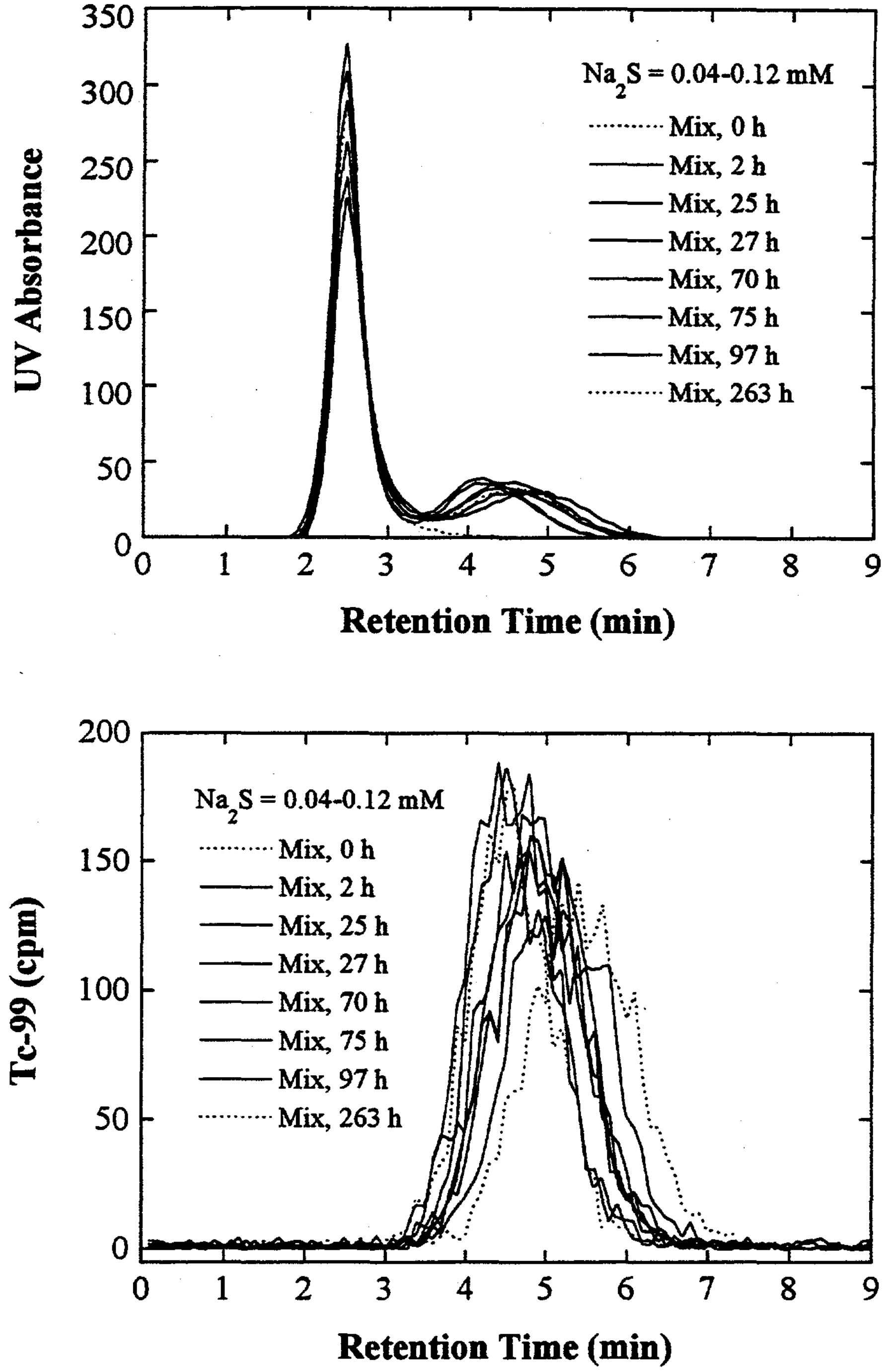


Fig. 1.8. Chromatographs of (a) NOM (by UV absorbance) and (b) Tc (by Radiomatic liquid scintillation counting) under a reducing conditions and at different reaction times using a PDX Gel-25 column.

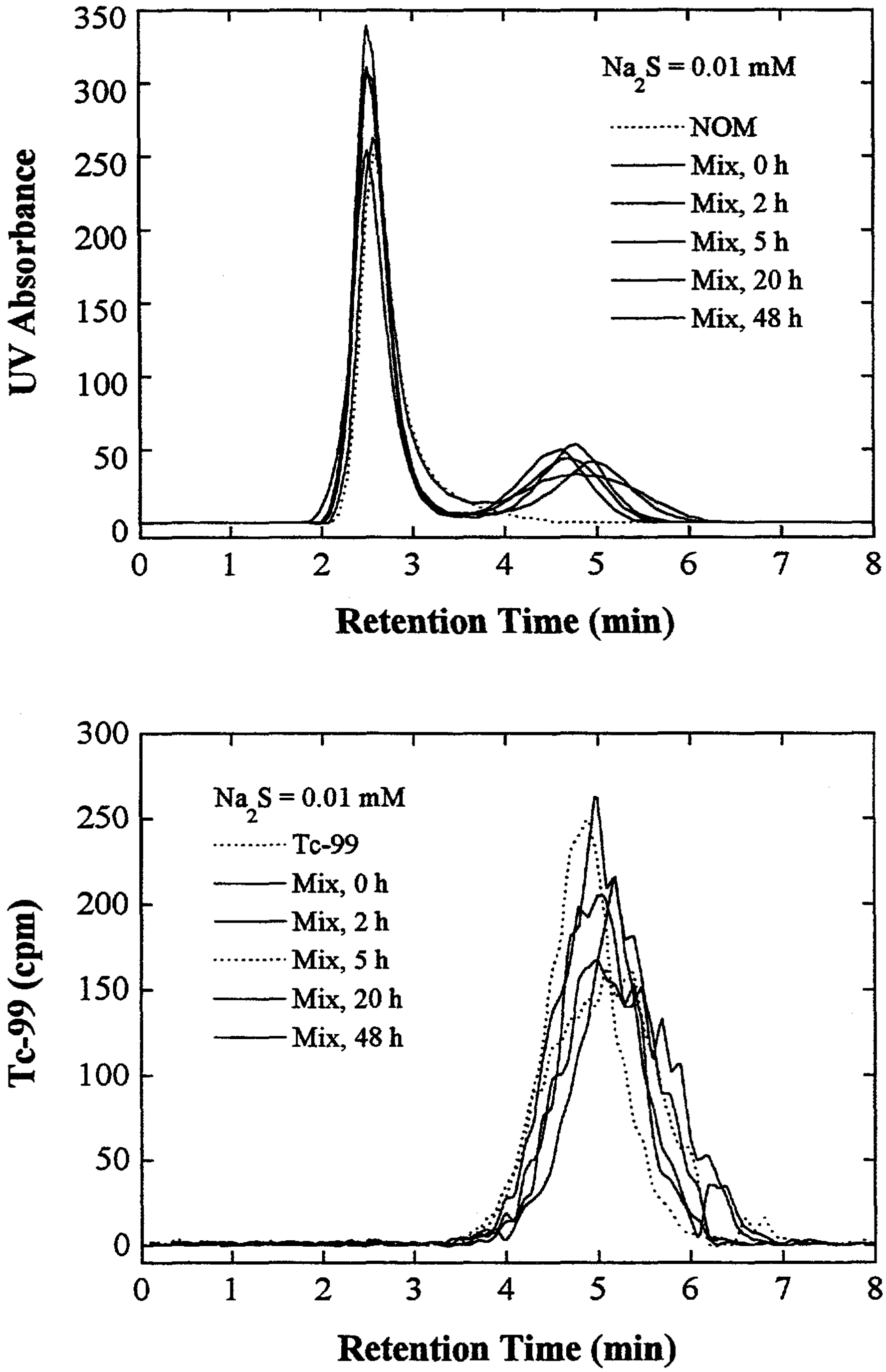


Fig. 1.9. Chromatographs of (a) NOM (by UV absorbance) and (b) Tc (by Radiomatic liquid scintillation counting) under a reducing conditions and at different reaction times using a PDX Gel-25 column.

1.3.3 Tc complexation Studies with Groundwater Organics from PGDP

Similar experiments to those in Section 1.3.2 were performed using the actual MW 66 groundwater from PGDP. The groundwater samples were spiked with reference TcO_4^- so that Tc activity was high enough to be detected. Initial results (Fig. 1.10) indicate Tc (in MW 66 groundwater) and the groundwater organics were eluted at about the same time; the retention time for Tc is ~3.6 min (Fig. 1.10), which is significantly longer than the Tc reference in 1 mM NaCl (Fig. 1.10, dotted line). These observations would appear to suggest that Tc may be complexed with the groundwater organics. However, further experiments using spiked Tc reference in 50 mM NaCl (Fig. 1.10) revealed an increased salt concentration resulted in a significant shift of the Tc elution peak to ~3.3 min. Therefore, the longer retention time of Tc in MW 66 groundwater versus the Tc reference is not attributed to its complexation with the groundwater organics, but is likely due to the high salt concentration in the concentrated MW 66 groundwater. These results again suggest that Tc complexation with PGDP groundwater organics is negligible.

1.3.4 Membrane Ultrafiltration Studies

Membrane filtration techniques were also applied to study Tc complexation with groundwater organics at PGDP. It was assumed that most groundwater organics have a nominal molecular weight above 500 dalton so free TcO_4^- (if uncomplexed with NOM), in solution, will pass through the membrane whereas the organic macromolecules will be retained. Two filtration apparatus (Amicon 10 mL and 50 mL) were used with an ultrafiltration membrane having a nominal molecular weight cut-off of 500 dalton. Samples of MW66 water (untreated), the concentrated MW 66 water, a mixture of 0.5 mg C/L GT-NOM and 6 pCi/mL Tc, and a solution of 6 pCi Tc/mL were analyzed for Tc activity before and after filtration. All Eh/pH values were recorded using an AT Orison model 920A advanced IS/pH meter. The Tc stock solutions were prepared from a standard reference solution from Isotope Products Laboratories, CA.

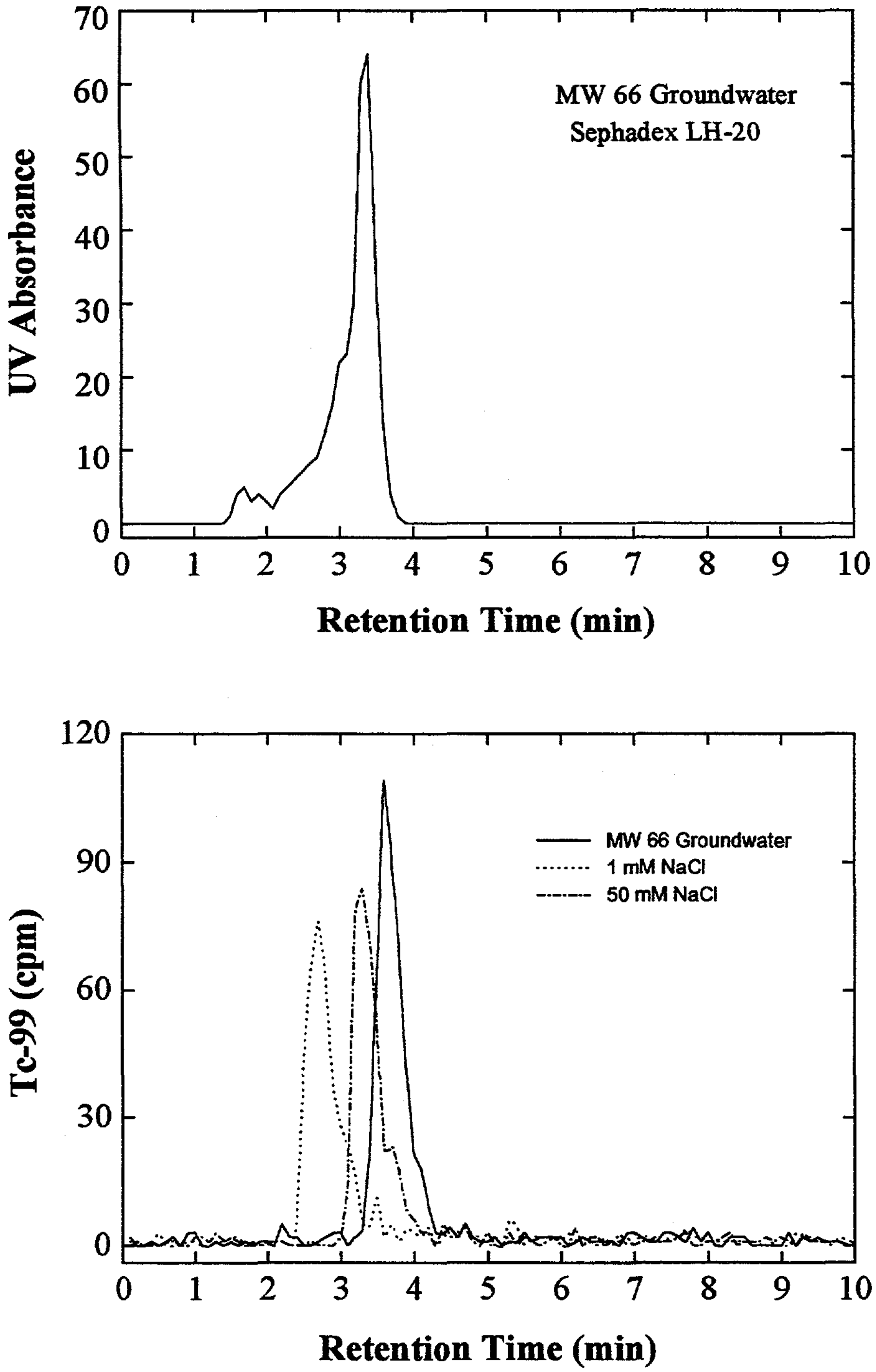


Fig. 1.10. Chromatographs of (a) MW 66 groundwater NOM (by UV absorbance) and (b) Tc (spiked in MW 66 groundwater and NaCl solutions) using a Sephadex LH-20 column.

Membrane filtration experiment results (Table 1.2) indicate, within experimental error, Tc does not appear to be complexed with groundwater organics from PGDP. The Tc concentration in solution did not change appreciably before and after filtration (Table 1.2).

Table 1.2. Tc activity in aqueous solution before and after filtration through an ultrafiltration membrane with a nominal molecular weight cut-off at 500 dalton.

Sample	Before Filtration (pCi/L)	After Filtration (pCi/L)
	10 mL Amicon Cell	
Tc Reference	5460	5680
MW-66 Groundwater	2800	3080
MW-66 Concentrated	7200	8120
Tc + GT-NOM	5980	4420
	50 mL Amicon Cell	
Tc Reference	7400	7390
MW-66 Groundwater	3410	3420
MW-66 Concentrated	8590	6350
Tc + GT-NOM	6630	6670

1.3.5 Effect of NOM on Tc precipitation and solubility under reducing conditions

The effect of NOM on the solubility of Tc under reducing conditions was studied by addition of various amounts of Na_2S and GT-NOM into a given Tc solution (Table 1.3). Two Tc concentration levels were studied (~33 and ~610 pCi/mL). Without GT-NOM addition, Tc concentration in solution decreased as Na_2S concentration increased from 0 to 0.1 M (Table 1.3), which is in agreement with our previous observations. With the addition of 1 mg C/L GT-NOM, Tc concentration in solution also decreased but to a lesser extent than without GT-NOM addition. When addition of GT-NOM increased to 10 mg C/L, the Tc concentration in solution also increased, especially with high Na_2S concentrations. These results indicate the presence of NOM reduced or prevented Tc from precipitation as Tc-sulfides or as TcO_2 under reducing conditions. The observations are also in agreement with Wildung et al. (1986) who found that low molecular weight organic matter (or ligands) to form complexes with Tc, especially with reduced forms of Tc. The Tc complexes increased the solubility of Tc. Similarly, Pilkington (1990) found pH had little effect on the measured solubility of TcO_2 over the range of 1 to 12.5. On the other hand, the presence of small amounts of organic compounds increased the measured solubility of Tc by about a factor of 10.

Because data in Figs. 1.2 - 1.10 suggest Tc may not be complexed with NOM or groundwater organic compounds, the exact mechanisms why GT-NOM decreases Tc precipitation is unclear at present. It is possible, however, that the fraction of Tc complexed with NOM was small so our technique to detect Tc–NOM complexes was not sensitive enough. As discussed previously, the radiomatic detector requires to use a relatively high Tc activity in order to obtain a sufficiently high signal to noise ratio. This could have limited our ability to identify very small fractions of Tc complexed with NOM. However, even these results suggest the Tc-NOM complexation in aqueous media may not be significant.

Table 1.3. Effect of organic matter and Na_2S on the solubility of Tc

	Low Tc (pCi/mL)			High Tc (pCi/mL)		
Na_2S (M)	NOM-0	NOM-1	NOM-10	NOM-0	NOM-1	NOM-10
0	33.4±0.1	33.6±0.9	33.1±0.8	615±3	614±1	607±2
0.001	33.0±0.2	32.7±0.4	32.2±0.2	612±2	616±7	600±2
0.01	32.2±0.4	31.9±0.5	30.8±0.9	599±9	596±2	598±5
0.1	21.0±0.7	29.6±0.2	29.9±0.1	450±17	510±34	565±6

1.3.6 Tc Complexation Studies with Salicylic and Phthalic Acids

Because NOM and groundwater organics are such complex mixtures of natural organic compounds, the exact structure and functional groups of these organic materials are still unclear. This has been a serious drawback in studies of NOM and its roles in contaminant binding and transport (Gu et al., 1994, 1995). To over come such a difficulty, model compounds with known molecular structure and functional groups are often used in these studies (Gu et al., 1995). In this study, two model organic compounds, namely, salicylic and phthalic acids were used. However, different preparative columns were used for the separation of Tc from these two organic compounds. Phthalate and Tc were found to be separated best on the PDX Gel-25 column whereas salicylate and Tc were best separated on the Sephadex LH-20 column. Retention time of Tc on the PDX Gel-25 columns and Sephadex LH-20 were ~4.8 and ~2.2 min, respectively, in agreement with the previous experiment (Figs. 1.2 - 1.5).

Chromatographs of phthalate, Tc, and Tc-phthalate mixture were plotted in Fig. 1.11. The retention time of phthalate (measured by UV absorption) on this column was ~2.8 min. A small UV absorption peak was also observed at ~4.8 min, which was again due to TcO_4^- in the solution. By examining the Tc activity in the effluent, only a single Tc peak was observed, which corresponded to the small UV absorption peak in Fig. 1.11a. Note that a time delay ~30 s between the UV detector and the Radiomatic detector was not corrected in this graph. Therefore, the Tc and phthalate were well separated by the PDX Gel-25 column; no significant complexation reactions were confirmed from this experiment.

On the other hand, the retention times of salicylate (without Tc) and Tc (without salicylate)on Sephadex LH-20 were about ~2.2 and 3.7 min respectively (Fig. 1.12). When a mixture of Tc-salicylate solution was injected, the Tc activity peak shifted to ~3.8 min whereas salicylate (or complexed with Tc) elution peaks remained unchanged (~3.6 min). These observations suggest Tc is likely complexed with salicylate, which resulted in a longer retention time of Tc (complexed with salicylate). More importantly, the Tc activity peak (of the mixture) coincided with the UV absorption peak at ~3.6 min. An increased UV peak height (Fig. 1.12b)

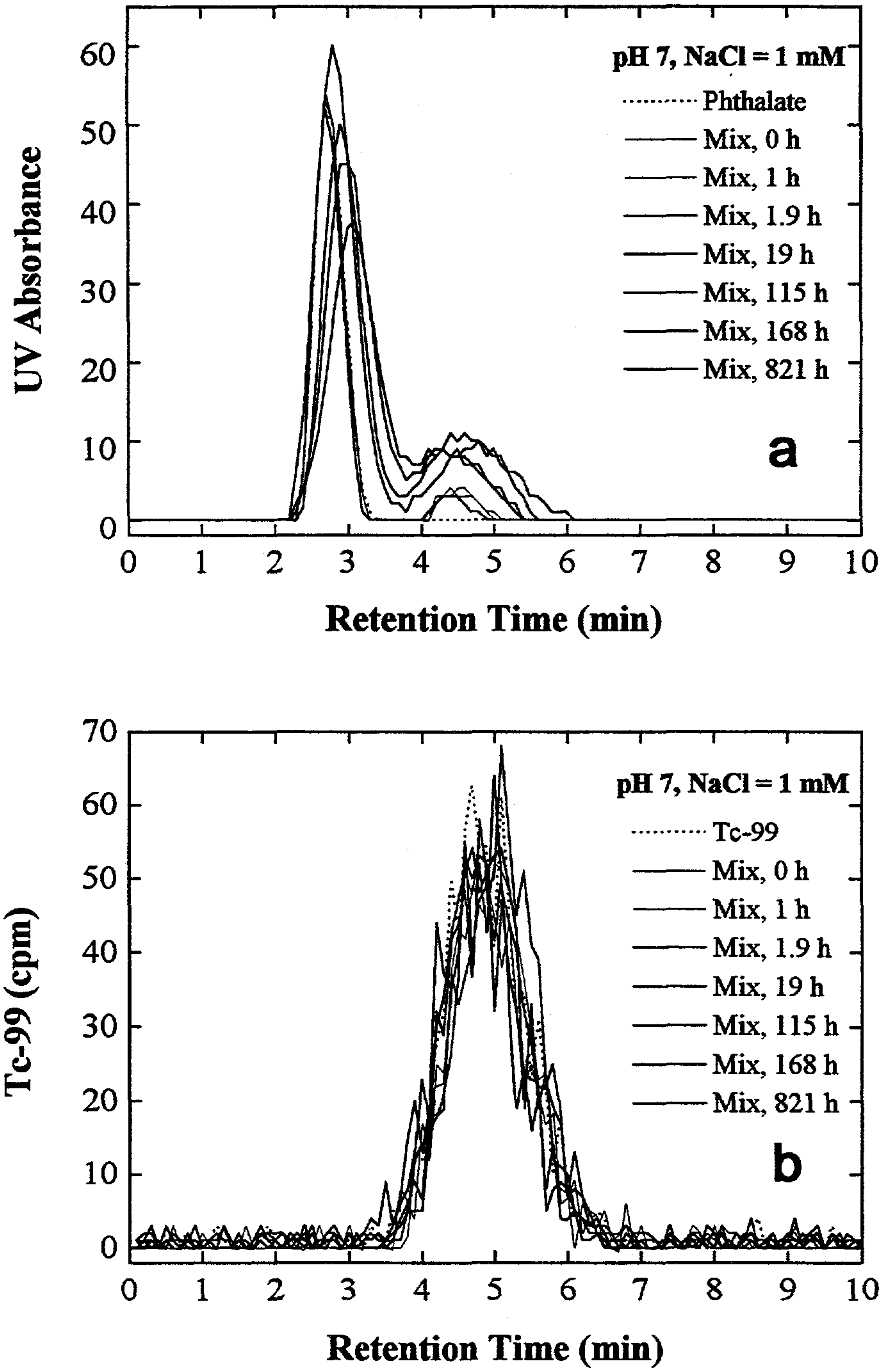


Fig. 1.11. Chromatographs of (a) phthalate (by UV absorbance) and (b) Tc (by Radiomatic liquid scintillation counting) at different reaction times using a PDX Gel-25 column.

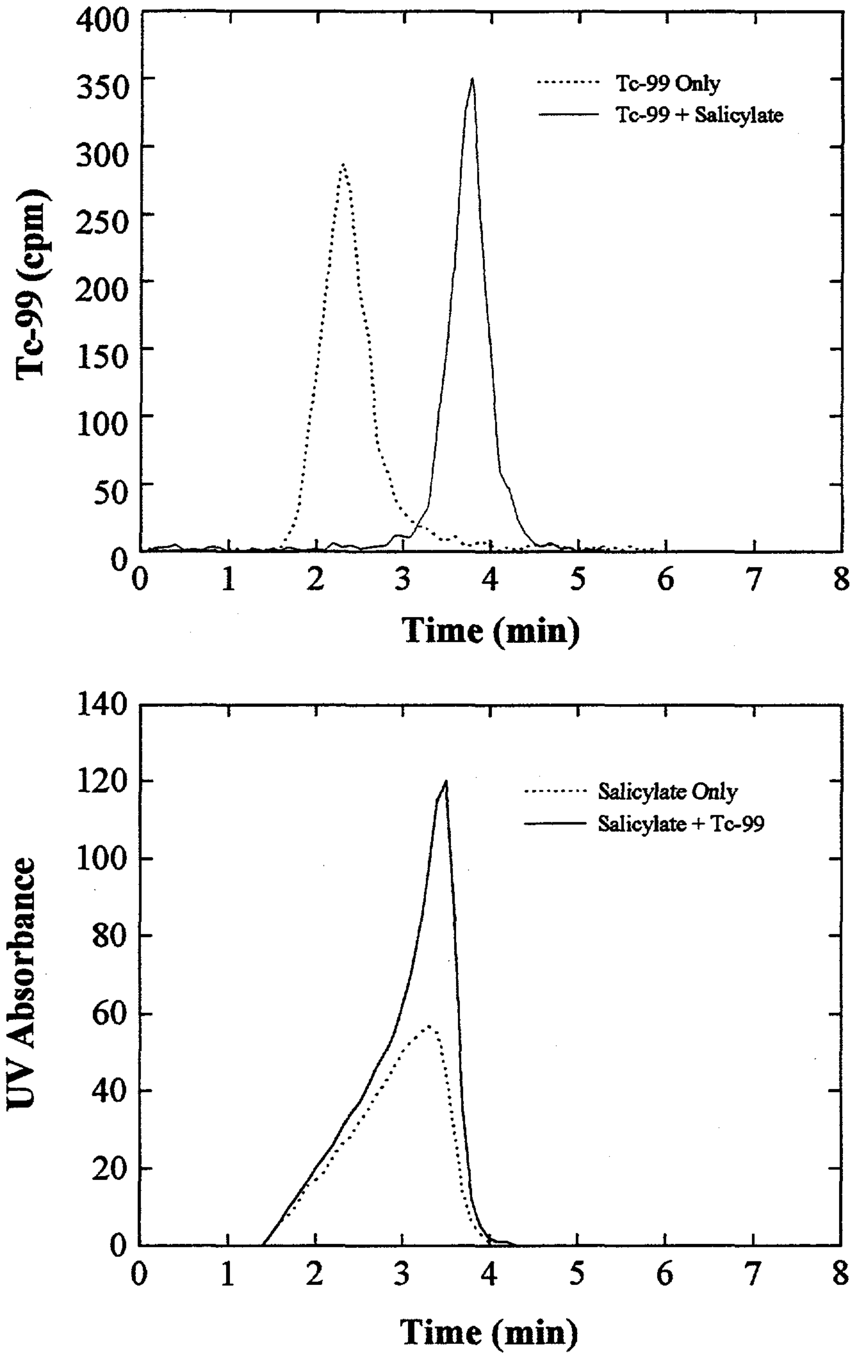


Fig. 1.12. Chromatographs of (a) salicylate (by UV absorbance) and (b) Tc (by Radiomatic liquid scintillation counting) at different reaction times using a Sephadex LH-20 column.

for the mixture was attributed to both salicylate and TcO_4^- which absorb UV and the relatively high Tc concentration.

2. COMPLEXATION STUDIES OF TRICHLOROETHYLENE WITH Tc

A good correlation between trichloroethylene (TCE) and Tc concentration is found at many monitoring wells at the PGDP site (Clausen and Early 1992). There is a concern Tc may be complexed with TCE and therefore co-transported with TCE in groundwater. Therefore, the main objective of this part of the study is to identify if Tc forms complexes with TCE under both oxidizing and reducing conditions.

2.1 MATERIALS AND METHODS

2.1.1 Liquid–Liquid Extraction

TcO_4^- is very soluble in water. However, TCE is insoluble in water but soluble in organic solvents such as hexane. Previous studies have shown that >99% of TCE can be extracted from the aqueous solution by a single extraction. If Tc and TCE are complexed, one would expect an increased proportion of Tc (complexed with TCE) being extracted by hexane because TCE–Tc complexes (if any) should have a higher affinity for organic solvents in comparison with TcO_4^-. The experiment was performed as follows. First, a mixture of TCE (200 mg/L) and TcO_4^- (~23 nCi/L) was prepared in aqueous solution. The reaction was monitored over a 72-h period. A 0.5 mL sample was withdrawn periodically at 2, 4.5, 7, and 72 h intervals and mixed immediately with 3 mL hexane. Samples were then shaken for 10 min, and 2 mL of the hexane extract was mixed with 13 mL scintillation cocktail for the determination of Tc activity in hexane. Second, the above procedures were repeated under (1) reducing conditions by addition of 10 mg/L Na_2S, and (2) using a higher concentration of TCE at 400 mg/L. The Eh of the samples under reducing conditions ranged from -170 - 300 mV (or an average of ~ -250 mV). A reference TcO_4^- sample (without TCE) was also prepared and analyzed using exactly the same procedure as described above.

2.1.2 Chromatographic Separation and Identification

Possible complexation between TCE and Tc was studied by chromatographic separation and identification using a Prodigy ODS column (Phenomenex, CA). The experiment was performed under both atmospheric and reducing conditions. Aqueous solutions of TCE (20 mg/L), TcO_4^- (0.2 mCi/L), or their mixtures were prepared. At a given time interval, 100 μL solution was injected into the column for analysis. The mobile phase was a 50% acetonitrile aqueous solution with 1 mM NaCl, and the flow rate was 1 mL/min. TCE was monitored with a UV/VIS detector at a wavelength of 210 nm whereas Tc was determined by a Radiomatic flow-through detector, as described previously. Similar procedures were followed under reducing conditions using 0.5 mM Na_2S. These experiments were limited to 3 days because the TCE concentration decreased rapidly with time due to volatilization of the TCE.

2.2 RESULTS AND DISCUSSION

Results of hexane extraction of Tc-TCE complexes are shown in Table 2.1 (at 200 mg/L TCE) and Table 2.2 (at 400 mg/L TCE) under both atmospheric and reducing conditions. The initial Tc activity in aqueous solution was ~23,500 pCi/mL. As expected, hexane extraction of TcO_4^- from aqueous solution (without TCE) was very low and ranged from ~0.03% to 0.1%. Mixing a TCE aqueous solution with TcO_4^- solution did not result in a significant increase in Tc activity in the hexane extract, which ranged from ~0.03% to 0.12% under oxidizing conditions. Similarly, under reducing conditions, only an insignificant amount of Tc was extracted by hexane regardless of the TCE concentration. These results suggest Tc is not complexed with TCE.

Chromatographic separation and identification of TcO_4^- and TCE mixture was then tested by using a variety of preparative and analytical HPLC columns. By trial and error, the most satisfactory separation and identification of Tc and TCE mixture were accomplished by using a Prodigy analytical column obtained from Phenomenex, CA (Figs. 2.1-2.3). Fig. 2.1 shows a retention time of ~2.2 min for TcO_4^-. The Tc radioactivity and retention time did not change with time (over a 72-h period) as expected. On the other hand, TCE concentration decreased

Table 2.1. Hexane extraction of TCE or TCE complexed with Tc from the aqueous solution containing 23,500 pCi/mL Tc and 200 mg/L TCE. Data are the average of two duplicate measurements.

	Tc Extracted (pCi/mL)			
Sample	2 h	4.5 h	7 h	72 h
	Under oxidizing conditions			
TCE + Tc	28.8	18	20	18.2
Tc Reference	15.6	13.8	12.2	9.6
	Under reducing conditions			
TCE + Tc + Na_2S	9.6	8.6	8.4	7.8
Tc + Na_2S	13.6	10.2	13.8	11.6

Table 2.2. Hexane extraction of TCE or TCE complexed with Tc from the aqueous solution containing 22,548 pCi/mL Tc and 400 mg/L TCE. Data are the average of two duplicate measurements.

	Tc Extracted (pCi/mL)			
Sample	2 h	5 h	7 h	24 h
	Under oxidizing conditions			
TCE + Tc	7.9	6.2	8.7	24.4
Tc Reference	7.7	6.9	22.3	18.3
	Under reducing conditions			
TCE + Tc + Na_2S	9.1	6.3	9	19.1
Tc + Na_2S	9.7	5.6	6.1	16.7

substantially with storage time although its retention time remains unchanged (~9.7 min, Fig. 2.2). The decreased TCE concentration is primarily attributed to its volatilization loss during storage. A previous study (West et al., 1994) revealed that TCE loss to head space could occur rapidly. In addition, TCE also leaked through the septum of the standard 40 mL or 20 mL vials. Therefore, a periodic sampling of Tc inevitably lead to a loss of TCE to the headspace, which accounted for a decreased TCE peak height with time (Fig. 2.2).

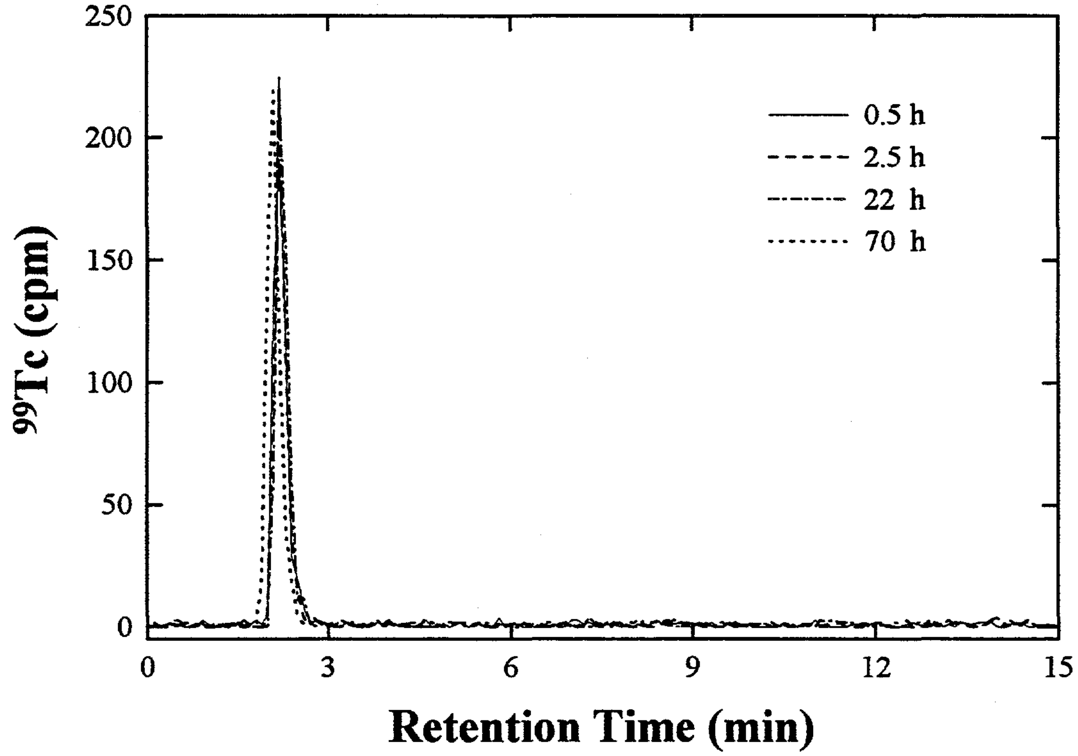


Fig. 2.1. Chromatographs of Tc (by Radiomatic liquid scintillation counting) at different time intervals using a Prodigy analytical column.

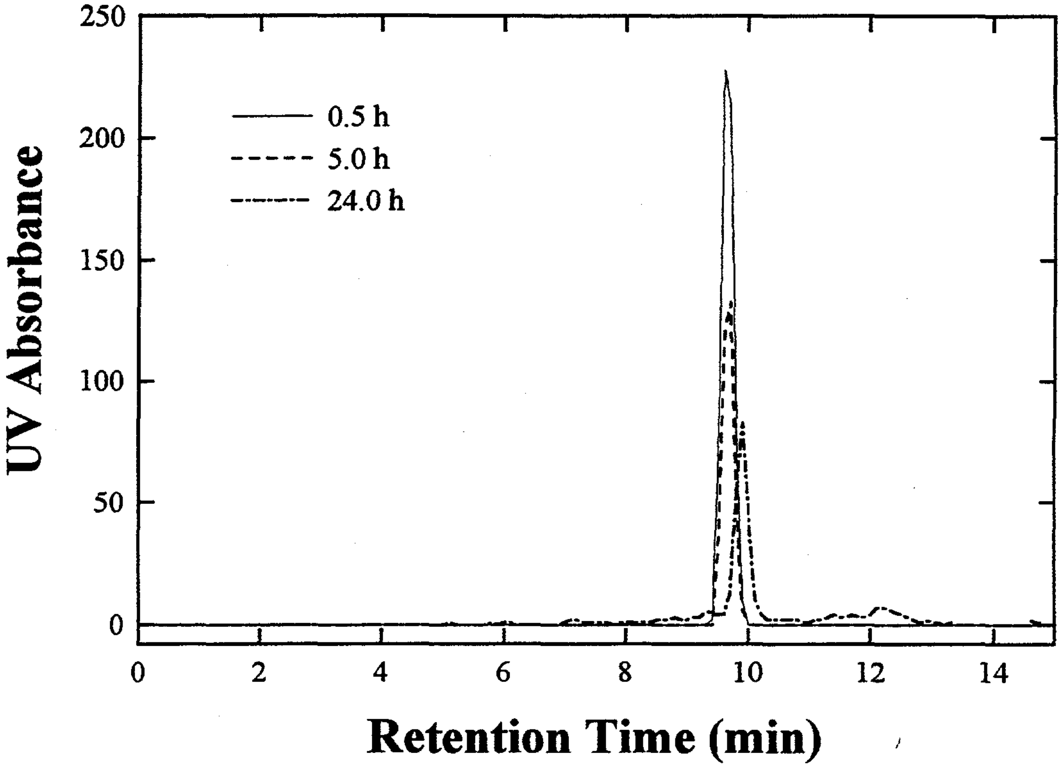


Fig. 2.2. Chromatographs of trichloroethylene (by UV absorbance) at different time intervals using a Prodigy analytical column.

By mixing TcO_4^- with TCE in aqueous solution (simulated groundwater), and then injecting an aliquot of Tc-TCE mixture into the HPLC column, we observed that Tc and TCE were eluted out of the column independently (Fig. 2.3). Tc and TCE retention times were ~2.2 and 9.7 min, respectively, and were the same as those shown in Figs. 2.1 and 2.2. There was no indication of the Tc complexation with TCE. This is because, if Tc was complexed with TCE, we would expect a relatively retarded TCE peak (or UV absorbance peak) and a corresponding Tc peak with a same retention time in Fig. 2.3. Note that a small UV-absorbance peak at ~2 min in Fig. 2.3b was sue to the presence of TcO_4^-, as has been indicated previously. Similarly, the above experiments were repeated under reducing conditions by addition of 0.5 mM Na_2S (Figs.

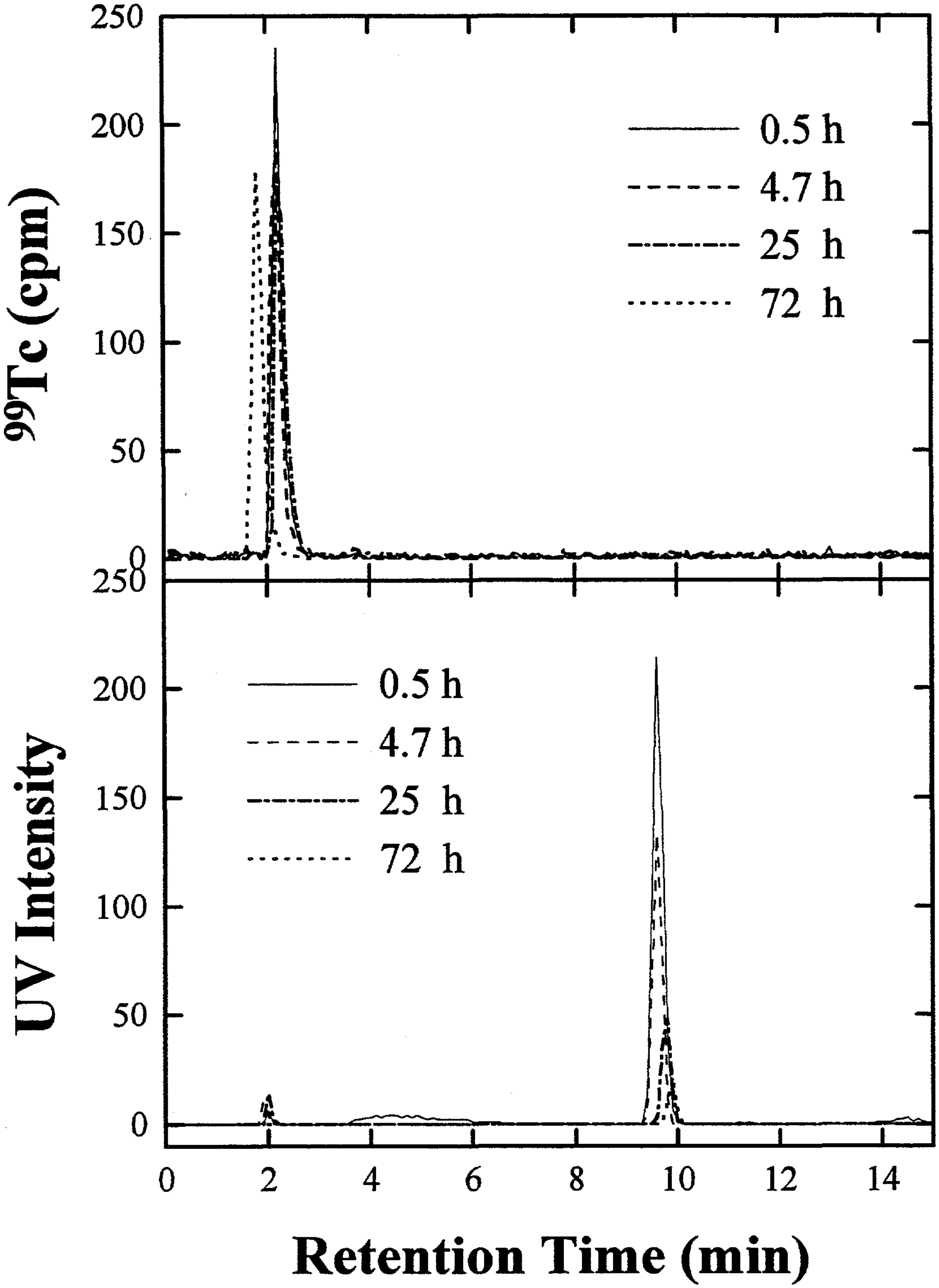


Fig. 2.3. Chromatographs of trichloroethylene (by UV absorbance) and Tc (by Radiomatic liquid scintillation counting) at different reaction times using a Prodigy analytical column.

2.4-2.6). Again, all results suggest Tc and TCE was not complexed under the given experimental conditions. The UV-absorbance peaks at ~1.3 and 2.5 min were due to the presence of S^{2-} and possibly $S_2O_3^{2-}$ ions. Therefore, these observations are in agreement with the observations from the liquid-liquid extraction experiments (Tables 2.1 and 2.2). These results confirm that TCE and Tc were not complexed under the experimental conditions. The good correlation between Tc and TCE concentrations observed in PGDP groundwater is probably due to the fact that TcO_4^- and TCE were both present in the waste stream and then transported as a dissolved phase with both TcO_4^- and TCE poorly adsorbed by soil minerals.

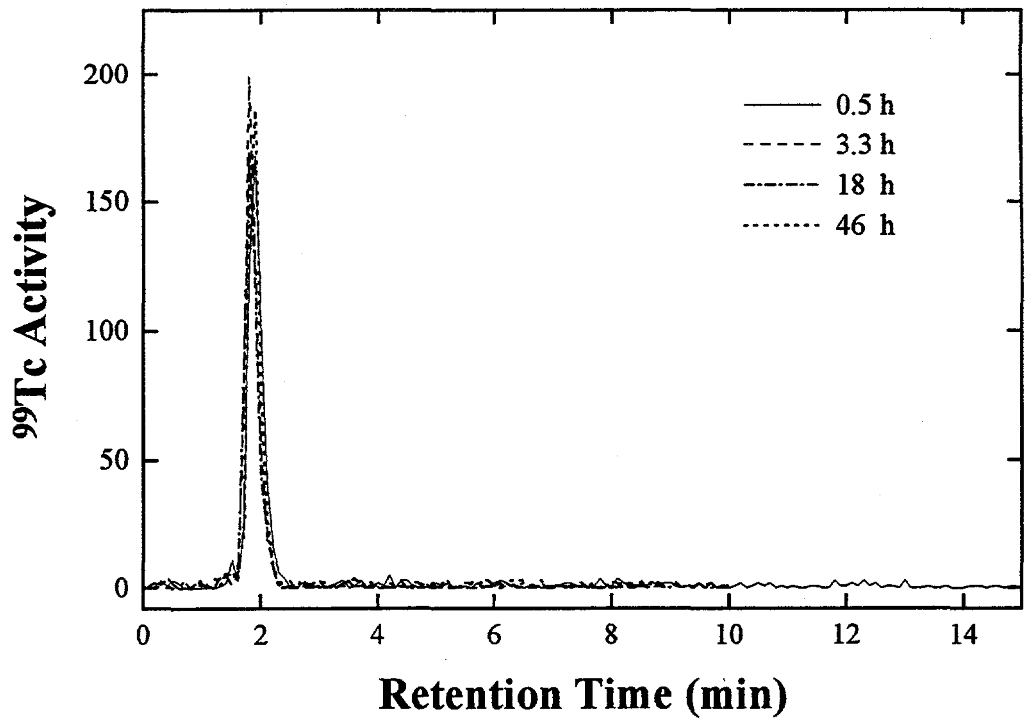


Fig. 2.4. Chromatographs of Tc (by Radiomatic liquid scintillation counting) under reducing conditions and at different time intervals using a Prodigy analytical column.

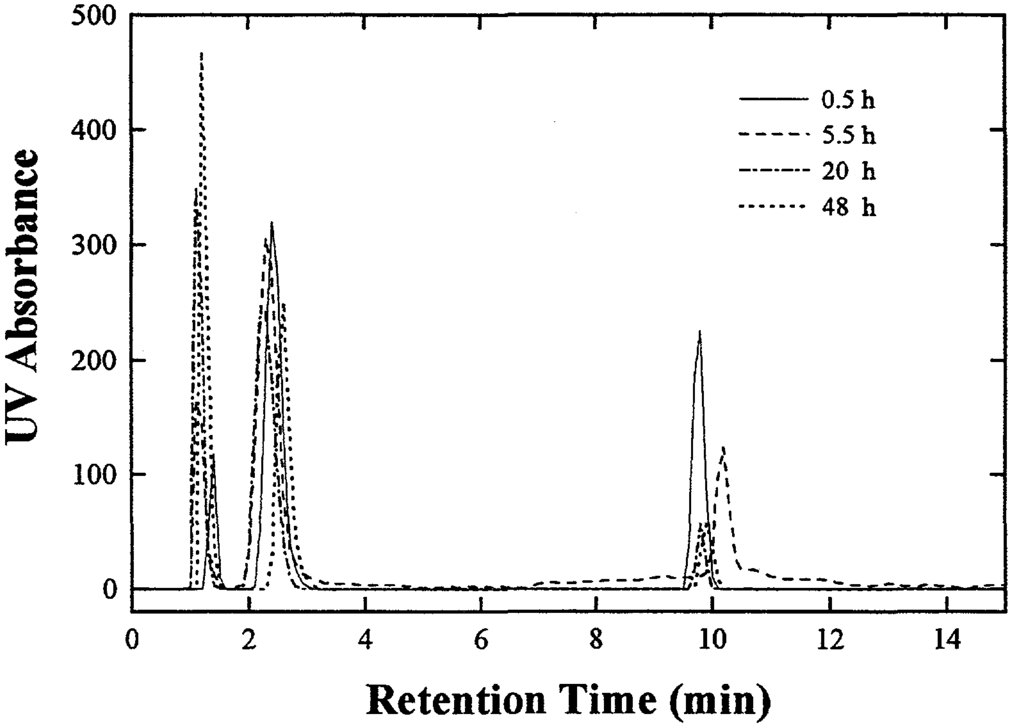


Fig. 2.5. Chromatographs of trichloroethylene (by UV absorbance) under reducing conditions and at different time intervals using a Prodigy analytical column.

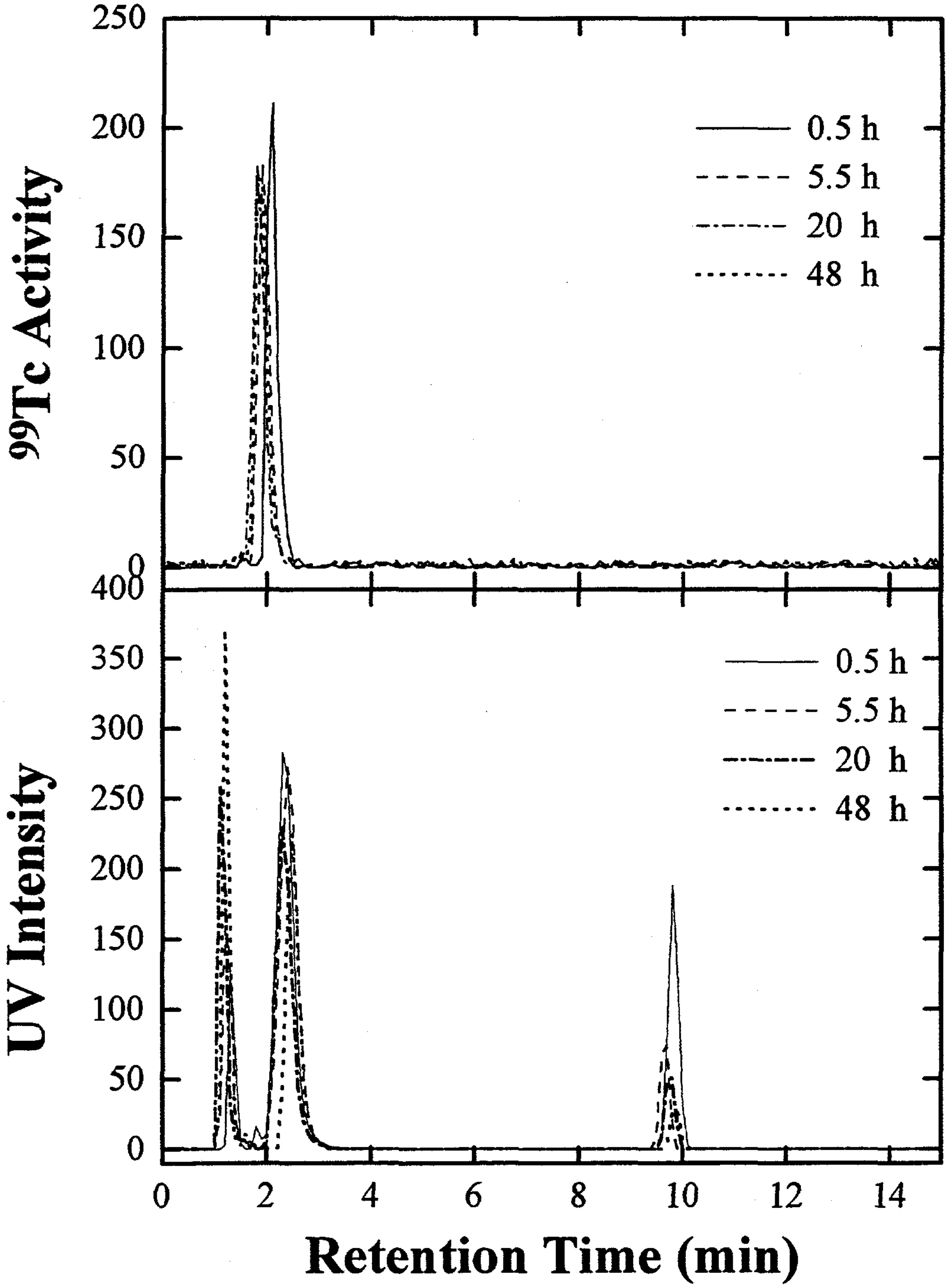


Fig. 2.6. Chromatographs of trichloroethylene (by UV absorbance) and Tc (by Radiomatic liquid scintillation counting) under reducing conditions and at different reaction times using a Prodigy analytical column

3. Tc ADSORPTION ON SOILS FROM PADUCAH, KENTUCKY

3.1 MATERIALS AND METHODS

3.1.1 Soil Samples and Preparation

Soil samples were obtained during the installation of the monitoring wells MW 261 and MW 262 at the PGDP site. Both monitoring wells are located within a security fence in the north-central area of the plant, approximately 2,000 ft southeast of MW 66. The soil samples collected represent each of the five hydrogeologic units (HU) present at the PGDP site (Clausen et al., 1992). Sample SPT-1 is a representative of HU-1 and consists of a silty clay and was collected at a depth of 8 to 10 ft. Typically, HU-1 extends from the ground surface to a depth of 20 ft whereas HU-2 section extends from 20 to 30 ft. Samples SS-1, 2B, and 3B are representative of HU-3 and were collected at a depth of 40 to 45 ft. This unit consists of a sandy clay. This unit typically extends from 30 to 50 ft below the ground surface. Sample SPT-8 represents HU-4 and is a gravelly sand unit. Typically, HU-4 ranges from a depth of 50 to 60 ft. The final sample, SPT-12, was collected at a depth of 92 to 94 ft and represents HU-5 or the regional gravel aquifer at the PGDP site. This unit consists of a poorly sorted very coarse gravel. This unit typically ranges from a depth of 60 to 100 ft below the ground surface.

Soil preparation and washing procedures were as follows. Approximately 500 g soil from each of four bags from MW 261 (SPT-1,6,8,12) and three bags from MW 262 (SS-3B, SS-1, and SS-2B) were collected into glass beakers and dried over 24 hours at 105 °C. A soil grinder was used to collect soil which passed through 1 mm sieve into large mouth plastic containers.

3.1.2 Soil Batch Adsorption Experiments

Under Atmospheric Conditions

Two grams of soil were carefully weighed into a series of 10 mL centrifuge tubes. A total of 16 soil samples, 8 reference samples, and 2 blanks were prepared for each soil type. Calcium chloride was added to each sample to give a final concentration of 0.01 M $CaCl_2$. A Tc stock solution of known activity was then added. The initial Tc concentration ranged from 0 to ~25 pCi/mL. Samples were shaken for 2 h end-by-end, centrifuged for 30 min at 2000 rpm, and allowed to sit overnight for soil settlement. An aliquot of clear supernatant was then mixed with Ultima-Gold scintillation cocktail and Tc activity was measured as described previously.

Under Reducing Conditions

Two sets of experiment were performed under reducing conditions. In the first set of experiments, all reagent solutions, water, and soil were degassed within an anaerobic chamber (glove-box) using a mixture of H_2 (10%) and N_2 (90%). The absence of oxygen within the anaerobic chamber was maintained using a palladium catalyst with a continued flow of H_2/N_2. The Eh of soil samples was measured to be ~ –250 mV on average. The batch adsorption experiments were then carried out similarly as described above under atmospheric conditions.

The second set of experiments was performed under more drastic reducing conditions by addition of 5 mg/L Na_2S within the anaerobic chamber. A soil discoloring from yellow to gray was noticed after addition of Na_2S and equilibration for overnight. The adsorption procedures were the same as previous experiments.

3.2 RESULTS AND DISCUSSION

Fig. 3.1 shows the adsorption of TcO_4^- for five different soil types from PGDP under atmospheric conditions. Within the experimental error, adsorption of Tc on these soils is negligible. These results are not surprising since soil surfaces are negatively charged and TcO_4^- is an anion, so that TcO_4^- is repelled from the surface of the soil minerals. Similar results have been reported previously (Bondietti and Francis 1979; Schulte and Scoppa 1987; Sheppard et al., 1990; Wolfrum and Bunzl 1986). For example, Sheppard et al. (1990) reported, under aerobic conditions, Tc was not significantly retained by seven types of soils, and was only slightly retained by the organic soils.

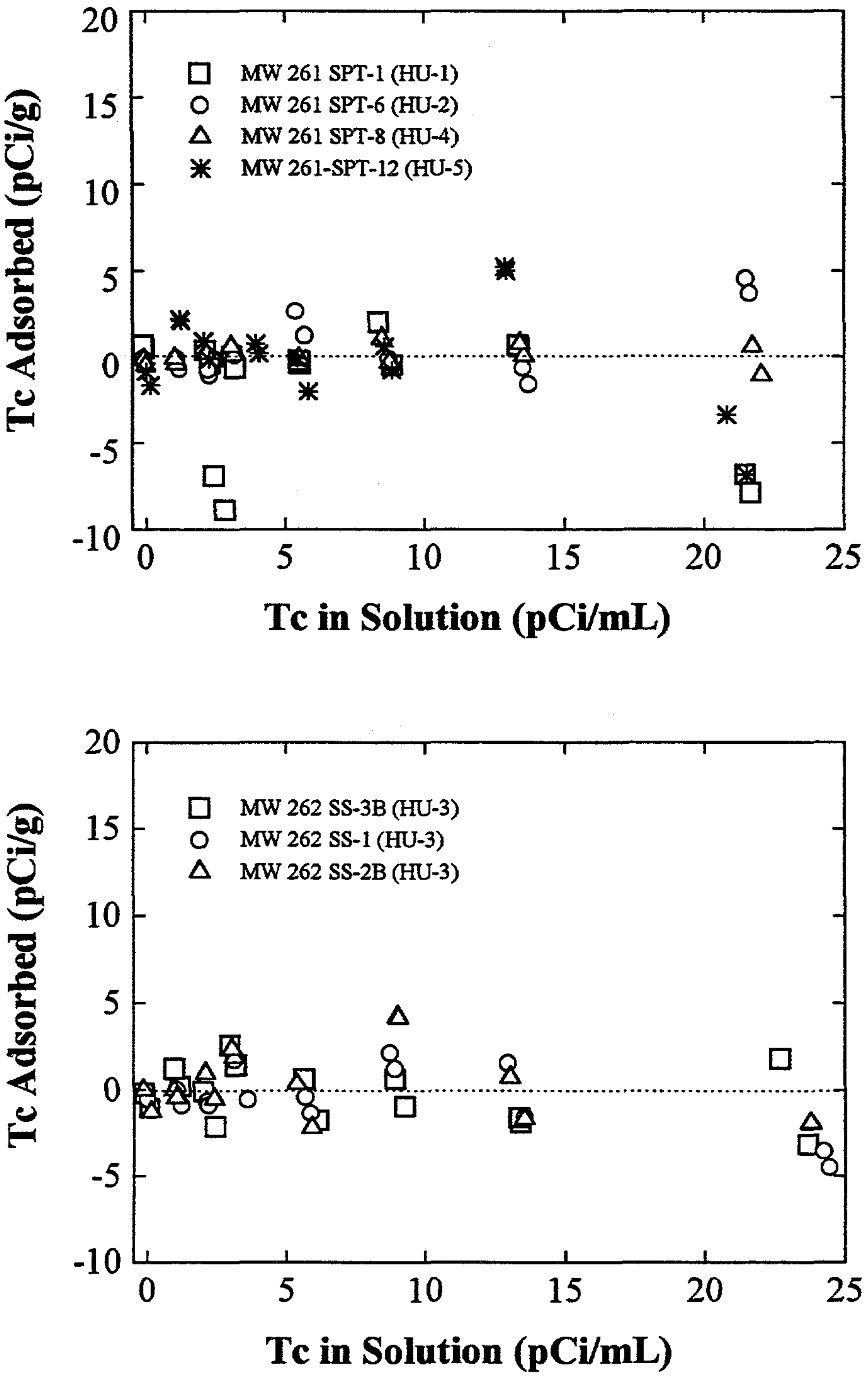


Fig. 3.1. Adsorption of Tc by soils from Paducah, Kentucky, under atmospheric conditions.

When the adsorption experiment was performed under H_2/N_2 atmosphere (Fig. 3.2), we observed that Tc adsorption was only slightly increased for certain soils but, in general, Tc was not significantly retained by the soils within the experimental error. However, Sheppard et al. (1990) reported that Tc adsorption increased about 2 orders of magnitude under reducing conditions than under oxidizing conditions. A possible explanation for the observed low Tc adsorption under H_2/N_2 atmosphere is probably the result of a true reducing environment not being attained in our experiment by simply purging the soil reagent solutions with H_2/N_2. Possible evidence for this includes soil sediments at the end of adsorption experiment that still appear to be yellow in color, suggesting the presence of Fe(III). This implies that the redox (Eh) of the soil suspension was not sufficiently reduced.

In contrast, when the adsorption experiment was performed under a H_2/N_2 atmosphere with the addition of 5 mg/L Na_2S, it was observed that adsorption of Tc was significantly increased (Fig. 3.3). The partitioning coefficients ranged from ~20 to ~100 mL/g. These results are therefore in agreement with that of Sheppard et al. (1990) and other investigators (Bondietti and Francis 1979). However, it is pointed out that Tc removed under reducing conditions may not be simply due to the adsorption process but a combination of adsorption and precipitation (as TcO_2 or Tc-sulfides). To verify the precipitation loss of Tc under low Tc concentration ($\sim 10^{-8}$ M) and reducing conditions, we added different amounts of Na_2S into a Tc-reference solution. After equilibration for overnight, clear Tc-reference solution was analyzed. Results (Fig. 3.4) indicate Tc precipitation loss increased as the Na_2S solution concentration increased, especially at a relatively high Na_2S concentration (>0.01 M). At Na_2S concentrations below 0.005 M, Tc concentration in reference solutions remained relatively stable, suggesting that no apparent precipitation of Tc occurred. These observations indicate an increased Tc retention by soils with the addition of 5 mg/L Na_2S (Fig. 3.3a,b) may be primarily due to adsorption of TcO_2 but not due to the precipitation of Tc-sulfides. The results also imply that if reducing conditions existed at PGDP the loss of Tc from solution would be limited by adsorption to the soil surfaces.

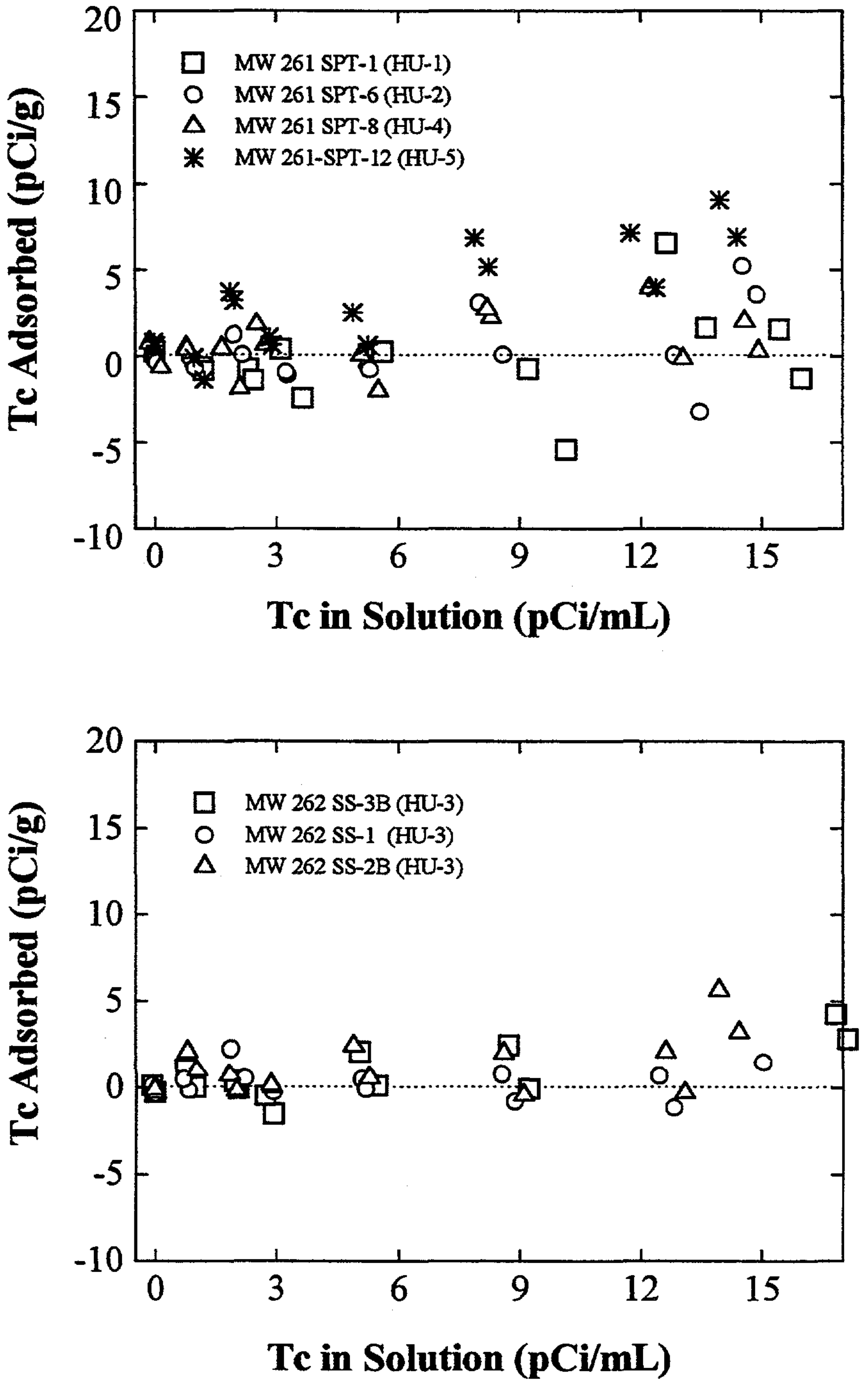


Fig. 3.2. Adsorption of Tc by soils from Paducah, Kentucky, under H_2/N_2 atmosphere in a glove-box.

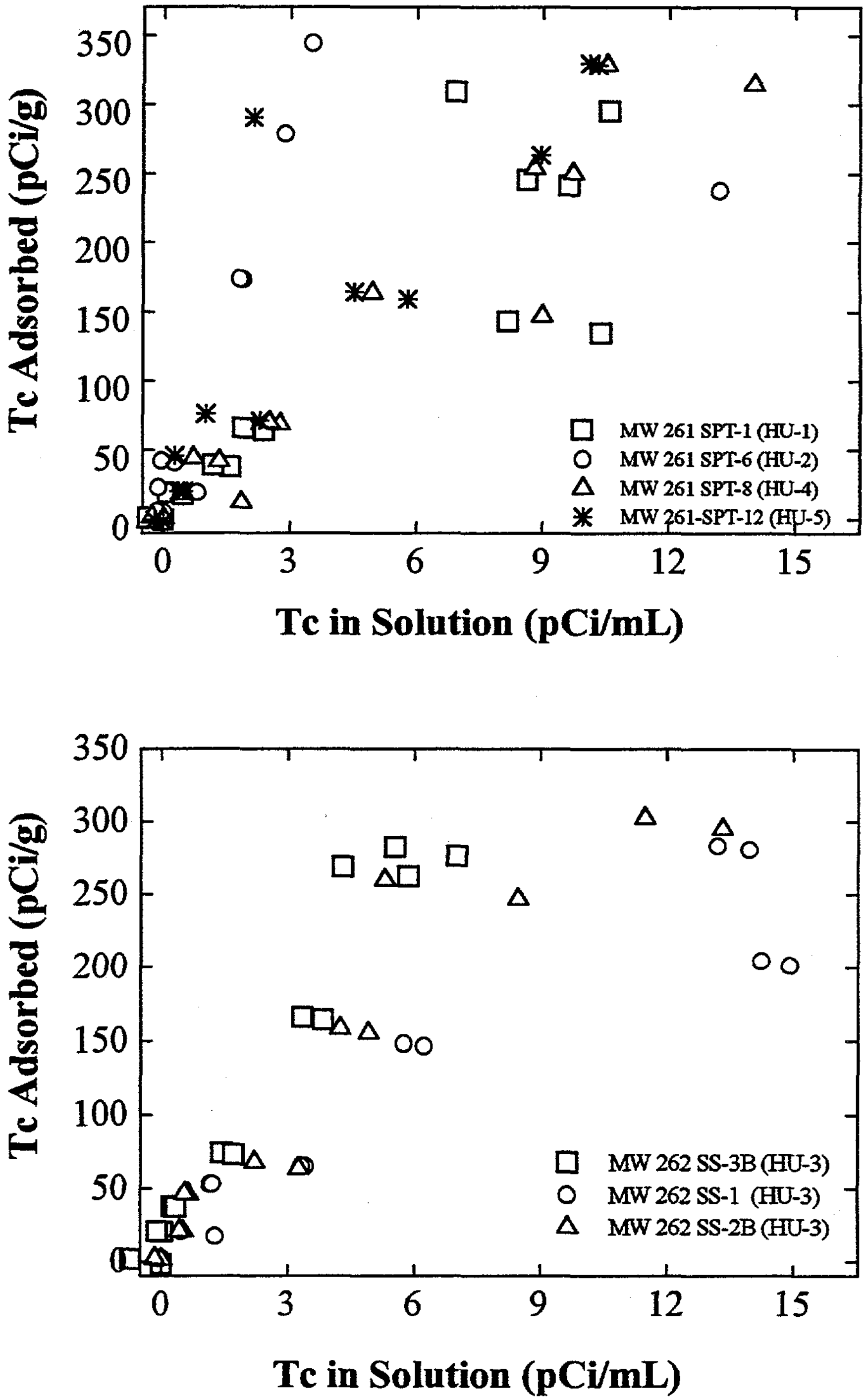


Fig. 3.3. Adsorption of Tc by soils from Paducah, Kentucky, in 5 mg/L Na_2S solution and under H_2/N_2 atmosphere in a glove-box.

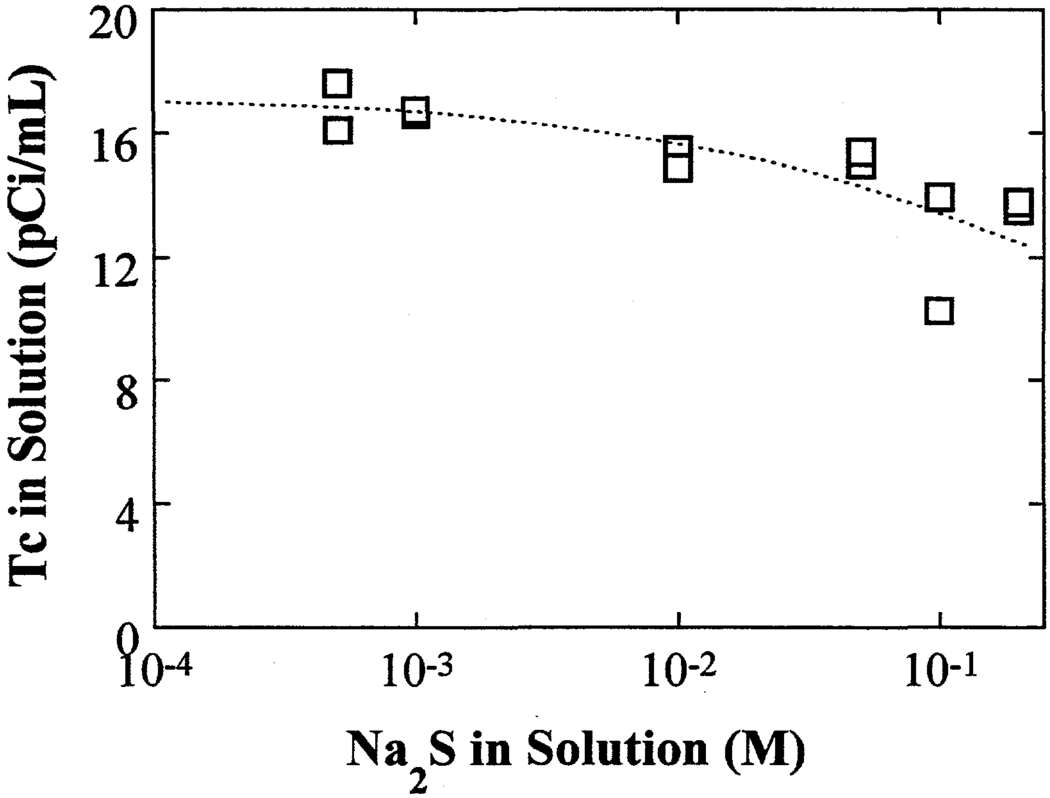


Fig. 3.4. Effects of Na_2S concentration on the precipitation of Tc from aqueous solution.

4. SELECTIVE ADSORPTION RECOVERY OF Tc BY ACTIVATED CARBON

4.1 INTRODUCTION

Remediation of Tc-contaminated groundwater has become an increasingly important public concern. Millions of dollars are being spent each year by DOE on site investigations, technology development, and remedial activities related to Tc contamination. Existing remedial technologies for Tc using synthetic exchange resins or liquid-liquid extraction are unsatisfactory; they are relatively inefficient, expensive, kinetically slow, and generate large quantities of secondary wastes. Previous studies have examined several anion exchange resins, such as AG1-X4 (Chen et al., 1990), Dowex SRB-OH and Reillex (Del-Cul et al., 1993), Dowex 1-X8 (Ihsanullah 1994; Kawasaki et al., 1993) or the use of solvent extraction techniques (Karalova et al., 1991; Takeuchi et al., 1993) to remove Tc. However, the disadvantages of using these techniques limit their application. First, a relatively low efficiency was reported when using anion exchange resins to remove TcO_4^-, because of a competition or exchange reactions by the background anions in solution (normally at a much higher concentration than TcO_4^- in solution). Second, the reaction kinetics are relatively slow and can range from a few hours to several days for many of these synthetic resins. For example, Del Cul et al. (1993) found that ~90% of Tc from PGDP groundwater (1 L) was removed with 1 g resin, but after 4 days of equilibration. Third, Tc adsorbed on resins is usually difficult to desorb (Del-Cul et al., 1993), and the process generates large volumes of spent sorbents needing to be stored or disposed. Secondary waste generation is also a serious problem when using liquid-liquid extraction techniques.

In a course of study of Tc complexation with various organic compounds, we observed that activated carbon adsorbed both organics and TcO_4^- effectively and selectively. A literature review revealed that porous graphitic carbon was used to remove cationic Tc-99m amine complexes (Emery and Lim 1989) and to separate Tc from high-level liquid waste, such as raffinates generated in the solvent extraction of transuranic elements (Yamagishi and Kubota 1993; Yamagishi and Kubota 1989). The adsorption capacity of Tc was reported to be as high as 0.60

meq/g (Yamagishi and Kubota 1989). However, a much lower maximum adsorption (on the order of 10^{-5} meq/g) is expected for the treatment of only slightly contaminated groundwater (e.g., containing 3000 pCi Tc/L or ~10^{-6} mmol Tc/L). The present study was undertaken to investigate the ability of activated carbon to remove low levels of Tc under a variety of environmental conditions, such as pH, electrolyte composition, and concentration. Column transport and recovery studies were performed with actual contaminated groundwater to determine the feasibility of using activated carbon to remediate Tc-contaminated groundwater.

4.2 MATERIALS AND METHODS

4.2.1 Activated carbon and Tc standard

A granular activated carbon sample (Nuchar WV-G) was obtained from West Virginia Pulp and Paper in Covington, Virginia. Before use, the sample was washed with purified water (Milli-Q plus system, Bedford, MA) by repeated decanting and sedimentation to remove fine carbon particles and then air dried and stored in a plastic bottle. The Tc standard solution (NH_4TcO_4 dissolved in water) was obtained from Isotope Products Laboratories in Burbank, California. The Tc radioactivity was 37.1 µCi/g ± 2.2%.

4.2.2 Adsorption Experiment

Adsorption of TcO_4^- on activated carbon was performed in various background electrolyte solutions including 0.01 M $CaCl_2$, 0.01 M $NaNO_3$, 0.01 M Na_2SO_4, Na-salicylate and phthalate at pH ~6.5, and two groundwater samples from monitoring wells (MW) 66 and 106 at PGDP in Paducah, Kentucky. MW 66 is contaminated with Tc at ~3000 pCi/L (or ~0.18 µg/L), whereas MW 106 is not contaminated.

The adsorption experiments were initiated by mixing 0.1 g activated carbon with 14.9 mL of the background electrolyte solution in 25 mL Teflon centrifuge tubes to which 0.1 mL of Tc stock solution (varying in concentration) was added. The initial Tc concentrations ranged from 0 to 110,000 pCi/L (or 6.5 µg/L) and equilibrium concentrations from 0 to 6500 pCi/L (or 0.38

μg/L). Samples were interverted 3 to 4 times every 15 min for 1 h and then equilibrated overnight. Rigorous shaking was avoided because it would break up the carbon particles by abrasion; therefore, the above equilibration procedure may cause a slight underestimation of Tc adsorption by activated carbon. However, the procedure may provide a realistic estimation of Tc removal efficiency when an activated carbon column is used to remove Tc from contaminated groundwater. After equilibration, 10 mL of clear supernatant solution was pipetted into 10 mL of scintillation cocktail (Ultima-Gold XR, Packard Instrument Co., CT). The Tc radioactivity in each vial was then determined with a liquid scintillation analyzer (Tri-Carb, Model 2000, Packard). The measured counts per minute were converted to actual disintegrations per minute or pCi by the external standard method (Gu et al., 1995). All samples were prepared in duplicate with two blanks.

The pH-dependent adsorption of TcO_4^- was studied with an initial Tc concentration of ~18 μCi/L (or ~1.1 mg/L) and 0.2 g activated carbon in 5 mL aqueous solution. The equilibrium concentrations ranged from 0.02 to 0.14 μCi/L. The pH was adjusted by adding known amounts of dilute acid (HCl) or base (NaOH), which were estimated through a trial titration to be from pH ~4 to 10. After overnight equilibration, 2 mL of clear supernatant was pipetted into 5 mL Ultima-Gold scintillation cocktail to determine Tc radioactivity.

4.2.3 Separation and Recovery of Tc

Recovery of TcO_4^- adsorbed on activated carbon was studied by using a 3 x 50 mm glass chromatographic column. Activated carbon particles (0.15 g) were wet-packed into the column, and purified water was fed into the column at a flow rate of 0.1 mL/min, which was achieved with a high-performance liquid chromatographic (HPLC) pump (Model 2350, ISCO, Lincoln, NE). The Tc stock solution in the desired concentration was injected into the column through a Rheodyne injector having a 100 μL sample loop. After ~25 pore volumes of water passed through the column, the mobile phase was switched to a 0.5 M salicylate solution at pH 8.8 to initiate the desorption of Tc that had been adsorbed on the activated carbon. A fraction collector

(Spectra/Chrom CF-1) was used to collect the effluent every 30 min (for a total volume of 3 mL). An aliquot (2 mL) was then mixed with a 5 mL scintillation cocktail in 9 mL scintillation vials and assayed for Tc radioactivity as described previously. The recovery of Tc was estimated by comparing the Tc injected into the column to the amount of Tc in the effluent. Different chemical reagents were examined for their ability to desorb TcO_4^- from activated carbon, and include 0.5 M Na-salicylate, Na-phthalate, NaCl, $NaNO_3$, and Na_2SO_4.

4.2.4 Tc Removal from Contaminated Groundwater

Column experiments were performed to test the ability of activated carbon to remove Tc from actual contaminated groundwater. The initial experiment used 0.5 g activated carbon packed in a 6.6 x 30 mm glass column. About 18 L of Tc-contaminated groundwater (MW 66) from PGDP was continuously pumped into the column. For convenience, the flow rate varied from 2 mL/min during the day to 1 mL/min at night. The effluent was collected in 1 L plastic bottles, and 10 mL aliquots were used to measure the Tc activity with a liquid scintillation analyzer. The above experiment was repeated using 1.5 g activated carbon with a constant flow rate of 1 mL/min. After 12 L of MW 66 groundwater passed through the column, the input solution was switched to a synthetic groundwater containing high levels of TcO_4^- (ranging from ~28,000 to 40,000 pCi Tc/L). The synthetic groundwater was composed of 2 mM $CaCl_2$, 2 mM Na_2SO_4, 1 mM $NaNO_3$, and 0.5 mg/L dissolved organic carbon obtained from a wetland pond in Georgetown, South Carolina (Gu et al., 1994). A total of ~6 L synthetic groundwater was pumped through the column. To recover the Tc adsorbed on activated carbon, 0.5 M salicylate at pH 8.8 was pumped into the column at a flow rate of 0.2 mL/min. The effluent was collected and analyzed as described previously.

4.3 RESULTS AND DISCUSSION

4.3.1 Adsorption of Tc by Activated Carbon

Adsorption of TcO_4^- on activated carbon yielded linear adsorption isotherms in various background solutions (Fig. 4.1); the Kd values are listed in Table 4.1. Results indicate that, in dilute electrolyte solutions of 0.01 M $CaCl_2$, $NaNO_3$, and Na_2SO_4, TcO_4^- can be selectively and effectively removed by activated carbon. The observed Kd values ranged from 2110 to 14,350 mL/g (Table 4.1). When using groundwater from MW 66 and MW 106 as a background, the Kd values were even higher, ~27,000 mL/g. Except in a background of 0.01 M $NaNO_3$, the removal efficiency of TcO_4^- by activated carbon exceeded 99%. The molar concentration of TcO_4^- in solution was trivial (on the order of 10^{-8} M) compared to that of Cl^-, $SO_4^=$, or NO_3^- (0.01 M). The ratio of molar concentration of background anions to that of TcO_4^- ranged from 5.8×10^5 to 1.1×10^7 (Table 4.1). These results suggest that TcO_4^- is preferentially adsorbed by activated carbon over other anions such as Cl^-, $SO_4^=$, and NO_3^-, although NO_3^- appears more effective in reducing TcO_4^- adsorption.

Table 4.1 Partitioning coefficients (Kd) of TcO_4^- on activated carbon in varying background electrolyte solutions, where S_N is the ratio of normal concentration of anions in the background to that of TcO_4^-, σ is the standard error, and R is the regression coefficient

Background Electrolyte	S_N	Kd (mL/g)	σ	R
0.01 M $CaCl_2$	1.1×10^7	14350	216	0.966
0.01 M $NaNO_3$	5.05×10^6	2110	7	0.998
0.01 M Na_2SO_4	1.1×10^6	12197	145	0.976
MW 66 Groundwater	8.4×10^5	26858	781	0.84
MW 106 Groundwater	5.8×10^5	27418	838	0.88

By using high ionic strength solutions (Cl^-, $SO_4^=$) or organic anions as a background, the adsorption of TcO_4^- was reduced significantly (Fig. 4.2 and Table 4.2). In particular, Kd values in 0.01 M Na-salicylate were reduced to ~8.7 mL/g, and to ~37 mL/g in 0.01 M Na-phthalate. These observations indicate that organic anions are more competitive than NO_3^-, Cl^-, and $SO_4^=$ for adsorption onto activated carbon, therefore reducing the adsorption of TcO_4^-.

Anion exchange has been proposed as the reaction mechanism between TcO_4^- and carbon surfaces (Yamagishi and Kubota 1993; Yamagishi and Kubota 1989). However, our results do not appear to support this conclusion. If anion exchange is the dominant reaction mechanism, one would expect a much smaller adsorption of TcO_4^- because the background electrolyte concentration (0.01 M Cl^-, $SO_4^=$, or NO_3^-) was about 5–7 orders of magnitude higher than that of TcO_4^- (~10^{-8} M) in solution. These anions would compete with TcO_4^- for adsorption (or exchange) by the electrostatic interactions. Thus, we propose that the surface reactions (or specific adsorption) and possible H-bonding between TcO_4^- anions and the –C-O or –C-OH functional groups on activated carbon are the dominant interaction mechanism, whereas the electrostatic interactions enhance the adsorption process or reduce the free energy of TcO_4^- adsorption. The presence of oxygen-containing functional groups (e.g., –OH, C–O–C) on activated carbon surfaces is well known. These functional groups have played a remarkable role in the processes of carbon utilization (Gomezserrano et al., 1994; Newcombe et al., 1993). Upon oxidation with H_2O_2, other oxygen functional groups, such as C=O and COO^-, have also been identified by FTIR spectroscopy (Gomezserrano et al., 1994). These oxygen functional groups are believed to be important for the removal of many organic compounds during water treatment (Gomezserrano et al., 1994; Newcombe et al., 1993; Warta et al., 1995). For example, Warta et al. (1995) have observed that, under oxic conditions, more dissolved organic compounds can be adsorbed by activated carbon than under reducing conditions. They suggest the oxidation of activated carbon surfaces results in an increase in surface oxygen functional groups which thereby enhances the surface complexation reactions between activated carbon and the organic compounds in water.

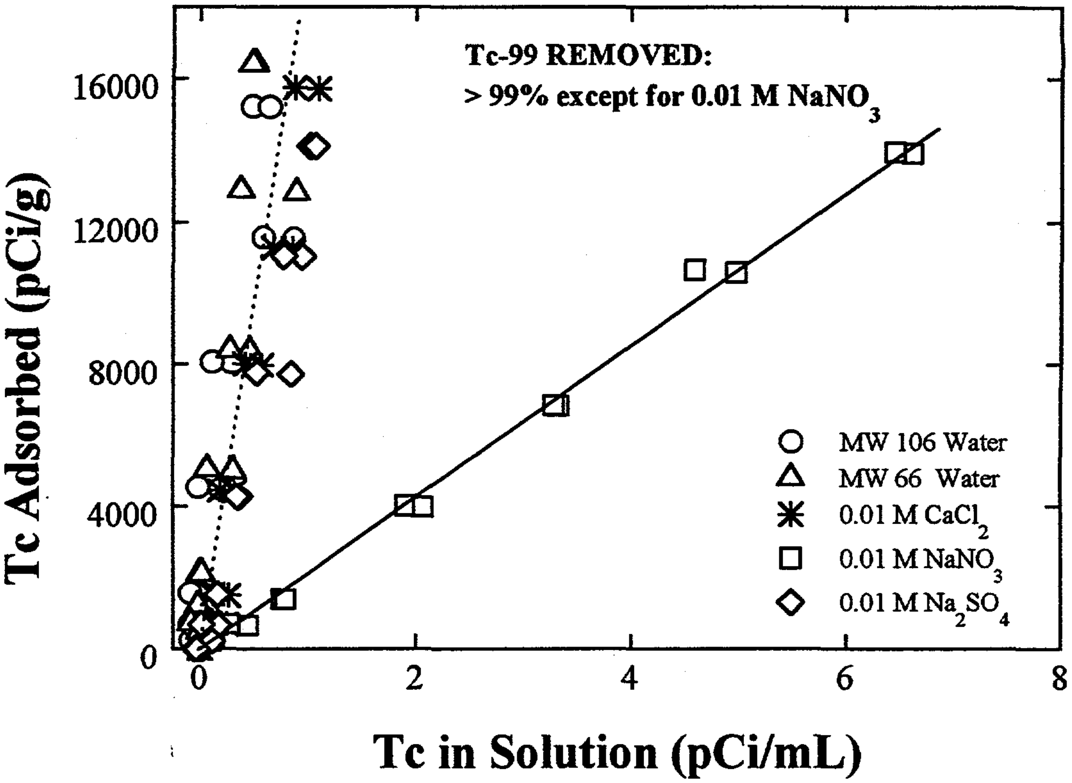


Fig. 4.1. Adsorption or partitioning of TcO_4^- by activated carbon in varying electrolyte backgrounds.

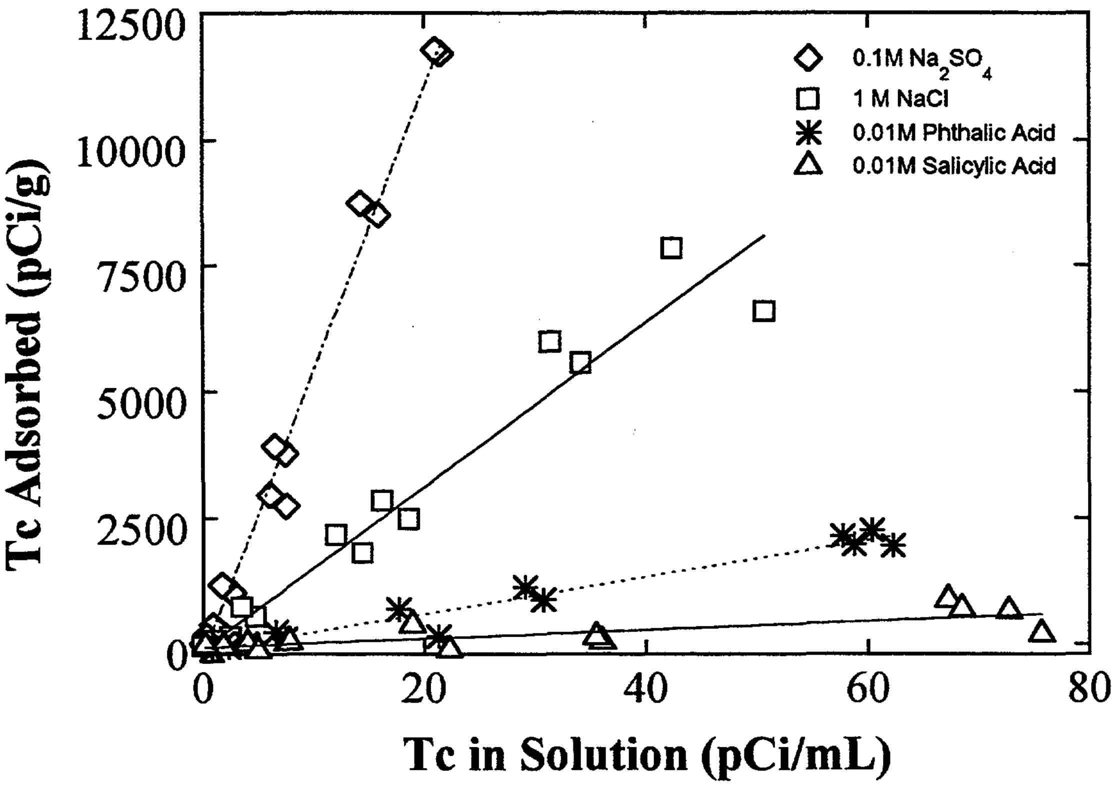


Fig. 4.2. Adsorption or partitioning of TcO_4^- by activated carbon in different organic and inorganic electrolyte backgrounds.

Table 4.2 Partitioning coefficients (Kd) of TcO_4^- on activated carbon in varying background electrolyte solutions, where S_N is the ratio of normal concentration of anions in the background to that of TcO_4^-, σ is the standard error, and R is the regression coefficient

Background Electrolyte	S_N	Kd (mL/g)	σ	R
1 M NaCl	5.05×10^8	161	10	0.975
0.1 M Na_2SO_4	1.1×10^8	562	17	0.994
0.01 M Na-salicylate	5.05×10^6	8.7	2	0.80
0.01 M Na-phthalate	1.1×10^7	37	2	0.98

TcO_4^- is also known to form complexes with organic compounds containing –C-O and –COO functional groups, especially under reducing conditions. Such a complexation reaction is thermodynamically possible based on the coordination chemistry of technetium (Schwochau and Pleger 1993). For example, organic compounds such as ethylenediaminetetraacetate (EDTA) and polyethylene glycol have been reported to form complexes with TcO_4^- (Colombo et al., 1990; Hashimoto et al., 1993; Havranek et al., 1994; Seifert et al., 1992; Zhang et al., 1995). Our experiments (Fig. 1.12) also indicate TcO_4^- may form complexes with salicylate. Using a preparative HPLC column, we observed that the elution peaks of TcO_4^- and salicylate in a mixture coincided but were separated if TcO_4^- or salicylate were injected into the column individually. The fact that salicylate can effectively reduce TcO_4^- adsorption (Fig. 2) and effectively desorb TcO_4^- adsorbed on activated carbon (discussed below) also suggests a possible complexation between TcO_4^- and salicylate. Therefore, these observations support our conclusion the surface reactions and possible H-bonding between TcO_4^- anions and the C-O (or –C-OH) functional groups on activated carbon are the dominant interaction mechanisms. Anion exchange reactions can not be completely ruled out because an increase in ionic strength (Fig. 4.2) appeared to reduce Kd values of TcO_4^- adsorption on activated carbon.

4.3.2 pH-dependent Adsorption of TcO_4^-

The pH-dependent adsorption of TcO_4^- on activated carbon was studied between pH ~4.5 and ~9.5 (Fig. 4.4). This pH range represents the groundwater pH at many contaminated sites. Results indicate adsorption of TcO_4^- on activated carbon decreases slightly as pH increases from 4.5 to 9.5. At pH ~9.5, however, adsorption of TcO_4^- remained relatively high, about 94% of that observed at pH ~4.5. These results demonstrate TcO_4^- can be effectively removed from groundwater in a wide range of pH values by activated carbon.

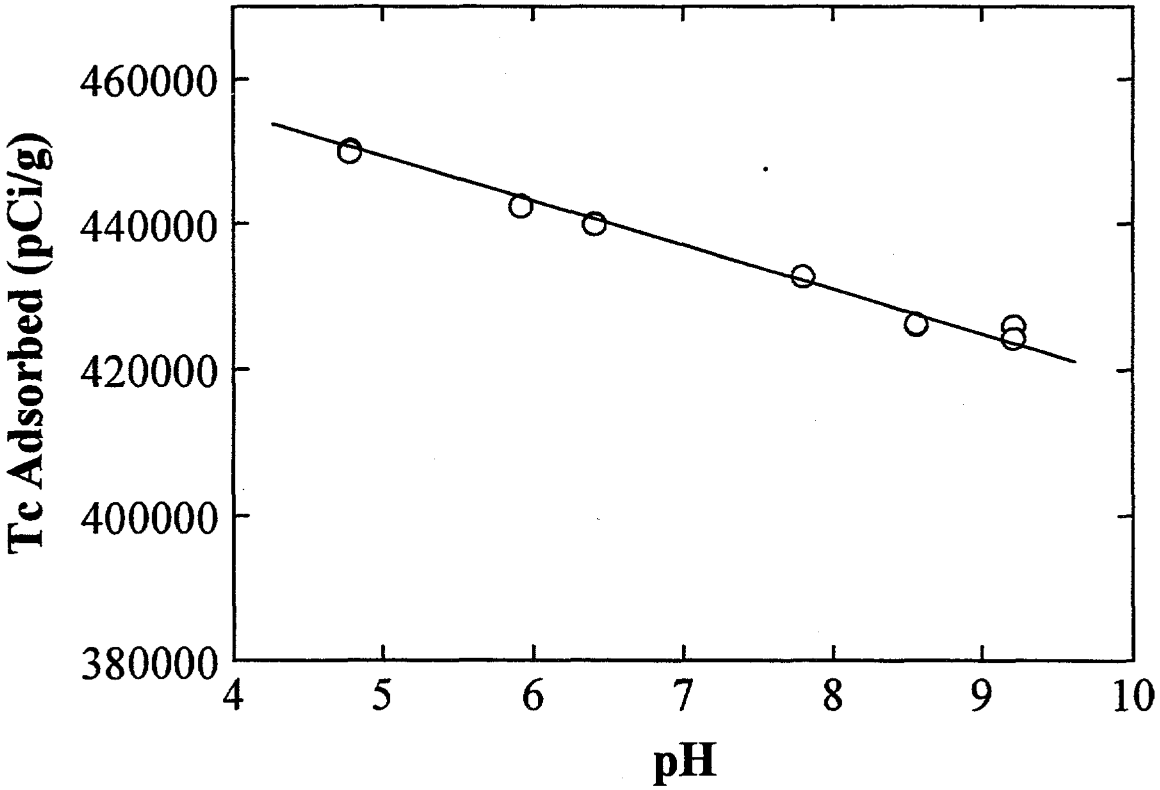


Fig. 4.3. pH-dependent adsorption of TcO_4^- by activated carbon at an initial concentration of ~18 μCi/L (or 1.1 mg Tc/L).

Because of the high adsorption capacity and affinity of TcO_4^- for activated carbon, more than 98% of TcO_4^- was removed from the solution phase at pH ~9.5 and more than 99.8% at pH ~4.5. The initial Tc concentration was ~18 µCi/L (or ~1.1 mg/L). Given the experimental conditions, the surface of the activated carbon was far from being saturated with TcO_4^-. Therefore, the slope of the pH-dependent adsorption curve (Fig. 4.3) could become steeper if the initial TcO_4^- concentration was sufficiently high. In other words, much more TcO_4^- may be adsorbed at pH 4.5 than what is shown in Fig. 4.4 if enough initial TcO_4^- is available. No further experiments were performed because only limited amounts of Tc reference were available and a relatively high concentration of Tc was needed for the experiment. Nevertheless, these results suggest TcO_4^- can be effectively removed from aqueous solutions over a relatively wide pH range.

Both adsorption isotherms and pH-dependent adsorption experiments demonstrate that TcO_4^- removal by activated carbon combined with the pump-and-treat technology can be a promising technique to remediate Tc-contaminated groundwater. Because of the low cost of activated carbon and an overall simplicity of the treatment process, the technology is very cost-effective compared to synthetic anion exchange resins or liquid-liquid extraction techniques (Brown et al., 1995; Chen et al., 1990; Del-Cul et al., 1993; Ihsanullah 1994; Kawasaki et al., 1993).

In comparison with many known synthetic resins, the TcO_4^- removal efficiency by activated carbon is superior. Anion exchange resins such as AG1-X4, Dowex SRB-OH, Dowex 1-X8, and Reillex have been tested for their ability to remove TcO_4^- (Chen et al., 1990; Del-Cul et al., 1993; Ihsanullah 1994; Kawasaki et al., 1993). Historically, anion exchange with a type 1 (quaternary amine) strong-base resin (e.g., Dowex SRB-OH) has been used to remove TcO_4^- at the Portsmouth Gaseous Diffusion Plant in Ohio (Del-Cul et al., 1993). However, this process has been known to be unsatisfactory because of its low efficiency, a result of competition by other anions in the solution. The process usually generates a relatively large volume of spent sorbent that needs storage and disposal (Del-Cul et al., 1993). Dowex 1-X8 anion exchange resin was also examined for its ability to remove TcO_4^- from Cl^-, NO_3^-, and ClO_4^- solutions (Kawasaki et al., 1993). The Kd values for this process ranged from only 2.5 to 1500 at an ionic strength of 2.0. Del Cul et al. (1993) reported that Reillex 402 (a poly-4-vinylpyridine cross-linked with 2% divinylbenzene from Reilly Industries, Inc.) performed better than Dowex SRB-OH in TcO_4^- removal. However, they also found the industrial grade Reillex 402 did not perform as well as Dowex SRB-OH in removing TcO_4^-. In addition, a relatively large amount of resins and a longer equilibration time (ranging from 24 h to 6 weeks) were reported as necessary for these resins to reach equilibrium. Del Cul et al. (1993) found that only ~90% of TcO_4^- was removed from the Paducah groundwater (1 L) with ~1 g Dowex SRB-OH resin after 4 days of equilibration. In contrast, TcO_4^- adsorption on activated carbon is almost instantaneous and much more effective, as will be discussed below. Iron metal fillings and ferrous sulfide were found to be very effective in removing TcO_4^- because of a reduction of TcO_4^- to TcO_2. The disadvantages of this technique, however, are that a relatively long equilibrium time is required for the chemical reduction to occur (Del-Cul et al., 1993), and the process may suffer pore clogging problems and potential re-release of TcO_4^- after an extended period as a result of re-oxidation.

4.3.3 Separation of TcO_4^- from Contaminated Groundwater

To verify the ability of activated carbon to remove TcO_4^- from actual contaminated groundwater, a small column (6.6 x 30 mm) was wet-packed with only 0.5 g activated carbon. A small column was prepared to limit the amount of groundwater (containing ~3000 pCi Tc/L) required to pass through a larger column before a breakthrough of TcO_4^- could be observed. Adsorption capacity of TcO_4^- on activated carbon is reported to range from 0.26 to 0.6 mmol/g (Yamagishi and Kubota 1993; Yamagishi and Kubota 1989) whereas the PGDP groundwater Tc concentration was on the order of 10^{-8} M. Column results (Fig. 4.4) indicate no Tc breakthrough was observed when more than 14,000 pore volumes of contaminated groundwater (from MW 66) was passed through the column. A full breakthrough of TcO_4^- was not observed, even after ~23,000 pore volumes of groundwater was pumped through the column. In a separate experiment, a longer column (6.6 x 85 mm) was prepared with 1.5 g activated carbon. After an input of ~12 L (or 5300 pore volumes) of Tc-contaminated groundwater (from MW 66), no significant amount of Tc breakthrough was observed within the experimental error (data not shown). The input solution was then switched to a synthetic groundwater containing high levels of Tc (~10 fold increase) as compared with MW 66. After ~6 L of the solution passed through the column, C/C_0 was <3%. Again, a full breakthrough was not achieved.

These results confirm our previous conclusion that remediation of Tc-contaminated groundwater by activated carbon is feasible because of its low cost, high efficiency, and capacity. As a conservative estimate (based on Fig. 4.4), if our treatment goal is <200 pCi/L in the water, one hundred kilograms of activated carbon should treat ~500,000 gal of Tc-contaminated groundwater containing about 12,000 pCi/gal Tc (or a total of 6 mCi or ~350 mg Tc equivalent). The treatment efficiency is expected to be even higher with a larger and longer column because preferential flow paths and wall-effects may exist when using such a small analytical column. The theoretical adsorption capacity of TcO_4^- on activated carbon (0.26–0.6 mmol/g) is obtained under saturated conditions (or at a much higher solution Tc concentration). Because Tc concentration in MW 66 groundwater is only about 3000 pCi/L (or 0.2×10^{-8} M), the maximum adsorption capacity under these conditions is only ~4.8×10^{-5} mmol/g (or ~4.8 mg/kg), based on the adsorption isotherm shown in Fig. 4.1 (or the Kd value in Table 4.1). These data were in general agreement with the estimate made on the basis of the column experiment (Fig. 4a).

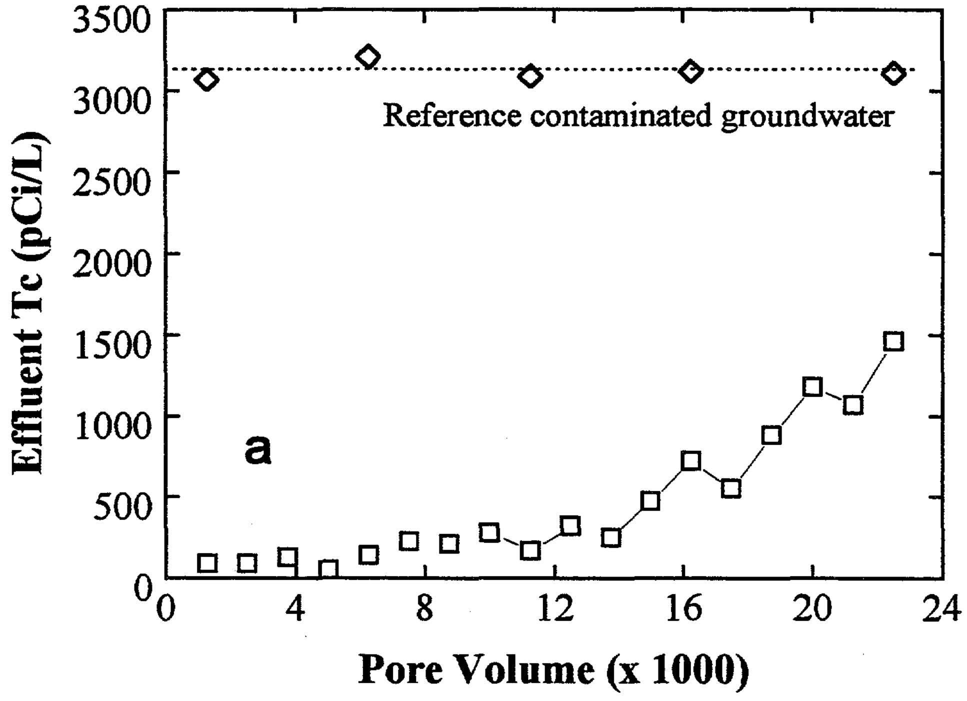


Fig. 4.4. Breakthrough of (a) TcO_4^- from MW 66 groundwater in a packed column (6.6 x 30 mm) with 0.5 g activated carbon.

4.3.4 Recovery of TcO_4^- from Activated Carbon

Recovery of adsorbed Tc from activated carbon was performed in packed columns to evaluate recovery of Tc and for possible reuse of the carbon (Fig. 4.5). Desorption of Tc from carbon would be necessary to minimize waste disposal of spent carbon if the technique is applied to remediate Tc-contaminated groundwater. Results indicate (Fig. 4.5) injected Tc (100 μL at varying concentrations) was completely adsorbed by activated carbon in all experiments. These results are consistent with the batch adsorption experiments (Fig. 4.1), which show >99% Tc removal from the aqueous solution. The TcO_4^- solution was injected at ~25 pore volumes and eluted with an additional 25 pore volumes of water before the eluent was switched to a recovery reagent (Fig. 4.5). When the input solution was switched to 0.5 M Na-salicylate, desorption of TcO_4^- occurred rapidly. A complete recovery (~100%) of adsorbed Tc was observed except for the column injected with a high level of Tc (100,000 pCi), where a significant tailing occurred (inset plotted on a log-scale in Fig. 4.5a).

Desorption of adsorbed Tc on activated carbon was also evaluated using Na-phthalate, $NaNO_3$, Na_2SO_4, and NaCl, respectively (Fig. 4.6). Compared with salicylate, these electrolytes were less effective in recovering TcO_4^- adsorbed on activated carbon. Although Na-phthalate and $NaNO_3$ were able to completely desorb adsorbed Tc, a much longer time (or more pore volumes of eluent) was required to wash TcO_4^- off the carbon. On the other hand, NaCl and Na_2SO_4 were incapable of desorbing TcO_4^- from activated carbon, especially Na_2SO_4. Less than 4% and 32% of the adsorbed Tc was desorbed by Na_2SO_4 and NaCl, respectively, after about 160 mL of the electrolyte solution passed through the column (during ~27 h equilibration time). Particularly significant is that $SO_4^=$ anions are less effective in desorbing TcO_4^- than Cl^-, although $SO_4^=$ carries two negative charges on a molar basis. Similar results were obtained when this experiment was repeated. From the batch adsorption experiment, we also observed a relatively high Kd value for Tc adsorption in Na_2SO_4 than in NaCl. No satisfactory explanations can be given at the present. These results nevertheless provide additional evidence that TcO_4^- adsorption on activated carbon is not simply by the anion exchange mechanism because, on a molar concentration basis, $SO_4^=$ anions were less effective than Cl^- in inhibiting TcO_4^- adsorption.

4.4 CONCLUSIONS

Results of this work provide a simple yet extremely effective technology to remediate Tc (as TcO_4^-) contaminated groundwaters. Activated carbon adsorbs TcO_4^- selectively and effectively over a wide range of pH values and from various dilute electrolyte solutions (<0.01 M). The partitioning coefficient (Kd) of TcO_4^- exceeded 27,000 when using the actual groundwater from the PGDP site, and exceeded 12,000 mL/g in 0.01 M $CaCl_2$ and Na_2SO_4. TcO_4^- removal efficiency was >99% under these conditions, except in a 0.01 M $NaNO_3$ background solution. Organic anions such as salicylate and phthalate and NO_3^- compete with TcO_4^- for adsorption on activated carbon, especially at a high ionic strength (e.g., >0.5). Salicylate

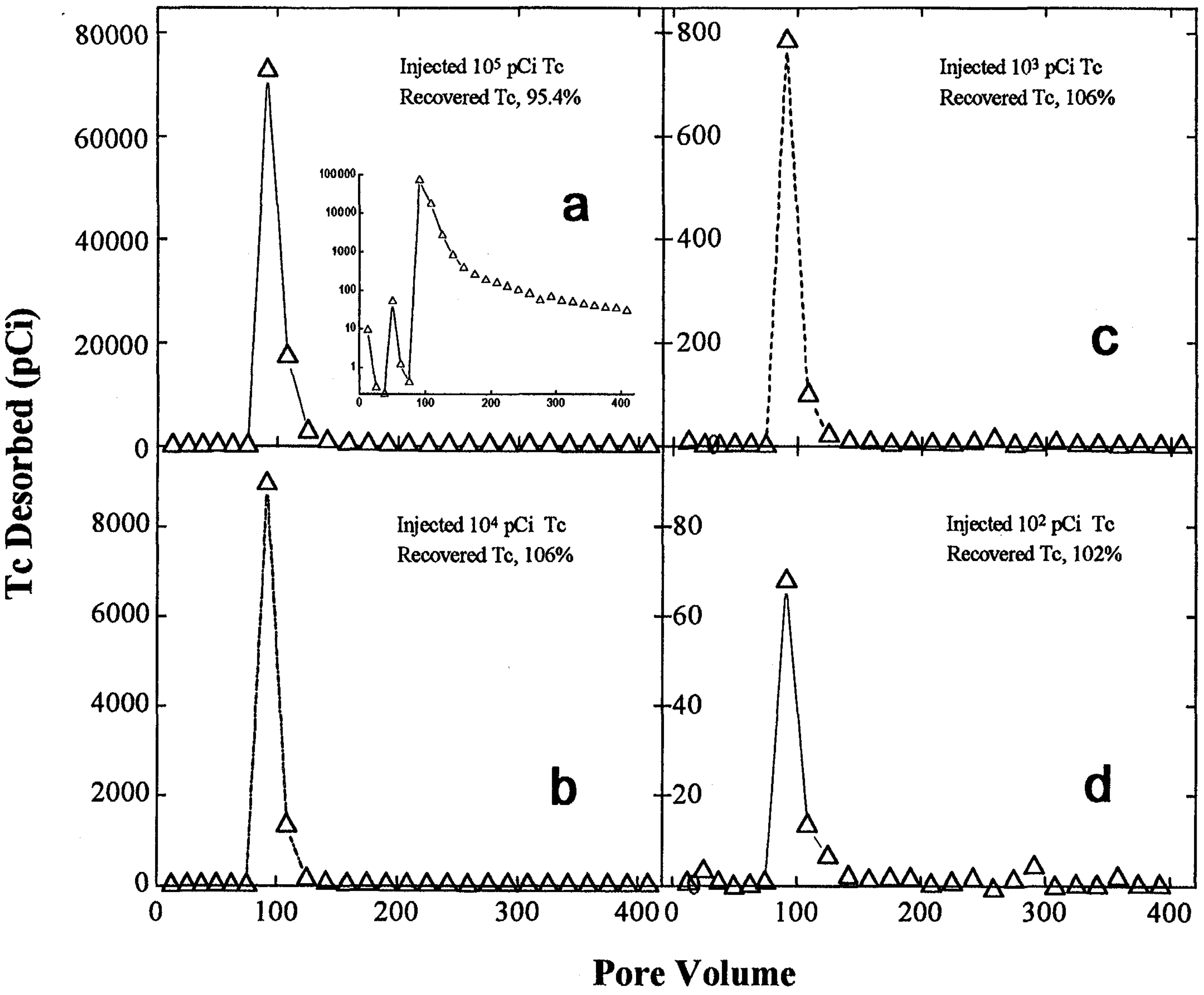


Fig. 4.5. Recovery of TcO_4^- adsorbed on activated carbon by 0.5 M Na-salicylate using a 3 x 50 mm glass column at varying initial TcO_4^- loadings.

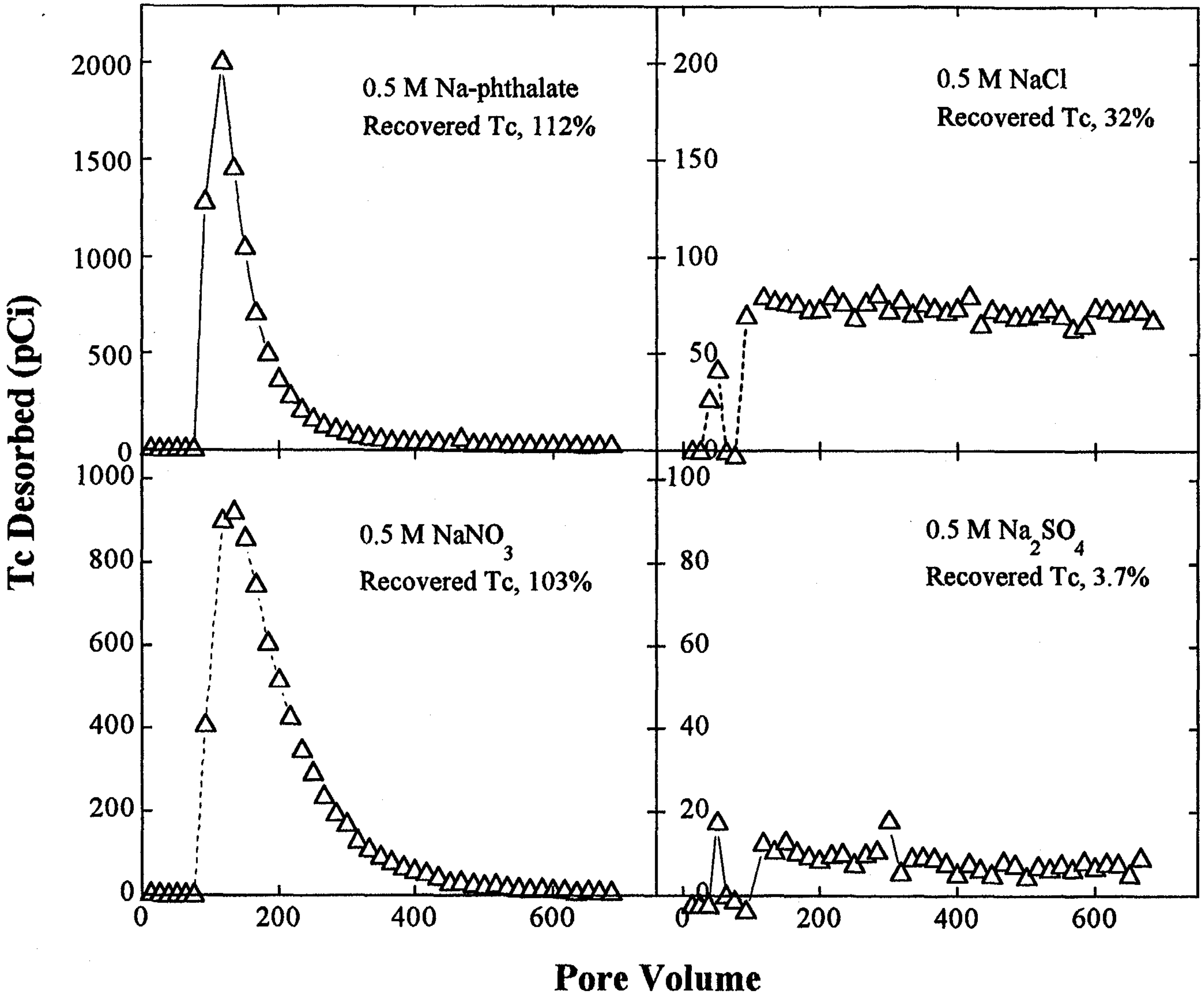


Fig. 4.6. Recovery of TcO_4^- adsorbed on activated carbon by different electrolyte solutions using a 3 x 50 mm glass column at an initial TcO_4^- loading of 8000 pCi.

Salicylate is more effective than phthalate in desorbing the adsorbed TcO_4^- from activated carbon but, on the other hand, offers an effective way to recover the adsorbed Tc for possible reuse and for regeneration of activated carbon and waste minimization. Therefore, the use of activated carbon to remediate TcO_4^--contaminated groundwater is a promising technology that is cost-effective and requires minimal installation and maintenance. A treatment module (or column) can be used as part of a pump-and-treat facility to remove TcO_4^- from contaminated groundwater.

Because adsorbed TcO_4^- can be recovered quantitatively from activated carbon, another important application of this technique is for quantitative analysis of TcO_4^- in environmental samples containing low levels of Tc (i.e., <100 pCi/L). Existing methodologies for analyzing low levels of Tc are tedious and expensive. In a number of separation methods for the enrichment of Tc, the main step consists of an adsorption on an anion exchanger. This step is time consuming and the yield is quite low (Sattelberger et al., 1989). In comparison, solvent extraction (e.g., by tetraphenylarsonium chloride) is preferred (Karalova et al., 1991; Sattelberger et al., 1989). However, solvent extraction requires the use of expensive and toxic chemical reagents such as tetraphenylarsonium chloride and chloroform. More importantly, perhaps, it generates a relatively large quantity of secondary waste and the yield is between 80 and 85% (Sattelberger et al., 1989). Therefore, a relatively simple analytical procedure is proposed on the basis of this research. The methodology includes the following steps, provided that the groundwater has a low dissolved organic carbon (e.g., < 1 mg C/L) and ionic strength (<0.01): (1) a small activated carbon column (e.g., 5 x 100 mm) is prepared and washed with purified water; (2) a sufficient amount of contaminated groundwater (e.g., 1 L if groundwater contains >10 pCi/L TcO_4^-) is quantitatively pumped through the column, (3) the input solution is then switched to salicylate at pH ~8.5–9 to initiate the desorption process (a low flow rate is recommended to allow sufficient equilibrium time for desorption to occur), and (4) finally, the effluent is collected and mixed with an appropriate scintillation cocktail for liquid scintillation analysis. If a large number of samples are to be analyzed, the above procedure may be simplified by using a special separation funnel instead of a chromatographic column and a HPLC pump.

SUMMARY AND RECOMMENDATIONS

Various experimental techniques have been applied to characterize and identify Tc complexation with groundwater organic compounds and TCE. Results suggest, within the experimental error, Tc (as TcO_4^-) is not significantly complexed with groundwater or natural organic matter. Tc presents in PGDP groundwater primarily as TcO_4^- given a relatively high DO concentration in the groundwater. Similarly, Tc does not appear to form complexes with TCE in aqueous solution. Both liquid-liquid extraction and HPLC analyses give no indication Tc is complexed with TCE.

No significant adsorption of TcO_4^- is observed by soils from PGDP under both atmospheric and H_2/N_2 atmosphere. However, under strong reducing environment (e.g., by addition of 5 mg/L Na_2S), a relatively high amount of Tc can be removed or adsorbed by the PGDP soil. The removal of Tc under such conditions is attributed to both adsorption and precipitation processes. These observations are consistent with previous studies which have shown TcO4- anions are not significantly adsorbed by silicate minerals. However, under strongly reducing conditions, a large percentage of Tc may be retained by the soil.

This study supports the pump-and-treat technology to remediate TcO_4^- contaminated groundwater plume. Because TcO_4^- anions are not significantly retained by the soil, one would expect only a limited tailing during the pump-and-treat process. Both batch and column studies revealed that TcO_4^- anions can be selectively and effectively adsorbed by activated carbon. Because of a low cost, high efficiency, and capacity of activated carbon for TcO_4^- removal, the pump-and-treat technology coupled with the activated carbon adsorption could potentially be the most cost-effective technique to remediate TcO_4^- contaminated groundwater plume. A field-scale demonstration of this technology is thus recommended and is expected to have a great impact on the restoration of Tc-contaminated groundwater.

REFERENCES

Bondietti, E.A., and C.W. Francis. 1979. Geologic migration potentials of technetium-99 and neptunium-237. Sci. 203:1337-1340.

Brown, D.J. 1967. Migration characteristics of radionuclides through sediments underlying the Hanford reservation. In Disposal of radioactive wastes into the ground. Int. Atomic Energy Agency Symp., Vienna, Austria. USAEC Symp. Ser., CONF-670512. Natl. Tech. Inf. Serv., Springfield, VA.

Brown, G.M., S.D. Alexandratos, L.M. Bates, P.V. Bonnesen, L.A. Hussain, B.A. Moyer, and V. Patel. 1995. Pertechnetate selective resins for remediation of groundwater. in *Program and Abstracts, Ninth Symposium on Separation Science and Technoogy for Energy Applications. October 22-26, 1995*. Gatlinburg, TN.

Chen, Q.J., H. Dahlgaard, H.J.M. Hansen, and A. Aarkrog. 1990. Determination of Tc-99 in environmental samples by anion exchange and liquid liquid extraction at controlled valency. Anal. Chim. Acta 228:163-167.

Clausen, J.L., K.R. Davis, J.W. Dorthitt, and B.E. Phillips. 1992. Report of the Paducah Geseous Diffusion Plant groundwater investigation. Phase III. KY/E-150. Martin Marietta Energy Systems. Paducah, KY.

Clausen, J.L., and T.O. Early. 1992. The migration of trichloroethylene and technetium in groundwater at the Paducah Gaseous Diffusion Plant. Proceedings of the Subsurface Restoration Conference. June 21-24, 1992. Dallas, TX. 133-135.

Clausen, J.L., J.L. Zutman, D.A. Pickering, and N.D. Farrow. 1995. Final report on drive-point profiling of the northwest plume and analysis of related data. Martin Marietta Energy Systems, Kevil, Kentucky. KY/ER-66.

Colombo, F., M. Matarrese, F. Fazio, and E.D. E. 1990. Tc-99m complexes of alpha,alpha-disubstituted, alpha-hydroxy carboxylic acids. Appl. Rad. Isot.-Intl. J. Rad. Appl. Instr. Part A 41:221.

Del-Cul ,G.D., W.D. Bostick, D.R. Trotter, and P.E. Osborne. 1993. Technetium-99 removal from process solutions and contaminated groundwater. Sep. Sci. Technol. 28:551-564.

Emery, M.F., and C.K. Lim. 1989. Separation of cationic technetium-99m amine complexes on porous graphitic carbon. J. Chrom. 479:212-215.

Gomezserrano, V., M. Acedoramos, A.J. Lopezpeinado, and C. Valenzuelacalahorro. 1994. Oxidation of activated carbon by hydrogen peroxide - study of surface functional groups by FT-IR. Fuel 73:387-395.

Gu, B., J. Schmitt, Z. Chen, L. Liang, and J.F. McCarthy. 1994. Adsorption and desorption of natural organic matter on iron oxide: mechanisms and models. Environ. Sci. Technol. 28:38-46.

Gu, B., O.R. West, and R.L. Siegrist. 1995. Using ^{14}C-radiochemicals can cause experimental error in studies of the behavior of volatile organic compounds. Environ. Sci. Technol. 29:1210-1214.

Hashimoto, M., H. Wada, T. Omori, and K. Yoshihara. 1993. Formation of Tc(III) complexes with EDTA and HEDTA. Radiochimica Acta 63:173-177.

Havranek, E., A. Bumbalova, P. Krenek, M. Komova, and M. Belakova. 1994. Development of new radiopharmaceuticals - Technetium aminopolycarboxylate complexes. Pharmazie 49:369-370.

Ihsanullah. 1994. Optimization of various factors for the separation of technetium using anion-exchange resins. Sep. Sci. Technol. 29:239-247.

Karalova, Z.K., E.A. Lavrinovich, and B.F. Myasoedov. 1991. Separation of technetium from accompanying elements in basic solutions by extraction with triphenyltetrazolium chloride. Soviet Radiochem. 33:266-269.

Kawasaki, M., T. Omori, and K. Hasegawa. 1993. Adsorption of pertechnetate on an anion exchange resin. Radiochim. Acta 63:53-56.

Newcombe, G., R. Hayes, and M. Drikas. 1993. Granular activated carbon - Importance of surface properties in the adsorption of naturally occurring organics. Coll. Surf. A-physicochem. Eng. Aspects 78:65-71.

Pilkington, N.J. 1990. The solubility of technetium in the near-field environment of a radioactive repository. J. Less-Common Metals 161:203-212.

Sattelberger, P., M. Mang, G. Herrmann, J. Riegel, H. Rimke, N. Trautmann, F. Ames, and H.-J. Kluge. 1989. Separation and detection of trace amounts of technetium. Radiochim. Acta 48:165-169.

Schulte, E.H., and P. Scoppa. 1987. Sources and behavior of technetium in the environment. Sci. Total Environ. 64:163-179.

Schwochau, K., and U. Pleger. 1993. Basic coordination chemistry of technetium. Radiochim. Acta 63:103-110.

Seifert, S., R. Muenze, P. Leibnitz, G. Reck, and J. Stach. 1992. Preparation, characterization and crystal structure of a mixed ligand complex of technetium with DPPE and oxalic acid -

oxalato-bis(1,2-bis(diphenylphosphino)ethane) technetium(II). Inorg. Chim. Acta 193:167-172.

Sheppard, S.C., M.I. Sheppard, and W.G. Evenden. 1990. A novel method used to examine variation in Tc sorption among 34 soils, aerated and anoxic. J. Environ. Radioactivity 11:215-233.

Takeuchi, M., S. Tanaka, and M. Yamawaki. 1993. Solvent extraction of Tc(vii) and Re(vii) from nitric acid solution with the mixture of CMPO and TBP. Radiochim. Acta 63:97-100.

Warta, C.L., S.P. Papadimas, G.A. Sorial, M.T. Suidan, and T.F. Speth. 1995. The effect of molecular oxygen on the activated carbon adsorption of natural organic matter in Ohio river water. Water Res. 29:551-562.

Wildung, R.E., T.R. Garland, K.M. McFadden, and C.E. Cowan. 1986. Technetium sorption in surface soils. Elsevier Appl. Sci. Publishers: London. p. 115-129.

Wolfrum, C., and K. Bunzl. 1986. Sorption and desorption of technetium by humic substances under oxic and anoxic conditions. J. Radioanal. Nucl. Chem. 99:315-323.

Yamagishi, I., and M. Kubota. 1993. Recovery of technetium with active carbon column in partitioning process of high-level liquid waste. J. Nucl. Sci. Technol. 30:717-719.

Yamagishi, I., and M. Kubota. 1989. Separation of technetium with active carbon. J. Nucl. Sci. Technol. 26:1038-1044.

Zhang, J., S.T. Griffin, and R.D. Rogers. 1995. The effects of halide anions on the partitioning behavior of pertechnetate in polyethylene glycol-based aqueous biphasic systems. in *Program and Abstracts, Ninth Symposium on Separation Science and Technoogy for Energy Applications. October 22-26, 1995*. Gatlinburg, TN.

INTERNAL DISTRIBUTION

J. L. Collins, 4501, MS-6221
V. H. Dale, 1505, MS-6035
D. T. Davenport, X7725, MS-7602
T. O. Early, 1509, MS-6400
B. Gu, 1505, MS-6036(6)
S. G. Hildebrand, 1505, MS-6037
G. K. Jacobs, 1505, MS-6036
L. Liang, 1505, MS-6038
A. P. Malinauskas, 1001, MS-7172
D. E. Reichle, 4500N, MS-6253
R. Siegrist, 1505, MS-6037
S. H. Stow, 1505, MS-6035
J. S. Watson, 4500N, MS-6178
Central Research Library
ESD Library (15)
Laboratory Records Dept. (2)
Laboratory Records, ORNL-RC
ORNL Y-12 Technical Library

EXTERNAL DISTRIBUTION

J. A. Clausen, Environmental Restoration and Waste Management, 761 Veterans Avenue, Room 2-6, Kevil, Kentucky 42053 (5)

J. W. Douthitt, Hydrological Services Section, Martin Marietta Energy Systems, Paducah Gaseous Diffusion Plant, 761 Veterans Ave., Kevil, Kentucky 42053

D. J. Grimes, U.S. Department of Energy, 19901 Germantown Road, ER-74, Germantown, MD. 20874

Nic Korte, Oak Ridge National Laboratory, P. O. Box 2567, Grand Junction, CO. 81502

Office of Assistant Manager for Energy Research and Development, U.S. Department of Energy, Oak Ridge Operations, P. O. Box 2001, Oak Ridge, Tennessee 37831-8600

A. Patrinos, Director, Environmental Sciences Division, Office of Health and Environmental Research, ER-74, U. S. Department of Energy, Washington, D.C. 20585

Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, Tennessee 37831
(2 copies)