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DOE/MC/11076--2956

DE91 002034

Determination of Sulfur Anions in Spent Oil Shale Leachates by Ion Chromatography

Topical Report

N.D. Niss

July 1989

Work Performed Under Cooperative Agreement No.: DE-FC21-86MC11076

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Western Research Institute
Laramie, Wyoming

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(DE91002034)

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SUMMARY

The leaching and transport of chemical constituents from spent oil shale disposal areas is an area of environmental concern at the present time. Sulfur-containing compounds are prevalent in spent oil shales and have the potential to leach into aqueous systems surrounding disposal sites. Computer modeling has been used in recent years to predict the transport of species in an aqueous environment. The quality of model predictions, however, depends on the validation steps taken in comparing model predictions with laboratory data on ion speciation. Further, the quality of the validation step depends on the reliability of laboratory methods in generating ion speciation data.

The purpose of this study was to develop methods to separate and quantify sulfur-containing anions in spent oil shale leachates by suppressed ion chromatography. The anions studied were S^{2-} (sulfide), SO_3^{2-} (sulfite), SO_4^{2-} (sulfate), SCN^- (thiocyanate), $S_2O_3^{2-}$ (thiosulfate), and $S_4O_6^{2-}$ (tetrathionate). After the separations were developed, a series of method-challenging experiments were performed to test the reliability of the methods and assure the development of an analytically sound product.

INTRODUCTION

Background

The chemical form of sulfur in an aqueous environment determines its mobility, solubility, interaction with other compounds, and, therefore, its environmental impact. Volatile species such as sulfide or sulfite may react one way, but more stable species, such as sulfate or thiosulfate, may react another. The behavior of these species in a spent oil shale-water system is an area of increasing concern in predicting water quality and characterizing the partitioning behavior between solid and solution phases.

Computer modeling is being used to a greater extent in predicting the distribution of elements in leachates and the mobility of species through porous media. Before model predictions can be applied to a real environment, however, they must be validated. This may be accomplished by comparing ion speciation data obtained from laboratory analyses with geochemical model predictions. Further, because the validation step depends on the quality of the laboratory data, accurate and reliable methods are needed to separate and quantify the ions of interest.

The purpose of this study was to develop methods to separate and quantify inorganic sulfur anions in spent oil shale leachates using suppressed ion chromatography. Based on the analyses performed by Stuber et al. (1978) on waste waters generated from in situ oil shale processing, the anions chosen for study were S^{2-} (sulfide), SO_3^{2-} (sulfite), SO_4^{2-} (sulfate), SCN^- (thiocyanate), $S_2O_3^{2-}$ (thiosulfate), and $S_4O_6^{2-}$ (tetrathionate).

Analysis of Sulfur Anions

Previous Work

The determination of inorganic sulfur anions such as sulfide, sulfite, sulfate, and thiosulfate in aqueous solutions has been a difficult, if not impossible, task in the past. These species have a tendency to react with one another and may be unstable during sampling and sample stabilization in a variety of conditions. Traditional wet chemical analyses of three or more sulfur-containing anions require several iodometric titrations and precipitations, typically including at least one barium sulfate gravimetric step. Individual polythionates cannot be determined using these procedures (Story 1983). Colorimetric procedures used to determine sulfide and thiocyanate are subject to interference problems, especially if other sulfur-containing anions are present in solution (Karchmer 1970; APHA 1981). A comprehensive study was conducted by Mancy and Weber (1971) to compare the analytical methods available to determine low levels of thiocyanate. The study compared colorimetry, high-performance liquid/ion chromatography (HPLC/HPIC), and atomic absorption (AA) spectroscopy of SCN-copper ligand complexes. They concluded that HPLC/HPIC is the best approach to follow.

Many studies have been conducted using ion chromatography to determine various inorganic sulfur anions in aqueous solution. The lower sulfur anions (i.e., sulfide, sulfite, sulfate, thiocyanate, and thiosulfate) have been the subject of several previous studies.

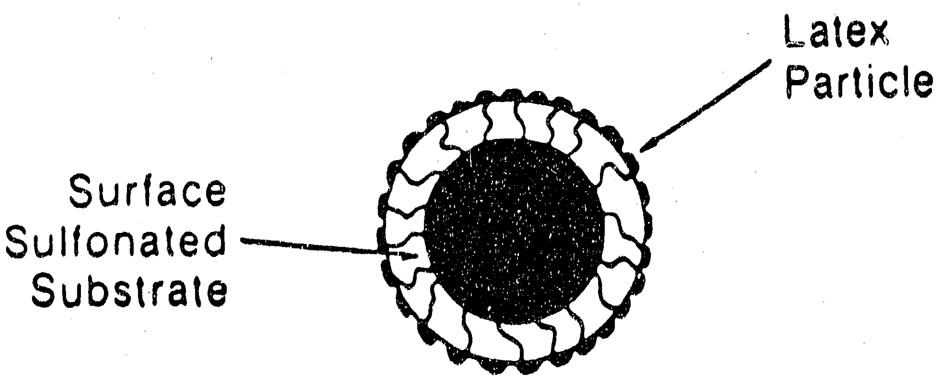
Holcombe et al. (1979) separated sulfite, sulfate, and thiosulfate using suppressed ion chromatography. The technique required two different runs with two different eluents to separate the three anions. Gjerde et al. (1980) separated thiosulfate and sulfate in one run using suppressed ion chromatography, but sulfate and sulfite were not completely resolved. Sunden et al. (1983) separated the same three anions using suppressed ion chromatography with gradient elution. There were some baseline disturbance problems associated with the gradient program, and adsorption of thiosulfate in the separator column resulted in severe tailing of the thiosulfate peak.

Conventional HPLC and single-column ion chromatography (SCIC) techniques have also been used to separate the lower sulfur anions. Kokkonen and Hyvarinen (1988) separated sulfide, sulfite, sulfate, and thiosulfate under acidic conditions (pH 4.0-6.5) with both silica-based and resin-based low-capacity anion exchange columns. The ions were detected using both indirect ultraviolet absorption and conductivity. The sensitivity using the conductivity detection was in the 1-3 mg/L range and about four times lower using the ultraviolet detector. Story (1983) separated sulfide, sulfite, sulfate, thiosulfate and several polythionates using an ion exchange column with continuous analysis of the column effluent by in-stream oxidation with bromine. The resulting sulfate ion was then measured spectrophotometrically after addition of iron(III) perchlorate to the effluent stream. The procedure is not highly sensitive; however, it is most applicable to aqueous solutions containing 10 mg/L or more of the anion of interest. Poulson and Borg (1984) separated sulfide, sulfite, sulfate, thiocyanate, and thiosulfate using SCIC techniques with both silica-based and resin-based anion exchange columns. They used phthalate/borate and gluconate/borate eluents with indirect and direct photometric detection. The indirect photometric detection response was comparable to conductivity detection. However, sulfide could not be separated from early interferences, and neither column provided a good separation of sulfite and sulfate.

The lower polythionates (i.e., trithionate, tetrathionate, pentathionate, and hexathionate) were separated by Pollard et al. (1964) and Iguchi (1958) on anion exchange resin using gravity flow, fraction collection, and analysis of the separate fractions. This method is very slow, however, and not applicable to trace-level analyses. Several polythionates were determined by Wolkoff and Larose (1975) using citrate eluents and cerium(IV) fluorescence detection. This method was not specific enough to be reliable. The detector responds to any oxidizable materials and is insensitive to sulfate.

Recent Developments

Recent developments in ion exchange resins and ion chromatography techniques have made the analysis of sulfur anions much faster and easier than before. A major problem in separating sulfide, sulfite, sulfate, and thiosulfate in the past was the very long retention of thiosulfate compared to the other ions. Johnson (1986) developed columns with special resins for use in separating hydrophobic anions such as thiocyanate and thiosulfate. The ion exchange resins used for the separation of hydrophilic ions (e.g., fluoride, chloride, bromide) are composed of a surface-sulphonated polystyrene/divinylbenzene core surrounded by a porous latex particle that is completely aminated (Figure 1). The latex particles carry the actual ion exchange function $-NR_3^+$, a quaternary ammonium base material. The functional groups on these resins are hydrophobic so that hydrophilic ions are retained longer (Johnson 1986).



Latex-Anion Exchange Particle

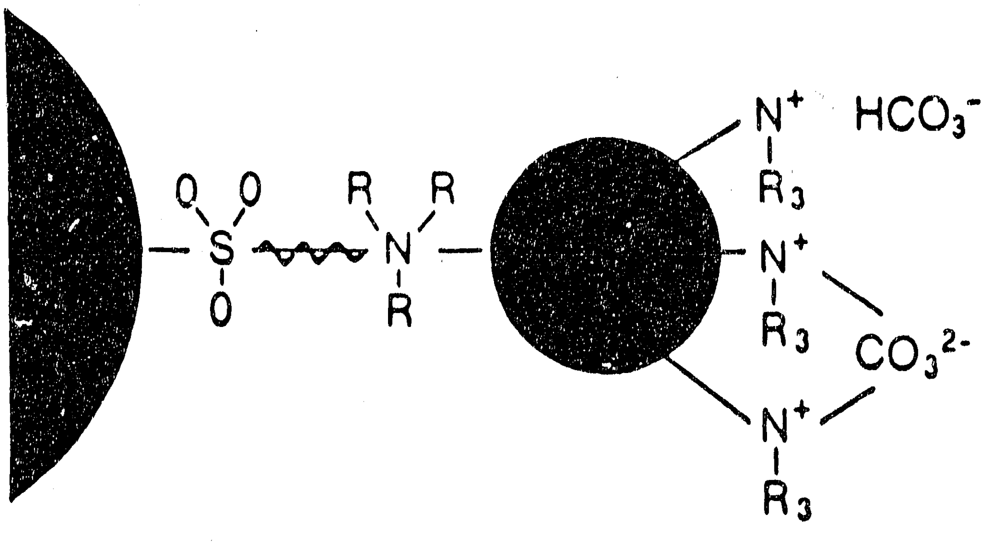


Figure 1. **Structure of a Latex Anion Exchange Resin (Modified from Johnson 1986).**

The AS5 column was developed with a resin designed for separating hydrophobic anions. The structure of the resin is the same as shown in Figure 1, except that the functional groups on the latex particles are more hydrophilic. Hydrophobic anions are not adsorbed onto the stationary phase, and separations can be carried out with standard carbonate/hydrogen carbonate eluents. In order to minimize adsorption effects, a small amount of p-cyanophenol can be added to the eluent. Figure 2 illustrates the effect of p-cyanophenol on iodide and thiocyanate peak tailing (Johnson 1986). However, polythionates, such as tetrathionate, exhibit such strong affinities for the stationary phase that ion exchange technology is of no use in their analysis. A technique called mobile-phase ion chromatography (MPIC) or ion pair chromatography has been successfully used to separate these anions.

Mobile-Phase Ion Chromatography

Wittmer et al. (1975) and Sood et al. (1976) as well as Waters Associates (1975) have found that the addition of lipophilic ions (i.e., alkyl sulphonic acids or quaternary aliphatic amines) to the mobile phase allows solutes with charges opposite to the added material to be separated on reversed-phase (i.e., C18) silica-based columns. This technique was termed reversed-phase ion pair chromatography (RPIPC). The term mobile-phase ion chromatography is essentially the same as RPIPC, except that detection is by conductivity after chemical suppression of the eluent background conductivity. The stationary phase used for this technique is a neutral macroporous polystyrene/divinylbenzene resin with a nonpolar character (Johnson 1986).

MPIC Retention Mechanisms

The retention mechanisms associated with MPIC have not yet been fully investigated. At the present time, three main hypotheses exist. Horvath et al. (1976, 1977) propose that the solute ions form neutral ion pairs with the lipophilic ions in the aqueous phase and are adsorbed onto the neutral stationary phase. The equilibria can be formulated as follows:

$$E + H \underset{}{\overset{K_1}{\rightleftharpoons}} EH$$

$$EH + L \underset{}{\overset{K_2}{\rightleftharpoons}} LEH$$

$$K_1 = \frac{[EH]_m}{[E]_m \cdot [H]_m}$$

$$K_2 = \frac{[LEH]_s}{[EH]_m \cdot [L]_s}$$

The solute ion, E, interacts with the lipophilic ion, H, and forms a complex, EH. This complex is reversibly bound to the stationary phase, L, in the form, LEH. The equilibrium constants K_1 and K_2 indicate the concentrations of individual ions in the mobile and stationary phases by the subscripts m and s, respectively. $[L]_s$ is a measure of the available free surface of the stationary phase (Horvath et al. 1977).

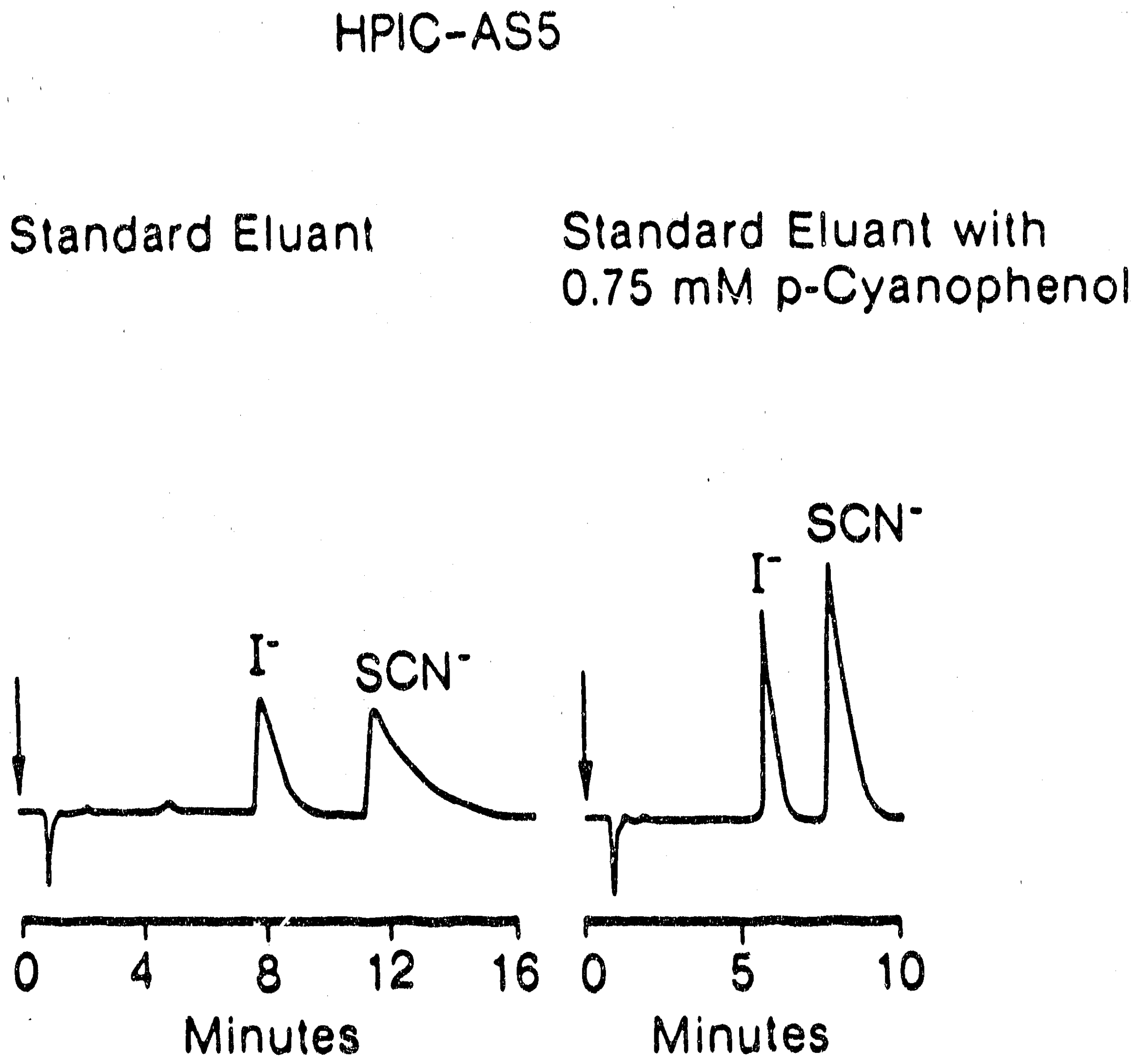


Figure 2. **Influence of p-Cyanophenol on Iodide and Thiocyanate Peak Tailing (Modified from Johnson 1986).**

The second hypothesis is called the ion exchange model and was proposed by Hoffman and Liao (1977) and Kissinger (1977). They propose that the lipophilic ions are adsorbed onto the surface of the stationary phase, forming the complex LH, and effectively turning the stationary phase into an ion exchange material. The solute ion, E, interacts with LH:

$$\mathrm{H} + \mathrm{L} \overset{K_3}{\rightleftharpoons} \mathrm{LH}$$

$$\mathrm{LH} + \mathrm{E} \overset{K_4}{\rightleftharpoons} \mathrm{LEH}$$

$$K_3 = \frac{[\mathrm{LH}]_s}{[\mathrm{H}]_m \cdot [\mathrm{L}]_s}$$

$$K_4 = \frac{[\mathrm{LEH}]_s}{[\mathrm{LH}]_s \cdot [\mathrm{E}]_m}$$

Bidlingmeyer et al. (1979) and Bidlingmeyer (1980) proposed an ion interaction model to explain retention mechanisms involved in MPIC separations. The model was derived from conductivity measurements and does not assume the formation of ion pairs or the presence of ion exchange processes. The model proposes that due to the nonpolar character of the stationary phase and the polar character of the mobile phase, high surface tension exists at the phase boundary. The stationary phase has an affinity for components in the mobile phase, such as quaternary ammonium bases, that can reduce the surface tension. An electrical double-layer develops on the surface of the stationary phase, while lipophilic ions added to the mobile phase (i.e., quaternary ammonium cations) and the organic modifier (acetonitrile) are adsorbed onto the surface of the stationary phase. The corresponding counterions (OH^- with conductivity detection) and the analyte anions (A^-) make up the diffuse outer region. This concept is illustrated in Figure 3. The selectivity of the system is derived from the dependence of the charge density in the double layer outer region on the degree of hydration of the counterions. In short, the ions with the smallest enthalpy of hydration have the longest retention times.

MPIC Applications

Mobile-phase ion chromatography is a very powerful tool with applications in many areas. Hydrophobic ions previously not analyzable by ion chromatography may be separated using MPIC techniques. Johnson (1986) successfully separated many inorganic polythionates as well as organic sulfur-containing compounds, such as mercaptans, polysulfides, and di- and polysulfuric acids. Figure 4 shows a chromatogram separating the lower polythionates. In order to analyze higher polythionates ($S_nO_6^{2-}$), (n > 2) only the concentration of acetonitrile in the eluent needs to be increased.

Objective

The objective of this study was to develop suppressed ion chromatography methods to determine the sulfur anions: sulfide, sulfite, sulfate, thiocyanate, thiosulfate, and tetrathionate. Ideally, the final method will separate all the anions of interest in one run with minimal background interferences. Method-challenging steps include repeatability, sample size variation, sensitivity, and spiking experiments to assure that quality control measures are adequately met.

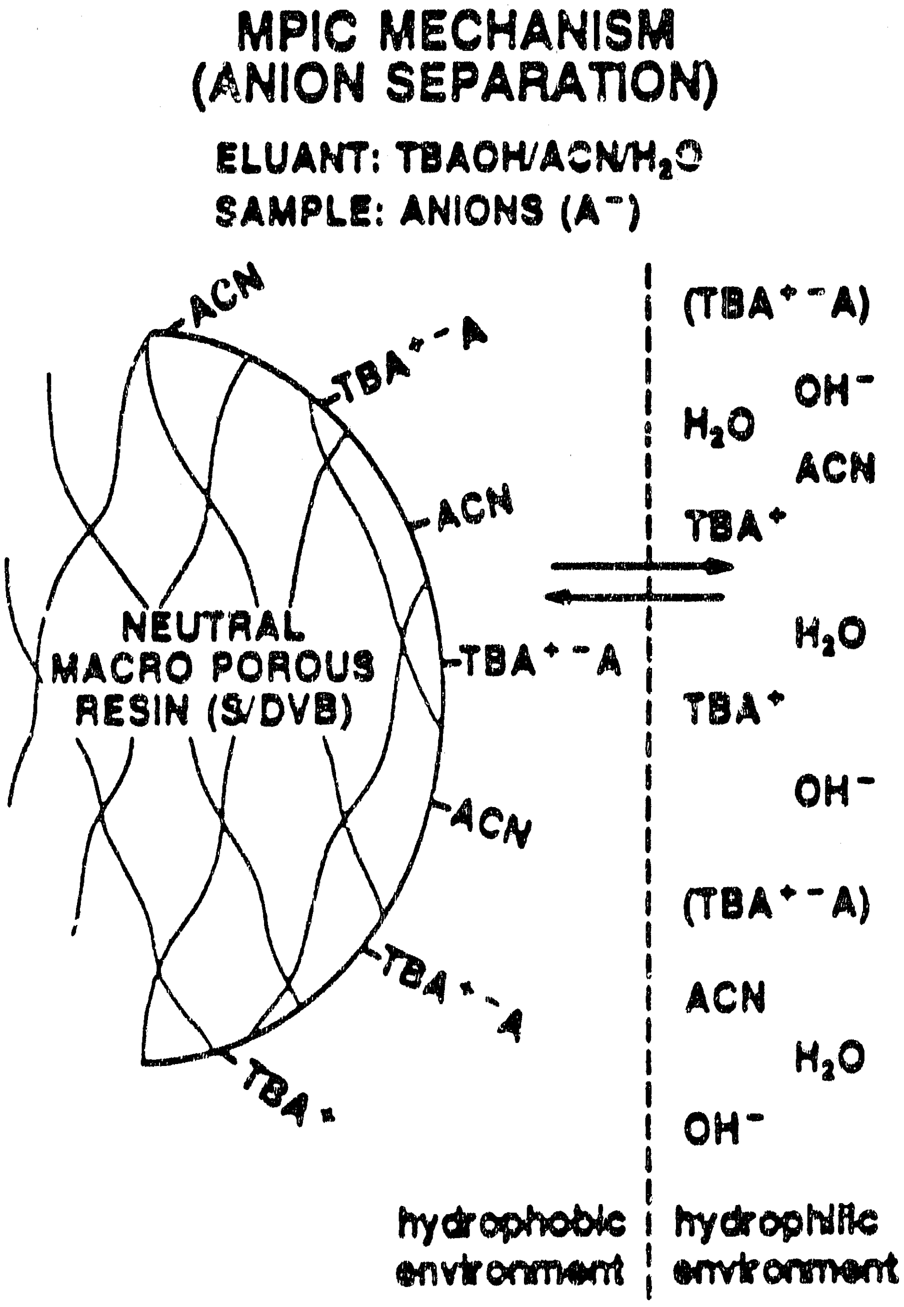
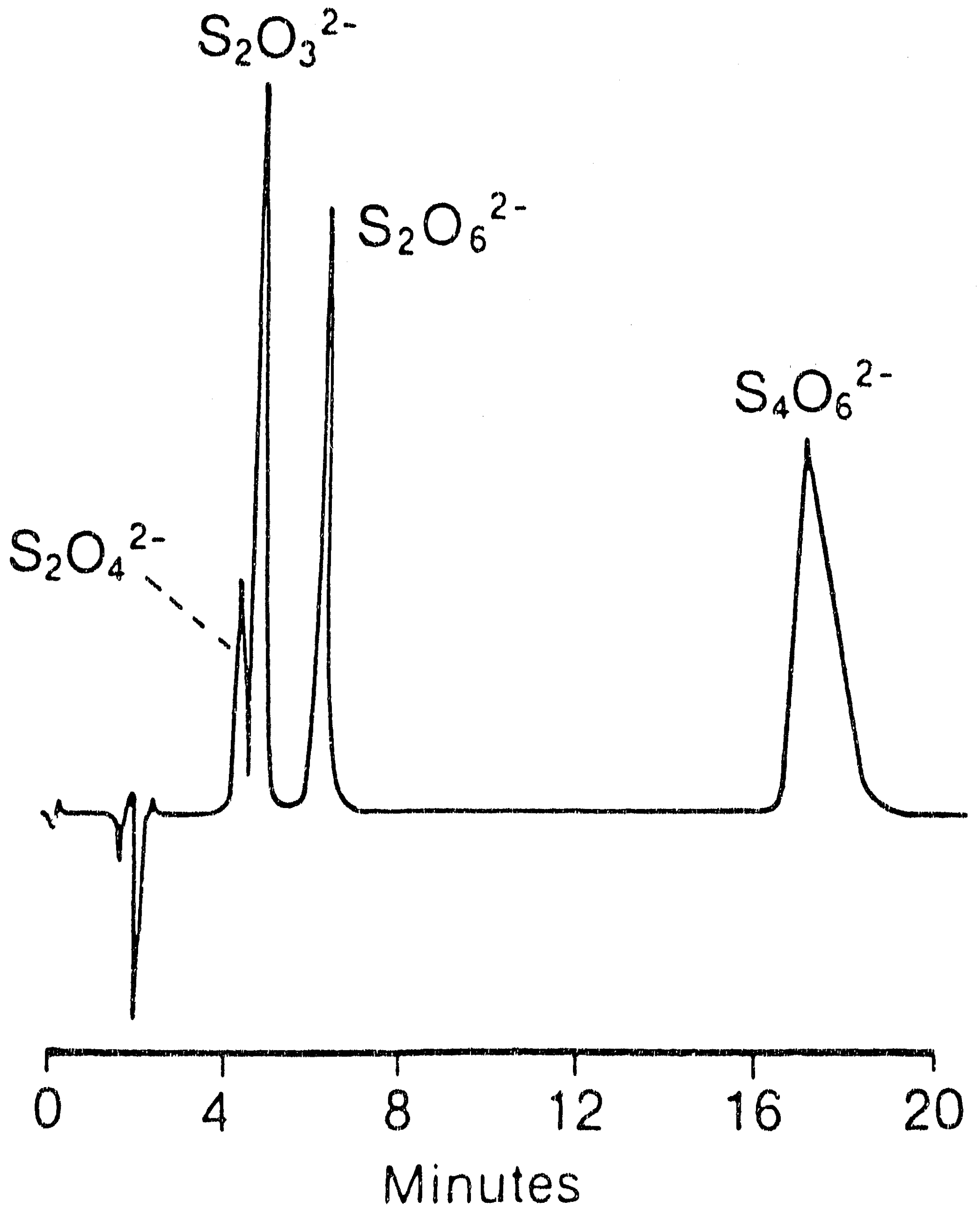


Figure 3. Ion Interaction Model for MPIC Separations (Modified from Johnson 1986).



Analysis of Sulfur Species Using MPIC

Eluent: 2 mM TBAOH + 1 mM Na_2CO_3 + 20% acetonitrile

Figure 4. **Analysis of Polythionates by MPIC (Modified from Johnsen 1986).**

EXPERIMENTAL

Instrumentation

A Dionex model 4040i dual channel ion chromatograph was used in this study. The instrument was equipped with a model CHA-6 valve module, an eluent degassing module, a computer interface module, an Autoion 400 control system, and a micromembrane suppression system. An autosampler was used for sample injection into 50-μL and 100-μL sample loops. The sulfur anions were detected with a Dionex conductivity detector. Data were collected and stored with a Mitsubishi IMS286 computer and disc drive.

Ion Chromatograph Operating Conditions

The operating conditions for the ion chromatograph are listed in Table 1. Two types of columns were used in this study. The lower sulfur anions were separated using an HPIC AG5 guard column and an AS5 high capacity anion exchange column. Tetrathionate was chromatographed using an Ionpac NG1 guard column and NS1 separator column. The NS1 column is packed with a highly crosslinked macroporous resin suitable for MPIC separations with suppressed conductivity detection.

A bicarbonate/carbonate eluent was used with the AS5 column. The eluent contained p-cyanophenol in 2 vol % acetonitrile to improve the peak shapes of strongly retained anions. Isopropanol was added to the eluent as a preservative to prevent oxidation of unstable ions. Several eluents were tried with the NS1 column. The eluent providing the most efficient analysis of tetrathionate contained tetrapropylammonium hydroxide (TPAOH) as the ion pairing reagent, sodium hydroxide as the inorganic modifier, and acetonitrile as the organic modifier. The regenerant was the same for both suppressor systems.

Table 1. Chromatographic Conditions

	AS5 Column	NS1 Column
Eluent	0.0040 M Na_2CO_3 plus 0.0043 M $NaHCO_3$ plus 0.0008 M p-cyanophenol in 2% v/v acetonitrile 10% isopropanol	0.0020 M TPAOH plus 0.0010 M Na_2CO_3 plus 15% v/v acetonitrile
Eluent Flow	1.5 mL/minute	1.0 mL/minute
Analytical Column	HPIC AS5 Anion Exchange	Ionpac NS1 MPIC Ion Pairing
Suppressor	Anion Suppressor (Dionex)	Anion-MPIC Suppressor (Dionex)
Regenerant	0.025 N H_2SO_4 in deionized water	0.025 N H_2SO_4 in deionized water

Reagents

All inorganic reagents used were 98%+ purity. Deionized-distilled water was prepared daily and had a background resistance of greater than 18 megaohms. The standards used were sodium sulfite, sodium sulfate, potassium thiocyanate, sodium thiosulfate, and sodium tetrathionate. The eluent for the AS5 column was prepared from Primary Standard sodium carbonate, sodium bicarbonate, p-cyanophenol, HPLC-grade acetonitrile, and HPLC-grade isopropanol. The eluent for the NS1 column was prepared by diluting 1.0 M tetrapropylammonium hydroxide to the desired concentration and adding Primary Standard sodium carbonate and HPLC-grade acetonitrile. The eluents were prepared using deionized-distilled water of greater than 18-megaohm purity and were continually degassed and pressurized under a helium atmosphere while in use.

Standard Solutions

The problem of sulfite oxidation exists when preparing sulfite standards. Oxidation inhibitors such as isopropanol, formaldehyde, or D-mannitol may be added to the standard solution to prevent oxidation. Dionex Corporation recommends using D-mannitol as an oxidation inhibitor. Concentrations of D-mannitol as high as 50 mM were added to the standard solutions and the eluent, but significant oxidation of sulfite to sulfate still occurred. Figure 5 shows a chromatogram of a 10-mg/L sulfite standard preserved with 50 mM D-mannitol. Two peaks are evident, a small sulfite peak, and a larger sulfate peak. Formaldehyde was also tried as an oxidation inhibitor, but it forms a complex with sulfite making it an unsuitable preservative. The addition of 10 vol % isopropanol to the standard solutions and eluent proved to be the most satisfactory preservation technique. Figure 6 shows a chromatogram of a 10-mg/L sulfite standard preserved with 10 vol % isopropanol. The sulfate peak that was evident in Figure 5 is negligible when isopropanol is used as a preservative.

Stock standard solutions with 1000-mg/L concentrations were prepared in deionized-distilled water. The stock sulfite standard was prepared in deionized-distilled water with 10 vol % isopropanol added as an oxidation inhibitor. Appropriate dilutions were made into eluent solution just prior to injection. Multilevel calibration runs were performed using 1-, 5-, and 10-mg/L standards. Method challenging procedures were followed to determined the precision and accuracy of the two analyses. Calibration curves were constructed through the data using least-squares regression analysis. Concentrations of components in sample leachates were calculated by relating the measured area of the component to its individual calibration curve.

Preparation of Leachates

The spent oil shale leachates were prepared as follows: reference eastern, reference western, and Rio Blanco spent oil shales were placed in vessels, and humidified air was continuously passed over them. Every seven days, deionized-distilled water was added to the vessel to establish a 1:1 solid-to-solution ratio. After one hour, the solution was separated from the spent oil shale by filtration through Whatman #42 filter paper. The shales were then allowed to air dry, and the seven-day cycle was repeated. The filtrates were preserved with isopropanol and stored at 4°F until they were analyzed for sulfur-containing anions.

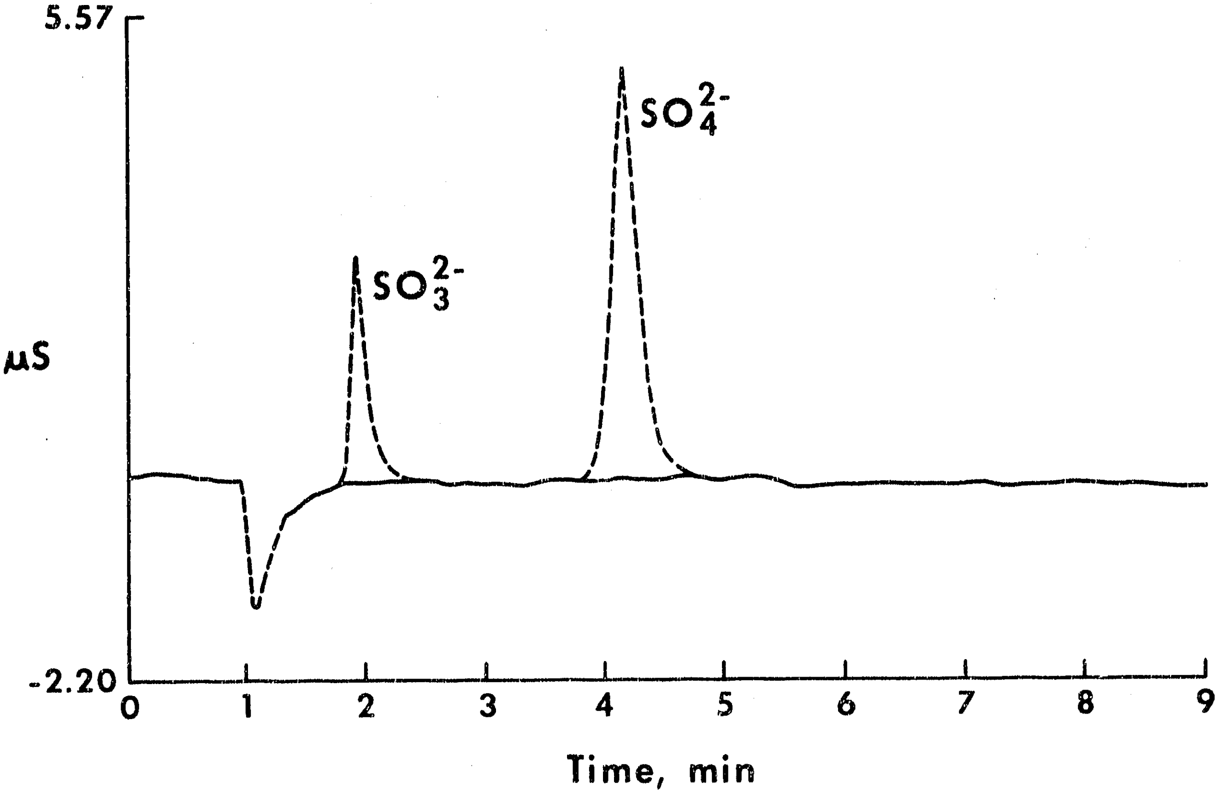


Figure 5. Sulfite Standard Preserved with 50 mM D-mannitol. Column, Dionex AS5; Eluent, 4.3 mM $NaHCO_3$, 4.0 mM Na_2CO_3, 0.8 mM p-cyanophenol, 2 v/v% Acetonitrile, 50 mM d-mannitol; Conductivity Detection.

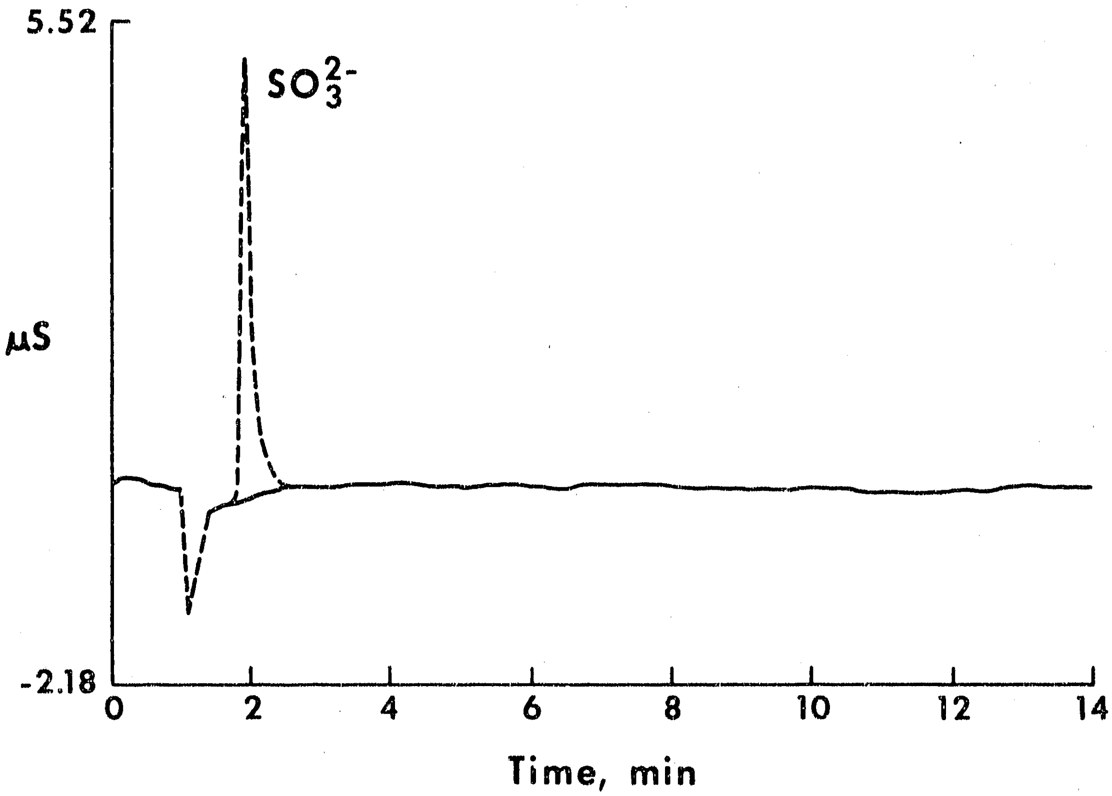


Figure 6. **Sulfite Standard Preserved with 10 % Isopropanol. Column, Dionex AS5; Eluent, 4.3 mM $NaHCO_3$, 4.0 mM Na_2CO_3, 0.8 mM p-cyanophenol, 2 v/v% Acetonitrile, to mM d-mannitol, Conductivity Detection.**

RESULTS AND DISCUSSION

Optimization of Mobile Phase

MPIC techniques using the HPIC-NS1 column were evaluated initially to separate sulfide, sulfite, sulfate, thiocyanate, thiosulfate, and tetrathionate in one run. The eluent composition chosen for this separation was based on three main factors affecting retention and detection: (1) type and concentration of ion-pairing reagent, (2) type and concentration of organic modifiers, and (3) addition of inorganic modifiers.

The most common ion-pairing reagents used in MPIC are ammonium hydroxide (NH_4OH), tetrapropylammonium hydroxide (TPAOH), and tetrabutylammonium hydroxide (TBAOH). The selection of ion-pairing reagent depends on the hydrophobicity of the analyte. Hydrophilic anions are best separated with a hydrophobic ion-pairing reagent such as TBAOH. More hydrophobic ions require a hydrophilic ion-pairing regent, such as NH_4OH. The next major constituent in the eluent is the organic modifier. The addition of an organic modifier such as acetonitrile or methanol makes the mobile phase more like the stationary phase and, thus, decreases retention. By using different combinations of ion-pairing reagents and organic modifiers, a separation can be optimized according to the desired resolution and run time. When using TBAOH or TPAOH as an ion-pairing reagent, sodium carbonate is usually added to the eluent as an inorganic modifier. Although the behavior or influence of CO_3^{2-} in the separation process is not clearly understood, it is thought to compete with the analyte ion for the pairing reagent. Its effect on the separation is to decrease retention times and improve peak shapes. The normal range of CO_3^{2-} added to the eluent is from 0.1 to 1.0 mM Na_2CO_3.

In this study, several combinations of ion-pairing reagents and organic modifiers were used. Tetrabutylammonium hydroxide was chosen first as the ion-pairing reagent. The eluent was composed of 0.002 M TBAOH, 0.001 M sodium carbonate, and acetonitrile concentrations that range from 15-25 vol %. This eluent successfully eluted tetrathionate in a reasonable time, but it provided a poor separation between sulfate and thiosulfate. The ion-pairing reagent was changed to tetrapropylammonium hydroxide to improve the resolution between sulfate and thiosulfate. The TPAOH is a smaller pairing reagent, so separations are based more on the molecular structure of the analyte than on the contribution of the ion-pairing reagent. The eluent using TPAOH consisted of several different combinations of 1-2 mM TPAOH, 0.5-1 mM Na_2CO_3, and 5-10 vol % acetonitrile. All the eluent combinations successfully eluted tetrathionate in a reasonable time, but none of the eluents provided good resolution between sulfate and thiosulfate. The similar retention of sulfate and thiosulfate seemed to be a function of the column and its efficiency. Dionex Corporation has since introduced a NS1 column with smaller particle diameters and higher efficiency that will better suit this separation.

Because the NS1 column did not acceptably separate sulfate and thiosulfate, we decided to separate the lower sulfur-containing anions using ion exchange chromatography with the AS5 column. This column is more suited to separating hydrophobic anions like thiosulfate, but efficient enough to separate similar species, such as sulfite and sulfate. A standard bicarbonate/carbonate eluent was used with p-cyanophenol added to improve the peak shapes of strongly adsorbed ions. Isopropanol was added to prevent oxidation of unstable ions. Although the technique separated all the anions (sulfide, sulfite, sulfate, thiocyanate, and thiosulfate) satisfactorily, the sulfide response to conductivity detection was very poor. The low response is due to reactions that take place in the suppressor system. The background conductivity is reduced by replacing the counterions from the electrolyte with either H$^+$ or OH$^-$ (Small 1983). The low-conductance acid, H$_2$S, is formed from the sulfide ions and leads to poor response with conductivity detection. The use of amperometric detection in conjunction with conductivity detection is necessary to accurately quantify sulfide. This will be the subject of future work.

The polythionate ion tetrathionate was too strongly adsorbed on the AS5 column to be chromatographed, so the NS1 column with MPIC was used. The eluent consisted of tetrapropylammonium hydroxide, sodium carbonate, and acetonitrile in concentrations to produce a run time of about 5 minutes.

Precision

The precision of the two methods was tested by ten repeat injections of standards ranging from 1 to 10 mg/L (Table 2). The standard deviations of measured concentrations using a 50-μL loop ranged from 0.15 to 0.51 with the AS5 column and 0.15 to 0.29 with the NS1 column.

Detection Limits

The method detection limit (MDL) for both methods using a 50-μL sample loop was calculated as the threefold signal-to-noise ratio of the baseline ($S/N = 3$). The MDLs for each analyte are listed in Table 3.

Calibration Plots

Calibration plots of peak area versus solute ion concentration were linear for all anions in concentrations ranging from 0 to 10 mg/L. The coefficient of correlation, r, was greater than 0.995 in all cases.

Spiking Experiments

Several spiking experiments were performed to ensure adequate recovery of the analyte. A laboratory quality control check sample was prepared as follows. Using stock standards, a 1000-mg/L check sample was prepared in reagent water preserved with 10 v/v % isopropanol. Four 10-mg/L aliquots of the check sample were then made by dilution in 100 mL of reagent water. Each aliquot was then analyzed using the AS5 column for the lower sulfur-containing anions and the NS1 column for tetrathionate. A leachate sample was selected at random and spiked with 10 mg/L of the standards. Four aliquots of the spiked sample were run to monitor analyte recoveries. The average percent recovery (R) and the standard deviation (s) of the percent recovery are listed in Table 4. The data show essentially quantitative recovery in all cases.

Table 2. Precision of IC Analysis Using AS5 Column[a]

	Injection Volume, μL	Concentration, mg/L	Std. Dev. mg/L
<u>AS5 Column[a]</u>			
SO_3^{2-}	50	10	0.51
	100	5	0.21
SO_4^{2-}	50	1	0.15
	100	10	0.24
SCN^-	50	5	0.22
	100	10	0.23
$S_2O_3^{2-}$	50	10	0.31
	100	10	0.29
<u>NSI Column[b]</u>			
$S_4O_6^{2-}$	50	1	0.15
		5	0.20
		10	0.28
	100	1	0.18
		5	0.22
		10	0.29

[a] Column, HPIC-AS5; Eluent, 4 mM Na_2CO_3, 4.3 mM $NaHCO_3$, 0.8 mM p-cyanophenol, 2% acetonitrile, 10% isopropanol; detection, conductivity

[b] Column, Ionpac NS1; Eluent, 2 mM TPAOH, 1 mM Na_2CO_3, 15% acetonitrile; detection, conductivity

Table 3. Detection Limits for Sulfur Anions, mg/L

Injection Volume	SO_3^{2-}	SO_4^{2-}	SCN^-	$S_2O_3^{2-}$	$S_4O_6^{2-}$
50 μL loop	0.10	0.01	0.02	0.02	0.09

Chromatographic conditions as in Table 1.

Detection limit calculated from data obtained using a detector setting of 100 μS full scale.

Table 4. Single-Operator Accuracy and Precision

Analyte	Sample Type	Spike, mg/L	No. Replicates	Mean Recovery, %	Standard Deviation, mg/L
SO_3^{2-}	RW	10.0	4	101	0.62
	LW	10.0	4	106	0.30
SO_4^{2-}	RW	10.0	4	105	0.18
	LW	10.0	4	101	0.35
SCN^-	RW	10.0	4	101	0.29
	LW	10.0	4	99.5	0.12
$S_2O_3^{2-}$	RW	10.0	4	102	0.06
	LW	10.0	4	96.8	0.10
$S_4O_6^{2-}$	RW	10.0	4	98.3	0.33
	LW	10.0	4	99.1	0.33

RW = Reagent Water preserved with 10 v/v% isopropanol
LW = Leachate Water, unpreserved

Leachate Analyses

A typical chromatogram from a spent western reference oil shale leachate is shown in Figure 7. The results of leachates analyses are listed in Table 5. They were not preserved before analysis. The leachates with the prefix BW are blank waters submitted with each successive leachate set. The main constituent of all the leachates is sulfate with minor amounts of thiocyanate and thiosulfate. None of the leachates analyzed contained sulfite or tetrathionate.

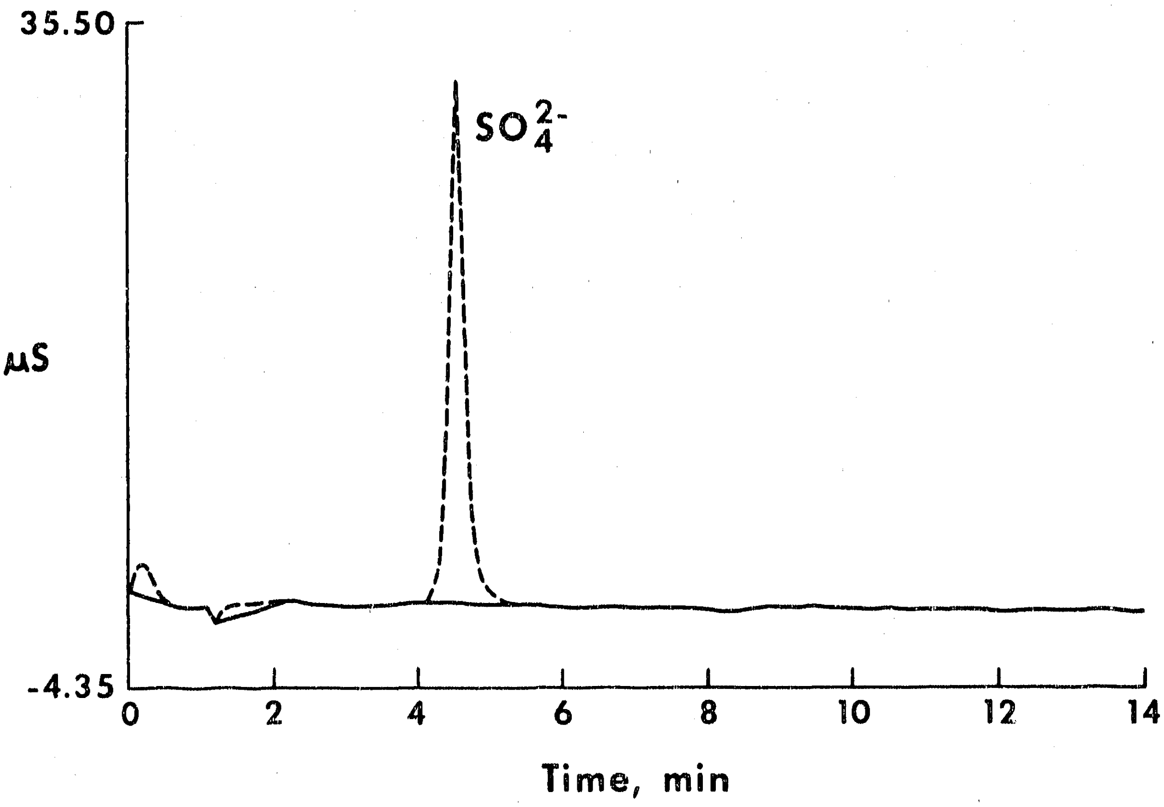


Figure 7. Ion Chromatogram of Western Refernce Spent Oil Shale Leachate. Sample CW1-E. Dilution, 100x, Column, Dionex AS5. Eluent, 4.3 mM $NaHCO_3$, 4.0 mM Na_2CO_3, 0.8 mM p-cyanophenol, 2 v/v% Acetonitrile, 10% Isopropanol, Conductivity Detection.

Table 5. Spent Oil Shale Leachates Analysis for Sulfur-Containing Anions, mg/L

Sample	SO_3^{2-}	SO_4^{2-}	SCN^-	$S_2O_3^{2-}$	$S_4O_6^{2-}$
BW-1	<0.1	<0.01	<0.02	<0.01	<0.1
BW1-B	<0.1	<0.01	<0.02	<0.01	<0.1
BW1-C	<0.1	<0.01	<0.02	<0.01	<0.1
BW1-D	<0.1	<0.01	<0.02	<0.01	<0.1
BW1-E	<0.1	<0.01	<0.02	<0.01	<0.1
BW1-F	<0.1	<0.01	<0.02	<0.01	<0.1
BW1-G	<0.1	<0.01	<0.02	<0.01	<0.1
BW1-H	<0.1	<0.01	<0.02	<0.01	<0.1
BW1-I	<0.1	<0.01	<0.02	<0.01	<0.1
BW1-J	<0.1	<0.01	<0.02	<0.01	<0.1
RB1	<0.1	1,910.	0.60	12.9	<0.1
RB1-B	<0.1	2,050.	0.48	19.7	<0.1
RB1-C	<0.1	3,640.	0.52	2.81	<0.1
RB1-D	<0.1	2,850.	<0.02	2.45	<0.1
RB1-E	<0.1	3,320.	<0.02	0.66	<0.1
RB1-F	<0.1	2,510.	0.68	1.79	<0.1
RB1-G	<0.1	1,670.	<0.02	0.53	<0.1
RB1-H	<0.1	1,130.	<0.02	1.29	<0.1
RB1-I	<0.1	900.	<0.02	1.24	<0.1
RB1-J	<0.1	814.	<0.02	0.74	<0.1
RB2	<0.1	2,070.	0.60	14.9	<0.1
RB2-B	<0.1	1,880.	0.79	19.1	<0.1
RB2-C	<0.1	2,920.	0.61	7.73	<0.1
RB2-D	<0.1	2,820.	<0.02	1.17	<0.1
RB2-E	<0.1	2,970.	<0.02	0.81	<0.1
RB2-F	<0.1	2,420.	0.49	0.76	<0.1
RB2-G	<0.1	1,510.	<0.02	0.56	<0.1
RB2-H	<0.1	975.	<0.02	0.65	<0.1
RB2-I	<0.1	954.	<0.02	0.86	<0.1
RB2-J	<0.1	1,020.	<0.02	0.75	<0.1
CW1	<0.1	5,070.	0.81	8.11	<0.1
CW1-B	<0.1	3,770.	2.58	16.7	<0.1
CW1-C	<0.1	3,230.	0.98	5.31	<0.1
CW1-D	<0.1	3,270.	0.40	1.61	<0.1
CW1-E	<0.1	3,500.	0.91	4.99	<0.1
CW1-F	<0.1	4,400.	0.77	2.80	<0.1
CW1-G	<0.1	4,760	0.51	1.21	<0.1
CW1-H	<0.1	4,340	0.74	1.53	<0.1
CW1-I	<0.1	4,530.	0.80	0.85	<0.1
CW1-J	<0.1	4,560.	0.43	<0.01	<0.1

Table 5. Spent Oil Shale Leachates Analysis for Sulfur-Containing Anions, mg/L (continued)

Sample	SO_3^{2-}	SO_4^{2-}	SCN^-	$S_2O_3^{2-}$	$S_4O_6^{2-}$
CW2	<0.1	4,440.	0.54	9.31	<0.1
CW2-B	<0.1	3,490.	0.47	13.8	<0.1
CW2-C	<0.1	3,440.	0.91	4.99	<0.1
CW2-D	<0.1	3,410.	0.84	1.14	<0.1
CW2-E	<0.1	3,750.	0.95	1.20	<0.1
CW2-F	<0.1	5,230.	0.52	0.75	<0.1
CW2-G	<0.1	4,640.	0.41	<0.01	<0.1
CW2-H	<0.1	4,860.	0.43	<0.01	<0.1
CW2-I	<0.1	4,330.	<0.02	<0.01	<0.1
CW2-J	<0.1	3,300.	<0.02	<0.01	<0.1
TR23-1	<0.1	5,600.	9.78	13.2	<0.1
TR23-1B	<0.1	3,970.	16.2	0.51	<0.1
TR23-1C	<0.1	3,510.	7.77	2.80	<0.1
TR23-1D	<0.1	2,470.	3.75	2.06	<0.1
TR23-1E	<0.1	2,130.	2.17	1.15	<0.1
TR23-1F	<0.1	1,940.	1.42	0.72	<0.1
TR23-1G	<0.1	1,630.	0.87	0.75	<0.1
TR23-1H	<0.1	1,760.	0.86	0.77	<0.1
TR23-1I	<0.1	998.	1.57	<0.01	<0.1
TR23-1J	<0.1	995.	1.19	<0.01	<0.1
TR23-2	<0.1	5,900.	7.22	12.7	<0.1
TR23-2B	<0.1	3,400.	14.5	0.58	<0.1
TR23-2C	<0.1	3,350.	9.11	2.14	<0.1
TR23-2D	<0.1	2,300.	2.81	1.45	<0.1
TR23-2E	<0.1	1,900.	2.12	0.68	<0.1
TR23-2F	<0.1	2,150.	1.65	<0.01	<0.1
TR23-2G	<0.1	1,690.	1.01	<0.01	<0.1
TR23-2H	<0.1	1,550.	1.00	<0.01	<0.1
TR23-2I	<0.1	1,280.	0.56	<0.01	<0.1
TR23-2J	<0.1	950.	0.83	0.63	<0.1

CONCLUSIONS

- Recent developments in ion exchange resins have made the analysis of hydrophobic sulfur-containing anions much faster and more efficient. These developments include a new ion exchange resin with hydrophilic functional groups so hydrophobic anions are not adsorbed onto the stationary phase, and separations can be carried out with standard bicarbonate/carbonate eluents. The addition of p-cyanophenol to the eluent solves the problem of peak tailing on hydrophobic anions.

- The development of mobile-phase ion chromatography (MPIC) techniques have made the determination of polythionates possible with ion chromatography. The technique is similar to reversed-phase ion pair chromatography, except that detection is by suppressed conductivity.

- MPIC was used in this study to try and separate sulfide, sulfite, sulfate, thiocyanate, thiosulfate, and tetrathionate in one run. Several combinations of ion-pairing reagents and modifiers were tried, but the column did not provide adequate resolution between sulfate and thiosulfate.

- An AS5 column was used to separate sulfide, sulfite, sulfate, thiocyanate, and thiosulfate. The sulfide response to conductivity detection was very poor, so it was dropped from the current study. The addition of an amperometric detector is necessary to accurately quantify sulfide, and this will be used in conjunction with conductivity detection in this method in future work.

- The MPIC-NS1 column was used to determine tetrathionate. The eluent was adjusted to elute tetrathionate in about 5 minutes.

- Method-challenging experiments performed included repeatability, sample size variation, and spiking studies. All analytes displayed acceptable recoveries in the spiking experiments. Calibration plots were constructed for each analyte, and the coefficient of correlation was greater than 0.995 in each case.

ACKNOWLEDGMENT

The support for this work from the United States Department of Energy under Cooperative Agreement Number DE-FC21-86MC11076 is greatly appreciated.

DISCLAIMER

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