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DETERMINATION OF SULFUR SPECIES IN OIL SHALE WASTE WATERS BY ION CHROMATOGRAPHY

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ABSTRACT

Ion chromatography was evaluated for analysis of sulfur (S) species in oil shale waste waters. Chromatographic separation of $S_2O_3^{2-}$ and SCN^-, the effect of high salt concentration on the elution of SO_4^{2-}, and the inherent instability of S species in the samples are discussed. Several sulfur-oxide anions, including $S_2O_4^{2-}$, $S_2O_5^{2-}$, $S_2O_6^{2-}$, and $S_2O_7^{2-}$ were unstable when added to solution, forming SO_3^{2-} and SO_4^{2-}. However the method proved applicable to determination of SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$ and SCN^- in oil shale retort water and from retorted shale in both laboratory and field studies.

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DETERMINATION OF SULFUR SPECIES IN OIL SHALE WASTE WATERS BY ION CHROMATOGRAPHY

INTRODUCTION

Oil shale deposits of greatest current economic potential occur within the Green River formation in Colorado, Utah, and Wyoming (Figure 1). Shaded areas on the map represent other oil shale deposits of lesser potential yield. Research directed toward the environmental impact of the development of an oil shale industry has included a multi-disciplinary team of chemists, microbiologists, soil scientists, plant physiologists, and hydrologists at Pacific Northwest Laboratory.

Our studies are currently centered in the Piceance Basin in northwestern Colorado (Figure 2). This is the location of several shale mining and process development sites -- such as modified in situ retorting processes at Occidental and Rio Blanco, and the above-ground retorting Paraho process at Anvil Points.

The oil shale is heated (retorted) to produce oil and the various processes yield large volumes of retorted shale and waste water. It is the interaction of these wastes with surface or ground water that is of great environmental concern. Early laboratory studies indicated that leaching of retorted shale by natural precipitation gave highly saline, caustic solutions, with pH values greater than 11. The exact values were somewhat dependent on retorting conditions, such as process type, temperature, and time of contact. Therefore, this study was to determine the sulfur species that were found in waters leached from retorted shale.

Our field studies, conducted with retorted shale from the Paraho process, revealed a significant reduction in pH in percolates from large irrigated retorted-shale lysimeters after one year of weathering. Subsequent studies indicated that this pH reduction probably resulted from oxidation of reduced sulfur species. Mechanisms of sulfur oxidation in these waters must be established in order to predict the long-term effects of weathering. We therefore are developing analytical methods that could rapidly and precisely measure sulfate and reduced sulfur species in water solutions of highly variable composition.

METHODS AND RESULTS

The Dionex Model 10 Ion Chromatograph satisfies many of these criteria (Figure 3). Ion chromatography (IC) is ion exchange separation followed by eluent suppression and conductimetric detection. For anion analyses done here, a low-capacity anion exchange resin separated the anions in the eluent stream. This stream passed through the suppressor column, a high-capacity cation exchange resin, where eluent and sample ions were converted to their acidic forms.

Eluents were chosen that resulted in low-conducting species at this point. The eluent stream proceeded to the conductivity cell, where the ions of interest were detected as peaks against the eluent's low-conductance background. Over a wide range of concentrations, the peak height is linear with concentration. For most anions studied, concentrations of less than 1 ppm were easily seen unless greatly obscured by high concentrations of neighboring ions.

Sulfur-containing anions of current interest are listed in Table 1. Sulfide was analyzed via specific ion electrode, since its acidic form (H_2S) has very low conductivity and therefore poor sensitivity on the IC in its normal operating mode.

SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, and SCN^- are now analyzed on a routine basis. The potential for presence of the larger sulfur-oxy anions listed will be discussed below; their structures are included here to show their similarities. The lack of stability of SO_3^{2-} has been a long-standing problem. Addition of formaldehyde stabilizes SO_3^{2-}, but in the IC, it also shifts SO_3^{2-} peaks to a shorter elution time and decreases its sensitivity. Thiosulfate also stabilizes sulfite. However, addition of this ion would mask the presence of any $S_2O_3^{2-}$ in the original sample. Isopropanol has been shown to be inferior to formaldehyde as a preservative. EDTA cannot be used because it adds interfering peaks in the IC analysis. We concluded that the best policy was to assure a minimum holding time between sampling and analysis.

We therefore took the IC in a lab trailer directly to the Paraho site. Samples collected in the field could then be analyzed within minutes, if necessary. Samples collected from the more distant sites were sealed and chilled and analyzed within a few hours. Immediate analysis was preferred for both SO_3^{2-} and S^{2-} determination. Their instability may be the cause of the observed change with time in E_h and pH of some samples.

Several IC eluent systems have been investigated for speed and accuracy of anion separations. For sulfite and sulfate, the so-called "standard eluent," 3m$\underline{M}$ $NaHCO_3$ + 2.4 m$\underline{M}$ Na_2CO_3, is still preferred. Figure 4 shows relative peak heights and elution times of SO_3^{2-} and SO_4^{2-} with several other ions which could potentially be present in samples. These are not detection limits, which are usually much less than 1 ppm under routine conditions, but are merely chromatograms run about midrange of IC instrumental capability.

A method using standard eluent to separate SO_3^{2-} and SO_4^{2-}, followed by triple strength standard eluent to elute $S_2O_3^{2-}$ has been published.* However, we found that if SCN^- is also present, it would elute in combination with $S_2O_3^{2-}$ under such a program. Conclusive separation of SCN^- and $S_2O_3^{2-}$ (Figure 5) required use of triple-strength standard eluent alone, sacrificing SO_3^{2-} resolution. This was still no problem in the many samples lacking SO_3^{2-}. Here again, peaks are shown for their relative sensitivities, not detection limits. Of the other eluents studied for $S_2O_3^{2-}$ and SCN^- resolution, 6 m$\underline{M}$ CO_3^{2-} showed partial separation which was only slightly improved by the addition of 1 m$\underline{M}$ hydroxide; 0.5 m$\underline{M}$ citrate proved to be a very fast and efficient eluent for SO_4^{2-}, $S_2O_3^{2-}$, and SCN^-, provided SO_3^{2-} was absent. Nonreproducible profiles in the SO_3^{2-} to SO_4^{2-} region resulted from the addition of SO_3^{2-}, suggesting some reaction within the column system due to presence of citrate eluent.

Of the other sulfur-oxy anions in Table 1, several showed instability in aqueous solutions of their salts when analyzed by IC (Table 2). $S_2O_4^{2-}$

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* Holcombe, L. J., and B. F. Jones, F. B. Meserole. The quantitative determination of aqueous solutions of sulfite, sulfate and thiosulfate using ion chromatography. Second National Symposium on Ion Chromatographic Analysis of Environmental Pollutants - Oct. 11-13, 1978, Raleigh, N.C.

shows partial breakdown, with a significant unaccounted portion. $S_2O_5{}^{2-}$ converts nearly completely to $SO_3{}^{2-}$. $S_2O_6{}^{2-}$ has been shown to elute after SCN^-, but with much poorer sensitivity, bad tailing, and an elution time highly dependent on concentration. $S_2O_7{}^{2-}$ hydrolizes fairly rapidly to $SO_4{}^{2-}$. $S_2O_8{}^{2-}$ and $S_4O_6{}^{2-}$ were not eluted even under very stringent conditions. $S_2O_8{}^{2-}$ would elute only if the separator column was totally bypassed. Since this is a powerful oxidizing agent, it would not be expected to remain intact in other than a pure solution. This was demonstrated when an aliquot of $S_2O_8{}^{2-}$ added to retort H_2O resulted in an increase in $SO_4{}^{2-}$ and decrease in original $S_2O_3{}^{2-}$ peak. $S_2O_6{}^{2-}$ remained stable when added to retort water. Addition of other oxy-anions to retort water altered the original $SO_3{}^{2-}$ - $SO_4{}^{2-}$ - $S_2O_3{}^{2-}$ ratios, usually in favor of $SO_3{}^{2-}$. This is in contrast to the values listed in Table 2 for $S_2O_7{}^{2-}$ and $S_4O_6{}^{2-}$ for pure solutions, but is not unusual, since the water hydrolysis of $S_2O_7{}^{2-}$ to form $SO_4{}^{2-}$ occurs slowly enough to allow time to react in a nonpure solution to form $SO_3{}^{2-}$, and polythio groups such as $S_4O_6{}^{2-}$ are much more easly oxidized than $S_2O_3{}^{2-}$.

During the course of our lab studies, it was necessary to analyze some neutralized nitric acid leach solutions of retorted oil shale. Under these high nitrate conditions, the $SO_4{}^{2-}$ peak was deformed in a reproducible manner as shown in Figure 6.

The normal $SO_4{}^{2-}$ peak (100 ppm) in the absence of any interfering ions is given for comparison. Although not shown on this figure, In the presence of 0.015 $\underline{M}$ $NO_3{}^-$ (900 ppm) the $SO_4{}^{2-}$ peak already shows a very slight change in elution time and peak height. With 0.1 $\underline{M}$ $NO_3{}^-$ the effects are more more pronounced. With 0.2 $\underline{M}$ $NO_3{}^-$, the first shoulder appears on the $SO_4{}^{2-}$ peak. Incidentally, this was the actual $NO_3{}^-$ concentration in the leaching study. At 0.3 $\underline{M}$ two shoulders appear in the $SO_4{}^{2-}$ elution profile at 0.4 $\underline{M}$ and at higher NO_3 concentrations the $SO_4{}^{2-}$ peak gradually merges with $NO_3{}^-$ peak. The number of shoulders observed was independent of $SO_4{}^{2-}$ concentration at a given $NO_3{}^-$ concentration over the 50-200 ppm $SO_4{}^{2-}$ range checked. Dilution of the solutions to a level below 0.1 $\underline{M}$ nitrate resulted in normal $SO_4{}^{2-}$ peaks. $SO_3{}^{2-}$ also produced a profile of shoulders in 0.2 $\underline{M}$ $NO_3{}^-$.

The nitrate effect prompted us to look at other salt effects. We found that with Cl^-, the splitting of SO_4^{2-} peak did not appear until chloride concentration reached 0.3 M, though reduction in peak height occurred earlier. The effect of phosphate on SO_4^{2-} peak was extremely sensitive to the basicity of the salt used, with significant SO_4^{2-} peak reduction already occurring at 0.01 M PO_4^{3-} when supplied as Na_3PO_4. Apparently, localized pH changes due to the added salts can greatly alter the elution characteristics at salt concentrations below the 0.1 M level suggested by Dionex as the upper salt limit on anion brine columns. For accurate analysis, standards should be analyzed in a matrix similar to the samples, or by standard addition. Due to the great sensitivity of the IC, however, a simple dilution is usually an adequate solution to a salt effect.

As a test of the accuracy of analysis by IC, several actual samples were run for $S_2O_3^{2-}$ and SCN^-, both on IC and by classical methods (Table 3). Sulfate was not analyzed on the first five samples by the classical method, which involves barium sulfate precipitation. The standard analysis for SCN^- involves colorimetric determination as the intense red ferric-SCN^- complex. Reducing agents, organics, and color in the original sample cause interferences. The classical $S_2O_3^{2-}$ analysis is iodometric titration. S^{2-} and SO_3^{2-}, and probably other sulfur-oxy anions, will interfere if not removed or complexed. Since iodine is a relatively nonspecific titrant, care must be taken in ensuring other reducing species are absent from the sample. This can be extremely difficult, even if the sample history is well-known. In contrast, IC analysis seldom requires any sample preparation other than filtration and probable dilution. Analysis by IC takes about 20 minutes using triple strength standard or 10 minutes using citrate eluent.

While SCN^- values shown in Table 3 agree rather well, considerable discrepancy is seen in a few of the $S_2O_3^{2-}$ values. We suspect interference by other reducing species in the samples to cause the elevated values with the classical iodometric titration. Care must also be taken in interpreting titration data, since under the proper conditions, $S_2O_3^{2-}$ can be titrated past the $S_4O_6^{2-}$ endpoint all the way to SO_4^{2-}.

Table 4 shows typical anion concentration ranges found in a variety of actual samples. The ranges involved speak highly of the versatility of the IC. The percolate samples resulted from the weathering study of retorted shale at Paraho. Stream and wells in the vicinity of the Paraho plant are also being sampled. The higher stream concentrations usually resulted from sampling of renewed runoff after dry periods in the creek beds. Retort waters and related waste waters from above-ground and in situ processes have been analyzed. Laboratory mockups include leachings and percolates from retorted shale columns, as well as analysis of solutions from related microbial studies. F^-, Cl^-, and NO_3^- are examples of some of the other ions we can detect, while our main interest lies with the sulfur-containing species. In all cases, sulfate was the predominant anion present. The presence of SO_3^{2-}, $S_2O_3^{2-}$ and SCN^- in retort waters necessitates the continual environmental monitoring for these anions.

SUMMARY AND CONCLUSIONS

Oil shale field and laboratory studies of simulated field conditions have benefitted from the use of IC analysis. Since the method requires very little sample preparation, and allows for the analysis of several anions simultaneously with good sensitivity and few interferences, it already has been used on a routine basis for analysis of SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, and SCN^-. Further experimentation with other eluent and column systems should result in the separation and identification of other sulfur-oxy anions as well as identification of those peaks that have been observed and recorded but are not yet identified. Also, the value of the positive proof by IC of the absence of any of these anions should not be understated. Since incorporating the IC into the mobile laboratory trailer, we have been able to analyze samples from the Paraho and Rio Blanco sites with minimal time lapse between sampling and analysis. Ultimately, we hope to use the IC to identify organic and metal-organic anions as well as the sulfur-containing anions.

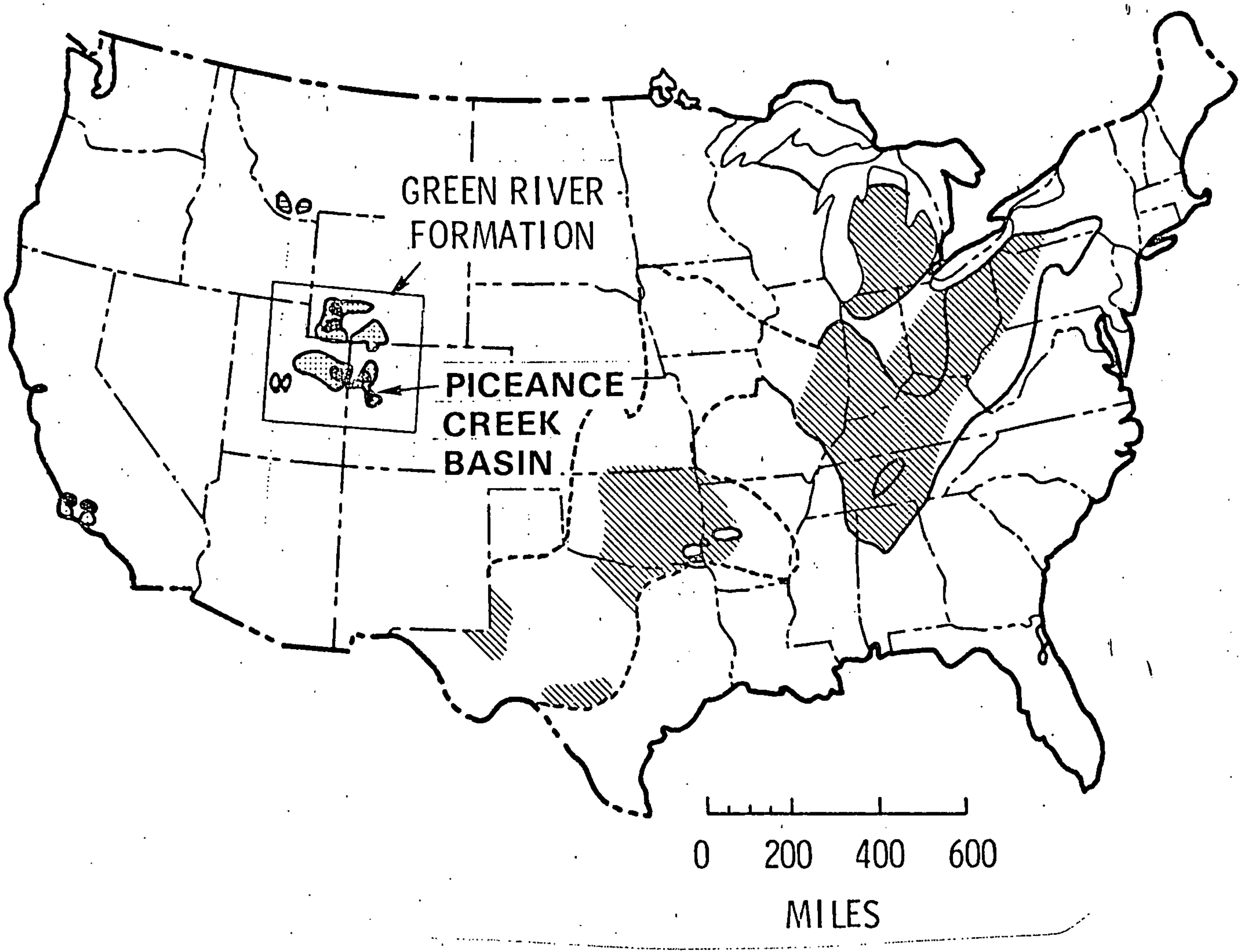


FIGURE 1. Oil Shale Deposits of the Green River Formation

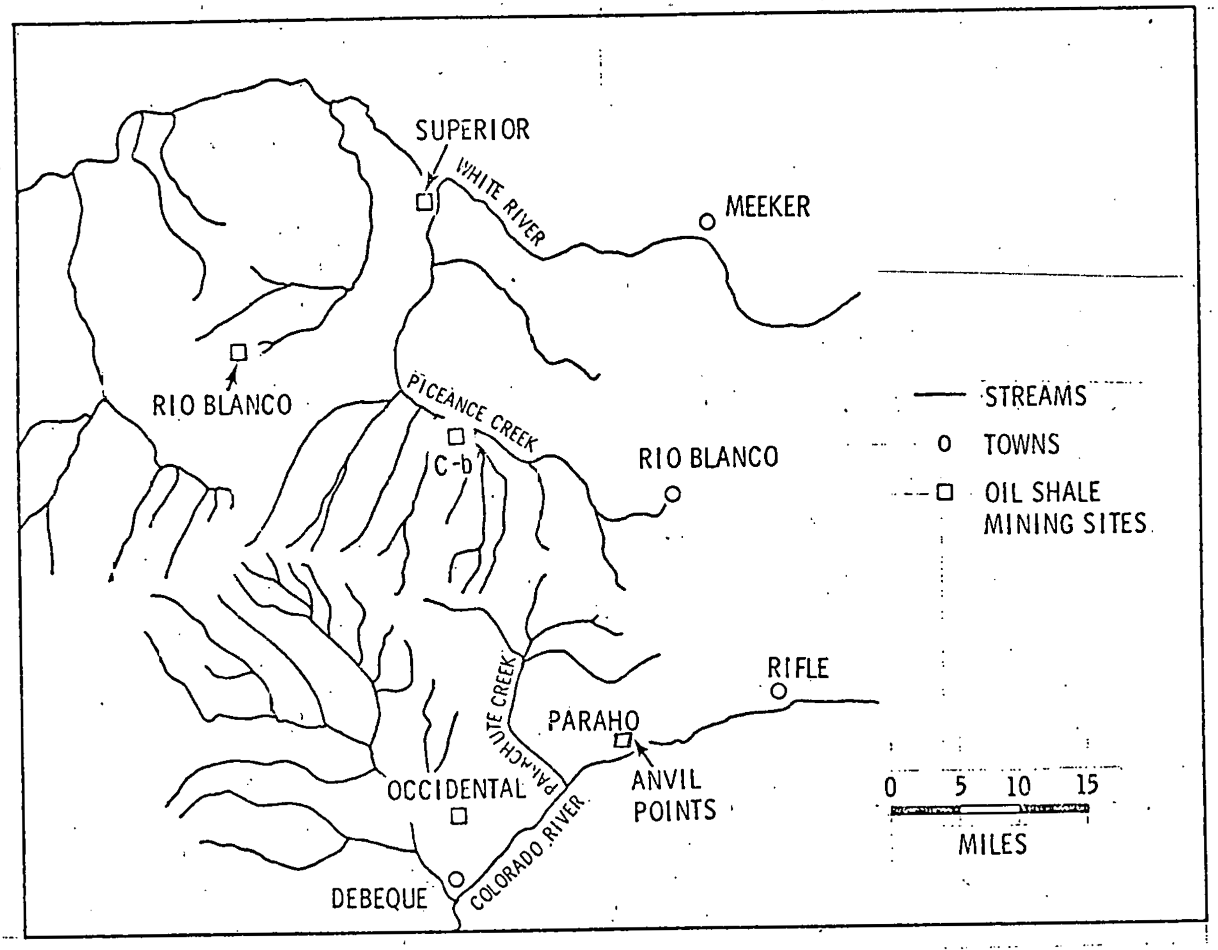


FIGURE 2. Piceance Creek Basin, Colorado

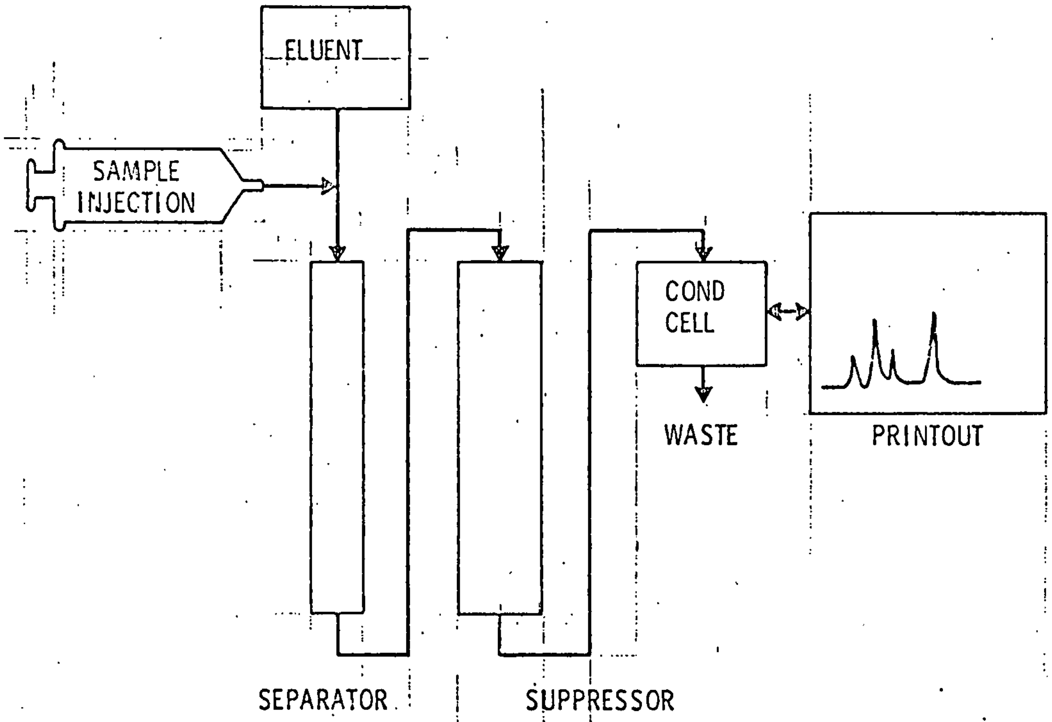


FIGURE 3. Basics of Ion Chromatography (IC)

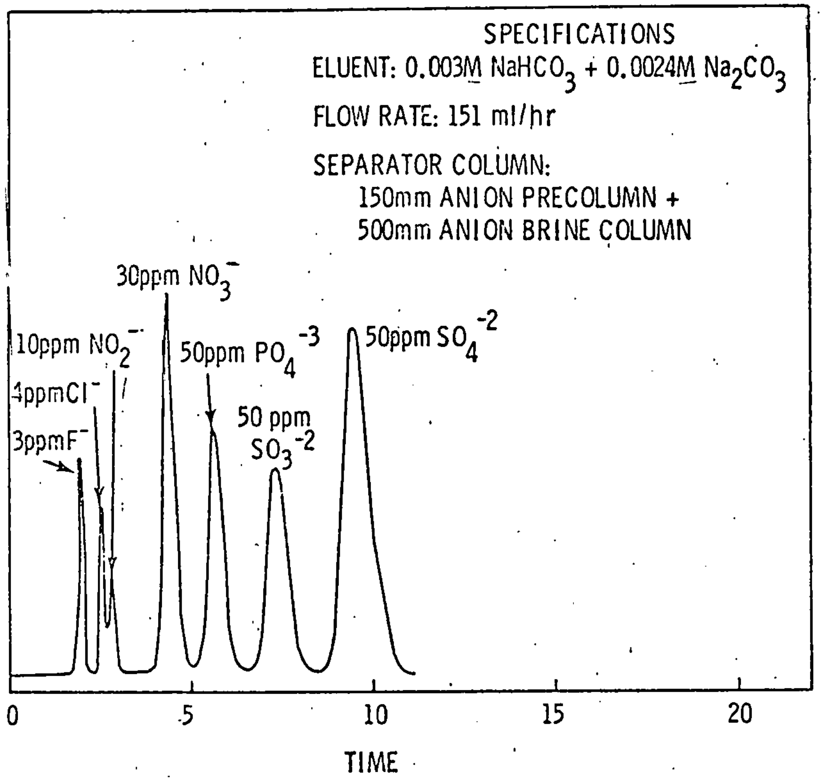


FIGURE 4. Typical Spectrum - Common Anions

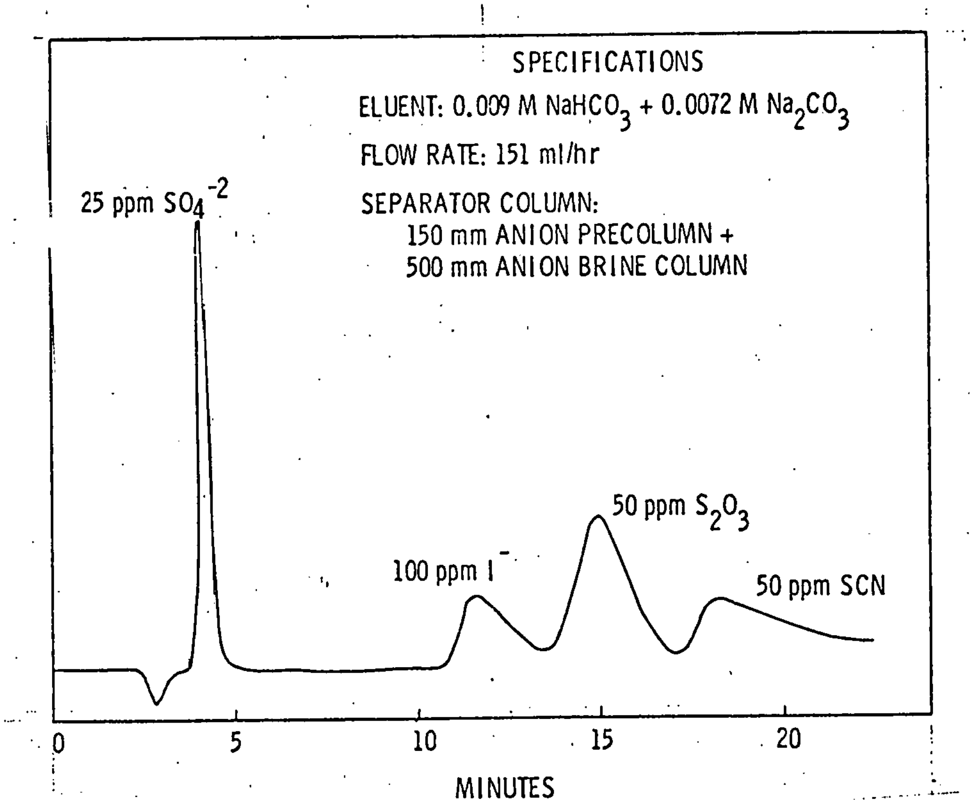


FIGURE 5. Typical Spectrum - Large Anions

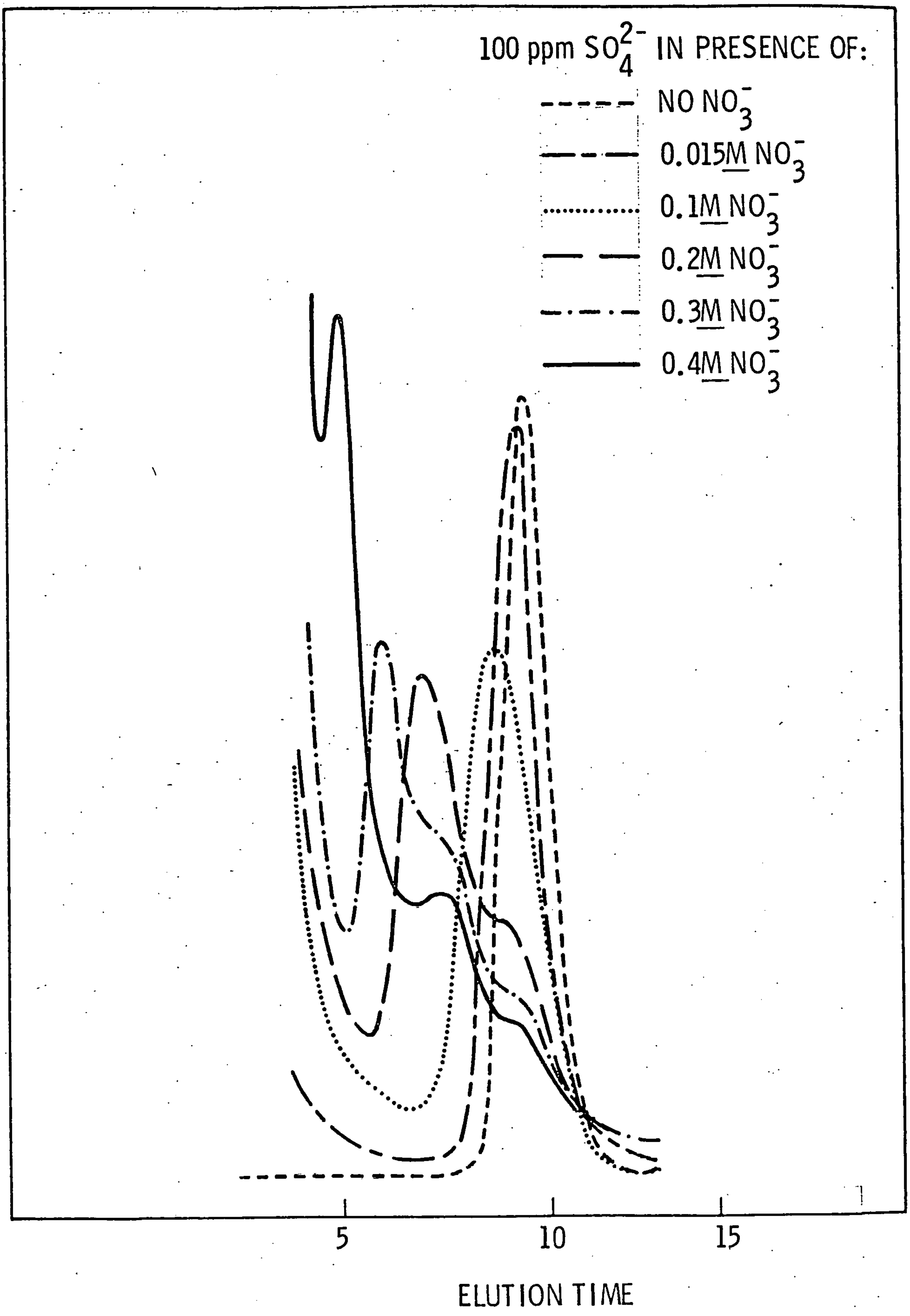


FIGURE 6. Effect of NO_3^- Concentration on SO_4^{-2} Elution

TABLE 1. Sulfur-Containing Anions

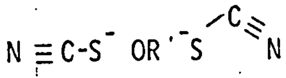
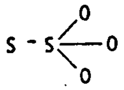
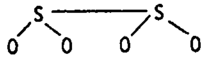
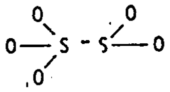
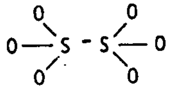
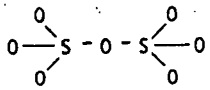
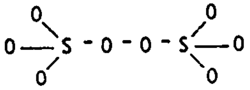
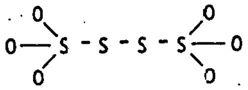
SPECIES	FORMULA	STRUCTURE
SULFIDE	S^{-2}	
THIOCYANATE	SCN^{-}	
SULFITE	SO_3^{-2}	
SULFATE	SO_4^{-2}	
THIOSULFATE	$S_2O_3^{-2}$	
DITHIONITE	$S_2O_4^{-2}$	
BISULFITE	$S_2O_5^{-2}$	
DITHIONATE	$S_2O_6^{-2}$	
PYROSULFATE	$S_2O_7^{-2}$	
PERSULFATE	$S_2O_8^{-2}$	
TETRATHIONATE	$S_4O_6^{-2}$	

TABLE 2. Instability of Sulfur-Oxy Anions

Anion	% as SO_3^{-2}	% as SO_4^{-2}	% as S_2O_3	% Not Accounted For
$S_2O_4^{-2}$	39	20	0	41
$S_2O_5^{-2}$	98	<1	1	0
$S_2O_6^{-2}$				
$S_2O_7^{-2}$	0	100	0	0
$S_2O_8^{-2}$	0	0	0	100
$S_4O_6^{-2}$	0	0.1	0	100

TABLE 3. IC vs Classical Analysis

	SO_4^{-2}		$S_2O_3^{-2}$ (ppm)		SCN^- (ppm)	
	IC	CLASSICAL	IC	CLASSICAL	IC	CLASSICAL
1	1010	ND*	550	1090	245	250
2	~850		1990	ND	303	270
3	2500		<20	<50	67	64
4	2480		<20	<50	57	51
5	8600		175	685	366	310

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* ND = not determined

TABLE 4. Typical Concentration Ranges

			Ion				
Sample Type	F^-	Cl^-	NO_3^-	SO_3^{-2}	SO_4^{-2}	$S_2O_3^{-2}$	SCN^-
				ppm			
Percolate	<2-10	60-150	6-150	<1	200-18,700	<1-2,330	<1
Streams				<1	800-11,000	<1	<1
Wells	2	10	0.2	<1	240-7000	<1	<1
Retort Waters				<100-11,000	1000-16,000	100-45,600	<1-100
Laboratory Mockups			0.2-12,000	<1-150	2-12,000	<1-3500	<1