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The Analysis of Anions in Geological Brines Using Ion Chromatography

R. M. Merrill

Prepared by
Sandia National Laboratories
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ABSTRACT

Ion chromatograpic procedures for the determination of the anions bromide, sulfate, nitrite, nitrate, phosphate, and iodide in brine samples have been developed and are described. The techniques have been applied to the analysis of natural brines, and geologic evaporites. Sample matrices varied over a range from 15,000 mg/L to 200,000 mg/L total halogens, nearly all of which is chloride. The analyzed anion concentrations ranged from less than 5 mg/L in the cases of nitrite, nitrate, and phosphate, to 20,000 mg/L in the case of sulfate. A technique for suppressing chloride and sulfate ions to facilitate the analysis of lower concentration anions is presented. Analysis times are typically less than 20 minutes for each procedure and the ion chromatographic results compare well with those obtained using more time consuming classical chemical analyses.

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*This work was performed at Sandia National Laboratories supported by the U. S. Department of Energy under Contract No. DE-AC04-76DP00789.

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INTRODUCTION

Chemical analyses of brines are important to geochemists in determining the history or source of the solutions. In addition, the presence or absence of certain chemical species can be used to calculate the oxidation potential which is helpful in determining elemental oxidation states. Instrumental techniques for the analysis of the metallic elements, for example atomic absorption spectroscopy, have been in existence for some time. Until recently however, the determination of anionic species has required the use of selective-ion electrodes which lack specificity and are particularly sensitive to matrix effects,[1] or depended on individual wet chemical analyses which are labor intensive and time comsuming.[2]

Ion chromatography, introduced in 1975 by H. Small and his co-workers,[3] is a new approach to the analysis of ionic species in solution. The technique is a variation on high performance liquid chromatography which employs columns packed with pellicular ion exchange resins having high resolution and low ion exchange capacity. Solutions containing the sample ions are injected into a continuously flowing eluent stream at the top of the column, and are dynamically separated into individual bands according to each ion's affinity for the resin. A second ion exchange column is used to chemically convert the eluent into a compound with a lower conductivity. The sample ions are subsequently detected by electrical conductivity. (See Figure 1 for a schematic diagram.) The technique is particularly attractive for the analysis of anionic species due the wide variety of anions which can be analyzed, and because it provides the first instrumental method for multiple anion analysis. Since its advent, ion chromatography has been used to analyze anions in samples such as radioactive wastes,[4] geothermal well waters,[5] soil samples,[6] and a large number of environmental pollutants.[7]

Ion chromatography is an ideal tool for the analysis of anions in brines because a number of anions can be separated and analyzed with a single injection. This paper describes the use of ion chromatography to determine anions in brine samples from the Delaware Basin (site of the Waste Isolation Pilot Plant WIPP) in southeastern New Mexico and in brines from several salt domes in southeastern Texas and southwestern Louisiana. Some of the salt dome brines were prepared in the laboratory by dissolving salt core samples in deionized water. For the purposes of this report, a brine is defined as a solution having in excess of 15,000 mg/L total dissolved halogens.

EXPERIMENTAL

Equipment - Brine analyses were done using Dionex Models 16 and 2020i ion chromatographs. Chromatograms were recorded using a Honeywell dual channel strip chart recorder. Either a Hewlett Packard Model 3370A electronic integrator or a Spectra Physics Model SP 4270 computing integrator were used to determine peak heights and areas. All chromatographic separator and suppressor columns were purchased from Dionex Corporation.

Reagents - Reagent grade chemicals were used without further purification to make eluents and standards. Stock solutions of standards were prepared to contain 1000 mg of the ion of interest per liter of solution, and working standards were prepared from these by dilution. All solutions were prepared in deionized water.

Hydrogen form Biorad AG-50W-XB, 100-200 mesh, cation exchange resin was converted to the silver form by overnight batch equilibration with an excess of reagent grade $AgNO_3$. After equilibration, nitric acid was removed from the resin by multiple rinsings with deionized water.

Column Conditions - Fluoride, bromide, sulfate, nitrite, nitrate and phosphate were analyzed using the following columns and conditions:

Precolumn: A Model AG3 or AG4 anion guard column.

Separator Column: A Model AS3 or AS4 anion separator.

Suppressor Column: Packed bed or fiber anion suppressors.

Eluent: An aqueous solution containing 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3 (standard anion eluent).

Flow Rate: 2.0 mL/min.

Column conditions for iodide were the same as listed above with the exceptions that the separator column was shortened by eliminating the precolumn, and a 0.008 molar solution of sodium carbonate was used as an eluent.

RESULTS AND DISCUSSION

Using the conditions detailed in the experimental section, the seven anions: fluoride, chloride, nitrite, phosphate, bromide, nitrate, and sulfate, can be routinely analyzed in the times and at the levels shown in Figure 2. The major difficulty encountered in analyzing brine solutions arises from the very high chloride levels which tend to swamp out other anions. The magnitude of this interference depends on the ratio of the anion of interest to the chloride concentration, and the difference in their respective retention times. In many cases, the anions of interest have concentrations great enough, and are well enough separated from the chloride peak, that the only sample preparation needed is dilution with deionized water. In other cases, however, the analyte anions very close to the chloride peak and/or are at the low parts per million levels and techniques other than dilution are needed to suppress the chloride concentration.

The Determination of Bromide and Sulfate

The sulfate and bromide levels in the brines analyzed in this study ranged from less than 5 to 20,000 mg/L and from 20 to 600 mg/L respectively. The only sample preparation needed prior to analysis for these constituents was dilution with deionized water. Figure 3 shows ion chromatograms of a brine which had been diluted 1:20 prior to analysis. To verify the identity of the peaks, the brine was spiked first with a known amount of bromide, then with a known amount of sulfate. The results of the spiking experiments are also shown in Figure 3. The undiluted brine used to obtain the chromatograms in Figure 3 contained 1400 mg sulfate per liter. Figure 4 is the chromatogram of a brine diluted 3:100 and which originally had a sulfate concentration of 20,000 mg/L. This very high sulfate concentration caused the apparent change in the shape and shift in the retention time of the sulfate peak.

In early literature dealing with ion chromatography, peak heights are used to quantitate the ions.[8,9,10] Geological brine solutions, however, have such large variations in sample matrix and anion concentrations, that the already noted peak fluctuations lead to errors when peak heights alone are used to determine the analyte ions over their full range of concentrations. Figure 5 shows that in the range of interest, linear plots of the bromide concentration can be obtained using either peak heights or peak areas. Figure 6 shows however, that peak areas must be used if the sulfate plots are to remain linear over the entire range of concentration. These changes in peak height are related to the noted change in peak shape at high concentrations and is caused by column overloading. Overloading is also responsible for the shortening of sulfate peak retention times delineated in Figure 7.

The effect of chloride concentration on the bromide and sulfate peak characteristics were determined by preparing a series of solutions in a range of 2.5 to 15 grams of sodium chloride per liter. The solutions contained fixed concentrations of either 20 mg or 600 mg sulfate/liter and either 20 or 60 mg bromide/liter. Ion chromatograms of the solutions were obtained and bromide and sulfate peak heights and areas were determined. The results of the experiments are presented in figures 8 and 9. Figure 8 shows that the chloride concentration has very little effect on the bromide peak height at 20 mg/L and causes minor pertubations at 60 mg/L. The sulfate peak heights at both 20 mg/L and 600 mg/L are suppressed by increasing chloride concentration (Figure 9). Peak areas were constant at constant concentration of bromide and sulfate over the range of sodium chloride concentrations studied.

The accuracy of the ion chromatographic analyses were determined by preparing and analyzing a series of known brine solutions and the results of these analyses are presented in Figure 10. The r^2 values shown in the figure are the coefficients of linearity and have a theoretical value of 1.0. The figure shows that the slope for the anionic recoveries are also very close to the theoretical. These results indicate that ion chromatography can be used to analyze for bromide and sulfate in brine solutions with good precision and accuracy. Figure 11 shows the results of a comparison of ion chromatographic and classical wet chemical analyses of several brine samples obtained from the Delaware Basin. The systematic differences which occur between the iodimetric and ion chromatographic bromide are due to the presence of iodide in the sample solutions. The iodimetric procedure determines iodide and bromide as a single species, while ion chromatography separates all of the halogens. The ion chromatographic analyses for sulfate agree well with the classical barium sulfate analyses.

The Determination of Iodide

Iodide is very strongly retained by the separator column. Under the conditions used to analyze bromide and sulfate, iodide is retained for periods in excess of an hour resulting in considerable peak broadening. By shortening the separator column with the elimination of the precolumn, and using a much stronger 0.008 M sodium carbonate eluent, iodide retention times can be reduced to less than twenty minutes. All of the weakly retained anions are eluted with the cloride when these column conditions are employed.

A calibration curve was constructed over a range of 1 to 10 mg iodide per liter in a matrix of 10 gm sodium chloride per liter, and a linear plot of peak areas versus iodide concentration was obtained even though the iodide retention times varied considerably with iodide concentration and sample matrix. Figure 12 is a comparison of the chromatogram from a synthetic brine containing 1 mg iodide/L to the chromatogram from a sample of a natural brine which had been diluted 1:5. The sensitive 1 microsiemen scale was used, accounting for the noisy baseline apparent in the figure.

In the previous section it was noted that the presence of iodide in the solutions would cause the iodimetric bromide analyses to be erroneously high. A typical ion chromatographic iodide analysis of brines from the WIPP site was approximately 20 mg iodide/L which is equivalent to 13 mg bromide/L, a value comparable to the differences noted between the iodimetric and ion chromatographic bromide determinations.

The Determination of Trace Level Anions in Brines

The concentrations of nitrite and nitrate ions are of interest since their ratio can be used to determine the oxidation potential of the solutions, and the phosphate concentration is useful in determining the history of the brine. These anions if present at all, exist at low concentrations, typically less than 5 mg/L. In order to analyze for them using ion chromatography it is necessary to suppress the high chloride levels by some method other than dilution. This suppression must necessarily also be accomplished without the addition of extraneous anions to the sample.

A standard solution was prepared containing the following anions: 0.3 ppm fluoride, 1.0 ppm nitrite, 5.0 ppm phosphate, 1.0 ppm bromide, 3.0 ppm nitrate, 5.0 ppm sulfate and enough sodium chloride so that the final chloride concentration was 3.0% (30,000 mg/L). An aliquot of this solution was passed through a column packed with high capacity cation exchange resin in the silver form. Brine sodium ions exchanged with the silver which subsequently precipitated as silver chloride, and the effluent solution was clear and virtually free from chloride. Ion chromatograms were run on this solution along with an identical solution prepared without the addition of chloride. The results of the experiment are shown in Figure 13. The third chromatogram shown in the figure is one of a 1:10 dilution of the above standard with enough additional sodium chloride added to make it a 3% chloride brine. These results show that accurate recoveries of trace level anions can be obtained from brines following the suppression of chloride with silver form ion exchange resin.

Most of the actual brine samples, whether from the salt domes of Texas and Louisiana or from the WIPP site, contain high concentrations of sulfate ion. The first chromatogram in Figure 14 is from a 1:5 dilution of a brine which contained 175,000 mg/L total halogens, and was nearly saturated with calcium sulfate. This high sulfate concentration so perturbed the retention of the trace anions, the chromatogram was unuseable. The sulfate can be reduced or removed form these high sulfate brines by adding barium chloride crystals prior to chloride suppression with the silver resin column. The resulting barium sulfate precipitate is added to the silver column and the column allowed to act as a filter, and the effluent is clear of suspended particles. The second and third chromatograms in the figure are from high sulfate brines which had been treated with barium chloride prior to passing through the silver form ion exchange column. By using these matrix modification techniques, nitrate and phosphate concentrations were determined in salt dome samples at levels of from 1 to 11 mg/L, and nitrite/nitrate concentrations in Delaware Basin brines were analyzed at levels down to 0.24 mg/L.

CONCLUSIONS

Ion chromatography has been used to determine the anions normally found in geological brine samples with good results. If the ions to be analyzed are concentrated enough, the only sample preparation needed prior to analysis is a simple dilution. Due to the variations in brine composition, it was determined that more accurate analyses are obtained if peak areas rather than heights are used to quantitate bromide and sulfate.

In cases where analyte anion concentrations are very low, chloride can be removed from the solutions by passing them through a silver form cation exchange column. Interferences from large sulfate concentrations can be eliminated by the addition of barium chloride to the samples prior to treatment with the silver resin.

Usually more than one anion can be analyzed with a single injection onto the ion chromatograph, and the results are obtained in less than twenty minutes. Classical chemical analyses typically require several hours to perform and new sample aliquots must be taken for each ion analyzed. The accuracy of the results obtained from ion chromatography compares favorably with results from classical wet chemical analyses. In some cases, for instance, the determination of bromide in the presence of iodide, ion chromatography offers a more selective method of analysis.

REFERENCES

1. J. Vesely, D. Weiss, and K. Stulik, Analysis With Ion-Selective Electrodes, John Wiley and Sons, New York, NY, 1978.
2. N. H. Furman, Ed., Standard Methods of Chemical Analysis, 6th ed., VanNostrand Co., Inc., Princeton, NJ, 1968.
3. H. Small, T. S. Stevens and W. C. Bauman, Anal. Chem., 47 (11), (1975) 1801.
4. S. J. Johnson and M. J. Kupfer, "Application of Ion Chromatography to the Analyses of Anions in Radioactive Sludge Wastes and Silicate Glasses," RHO-SA-74, Rockwell International, Rockford Hanford Operations, Richland, WA, 1979.
5. R. P. Lash and C. J. Hill, Anal. Chim. Acta, 108 (1979) 405.
6. W. A. Dick and M. A. Tabatabai, Soil Sci. Am. J., 43 (1979).
7. E. Sawicki, J. D. Mulik and E. Wittgenstein, Eds., Ion Chromatographic Analyses of Environmental Pollutants, 2 volumes, Ann Arbor Science, Ann Arbor, MI, 1979.
8. J. F. Colaroutolo and R. S. Eddy, Anal. Chem., 49 (6), (1977) 84.
9. R. A. Wetzel, C. L. Anderson, Helmut Schleicher, and G. D. Crook, Anal. Chem., 51 (9) (1979) 1532.
10. C. A. Pohl and E. L. Johnson, J. Chrom. Sci., 18 (1980) 442.

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Figure 11 A comparison of ion chromatographic analysis of geological brine solutions with the iodimetric bromide, and gravimetric sulfate analysis of the same solutions. The theoretical 45° slopes are depicted by the solid lines.

Figure 12 Iodide ion chromatograms of an artificial brine standard and of an actual geological brine from the WIPP site.

Figure 13 The ion chromatographs of standard solutions which were matrix adjusted with silver-resin to remove high levels of chloride.

Figure 14 The ion chromatographs of brine solutions which were matrix adjusted to remove both high levels of chloride and high levels of sulfate.

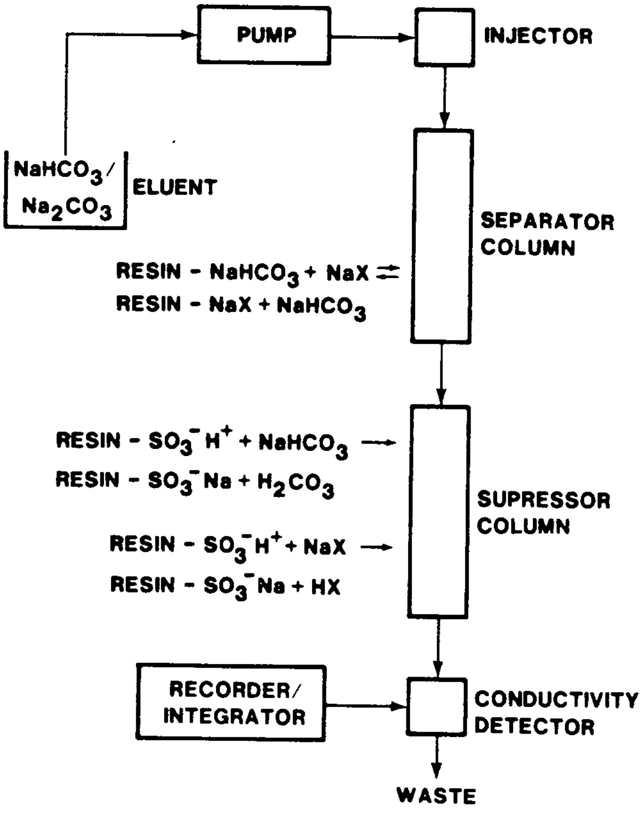
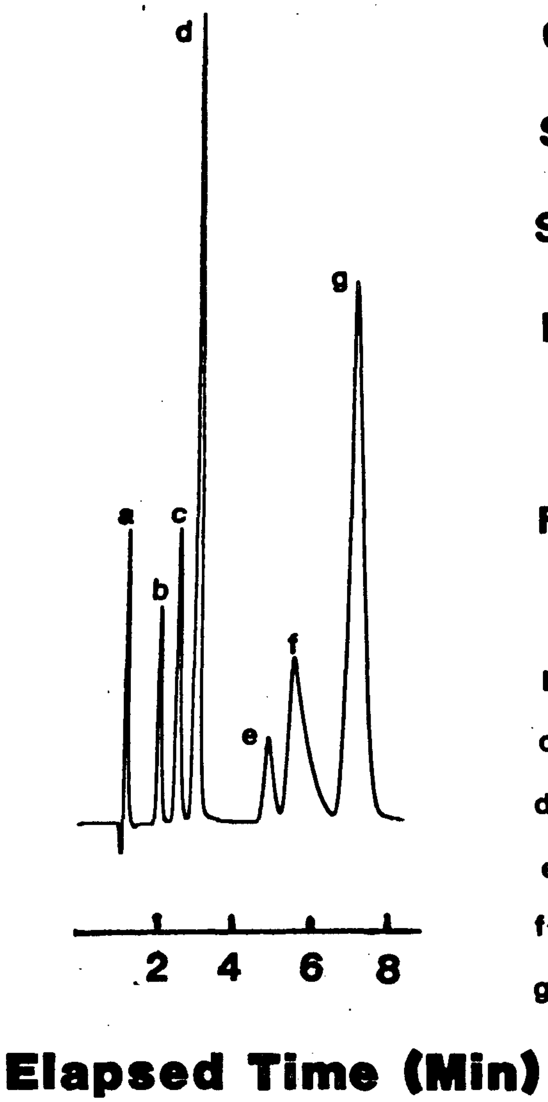

PUMP
INJECTOR
NaHCO3/ Na2CO3
ELUENT
SEPARATOR COLUMN
RESIN - NaHCO3 + NaX ⇌ RESIN - NaX + NaHCO3
RESIN - SO3⁻H⁺ + NaHCO3 → RESIN - SO3⁻Na + H2CO3
SUPRESSOR COLUMN
RESIN - SO3⁻H⁺ + NaX → RESIN - SO3⁻Na + HX
RECORDER/ INTEGRATOR
CONDUCTIVITY DETECTOR
WASTE

Figure 1



Column Conditions

Separator: AG4-AS4

Suppressor: AFS-1

Eluent: 0.0024M Na_2CO_3

0.003M $NaHCO_3$

Flow Rate: 2.0 mL/Min

a- 3ppm F^-
b- 4 ppm Cl^-
c- 10 ppm NO_2^-
d- 50 ppm HPO_4^{2-}
e- 10 ppm Br^-
f- 30 ppm NO_3^-
g- 50 ppm SO_4^{2-}

Figure 2

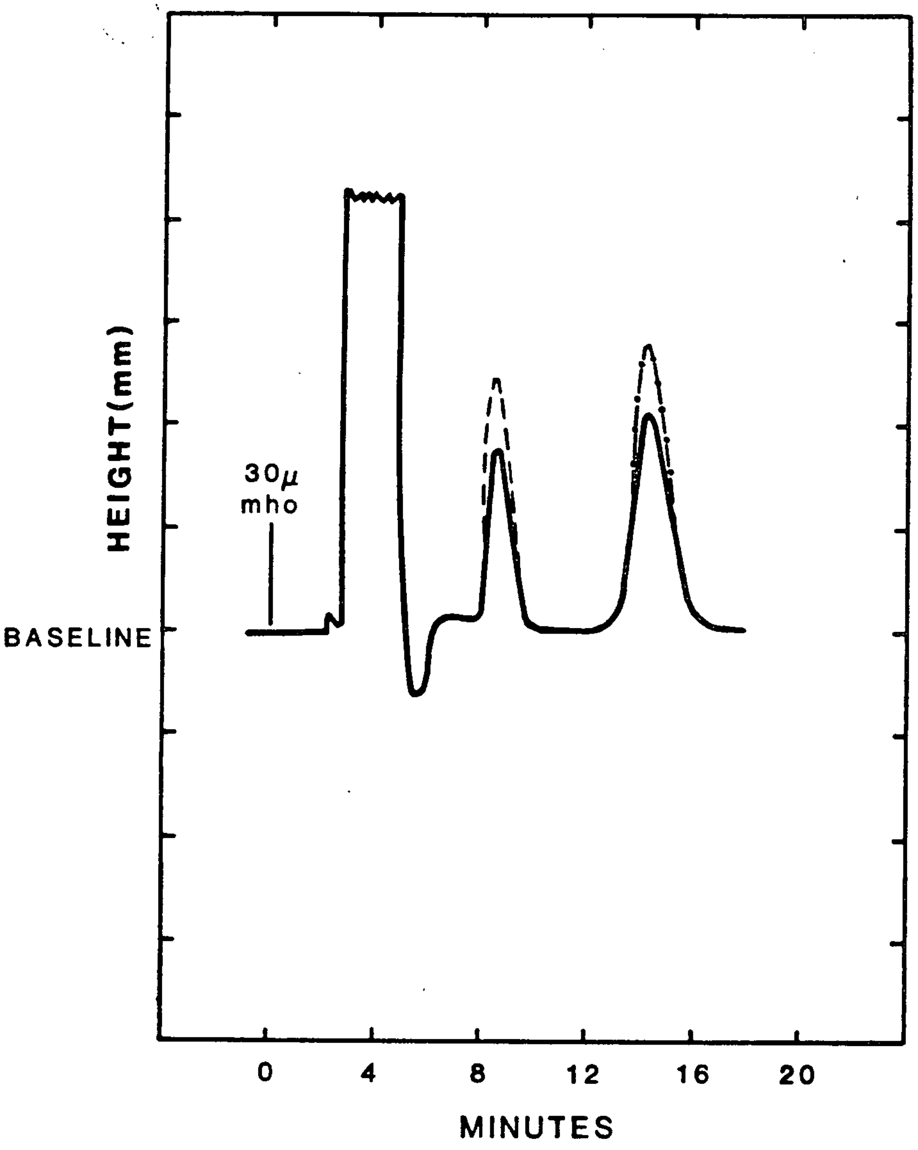
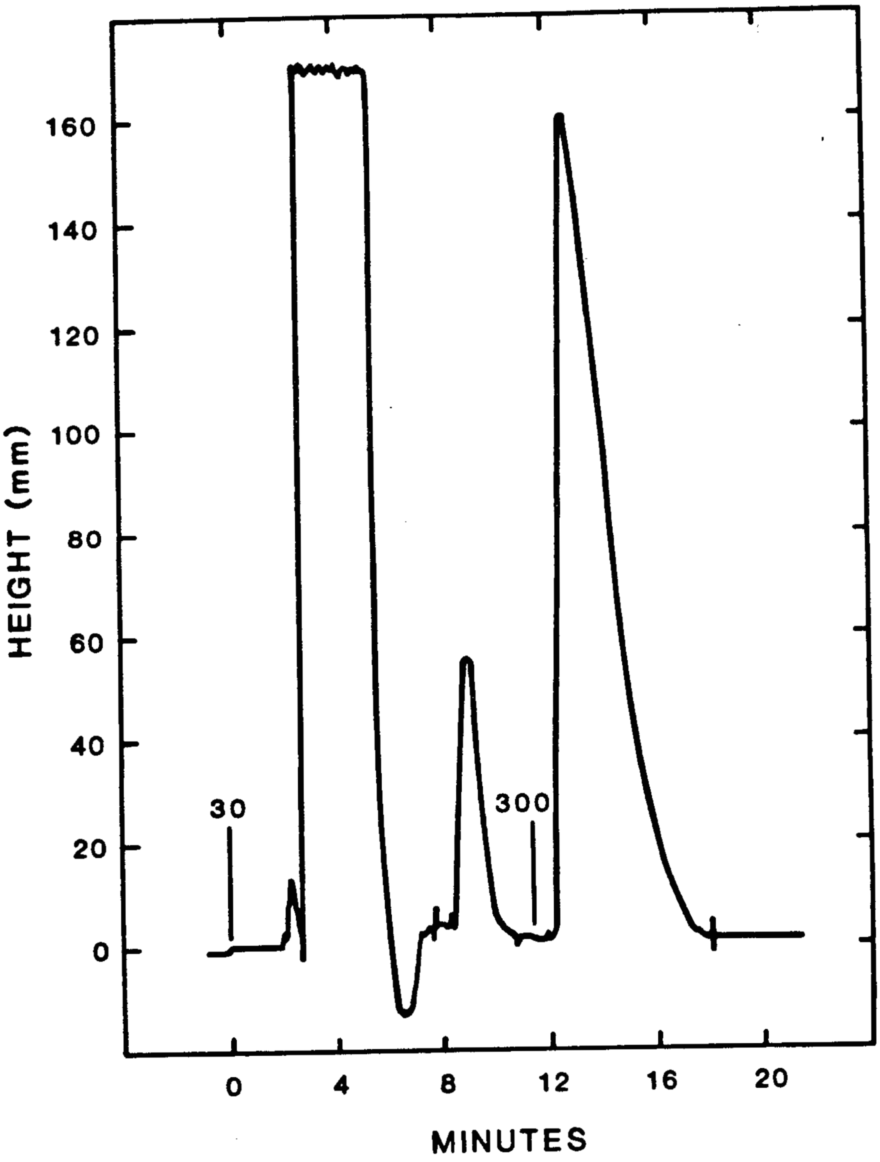


Figure 3



HEIGHT (mm)
160
140
120
100
80
60
40
20
0
30
300
0
4
8
12
16
20
MINUTES

Figure 4

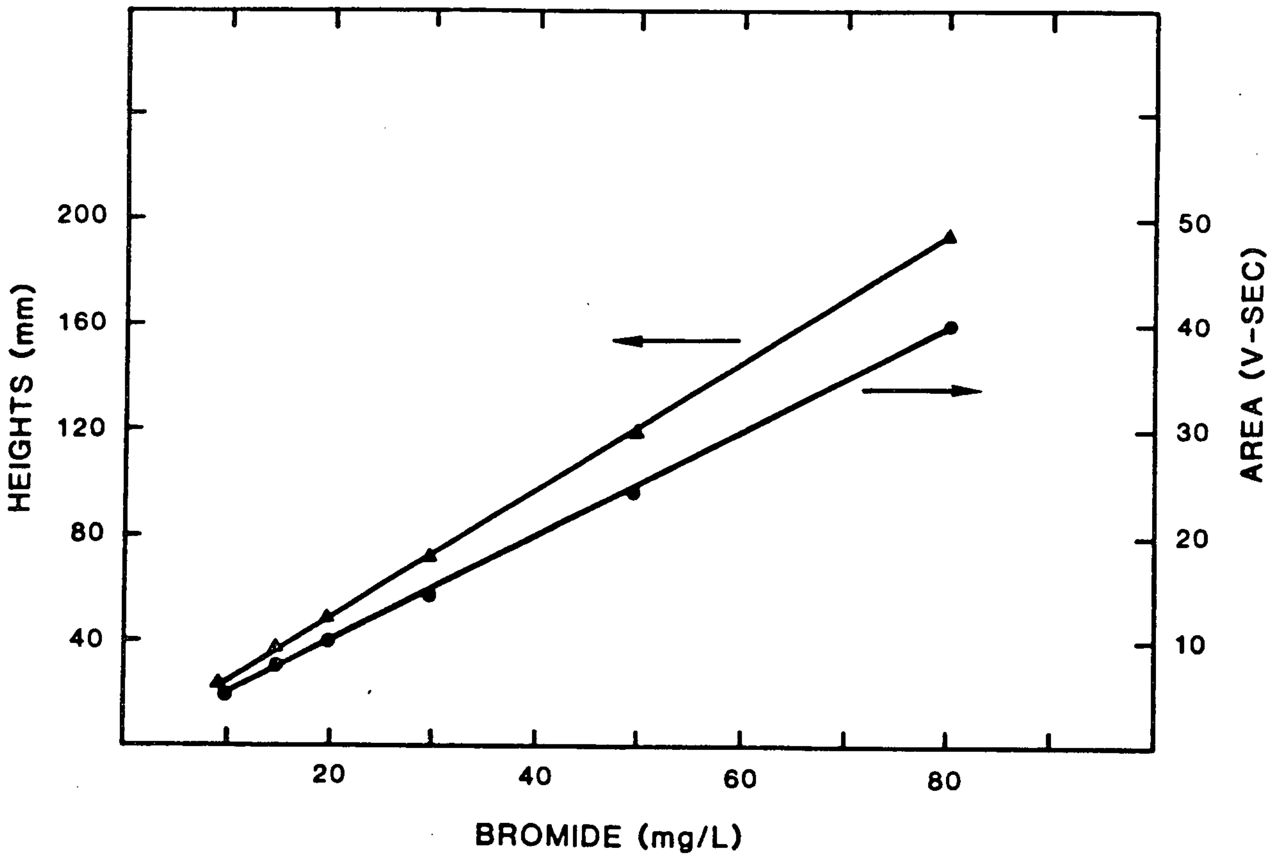

200
160
120
80
40
HEIGHTS (mm)
50
40
30
20
10
AREA (V-SEC)
20
40
60
80
BROMIDE (mg/L)

Figure 5

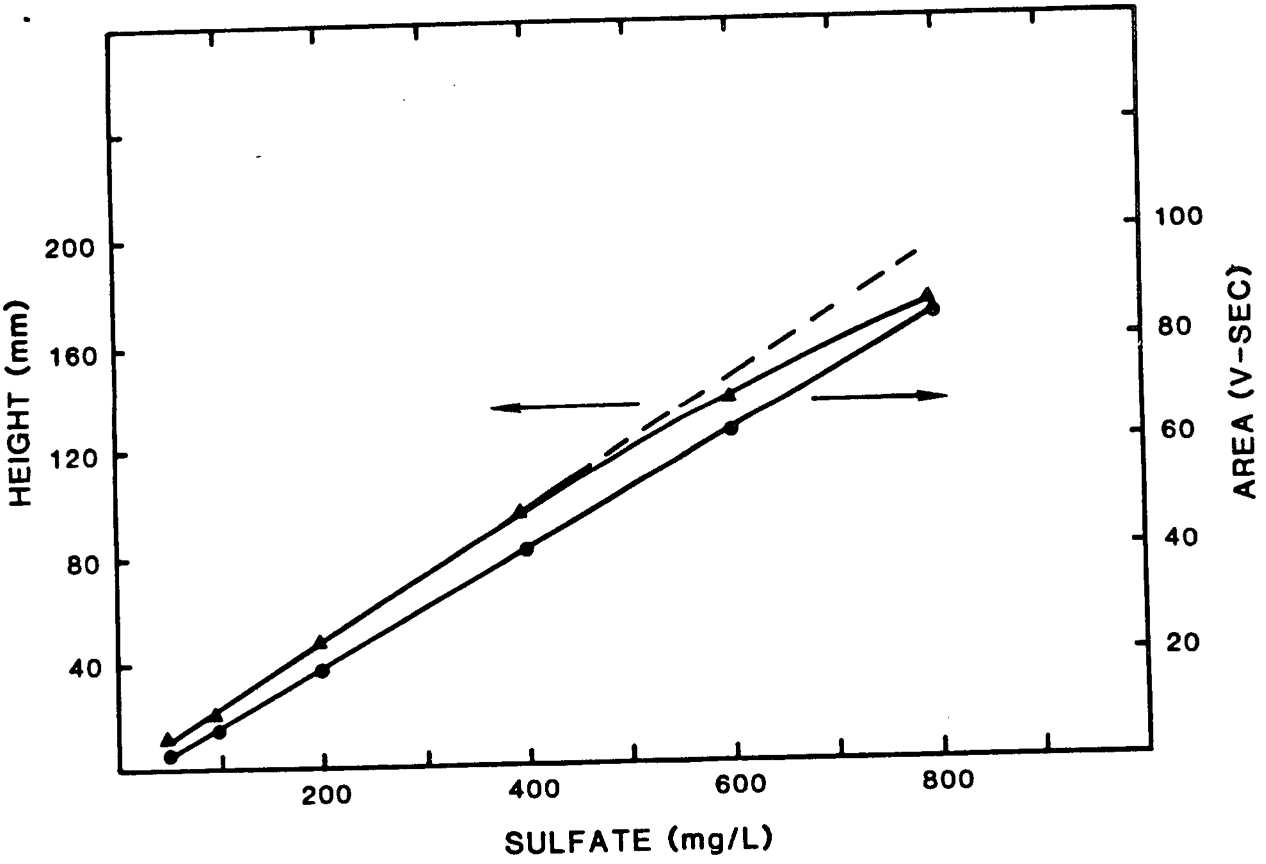

HEIGHT (mm)
200
160
120
80
40
AREA (V-SEC)
100
80
60
40
20
200
400
600
800
SULFATE (mg/L)

Figure 6

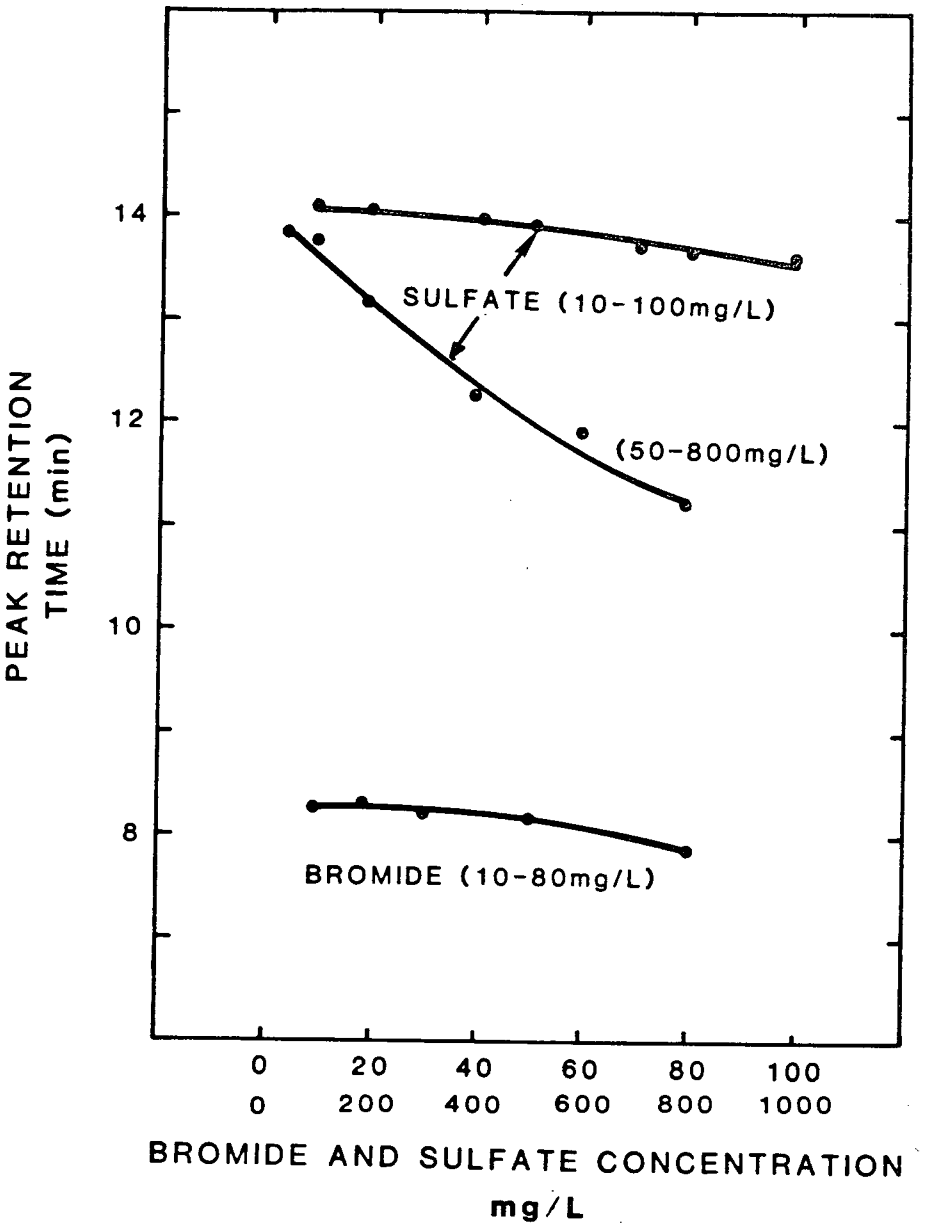

PEAK RETENTION TIME (min)
14
12
10
8
SULFATE (10-100mg/L)
(50-800mg/L)
BROMIDE (10-80mg/L)
0 20 40 60 80 100
0 200 400 600 800 1000
BROMIDE AND SULFATE CONCENTRATION mg/L

Figure 7

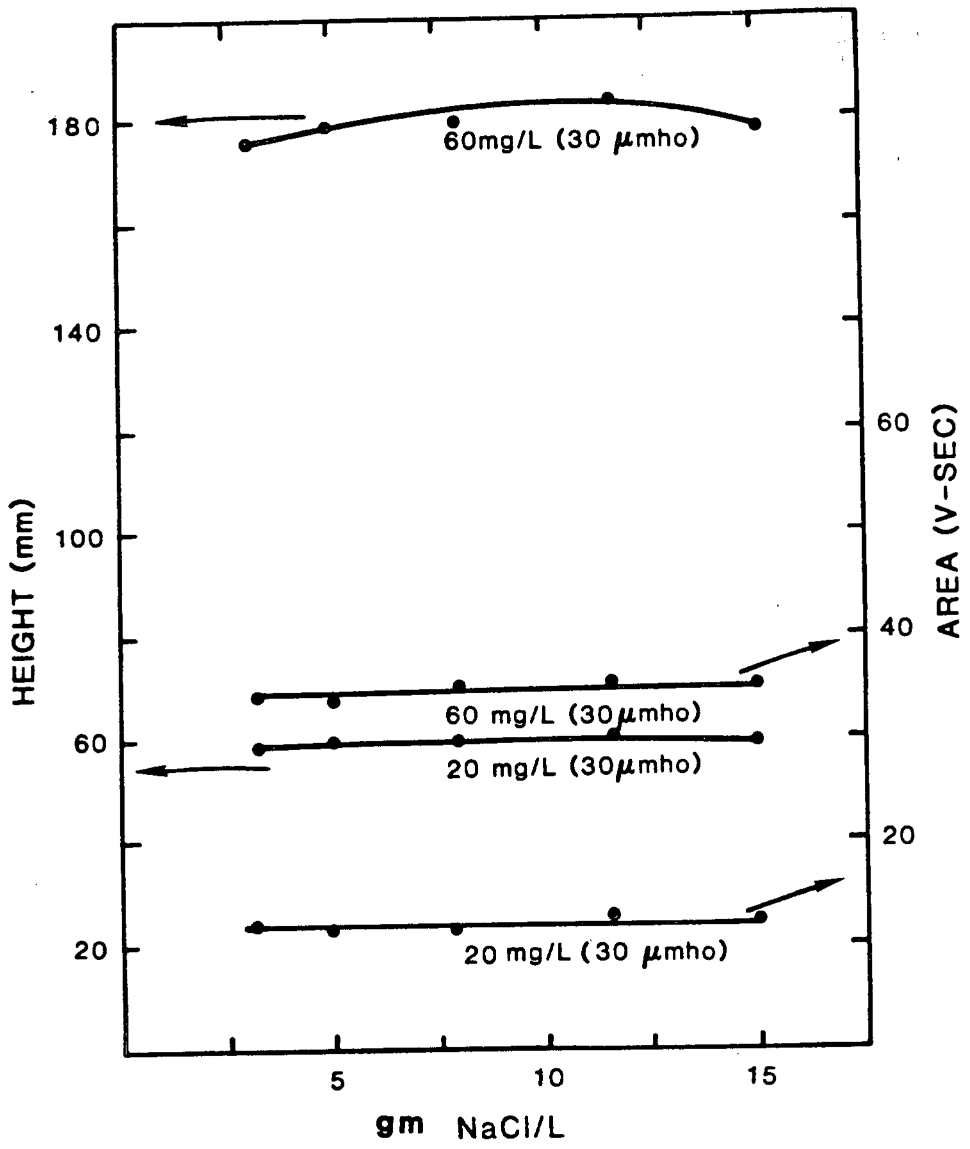

HEIGHT (mm)
180
140
100
60
20
AREA (V-SEC)
60
40
20
60mg/L (30 μmho)
60 mg/L (30μmho)
20 mg/L (30μmho)
20 mg/L (30 μmho)
5
10
15
gm NaCl/L

Figure 8

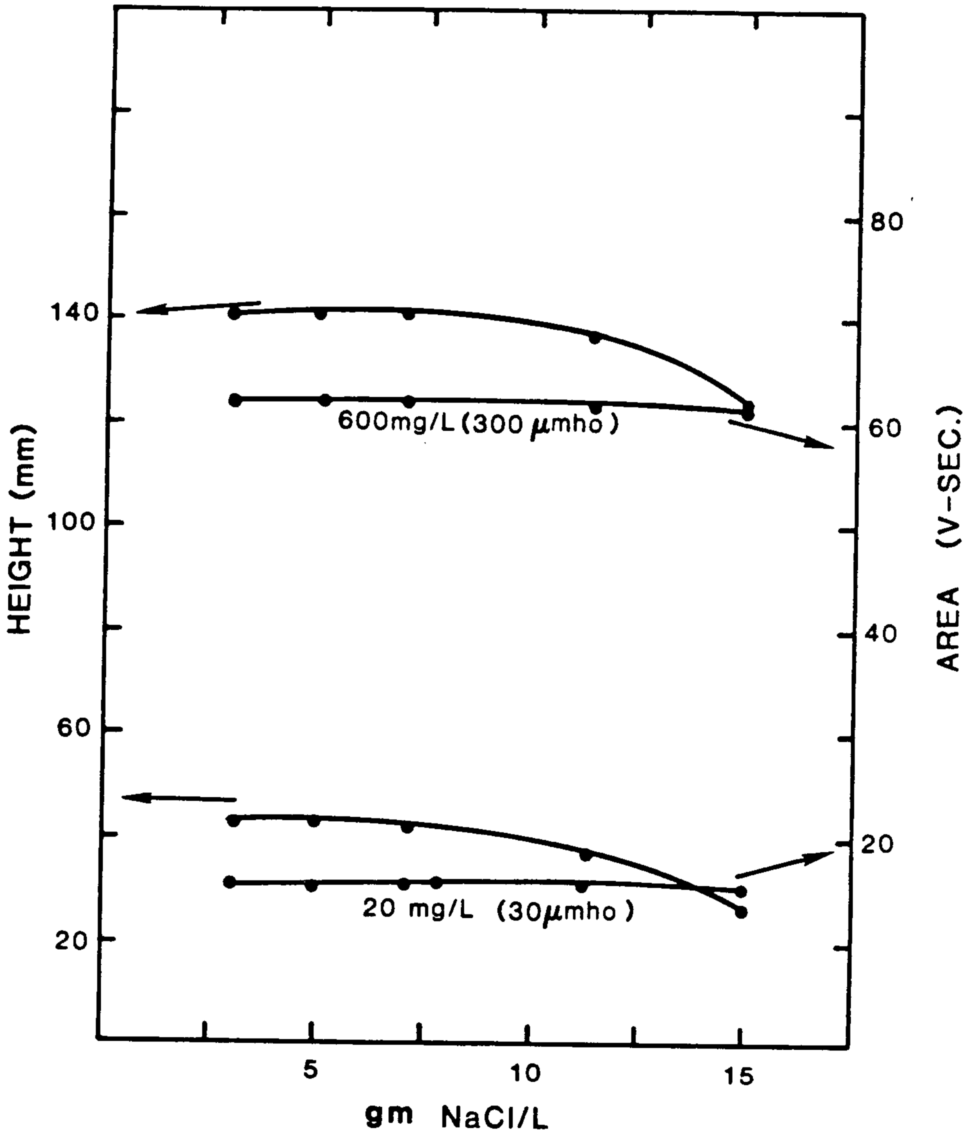

140
100
60
20
HEIGHT (mm)
80
60
40
20
AREA (V-SEC.)
600mg/L (300 μmho)
20 mg/L (30μmho)
5
10
15
gm NaCl/L

Figure 9

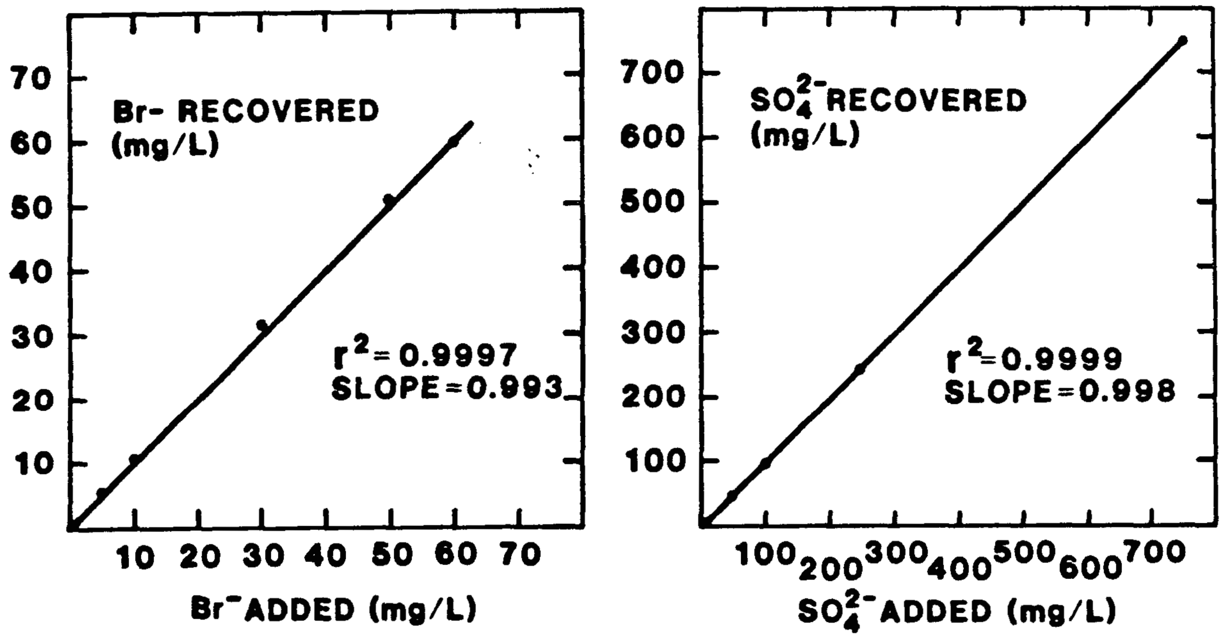
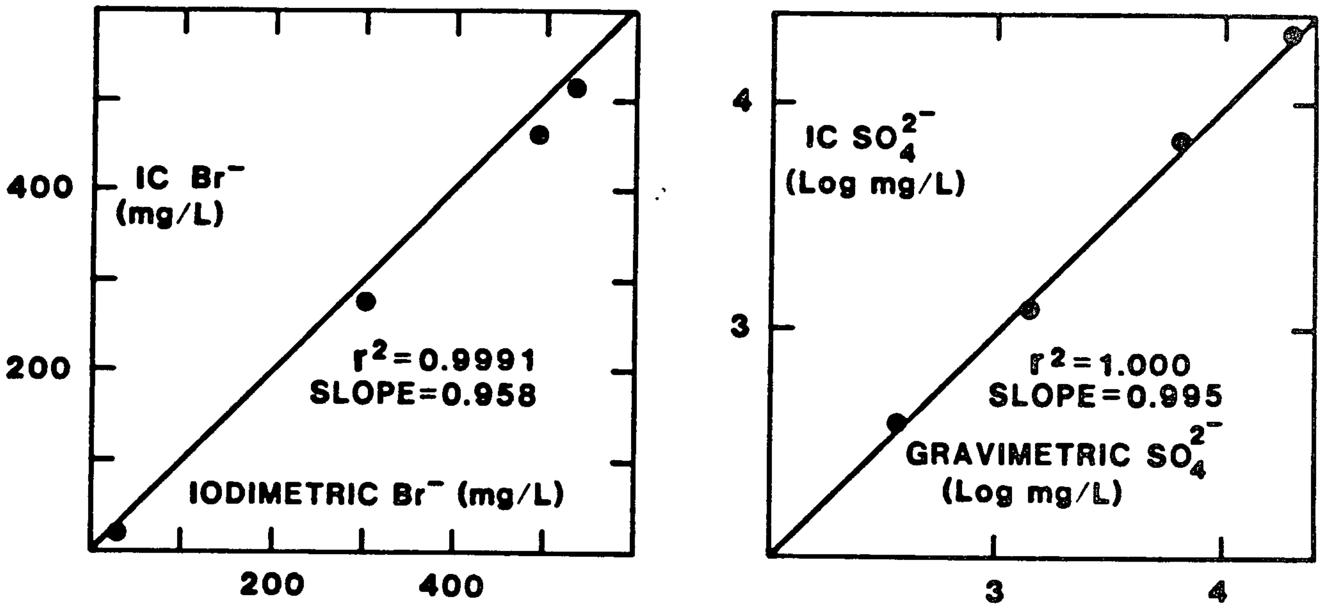

70
60
50
40
30
20
10
Br- RECOVERED
(mg/L)
r^2= 0.9997
SLOPE=0.993
10 20 30 40 50 60 70
Br⁻ ADDED (mg/L)
700
600
500
400
300
200
100
SO_4^{2-} RECOVERED
(mg/L)
r^2=0.9999
SLOPE=0.998
100 200 300 400 500 600 700
SO_4^{2-} ADDED (mg/L)

Figure 10



400
200
IC Br⁻ (mg/L)
r² = 0.9991
SLOPE = 0.958
IODIMETRIC Br⁻ (mg/L)
200
400
4
3
IC SO₄²⁻ (Log mg/L)
r² = 1.000
SLOPE = 0.995
GRAVIMETRIC SO₄²⁻ (Log mg/L)
3
4

Figure 11

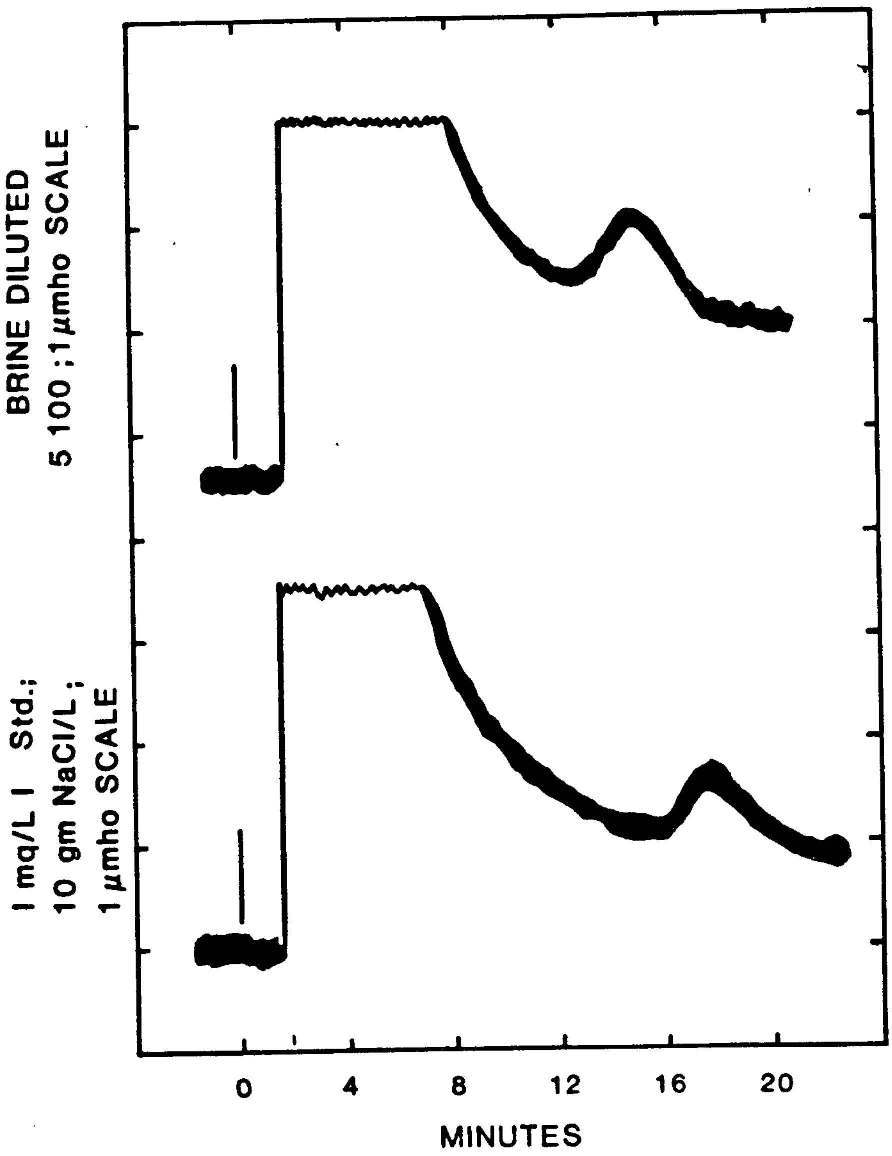

BRINE DILUTED
5 100 ;1 μmho SCALE
I mq/L I Std.;
10 gm NaCl/L ;
1 μmho SCALE
0
4
8
12
16
20
MINUTES

Figure 12

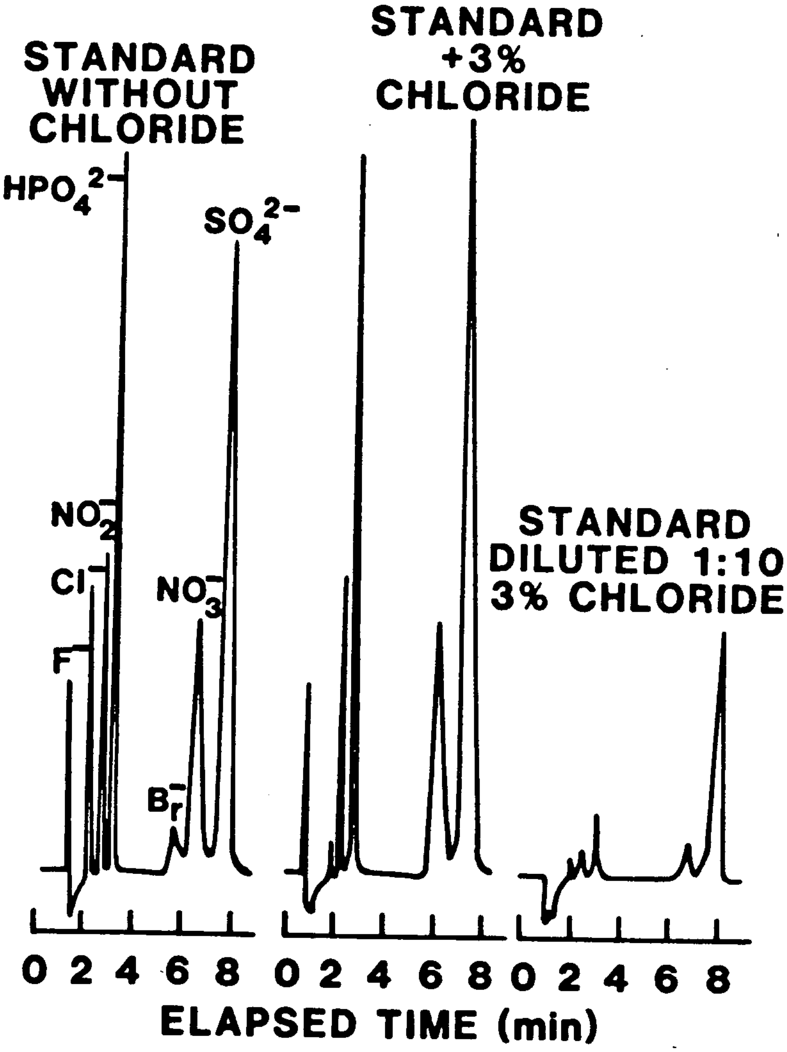

STANDARD WITHOUT CHLORIDE
STANDARD +3% CHLORIDE
STANDARD DILUTED 1:10 3% CHLORIDE
HPO$_4^{2-}$
SO$_4^{2-}$
NO$_2^-$
Cl$^-$
F$^-$
NO$_3^-$
Br$^-$
0 2 4 6 8 0 2 4 6 8 0 2 4 6 8
ELAPSED TIME (min)

Figure 13

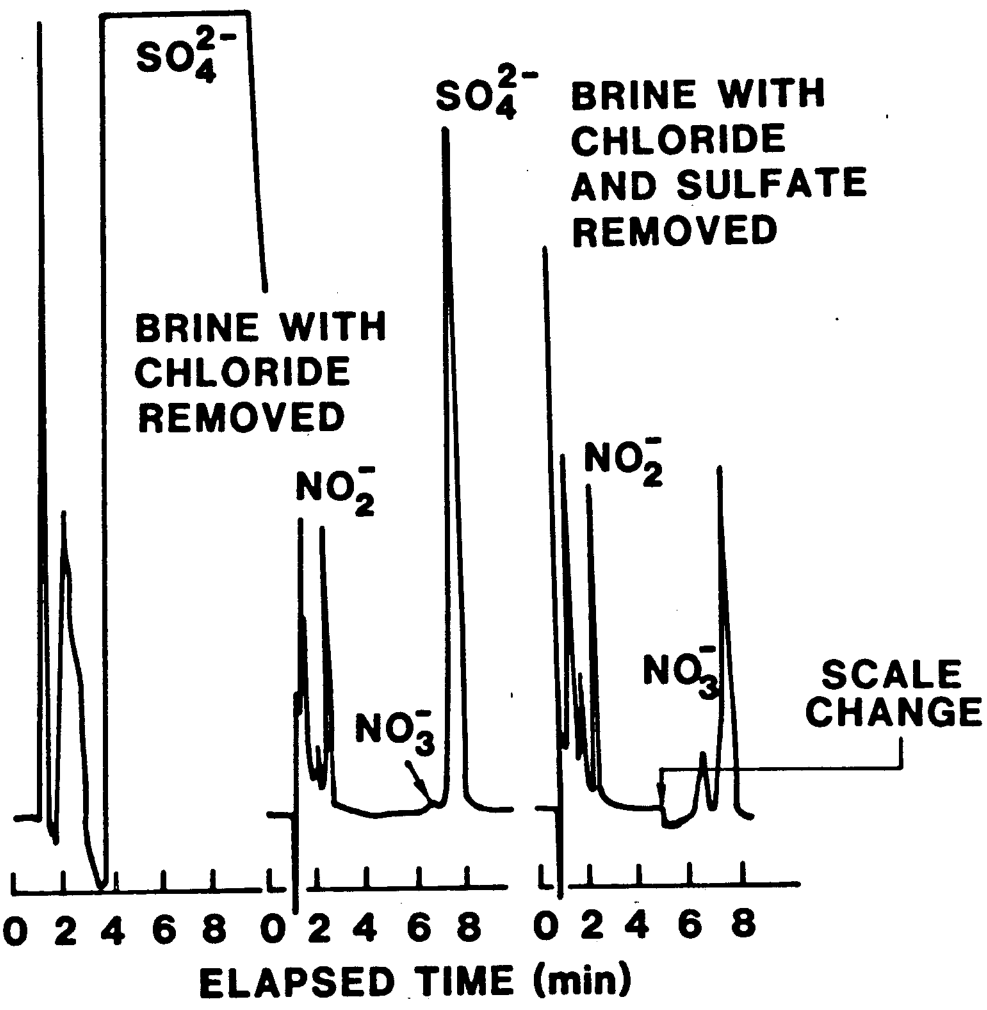

SO_4^{2-}
BRINE WITH CHLORIDE REMOVED
NO_2^-
NO_3^-
SO_4^{2-}
BRINE WITH CHLORIDE AND SULFATE REMOVED
NO_2^-
NO_3^-
SCALE CHANGE
0 2 4 6 8 0 2 4 6 8 0 2 4 6 8
ELAPSED TIME (min)

Figure 14

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