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Ion Chromatographic Analysis of
Oil Shale Leachates

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INTRODUCTION

Ion chromatography can be used for the rapid separation and determination of ions in aqueous solutions that would otherwise require a plethora of classical wet chemical techniques. Ion chromatography is finding increasing use in environmental analysis as well as the petroleum and fossil fuel industries.

In the present work an investigation of the use of ion chromatography to determine environmentally significant anions present in oil shale leachates was undertaken. Nadkarni et al. have used ion chromatography to separate and quantify halogen, sulfur and nitrogen species in oil shales after combustion in a Parr bomb.^{1,2} Potts and Potas used ion chromatography to monitor inorganic ions in cooling tower wastewater from coal gasification.³ Wallace and coworkers⁴ have used ion chromatography to determine anions encountered in retort wastewaters. The ions of interest in this work were the ions of sulfur oxides including sulfite (SO_3^{2-}), sulfate (SO_4^{2-}), thiosulfate ($\text{S}_2\text{O}_3^{2-}$), dithionite ($\text{S}_2\text{O}_4^{2-}$), dithionate ($\text{S}_2\text{O}_6^{2-}$), peroxydisulfate ($\text{S}_2\text{O}_8^{2-}$), and tetrathionate ($\text{S}_4\text{O}_6^{2-}$), and thiocyanate (SCN^-), sulfide (S^{2-}), hydrosulfide (HS^-), cyanide (CN^-), thiocyanate (SCN^-), and cyanate (OCN^-). A literature search was completed and a leaching procedure developed.

EXPERIMENTAL

Reagents and Standard Solution

Tetrabutylammonium hydroxide (TBAOH), sodium carbonate and sodium bicarbonate concentrates were obtained from Dionex. Burdick and Jackson UV grade, high purity acetonitrile was used. Water used in this work was either doubly distilled water from a Corning LD-2A water purifying system or high purity water from a Millipore Milli-Q ion exchange system. Sulfur oxide standards were made using the sodium and ammonium salts of the highest purity available. Standard sulfite solution (1000 ppm) was prepared by the method described by McCormick and Dixon.⁵ In a 500 ml volumetric flask 10 ml of formaldehyde was added to ~300 ml of water, then 0.5942 g $\text{Na}_2\text{S}_2\text{O}_5$ was added and the solution diluted to the mark with high purity water. For sulfite analysis, samples were diluted with 2% V/V formaldehyde.

Leaching Procedure

The leaching apparatus consisted of a 50-ml round bottom flask, equipped with a water-cooled reflux condenser and an argon inlet. The oil shale sample (2-4 g) was charged into the round bottom flask and high purity Millipore water (10 ml / 2 g of shale)

was added by serological pipet. The sample was heated at reflux, under argon with stirring for 24-48 hours, then left to stir at room temperature for 5 to 7 days. A one ml aliquot was withdrawn, filtered through a 0.2 μm Nylon filter and diluted to 25 ml in a volumetric flask. This sample was used for ion chromatography with further dilution if necessary. Determinations made in this work were qualitative rather than quantitative.

All glassware used in this work was cleaned by successive sonications in $\sim 2\text{ N}$ HNO_3 , deionized water, and high purity water. The glassware was then given a final rinse in high purity water.

Samples from New Albany shale formation (NA-13-GS-24) as well as four Green River formations were subjected to the leaching process. The Green River shales were received identified as follows: S.S. Spent G-19; S.S. comb drum #1G-19; S.S. pot product #1G-19-20; S.S. spent comb. G-22#2. In addition, two aliquots of New Albany shale were spiked, one with SO_3^{2-} and the other with $\text{S}_2\text{O}_3^{2-}$, and then leached.

Equipment

A Dionex model 2110i ion chromatograph equipped with a conductivity detector, eluant pump, separator column, and membrane suppressor device were used for separation and detection of the ions. The suppressor regenerant was 0.02 N H_2SO_4 . A Nelson Analytical Series model 4400X chromatography data system was used to store and analyze the signal from the detector.

RESULTS AND DISCUSSION

In the work of Wallace and co-workers, four separate protocols were used to achieve the determination of acetate, Cl^- , NO_2^- , NO_3^- , SO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, and SCN^- . One problem that they site in this work is the shift in the acetate peak to a shorter retention time as the suppressor is exhausted⁴ (i.e., the resin changes from the hydrogen-form to the sodium-form). Acetate is retained by the hydrogen-form of the resin but not the sodium-form. Their work was done using a packed bed suppressor which required periodic regeneration. The problem has been eliminated with the development of membrane suppressors which are continuously regenerated throughout the run.

Mobile phase ion chromatographic techniques have been developed previously for the analysis of di and polysulfonic acids⁶. The method utilizes a hydrophobic column packing, a hydrophilic mobile phase containing an ion pairing agent and organic modifier and a suppressor to lower the background conductivity. The column is a neutral polystyrene resin which contains no fixed ion exchange sites. This allows the column to be

used for both anion and cation analysis, dependent on the choice of pairing agent. Quaternary ammonium bases chosen from ammonium hydroxide, tripropylammonium hydroxide or TBAOH, are used for the separation of anions. Cations are separated using long chain sulfonic acids. The organic modifier is usually acetonitrile or methanol. Increasing the organic modifier shortens retention times. Smaller pairing agents give better resolution while larger pairing agents increase retention time. Using an MPIC-NS1 separator column, an MPIC-NG1 guard column, an anion micro membrane suppressor (AMMS) and an eluant consisting of 2 mM TBAOH + 1 mM Na_2CO_3 in 20 vol-% acetonitrile, a complete chromatographic analysis of SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_2\text{O}_6^{2-}$, $\text{S}_4\text{O}_6^{2-}$ was obtained in less than 20 minutes.

The MPIC eluant used in this work was the same as the eluant described above, with the exception that the acetonitrile content was increased to 23-25 vol-% which allowed the complete chromatogram to be obtained in 15 minutes or less. In all of the oil shale leachates investigated in the present work, sulfate was the principal ion identified. Ions such as F^- , Cl^- , NO_2^- , and NO_3^- were not observed. In all of these leachates with the exception of the New Albany Shale, SO_4^{2-} was the only ion observed. A typical chromatogram of the New Albany leachate is shown in Figure 1. Three peaks are observed with retention times of 4.37, 7.46 and 11.03 minutes. Table 1 gives retention times of several sulfur oxide standards run under the same conditions as the New Albany leachate. In another experiment, chromatography of the New Albany leachate gave three peaks with retention times of 4.27, 7.02 and 10.15 minutes while SO_4^{2-} , SCN^- , and $\text{S}_4\text{O}_6^{2-}$ had retention times of 4.20, 5.96, and 10.17 minutes respectively. Based on this data, the first and third peaks in the New Albany leachate were identified as SO_4^{2-} and $\text{S}_4\text{O}_6^{2-}$. This identification was further confirmed by spiking experiments as shown in Figures 2, 3 and 4. Attempts to identify the second peak in the New Albany shale chromatogram have thus far been unsuccessful.

Since SO_3^{2-} , SO_4^{2-} , and $\text{S}_2\text{O}_3^{2-}$ all elute between 4.5 and 4.9 minutes under the conditions described above, different conditions must be used to achieve separation of these early eluting hydrophilic ions. Furthermore, unless it is stabilized, sulfite oxidizes to sulfate during chromatography and therefore can not be determined directly. A procedure has been developed⁵ whereby sulfite is stabilized by the addition of formaldehyde, forming a formaldehyde-sulfite adduct, and it is this stabilized adduct ($\text{HOCH}_2\text{SO}_3^-$) which is subsequently chromatographed. Using this procedure, the sulfite stock solution was prepared as described in the experimental section. Leachate samples were diluted in 2 vol-% formaldehyde. The eluant consisted of 3 mM NaHCO_3 /2.4 mM Na_2CO_3 in 0.2%

Figure 1. New Albany Shale Leachate. Column: MPIC-NS1. Eluant: 2 mM TBAOH + 1 mM Na₂CO₃ + 25 vol-% acetonitrile. Flow rate: 1 ml/min. Detection: Suppressed conductivity. Sample: 50 ml.

Table 1

Ion	Retention Time (min)
SO ₄ ²⁻	4.35
S ₂ O ₃ ²⁻	4.76
S ₂ O ₆ ²⁻	5.76
S ₂ O ₈ ²⁻	8.94
S ₄ O ₆ ²⁻	11.03

Figure 2. Unspiked New Albany Shale Leachate

Figure 3. SO_4^{2-} spiked New Albany Shale Leachate

Figure 4. $\text{S}_4\text{O}_6^{2-}$ spiked New Albany Leachate

Column: MPIC-NS1
 Eluant: 2 mM TBAOH + 1 mM Na_2CO_3 + 23 vol-% acetonitrile
 Flow rate: 1 ml/min
 Detection: Suppressed conductivity
 Sample size: 50 μl

formaldehyde. Chromatography was achieved using an HPIC-AS3 separator column, HPIC-AS3 guard column, and a 2 ml/min. flow rate. A sample was prepared containing both sulfate and the derivatized sulfite. Under the conditions described, the derivatized sulfite and sulfate are well separated with retention times of 1.75 and 6.20 minutes respectively as shown in figure 5a. Chromatograms of unspiked and SO_3^{2-} spiked New Albany shale are shown in 5b and c respectively. The spiked sample does not show a significant increase in the sulfite peak at 1.74 minutes. Apparently the SO_3^{2-} that was used to spike the leachate has oxidized to sulfate as shown by the increase in sulfate peak at 6.21 minutes shown in figure 5c. This would be an expected result since sulfite is very easily oxidized. Formaldehyde could be added to the leaching solvent in order to stabilize any sulfite present.

The retention time for thiosulfate using the bicarbonate eluant is unacceptably long (>20 min.). Thiosulfate can be eluted at shorter retention time by using a stronger eluant, but under such conditions, sulfite and sulfate coelute.⁶ When thiosulfate was chromatographed using the mobile phase technique, a sharp peak was obtained with no significant tailing (Figure 6). Traditionally the separation of sulfite, sulfate and thiosulfate requires two separate runs. Sundren and coworkers⁸ have developed a method by which these three ions, can be separated in a single run in 15 min. using a gradient elution technique. A drawback to this technique, however, is the severe tailing of the thiosulfate peak.

FUTURE WORK

Experience in this laboratory has shown ion chromatography to be a promising technique for the determination of anions in oil shale leachates. Further work is required, however, before this technique can be applied routinely. While the investigation undertaken here, and reports in the literature, indicate that the anions of interest in this report can be separated when each is injected as a pure component, the stability of these anions when they occur together in solution remains to be determined. Model mixed anion studies could be used to better understand how the species under investigation interact with each other. Spiking experiments need to be done in order to test the stability of these ions during the leaching process.

High purity water was the only leaching solvent used in this work. Other solvents that should be tested include 1 N NaOH, $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ buffer and 0.2 N EDTA. The effects of leaching solvent, pH, time and temperature need to be investigated.

Figure 5. a) $\text{HOCH}_2\text{SO}_3^- / \text{SO}_4^{2-}$ standard. b) New Albany Shale unspiked; c) New Albany Shale SO_3^{2-} spiked.
Column: AS3
Eluant: 2.4 mM Na_2CO_3 + 3 mM NaHCO_3 + 0.2% formalin
Flow rate: 2.0 ml/min
Detection: Suppressed conductivity

Figure 6. 25ppm $\text{S}_2\text{O}_3^{2-}$
Column: MPIC-NS1.
Eluant: 2 mM TBAOH + 1 mM Na_2CO_3 + 24 vol.-%
acetonitrile
Flow rate: 1 ml/min.

Methods for separation and detection of cyanide and sulfide by ion chromatography using electrochemical detection also remain to be investigated in this laboratory. There are well documented methods for the separation and determination of CN^- , and S^- using electrochemical detection^{9,10,11}. Classical wet chemical techniques for determining sulfide and cyanide are subject to interferences and a distillation step is usually involved. Cyanide and sulfide are easily separated by ion exchange, but their detection via conductivity is poor. This is because the HCN and H_2S which are formed in the suppressor are weakly acidic and therefore only slightly dissociated. When using electrochemical detection, it is important to place the detector before the suppressor device, because when the suppressor lowers eluant conductivity it decreases the concentration of the supporting electrolyte. In fact, when electrochemical detection is used, the suppressor device is not needed, unless it is being used in tandem with a conductivity detector for a simultaneous multielement analysis.

To date no method has been developed for the direct ion chromatographic determination of cyanate ion. One reason is that cyanate reacts with the dilute sulfuric used as suppressor regenerant and forms ammonia according to Equation 1.

This equation is the basis for a wet chemical determination of cyanate. The approach involves the ion exchange separation of cyanate from any ammonia present, conversion of cyanate to ammonia by reaction with 0.05 M H_2SO_4 and the determination of ammonia using Nessler's reagent.¹² Two possible routes are recommended for the ion chromatographic analysis of cyanate. First, since electrochemical detection does not require the use of a suppressor device, acidic conditions are not encountered. This suggests the possibility of using electrochemical detection to develop a method for the ion chromatographic determination of cyanate ion. This would require the selection of an eluant in which cyanate ion remains stable for a reasonable period of time. Secondly, the reaction in Equation 1 could be used to develop an indirect method of cyanate analysis. The method would require two sample pretreatment steps. Namely, the ion exchange separation of any ammonia already present and the conversion of cyanate to ammonia. The ammonium cation thus formed could then be analyzed by established ion chromatographic protocols.^{14,15}

The middle peak observed in the chromatogram of the New Albany Shale leachate (see Figure 1) needs to be identified. Retention times given in Table 1 and for SCN^- in this

paper, indicate that none of the anions listed can account for the unidentified peak. Possibilities include $\text{Fe}(\text{CN})_6^{3-}$ (hexacyanoferrate)¹⁵, and $\text{S}_3\text{O}_6^{2-}$ (trithionate).

The identity of the anions found in the New Albany shale leachate could be further confirmed by an independent technique such as thin layer chromatography.

Complete anion analysis of oil shale leaches requires the determination of many different species, with widely varying solubilities and detection sensitivities. This requires the use of different columns, eluants and modes of detection. For example, ions such as F^- , Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , and SO_3^{2-} are best separated using an ion exchange column, carbonate/bicarbonate eluant and conductivity detection. However, the polythionates are best separated using a mobile phase column with an eluant consisting of an ion pairing agent such as TBAOH and an organic modifier. Ions such as CN^- , S^- which form weakly dissociated acids are not sufficiently detected by conductivity. An important goal in further work would be to develop methods for determination of the maximum number of species with a minimum number of component changes. This will require the development of protocols which employ gradient elution techniques, simultaneous multi-element analysis by using two or more detection modes in tandem, and column switching techniques.

REFERENCES

1. R.A. Nadkarni and D.M. Pond, Anal. Chem. Acta, 146, 261 (1983).
2. R.A. Nadkarni and J.M. Brewer, American Laboratory, 57, 50 (1987).
3. M.E. Potts and T.A. Potas, J. Chromat. Sci. 23, 411 (1985).
4. J.R. Wallace, L. Alden, F.S. Bonomo, J. Nichols and E. Sexton, "Method of Chemical Analysis for Oil Shale", EPA/600/2848/110, 1984 [NTIS #PB84-211226].
5. M.J. McCormick and L.M. Dixon, J. Chromatogr. 322, 478 (1985).
6. J. Weiss, "Handbook of Ion Chromatography," Dionex Corp., Sunnyvale, California, P. 193 (1986).
7. F.J. Trijillo, M.M. Miller, R.K. Skogerboe, H.E. Taylor, C.L. Grant, J. Chromatogr. 53, 1944 (1981).
8. T. Sundren, M. Lindgren, A. Cedergren, Anal. Chem. 55, 2 (1983).
9. R.D. Rocklin and E.L. Johnson, Anal. Chem. 55, 4 (1983).
10. A.M. Bond, I.D. Heritage, G.G. Wallace, M.J. McCormich, Anal. Chem. 54, 583 (1984).
11. Dionex Application Update Au107, April, 1986.
12. W. John Williams, Handbook of Anion Determination, Butterworth and Company, Boston, Mass. p. 68 (1979).
13. Ibid p. 77.
14. F.C. Smith, Jr. and R.C. Chang, The Practice of Ion Chromatography, John Wiley and Sons, New York (1983) p. 32.
15. J. Weiss, ibid p. 127.

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