

# Study of permanently coated columns for the high-performance liquid chromatographic determination of sulphur anions in environmental samples from metallurgical processes

D. J. Barkley\*, J. R. Charbonneau, M. J. Chenier, C. C. Glasgow\* and J. A. Graham

*Mineral Sciences Laboratories, Canada Centre for Mineral and Energy Technology, Ottawa, Ontario K1A 0G1 (Canada)*

---

## ABSTRACT

The behaviour of styrene–divinylbenzene and bonded C<sub>18</sub> reversed-phases permanently coated with cetylpyridinium ion or hexadecyltrimethylammonium ion (“permanent coating” ion–interaction chromatography) were investigated for the determination of sulphur species in samples from studies on environmental control in metallurgical processes. The advantages of these types of exchanger are the ability to vary the ion-exchange capacity and the attainment of high column efficiency. Also demonstrated is the effect of an organic modifier on the control of retention and the wide linear range calibration curves obtained with these columns. Examples of application to the analysis of effluents and acid-tailings residues from metallurgical processing operations for the determination of sulphate, thiosulphate and thiocyanate anions are given. Detection was by indirect UV absorption.

---

## INTRODUCTION

The Canada Centre for Mineral and Energy Technology (CANMET) is committed to the development of technology for the effective removal or disposal of potential environmental contaminants discharged from metallurgical processing operations. The analysis of mixtures of anions including sulphur anions is of interest in studies of environmental problems. Recently much effort has been applied to use of HPLC for the separation and determination of these anions.

There are two main approaches for separation methods applicable to sulphur anion analysis: (a) ion-exchange using fixed-site exchange resins of various composition and, (b) ion-interaction meth-

ods with a variety of sorbents that support dynamically exchanged or permanently bonded ionic functionalities.

It is convenient to subdivide ion-exchange methods into two groups: those in which a suppressor column is used and those in which it is not. The first group includes those methods which are predominantly based on the system originally described by Small *et al.* [1] and commercialized by Dionex and generally described by the term suppressed-ion chromatography. Single-column chromatography methods for anions make up the second group. They were introduced by Gjerde *et al.* [2]. The determination of inorganic anions by non-suppressed ion chromatography generally involves the use of low-capacity, resin-based or silica-based ion-exchange materials combined with a low-conductance eluent.

In ion-interaction chromatography, pioneered by Skelly [3], Molnar *et al.* [4], and Cassidy and Elchuk [5], an ionic hydrophobic reagent is added to the

---

\* Corresponding author. Address for correspondence: 59 Ridgefield Crs., Nepean, Ontario K2H 6S6, Canada.

\* Present address: University of Waterloo, Waterloo, ON, Canada.

mobile phase of a reversed-phase chromatographic system in order to increase the retention of an oppositely charged ionic solute. Two distinct approaches for coating the column with ion-interaction reagent are dynamic coating and permanent coating. In the first approach a reagent of relatively low hydrophobicity is used initially to condition the column and is maintained in the mobile phase for all subsequent chromatography. In the permanent-coating method, a much more hydrophobic reagent is used for initial column conditioning, after which it is removed from the mobile phase.

Our studies [6] with reversed-phase columns that are permanently coated to give a charged surface that can be used for ion exchange have shown that such columns can offer distinct advantages over either dynamically coated or fixed-site ion-exchange separations. We now describe the results of a study to compare the behaviour of styrene–divinylbenzene and bonded C<sub>18</sub> reversed-phase columns coated with hydrophobic reagents, cetylpyridinium bromide (CTP) and hexadecyltrimethylammonium bromide (cetrimide). Applications of these columns to the determination of sulphur anions in various types of environmental samples are shown, and the advantages of this approach are presented.

## EXPERIMENTAL

### Apparatus

The chromatographic pumps were a Waters M-625 pump for chromatographic determinations and a Waters M-45 pump for coating the columns (Waters, Milford, MA, USA). Sample injection was by a Rheodyne Model 9125 sample valve (Rheodyne, Berkeley, CA, USA). Spectra Physics 2000 and Linear 100 variable-wavelength detectors were used for absorbency detection. Data handling was done by Spectra-Physics ChromJet integrators. (Spectra Physics, Santa Clara, CA, USA).

The columns used were 5- $\mu$ m PRP-1 styrene–divinylbenzene, 150  $\times$  4.1 mm I.D. (Hamilton, Reno, NV, USA) and 5- $\mu$ m Supelcosil LC-18-DB, 150  $\times$  4.6 mm I.D. (Supelco Canada, Oakville, Canada).

### Reagents

All solutions were prepared with water which was freshly distilled and passed through a Milli-Q water system (Millipore, Bedford, MA, USA). A stock so-

lution (5 mM) of the eluent acid, 1,3,5-benzenetricarboxylic, was dissolved in water by adding NaOH to a pH value of *ca.* 5. Eluents were prepared by diluting the stock solution with water and adjusting to the optimum pH (refer to Experimental conditions) with tris(hydroxymethyl)aminomethane (THAM). Hexadecyltrimethylammonium bromide (cetrimide) and cetylpyridinium bromide (CTP) were used for coating the columns. These reagents were used as received from the supplier (Sigma, St. Louis, MO, USA). All solvents were HPLC-grade and were obtained from Caledon Labs. (Georgetown, Canada).

### Procedure for coating columns

Solutions containing the coating reagent, CTP or cetrimide, were prepared in water–acetonitrile mixtures (0.5 mM of reagent with 15–30% of acetonitrile). The pH of these coating solutions was 5.5 and no further adjustment was made. The analytical column was first washed with a solution of acetonitrile without the coating reagent (the percentage of acetonitrile determined column capacity). A solution of the coating reagent containing this same percentage of acetonitrile was then pumped through the column. The breakthrough curve was recorded by monitoring the bromide ion with a UV detector at 210 nm. A 1-mM salicylic acid solution (5% acetonitrile and pH 6.5) was pumped through the column until breakthrough of the salicylic anion as recorded at 290 nm. This was followed by equilibrating the column with the eluent. To remove the sorbed coating reagent, a solution of 0.1 M potassium bromide containing 70% acetonitrile was passed through the column for at least 1 h followed by washing with acetonitrile for 10 min.

### Sample preparation

*Nickel process effluent.* To a sample was added 0.1 M NaOH to give a pH of 4.8–5.2. This was followed by the addition of a solution of THAM to a pH of 6.8. The sample was then diluted to an appropriate volume with eluent.

*Gold process effluent.* The samples from the cyanide removal process were preserved by adding sodium hydroxide to a pH of 12. An aliquot of sample was adjusted to pH 5.5–6.0 with eluent acid and then a solution of THAM was added to give a pH of 7.0. The sample was transferred to a 50-ml volu-

metric flask and diluted to the mark with eluent.

**Sulphide concentrate and tailing samples.** The procedure as described by Guillas and Blanchette [7] for dissolving the samples and oxidation of sulphur species to sulphate ion was used. Weighed aliquots from the sample solutions were adjusted to a pH of 6.8 with a solution of THAM, and then transferred to 500 ml volumetric flasks and diluted with eluent.

#### Sample analysis

An aliquot (normally 50  $\mu$ l) was injected into the chromatograph; chromatographic conditions recommended for the samples are those given in Figs. 3 and 4.

## RESULTS AND DISCUSSION

### Comparison of column systems

Both bonded silica ( $C_{18}$ ) and styrene–divinylbenzene (PRP-1) reversed-phases were used in these studies. These columns were coated with the hydrophobic quaternary amines: CTP or cetrimide. The amount of reagent sorbed by a column was studied as a function of concentration of acetonitrile in the coating solution. The concentration of the coating reagent was 0.5 mM. The pH of the coating solution was 5.5. The anion-exchange capacity, which is calculated from the amount of sorbed quaternary amine, might not be necessarily the same as the effective capacity. This is because the amine sorbed by electrostatic interaction through a silanol group does not perform as an anion-exchange site [8]. Therefore, the anion-exchange capacities were calculated from the difference in breakthrough volumes of salicylate between the columns coated and uncoated.

The data in Fig. 1 show the amount of sorbed CTP with concentration of acetonitrile for the  $C_{18}$  and PRP-1 columns. Under the coating conditions used, the coating weights sorbed on the  $C_{18}$  column were higher than for the PRP-1 column for a given concentration of acetonitrile. In previous work [9] we showed that there were only small differences in the weights of the two quaternary amines that sorbed on the  $C_{18}$  column for a given percentage of acetonitrile. This indicated that the cetyl group in these reagents is the main contributor in the hydrophobic interactions with the octadecyl groups of the  $C_{18}$  column.

The  $C_{18}$  phase coated column was found to be more efficient than the PRP-1 column. The column efficiency as given by the height equivalent of a theoretical plate (HETP values) [10] were generally in the range of 0.1–0.15 mm at 1 ml/min for the  $C_{18}$  column when coated with either of the reagents, and the peak shapes of the anions tested,  $Cl^-$ ,  $CNO^-$ ,  $SO_4^{2-}$ ,  $S_2O_3^{2-}$ , and  $CNS^-$ , were similar. Fig. 2 shows the dependence of the capacity factor  $k'$  of the anions on the concentration of the two reagents. As can be seen the effective capacity of a column coated with cetrimide is greater than for a column coated with the same weight of CTP.

Both PRP-1 and  $C_{18}$  columns were stripped and recoated several times for a period of 8 months during these studies, and only small changes in column efficiency and retention times were noted. In general, the columns did not appear to be susceptible to poisoning from extraneous ions in the samples analyzed. However, when an occasional problem was encountered, the ion exchanger was stripped and the column recoated.

### Application of permanently coated column systems

#### Determination of $\mu$ g/ml sulphate in presence of high concentrations of chloride

Sulphate ion at the  $\mu$ g/ml level along with transition metals are monitored in effluents from nickel

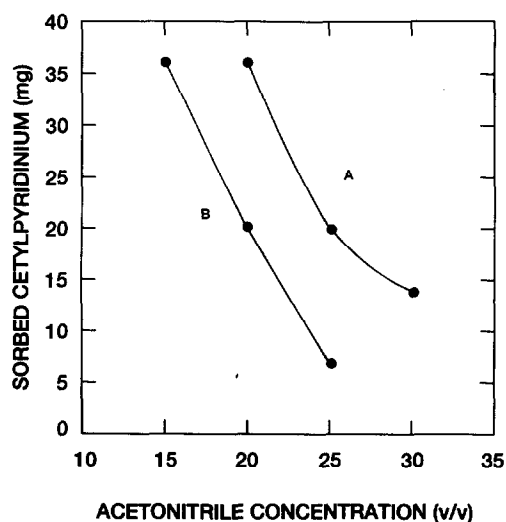


Fig. 1. Variation of amount of sorbed CTP with concentration of acetonitrile in coating solution. (A) Supelcosil LC-18-DB  $C_{18}$  column, (B) Hamilton PRP-1 styrene–divinylbenzene column.

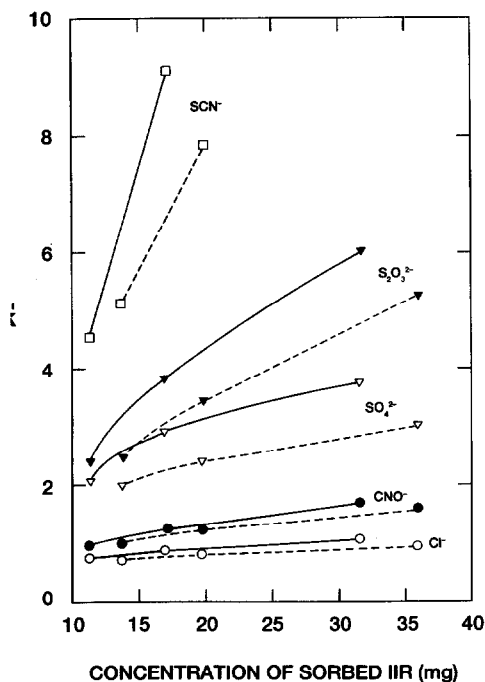


Fig. 2. Relationship between the amount of a coating reagent (IIR) sorbed on  $C_{18}$  column and  $k'$  for anions. The broken curves are for the column coated with cetylpyridinium, and the solid curves are for hexadecyltrimethylammonium coated column; eluent,  $0.5 \cdot 10^{-3}$  mol/l 1,3,5-benzenetricarboxylic acid, neutralized to pH 6.8 with THAM; flow-rate, 1 ml/min; detection by indirect UV at 254 nm.

processing operations. The addition of hydrochloric acid to the samples at the collection site, to prevent hydrolysis of metals, complicated the determination of sulphate.

With both suppressed-ion chromatography and single-column ion chromatography, high concentrations of chloride generally are eluted with sulphate and obscures the sulphate peak in the chromatogram. Pretreating the sample with silver compounds to separate large amounts of chloride has been used [11], but this is time consuming and introduction of contaminants into the sample may take place. Also, peak broadening occurs with this technique.

A high-capacity (32 mg of cetrinide), permanently coated column system gave efficient separation of the sulphate ion from the chloride matrix ion, as shown in Fig. 3. In this example the concentration

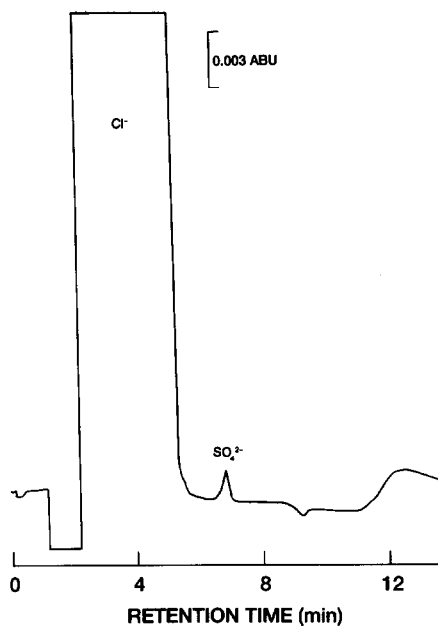


Fig. 3. Separation of sulphate in effluent containing 0.5 M HCl. Experimental conditions: Supelcosil LC-18-DB column coated with 36 mg of hexadecyltrimethylammonium; eluent,  $0.5 \cdot 10^{-3}$  mol/l 1,3,5-benzenetricarboxylic acid, neutralized to pH 6.8 with THAM; flow-rate, 1 ml/min; detection by indirect UV at 254 nm (ABU = absorbance units).

of the sulphate was determined to be 1 ppm in a sample containing 0.5 M of chloride. There is little tailing of the large chloride peak, and this reflects the rapid mass transfer characteristics of permanently coated ion exchangers. A small "reaction peak" from an overloading effect of the high chloride appears after the sulphate. With a lower-capacity column this peak increased in size and obscured the sulphate peak. The ability to adjust the ion-exchange capacity was an important factor in being able to optimize separation of low levels of sulphate from high concentrations of chloride ion.

#### *Determination of thiosulphate, thiocyanate, and sulphate in gold process effluents*

There is an urgent need to develop technology for the effective removal of cyanide from gold process effluents. In projects carried out in this area at CANMET, thiosulphate, thiocyanate, and sulphate, as well as chloride and cyanate, needed to be closely monitored.

TABLE I  
EFFECT OF ORGANIC MODIFIER ON RETENTION TIMES

Eluent acid was  $0.5 \cdot 10^{-3}$  mol/l 1,3,5-benzenetricarboxylic acid adjusted to pH 7.0 with THAM, and contained 5% (v/v) of the solvent; flow-rate was 1 ml/min; detection by indirect UV at 254 nm.

Anion	Retention times (min)		
	Acetonitrile	Methanol	<i>n</i> -Butanol
Cl <sup>-</sup>	2.56	2.46	2.33
SO <sub>4</sub> <sup>2-</sup>	5.05	4.51	4.30
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	6.42	5.84	5.35
CNS <sup>-</sup>	12.54	9.28	6.08

One of the major problems in the determination of thiosulphate and thiocyanate by available chromatography techniques is that the conditions required to separate chloride and cyanate results in rather long retention times for thiosulphate and thiocyanate. Also the sensitivity of reported methods was found to be insufficient [12,13].

In our studies to devise chromatographic conditions for the determination of these anions in one chromatographic run, it was found that the type of organic solvent added to the eluent caused differences in the relative retention of the anions. Table I summarizes some of the retention patterns observed. A change in the solvent concentration from 2 to 6% had much smaller effects than observed when the nature of the solvent was changed. The data shows that a change in solvent from acetonitrile to *n*-butanol decreased the retention of thiosulphate and thiocyanate ion significantly relative to sulphate. This effect was likely due to specific solvation effect on the more polar thiosulphate and thiocyanate anions. Retention time for a pure aqueous system were similar to that observed with methanol. The different solvents had little effect on the retention times of cyanate and chloride.

Fig. 4 shows the separation of chloride, cyanate, sulphate, thiosulphate, and thiocyanate in a typical gold process effluent. The pH of the eluent affected peak shape for cyanate and the size of the system peak, which could interfere with thiocyanate quantitation. The eluent pH was tested over the pH range of 5.5 to 8.0 and interference effects were min-

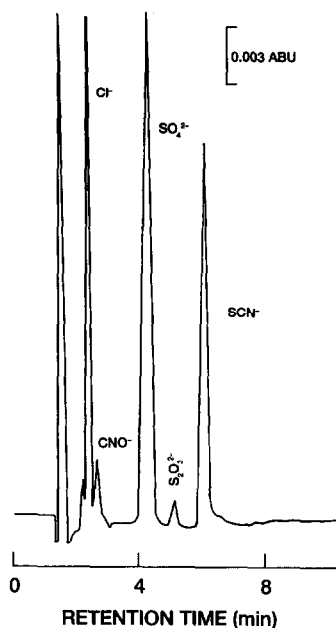


Fig. 4. Separation of chloride, cyanate, sulphate, thiosulphate and thiocyanate in a gold process effluent. Experimental conditions: Supelcosil LC-18-DB column coated with 24 mg of cetylpyridinium; eluent,  $0.5 \times 10^{-3}$  mol/l 1,3,5-benzenetricarboxylic acid, neutralized to pH 7.0 with THAM; modifier, 2.5% (v/v) *n*-butanol; flow-rate, 1 ml/min; detection by indirect UV at 254 nm; Sample, 50  $\mu$ l of diluted sample (10:1) (ABU = absorbance units).

imized when the eluent was adjusted to a pH of 7.0–7.2. The initial system peak in this chromatogram was caused by the high concentration of NaOH present in the sample. Both the early-eluted anions and the more highly retained sulphur species were determined in less than 8 min with good resolution. This system illustrates that exploitation of eluent composition is an attractive feature of these permanently coated reversed-phases, as it is another parameter that can be used to optimize separations.

#### *Analysis of sulphide concentrates and tailings for total sulphur*

The emission of sulphur dioxide in the pyrometallurgy of sulphide concentrates can be monitored by measuring the sulphur content in feed and in materials remaining after processing, *i.e.* tailings. Total sulphur in these materials is determined routinely by combustion techniques. The accuracy of these determinations is dependent on the availabil-

ity of matrix matched and certified standards to be used for instrument calibration.

Methods used to collect analytical data for certification of sulphur standards have been restricted to the classical gravimetric procedure and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) [14], since these are the only techniques for the analysis of total sulphur which are not matrix-dependent and are independent of compositional reference materials for calibration purposes.

The present authors experience with HPLC dynamic ion-exchange techniques has shown that a peak-height repeatability ( $1\sigma$ ) of  $<1\%$  was obtained for the determination of rare earths in samples from uranium ore refining processes [15]. Further, our application of permanently coated anion-exchange systems has indicated that wide linear range calibration curves are obtained, and large weights of an anion, up to  $10\ \mu\text{g}$ , can be used for sample injection [9]. Errors associated with the sample loop are not a concern, as repeatabilities are expected to be  $\pm 0.1\%$  [16]. Consequently, the permanently coated column chromatographic approach was investigated for the determination of total sulphur in tailings and concentrates as an alternative technique to the gravimetric and ICP-AES methods.

Samples used in this study were Canadian Certified Reference Materials from CANMET. Three samples of acid tailings and a copper concentrate were analyzed. The wet chemical procedure described by Guillas and Blanchette [7] for dissolving the samples and oxidation of sulphur species to sulphate ion was used. Dilutions were made of accurately weighed aliquots from the sample solution. The chromatographic conditions for the samples are those given in Fig. 3. The weight of sulphate ion in the injected samples was 5–7 ng.

The results obtained for the samples are shown in Table II along with the corresponding values for these samples from the CANMET certification program for comparison. The HPLC data were obtained from the average of five samples, each analyzed in duplicate. The average relative standard deviation (R.S.D.) was 0.48%. The data show that excellent agreement was obtained between the values recommended by the Canadian Certified Reference Materials Project and the HPLC results. The concentrations of sulphur were calculated from

TABLE II

HPLC ANALYSIS OF CANMET CANADIAN CERTIFIED REFERENCE MATERIALS FOR TOTAL SULPHUR

Reference material	Type of material	CCRMP <sup>a</sup> value	HPLC <sup>d</sup> value	HPLC S.D.
RTS-2	Tailings	19.5 <sup>b</sup>	19.5	0.076
RTS-3	Tailings	10.3 <sup>b</sup>	10.2	0.042
RTS-4	Tailings	35.6 <sup>b</sup>	34.6	0.17
CCU-a1a	Copper concentrate	33.8 <sup>c</sup>	33.8	0.18

<sup>a</sup> Canadian Certified Reference Materials Project (CCRMP) of CANMET.

<sup>b</sup> CCRMP recommended value.

<sup>c</sup> Certified value,  $\pm 95\%$ ; confidence interval = 0.3%.

<sup>d</sup> Average of results of 5 samples, each analyzed in duplicate.

peak area calibration curves prepared from standards that did not contain ions to simulate the sample matrix, and illustrates non-biased recovery of the sulphur by this HPLC system. This study has shown that permanent coated column techniques can be used to determine total sulphur in tailings and concentrates with a precision ( $1\sigma$ ) of  $<1\%$ .

## CONCLUSIONS

Anion exchangers formed by the sorption of hydrophobic cations on reversed-phase columns can offer significant advantages over bonded fixed-site exchangers for the separation of sulphur anions. These exchangers give greater chromatographic efficiency and greater flexibility with regard to choice of column capacity and eluent composition for the development of separations that may be difficult on other types of ion exchangers. This kind of chromatography has given reliable analysis of samples from the environmental area of metallurgical processing for anions and is applied in our Laboratory to the resolution of difficult sample matrices.

## REFERENCES

- 1 H. Small, T. S. Stevens and W. C. Bauman, *Anal. Chem.*, 47 (1975) 1801.
- 2 D. T. Gjerde, J. S. Fritz and G. Schmuckler, *J. Chromatogr.*, 187 (1980) 35.
- 3 N. E. Skelly, *Anal. Chem.*, 54 (1982) 57.
- 4 I. Molnar, H. Knauer and D. Wilk, *J. Chromatogr.*, 201 (1980) 225.

- 5 R. M. Cassidy and S. Elchuk, *Anal. Chem.*, 54 (1982) 1558.
- 6 D. J. Barkley, T. E. Dahams and K. N. Villeneuve, *J. Chromatogr.*, 395 (1987) 631.
- 7 R. J. Guillas and M. C. Blanchette, *Report, MSL 89-36 (TR)*, CANMET, Ottawa, 1989.
- 8 T. Takeuchi and E. S. Yeung, *J. Chromatogr.*, 483 (1989) 145.
- 9 D. J. Barkley, L. A. Bennett, J. R. Charbonneau and L. A. Pokrajac, *J. Chromatogr.*, 606 (1992) 195.
- 10 L. R. Snyder and J. J. Kirkland, *Introduction to Modern Liquid Chromatography*, Wiley-Interscience, New York, 2nd ed., 1979, p. 28.
- 11 P. R. Haddad and P. E. Jackson, *Ion Chromatography, Principles and Applications*, Elsevier, Amsterdam, 1990, p. 429.
- 12 J. Weisz and M. Gobl, *Fresenius' Z. Anal. Chem.*, 320 (1985) 439.
- 13 J. N. Story, *J. Chromatogr. Sci.*, 21 (1983) 272.
- 14 H. F. Steger, *Report, MSL 89-45 (TR)*, CANMET, Ottawa, 1989.
- 15 D. J. Barkley, M. Blanchette, R. M. Cassidy and S. Elchuk, *Anal. Chem.*, 58 (1986) 2222.
- 16 C. H. Knight, R. M. Cassidy, B. M. Recoskie, and L. W. Green, *Anal. Chem.*, 56 (1984) 476.