

CHROMSYMP. 1176

## PERMANENTLY COATED ION EXCHANGERS FOR LIQUID CHROMATOGRAPHIC DETERMINATION OF ANIONIC SPECIES IN SAMPLES FROM ENVIRONMENTAL CONTROL PROCESSES

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### SUMMARY

Reversed phases coated with a “permanently” sorbed ion exchanger and indirect UV detection were investigated for the determination of a number of anions in solutions from some environmental control process studies. The advantages of permanently coated systems and indirect UV detection are discussed, and the ability to vary the column selectivity by eluent–solvent combinations and the ion exchange capacity of these ion exchangers for optimization of resolution are illustrated. Low-molecular-weight organic acids were determined in solutions from studies into the use of biological oxygen barriers on the surface of mine tailing deposits, and samples from tests to reduce toxic materials in gold process effluents were analyzed for chloride, cyanate, sulphate, thiosulphate and thiocyanate. The limit of detection by indirect UV for the low-molecular-organic acids is *ca.* 0.1  $\mu\text{g/ml}$  and for the inorganic anions is *ca.* 0.05  $\mu\text{g/ml}$ .

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### INTRODUCTION

The Canada Centre for Mineral and Energy Technology (CANMET) contributes to the development of technology for the effective removal or disposal of potential environmental contaminants discharged from metallurgical processing operations. Reverse osmosis and acidification techniques are being investigated for the removal of cyanide from gold process effluents, and to optimize conditions, the determination of chloride, cyanate, sulphate, thiosulphate and thiocyanate are required. Another area of environmental technology under study is the use of vegetation on the surface of pyrite-containing mine tailings to inhibit bacterial sulphide mineral oxidation, which is the primary cause of sulphuric acid generation from these deposits. In this investigation, the determination of acetic, propionic, lactic, and pyruvic acids is desired to assist in identifying microbial mechanism.

Low-molecular-weight organic acids have been determined by gas chromatography, and there are chemical procedures for detecting thiocyanate, thiosulphate

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and cyanate, but these methods are labour intensive and have limited sensitivity. High-performance liquid chromatography (HPLC) can be applied to these analyses. However, most of the methods reported for determining low-molecular-weight organic acids have the disadvantage that they are either not sensitive enough<sup>1</sup> or because of a high concentration of sulphate, the analysis time would be excessively long<sup>2</sup>. One of the major problems in the analysis of thiosulphate and thiocyanate is that the retention times for these anions are rather long when chloride is to be determined; also the sensitivity of reported methods was found to be insufficient<sup>3,4</sup>.

Recent studies have been conducted with dynamic ion exchangers produced by the sorption of a hydrophobic ionic modifier from the eluent onto the hydrophobic surface of a reversed phase to produce a charged double layer,<sup>5,6</sup> and with reversed-phase columns that are permanently coated with large, hydrophobic, quaternary amines to give a charged surface<sup>7</sup>. Results have shown that these systems have several advantages for separations over conventional bonded-phase ion-exchange columns. These exchangers gave greater flexibility with regard to choice of variables for the optimization of resolution and are compatible with conductivity and indirect UV absorbance detection.

This paper reports the results of studies of these systems with conductivity and indirect UV detection and effect of the ion-exchange capacity, the eluent acid, the organic solvent composition, and the eluent pH for the optimization of chromatographic conditions to determine the anions in these samples. The organic acids of interest were acetic, lactic, propionic and pyruvic acid, and the samples were effluents from lysimeter leaching tests, in which water is percolated through vegetation covered tailings beds. These solutions can also contain large concentrations of sulphate and iron. Samples for the determination of sulphate, thiosulphate, thiocyanate, cyanate and chloride were from acidification and reverse osmosis tests for the removal of cyanide from gold process effluents, and contain a relatively high concentration of sulphate ion.

## EXPERIMENTAL

### *Apparatus*

The chromatographic systems consisted of a Spectra Physics SP8700 pump (Spectra Physics, Santa Clara, CA, U.S.A.), a Waters M-45 pump (Waters, Milford, MA, U.S.A.), Rheodyne Model 7125 sample valves (Rheodyne, Berkeley, CA, U.S.A.), Kratos SF753 and SF773 absorbance detectors (Kratos Analytical Instruments, Westwood, NJ, U.S.A.), a Waters 430 conductivity detector, and Spectra Physics SP4270 integrators.

The columns used were as follows: 5- $\mu$ m PLPR-S styrene-divinylbenzene, 150  $\times$  4.6 mm (Polymer Lab., Stow, OH, U.S.A.); 5- $\mu$ m PRP-1 styrene-divinylbenzene, 150  $\times$  4.1 mm (Hamilton, Reno, NV, U.S.A.); 5- $\mu$ m Supelcosil LC-18, 150  $\times$  4.6 mm (Supelco Canada, Oakville, Canada); and 5- $\mu$ m Supelcosil LC-18DB, 150  $\times$  4.6 mm.

### *Reagents*

The organic acids used for elution and for indirect detection of sample ions were salicylic, phthalic, 1,2,4-benzenetricarboxylic, 1,3,5-benzenetricarboxylic and

5-sulphosalicylic acid. The co-ions used to neutralize the eluent acids were tris(hydroxymethyl)aminomethane (THAM), tetramethyl-ammonium hydroxide (TMA), and tetraethylammonium hydroxide (TEA). These reagents were used as received from the supplier (Sigma, St. Louis, MO, USA). HPLC-grade solvents were obtained from Caledon Labs. (Georgetown, Canada). Tetrabutylammonium hydroxide, 40% (v/v) (Sigma) was used as received. Standards were made from reagent-grade salts. All reagents solutions were prepared from distilled water purified with a Milli-Q deionizing unit (Millipore, Bedford, MA, U.S.A.).

#### *Column coating*

The analytical columns were prewashed with 100 ml of acetonitrile–water (7:1) followed by 1200 ml of  $5 \cdot 10^{-4}$  M cetylpyridinium chloride in 18% aq. acetonitrile (for a high-capacity column) or 23% aq. acetonitrile (for a low-capacity column) at a flow-rate of 1 ml/min. The eluent was then passed through the column until equilibrium was obtained (*ca.* 150 ml). The amount of sorbed modifier was determined by elution of the cetylpyridinium ion with acetonitrile–water (7:1), and spectrophotometric analysis of the eluate at 257 nm.

#### *Sample analysis*

The samples for organic acid analysis were at pH 2–6. A small amount of chloroform was added as a biocide. An aliquot was adjusted to pH 5.0 with THAM and diluted to 50 ml with the eluent. The samples from the cyanide acidification process had been neutralized to pH 9 or 12 with sodium carbonate or sodium hydroxide. An aliquot was adjusted to pH 6.0 with eluent acid and then diluted to 50 ml with eluent. A 50- $\mu$ l sample was injected into the chromatograph. Chromatographic conditions recommended for most of the samples are those given in Figs. 1 and 3. Quantitation was by comparison of peak areas with standard calibrations curves of peak areas for known volume concentrations of anions determined under the same chromatographic conditions.

## RESULTS AND DISCUSSION

#### *Column systems*

Bonded-silica ( $C_{18}$ ) and styrene–divinylbenzene (SDB) reversed phases used in these studies are listed in the Experimental section. The  $C_{18}$  phases were more efficient than the SDB phase columns, although the particle size was the same (5  $\mu$ m). Also the SDB phases were slower to equilibrate when elution conditions were changed. Dynamic and permanently coated ion-exchange separations were investigated on both these types of columns using tetrabutylammonium salts. The dynamic systems were slower to equilibrate when elution conditions were changed, and were more prone to induced and system peak interferences. Detection by conductivity was not as sensitive for dynamic ion exchange as for permanently coated systems due to higher background conductivity, which was caused by the  $TBA^+$  in the eluent. Consequently,  $C_{18}$  permanently coated columns were used to investigate the variables affecting selectivity and detection for analysis of the samples.

Two  $C_{18}$  reversed-phase (Supelcosil LC-18) columns were used in the investigation over a period of eight months. These were coated at two different concen-

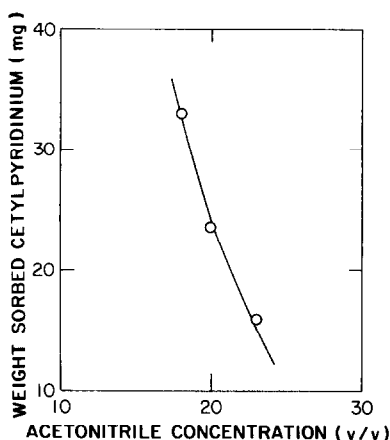


Fig. 1. Variation of amount of sorbed cetylpyridinium with concentration of acetonitrile in coating solution. Coating conditions as given in the Experimental section.

trations of cetylpyridinium ion (CPI); a "low"-capacity column (16 mg of sorbed CPI) and a "high"-capacity column (33 mg of CPI) which corresponds to column loadings of 0.02 mequiv/ml and 0.04 mequiv/ml, respectively. The data in Fig. 1 shows the variation of the amount of sorbed cetylpyridinium with concentration of acetonitrile in the coating solution. Changes in column efficiency and retention times were small at either concentration of CPI during the test period. Another bonded phase packing, Supelcosil LC-18 DB, was briefly studied and the difference found in efficiency and retention times between the two types of bonded phases was not significant.

### Detection

Detections of the anions by conductivity and by indirect UV absorption were compared. The low-molecular-weight organic acids with  $pK$  values around 4.5 gave low or no response to conductivity measurement, depending on the organic acid and the conductance of the eluent. Sensitivity was poor for thiocyanate with conducto-

TABLE I  
SENSITIVITY OF INDIRECT UV DETECTION

<i>Eluent acid</i>	<i>Wavelength maxima of eluent (nm)</i>	<i>Wavelength of maximum sensitivity (nm)</i>	<i>Relative* sensitivity for <math>SO_4^{2-}</math></i>
Salicylic	295	293	2.5
Phthalic	280	245	2.8
1,2,4-Benzenetricarboxylic	285	254	1.9
1,3,5-Benzenetricarboxylic	280	254	1.3
5-Sulphosalicylic	295	295	1.4

\* Experimental conditions: Supelcosil LC-18 column, 5  $\mu$ m, 150  $\times$  4.6 mm, coated with  $5 \cdot 10^{-4}$  M cetylpyridinium chloride in 23% (v/v) acetonitrile; all eluent acids were  $0.5 \cdot 10^{-3}$  M, adjusted to pH 7.0 with THAM, and contained 5% (v/v) of acetonitrile; the flow-rate was 1 ml/min.

metric detection. In indirect UV absorbance (or vacancy detection) the absorbance of the eluent is monitored and sample ions are detected by the decrease in absorbance resulting from the exchange of eluent anion for the sorbed sample anion. All the acids listed can be used as eluents for indirect UV absorbance detection. With this detection method, the sulphur species and the organic anions were detected without a wide variation in sensitivity for a given eluent.

The sensitivity of indirect detection is dependent on the charge on the eluent and sample ions and the molar absorptivity of the eluent ion<sup>8</sup>. Since the molar absorptivity of an eluent is dependent upon wavelength, maximum sensitivity with an eluent could be obtained by adjusting the detector wavelength to give maximum detection for the anions. Table I lists the wavelength for maximum sensitivity obtained experimentally for the anions and the absorption maxima for the eluents. This table also shows the relative sensitivity of sulphate at the wavelengths of maximum sensitivity for the eluents by indirect UV absorption, and indicates the dependence of the sensitivity on the eluent charge.

#### Parameters affecting column selectivity

The eluent acid, the solvent composition, the eluent pH and the ion-exchange capacity of the coated column all influenced column selectivity. The stronger eluents, 1,2,4-benzenetricarboxylic, 1,3,5-benzenetricarboxylic and 5-sulphosalicylic acid,

TABLE II

#### RELATIVE RETENTION TIMES FOR DIFFERENT ELUENT-SOLVENT COMBINATIONS

Retention times are given relative to acetonitrile and absolute retention (min) for acetonitrile are given in brackets. All eluent acids were  $0.5 \cdot 10^{-3} M$ , adjusted to pH 7.0 with THAM, and contained 5% (v/v) of the solvent. The flow-rate was 1 ml/min.

Anion	1,3,5-Benzenetricarboxylic acid				Phthalic acid	
	THF	Acetonitrile	Methanol	n-Butanol	Acetonitrile	n-Butanol
<i>Low capacity column*</i>						
Cl <sup>-</sup>	1.0	1.0 ( 2.56)	0.96	0.91	1.0 (4.18)	1.17
CNO <sup>-</sup>	1.15	1.0 ( 3.07)	0.91	0.86		
SO <sub>4</sub> <sup>2-</sup>	1.06	1.0 ( 5.95)	0.89	0.85	1.0 (19.5)	1.55
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	0.86	1.0 ( 6.42)	0.91	0.83		
SCN <sup>-</sup>	1.46	1.0 (12.45)	0.74	0.48		
<i>Salicylic acid</i>						
					<i>1,2,4-Benzene-tricarboxylic acid</i>	
	THF	Acetonitrile	Methanol	n-Butanol	Acetonitrile	n-Butanol
<i>High capacity column**</i>						
Acetate	1.49	1.0 (3.64)	1.16	2.54	1.0 (2.54)	0.84
Lactate	1.54	1.0 (3.63)	1.18	2.50	1.0 (2.33)	0.98
Propionate	1.87	1.0 (4.25)	1.28	2.42	1.0 (2.39)	0.96
Pyruvate	1.40	1.0 (4.35)	1.23	2.32		

\* Coating of CPI (16-mg) on a Supelcosil LC-18 column, 5  $\mu$ m, 150  $\times$  4.6 mm.

\*\* Coating of CPI (33-mg) on a Supelcosil LC-18 column, 5  $\mu$ m, 150  $\times$  4.6 mm.

TABLE III

## EFFECT OF pH AND SOLVENT ON RETENTION TIME

Eluent,  $0.5 \cdot 10^{-3}$  M 1,2,4-benzenetricarboxylic acid, 5% (v/v) of the solvent, pH adjusted with THAM, flow-rate 1.0 ml/min. Column: Supelcosil LC-18, 5  $\mu$ m, 150  $\times$  4.6 mm, coated with  $5 \cdot 10^{-4}$  M cetylpyridinium chloride in 23% acetonitrile. Retention times are given relative to pH 7, and absolute retention (min) for pH 7 are given in brackets.

Anion	Acetonitrile			<i>n</i> -Butanol		
	pH 7	pH 5.5	pH 4.5	pH 7	pH 5.5	pH 4.5
Cl <sup>-</sup>	1.0 ( 2.25)	1.00	1.29	1.0 (2.30)	1.02	1.20
CNO <sup>-</sup>	1.0 ( 2.90)	1.17	ND*	1.0 (2.58)	1.12	7.05
SO <sub>4</sub> <sup>2-</sup>	1.0 ( 4.40)	1.16	1.83	1.0 (4.16)	1.08	1.68
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	1.0 ( 6.15)	1.06	1.71	1.0 (5.16)	1.11	1.76
SCN <sup>-</sup>	1.0 (11.60)	1.05	1.38	1.0 (5.90)	1.14	1.41

\* Not detected.

were used for the separation of the more highly retained sulphur species, while salicylic and phthalic acid were used for eluting the weaker organic acids. All these eluents influenced selectivity. Eluents neutralized with TEA hydroxide gave the shortest retention times, while THAM produced the longest times. THAM was used, as it is a better buffer and did not reduce sensitivity in indirect UV detection.

The types of organic solvents added to the eluent caused differences in the relative retention of the anions. Table II summarizes some of the retention patterns observed relative to that obtained for acetonitrile. After a given eluent-solvent combination was tested, the column was reequilibrated with the eluent containing acetonitrile, and the test samples were again analysed before another eluent-solvent combination was examined. Retention time for a pure aqueous system were similar to that observed with methanol. The retention of the anions decreased with the ad-

TABLE IV

## EFFECT OF pH AND COLUMN CAPACITY ON RETENTION TIME

Eluent,  $5 \cdot 10^{-3}$  M salicylic acid, pH adjusted with THAM, flow-rate 1.0 ml/min. Retention times are given relative to pH 7, and absolute retentions (min) for pH 7 are given in brackets.

Anion	Column capacity* (mg)					
	33			16		
	pH 7	pH 5.5	pH 4.5	pH 7	pH 5.5	pH 4.5
Acetate	1.0 (4.91)	1.08	1.07	1.0 (3.64)	1.06	0.98
Lactate	1.0 (4.56)	1.23	1.22	1.0 (3.63)	1.10	1.13
Propionate	1.0 (5.79)	1.09	1.09	1.0 (4.25)	1.12	1.05
Pyruvate	1.0 (6.06)	1.13	1.12	1.0 (4.35)	1.09	1.10

\* Weight of cetylpyridinium ion sorbed onto Supelcosil LC-18, 5  $\mu$ m, 150  $\times$  4.6 mm columns.

dition of alcohols to the tricarboxylic acid eluents while the opposite effects were observed with salicylic and phthalic acid eluents. Tetrahydrofuran gave a mixture of effects for the inorganic anions. For a sulphosalicylic acid eluent (not shown) there was a small decrease in retention times when *n*-butanol replaced acetonitrile as the organic solvent. A change in the organic solvent concentration from 2 to 8% had much smaller effects than that observed when the nature of the solvent was changed; there was an increase or decrease in retention, and this depended on the solvent-eluent combination. The observed changes in retentions were likely related to changes in the bonded phase due to sorption of the organic solvent. This sorption could cause changes in the distribution of charged species within the bonded phase and thus influence ion exchange behavior. Hydrophobic interactions will also be changed and this would effect, in particular, hydrophobic anions such as the organic acids. A change in the solvent from acetonitrile to *n*-butanol in a tricarboxylic acid eluent resulted in a significant difference in relative retention for thiocyanate ion and this was likely due to specific solvation effects.

The effect of pH of the eluent on selectivity was studied over the range of 4.5 to 7.2 for some of the eluents. All the eluents became more effective with increasing pH. Some changes in selectivity with pH were observed and this is illustrated in Table III where butanol and acetonitrile are used as modifiers with 1,3,5-benzenetricarboxylic acid eluents for the separation of the inorganic anions. Cyanate, which would be hydrolyzed, was strongly adsorbed and thiosulphate and thiocyanate crossed over at the lower pH when butanol was present. Table IV shows the effect of pH and a change in capacity of the column on the relative retention of the organic acids. The data shows that the ion-exchange capacity of the permanently coated columns can be used to optimize selectivity.

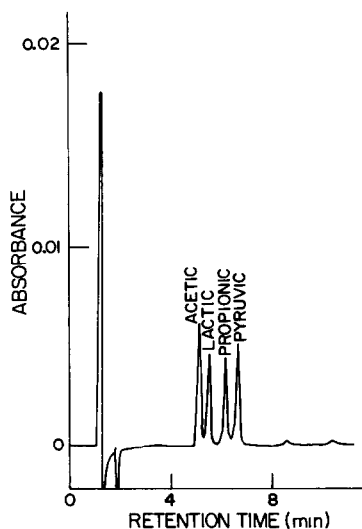


Fig. 2. Separation of acetic, lactic, propionic and pyruvic acids. Experimental conditions: Supelcosil LC-18 column,  $150 \times 4.6$  mm,  $5 \mu\text{m}$  coated with  $5 \cdot 10^{-4}$  M cetylpyridinium chloride in 18% (v/v) acetonitrile; eluent  $0.5 \cdot 10^{-3}$  M salicylic acid, neutralized to pH 5.5 with THAM, modifier 5% (v/v) acetonitrile, and flow-rate 1.0 ml/min; sample,  $50 \mu\text{l}$  of solution containing  $1 \mu\text{g/ml}$  of the above anions; detection by indirect UV at 293 nm.



Fig. 3. Calibration curves for organic acids. Experimental conditions as for Fig. 2.

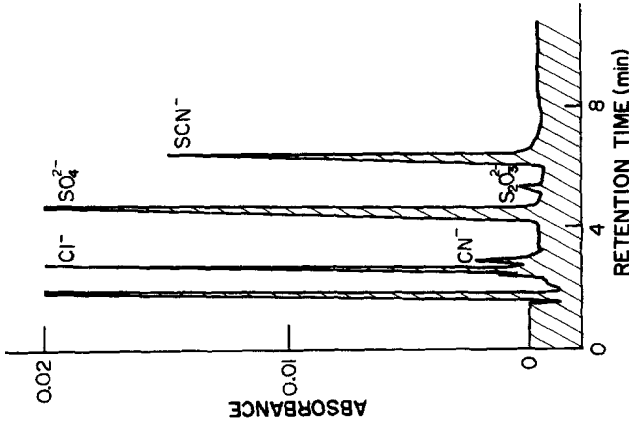


Fig. 4. Separation of chloride, cyanate, sulphate, thiosulphate and thiocyanate in a gold process effluent. Experimental conditions Supelcostil LC-18,  $150 \times 4.6$  mm,  $5\text{-}\mu\text{m}$  column coated with  $5 \cdot 10^{-4}$  M cetylpyridinium chloride in 23% (v/v) acetonitrile; eluent  $0.5 \cdot 10^{-3}$  M 1,3,5-benzenetricarboxylic acid, neutralized to pH 7 with THAM; Modifier, 2.5% (v/v) *n*-butanol and flow-rate 1 ml/min; sample,  $50 \mu\text{l}$  of diluted sample (10:1); detection by indirect UV at 254 nm.



TABLE V  
DETECTION LIMITS\*

Anion	$\mu\text{g/ml}^{**}$	Anion	$\mu\text{g/ml}^{***}$
Acetate	0.06	Chloride	0.02
Lactate	0.07	Cyanate	0.05
Propionate	0.09	Sulphate	0.05
Pyruvate	0.10	Thiosulphate	0.07
		Thiocyanate	0.1

\* Three times peak-to-peak base line noise.

\*\* Chromatographic conditions given in Fig. 2.

\*\*\* Chromatographic conditions given in Fig. 4.

#### *Analysis of lysimeter leaching test samples*

The column capacity, the eluent strength (*i.e.* salicylic acid), the eluent concentration, and the pH were optimized to give separation efficiency and sensitive detection for the organic acids. Fig. 2 shows the separation and essentially the same system was used for the analysis for the test samples. The calibration curves obtained for separations is shown in Fig. 3 and peak areas were used, because peak heights gave non-linear curves. The detection limits for these anions, calculated as three times baseline peak-to-peak noise are given in Table V. Lactic acid was found in the samples, and none of the other organic acids. The concentration of lactate was  $0.1 \cdot 10^{-3}$ – $0.3 \cdot 10^{-3}$  M. The samples also contained chloride, nitrate and sulphate ions, and with the system used, chloride was eluted before lactate, and nitrate after pyruvate. Sulphate was eluted as a large peak at 32 min. To reduce analysis time, a pre-separation of sulphate ion on a concentrator column is under investigation.

#### *Analysis of samples from a project to reduce cyanide in gold process effluents*

Fig. 4 shows the separation of chloride, cyanate, sulphate, thiosulphate and thiocyanate in a typical gold process effluent. The calibration curves obtained for the separations of these anions are shown in Fig. 5 and the curves were linear for the range tested. Peak areas were used for quantitation, because detection of peak heights by indirect detection was not reproducible. The detection limits are shown in Table V. The pH of the injected sample affected peak shape for cyanate and the size of the

TABLE VI  
RECOVERY OF ANIONS FROM A GOLD PROCESS EFFLUENT SAMPLE

Chromatograph of the sample and experimental conditions similar to that given in Fig. 4.

Anion	ppm	Standard deviation ( $\sigma$ )
Chloride	167	4.9
Cyanate	55	3.9
Sulphate	444	5.0
Thiosulphate	18.7	0.62
Thiocyanate	277	4.9

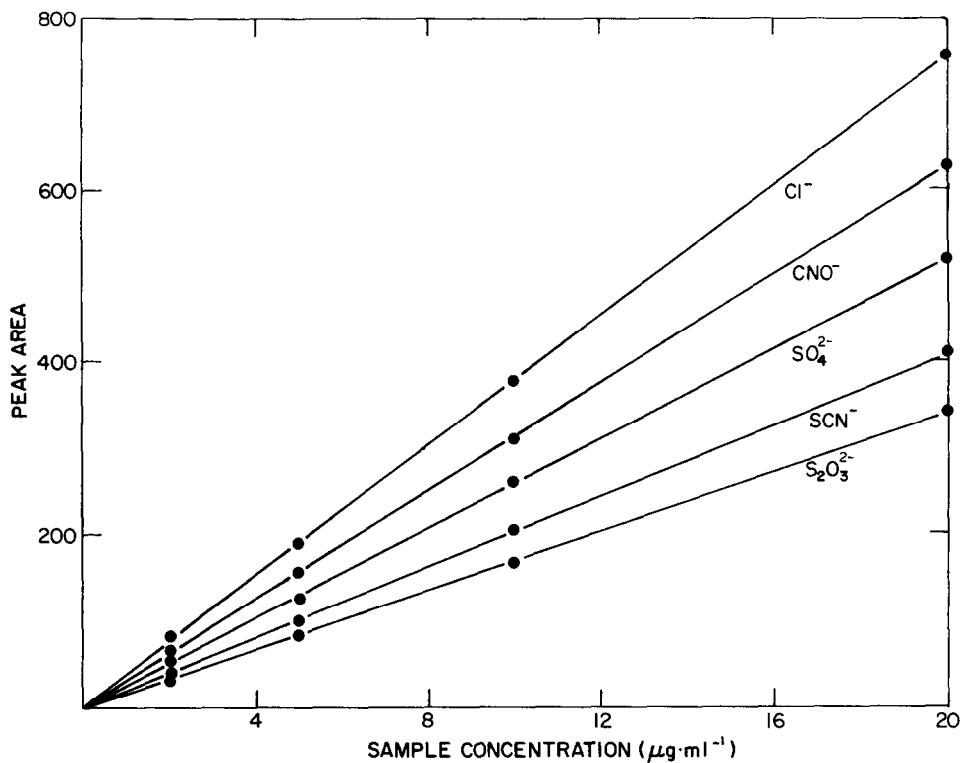


Fig. 5. Calibration curves for chloride, cyanate, sulphate, thiosulphate and thiocyanate. Experimental conditions as for Fig. 4.

system peak, which could interfere with thiocyanate quantitation. The concentration of the organic solvent could also affect the size of the system peak. The sample pH was tested over the pH range of 5.0 to 8.0, and interference effects were minimized when the sample was adjusted to pH 6.0–6.2 with the eluent acid. The separation time for these anions was 7 min. Reproducibility for the procedure is shown in Table VI and the data were obtained for a sample that had been analyzed eight times in a two week period. Results obtained by standard addition analysis were in agreement within  $\pm 5\%$  with those calculated from direct injection. This system illustrates that with appropriate adjustment in eluent strength, eluent concentration, solvent–eluent composition, and column capacity good resolution and sensitive detection was obtained for both the early eluting anions and for the more highly retained sulphur species.

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