# The application of single-column ion chromatography for the determination of sulphate in rain-water samples

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## Abstract

Single-column ion chromatography using potassium hydrogen phthalate at pH 5,0 or sodium benzoate at pH 6,8 as mobile phase, was compared to a methylthymol blue continuous flow method for the analysis of sulphate in rain-water samples. Statistical evaluation indicated comparable results between the ion chromatographic and continuous flow methods. Sulphate recovery using the ion chromatographic method was 96 to 100% and the continuous flow method 100 to 108%.

## Introduction

The separation of several common anions chromatographically in only a few minutes was described for the first time by Small et al. (1975). Their technique commonly known as suppressed ion chromatography used basic eluents to separate sample anions on a low capacity anion-exchange column. The eluent then flowed through a second suppressor column, which was a high capacity cation-exchange column in the hydrogen form. This converted the eluent into a low-conducting weak acid and the sample anions into highly conducting acids.

Gjerde et al. (1979; 1980) introduced a new system for anion chromatography, which allows for the elimination of the suppressor column, made possible by the use of a special anion-exchange resin of very low capacity and the adoption of an eluent having a very low conductivity.

Single-column chromatography has been used for water/environmental samples and acurate results have been obtained (Hern et al., 1983). An effective analytical method for determining parts per billion concentrations of chloride and sulphate in very pure water such as steam condensates using single-column ion chromatography was demonstrated by Roberts et al. (1981).

It is still widely believed that suppressed ion chromatography is the preferred method to single-column ion chromatography. This paper aims to illustrate that accurate analyses can be done without the need for a suppressor column, and compares 2 different methods for determining sulphate in rain-water samples, namely single-column ion chromatography and a continuous flow system method.

In addition to illustrating the effectiveness of single-column ion chromatography, it was decided to develop a method for the determination of sulphate in rain-water samples using ion chromatography. Although sulphate analysis can be done on the Auto Analyser at a higher rate with less cost per analysis, the ion chromatography technique exhibits a wider dynamic range (0,1 mg/$\ell$ to 40 mg/$\ell$) as well as being the more sensitive method and it is for this reason that ion chromatography is considered the conventional method for determining sulphate in rain-water samples. An added advantage of using ion chromatography is that a number of anions can be determined simultaneously, whereas with an Auto Analyser, a number of Auto Analysers with various methods are needed.

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## Experimental

### Apparatus

#### Ion chromatograph

A Shimadzu HIC-6A ion chromatograph with the following components was used for the evaluation of sulphate in rain-water samples:

- LC-6A liquid pump
- CTO-6A column oven
- COD-6A conductivity detector
- SCL-6B system controller
- SIL-6B auto injector

Parameter settings were as follows:

Flow rate : (i) sodium benzoate: 1,5 m$\ell$/min
            (ii) potassium hydrogen phthalate: 1,2 m$\ell$/min
Oven temp.: 30°C
Polarity : positive
Gain : 0,1 μS/cm
Range : 64
Response : standard

A Hamilton PRP-X100 column consisting of a trimethylammonium strong base ion exchanger was used.

The number of theoretical plates for the sulphate peak using a 2 mM solution of potassium hydrogen phthalate, at a flow rate of 1,2 m$\ell$/min and a pH of 5,0, was calculated to be 4399.

The areas of the chromatograph were calculated using a Hewlett Packard 3359A chromatographic work system.

### Auto analyser

The determination of sulphate is based on the reaction, at an acidic pH, of sulphate ions with barium ions to form barium sulphate (Badenhorst et al., 1992). This is followed by measurement, at high pH, of the increase in absorbance at 480 nm, due to the removal of the barium methylthymol blue complex. The sample is first passed through a sodium-type cation-exchange column to remove multivalent metal ions. Since the chemistry is non-linear, a solution containing 5 mg/$\ell$ sulphate is added to improve the linearity. The sample containing sulphate is then reacted with an alcohol

**TABLE 1**
**THE PRECISION OF THE 2 METHODS USED IN TERMS OF STANDARD DEVIATION**

| Auto Analyser | | Ion chromatograph | | | |
|---|---|---|---|---|---|
| Sulphate concentration (mg/$\ell$ $SO_4^{2-}$) | Standard deviation (%) | Potassium hydrogen phtalate: Sulphate concentration (mg/$\ell$ $SO_4^{2-}$) | Standard deviation (%) | Sodium benzoate: Sulphate concentration (mg/$\ell$ $SO_4^{2-}$) | Standard deviation (%) |
| 15 | 0,06 | 40 | 0,85 | 40 | 0,89 |
| 5 | 0,04 | 20 | 0,52 | 20 | 0,48 |
| 1 | 0,04 | 10 | 0,41 | 10 | 0,36 |

**TABLE 2**
**THE RECOVERY OF SULPHATE IN RAIN-WATER SAMPLES USING A SPIKING METHOD**

| Auto Analyser | | | Ion chromatograph | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Potassium hydrogen phthalate | | | Sodium benzoate | | |
| Expected (mg/$\ell$) | Obtained (mg/$\ell$) | Recovery (%) | Expected (mg/$\ell$) | Obtained (mg/$\ell$) | Recovery (%) | Expected (mg/$\ell$) | Obtained (mg/$\ell$) | Recovery (%) |
| 85,67 | 88,25 | 103 | 54,39 | 53,85 | 99,0 | 45,1 | 44,34 | 98,3 |
| 42,89 | 45,90 | 107 | 22,82 | 21,91 | 96,0 | 44,3 | 44,47 | 100,4 |
| 35,05 | 37,85 | 108 | 44,35 | 43,64 | 98,4 | 42,4 | 42,02 | 99,0 |
| 40,05 | 40,05 | 100 | 26,79 | 26,31 | 98,2 | 27,6 | 27,40 | 99,0 |
| 56,68 | 60,65 | 107 | 28,43 | 28,26 | 99,4 | 28,6 | 28,36 | 99,2 |
| Mean | | 105 | | | 98 | | | 99 |

solution of barium chloride and methylthymol blue (MTB) at a pH of 2,5 to 3,0 to form barium sulphate. The combined solution is raised to a pH of 12,5 to 13,0 so that the excess barium reacts with the MTB. The uncomplexed MTB colour is grey; if it is all chelated with barium, the colour is blue. The grey colour of the uncomplexed MTB is measured and is representative of the sulphate concentration in the sample. The optimum concentration range for the sulphate method is 0,5 mg/$\ell$ to 25 mg/$\ell$.

A Technicon Auto Analyser Sampler IV was used to present samples to a Technicon Auto Analyser model II peristaltic pump, fitted with standard Technicon pump tubes. A Technicon double channel colorimeter, with a 50,0 mm debubble type flow cell (internal diameter = 1,5 mm) was used.

## Materials and methods

Forty rain-water samples were collected from 2 different areas, namely the Olifants River catchment area and the Vaal Dam catchment area, using the bulk method. These samples include both dust and rain or any other form of atmospheric deposition. The sulphate content of these samples was determined using the ion chromatograph with 2 different mobile phases and an Auto Analyser using the MTB method (Badenhorst et al., 1992). AR-grade reagents and deionised water were used throughout. For the ion chromatograph, two mobile phases were prepared and used:

- 2 mM (0,4085 g/$\ell$) potassium hydrogen phthalate adjusted to pH 5,0 using a 1 N solution of sodium hydroxide.
- 6 mM (0,8647 g/$\ell$) sodium benzoate at pH 6,8.

Working sulphate standards of 40, 20, 10, 5 and 1 mg/$\ell$ were prepared from a stock solution containing 1 000 mg/$\ell$ $SO_4^{2-}$ (1,4787 g sodium sulphate in 1 $\ell$ water). Mobile phases, stock solutions, standards and samples were all filtered through a 0,22 $\mu$m membrane filter (Whatman GF/C).

All samples analysed using the ion chromatograph were repeated 3 times, with the run time for each sample being 12 min for the potassium hydrogen phthalate and 15 min for the sodium benzoate. The volume of sample added was 20 $\mu\ell$.

## Method evaluation

The precision of the methods was examined using a range of 1 to 15 mg/$\ell$ sulphate for the Auto Analyzer and 1 to 40 mg/$\ell$ sulphate for the ion chromatograph. The results are shown in Table 1.

Recovery results on a number of rain-water samples were determined using a spiking method (Table 2). The average recovery using the Auto Analyzer was 105%, whilst the average recoveries of the 2 mobile phases using the ion chromatograph were 98% for the potassium hydrogen phthalate and 99% for the sodium benzoate.

**TABLE 3**
**ANALYSIS OF VARIANCE FOR THE 2 MOBILE PHASES USED ON THE ION CHROMATOGRAPH AND THE AUTO ANALYSER**

| Source of variation | Sum of squares | Degrees freedom | Mean square | F-ratio | Significance level |
|---|---|---|---|---|---|
| Main effects | 35,83 | 2 | 17,91 | 0,203 | 0,8163 |
| Factor | 35,83 | 2 | 17,91 | 0,203 | 0,8163 |
| Residual | 8192 | 93 | 88,00 | | |
| Total (corr.) | 8228 | 95 | | | |

## Discussion

Statistical analysis of variance using Statgraphics 3.0I was done on the 3 methods used and the results are summarised in Table 3.

From Table 3, it can be seen that the significance level of 0,8163 is greater than 0,05 which means that working on a 95% confidence level there is no significant difference between the methods used. The F-ratio of 0,203 also indicates that there is no significant difference between the methods.

Figure 1 represents a graphic comparison of 5 samples using the different methods. From Fig. 1 it appears that the Auto Analyser is overreading and this fact is borne out by the mean recovery shown in Table 2.

When a conductivity detector is coupled directly to an anion-exchange separation column, it is important to choose the mobile phase carefully. A good mobile phase, is, in general, an aromatic organic anion which has a high selectivity coefficient for the anion-exchange resin. The cation, normally associated with the mobile phase may be sodium, potassium, ammonium or hydrogen. Benzoate and phthalate are among the mobile phases found to be successful.

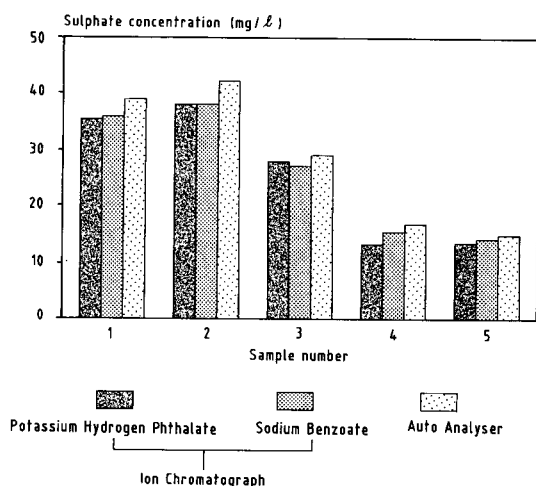Retention times of anions can be adjusted by varying the concentrations of the mobile phase. In general, the less concen-trated the mobile phase, the longer will be the retention time of the anions. When looking at early-eluting anions, such as fluoride and chloride, it is advisable to use a less concentrated mobile phase with a pH which allows for longer retention times, as these anions will then be better separated away from the characteristic water dip. Conversely, if one is interested in late-eluting anions, such as sulphate, a more concentrated mobile phase with a pH allowing for shorter retention times, is used. For the purpose of this study, sodium benzoate was used at a concentration of 6 mM, as an increased concentration shifts the retention time of the sulphate peak to under 15 min (Fig. 2). At lower concentrations (2 mM), very long retention times for the sulphate peak are observed, making the use of sodium benzoate at these low concentrations impractical for the determination of sulphate, but useful for separating early-eluting anions such as fluoride and nitrate.

Sodium or potassium phthalate is a more powerful mobile phase than benzoate and is used for the separation of divalent anions and other late-eluting anions such as sulphate (Fig. 3). The eluting abilities of benzoate and phthalate overlap, and it is usually possible to resolve a mixture of anions using one or both of these mobile phases.

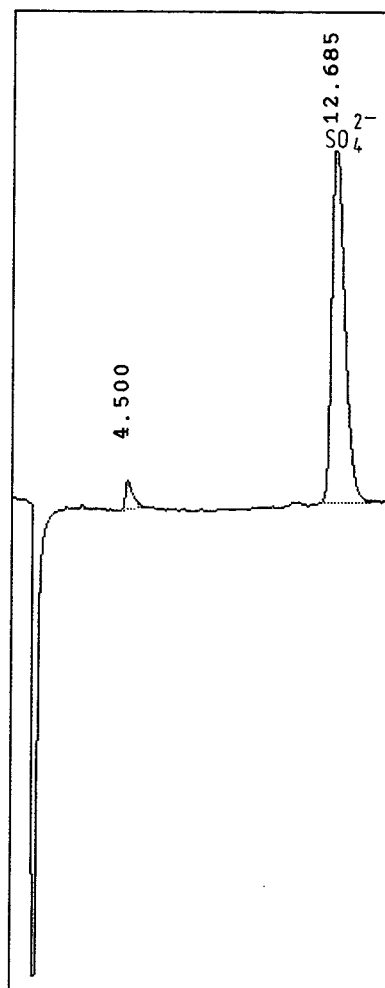Adjusting the pH of the mobile phase can also be very useful



*Figure 1*
*Graphic comparison of the different methods used*



*Figure 2*
*Chromatograph of 40 mg/ℓ sulphate, using a solution of 6 mM sodium benzoate, at a flow rate of 1,5 mℓ /min and a pH of 6,8. Retention time (in min) of the sulphate anion appears above the peak*
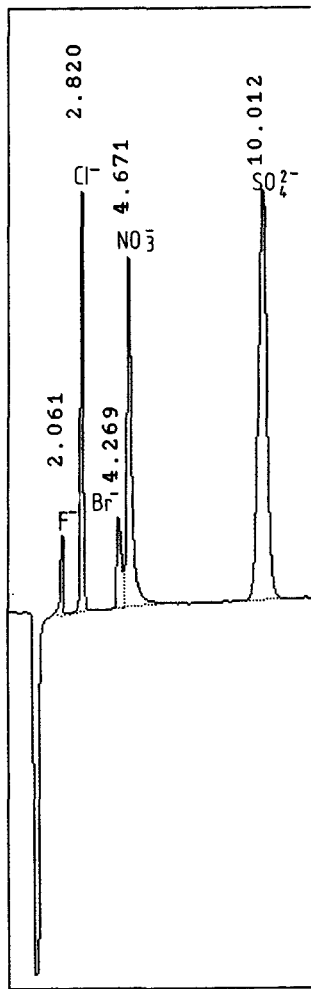
*Figure 3*

*Separation of 10 mg/ℓ fluoride, 10 mg/ℓ chloride, 10 mg/ℓ bromide, 30 mg/ℓ nitrate and 40 mg/ℓ sulphate, using a 2 mM solution of potassium hydrogen phthalate, at a pH of 5,0 and a flow rate of 1,2 mℓ/min. Retention times (in min) of each anion appear above each peak*

in adjusting the retention times of certain anions relative to most other anions. When a 2 mM solution of potassium hydrogen phthalate with a pH value of 4,0 is used as the mobile phase, the

retention time of the sulphate ion is approximately 27 min. (flow rate 1,2 mℓ/min). By adjusting the pH of the mobile phase to 5,0 (using 1N NaOH), the retention time of the sulphate ion is shifted dramatically to approximately 10 min (flow rate 1,2 mℓ/min). The retention times of other anions including chloride, bromide and nitrate, were also seen to shift, although to a far lesser degree.

The application of ion chromatography to the determination of anions in a large variety of samples, has demonstrated that relatively few interferences are encountered. However, large amounts of bicarbonate result in a substantial positive peak, which would not constitute interference in sulphate rain-water samples, but which may interfere with the determination of chloride and fluoride.

## Conclusion

The results of this study indicate that both the Auto Analyser and ion chromatography methods are adequate for the determination of sulphate in rain-water samples. Even though the recovery results indicate that the Auto Analyser is overreading, statistical analysis indicates that at the 95% confidence level, there is no significant difference between the 2 methods.

## Acknowledgements

## References

BADENHORST, JE, DAVIES, E, KEMPSTER, PL, KYRIACOU, P, SCHOONRAAD, IJ, TRUTER, E, and VAN VLIET, HR (1992) *Analytical Methods Manual* TR 151. Department of Water Affairs.

GJERDE, DT, FRITZ, JS and SCHMUCKLER, G (1979) Anion chromatography with low conductivity eluents. *J. Chromatogr.* **186** 509.

GJERDE, DT, FRITZ, JS and SCHMUCKLER, G (1980) Anion exchange with low conductivity eluents II. *J. Chromatogr.* **187** 35.

HERN, IA, RUTHERFORD, GK and VAN LOON, GW (1983) Determination of chloride, nitrate, sulphate and total sulphur in environmental samples by single-column ion chromatography. *Talanta* **30** 677-682.

ROBERTS, KN, GJERDE, DT and FRITZ, JS (1981) Single-column ion chromatography for the determination of chloride and sulphate in steam condensates and boiler feed. *Anal. Chem.* **53** 1691-1695.

SMALL, H, STEVENS, TS and BAUMAN, WS (1975) Novel ion exchange chromatographic method using conductimetric detection. *Anal. Chem.* **47** 1801-1809.