

CHROM. 14,801

Note

Analysis of anions by ion chromatography using ultraviolet detection

R. A. COCHRANE* and D. E. HILLMAN

Materials Quality Assurance Directorate, Royal Arsenal East, London SE18 6TD (Great Britain)

(Received February 10th, 1982)

Single-column anion chromatography has been reported by Gjerde *et al.*^{1,2} as a method for the analysis of anions. Separation is performed on a low-capacity, silica-based ion-exchange column and is achieved by using a very dilute solution of an aromatic acid salt (*e.g.* potassium hydrogen phthalate) as the eluent. An electrical conductivity detector is used to monitor the anion peaks. The system is simple to operate but is less sensitive than the two column system marketed by Dionex Corporation³ where the use of a suppressor column eliminates the background conductivity.

This note describes the use of an ultraviolet detection system which relies on the decrease in the background ultraviolet absorption of the potassium hydrogen phthalate buffer as the individual anions are eluted. The sensitivity of this system is approximately one order of magnitude greater than with the conductance detector.

EXPERIMENTAL

The chromatographic system consisted of the following parts in series: (1) Milton Roy mini pump set at a flow-rate of 1.5 ml/min; (2) a Rheodyne 7120 sample injection valve fitted with a 100- μ l sample loop; (3) Vydac 302 column, 25 cm \times 4.6 mm I.D. (Separations Group); (4) LDC Model 701 conducto monitor used in the differential mode at the most sensitive setting ($\times 10$); (5) Schoeffel SF770 variable-wavelength UV detector set at 308 nm detection wavelength and the zero suppression at -2 (maximum -5); (6) Servoscribe dual-pen recorder, set at 10 mV output and 1 cm/min chart speed.

Potassium hydrogen phthalate solution ($5 \cdot 10^{-3}$ M) at pH 4.6, filtered through a Millipore 0.65- μ m filter (type DA) was used as eluent. Sample solutions were prepared from analytical grade reagents dissolved in the eluent.

RESULTS AND DISCUSSION

UV detection of anions is not generally applicable except at very low wavelengths such as 215 nm⁴. An alternative method of detection of non-UV-absorbing species is to add a low level of UV-absorbing substance to the eluent. The emergence of a component is then shown by a negative detector response.

This effect is easily achieved in the ion chromatography system where the preferred buffer solution (potassium hydrogen phthalate) has a strong UV response

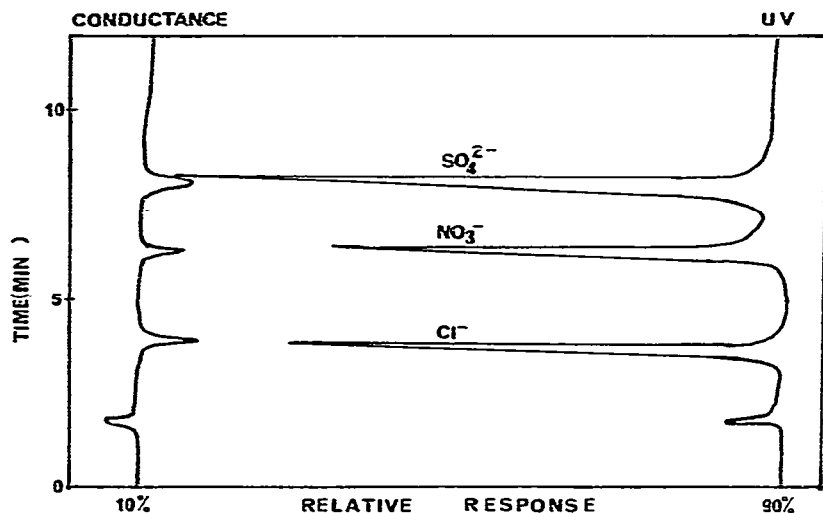


Fig. 1. Separation of chloride (10 ppm), nitrate (25 ppm) and sulphate (25 ppm) with UV and conductance detection.

with λ_{\max} at 280 nm. At this wavelength the excessively strong absorbance will not allow adequate zero suppression, and the wavelength was therefore increased to a much less absorbing region (308 nm) where the background response could be backed-off sufficiently for the detector to be used at maximum sensitivity. A comparison of the conductivity and UV detectors showed that:

- (1) The response is greater for UV detection by a factor of 5–30 (see Fig. 1 and

TABLE I

LIMITS OF DETECTION FOR A NUMBER OF ANIONS USING THE CONDUCTANCE AND UV DETECTORS

Anion	Limits of detection (ppm)*	
	Conductance	UV
Chloride	1	0.1
Bromide	1	0.2
Nitrite	1	0.2
Chlorate	2	0.2
Nitrate	3	0.3
Sulphate	3	0.3
Iodide	3	0.5
Phosphate	4	0.3
Bromate	5	0.2
Acetate	9	0.4
Formate	10	0.5
Iodate	12	0.4

* This is equivalent to twice the noise level at the most sensitive setting for both detectors.

TABLE II
LINEARITY RANGES FOR SOME ANIONS

<i>Anions</i>	<i>Linearity range (ppm)</i> <i>(upper limit)</i>	
	<i>Conductance</i>	<i>UV</i>
Chloride	25	50
Nitrate	60	60
Sulphate	80	100

Table I). A relatively stronger, negative UV response occurs for weakly acidic anions because there is no dependence on their ionisation.

(2) Linearity ranges using UV detection are greater than those for conductance (Table II).

(3) Conductance detection may give positive or negative peaks depending on eluent concentration and pH (ref. 2). UV detection of non-UV-absorbing ions gives a response in one direction only.

A number of water extracts have been analysed using the two detectors in series. The ultraviolet detection system has extended the range of application of single-column ion chromatography by overcoming one of the main limitations of the single-column system *i.e.* the level of sensitivity for trace analysis.

REFERENCES

- 1 D. T. Gjerde, J. S. Fritz and G. Schmuckler, *J. Chromatogr.*, 186 (1979) 509.
- 2 D. T. Gjerde, G. Schmuckler and J. S. Fritz, *J. Chromatogr.*, 187 (1980) 35.
- 3 C. A. Pohl, E. L. Johnson, *J. Chromatogr. Sci.*, 18 (1980) 442.
- 4 R. N. Reeve, *J. Chromatogr.*, 177 (1979) 393.