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## Note

### Novel eluent for the UV and conductometric detection of anions in unsuppressed ion chromatography

J. P. IVEY

*Australian Government Analytical Laboratories, Kingston, Tasmania (Australia)*

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Unsuppressed ion chromatography as reported by Gjerde *et al.*<sup>1,2</sup> has utilised either dilute acetate or aromatic acid salts as eluents. Reeve<sup>3</sup> has shown that reversed-phase systems with UV-transparent eluents could be used for the sensitive detection of selected anions. However, the strong absorbance of the eluents used in unsuppressed ion chromatography, at the wavelengths employed by Reeve, has prevented the use of UV detection in ion chromatography.

The sodium salt of methanesulphonic acid has been found to be an excellent eluent for the chromatography of inorganic anions allowing detection via UV absorption and conductivity.

#### EXPERIMENTAL

The chromatographic system consisted of the following elements: (1) a Waters M45 pump at a flow-rate of 2 ml/min; (2) Waters U6K variable-volume injector; (3) Wescan anion column (25 cm × 4.6 mm I.D.); (4) Waters 441 fixed-wavelength detector at 214 nm; (5) Wescan conductivity detector Model 213A; (6) Omniscrite dual pen recorder at 0.5 cm/min.

Sodium neutralised methanesulphonic acid (reagent grade, Merck) pH 5 was filtered through a Millipore 0.45- $\mu$ m filter and used as eluent. Standards were prepared from analytical grade reagent dissolved in distilled deionised water.

#### RESULTS AND DISCUSSION

The detection of ions by conductance in unsuppressed ion chromatography is achieved due to the difference in ionic conductances of the sample and eluent ions. The limiting equivalent conductances and UV absorption at 214 nm of common eluent and sample ions are listed in Table I. Methanesulphonate ion has a higher limiting equivalent conductance than the commonly used eluents in unsuppressed ion chromatography but is comparable to the equimolar solutions of monohydrogen and dihydrogen orthophosphates used by Molnár *et al.*<sup>4</sup>.

An example of detection by conductance and UV is shown in Fig. 1a for chloride and nitrate. The method has been applied to the analysis of precipitation from a pristine marine site, Fig. 1b, and to the detection of iodine in dairy products as the iodide ion, Fig. 2.

TABLE I

LIMITING EQUIVALENT CONDUCTANCES AND ABSORBANCES OF ANIONS IN AQUEOUS SOLUTION AT 25°C

Anion	Conductance ( $\text{mho} \cdot \text{cm}^2/\text{equiv.}$ )	Absorbance*
Carbonate	72	$3.4 \cdot 10^{-1}$
Bicarbonate	44.5	—
Monohydrogen phosphate	57	—
Dihydrogen phosphate	33	—
Chloride	76.4	—
Bromide	78.1	$4.0 \cdot 10^0$
Iodide	76.8	$3.6 \cdot 10^1$
Nitrate	71.4	$2.0 \cdot 10^2$
Nitrite	71.8	$6.5 \cdot 10^1$
Acetate	40.9	$1.3 \cdot 10^{-1}$
Benzoate	32.4	$1.6 \cdot 10^5$
Monohydrogen phthalate	29.4	$1.8 \cdot 10^5$
Methanesulphonate	48.8	$3.5 \cdot 10^{-4}$
Ethanesulphonate	39.6	—

\* 1-cm absorbance of a 5 mM solution of the sodium salt of the anion.

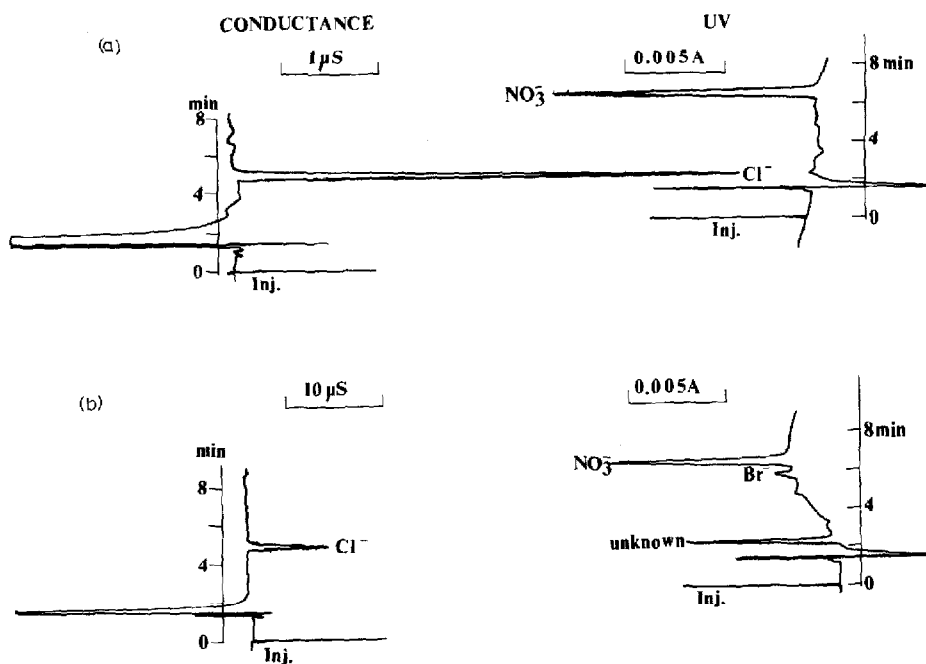


Fig. 1. Dual detection of chloride by conductance and nitrate by UV. (a) Standards, chloride 7.5  $\mu\text{g}$  and nitrate 45 ng; (b) precipitation from the Australian Background Air Pollution Monitoring Network Station, Cape Grim. Flow-rate: 2 ml/min. Mobile phase: 2 mM methanesulphonic acid sodium salt, pH 5. Injection volume: 150  $\mu\text{l}$ .

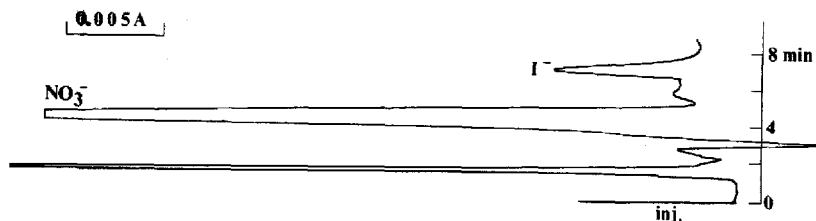


Fig. 2. Detection of iodide ( $0.2 \mu\text{g}$ ) in butter after alkaline ashing and neutralisation. Eluent:  $10 \text{ mM}$  methanesulphonate sodium salt. Flow-rate:  $2 \text{ ml/min}$ . Injection volume:  $150 \mu\text{l}$ .

Detection limits of ion chromatography with ion-pairing reagents in reversed-phase systems are limited by peak broadening at large sample injection volumes. Ion chromatography with low-capacity ion-exchange columns commonly employs preconcentration of ions via sample-loop precolumns or by loading of the sample onto the first portion of the analytical column. The detection limit of ion-exchange systems is therefore potentially much lower than reversed-phase systems. In Fig. 3 a 2-ml injection of laboratory distilled water is shown.

In the range of standards utilised,  $0\text{--}30 \mu\text{g}$  for chloride and  $0\text{--}100 \text{ ng}$  for nitrite, nitrate, bromide and iodide, the peak area gave a linear response with mass injected.

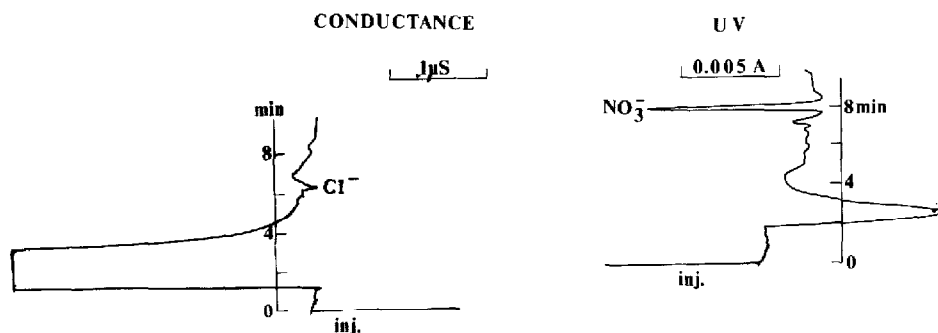


Fig. 3. A nitrate blank of  $10 \text{ ng/ml}$  is determined from a 2-ml injection of laboratory-distilled water. Conditions as for Fig. 1.

TABLE II

LIMITS OF DETECTION AND RETENTION TIMES OF SELECTED ANIONS USING CONDUCTANCE AND UV DETECTORS

Anion	Detection limit*	Retention time (min)
Chloride	$0.2 \mu\text{g}$ (Cond.)	4.72
Nitrite	$2 \text{ ng}$ (UV)	5.51
Nitrate	$1 \text{ ng}$ (UV)	6.20
Bromide	$4 \text{ ng}$ (UV)	5.62
Iodide	$30 \text{ ng}$ (UV)	7.05

\* At twice the peak to peak noise.

## CONCLUSIONS

Dual detection of anions in conductometric and UV modes has been established with a UV-transparent eluent of low equivalent conductance. The methodology should be particularly useful in the fields of water chemistry and food science.

## REFERENCES

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- 2 D. T. Gjerde, G. Schmuckler and J. S. Fritz, *J. Chromatogr.*, 187 (1980) 35.
- 3 R. N. Reeve, *J. Chromatogr.*, 177 (1979) 393.
- 4 I. Molnár, H. Knauer and D. Wilk, *J. Chromatogr.*, 201 (1980) 225.