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Note

Sensitive detection of anions in ion chromatography using UV detection at wavelengths less than 200 nm

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Recently UV detection has been suggested by a number of authors as an excellent alternative to conductometric detection for the determination of anions by unsuppressed ion chromatography¹⁻⁶. Two approaches have been taken. In the so called direct method conditions are chosen so that the UV absorbance of ions being determined significantly exceeds that of the eluting species, giving positive detection peaks¹⁻³. In the indirect method a strongly absorbing eluent is used so that the bands of separated ions have relatively low absorbance and are detected as negative UV peaks⁴⁻⁶. In both cases to date detection has been ≥ 205 nm¹⁻⁷.

The direct method usually has the advantage of being the more sensitive, with detection limits for a number of anions being at least as low as those achieved by suppressed ion chromatography/conductometric detection, but has suffered from an inability to detect "optically transparent" anions^{1,5}. In this note we suggest that at least for some ions this difficulty may be overcome by using detection wavelengths below 200 nm, a spectral region in which most anions have measurable extinction coefficients.

EXPERIMENTAL

The system used consisted of an LDC CCM (Chromatography Control Module), LDC Constametric III pump, Rheodyne 7125 injector, Vydac 302 anion column (25 cm \times 4.6 mm I.D.), and LDC spectro Monitor D variable wavelength UV detector. The injector sample loop was replaced by a 50-mm long concentrator column (4.6 mm I.D.) containing Vydac SC 30-40 micron pellicular packing material. All injections were 500 μ l; except where otherwise stated all chromatograms were recorded at a flow-rate of 3 ml/min.

Solutions were prepared from AR grade reagents and distilled, de-ionised water from a Milli-Q water purification system. The eluent used was methane sulphonic acid (Tokyo Kasai, 80% w/v) diluted to 0.02 M and filtered through a 0.45 μ m filter.

RESULTS AND DISCUSSION

The potential usefulness of detection at < 200 nm is well illustrated by a prob-

lem we have encountered in studies of cloud and rainwater composition at remote sites in the southern hemisphere. In this work there is interest in both chloride and nitrate ion concentrations, but in many cases nitrate concentrations are too low to be detected by unsuppressed ion chromatography using conductometric detection. On the other hand in some cases where nitrate could be determined chloride ion was sometimes so concentrated as to be off-scale, making a separate analysis necessary for each ion. Bromide ion is also of interest, but has never been quantifiable using conductometric detection.

Ivey⁷ largely overcame these difficulties by using methane sulphonic acid as eluent and a dual UV-conductometric detection system, UV at 214 nm for nitrate and bromide, and conductivity for chloride. Even so the weakness of the bromide response at natural levels in rainwater and the need for two detectors are undesirable features of the method. However in this note we show that both of these features can be eliminated by a change in detection wavelength to < 200 nm.

Fig. 1 shows chromatograms of a standard solution containing $50 \mu\text{M}$ chloride, $5 \mu\text{M}$ bromide and $5 \mu\text{M}$ nitrate, recorded at 190, 197 and 214 nm, respectively. It is clear from Fig. 1 that response for all three ions is considerably enhanced in going from 214 to 190 nm, the most dramatic enhancement being for chloride ion. This is more clearly demonstrated in Fig. 2, where change in response for each ion is plotted

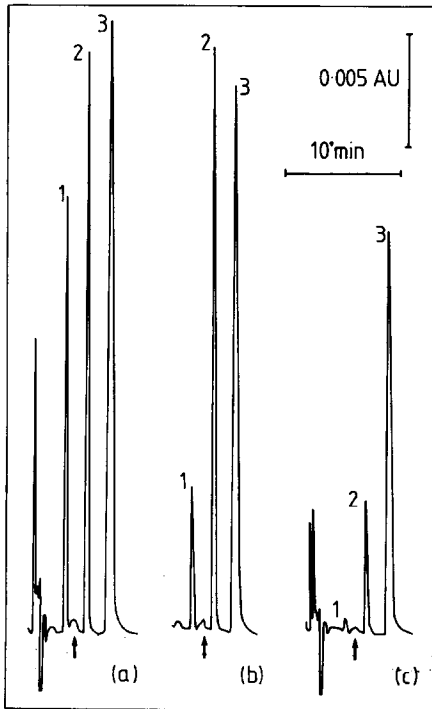


Fig. 1. Chromatograms of standard solution containing (1) $50 \mu\text{M}$ chloride, (2) $5 \mu\text{M}$ bromide and (3) $5 \mu\text{M}$ nitrate. Conditions given in text. (a) 190 nm, (b) 197 nm, (c) 214 nm. Peaks to the left of the chloride peak are associated with injection transients; the arrowed peak is an unknown contaminant in the de-ionised water.

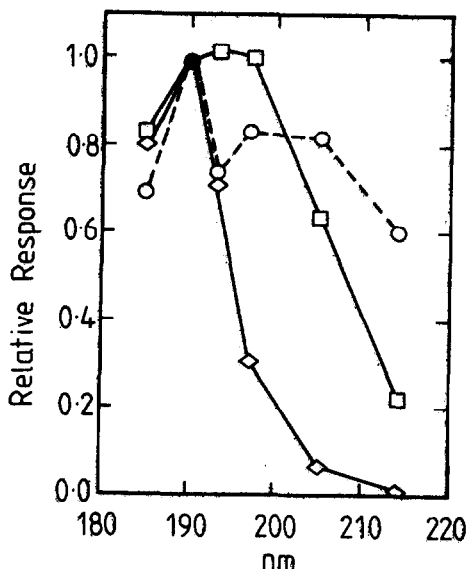


Fig. 2. Response (peak area) relative to that at 190 nm as a function of detection wavelength for chloride (◇), bromide (□) and nitrate (○).

as a function of wavelength. In Fig. 2 response (peak area) is normalised for each ion to the response for that ion at 190 nm.

Optimal sensitivity for this particular mixture of ions is attained at 190 nm, at which the absolute responses (peak areas) are in the ratio 1:0.58:0.034 for nitrate:bromide:chloride. However the differences between the wavelength dependences shown in Fig. 2 may also be used to give added flexibility to the analytical method. For example cloudwater samples collected in pristine conditions over the Southern Ocean contain considerable chloride, derived from sea salt, but only minute traces of nitrate. By changing the detection wavelength to 197 nm the response of chloride relative to that of nitrate is reduced by almost a factor of 3, while absolute nitrate response is only marginally reduced (see Fig. 2). In this way chromatograms having chloride and nitrate peaks of comparable height were obtained easily despite the disparity in concentrations. Another case is that where bromide is of particular interest. Using a detection wavelength between 197 and 205 nm it is possible to further suppress strong chloride peaks relative to bromide and nitrate and so reduce overlap between strong chloride and weak bromide peaks with only slight loss of bromide sensitivity.

As expected on the basis of Fig. 2 it was found in practice that detection at 190 nm gave a useful increase in sensitivity over detection at longer wavelengths for all three ions. Tests were carried out at 1.5 ml/min flow rate using very dilute standard solutions and the 0.002 a.u.f.s. detector range with 5-sec time constant. At a signal-to-noise ratio of 3 (peak height/baseline peak-to-peak noise level) estimated detection limits were 0.5 ng for nitrate and bromide and 3 ng for chloride. These values compare with Ivey's results at 214 nm of 1 ng, 4 ng and not detected⁷.

In order to confirm that detection at ≤ 200 nm has more general value, chromatograms for several other ions were also recorded at 190 nm. Retention times and

TABLE I

RETENTION TIMES AND DETECTION LIMITS FOR SOME ANIONS

Detection at 190 nm; eluent 0.02 *M* methanesulphonic acid, pH 1.7; Vydac 302 anion column. Other conditions as given in text.

<i>Anion</i>	<i>Retention time (min)</i>	<i>Detection limit (ng)</i>
Iodate	2.57	5
Bromate	3.22	6
Oxalate	3.29	11
Chloride	3.35	3
Bromide	4.96	0.5
Nitrate	7.02	0.5
Iodide	12.24	2
Thiocyanate	19.67	5
Thiosulphate	43.06	30

detection limits are given in Tables I and II. The change in eluent pH from 1.7 in Table I to 4.7 in Table II was made to enable separation and detection of weak acids, which remain unionized and thus undetected at the lower pH.

As an aside we note that the change in sulphonate concentration from 0.02 *M* in Table I to 0.012 *M* in Table II was effected because different Vydac 302 columns were used to obtain each set of results. Our experience with three different columns of this type is that although the order of elution is invariant, absolute retention times under standard conditions vary significantly from column to column. Thus while part of the reduction in chloride and nitrate retention times in Table II results from the change in eluent pH, it is mostly due to real differences in the performance of the two columns. Furthermore, at least for our rainwater samples, retention times have been found to decrease after several hundred injections on each column, so in practice column age and prior usage also contribute to differences in column characteristics.

Returning to Tables I and II, with the exception of sulphate and phosphate ions the detection limits found are generally as good as, and for some ions better than, those recently quoted in the literature¹⁻⁸, so the use of detection at < 200 nm

TABLE II

RETENTION TIMES AND DETECTION LIMITS FOR SOME ADDITIONAL ANIONS

Detection at 190 nm; eluent 0.012 *M* methanesulphonic acid brought to pH 4.7 with sodium hydroxide. A second Vydac 302 anion column was used for this work. Other conditions as given in text.

<i>Anion</i>	<i>Retention time (min)</i>	<i>Detection limit (ng)</i>
Isobutanoate	1.96	90
Phosphate	2.32	3000
Formate	2.61	20
Chloride	2.62	3
Nitrite	3.02	1
Nitrate	3.39	0.5
Sulphate	9.38	3000

appears to have general applicability. One interesting feature of the results is that although both sulphate and phosphate are usually thought to be UV-transparent, both were detected. However, the rather high detection limits shown reflect the small difference in extinction coefficients between these ions and the sulphonate eluent.

CONCLUSIONS

The use by Ivey⁷ of a relatively UV-transparent eluent such as methanesulphonic acid provides the key to the success of short wavelength UV detection. In this note we have shown that chloride ion, previously considered to be undetectable by the direct UV method, can be detected with high sensitivity at 190 nm. Sulphate and phosphate could also be detected at this wavelength, although with relatively low sensitivity. However the response of both nitrate and bromide was significantly enhanced at < 200 nm in comparison with detection at longer wavelengths, and a range of other ions was also found to be detected with high sensitivity at 190 nm.

REFERENCES

- 1 J. P. de Kleijn, *Analyst (London)*, 107 (1982) 233.
- 2 H. J. Cortes, *J. Chromatogr.*, 234 (1982) 517.
- 3 Z. Iskandarani and D. J. Pietrzyk, *Anal. Chem.*, 54 (1982) 2601.
- 4 R. A. Cochrane and D. E. Hillman, *J. Chromatogr.*, 241 (1982) 392.
- 5 T. Imanari, S. Tanabe, T. Toida and T. Kawanishi, *J. Chromatogr.*, 250 (1982) 55.
- 6 M. Dreux, M. Lafosse and M. Pequignot, *Chromatographia*, 15 (1982) 653.
- 7 J. P. Ivey, *J. Chromatogr.*, 267 (1983) 218.
- 8 B. B. Wheals, *J. Chromatogr.*, 262 (1983) 61.