

Note

Elimination of the peak of a major ion in anion chromatography with UV detection

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Since the introduction of ion chromatography (IC) by Small *et al.*¹, many inorganic anions have been determined by this method¹⁻⁶. One of the most important properties of this method is that all dissociated ions are detected by a conductivity detector regardless of their nature. On the other hand, as a UV detector, which is most generally used for high-performance liquid chromatography, is more selective than the conductivity detector, only some UV-absorbing anions (NO_2^- , NO_3^- , Br^- , etc.) can be detected in a direct photometric mode⁷⁻¹¹. However, indirect photometric chromatography (IPC) permitted the determination of non-UV-absorbing anions by using UV-absorbing eluents^{10,11}. When a major anion exists in a sample solution, its peak often interferes with the detection of the other anions in such universal detection modes.

Direct and indirect chromatographic modes can be alternated by changing the detection wavelength and the eluent used. In the present study, the elimination of the peak of a major anion was investigated by using these two UV-detection modes. When trace solutes of interest exist in a matrix, the following four cases can be distinguished:

- (1) Trace non-UV-absorbing solutes exist in a non-UV-absorbing matrix;
- (2) Trace UV-absorbing solutes exist in a non-UV-absorbing matrix;
- (3) Trace non-UV-absorbing solutes exist in a UV-absorbing matrix; and
- (4) Trace UV-absorbing solutes exist in a UV-absorbing matrix.

In the first case the elimination of the major peak is impossible since it appears in the indirect photometric mode or no peaks are observed in the direct photometric mode. In the second case, only UV-absorbing solutes of interest are detected by the direct photometric mode. In the third and fourth cases, the major peak can be eliminated by utilizing the difference in the UV-absorbing properties between the major ion and UV-absorbing or non-UV-absorbing solutes. If the absorbance is measured at an isobestic point between an eluent and the major anion, the peak of the major anion should be eliminated. In this way, the solutes of interest are measured as positive or negative peaks according to their absorptivity at the detection wavelength.

EXPERIMENTAL

Apparatus

The chromatographic system consisted of a computer-controlled pump, a sample injection valve, an anion-exchange column (50×4.6 mm I.D.) packed with TSKgel IC-Anion-PW (particle size 10 ± 1 μm , capacity 0.03 ± 0.005 mequiv./g), a UV-spectrophotometric detector (UV-8 Model II, Toyo Soda) and a Shimadzu integrator Model Chromatopack CR1A. The pump and the injection valve were parts of a Toyo Soda Model HLC-601 non-suppressed ion chromatograph. The volume of the sample loop was 100 or 45 μl . The flow-rate was maintained at 1.2 ml/min under a pressure of 25–30 kg/cm^2 . A Shimadzu Model UV-240 spectrophotometer was used to obtain UV spectra of organic and inorganic anions.

Reagents

A potassium hydroxide eluent was prepared daily by dissolving the guaranteed reagent in distilled deionized water (DDW). The eluents of organic and inorganic anions were prepared by dissolving the potassium or sodium salts in DDW, and deaerating.

Stock solutions (1000–2000 ppm) of inorganic anions were prepared by dissolving the potassium salts, dried *in vacuo* at 110°C overnight, in DDW. Working standard solutions were prepared by diluting the stock solutions.

RESULTS AND DISCUSSION

Determination of UV-absorbing solutes in a non-UV-absorbing matrix

Fig. 1 shows the UV spectra of inorganic anions. Except for chloride which is one of the most widespread non-UV-absorbing anions, the anions are selectively detectable in the wavelength range 190–240 nm. It is an advantage in this case that a non-UV-absorbing eluent can be freely chosen. If an eluent has a weak UV ab-

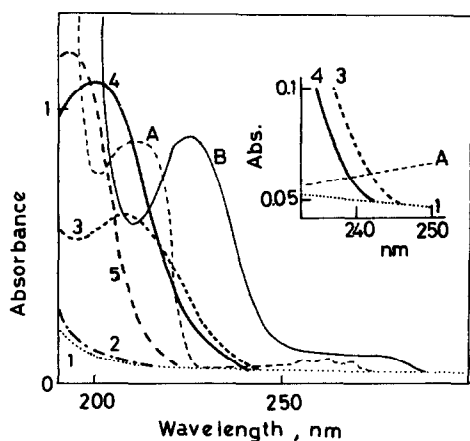


Fig. 1. UV spectra of inorganic and organic anions: 1 = blank (water); 2 = Cl^- ; 3 = NO_2^- ; 4 = NO_3^- ; 5 = Br^- . A = Benzenesulphonate; B = benzoate. The concentration was $1 \cdot 10^{-4}$ M.

sorptivity, the indirect photometric peak of chloride will appear and interfere with the determination of UV-absorbing solutes.

Fig. 2 shows chromatograms of nitrite and nitrate obtained by the use of potassium hydroxide as eluent in non-suppressed IC^{2,3}. The peak shapes and retention times vary depending on the concentration of coexistent chloride. Similar behaviour was reported in the determination of chloride in the presence of a large amount of sulphate^{12,13}. Although the peak heights of nitrite and nitrate increased with the concentration of existent chloride, their peak areas were hardly changed. This seems to be an advantage because of the increase in the numbers of theoretical plates for nitrite and nitrate. However, coexistent chloride depresses the resolution between the peaks of these two ions. It is desirable that a sample solution contains < 2000 ppm of chloride.

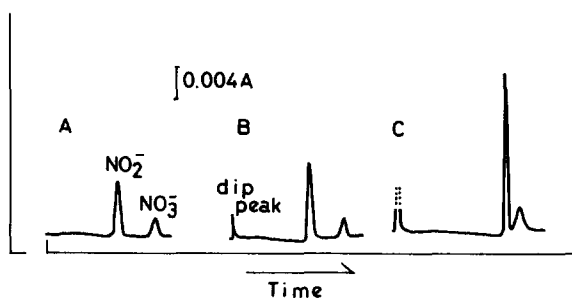


Fig. 2. Chromatograms of NO_2^- and NO_3^- . A, Without Cl^- ; B, with 100 ppm of Cl^- ; C, with 1000 ppm of Cl^- . Sample contained 1 ppm of NO_2^- and NO_3^- . The eluent was 1 mM potassium hydroxide solution. Detection wavelength: 230 nm. Other conditions as in text.

“Dip peaks”, which contained sample water, sample cations excluded by an anion-exchange resin and an eluent anion replaced by solute anions, were observed in non-suppressed IC¹⁴ or IPC¹⁰. In the present case, a small dip peak appears as shown in Fig. 2B and C. This peak is, however, so small that it does not interfere with the determination of the solutes of interest. Nitrite and nitrate in 1000 ppm of chloride could be determined at 10-ppb (10^9) levels by optimizing the conditions.

Determination of UV-absorbing or non-UV-absorbing solutes in an UV-absorbing matrix

If an eluent cation has no UV-absorption property, the response, A , of the UV detector is given by

$$A = (\varepsilon_{\lambda_s} - \varepsilon_{\lambda_e})lC_s$$

where ε_{λ_s} , ε_{λ_e} , l and C_s represent the molar absorptivities of a solute anion and an eluent anion, the light path length and the concentration of the solute anion, respectively. Positive or negative peaks are observed according to the sign of $(\varepsilon_{\lambda_s} - \varepsilon_{\lambda_e})$. In order to eliminate a UV-absorbing matrix peak, a wavelength must be chosen so as to make the value of $(\varepsilon_{\lambda_s} - \varepsilon_{\lambda_e})$ zero.

The following two methods are available for this purpose. First, the UV-ab-

sorbing anion (*e.g.*, organic acid) is used as an eluent and the absorbance is measured at the wavelength where the difference in absorptivity between the matrix and the eluent anion is zero. For example, when 1 mM benzoic acid is chosen as an eluent anion, the peaks of nitrate and nitrite are reduced in intensity at 210 nm and at 208 or 212 nm, respectively (Fig. 1). However, the sensitivity is markedly poor because of the baseline noise resulting from the high absorbance of benzoic acid at these wavelengths. It is desirable that the background absorbance is less than 1, that is, less than 0.1 in Fig. 1. Benzoic acid is not, therefore, a suitable eluent for this purpose. When benzenesulphonate was used as an eluent, cross-over points between its spectrum and those of the solutes occur at 210, 221 and 239 nm for nitrate and 220 and 242 nm for nitrite. By observing the absorbance at 239 nm (for nitrate) and 242 nm (for nitrite) their peaks can be eliminated without an increase in the background noise. Fig. 3 shows the elimination of 5 ppm of nitrate and nitrite. Nitrate and chloride are observed as indirect photometric peaks and the peak of nitrite is eliminated at 242 nm. At 239 nm the peak of nitrate is eliminated, and nitrite and chloride are observed as a direct and an indirect photometric peak, respectively. However, the lack of resolution of the spectrometer and the slight variation in the absorbance of the organic acid prevent complete elimination of the matrix peak at concentrations greater than 100 ppm. The use of a suitable eluent and a high-resolution spectrophotometer will permit elimination of matrix peaks only upon varying the detection wavelength.

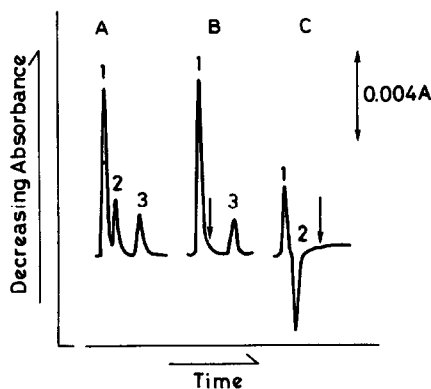


Fig. 3. Elimination of the peaks of UV-absorbing anions. Detection wavelengths: A, 255 nm; B, 242 nm; C, 239 nm. Peaks: 1 = Cl^- ; 2 = NO_2^- ; 3 = NO_3^- . The arrows in B and C show the elution positions of NO_2^- and NO_3^- , respectively. The eluent was 1 mM sodium benzenesulphonate. Other conditions as in text.

In the second method the matrix anion is used as an eluent anion. The value of $(\epsilon_{\lambda_s} - \epsilon_{\lambda_e})$ in the above equation is zero because the eluent and the matrix have the same anion. Similar considerations can be applied to elimination of the matrix peak using a conductivity detector, but the sensitivity is extremely low unless the difference in the equivalent conductance between the eluent (or matrix) and the solute anions is large. When chloride in a large amount of nitrate is determined by using nitrate as eluent and a conductivity detector, the difference in the equivalent conductance is only $4.9 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. In the UV-detection system, chloride can be

determined with high sensitivity since the difference in absorbance between chloride and nitrate is large enough at wavelengths less than 240 nm. The detection wavelength can be freely chosen, but the strength of the eluent is a problem. Fortunately, the matrix anions investigated in the present study were sufficiently strong eluents, but other methods must be considered when the matrix anion is a weak eluent. Fig. 4 shows the peaks of chloride and nitrate in a nitrite matrix obtained by using a nitrite eluent. For high sensitivity, the wavelength resulting in maximum absorbance (less than 1) must be selected. Therefore, 235 nm was used for detection. Both solutes were observed as negative peaks because of the large absorptivity of nitrite at this wavelength. An increase in the concentration of coexisting nitrite broadened the peaks of chloride and nitrate, and increased their retention times. The peaks were remarkably broadened under the coexistence of > 1000 ppm nitrite, and the determination of solutes was difficult. This phenomenon is due to the exhaustion of solute ions in the sample band from the matrix anion, and is more pronounced because the capacity of the column used in this study is low. Although the peak broadening will be lessened by using columns with higher capacities, the sensitivity will be reduced by the use of an eluent having a high concentration. The peak broadening and distortion were reduced by decreasing the sample volume to $45 \mu\text{l}$. Fig. 4A' and D' show chromatograms obtained by injecting $45 \mu\text{l}$ of a sample. Although the peaks are smaller than those obtained by injecting $100 \mu\text{l}$ of sample, this procedure is effective for samples containing a large amount of a matrix anion. The negative peak (increasing absorbance), observed ahead of the chloride peak upon injecting a sample of high concentration, is caused by an impurity having higher absorptivity than nitrite. The

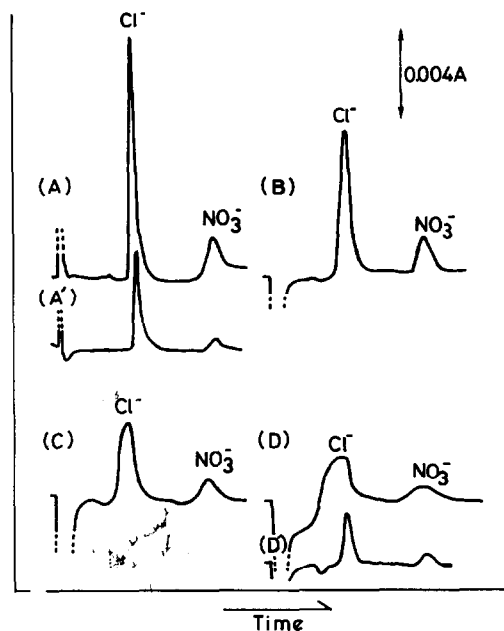


Fig. 4. Elimination of the peak of NO_2^- . A and A', without NO_2^- ; B, with 100 ppm of NO_2^- ; C, with 500 ppm of NO_2^- ; D and D', with 1000 ppm of NO_2^- . Sample volume: $100 \mu\text{l}$ in A–D; $45 \mu\text{l}$ in A' and D'. The eluent was 1 mM of NaNO_2 . Detection wavelength; 235 nm. Other conditions as in text.

degradation of the standard solution of nitrite was investigated by using this method. No peaks due to impurities are observed for the freshly prepared solution, but chloride and nitrate, arising from contamination and oxidation, are detected 2 months later.

This method was also applicable to the matrices of nitrate and bromide. The anions of interest were detected in a 1000 ppm solution of the matrix anion at sub-ppm levels. Impurities could not be detected in the standard solution of nitrate, but 2 ppm of chloride were detected in the standard solution of bromide.

The separation or the elimination of a major peak has been carried out by the use of a long column or the multidimensional method¹⁵. These methods were effective for the determination of some anions when using a poorly selective detector, but were tedious and time-consuming. The present method can be used for this purpose by selecting a suitable eluent and the detection wavelength, and will be applicable to the quality control of reagents, the determination of anions in a sample decomposed by nitric acid, etc. The method using organic acids as eluents is also effective for the reduction in size of a peak separated inadequately from a peak of interest.

REFERENCES

- 1 H. Small, T. S. Stevens and W. C. Bauman, *Anal. Chem.*, 47 (1975) 1801.
- 2 T. Okada and T. Kuwamoto, *Anal. Chem.*, 55 (1983) 1001.
- 3 T. Okada and T. Kuwamoto, *Anal. Chem.*, 57 (1985) 258.
- 4 D. T. Gjerde, J. S. Fritz and G. Schmuckler, *J. Chromatogr.*, 186 (1979) 509.
- 5 D. T. Gjerde, G. Schmuckler and J. S. Fritz, *J. Chromatogr.*, 187 (1980) 35.
- 6 R. E. Majors, H. G. Barth and C. H. Lochmüller, *Anal. Chem.*, 56 (1984) 300R.
- 7 S. A. Wilson and E. S. Yeung, *Anal. Chim. Acta*, 157 (1984) 53.
- 8 S. Rokushika, Z. Y. Qui, Z. L. Sun and H. Hatano, *J. Chromatogr.*, 280 (1983) 69.
- 9 R. N. Reeve, *J. Chromatogr.*, 177 (1979) 393.
- 10 H. Small and T. E. Miller, Jr., *Anal. Chem.*, 54 (1982) 462.
- 11 H. J. Cortes and T. S. Stevens, *J. Chromatogr.*, 295 (1984) 269.
- 12 R. E. Smith, *Anal. Chem.*, 55 (1983) 1427.
- 13 M. A. O. Bynum, S. Y. Tyree, Jr. and W. E. Weiser, *Anal. Chem.*, 53 (1981) 1936.
- 14 T. Okada and T. Kuwamoto, *Anal. Chem.*, 56 (1984) 2073.
- 15 T. B. Hoover and G. D. Yager, *Anal. Chem.*, 56 (1984) 221.