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Ion chromatographic determination of anions, especially sulphur-containing anions, with conductimetric and kinetic detection

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ABSTRACT

A new mode of detection in ion chromatography called "kinetic detection" is suggested. The technique uses an ion chromatograph with a conductimetric detector and a multichannel flow mounting with a spectrophotometric detector. The potassium bromate degradation reaction in hydrochloric acid accelerated by reducing anions, is used as a model indicator system. The sensitive determination of S^{2-} , SO_3^{2-} , $S_2O_3^{2-}$, SCN^- and NO_2^- has been performed. The simultaneous determination of weak and strong inorganic acid anions is shown to be possible.

INTRODUCTION

The determination of anions of weak inorganic acids, in particular sulphur-containing anions, is an important analytical problem. Ion chromatography is a convenient method for the determination of sulphur as anions [1–4], and can be used to determine S^{2-} , SO_3^{2-} , SO_4^{2-} , $S_2O_3^{2-}$, $S_2O_4^{2-}$, $S_2O_6^{2-}$, $S_2O_8^{2-}$, $S_4O_6^{2-}$ and SCN^- in the presence of other inorganic anions [5–8]. However, it is difficult, in most instances, to ensure the selective and sensitive determination of all such components of complicated samples by conventional ion chromatographic techniques. It seems reasonable to use a chromatograph with several detectors, each of which is selective for one or a number of anions.

The authors' laboratory uses a conventional ion chromatograph with a conductimetric detector in combination with a so-called "kinetic detector". The latter is a multichannel post-column kinetic reaction with spectrophotometric detection. The degradation of potassium bromate in hydrochloric acid is accelerated by S^{2-} , SCN^- , SO_3^{2-} , $S_2O_3^{2-}$, NO_2^- or AsO_2^- [9,10] and has been used as an indicator reaction. This method makes it possible to determine small concentrations of weak acidic anions and other inorganic anions (F^- , Cl^- , NO_3^- , HPO_4^{2-} , SO_4^{2-}) simultaneously, because the

former are not recorded by the conductimetric detector and the latter do not affect the indicator reaction.

EXPERIMENTAL

A Biotronik IC-5000 ion chromatograph with a 100×3 or 100×4 mm separator column and a 150×6 mm suppressor column, a conductimetric detector, and a Chromatopac CR 2A integrator were used. Oka-1 and Anieks N were used as the separator resins. Sodium carbonate solutions of various concentrations were used as eluents. The flow system for kinetic detection consisted of two Zalimp PP-2-15 peristaltic pumps, several reaction coils and pipelines, and a Biotronik BT-3030 spectrophotometric detector with a recorder. The inner diameter of all the pipelines was 0.7 mm and that of the reaction coils was 1 mm. The pH was controlled with a glass electrode using an EV-74 ionometer.

All solutions were prepared from dry analytical reagent-grade chemicals using doubly deionized water. Solutions containing S^{2-} , SO_3^{2-} , $S_2O_3^{2-}$ and SCN^- were prepared daily.

RESULTS AND DISCUSSION

Kinetic detection

Kinetic detection was accomplished in a multichannel flow system which was coupled to an ion chromatograph connected to a conductimetric detector. The indicator kinetic reaction, which is accelerated by the sample components, is performed; the sample components are detected spectrophotometrically after separation on a column.

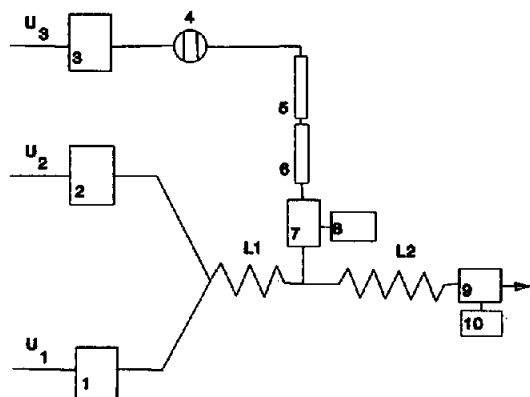


Fig. 1. Schematic diagram of an ion chromatographic experimental arrangement with kinetic detection. U_1 = Flow of methyl orange solution in hydrochloric acid; U_2 = potassium bromate flow; U_3 = eluent flow; 1,2 = peristaltic pumps; 3 = ion chromatograph pump; 4 = injection valve; 5 = separator column; 6 = suppressor column; 7 = conductimetric detector; 8 = integrator; 9 = spectrophotometric detector; 10 = recorder; L_1 , L_2 = reactors.

Ion chromatograph with kinetic detection

The degradation of potassium bromate in hydrochloric acid, one version of the Landolt system, was used as the indicator reaction, the catalysts being S^{2-} , SO_3^{2-} , NO_2^- , SCN^- , $S_2O_3^{2-}$, Br^- , I^- and AsO_2^- [9,10]. The study was carried out using the arrangement shown in Fig. 1.

The sample was injected into the eluent flow stream (U_3). After separation, the sample components were detected conductimetrically, then the eluent was mixed with the flows of potassium bromate (U_2) and methyl orange in hydrochloric acid (U_1). Through the reaction coil (L_2) the flow was driven into the flow cell of a spectrophotometric detector, where the absorption of the solution was measured (as a result of the reaction, the methyl orange became colourless, and the determination was accomplished over negative peaks).

Choice of flow system parameters

To provide sensitive detection with effective separation and minimum sample dispersion in the flow, the optimum experimental conditions were determined. It is known that the rate of the indicator reaction is proportional to $[KBrO_3]$ and $[H^+]$ [2]; however, the rate of the non-catalysed process increases considerably with increasing concentrations of the reactants. The determination of the sensitivity depends on the concentration of the indicator substance. However, at the same time, a high concentration of methyl orange causes noise and drift of the baseline. The results of the experiments have shown that the optimum parameters are as follows: flow-rates, $U_1 = U_2 = 0.5$ ml/min, $U_3 = 1.5$ ml/min; reactor lengths, $L_1 = 40$ cm, $L_2 = 1500$ cm, initial concentration, $c_{(initial)}$ [methyl orange] = 10^{-4} M, $c_{(initial)}$ [HCl] = $2.5 \cdot 10^{-1}$ M, $c_{(initial)}$ $[KBrO_3] = 1.5 \cdot 10^{-2}$ M, sample volume = 100 μ l, time of sample in the system = 4.5–7.5 min, spectrophotometric detector wavelength = 522 nm.

A dual-column variant of ion chromatography has been used. It was found that the suppressor column does not affect the spectrophotometric determination of the



Fig. 2. Chromatogram of a solution of 2 ppm F^- (1), 5 ppm Cl^- (2), 3 ppm S^{2-} (3), 25 ppm NO_3^- (4), 50 ppm HPO_4^{2-} (5), 6 ppm SO_3^{2-} (6) and 50 ppm SO_4^{2-} (7). Column, 100 \times 3 mm (Oka-1). Eluent, 0.0025 M sodium carbonate (1 ml/min). Solid line = conductimetric detector output; dotted line = spectrophotometric detector output.

Fig. 3. Chromatogram of a solution of 2 ppm F^- (1), 5 ppm Cl^- (2), 25 ppm NO_3^- (3), 1 ppm NO_2^- (4), 20 ppm HPO_4^{2-} (5), 12 ppm SO_3^{2-} (6) and 20 ppm SO_4^{2-} (7). Eluent, 0.0015 M sodium carbonate (1 ml/min).

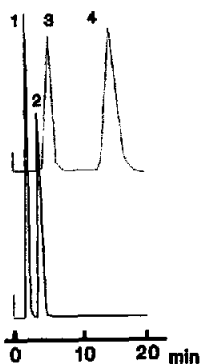


Fig. 4. Chromatogram of a solution of 5 ppm Cl^- (1), 50 ppm SO_4^{2-} (2), 0.2 ppm S^{2-} (3) and 1 ppm SCN^- (4). Column, 100 \times 4 mm (Oka-1). Eluent, 0.006 *M* sodium carbonate (1.5 ml/min).

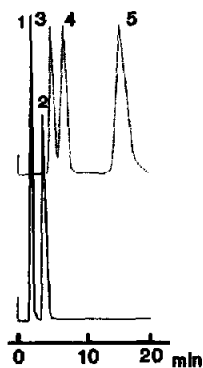


Fig. 5. Chromatogram of a solution of 5 ppm Cl^- (1), 50 ppm SO_4^{2-} (2), 1 ppm S^{2-} (3), 2 ppm SO_3^{2-} (4) and 5 ppm $\text{S}_2\text{O}_3^{2-}$ (5). Column, 100 \times 3 mm (Oka-1). Eluent, 0.005 *M* sodium carbonate (1.5 ml/min).

catalyst anions. In addition, it decreases the conductimetric signal of the weak acid anions, and these anions do not affect the conductimetric determination of other sample components.

Determination of inorganic anions

The determination of weak inorganic acid anions simultaneously with strong acid anions is a complicated analytical task. The described experimental arrangement allows such a determination. Figs. 2–5 show chromatograms of mixtures containing F^- , S^{2-} , Cl^- , NO_2^- , NO_3^- , HPO_4^{2-} , SO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$ and SCN^- , separated using the sorbent Oka-1. Figs. 2 and 3 are examples of the simultaneous determination of F^- , Cl^- , S^{2-} , NO_3^- , HPO_4^{2-} , SO_3^{2-} and SO_4^{2-} , and of F^- , Cl^- , NO_2^- , NO_3^- , HPO_4^{2-} , SO_3^{2-} and SO_4^{2-} , respectively. Examples of the simultaneous determination of weakly and strongly retained anions are shown by the chromatograms of Figs. 4 and 5. The reducing anions are detected kinetically; the other anions are detected

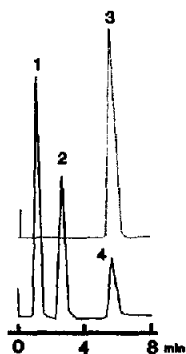


Fig. 6. Chromatogram of a solution of 2 ppm F^- (1), 5 ppm Cl^- (2), 0.2 ppm S^{2-} (3) and 5 ppm SO_4^{2-} (4). Column, 100 \times 4 mm (Anieks N). Eluent, 0.004 *M* sodium carbonate (1.5 ml/min).

conductimetrically. Using two detectors provides a rapid determination; for example, the determination of a mixture of F^- , S^{2-} , Cl^- and SO_4^{2-} can be achieved in 7 min (Fig. 6).

The detection limits calculated for a signal-to-noise ratio of 3:1 are (in ppm): 0.01 (S^{2-}), 0.05 (SO_3^{2-}), 0.05 ($S_2O_3^{2-}$) and 0.06 (SCN^-). These are essentially lower than the detection limits for conductimetric detection in single-column (direct and indirect methods) ion chromatography. The determination of the maximum concentration for each anion depends on the conditions of each individual task. The upper limit of the linear operating range of the calibration graphs is 50 ppm for each anion. The relative standard deviation in the determination of 1 ppm of S^{2-} , SO_3^{2-} , $S_2O_3^{2-}$ and SCN^- is 6%. The determination of 1 ppm of S^{2-} , SO_3^{2-} , SO_4^{2-} , $S_2O_3^{2-}$, SCN^- and NO_2^- is influenced by the presence of 0.01 ppm Br^- , 0.1 ppm I^- , 1000 ppm F^- , 1000 ppm Cl^- , 500 ppm NO_3^- , 500 ppm SO_4^{2-} , 500 ppm HPO_4^{2-} and 500 ppm CO_3^{2-} . All anions with reducing properties also affect the determination.

CONCLUSIONS

A new mode of detection in ion chromatography called "kinetic detection" has been proposed. The approach demonstrated makes it possible to solve a number of ion chromatographic problems, including the sensitive determination of sulphur-containing inorganic anions and the simultaneous determination of weak acid anions and strong inorganic acid anions.

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