Mendeleev Commun., 1991, 1(1), 38–39

Use of Kinetic Detection with Ion Chromatography for the Determination of some Anions

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The use of the kinetics of a post-column reaction with spectrophotometric detection, in combination with a conductometric detector for ion chromatography allows the sensitive simultaneous determination of anions of both weak and strong inorganic acids.

Ion chromatography is the most effective method for multicomponent analysis of complex mixtures of anions and cations. The determination of anions of weak inorganic acids, in particular sulphur-containing acids, is an important analytical problem. Ion chromatography is a convenient method for the determination of sulphur anions,[1–4] which allows the determination of 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 cases, to ensure selective and sensitive determination of all such components of complex samples using conventional ion chromatographic equipment. It seemed reasonable to use a chromatograph with several detectors, each of which responded selectively to one or a number of anions.

In our laboratory a conventional ion chromatograph has been used with a conductometric detector in combination with a so-called 'kinetic detector'. The latter uses a multichannel kinetic post-column reaction with spectrophotometric detection. The degradation of $KBrO_3$ in HCl catalysed by the anions S^{2-}, SCN^-, SO_3^{2-}, $S_2O_3^{2-}$, NO_2^- or AsO_2^- [9,10] was used as an indicator reaction. This method makes it possible to determine small concentrations of weak acid anions and other inorganic anions (F^-, Cl^-, NO_3^-, HPO_4^{2-}, SO_4^{2-}) simultaneously because the former do not give a conductometric signal and the latter do not affect the rate of the indicator reaction.

A Biotronik IC-5000 ion chromatograph with 100 × 3 or 100 × 4 mm i.d. separator column and 150 × 6 mm i.d. suppressor column, conductometric detector and Chromatopac CR 2A integrator were used. Oka-1 and Anieks N with a polymethacrylic matrix were used as separator resins, and Na_2CO_3 solutions of various concentrations were used as eluents. The flow system for kinetic detection consisted of two Zalimp PP-2-15 peristaltic pumps, systems of reaction coils and pipelines and a Biotronic BT-3030 spectrophotometric detector with a recorder. The internal diameter of all pipelines was 0.7 mm, and was 1 mm for the reaction coils. The pH was controlled with a glass electrode using an EV-74 ionometer.

The sample was introduced into the eluent stream (U_3) (Fig. 1). After separation the sample components were detected conductometrically, then the eluate was mixed with streams of $KBrO_3$ solution (U_2) and methyl orange in HCl (U_1). After passing through the reaction coil (L_2) the total stream was driven into the flow cell of the spectrophotometric detector where the absorption of the solution was measured (as a result of the reaction, methyl orange became colourless, and determination was accomplished according to the negative peaks).

In order to provide sensitive detection with effective separation and minimal sample dispersion in the steam we have found the optimal conditions at which to carry out the experiment. It is known[9,10] that the rate of the indicator reaction is proportional to $[KBrO_3]$ and $[H^+]^2$, however the rate of the noncatalytic process increases considerably as the concentrations of the components increase. The sensitivity of the determination depends on the concentration of the indicator substance, but at the same time, high concentrations of methyl orange cause noise and drift of the baseline. Experiments have shown that the optimal parameters are as follows: $U_1 = U_2 = 0.5$, $U_3 = 1.5$ ml min^{-1}, $L_1 = 40$, $L_2 = 1500$ cm, c_{initial} (methyl orange) $= 10^{-4}$, c_{initial} (HCl) $= 2.5 \times 10^{-1}$ c_{initial} ($KBrO_3$) $= 1.5 \times 10^{-2}$ mol dm^{-3} sample volume = 100 μl, residence time for sample in the system = 4.5–7.5 min, spectrophotometric detector wavelength = 522 nm.

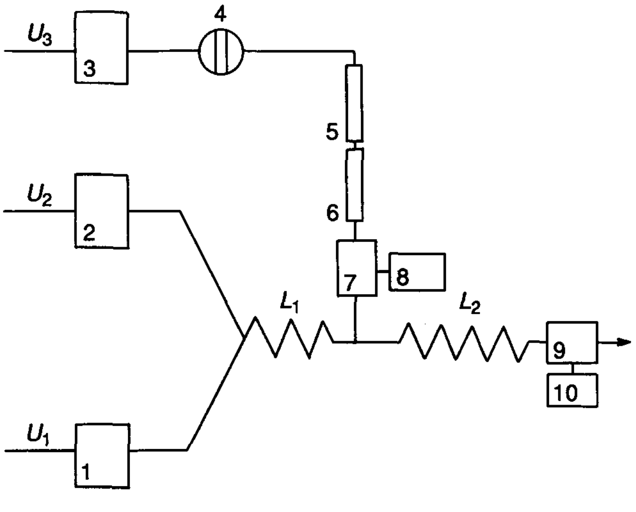

Fig. 1 Schematic drawing of ion-chromatographic mounting with kinetic detection. U_1, methyl orange solution in HCl stream; U_2, $KBrO_3$ stream; U_3, eluent stream; 1 and 2, peristaltic pumps; 3, ion chromatograph pump; 4, injection valve; 5, separator column; 6, suppressor column; 7, conductometric detector; 8, integrator; 9, spectrophotometric detector; 10, recorder; L_1 and L_2, reactors.

Dual-column ion chromatography has been used. It was found that the suppressor column does not affect the spectrophotometric output during the determination of ion-catalysts. In addition, it reduces the adverse influence of weak acid anions on the conductometric determination of other sample components.

The simultaneous determination of both weak and strong inorganic acid anions is a complex analytical problem. The arrangement described makes it possible to solve this. We have demonstrated the possibility of multicomponent analysis of various mixtures of anions, containing F^-, S^{2-}, Cl^-, NO_2^-, NO_3^-, HPO_4^{2-}, SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$ and SCN^-, which has been performed on the anion exchange resins Oka-1 and Anieks N. Reducing anions are detected kinetically, while other anions are detected conductometrically (Fig. 2). The use of two detectors also provides rapid determination: for example, the analysis of a mixture of F^-, S^{2-}, Cl^-, and SO_4^{2-} on Anieks N takes 7 min. The detection limits, calculated for a signal-to-noise ratio 3:1 are 0.01 (S^{2-}), 0.05 (SO_3^{2-}), 0.05 ($S_2O_3^{2-}$) and 0.06 ppm (SCN^-), which are significantly lower than those for conductometric detection by single-column ion chromatography (direct or indirect methods). The ability to

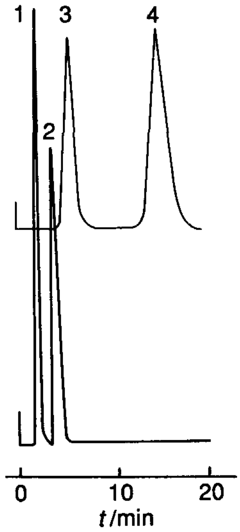

Fig. 2 Chromatogram of 5 ppm Cl^- (1), 50 ppm SO_4^{2-} (2), 0.2 ppm S^{2-} (3) and 1 ppm SCN^- (4). Column, 100 × 4 mm i.d. (Oka-1); eluent, 0.006 mol dm^{-3} Na_2CO_3 (1.5 ml min^{-1}).

optimise the determination of each anion depends on the relative concentrations present. The upper limit of the linear operating range of the calibration curves is 50 ppm for each anion. The relative standard deviation (RSD) for the determination of S-containing anions is not more than 0.06. Determination of 1 ppm 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 exert an adverse effect.

The approach demonstrated allows us to solve a number of ion-chromatographic problems, including the sensitive determination of sulphur-containing inorganic anions and the simultaneous determination of weak and strong inorganic acid anions.

Received in USSR, 22nd November 1990
Received in UK, 4th January 1991; Com. 0/05341D

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