Journal of Chromatography, 350 (1985) 317–323
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 18 160

Note

Trace analysis of anions by use of a back-flush method and large injection volumes in ion chromatography

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(First received June 17th, 1985; revised manuscript received September 2nd, 1985)

Anion chromatography using conductometric[1–5], indirect photometric[6,7] or direct UV detection[8] has widely been used for the analysis of inorganic anions, which is tedious and time-consuming with the conventional methods. Conductometric detection and indirect photometric detection are effective and practical methods since all solutes replacing an eluent anion can be detected regardless of their nature. These methods, however, have some disadvantages. One serious drawback is that the high detection limits, generally in the range 50–100 ppb*[1–7], restrict the applications.

Many workers have attempted to overcome this problem. Donnan dialysis using an ion-exchange membrane was applied to the preconcentration of both anions and cations prior to their voltammetric determination[9–11]. However, it has not yet been applied to anion chromatography because of the need for a receiver electrolyte of high ionic strength, whereas it was successfully applied to cation chromatography by use of Al^{3+} as a receiver cation and tartaric acid as an eluent[12].

An on-line concentration method with a concentrator column is being used widely and successfully[13,14]. Though an extremely diluted sample is concentrated easily by use of this method, there are some drawbacks: an extra pump and the concentrator column are required; the concentrator column has to be washed adequately to get rid of the contamination from the preceding sample; the recovery of trace anions decreases in the presence of one or more major elements in a sample. Haddad and Heckenberg[15] recently reported a single-pump concentration method, but the other problems remain unsolved.

The use of a large injection volume can solve these problems[16,17]. When a large volume of a sample solution is injected into a separator column, solutes contained in the solution are compressed at the top of the column and the sample bands do not move before an eluent is poured into the column. Major elements in a sample solution scarcely affect the compression of analytes because the separator column generally has a higher ion-exchange capacity than the concentrator column. Moreover, this method is applicable to the conventional high-performance liquid chromatographic instruments without the extra pump and column. However, a large injection peak (or first dip peak) does interfere with the peaks of some rapidly eluted anions, *e.g.*, F^-, Cl^-, and limits the maximum injection volume to 2 ml[16,17].

* Throughout the article the American billion (10^9) is meant.

0021-9673/85/$03.30

In the present paper, an improved method (back-flush cleaning method) is described.

EXPERIMENTAL

Reagents

The phthalate eluent (1 m*M*) was prepared by dissolving analytical grade sodium biphthalate in water, and adjusting the pH to 5.1 with 0.1 *M* sodium hydroxide. The borate eluent (10 m*M*) was prepared daily by dissolving analytical grade boric acid in water, and adjusting the pH to 9.0 with 0.1 *M* sodium hydroxide. All solutions were deaerated before use.

Stock solutions (1000 ppm) of inorganic anions were prepared by dissolving the potassium or sodium salts, dried in vacuum at 110°C overnight, in water. Working standard solutions were prepared by diluting the stock solutions.

When an extremely diluted sample (sub-ppb level) was examined, water was purified by a Milli-Q system (Millipore). Distilled deionized water was used in the other experiments.

Apparatus

The chromatographic system consisted of a computer-controlled pump, an anion-exchange column (50 × 4.6 mm I.D.) packed with TSK gel IC-Anion-PW (particle size 10 ± 1 μm, capacity 30 ± 5 μequiv./g), an UV spectrophotometric detector (UV-8 Model II, Toyo Soda), a conductivity detector, a six-port valve, a three-way valve, a column oven and a Shimadzu integrator Model Chromatopac CR1A. The pump, the conductivity detector, two valves and the column oven were parts of a Toyo Soda non-suppressed ion chromatograph Model HLC-601. The flow-rate was maintained at 1.2 ml/min under a pressure of 15–20 kg/cm^2. When the conductivity detector was used the column and the detector were kept at 30°C in the oven. The other experiments were carried out at room temperature.

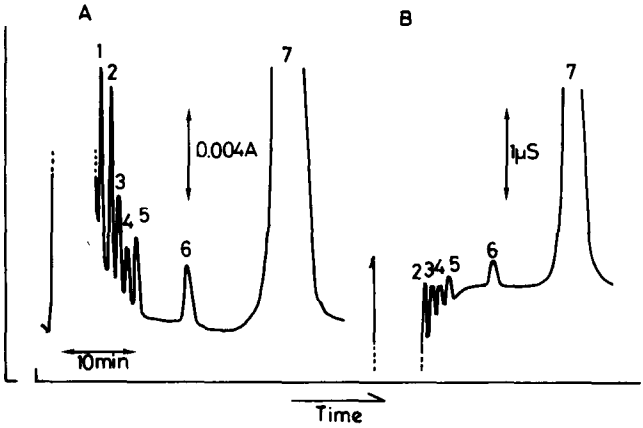

Fig. 1. Chromatogram of anions obtained by the use of a large injection volume. Eluent: 1 m*M* sodium phthalate (pH 5.1). Flow-rate: 1.2 ml/min. Column: TSK gel IC-Anion-PW (a) Indirect photometric detection at 270 nm. Sample: 5 ml of 40 ppb of each anion. (b) Conductivity detection. Sample: 5 ml of 50 ppb of each anion. Peaks: 1, F^-; 2, Cl^-; 3, NO_2^-; 4, Br^-; 5, NO_3^-; 6, SO_4^{2-}; 7, system peak.

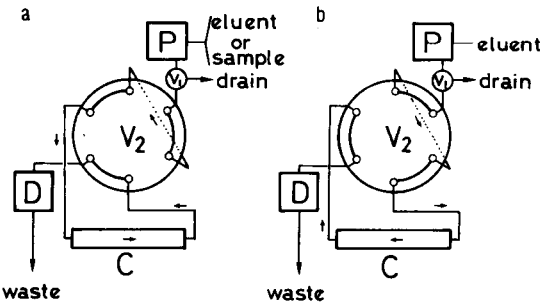

Fig. 2. Flow system for basck-flush method. P = Pump; C = separator column; D = detector; V_1 = drain valve; V_2 = six-port valve.

RESULTS AND DISCUSSION

Comparison of detection modes

The use of a large injection volume was first used for conductivity detection[16], and later for indirect photometric detection[17]. In the latter paper, Heckenberg and Haddad stated that indirect photometric detection was superior to conductivity detection as regards the stability of the baseline. Fig. 1 shows the comparison of detection modes. In conductivity detection, a peak for fluoride is not observed, and the other peaks are affected by the injection peak, while all peaks are observable by using indirect photometric detection. It is obvious that indirect photometric detection is more suitable.

The optimum conditions are given in the caption of Fig. 1.

Back-flush cleaning method

Only 2 ml of a sample solution are concentrated in the conventional method[16,17] because of the unstable baseline resulting from the large injection peak, while 15–50 ml could be concentrated by use of the on-line concentration column[13–15]. The former method was improved in order to solve this problem, and the proposed flow system is shown in Fig. 2. The device used consisted of a pump, a separator column, a six-port valve, a three-way valve and a detector. The three-way valve was used to minimize the dead volume. The solutes are concentrated at the top of the

TABLE I

PROCEDURE FOR BACK-FLUSH CLEANING

Step	*Solvent*	*Drain valve*	*Direction of solvent flow*	*Flow-rate (ml/min)*	*Time (s)*
Conditioning	Eluent	Shut	Usual	1.2	–
Purge	Sample	Open	–	5	60
Concentration	Sample	Shut	Usual	1.2	Definite time*
Purge	Eluent	Open	–	5	60
Back-flush Cleaning	Eluent	Shut	Opposite	1.2	20
Analysis	Eluent	Shut	Usual	1.2	–

* Corresponding to sample volume.

column by passing the sample solution through the column in the usual direction (Fig. 2a). In the conventional method, an eluent flows in the same direction immediately after concentration, and therefore sample water remaining in the column results in the large injection peak.

In the present method, the six-port valve is rotated after completion of the concentration step, and the sample water is replaced by an eluent flowing in the opposite direction (Fig. 2b). The injection peak is reduced by this procedure. The time for the back-flush cleaning has to be strictly controlled; interference from the injection peak is unavoidable if the time is short, and solutes concentrated on the column are lost if the time is long. Long back-flush times markedly depressed the recovery of SO_4^{2-}, which was the most strongly retained of the six solutes investigated. From this result, SO_4^{2-} may be concentrated near the entrance of the column, and be easily lost from the column during the back-flush procedure. Thus, a back-flush time of 20 s at the flow-rate of 1.2 ml/min was suitable. Sample water in the lower half of the column is replaced by the eluent in this procedure.

Analysis according to the procedure summarized in Table I permitted the detection of all solutes without losses and interference from the injection peak. A typical result is shown in Fig. 3. All peaks are fused from the effect of the injection peak by use of the back-flush (Fig. 3A). With conductivity detection, the back-flush step minimized the interference from the injection peak, but the peaks of fluoride and chloride were still affected (Fig. 3B).

Relative standard deviations obtained from six injections of 5 ml of 40 ppb of each anion were 2.1 (F^{-1}), 2.2 (Cl^{-1}), 1.0 (Br^-), 2.1 (NO_2^-), 3.7 (NO_3^-) and 5.1% (SO_4^{2-}). Though the value for SO_4^{2-} is slightly high, the other values are satisfasctory. The high value for SO_4^{2-} results from its unstable retention on the resin as mentioned above.

In the study on the effect of a major ion, the peak of fluoride (40 ppb) was found to be broadened in the presence of 1 ppm of chloride, and the peak of 5 ppm of chloride overlaps the peaks of fluoride and nitrite. However, no losses of solutes are observed during the concentration step. When the concentration of a major anion

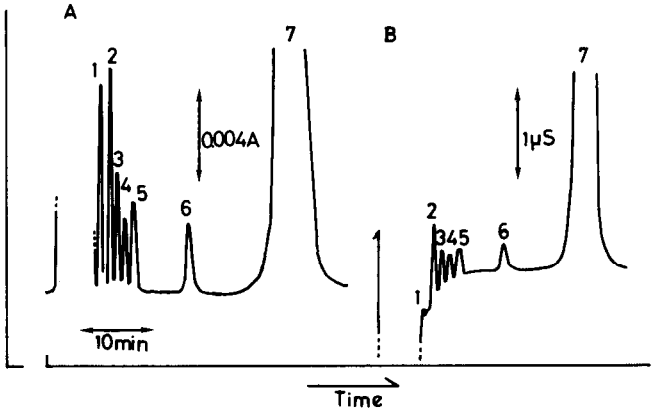

Fig. 3. Chromatograms of anions obtained by the use of a large injection volume with the back-flush method. (a) Indirect photometric detection at 270 nm. (b) Conductivity detection. Other conditions and peak identification as in Fig. 1.

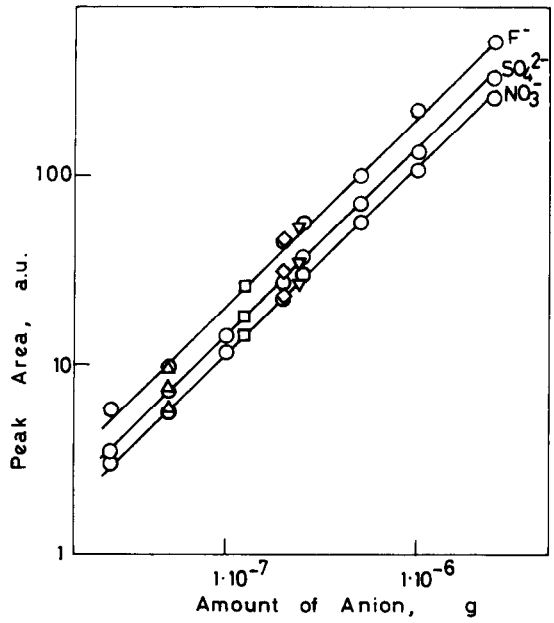

Fig. 4. Calibration curves for anions obtained by the present method. Injection volumes: ▽, 6 ml; ○, 5 ml; ◇, 4 ml; □, 2.5 ml; △, 1 ml.

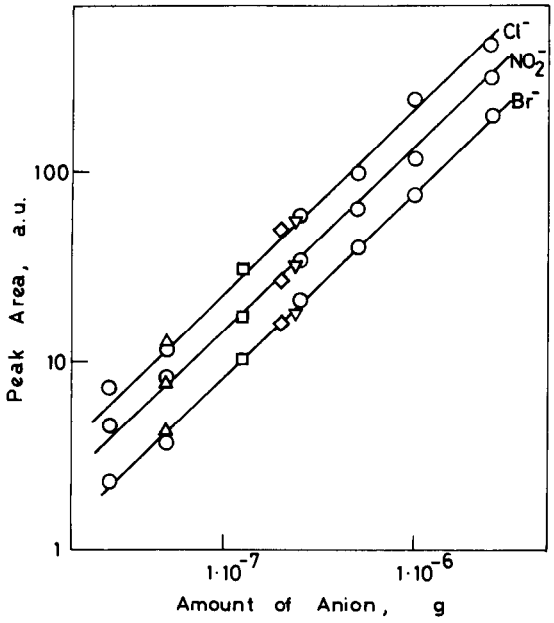

Fig. 5. Calibration curves for anions obtained as in Fig. 4.

TABLE II

COMPARISON OF DETECTION METHODS USING BACK-FLUSH CLEANING

Maximum injection volume was 6 ml in each case.

Method	*Detection limit (ppb)**					
	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}
Conductivity	–	4.5	10	12	12	15
Indirect UV	0.4	0.45	1.0	1.0	1.0	1.0

* Defined a signal-to-noise ratio of 3.

is larger than 20 ppm, the column is overloaded and the solutes are lost. The use of a column of higher capacity solves this problem, but the sensitivity is lowered because of the need for a high eluent concentration.

Calibration curves and sensitivity

Peak heights and areas were measured by injecting 1–10 ml of mixed standard solutions containing $2.5 \cdot 10^{-8}$–$2.5 \cdot 10^{-6}$ g of six solutes (fluoride, chloride, nitrite, bromide, nitrate, sulphate) into the present system. The peaks of F^-, Cl^- and NO_2^- were distorted by use of injection volumes >7 ml, but this distortion was not observed with injection volumes of <6 ml. By use of injection volumes of <6 ml, linear relationships were obtained between the amounts of solutes injected and the peak areas as shown in Figs. 4 and 5. These figures show that calibration curves can be obtained from arbitrary standard solutions regardless of the concentration and volume of the solution injected. Here the logarithms of both the amount of a solute and the peak area are plotted for convenience, but there is also linear relationship between the non-logarithmic values because the slope of every line is unity.

On the contrary, the peak heights obtained by injection of a small volume of a standard solution of high concentration were larger than that obtained from injection of a larger volume of a standard solution of lower concentration containing the same amounts of solutes. This shows that the sample bands are disturbed during the long concentration time by the flow of either sample water or the eluent diffusing into the sample solution. This distortion is not due to insufficient column capacity, because it was observed in the concentration of a extremely diluted solution (ppb level). Since the use of the concentrator column permitted the concentration of 15–30 ml of a solution, the maximum injection volume in the present method can be improved by the elucidation of this problem. The detection limits (signal-to-noise rates of 3) obtained from 6-ml injections with indirect photometric detection are in the range 0.4–1 ppb. The results are summarized in Table II.

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