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Note

High-performance electrochemical suppressor for ion chromatography

Z. W. TIAN*, R. Z. HU, H. S. LIN and J. T. WU
Chemistry Department, Xiamen University, Xiamen (China)

The conventional suppressor column, packed with a suitable ion-exchange resin, must be regenerated periodically. The elution times and detector response for some ions vary drastically according to the extent of exhaustion of the suppressor column. Band spreading and loss of resolution take place in the suppressor column. These drawbacks have been overcome by introduction of the ion-exchange fibre suppressor[1] (FS).

However, since the operation of FS is based on the diffusion principle, the following problems arise (taking anion chromatography as an example):

(1) Satisfactory replacement of Na^+ by H^+ cannot be achieved due to the back diffusion and the limitation in the rate of diffusion.

(2) A long fibre suppressor with very small diameter and very thin walls must be used to enhance the replacement. This construction causes some difficulties, such as an higher pressure drop along the fibre blockage by small gas bubbles and short lifetime owing to damage of the fibre during operation.

(3) To improve the replacement, a flowing scavenger solution is required. Hence the operating procedure is complicated and the running cost is raised.

Recently, the use of a micro-membrane suppressor[2] (MMS) has improved the above situation. However, as a derivative of FS, MMS is also based on the diffusion principle and cannot overcome the above problems fundamentally.

A new electrochemical suppressor (ES) has been developed by our laboratory. Since it is based on the electrochemical principle, the above problems encountered by the FS and MMS can be overcome.

PRINCIPLES AND ADVANTAGES OF THE ELECTROCHEMICAL SUPPRESSOR

A diagram of the structure and operating principle of the ES is given in Fig. 1.

The suppression compartment is a thin streamline channel filled with cation-exchange resin. The channel is about 6 cm long and 7 mm wide at its middle. The anolyte and catholyte are 0.1 *M* sulphuric acid. The anode and the cathode are made of platinum-plated titanium. The magnitude of the current depends on the eluent and flow-rate. For 5 m*M* sodium carbonate as the eluent at a flow-rate of 2 ml/min, a constant current of 50 mA is applied and the voltage across the suppressor is about 4 V. The electric power input is thus reduced to such a level that its heating effect on the eluent solution is acceptable[3].

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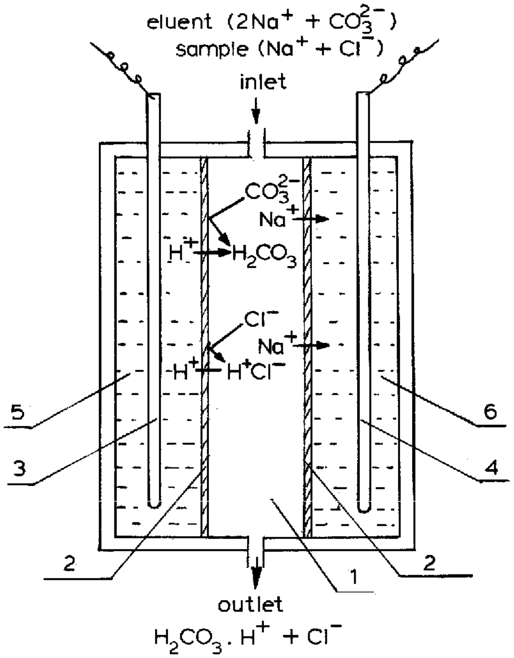

Fig. 1. Diagram of the electrochemical suppressor. 1 = Suppression compartment; 2 = cation-exchange membrane; 3 = anode; 4 = cathode; 5 = anolyte compartment; 6 = catholyte compartment.

The eluent with the sample from the separator column is passed through the suppression compartment. Under the influence of the electric field, the H^+ in the anolyte compartment move across the membrane into the eluent, and the Na^+ in the eluent move across the membrane into the catholyte compartment. Thus, sodium carbonate and sodium chloride in the eluent are converted into carbonic acid and hydrochloric acid.

From a thermodynamic point of view, the extent of suppression by diffusion must be restricted by the chemical equilibrium. However, an electrochemical suppressor is restricted only by the electrochemical equilibrium. The concentration of remnant sodium ions in the suppressed eluent can be further reduced in spite of the presence of sodium ions with an higher chemical potential outside the ion-exchange membrane. From a kinetic point of view, the sodium ions in the eluent are forced to cross the ion-exchange membrane by the chemical potential difference with a diffusion-type suppressors. In contrast, with an electrochemical-type suppressor the potential difference across the ion-exchange membrane can easily be controlled by the input electrical energy. In this case, sodium ions migrate under this potential difference much more rapidly.

According to the above discussion, for an electrochemical type suppressor, not only can the use of a flowing scavenger solution be avoided, but also the remnant sodium ion concentration can be further reduced to improve the suppression performance. The main advantages of the ES are as follows: (1) flowing scavenger solution is avoided; (2) suppression performance is improved; (3) operating procedure

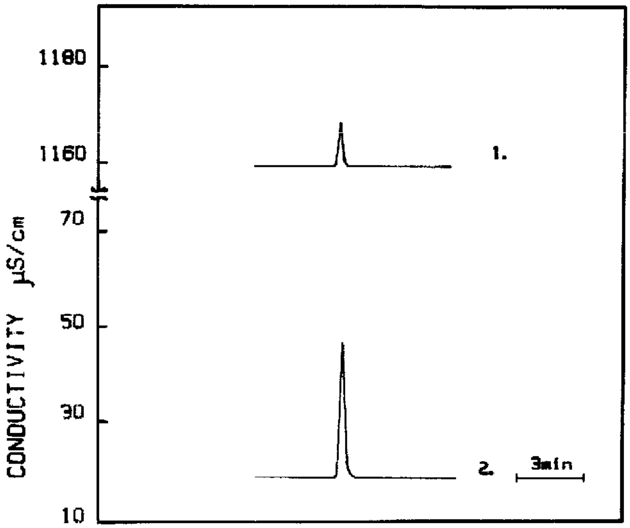

Fig. 2. Conductivity of peak and background before (1) and after (2) passage through the ES. Sample: 15 ppm F^-. Injection volume: 100 µl. Eluent: 5 m*M* sodium carbonate. Flow-rate: 2 ml/min.

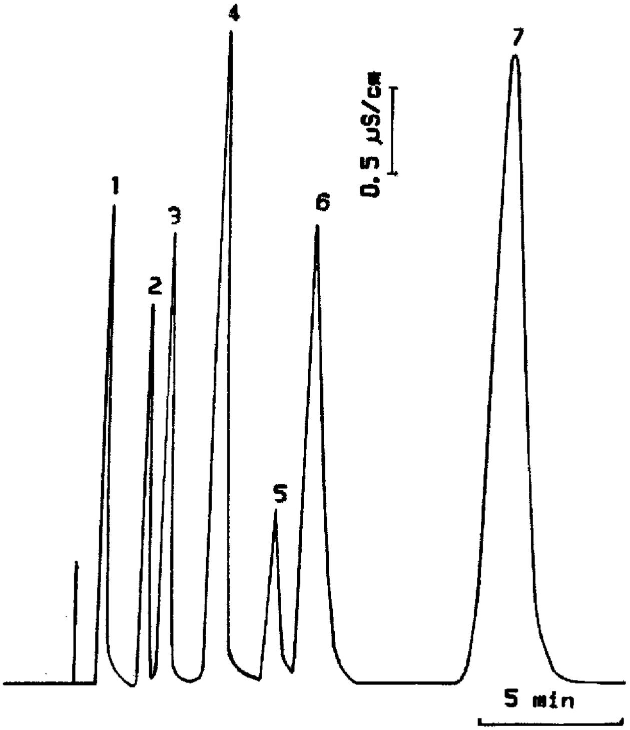

Fig. 3. Ion chromatogram of seven anions using the ES. Conditions as in Fig. 2. Sample: 1 = F^- (1 ppm); 2 = Cl^- (2 ppm); 3 = NO_2^- (5 ppm); 4 = PO_4^{3-} (20 ppm); 5 = Br^- (5 ppm); 6 = NO_3^- (15 ppm); 7 = SO_4^{2-} (20 ppm).

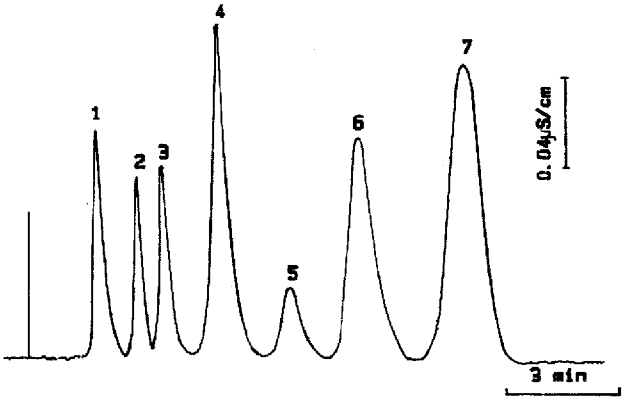

Fig. 4. Ion chromatogram of seven low concentration anions using the ES. Conditions as in Fig. 2. Sample: 1 = F^- (38 ppb); 2 = Cl^- (50 ppb); 3 = NO_2^- (125 ppb); 4 = PO_4^{3-} (625 ppb); 5 = Br^- (125 ppb); 6 = NO_3^- (375 ppb); 7 = SO_4^{2-} (625 ppb).

is simplified; (4) back pressure of suppressor is lowered; (5) lifetime of suppressor is lengthened; (6) cost of suppression is reduced.

EXPERIMENTAL

The equipment used was an YSIC-1 ion chromatograph (Shanghai Bioengineering Instrument Factory, Academia Sinica) based on our ES. The main features are as follows: separator column, Sinopak L-01A (250 mm × 4 mm I.D.); suppressor column, XYZ-1 electrochemical suppressor; conductivity detector (four electrodes), XWD-1. The chromatographic conditions were as follows: eluent, 5 m*M* sodium carbonate; flow-rate, 2.0 ml/min; pressure, 200 p.s.i.; injection volume, 100 μl. Sample solutions were prepared from reagent grade sodium salts.

RESULTS

The effect of the ES was examined without a separator by injecting 100 μl of 15 ppm fluoride ion. The background and peak conductivities before and after pas-

TABLE I

PERFORMANCE OF THE ES AND THE FS

Column	*Eluent*	*Flow-rate (ml/min)*	*Background specific conductivity (μS/cm)*	
			ES	*FS*
Anion suppressor	2.4 m*M* Na_2CO_3 + 3m*M* $NaHCO_3$	2.0–3.2	17–18	18–24 (ref. 5)
	2 m*M* NaOH	2.0	~2	10–15 (ref. 4)
Cation suppressor	5 m*M* HCl	2.4	~2	9–17 (ref. 5)
	2 m*M* HCl	2.0	~2	10–15 (ref. 4)

sage through the ES are shown in Fig. 2. The ratio of the peak signal to the background is increased from 0.017 to 1.67. The background conductivity decreased from 1.1 mS/cm to 17 μS/cm and the peak height increased by about a factor of 3.

The ion chromatograms of seven anions using the ES and the YSIC-1 are shown in Figs. 3 and 4. For 8 h of continuous operation, the deviations [relative standard deviations (R.S.D.)] for the peak heights and the retention times of a nitrite sample are less than 1 and 0.2% respectively.

Before and after passage through the ES (flow-rate 2 ml/min) the sodium ion concentration in the eluent (2.4 m*M* sodium carbonate + 3 m*M* sodium bicarbonate) is reduced from 179.4 to 0.1788 ppm as measured by a WFX-1D atomic absorption spectrometer. The suppression efficiency is 99.9%. A comparison of the background specific conductivity using the ES to that with a FS is shown in Table I.

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