Use of an Ion-selective Electrode as a Detector in Ion Pair Chromatography

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Synopsis. A chloride ion-selective electrode was used as a detector for inorganic anions separated by ion pair chromatography. Excellent performance of the electrode detector was demonstrated by detection of chloride, iodide, and thiocyanate.

While ion pair chromatography has been widely used in the separation of charged organic species,[1] little has been reported for the separation of inorganic anions.[2,3] This is seemingly ascribable to limitation in detectors which directly respond to inorganic anions under the conditions of the chromatography. Although detectable species are limited, ion-selective electrodes will be useful for detection of anions which have no or weak light absorption in the UV and visible regions.[4]

This paper describes the use of a solid state type chloride ion-selective electrode as a detector for some inorganic anions in ion pair chromatography.

Experimental

An HPLC system with an ion-selective electrode detector was reported in detail in a previous paper.[5] An Orion 94-17A chloride ion-selective electrode was used. A baseline supporting electrolyte solution (BLSS), which depresses streaming potential and stabilizes baseline potential, was mixed to a column effluent by a post column technique. The BLSS used was an aqueous solution containing potassium nitrate(1.0 M, 1 M=1 mol dm^{-3}) and sodium chloride(3.0×10^{-5} M). A LiChrosorb RP-18(Merck) or ODS 6013(Kyowa Seimitsu) was packed in a stainless steel coulmn(100 mm× 2.1 mm i.d.). Samples were injected with a Hamilton microsyringe HP-305(5 μl). The mobile phase was an aqueous solution containing tetrabutylammonium sulfate and sulfuric acid. The mobile phase and BLSS were doubly filtered with Mitex and Millipore MF filters, before use. All chemicals were of reagent grade and were used as received.

Results and Discussion

Since a chloride ion-selective electrode of solid membrane type responds to most anions which form sparingly soluble silver salts, the separation and detection of these kinds of anions were tested. In order to determine an appropriate pH range of the mobile phase, chloride, iodide, and thiocyanate were separately eluted with a mobile phase of various pH. When the pH of the mobile phase was greater than 1.5, marked tailing was observed for elution of iodide and thiocyanate. As an example, detector responses for iodide are shown in Fig. 1. Thus, further studies were made maintaining the pH of the mobile phase below 1.5, although the cause of the tailing was not clear.

Figure 2 shows detection of chloride and thiocyanate. Both anions were successfully separated within 10 min. The complete separation of iodide from chloride and thiocyanate was difficult under the conditions examined. In Table 1, an example of reproducibility for detector responses is given. The reproducibility is comparable to that of conventional detectors. Figure 3 shows an analytical curve for chloride separated

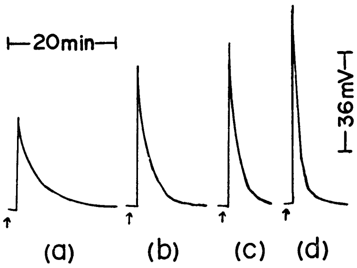

Fig. 1. Effect of pH of the mobile phase on elution of iodide.
Mobile phase: 2.0×10^{-3} M tetrabutylammonium sulfate in various concentrations of sulfuric acid, flow rate of mobile phase: 0.65 ml/min, flow rate of BLSS: 1.0 ml/min, sample: 50 nmol of sodium iodide, column: ODS 6013, pH of the mobile phase: (a) 2.80, (b) 1.95, (c) 1.47, (d) 1.08.

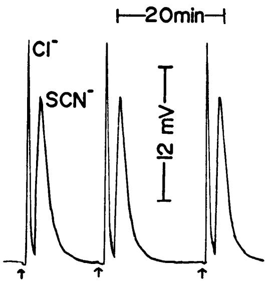

Fig. 2. Separation of chloride and thiocyanate.
Mobile phase: 6.0×10^{-3} M tetrabutylammonium sulfate in 0.1 M sulfuric acid, flow rate of mobile phase: 1.2 ml/min, flow rate of BLSS: 1.1 ml/min, sample: mixture of sodium chloride and sodium thiocyanate (50 nmol of each), column: Lichrosorb RP-18.

Table 1. Reproducibility of detector response[a]

Ion[b]	Peak height[c] / mV	Relative standard deviation/%
Chloride	17.0	2.5
Thiocyanate	21.5	4.1

a) Chromatographic conditions are given in Fig. 2. b) 50 nmol of each. c) Average of 12 determinations.

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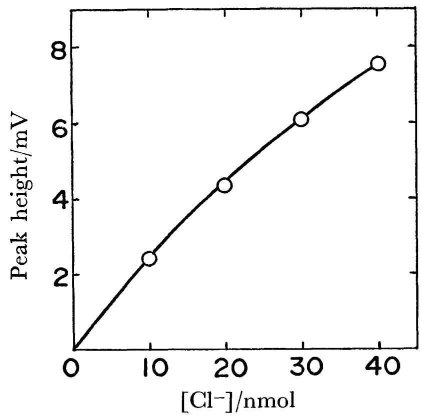

Fig. 3. Analytical curve for chloride separated from 50 nmol of thiocyanate.
Mobile phase: 4.0×10^{-3} M tetrabutylammonium sulfate in 0.1 M sulfuric acid, flow rate of mobile phase: 0.55 ml/min, flow rate of BLSS: 1.0 ml/min, sample: mixture of sodium chloride and sodium thiocyanate, column: ODS 6013.

from thiocyanate. The analytical curve is not linear. It shows slightly upward curvature. Lower detection limits are not examined, but it is not difficult to detect the anions down to orders of nano moles.

As is illustrated in this work, the chloride ion-selective electrode can be successfully used as one of the detectors in ion pair chromatography. Recently, reversed phase columns have drawn attention to the separation of charged inorganic species by ion pair chromatography[2,3] and by similar but somewhat different approaches.[6-8] Seemingly, ion-selective electrodes will be useful for expansion of this field, since problems encountered are detectors in chromatographic determination of inorganic species.

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