Determination of Iodide Ion Using Alkali-Free Lead Phosphate Glasses as Potentiometric Detector Sensors in Nonsuppressed Ion Chromatography

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(Received February 8, 1988)

Synopsis. Alkali-free lead phosphate glasses containing silver oxide show a linear relationship with the Nernstian slope for iodide concentration. By using these glass membranes as potentiometric detector sensors for ion chromatography, the limit of detection for iodide ion was extended down to 0.05 $\mu g\,cm^{-3}$. The high sensitivity can be interpreted in terms of the strong interaction between iodide ion and the silver ion incorporated in the membrane material.

A wide variety of detectors are presently used for the determination of iodide ion in ion chromatography, and have been quantified by the conductimetric method[1] and the UV absorbsnce method,[2,3] in addition to the electrochemical detector methods such as the amperometric method[4] and the potentiometric method.[5] The potentiometric detector method, chiefly using ion-selective electrodes, has been reported by a number of workers.[6,7] Various types of ion-selective glass electrodes are available. However, most of those glasses respond to cationic species,[8,9] and no reports on anion-responsive glass electrodes have apparently been published to date. We have already investigated some alkali-free phosphate glasses as sensing materials for nitrate ion[10] and as potentiometric detector sensors for ion chromatography.[11]

This paper reports on properties of lead phosphate glass membranes containing silver oxide and on their application to the analysis of iodide ion as potentiometric detector sensors for ion chromatography.

Experimental

Apparatus. Alkali-free lead phosphate glasses were prepared as previously described.[11] Chemical compositions of some of the tested glasses, their potential changes per decade change in iodide ion activity, and their physical and chemical properties are listed in Table 1.

A schematic diagram for an ion-chromatographic system is shown in Fig. 1. It consists of a Toso Co. HLC-803D pump with a Rheodyne sample injector with a 100 mm^3 sample loop, a combination of a TSK IC-A guard column and duplicated TSK Gel IC anion SW anion separator columns, two valves (V1 and V2) of a column changing switch, and a DKK Co. ion-selective flow cell with some improvements. Under the ordinary circumstances, the guard column and only separator column SW 1 were used. However, when the iodide concentration in seawater was determined, most of chloride ion was eluted by column SW 1, valve 2 was switched back on the line after about an 8 min period, and the chromatogram of iodide ion was obtained by column SW 2.

Both of peak height (potential difference, mV) and peak area gave essentially straight lines against the logarithmic iodide concentration. Therefore, the peak height was routinely used for the determination of iodide concentration.

Solutions. Aqueous solutions of inorganic anions and sodium citrate eluent were prepared by the corresponding sodium salts of analytical reagent grade with twice distilled water. Before use, the eluent was degassed under vacuum with sonication. Artificial seawater was prepared as previously described.[12]

Recommended Procedure. A 10 cm^3 sample solution containing a 0.03 $\mu g\,cm^{-3}$ iodide species was taken in a 50 cm^3 beaker, and 1.0 cm^3 of 10^{-3} mol dm^{-3} ascorbic acid was added to reduce the iodide species to iodide. Sodium citrate

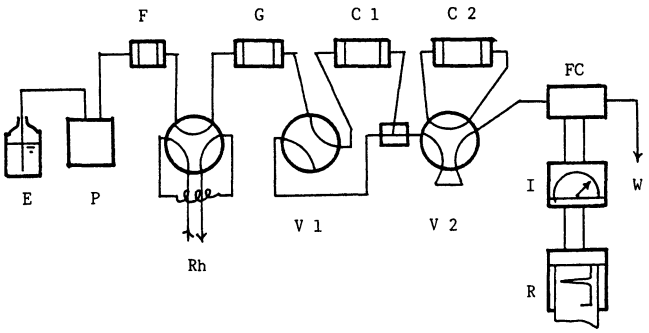

Fig. 1. The schematic diagram of the chromatographic system. E: eluent reservoir; P: pump; F: filter; RH: Rheodyne injector; G: guard column; V1: valve 1; C1: TSK Gel IC Anion SW 1 column; V2: valve 2; C2: SW 2 column; FC: flow cell; I: ion meter; R: recorder; W: waste.

Table 1. Chemical Compositions and Properties of Glasses

Glass no.	Chemical composition (Ag_2O : P_2O_5 : PbO : Al_2O_3) mol%				Physical and chemical property: Transition temp °C	Softening temp °C	Thermal expansion $10^7/cm\,°C^{-1}$	Membrane resist. $M\Omega\,cm^{-1}$	Chemical durability $10^4\,mg\,mm^{-2}$	Potential change mV/pI$^-$
1	—	55	35	10	433	506	102.4	37.6	8.96	35.2
2	5	55	30	10	447	536	118.1	24.4	7.78	52.3
3	10	55	25	10	506	567	113.4	29.6	16.5	58.2
4	15	55	20	10	493	552	120.6	39.2	14.6	48.9

eluent of 0.5 mmol dm^{-3} (pH about 5.0) was pumped at a flow rate of 1.0 cm^3 min^{-1}. For direct determination of iodide, a 100 mm^3 sample was injected and determined by comparison with the standard iodide concentration. Elution curves were obtained in the order: BrO_3^-, Cl^-, ClO_3^-, NO_2^-, Br^-, NO_3^- I^-, SCN^-, and ClO_4^-.

Results and Discussion

Properties of Glasses and Potential Response of Glass Electrodes. As is evident from Table 1, the values of physical and chemical properties of the lead phosphate glasses containing silver oxide are not so much different from those containing no silver oxide. The potential response for the glass number 3 in Table 1 is linear over the iodide ion activity range 10^{-1}—5×10^{-6} mol dm^{-3}, and it has a Nernstian response of about 58 mV per decade change in iodide activity at 25 °C. However, the glass electrode containing no silver oxide yields only a small unstable potential response for iodide.

Detection of Iodide Ion Using Lead Phosphate Glass Membrane Electrode in the Potentiometric Detector for Ion Chromatography. Figure 2 shows the chromatograms for 4 anions obtained with the potentiometric detectors for lead phosphate glass electrode No. 3(A) and No. 1(B) and with the conductivity detector (C), column SW 1 being used as the separator column and 0.5 mmol dm^{-3} sodium citrate (pH 4.96) as the eluent.

In measurement of peak heights for iodide ion, a negative dip peak is observed at the end of the iodide ion peak, and it increases with decreasing pH of the eluent and with increasing iodide ion concentration.

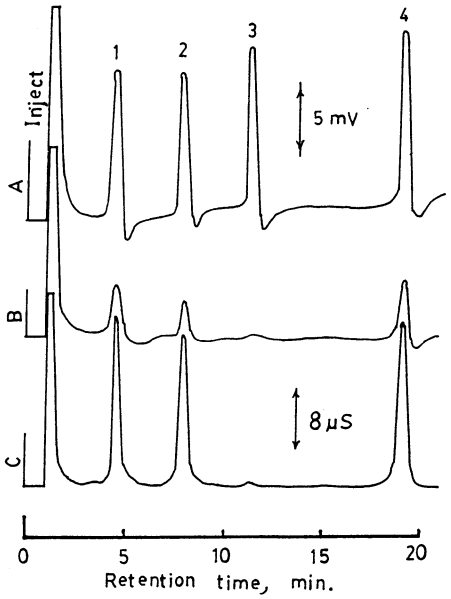

Fig. 2. Ion chromatograms of 4 anions with anion-exchange column. Eluent: 0.5 mol dm^{-3} sodium citrate (pH 4.96). Detector system: A: $10Ag_2O:55P_2O_5:25PbO:10Al_2O_3$ glass detector; B: $55P_2O_5:35PbO:10Al_2O_3$ glass detector; C: Conductivity detector. Anionic species: 1: 5 μg cm^{-3} Cl^-; 2: 10 μg cm^{-3} NO_3^-; 3: 0.4 μg cm^{-3} I^-; 4: 10 μg cm^{-3} ClO_4^-.

The glass number 3 detector is capable of detecting iodide ion with an extremely high sensitivity as compared with the other detectors. This suggests that the addition of silver ion in the glass material has led to the high sensitivity in potential response to iodide ion. Silver ion forms insoluble salts with anions such as Cl^-, Br^-, I^-, SCN^-, S^{2-}, and PO_4^{3-}, so that the insoluble silver iodide adsorbs strongly on the detector glass surface, resulting in the high sensitivity to iodide.

The sensitivity of UV absorbance method for the detection of iodide ion is as high as that of this method, but such anions as fluoride, chloride, and perchlorate ions will provide no sufficient absorbances for UV radiation.

Effect of Eluent pH on the Retention Time. Figure 3 shows the effect of eluent pH on the retention time of 5 anions. Decreasing the eluent pH produces good separation of peaks, but the accuracy for the measurement on these anions decreases due to the increase of the negative dip peak at the end of each peak. Therefore, the eluent pH around 5.0 yields only a small variation in the retention time for each anion, resulting in

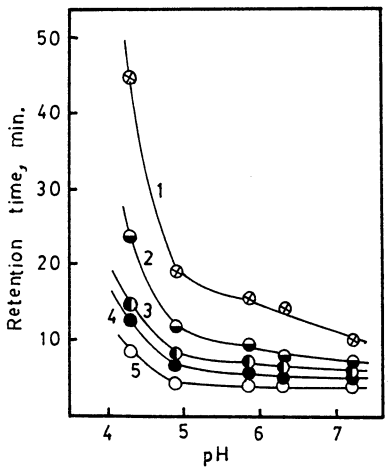

Fig. 3. Effect of pH on the retention time. Eluent: 0.5 mol dm^{-3} citric acid (pH 4.2—7.2). 1: ClO_4^-; 2: I^-; 3: NO_3^-; 4: Br^-; 5: Cl^-.

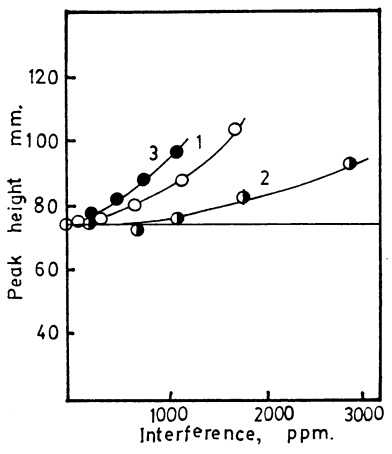

Fig. 4. Effect of diverse anions on the determination of 0.63 μg cm^{-3} iodide. Eluent: 0.5 mol dm^{-3} sodium citrate (pH≈5.0). 1: Br^-; 2: Cl^-; 3: NO_3^-.

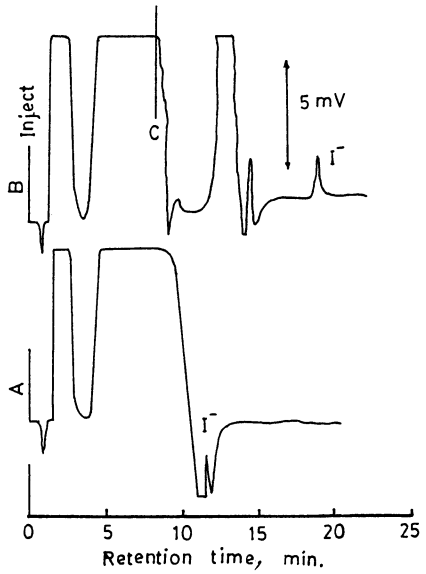

Fig. 5. Chromatograms of artificial seawater sample. Composition of artificial seawater: Cl^- 19 mg cm^{-3}, Br^- 65 μg cm^{-3}, I^- 0.06 μg cm^{-3} and IO_3^- 0.02 μg cm^{-3}. A: chromatogram of SW 1 column. B: chromatogram as similar to A when switched onto the line of SW 2 column after 8 minutes period. C: the place where the valve V 2 is switched onto the line of SW 2 column.

a favorable result will respect to the separation of each anion.

The peak height is considered to be proportional directly to the logarithmic concentration of iodide ion between 0.05 and 1.5 μg cm^{-3}. The relative standard deviation for five separate runs on 0.05 μg iodide ion in 100 mm^3 was about 4%. The detection limit of this procedure was estimated to be 3 ng for direct injection of 100 mm^3.

Interferences. Interferences of diverse ions, such as chloride, bromide, and nitrate ions, with the determination of 0.63 μg cm^{-3} of iodide ion are shown in Fig. 4. Of the anions examined, chloride, bromide, and nitrate ions cause interference if the specified amounts are exceeded (about 1500 for chloride, 400 for bromide, and 200 μg cm^{-3} for nitrate for the determination of 0.63 μg cm^{-3} of iodide). Iodate ion gives a small response and has a retention time different from that of iodide ion.

The amounts of the halogenic anions generally existing in seawater are about 0.05—0.06 μg cm^{-3} of total iodine, 65 μg cm^{-3} of bromide ion, and 19 mg cm^{-3} of chloride ion, so that the total iodine in seawater cannot be determined by the present procedure. When applying this procedure to the practical seawater, most of chloride ions must be removed by pretreatment.

The determination of total iodine in seawater is to be made as follows: (1) Ascorbic acid is added to reduce iodate to iodide, (2) a 200 mm^3 sample is injected, (3) chromatographic separation of anions is run with column SW 1 positioned as indicated in Fig. 1, (4) after most of chloride ions have passed through the detector (after 8 min), V2 valve is switched over to the line of column SW 2, and (5) the chromstogram of iodide ion is recorded with column SW 2.

Figure 5 shows typical chromatograms for the artificial seawater sample (Cl^- 19 mg cm^{-3} and Br^- 65, I^- 0.06, and IO_3^- 0.02 μg cm^{-3}) by both the ordinary method and the two column method. By the latter method, the large negative dip peak associated with chloride ion can be removed from the iodide peak, and the total iodide concentration can be determined accurately.

This work was supported by a Grant-in-Aid for General Scientific Research No. 62540433 from the Japanese Ministry of Education.

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