August, 1987] © 1987 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, **60**, 2861—2864 (1987) 2861

Properties of Alkali-Free Lead Phosphate Glasses as an Ion-Selective Electrode and Their Application to a Potentiometric Detector for Ion Chromatography

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(Received February 23, 1987)

The properties of alkali-free lead phosphate glasses containing silver oxide as an anion selective electrode were examined, and their application to a potentiometric detector for an ion chromatographic technique were developed. The series of these glasses are characterized by their low softening temperature and are only responsive to anionic substances. The featureless potential response of almost anions tested becomes a rather useful property as a detector for an ion chromatographic analysis of anions. The response characteristics and selectivity coefficients revealed that the glass composition of $10Ag_2O:55P_2O_5:25PbO:10Al_2O_3$ is the most suitable electrode materisl for anion chromatography. With this glass electrode, nonsuppressed anion chromatographic parameters were studied, including a comparison of an eluent composition, the flow rate and the retention time. This detector could be used in a high pH eluent without any interference of the large blank value. In paticular, the detector was highly sensitive to iodide ions. This may be due to the interaction of iodide ions with silver ions which are involved in membrane materials.

Ion-selective electrodes are versatile devices for the continuous monitoring of a wide range of processes and reactions such as titrations, industrial processes, enzyme reaction, flow injection analyses, and high-performance liquid chromatography.

It is well-known that various types of the ion-selective glass electrodes such as alkali silicate glasses,[1] chalcogenide glasses[2] and phosphate glasses[3,4] are available. All alkali-silicate and chalcogenide glasses have been utilized for measurements of cationic substances. On the other hand, it has been suggested that the replacement of aluminium in the sodium almino-silicate glasses by phosphorus can be expected to lead to anion-exchanger properties.[5] Since we had already investigated some phosphate glass membrane as materials of the nitrate ion selective electrode,[6] their alkali-free phosphate glass electrodes were characterized by their anion responsive properties.

Ion chromatography is a very effective method for the analysis of many common anions using an electrochemical detector[7,8] or a UV absorbance detector.[9] Electrochemical detection of inorganic anions by potentiometry, amperometry, or coulometry is generally applied to a restricted number of cases, but can exhibit a greater sensitivity than a conductivity detector. Nonsuppressed ion chromatographic techniques with TSK Gel IC Anion SW as an anion-exchanger column have been successful in a variety of applications.[10]

In this investigation, the physical and chemical characteristics of alkali-free lead phosphate glasses were measured, and a systematic check of the potential response and selectivity coefficients on the glass composition were performed; also, their applicability for an anion selective glass electrodes were examined. Moreover, the potentiometric detector based on the alkali-free lead phosphate glass electrode was constructed and utilized in order to determine various anions by the ion chromstographic technique.

Experimental

Preparation of the Glass Membrane. In order to obtain electrode glasses, the following analytical reagent grades were used: orthophosphoric acid (85%), silver carbonate, lead carbonate, and aluminium hydroxide. The preparation procedures of the phosphate glasses and the glass membranes have been described previously.[11] The chemical compositions of some of the tested glasses are listed in Table 1.

Measurements of physical and chemical properties and membrane potentials have been described previously.[6] The physical and chemical properties of some of the lead phosphate glasses containing Ag_2O and Al_2O_3 are summarized in Table 2.

Reagents and Solutions. Stock solutions were prepared by dissolving the reagent of KF, NaCl, $NaNO_3$, $NaNO_2$, Na_2SO_4, KBr, KI, $Na_2S_2O_3$, Na_2SO_3, $NaClO_4$, $NaBrO_3$, and $NaClO_3$ in twice-distilled water. Sodium tartrate eluents were prepared from the reagent grade tartaric acid in concentration ranging from 2×10^{-4} to 5×10^{-3} mol dm^{-3}; in general the eluents were buffered with sodium hydroxide. Citrate eluents with a pH range of 4.3 to 8.0 were prepared from sodium salt.

Chromatographic Procedure. Figure 1 shows a cross-sectional view of the flow-through type potentiometric detector, which consists of a combination of ion-selective

Table 1. Composition of the Glasses

Glass No.	Ag_2O	P_2O_5	PbO	Al_2O_3
1	—	55	35	10
2	5	48	37	10
3	5	50	35	10
4	5	55	30	10
5	10	48	32	10
6	10	50	30	10
7	10	55	25	10
8	15	48	27	10
9	15	55	20	10

Table 2. Physical and Chemical Properties of the Glasses

Glass No.	Transition temperature T_g/°C	Softening temperature T_s/°C	Thermal expansion $\alpha \times 10^7$/cm °C^{-1}	Chemical durability mg mm^{-2}	Membrane resistance MΩ cm^{-1}
1	433	506	102.4	8.96×10^{-4}	37.6
2	426	512	107.3	3.14×10^{-4}	53.8
3	—	—	—	—	21.9
4	447	536	118.1	7.78×10^{-4}	24.4
5	421	485	109.7	1.01×10^{-3}	13.7
6	—	—	—	—	36.7
7	506	567	113.4	1.65×10^{-3}	29.6
8	474	528	136.5	1.05×10^{-3}	32.6
9	493	552	120.6	1.46×10^{-3}	39.2

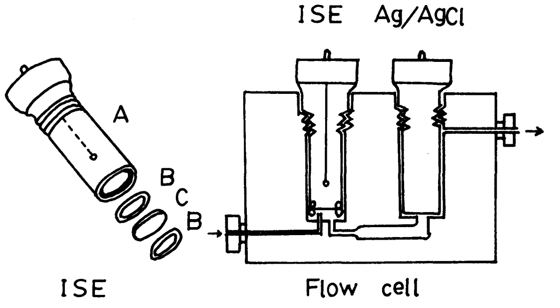

Fig. 1. Structure of ion-selective electrode and a cross section of flow cell. A: Ag/AgCl electrode; B: silicone rubber O-ring; C: glass membrane.

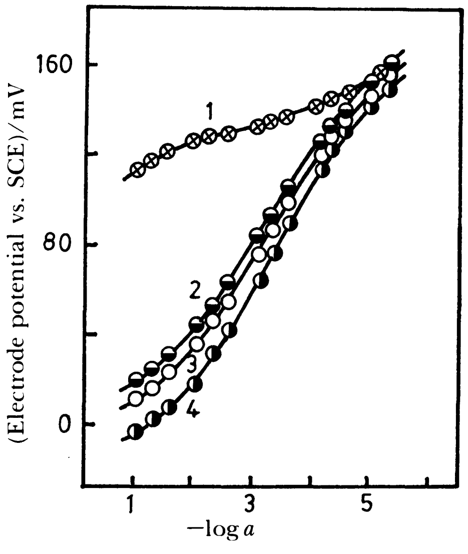

Fig. 2. Electrode response of No. 7 glass membrane electrode as a function of several ion activities. 1: SO_4^{2-}; 2: Cl^-; 3: NO_3^-; 4: I^-.

glass electrodes and an Ag/AgCl reference electrode, both with a direct internal contact.

The ion-selective electrode used consists of a lead phosphate glass working electrode of disks 8.0 mm in diameter and 0.4—0.6 mm thick tightened between a plastic detector body and an Ag/AgCl reference electrode with a silicone rubber O-ring on both sides. The detector cell, which has been developed for flow injection analyses by DKK Co., was used for this purpose with some improvements: a flow path diameter was thinned down by filling in the path way with ID 0.25 mm SUS pipe.

The chromatographic system employed comprised a Toyo Soda Co. HLC-803D pump, a 2 μm pore sintered ceramic filter, a TSK IC-A guard column, a TSK Gel IC Anion PW or SW anion-separator column, a DKK Co. ion-selective flow cell, a DKK COM-20 pH meter, and a Sekonic model SS-250F recorder. Unless otherwise specified, the injector sample loop volume was 100 mm^3, and samples of 1.0 cm^3 were introduced with a Hamilton syringe. The eluent flow rate was 1.0 cm^3 min^{-1}. A 0.1 mol dm^{-3} sodium citrate solution was used for column regeneration before the injection of a sample. The measurement temperature was maintained at 25±1 °C.

Results and Discussion

Physical and Chemical Properties of Glasses. As shown in Table 2, the values of T_g and T_s of the tested glasses were considerably lower than those of the other phosphate glasses.[6] This may be due to the addition of lead oxide instead of magnesium oxide in the glass compositions. Although the membrane resistance increased only slightly, the chemical durability of the tested glasses were better than the magnesium phosphate glasses.

Potential Response of the Lead Phosphate Glasses. The potential response curves of some of the alkali-free lead phosphate glass membranes (No. 7) for various anions are shown in Fig. 2. All the glasses investigated were sensitive to anions, except for sulfate, sulfide and thiosulfate ions. It is apparent that the potential response of the common anions examined were featureless to each others and gave calibration slopes of 45—50 mV per decade, except for iodide ions. It is a rather useful property for the potentiometric detector of ion chromatograph. However, iodide ions show a sensitive electrode response; the slope was at about 58 mV in the concentration range of 5×10^{-2} to 10^{-5} mol dm^{-3} of iodide ion and the analytical range was 10^{-1} to 10^{-6} mol dm^{-3}.

The potential response of several anions for all tested lead phosphate glass electrodes are listed in Table 3.

The response characteristics of the tested glass membranes depended upon its glass composition. In particular, glasses that do not contain Ag_2O show a small electrode response and an unsatisfactory poten-

Table 3. Electrode Function of Several Anions

Glass No.	NO_3^-	Cl^-	I^-	ClO_4^-	SO_4^{2-}
1	30.1	21.8	35.2	28.2	5.5
2	45.9	38.0	46.2	39.3	8.8
3	43.3	—	51.2	36.8	13.9
4	48.3	45.2	52.3	46.6	6.3
5	46.5	35.8	47.6	34.2	7.3
6	44.6	41.7	49.2	44.5	8.2
7	50.2	46.7	58.2	48.9	8.6
8	41.5	40.7	48.2	43.5	6.0
9	47.0	43.5	48.9	42.8	7.8

The numerical value shows a potential response of mV per decade.

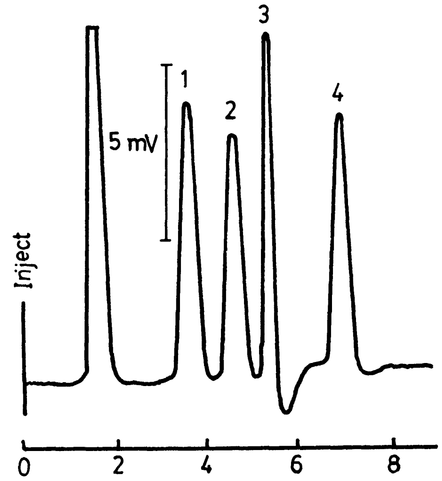

Fig. 3. Ion chromatogram of 4 anions with TSK Gel IC Anion SW column. Eluent: 0.5 mmol dm^{-3} sodium tartrate (pH 6.34), 1: 15 µg mm^{-3} Cl^-; 2: 20 µg mm^{-3} NO_3^-; 3: 2 µg mm^{-3} I^-; 4: 30 µg mm^{-3} ClO_4^-.

tial reproducibility. Moreover, it was observed that the response rate of the glasses with a lower P_2O_5 content (48 mol%) was rather worse than that of the higher P_2O_5 content glasses (55 mol%). This fact suggests that the ultraphosphate glasses corresponding to the branched structure seem to be more structurally useful than the polyphosphate glasses corresponding to the chain structure.

As the results of the potential response of various lead phosphate glass electrodes, the 10 Ag_2O : 55 P_2O_5 : 25 PbO : 10 Al_2O_3 glass membrane was concluded to be best in terms of the response speed, reproducibility of potential, and sensitivity of the electrode response for the determination of various anions.

Application of Lead Phosphate Glass Membrane Eectrode for the Potentiometric Detector of Ion Chromatography. The separation of 4 anions with TSK Gel IC Anion SW column using 0.5 mmol dm^{-3} sodium tartrate eluent is shown in Fig. 3.

Peaks of chloride, nitrate, iodide, and perchlorate ion appeared with very good separation. Sulfate, sulfide, and thiosulfate ion produce a small peak, and are unsuitable. The sensitivity of iodide ion is much higher than the other anions.

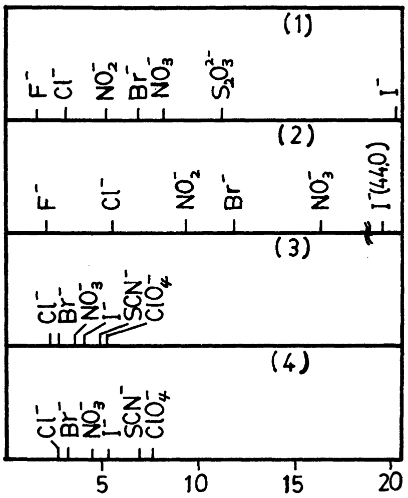

Fig. 4. Comparison of separation column. 1,2: TSK Gel IC Anion PW column; 3,4: TSK Gel IC Anion SW column; 1,3: 0.5 mmol dm^{-3} sodium citrate eluent (pH 6.80); 2,4: 0.5 mmol dm^{-3} sodium tartrate eluent (pH 6.34).

As shown in Fig. 3, a negative dip was observed at the end of the iodide ion peak. It increases with a decrease in the pH of the eluent, and with an increase in the iodide concentration. A negative dip peak signal similar to the present case has been reported when using an iodide selective electrode as the potentiometric detector of ion chromatography.[12] In the present experiment, even if the recorder was operated at much faster chart speed, the elution curve of iodide ion was not splited into its positive and negative parts.

Comparison of the Anion-Exchanger Column. Figure 4 lists the retention times of selected anions using both the TSK Gel IC Anion PW and SW as the separation column, and sodium citrate and sodium tartrate as the eluents. Anions such as chloride, nitrate, nitrite, and bromide show rather small changes in the order of the retention time from one eluent to another. However, iodide shows considerable variations between two columns, changing from a retention time of 5.16 min for SW to 44.0 min for PW wi 0.5 mmol dm^{-3} sodium tartrate eluent. It was considered that a large lag of the retention time of iodide ion with PW column is caused by a characteristics of hydrophobic group anions such as iodide, perchlorate, and thiocyanate.[10]

Effect of Retention Time on the pH and the Concentration of Eluent. The equilibrium reaction for anions exchanging on a strong base anion exchanger is expressed as

$$xA^{-y}+yB\text{-}R_x \rightleftarrows yB^{-x}+xA\text{-}R_y, \qquad (1)$$

where R represents the anion exchanger, A and B are competing anions, and y and x are the charge of the anion in the sample solution and the eluent, respectively.

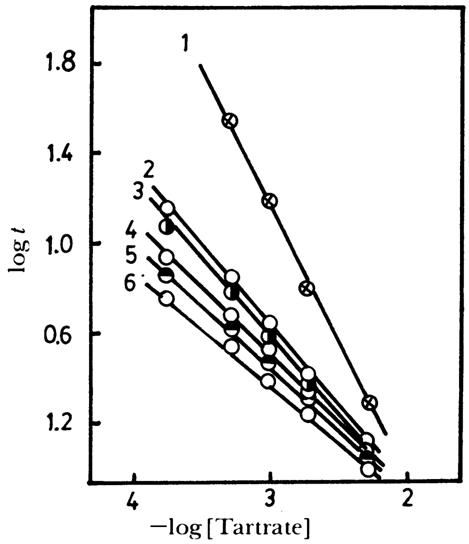

Fig. 5. Effect of eluent concentration on the retention time. TSK Gel IC Anion SW column, sodium tartrate eluent (pH 6.0—6.5), 1: $S_2O_3^{2-}$, 2: ClO_4^-, 3: SCN^-, 4: I^-, 5: NO_3^-, 6: Cl^-.

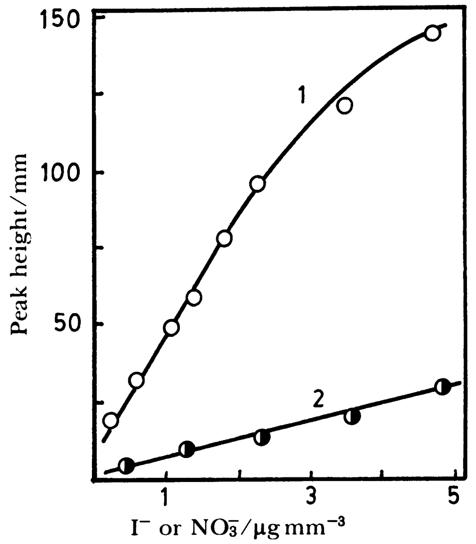

Fig. 6. Calibration curves of nitrate and iodide ion. TSK Gel IC Anion SW column, 0.5 mmol dm^{-3} sodium tartrate eluent (pH 6.34), 1: iodide ion; 2: nitrate ion.

From a consideration of the retention time, t, and the eluent concentration, [eluent], Eq. 2 can be obtained:[13]

$$\log t = \frac{-y}{x} \log \text{[eluent]} - \text{constant}. \qquad (2)$$

This shows that a change in the logarithm of the eluent concentration versus the logarithm of the retention time will have the straight line relationship with the slope of $-y/x$, which varies with the charge of the anions involved.

Figure 5 show the relation of the retention time and the concentration of sodium tartrate eluent for the TSK Gel IC Anion SW column. All anions show a straight line. The slopes of the perchlorate and thiocyanate ions are close to the theoretical value of −1, but the slopes of most of the monovalent anions are lower than the predicted values. Sulfate, sulfite, and thiosulfate have a slope of approximately −1.6.

The effect of the pH of the eluent on the retention time, using 0.5 mmol dm^{-3} sodium citrate as the eluent, was examined and revealed that the lower pH of the eluent below about 6.5 caused the larger difference of the retention time. However, the retention time remained almost constant for an eluent with a pH above 6.5.

Sensitivity of Various Anions and the Determination of Iodide Ion. As is shown in Fig. 4, the retention time of anions remains fixed in terms of the species of eluent, the pH of the eluent and the characteristics of anion-exchanger column.

By using the lead phosphate glass membrane as a potentiometric detector and the TSK Gel IC Anion SW as an anion-exchanger column, calibration curves of nitrate and iodide ion were examined; the results are shown in Fig. 6.

With a 100 mm^3 injection loop and 0.5 mmol dm^{-3} sodium tartrate at pH 6.34 as an eluent, calibration curves of the peak hight as a function of these concentration are almost linear at concentrations from 0.5 to 30 μg cm^{-3} for nitrate ion and from 0.1 to 5 μg cm^{-3} for iodide ion. The detection limit for nitrate and iodide are 0.2 and 0.05 μg cm^{-3}, respectively. The detection limit of iodide ions reported here is approximately several times lower than those reported with the use of the conductivity detector.[10]

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