

Indirect Determination of Alkali Metals and Lead by Fractional Dissolution/Ion Chromatography of Sulfates Deposited on Surface of Sulfur Dioxide-Treated Lead Glass

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二酸化硫黄処理された鉛ガラス表面上硫酸塩の分別溶解/イオンクロマト分析によるアルカリ金属と鉛の間接定量

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An indirect determination of alkali metals and lead by fractional dissolution/ion chromatography of sulfates deposited on the surface of sulfur dioxide-treated lead glass was investigated. This method involves the following procedures: 1) Sodium sulfate and potassium sulfate are dissolved in 50% (v/v) ethanol. 2) Remaining lead sulfate is dissolved in 20 mM sodium hydroxide. 3) From the concentration of sulfate in each sample solution, the surface concentrations of the corresponding alkali metals and lead are calculated. From the analytical results for lead glass samples, we have ensured that treating the glass with sulfur dioxide resulted in the formation of high concentrations of sodium sulfate and potassium sulfate, in addition to traces of lead sulfate, on the glass surface.

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1. Introduction

Lead glass has been used for the funnel tube, neck tube and stem tube in cathode-ray tubes because of its high electric insulation index and high absorption coefficient of X-rays, for the stem tube of the bulb lamp and fluorescent lamp because of its high electric insulation index, and for optical lenses and crystals due to its high refractive index.¹⁾ The physical and chemical properties of lead glass depend heavily upon the glass' composition. As one of the strengthening treatment for the surface of glass, the chemical strengthening method using sulfur dioxide gas has been developed.^{1)–4)} In this method, sodium and potassium ions, among other ions on the surface of lead glass, react with moistened sulfur dioxide gas at temperatures below 1100°C to deposit sodium sulfate and potassium sulfate, in addition to other sulfates. Consequently, silicon oxide, which has a low coefficient of expansion, becomes abundant on the surface of lead glass. Thus, to examine the improvement in the physical and chemical properties of the surface of lead glass, it is very important to determine alkali metals and lead in sulfates deposited on the surface of lead glass. The determination of sodium sulfate deposited on the surface of soda-lime silicate glass by treating the sample with water and measuring electric conductivity of the sample solution was reported.⁵⁾ However there appear to be no reports on the method of separation-determination for alkali metals and lead in sulfates deposited on the surface of lead glass.

Sodium sulfate and potassium sulfate are soluble in both water and aqueous ethanol. Lead sulfate is more or less soluble in water,⁶⁾ but only slightly soluble in aqueous ethanol solution.⁷⁾ Fortunately, lead sulfate is dissolved in sodium hydroxide solution.⁶⁾ By taking advantage of these chemical properties, we have devised a fractional dissolution method that employs the difference between the solubility of the two former sulfates, sodium sulfate and potassium sulfate, and the latter, lead sulfate. The concentrations of each sulfate ion in aqueous ethanol solution and sodium hydroxide solution ob-

tained were determined by ion chromatography (IC). From each concentration of sulfate ion, we calculated the surface concentrations of the corresponding alkali metals (sodium plus potassium) and lead.

2. Experimental

2.1 Apparatus, operating conditions and reagents

For this experiment, we employed a DX-500 (Dionex, Sunnyvale, CA, USA) IC system. The system consisted of an IonPac AG 17 (Dionex) guard column, an IonPac AS 17 (Dionex) separator column, an anion self-regenerating suppressor ASRS (Dionex), a conductivity detector (CD-20), a chromatography enclosure (LC-20), and an eluent organizer (EO-1). The ASRS was used with a scavenger, 12.5 mM sulfuric acid, acting as a chemical suppressor to obtain a more stable baseline. The IC operating conditions are summarized in Table 1. We used glass vessels sealed with a screw cap for pretreatment using 50% (v/v) ethanol, and polypropylene vessels sealed with a screw cap for pretreatment using 20 mM sodium hydroxide. A 1000 µg ml⁻¹ sulfate ion stock standard solution (Kanto Chemical, Tokyo) was used as stock solution and diluted as desired. In addition, we prepared 15 mM and 20 mM sodium hydroxide solutions by diluting 50% sodium hydroxide (Fisher Scientific, Fair Lawn, USA). Ninety seven

Table 1. IC Operating Conditions

Column	IonPac AG17 (4 mm i.d. × 50 mm) and AS17 (4 mm i.d. × 250 mm, Dionex)
Eluent	15 mM NaOH
Flow rate	1.50 ml min ⁻¹
Column temperature	30°C
Injection volume	100 µl
Scavenger	12.5 mM H ₂ SO ₄
Detection	Conductivity
Determination	Peak area method

percents sulfuric acid, ethanol of analytical reagent grade (Nacalai Tesque, Kyoto) and deionized water obtained from a Millipore-Q SP water purification system were used.

2.2 Samples

We used synthetic samples containing sodium sulfate, potassium sulfate, and lead sulfate, and lead glass samples with 7.5% (w/w) sodium oxide, 4.5% (w/w) potassium oxide, 28.0% (w/w) lead monoxide, and 59.0% (w/w) silicon dioxide. Funnel-shaped lead glass samples with a total surface area of 16.8 cm² were prepared by treating lead glass tubes at temperatures below 1100°C with a chemical flame (natural fuel gas-air-oxygen doped with approximately 1% (v/v) sulfur dioxide). On the surface of each lead glass sample, lead metal was precipitated as a metallic black mirror by reduction melting.

2.3 Procedure

Fifty milliliters of 50% (v/v) ethanol was added to five lead glass samples placed in a glass vessel. After sealing the vessel, it was kept at 60°C in a water bath for 4 h, and occasionally shaken. After cooling, the content was filtered through No.5C filter paper (Advantec Toyo). We then used the filtrate for determination of sulfate ion from sodium sulfate and potassium sulfate using the IC system.

Next, five lead glass samples treated with 50% (v/v) ethanol and the filter paper were washed five times with 10 ml of 50% (v/v) ethanol. These lead glass samples washed with 50% (v/v) ethanol and lead sulfate were transferred to a polypropylene vessel with the filter. We added 50 ml of 20 mM sodium hydroxide to the vessel, and heated the mixture in the same manner as described above and cooled. We then used the mixture for determination of sulfate ion from lead sulfate using the IC system.

Each lead glass sample solution was filtered through a 0.20-μm membrane filter, which was washed twice with each sample solution before use. Each blank solution was also prepared by performing the same procedure without any sample. Each sample solution and each blank solution was injected into the IC system. The retention time obtained for sulfate was approximately 5.5 min. We then calculated the concentrations of the corresponding alkali metals and lead from each sulfate concentration.

3. Results and discussion

3.1 Selection of analyte ion

The purpose of this work is to analyze sodium, potassium and lead, which are typical elements on the surface of the lead glass samples. The use of the direct method by which sodium, potassium and lead ions are measured results in a positive error in determining the concentration of lead, because not only lead sulfate⁶⁾ deposited on the surface of lead glass samples but also lead (i.e., metal and monoxide) in the lead glass samples is dissolved by treatment with 20 mM sodium hydroxide. Thus, we employed the indirect method by which the concentrations of sulfate in 50% (v/v) ethanol and 20 mM sodium hydroxide are measured. In the indirect method, the total amounts of sodium and potassium are calculated without the analytical value for each because of the above-mentioned pretreatment.

3.2 Effect of concentration of sodium hydroxide on dissolution of lead sulfate

As mentioned above, lead sulfate is more or less soluble in water and soluble in an alkali solution.⁷⁾ Thus, in this work, we investigated the suitability of a sodium hydroxide aqueous solution for dissolving lead sulfate. We treated 10 mg of lead sulfate with 100 ml of sodium hydroxide solution at concen-

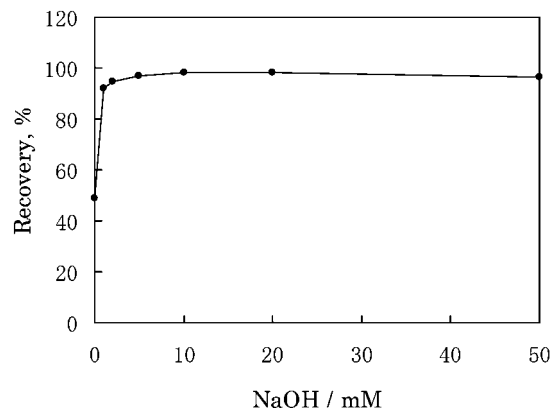


Fig. 1. Effect of sodium hydroxide concentration on dissolution of lead sulfate. PbSO₄: 10 mg; NaOH: 100 ml; heating: 60°C, 4h; sample dilution factor before measurement: 10.

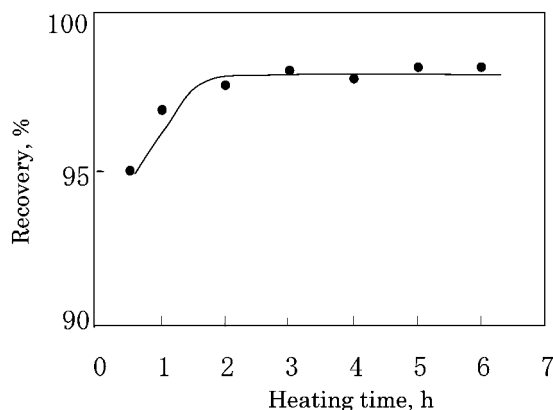


Fig. 2. Effect of heating time on recovery of lead sulfate. PbSO₄: 10 mg; 20 mM NaOH: 100 ml; heating: 60°C; sample dilution factor before measurement: 10.

trations ranging from 0 to 50 mM in a stepwise manner. Dissolution was carried out at 60°C in a water bath for 4 h, and the recovery percentage of lead was obtained by measuring sulfate concentration. The results are shown in Fig. 1. In the case of using water, we only recorded a low lead recovery percentage of approximately 50%. However, in the use of sodium hydroxide at concentrations higher than 2 mM, the lead recovery percentage sharply increased, exceeding 95%. We were able to attain a constant recovery percentage for lead using sodium hydroxide of more than 5 mM.

3.3 Effect of heating time on lead sulfate recovery

Ten milligrams of lead sulfate was treated with 100 ml of 20 mM sodium hydroxide at concentrations ranging from 0.5 to 6 h in a stepwise manner. The dissolution was carried out at 60°C in a water bath. Recovery percentage was obtained from the analytical concentration of sulfate, and the results are shown in Fig. 2. Recovery percentages of lead reached approximately 98% by heating the solution for longer than 2 h.

3.4 Suppression of lead sulfate dissolution

When sodium sulfate, potassium sulfate and lead sulfate are treated with water at 60°C for 4 h, the former two compounds dissolved perfectly, while the latter may be more or less dissolved. To chemically separate the latter from the former two, it is necessary that the latter be insoluble. Ethanol has been used for suppressing dissolution of lead sulfate in the gravimetry.⁷⁾ Thus, in this work the addition of ethanol was exa-

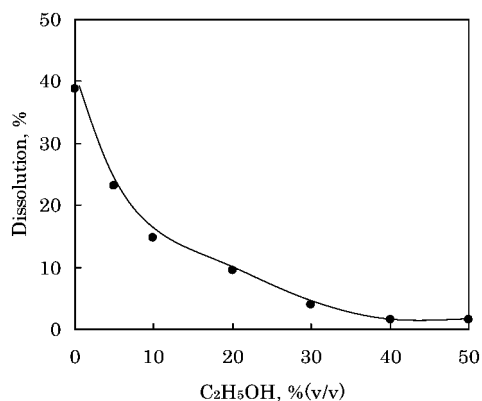


Fig. 3. Suppression of dissolution of lead sulfate in aqueous ethanol. PbSO₄: 10 mg; 20 mM NaOH: 100 ml; heating: 60°C, 4 h; sample dilution factor before measurement: 10.

Table 2. Analytical Results for Synthetic Samples

Sample	Na added/ mg	mmol	K added/ mg	mmol	Pb added/ mg	mmol	[SO ₄ ·bound] (Na+K)found/ mg	mmol
A	3.26	0.142	4.61	0.118	7.40	0.0357	12.3	0.128
B	3.66	0.159	4.79	0.122	8.20	0.0396	13.5	0.140
C	3.50	0.152	4.32	0.110	8.13	0.0393	12.5	0.130

Sample	[SO ₄ ·bound] Pb found/ mg	mmol	(Na+K) found/ mmol	Pb found/ mmol	Recovery, % (Na+K)	Pb
A	3.37	0.0351	0.257	0.0351	98.8	98.3
B	3.72	0.0387	0.280	0.0387	99.6	97.7
C	3.70	0.0385	0.260	0.0385	99.2	98.0

Sample dilution factor before measurement: 10

mined. We dissolved 10 mg of lead sulfate in 100 ml of the aqueous ethanol solution at concentrations ranging from 0 to 50% (v/v) in a stepwise manner. The dissolution in the water bath was carried out in the same way as mentioned above. We obtained the dissolution percentage for lead sulfate from the analytical concentration of sulfate, and the results are shown in Fig. 3. Using water, we obtained a high dissolution percentage of approximately 40%, although the higher the increase in ethanol concentration, the higher the decrease in the dissolution percentage of lead sulfate. A constant dissolution percentage for lead sulfate, approximately 2%, was obtained using ethanol of more than 40% (v/v).

3.5 Calibration curve and detection limit

The calibration curve obtained from the peak areas of sulfate at concentrations ranging from 0.25 to 2.0 $\mu\text{g ml}^{-1}$ was linear, with a high correlation coefficient (r) of more than 0.999 and good relative standard deviations (RSD) of 0.28% for 5% (v/v) ethanol and 0.46% for 20 mM sodium hydroxide; namely, those of alkali metals (sodium plus potassium) and lead were the same as above. The detection limits from the peak area ($S/N=3$) were 2 $\mu\text{g l}^{-1}$ for sulfate, 1 $\mu\text{g l}^{-1}$ for alkali metals and approximately 4 $\mu\text{g l}^{-1}$ for lead.

3.6 Analysis of synthetic samples

We prepared two synthetic samples containing various concentrations of sodium sulfate, potassium sulfate and lead sulfate, and their analytical results are shown in Table 2. Quantitative recovery percentages were obtained for alkali metals and lead. These results suggest that the proposed method is suitable for the fractional determination of alkali metals and lead in samples containing sodium sulfate, potassium sulfate and lead sulfate.

3.7 Application to lead glass samples

We prepared two types of lead glass sample: those with sul-

Table 3. Analytical Results for Alkali Metals (Sodium Plus Potassium) and Lead on Surface of Lead Glass Samples without Sulfur Dioxide Treatment

Sample	[SO ₄ ·bound] (Na + K)/ μg	nmolcm ⁻²	[SO ₄ ·bound] Pb/ μg	nmolcm ⁻²
D	15	1.8	<0.5	<0.06
E	15	1.8	<0.5	<0.06
F	15	1.8	<0.5	<0.06

Sample	[(Na + K)·bound] SO ₄ / nmolcm ⁻²	[Pb·bound] SO ₄ / nmolcm ⁻²
D	3.7	<0.06
E	3.7	<0.06
F	3.7	<0.06

The surface area of each lead glass sample was 16.8 cm². Five samples were used.

Table 4. Analytical Results for Alkali Metals (Sodium Plus Potassium) and Lead on Surface of Lead Glass Samples with Sulfur Dioxide Treatment

Sample	[SO ₄ ·bound] (Na + K) μg	nmolcm ⁻²	[SO ₄ ·bound] Pb μg	nmolcm ⁻²
G	300	37	1.8	0.22
H	302	37	1.8	0.22
I	335	42	1.8	0.22

Sample	[(Na + K)·bound] SO ₄ nmolcm ⁻²	[Pb·bound] SO ₄ nmolcm ⁻²
G	74	0.22
H	74	0.22
I	84	0.22

The surface area of each lead glass sample was 16.8 cm². Five samples were used.

fur dioxide treatment and those without sulfur dioxide treatment at temperatures below 1100°C. The analytical results of the samples are shown in Tables 3 and 4, respectively. We have ensured that treating the glass with sulfur dioxide results in the formation of higher concentrations of sodium sulfate and potassium sulfate, in addition to traces of lead sulfate, on the glass surface. Analytical results for samples G, H, and I for the heating time of 3 h in 20 mM sodium hydroxide were almost the same as those for the samples for the heating time of 4 h, although these results are not shown in Table 4.

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