Isotachophoretic determination of the cationic constituents in mixtures of raw materials for glass manufacturing

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Note

Isotachophoretic determination of the cationic constituents in mixtures of raw materials for glass manufacturing

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Glasses generally contain alkali, alkaline earth and other metal oxides. Especially glasses for television applications are quite complex and may consist of up to ten or more constituents^{1,2}. Such glasses are produced by melting a mixture of raw materials in a furnace in a continuous process. The raw materials are of mineral origin, such as quartz sand, feldspar and dolomite, and also of chemical origin, such as potassium carbonate and sodium carbonate. The mixture is produced in batches of *ca.* 1000 kg. The average composition and homogeneity of each batch is of vital importance for the resulting glass quality^{3,4}. Therefore, methods are required for the analysis of such mixtures with a precision of 1%.

A variety of analytical methods have been applied for the determination of alkali and alkaline earth metals and aluminium, *e.g.*, atomic absorption, ion-selective electrodes, X-ray fluorescence spectrometry and ion-exchange chromatography. This paper describes a preliminary investigation into the applicability of isotachophoresis for the analysis of a mixture of raw materials, with special emphasis on the determination of sodium, potassium, magnesium, calcium, barium and aluminium. Isotachophoresis has been applied to the determination of alkali and alkaline earth metals^{5–9}. Because of the small differences in mobility of the metal ions, complex-forming agents have been used for the separation of alkaline earth metals^{6,7}. CyDTA (1,2-cyclohexanediamine-N,N,N',N'-tetraacetate) was used as a co-counter ion for the separation of sodium, magnesium, calcium, strontium and barium in the range pH 4–6. Fukushi and Hiroyoshi used EDTA complexes of alkaline earth metals, which could be separated as anions for the determination of magnesium, calcium^{8,9} and strontium¹⁰ in sea-water. For the separation of alkali and alkaline earth metals, moreover, uncharged neutral ligands, like 18-crown-6 ether, have been described^{7,11,12}. In this feasibility study the simultaneous determination of sodium, potassium, magnesium, calcium, barium and aluminium with acceptable precision (1–2%) was investigated.

EXPERIMENTAL

Equipment

The analyses were performed in isotachophoretic equipment developed and built by Everaerts *et al.*¹³. The separation compartment consisted of a PTFE tube (ca. 250 mm × 0.45 mm I.D.). As (universal) detector an a.c. conductivity detector was used. The zone lengths were determined by a computer in order to achieve an high accuracy. Therefore, the analogue signal was digitized by an analog-to-digital converter (ADC; A-Micro Computer Ltd., Warrington, U.K.) with an accuracy of 12 bit. The digitized signals were stored in the memory of an Apple IIe microcomputer and on a floppy disc after each experiment. The zone lengths were determined on screen after digital differentiation by a Savitzky-Golay digital filter¹⁴. The filtering procedures were performed by a machine language routine.

The electrolyte system (Table I) used is a modification of that used for the determination of heavy metals. In this system, sodium, magnesium, calcium, barium¹⁵ and aluminium¹⁶ could be separated. Using potassium as the leading ion, the amount of potassium in a sample may be determined only by measuring the extension time of appearance of the first zone. In order to achieve high reproducibility of the potassium determination by this method, careful operation of the equipment is required. Therefore, in the present investigation, caesium was used as the leading ion in order to ensure reproducible determination of potassium. The difference in effective electrophoretic mobilities between caesium and potassium is low, however. At high concentration levels of potassium easily mixed zones of potassium and caesium can be formed, which result in too low a quantitation.

Therefore, crown ethers were used to alter the effective electrophoretic mobility of potassium. The effective ionic diameter and the crown ether chosen determine the effective mobilities of the cations. The various complexing constants of the cations under investigation are given in Table II.

The operational conditions were optimized with respect to the pH, ionic strength, the concentrations of the complexation agents α -hydroxyisobutyric acid (α -HIBA) and 18-crown-6 for the separation of the metals under investigation.

TABLE I

OPERATIONAL CONDITIONS FOR THE SIMULTANEOUS DETERMINATION OF POTASSIUM, SODIUM, MAGNESIUM, CALCIUM, BARIUM AND ALUMINIUM BY ISOTACHOPHORESIS

<i>Parameter</i>	<i>Leading electrolyte</i>	<i>Terminator electrolyte</i>
Cation	Cs ⁺	H ⁺
Concentration (<i>M</i>)	0.025	ca. 0.005
pH	4.4-4.5	—
Counter ion	Acetate*	Acetate
Complexation agents	0.0225 <i>M</i> α HIBA 18-crown-6 ether*	

* For further information see text.

TABLE II

STABILITY CONSTANTS, K , OF CATION-(18-CROWN-6) ETHER COMPLEXES

Ring size of 18-crown-6 ether: 0.26–0.32 nm.

Cation	log K		Ionic diameter (nm)
	Ref. 17	Ref. 18	
Na ⁺	0.82	0.8	0.190 ¹⁷
K ⁺	2.05	2.03	0.270 ¹⁷
Cs ⁺	0.98	0.99	0.330 ¹⁷
Ca ²⁺	0.48	<0.5	0.210 ¹⁷
Ba ²⁺	—	3.87	0.280 ¹⁷
Sr ²⁺	—	2.72	0.224 ¹⁹
Pb ²⁺	—	4.72	0.240 ¹⁹
Al ³⁺	—	—	0.102 ¹⁹
Mg ²⁺	—	—	0.132 ¹⁹

A leading ion concentration of 0.025 M was necessary to achieve a sufficient ionic strength. The complexation agent α -HIBA was adjusted to a concentration of 0.0225 M .

In order to investigate the effect of the 18-crown-6 ether on the effective mobility step height, the crown ether was added in varying amounts from 0 to 30 mM. A solution of 20% aqueous acetic acid was added until a pH in the range of 4.4–4.5 was reached.

Calibration lines were made by using 1000 ppm standard solutions of the metals dissolved in 1 M nitric acid as commonly used for atomic absorption (BDH, Poole, U.K.). Because of the low pH and high conductivity, the standard solutions were evaporated to dryness in a Speed Vac concentrator/evaporator (Savant, Farmingdale, NY, U.S.A.). The nitric acid was totally removed and the pressurized recoveries of the metals by this the method were $100.0 \pm 0.1\%$. The dried samples were dissolved in 5 mM acetic acid prior to the isotachophoretic analysis.

Mixtures of the metals were prepared in the expected composition range for mixtures of raw materials. The solutions of the metals under investigation were injected with a 10- μ l Hamilton micro syringe (Hamilton, Bonaduz, Switzerland).

For isotachophoretic determination, it is necessary that the metal ions in a mixture of raw materials are dissolved in an aqueous solution. Therefore, the matrix components were totally decomposed using hydrofluoric acid and silicon tetrafluoride formed was evaporated. The pretreatment procedure consisted of two stages. First the components soluble in acetic acid were dissolved in 2 M acetic acid and evaporated to dryness. The non-soluble residues were dissolved in hydrofluoric acid and evaporated to dryness.

RESULTS AND DISCUSSION

In Fig. 1 the step heights of potassium, sodium, calcium, magnesium, barium and aluminium relative to magnesium are plotted *versus* the 18-crown-6 concentration in the leading electrolyte. Similar results were found by Tazaki *et al.*⁷, with H⁺

Fig. 1. Step heights (RSHs) of sodium (O), potassium (Δ), magnesium ($\blacktriangle$), calcium (+), barium (+) and aluminium ($\bullet$) relative to magnesium as a function of the 18-crown-6 ether concentration in the leading electrolyte as listed in Table 1.

as the leading ion and *p*-toluic acid as the counter constituent. The increase in the potassium step height is almost linear with the 18-crown-6 concentration. The barium step height shows a large increase at low 18-crown-6 concentrations and reaches a

Fig. 2. Isotachopheric analysis of a standard mixture of sodium, potassium, magnesium, calcium, barium and aluminium. R = Increasing resistance; t = time.

TABLE III
PARAMETERS OF THE CALIBRATION LINES

N = Number of measurement points.

Cation	N	Slope (s/nmol)	Intercept (s)	Correlation coefficient	Range (nmol)
Potassium	10	1.43	0.4	0.9999	5–12
Sodium	12	1.61	0.05	0.9999	12–30
Calcium	12	3.03	0.59	0.9998	1–6
Magnesium	12	3.18	0.28	0.9999	1–7
Barium	12	3.68	0.36	0.9995	3–9
Aluminium	12	3.64	–1.8	0.997	1–7

plateau above 5 mM 18-crown-6. The influence on the step height of sodium, calcium, magnesium and aluminium is small.

To achieve a complete separation of the cations, a concentration of 3.75 mM 18-crown-6 in the leading electrolyte was chosen. Fig. 2 shows the analysis of a standard mixture of the metals under investigation. Higher concentrations of 18-crown-6 resulted in a mixed zone of potassium with one of the other components described, and lower concentrations resulted in a mixed zone with the leading ion. In the operational system with 3.75 mM 18-crown-6 ether, strontium and magnesium migrate with equal effective mobilities. Strontium is present in the barium raw material as an impurity of about 1%. The effect on the determination of the magnesium zone length is low compared to the required precision.

The parameters of the calibration lines as determined by the least-squares linear regression method are listed in Table III. Fig. 3 shows the calibration lines for

Fig. 3. Calibration lines for sodium, potassium, calcium and barium.

TABLE IV

RESULTS OF THE QUANTITATIVE ANALYSIS OF A MIXTURE OF RAW MATERIALS OF KNOWN COMPOSITION (A) AND THE AMOUNT DETERMINED (B) IN WEIGHT PERCENTAGE OF THE SAMPLE

Compound	% (w/w)		
	A	B	A - B
Al ₂ O ₃	2.6	2.0	0.6
Na ₂ O	8.7	8.7	0.0
K ₂ O	6.0	5.9	0.1
MgO	0.33	0.32	0.01
CaO	0.28	0.25	0.03
BaO	10.8	10.9	-0.1

sodium, potassium, calcium and barium. Except for aluminium, the linear regression revealed an high correlation between the amount sampled and the zone length detected. The lower reproducibility of the aluminium zone length suggests critical sampling conditions. For instance, experiments showed that attention has to be paid to the pH of both the sample and the terminating electrolyte. The use of other terminating electrolytes, ϵ -aminocaproic acid, γ -aminobutyric acid, α -alanine and tris(hydroxymethyl)aminomethane, did not improve the separation of aluminium.

In order to investigate the applicability of the isotachophoretic determination of the cationic constituents, a mixture of raw materials of known composition was analyzed (Fig. 4). The sample was dissolved and pretreated by the method described. In Table IV the results of the quantitative analysis are listed. Although the concen-

Fig. 4. Isotachopherogram of a mixture of raw materials for glass manufacturing. The sample pretreatment is described in the text. The analysis was performed under the conditions listed in Table I.

trations of magnesium and calcium in the sample were below the concentration range under investigation, the recoveries of those metals are acceptable. The recoveries of sodium, potassium and barium are nearly 100% with a precision smaller than 1%. The recovery of aluminium is unacceptable and further investigation is necessary.

CONCLUSIONS

The feasibility study shows that the isotachophoretic procedure described is suitable for the determination of sodium, potassium, magnesium, calcium and barium in mixtures of raw materials for glass manufacturing. A precision of 1% seems attainable. The low reproducibility of the aluminium zone length suggests critical sampling conditions. The sample pretreatment procedure with respect to the optimization of recovery of the metals from the samples and the determination of lead and strontium are under investigation.

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