

Use of isotachophoresis as a reference method for the simultaneous determination of barium and strontium

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ABSTRACT

When using X-ray fluorescence spectrometry for the determination of alkali and alkaline earth metals in a silica matrix, frequent recalibration with reference samples is necessary. Determination of metals in these reference samples is carried out using classical analysis. The latter was not possible with barium and strontium in the presence of each other owing to mutual interference. Isotachophoresis, using a 0.02 mol/l potassium-citrate leading electrolyte of pH 5.0 and magnesium chloride as a terminator proved suitable. At concentration ratios in the range 1:10 to 10:1 the accuracy and precision were well within the 1% requirement.

INTRODUCTION

Routine methods require reference samples as analytical standards, the purpose being calibration, taking into account possible sample matrix effects. The average composition of glass consists of, in addition to SiO₂, oxides K₂O, MgO, CaO, TiO₂, Fe₂O₃, Sb₂O₃, CeO₂, ZrO₂, Al₂O₃, Na₂O, SrO, BaO. For X-ray fluorescence spectrometry which is a rapid routine method for the simultaneous determination of glass components, the silica matrix requires recalibration with reference samples including this matrix. The composition of the reference sample should be known with an accuracy and precision exceeding that obtained by the routine method.

Classical analysis, *e.g.*, titration, is often used. However, barium and strontium have almost identical physical and chemical properties and hence mutual interference occurs in most commonly used determinations. The use of a separation technique prior to determination is therefore essential.

With capillary isotachophoresis, separation and determination can be combined. Isotachophoresis has been used previously for the determination of cations in glass-related samples [1]. Complex-forming agents such as crown ethers, hydroxyiso-

butyric acid (HIBA) and polyethylene glycol (PEG) are necessary to improve the separation of alkali and alkaline earth metals when analysed in one run [2–7]. HIBA is a mild complexing agent, also used for the separation of lanthanides [8]. In the system mentioned [1], separation is not optimized for alkaline earth metals and strontium will still interfere in the determination of calcium, magnesium and barium. In this study, attention was focused on the separation of barium and strontium, a highly selective operational system being sought for these two species.

EXPERIMENTAL

Equipment

Analyses were performed with laboratory-made equipment described previously [9]. The separation compartment was a PTFE capillary (200 mm × 0.2 mm I.D.). An a.c. conductivity detector was used. The constant driving current was ca. 50 μA during separation and 25.0 μA during detection. The conductivity signal and its differential were recorded on a potentiometric flat-bed recorder with a paper speed of 2 mm/s. The time of analysis was up to 20 min. The samples were injected with a Type 701 10- μl syringe (Hamilton, Bonaduz, Switzerland), equipped with a Chaney fixed-volume adaptor, adjusted to 1 μl . The sample was introduced 2 mm below the leading/terminating electrolyte boundary to ensure complete recovery of strontium.

Operational system

In earlier work [10] we investigated the decrease in the effective mobility of alkaline earth metals by citric acid as a co-counter ion at pH 5.0. The results showed that eventually the alkaline earth metal ions have a mobility lower than that of sodium. This is necessary for a good separation, because the mobility interval between sodium and potassium is not sufficient. A citrate concentration exceeding 0.001 mol/l is necessary. A leading electrolyte concentration of 0.02 mol/l potassium was chosen for two reasons: at increasing ionic strength the absolute mobilities of bivalent ions decrease more than those of monovalent ions, and a higher citrate concentrations at pH 5.0 is possible.

The leading electrolyte was prepared by dissolving analytical-reagent grade potassium hydrogencarbonate in water. This was preferred to potassium hydroxide because of the lower sodium content. Citric acid addition was calculated by weight. It should be noted that the order of mobility of the alkaline earth metal ions was reversed with respect to that with HIBA complexation [1]. This follows directly from the corresponding complex stability constants, found in the literature [11]. Therefore, magnesium could be used as a terminator, using 0.01 mol/l magnesium chloride solution. The effective mobilities of barium, strontium and magnesium were $30 \cdot 10^{-9}$, $27 \cdot 10^{-9}$ and $23 \cdot 10^{-9}$ $\text{m}^2/\text{V} \cdot \text{s}$, respectively. These 10% differences ensure adequate separation capability. Of the ions present in solution after pretreatment of the glass samples, only sodium, barium and strontium migrate within the leading-terminator mobility interval (Fig. 1).

Sample pretreatment

Approximately 1 g of solid glass sample was dissolved in 25 ml concentrated hydrofluoric acid–perchloric acid (1:1), the solution was evaporated to dryness, the

residue was dissolved in 40 ml of 6 mol/l hydrochloric acid and the mixture was evaporated to dryness. The latter procedure was repeated twice with 10 ml of 99% acetic acid instead of 40 ml 6 M hydrochloric acid. The residue was dissolved in deionized water with heating. After cooling to room temperature, the solution was filtered and transferred into a 200-ml volumetric flask, diluted to volume with deionized water and transferred into a polyethene container. The pH was measured. The filter-paper with the solid residue was ashed in a platinum crucible and checked for the absence of barium and strontium by energy-dispersive X-ray analysis.

Internal standard

A solution of 200 μ l of triethylamine (Fluka) in 500 ml of deionized water (*ca.* 2.8 mmol/l) was used as an internal standard (I.S.). The pH of this solution was 8–9, resulting in partial neutralization of the acidic samples. The sample and I.S. were mixed in equal volumes, using a 1000- μ l pipette with disposable tips. An analytical balance with a resolution of 0.1 mg was used to check the I.S. to sample ratio on a mass basis. The zone-length ratio measured on the isotachopherogram was multiplied by this mass ratio to correct for minor fluctuations in the use of the pipette. Owing to the extensive sample pretreatment, fluctuations in sample density were sufficiently small to allow this procedure.

Syringe-rinsing procedure

A syringe-rinsing procedure was developed to eliminate cross-contamination from subsequent injections. After sample injection, the syringe was rinsed successively in water, a tracer solution, water and the next sample solution. Each rinsing consisted of a fixed number of plunger displacements in the corresponding solution. The tracer solution consisted of 30 μ l of *n*-butylamine in 50 ml of deionized water (*ca.* 6 mmol/l). The idea was that if no zone occurs at the *n*-butylamine step height (between sodium and I.S.), cross-contamination with the previously injected sample can be excluded. If an additional zone is present, the results of the analysis are not valid.

Calibration

Barium and strontium standards were prepared from standard solutions of 1000 ppm (Baker) and were used for calibration. Using calibrated precision glassware, a number of standard solutions were made containing both elements at concentrations of *ca.* 0, 1, 2, 3 and 5 mg/ml. These standards were subsequently kept in plastic containers.

RESULTS AND DISCUSSION

Calibration graphs were constructed by analysing each of the standards twice. A difference of 1% between the duplicate results was considered acceptable, otherwise the analysis was repeated until good duplicate results were obtained. The Ba/I.S. and Sr/I.S. zone length ratios were multiplied by the I.S./samples volume ratio and plotted against the concentration of the corresponding element. The resulting calibration graphs (see Fig. 2) have been a correlation coefficient of 0.9998 or better. Duplicate analyses of samples were also within 1%.

Over a 1-month period, a number of calibration graphs were constructed. The

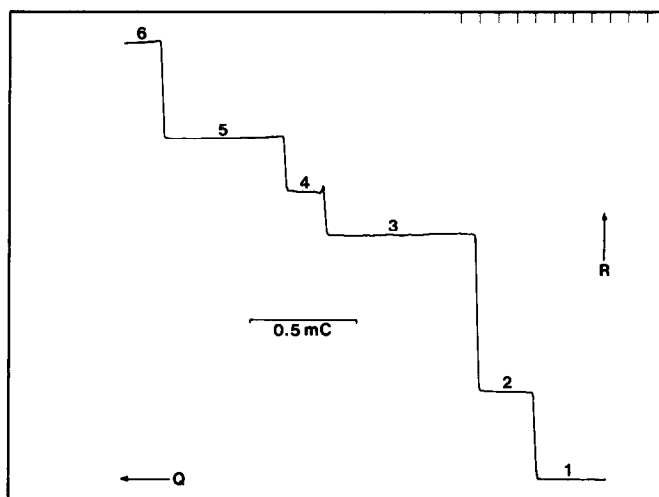


Fig. 1. Isotachopherogram of a typical glass sample. Resistance R is plotted against charge Q , the product of current and time. 1 = Potassium; 2 = sodium; 3 = triethylamine as I.S.; 4 = barium; 5 = strontium; 6 = magnesium. See text for operational conditions.

intercept of the calibration graphs was sufficiently small not to introduce an additional systematic error. The front of the barium zone shows a distinct detector overshoot, possibly owing to electrode reactions with the counter ion. This overshoot should be included in the zone length of barium because it does not originate from an additional component. The slopes of the calibration graphs show a day-to-day variation of 3 and 2% for barium and strontium, respectively, which means that daily recalibration is necessary.

Precision was determined by analysing a sample fourteen times. This included dilution with the internal standard, injection, analysis and zone length measurement. The relative standard deviations of the calculated concentration were 0.8 and 0.7% for barium and strontium, respectively. Accuracy was determined by analysing dried

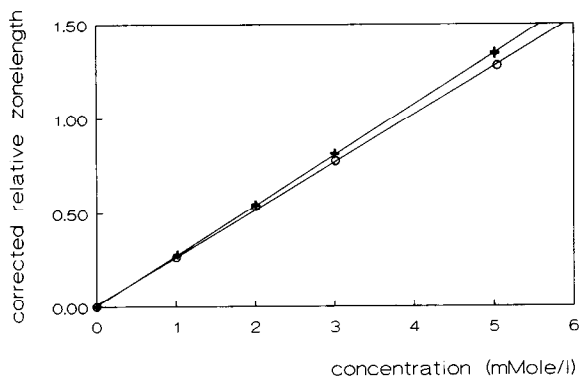


Fig. 2. Calibration graphs for (O) barium and (+) strontium. Correlation = 0.9998 and 0.9999, respectively ($n = 10$).

barium and strontium carbonates of super-pure quality. The result was 99.9% with a standard deviation of 0.2%.

The syringe-rinsing method was found useful and is recommended for precision analysis with any separation technique using syringe injection. An obvious requirement is that the tracer is not present in any of the samples. The sensitivity of the method can be changed by means of the tracer concentration.

It is concluded that isotachopheresis can be used as a reference method for glass standards containing both barium and strontium in the usual silica matrix. Provided that barium and strontium are not lost through precipitation in the sample pretreatment (this has been verified), it can be used to label reference samples for X-ray fluorescence spectrometry.

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