

Selective Extraction of Calcium on Tri-*n*-butyl Phosphate Plasticized Selective Extraction of Calcium on Tri-*n*-butyl Phosphate Plasticized Polyurethane Foam for Its Spectrophotometric Determination in Glass and Ceramics

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The present paper describes the application of a solid phase extraction system in order to separate traces of calcium from glass and ceramics for its spectrophotometric determination. The method is based on the extraction of calcium from sodium hydroxide solution by tri-*n*-butyl phosphate (TBP) loaded polyurethane foam (PUF), followed by its elution in hydrochloric acid. The spectrophotometric measurement of the absorbance of calcium complex with calconcarboxylic acid (2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid) takes place at pH 12. The following parameters were studied: effects of sodium hydroxide concentration and temperature on the extraction of calcium, time of equilibration for quantitative calcium extraction, effect of TBP concentration, effect of hydrochloric acid concentration for quantitative elution of calcium from PUF, effect of pH and concentration of calconcarboxylic acid for quantitative formation of the complex with calcium, effect of acetone on the stability of calcium-calconcarboxylic acid complex and influence of diverse ions on calcium sorption by TBP-loaded PUF. The results show that calcium traces can be separated onto TBP-loaded PUF from 0.25 mol l⁻¹ NaOH at 30 ± 5 °C within 30 min. PUF was loaded with TBP in CCl₄ (40% v/v). Elution of calcium was done in 1.0 mol l⁻¹ HCl. The calcium formed a complex with calconcarboxylic acid at pH 12 and absorbance was measured at 560 nm in acetone-water medium. Molar absorptivity was found to be 1.082 × 10⁴ l mol⁻¹ cm⁻¹. The method obeys Beer's law from 0.10 to 5.0 µg ml⁻¹ Ca. The validity of the method was established by its successful application in NIST standard reference materials. The method proposed was applied to determine calcium in glass and ceramic materials. The results of the proposed method are comparable with the results of ICP-AES analysis and they are found to be in good agreement.

(Received January 20, 2005; Accepted May 23, 2005)

Introduction

Traces of calcium are usually present in different glass and ceramic materials. Determination of calcium in such special glasses and ceramics is essential for their characterization, evaluation and quality control. Several methods have been reported for the determination of calcium. The use of flame emission photometry is complicated due to anionic suppression of calcium by sulfate, phosphate and aluminate.¹ Atomic absorption spectrometry is ineffective due to interfering effects of aluminium and silicon.² Some spectrophotometric methods³⁻⁶ have been reported for the determination of minor amounts or traces of calcium in various materials. But most of them suffer from matrix interference. Hence, selective extraction of calcium traces followed by its determination has been of considerable importance.

Polyurethane foam (PUF) has been used as a sorbent to preconcentrate and separate a wide variety of inorganic and organic compounds from different media by conventional methods. It was first proposed by Bowen⁷ in 1970. Braun⁸⁻¹¹ and Palagyi¹² published some reviews about the use of PUF in

separation and preconcentration procedures applied to several systems of analytical interest. PUF can be used without pretreatment¹³⁻¹⁷ and also after reagent immobilization or plasticizing.¹⁸⁻²³ Braun and Farag suggested the loading of PUF membranes with tri-*n*-butyl phosphate (TBP) and described the analytical use of TBP-foam membranes in batch and column operations.²⁴

The aim of this work was to demonstrate the feasibility of PUF loaded with TBP in CCl₄ for preconcentration of calcium traces from aqueous alkaline medium. After acid elution, calcium was determined spectrophotometrically prior to its complex formation with calconcarboxylic acid, a chromogenic reagent. The main advantages of this method reside in the use of TBP-loaded PUF, an efficient extractant and in the low instrumental cost available by spectrophotometric measurement. The method was validated by its successful application in NIST standard reference materials. The method showed a detection limit of 0.10 µg ml⁻¹ of calcium. The developed method can be easily applied to glass and ceramic samples.

Experimental

Apparatus

UV-visible absorbance spectra were recorded on a Shimadzu

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2100 spectrophotometer. The ICP-AES instrument used in this study was Spectroflame Modula (Spectro Analytical Instruments, Germany). Measurement of pH was done with an Orion 920A pH meter.

Reagents

All the chemicals used were of analytical reagent grade. Doubly distilled water was used throughout this experiment. A stock calcium solution ($1000 \mu\text{g ml}^{-1}$, ICP standard solution, Merck, Germany), was used. Working standard solutions were prepared by suitable dilution of this stock solution. Sodium hydroxide, tri-*n*-butyl phosphate, carbon tetrachloride, hydrofluoric acid, hydrochloric acid and perchloric acid were of Suprapur (Merck) quality. Calconcarboxylic acid solution (0.2% m/v) was prepared in water.

TBP-loaded PUF was prepared from polyether-based polyurethane foam. PUF (cylinder ~ 0.5 cm diameter, 2 cm height and average weight 10 mg/chip) was washed with 3 mol l^{-1} hydrochloric acid in a batch extractor followed by washing with water and acetone and dried in air. Dried foam chips were equilibrated with TBP in CCl_4 (40% v/v) with sufficient stirring and allowed to stand for 24 h to ensure complete saturation. Loaded foam chips were then dried by pressing with filter paper to remove excess solvent.

Procedures

General procedure for the determination of calcium. An aliquot of sample solution was transferred into a 100 ml polyethylen beaker. The solution was neutralized with 0.5 mol l^{-1} NaOH solution and diluted to 40 ml while maintaining the desired NaOH concentration. TBP-loaded PUF chips were added to the solution and the mixture was squeezed thoroughly with a plastic plunger (10 – 15 strokes at a time at 10 min intervals). The solution was equilibrated with foam chips for 1 h at $25 - 30^\circ\text{C}$. The foam chips were then removed from the solution, transferred to a plastic 5 ml disposable syringe, squeezed to remove the solution held in the foam and washed 3 times with 0.25 mol l^{-1} NaOH solution. The sorbed calcium was eluted from CCl_4 -TBP-plasticized polyurethane foam by repeated washing (5 times) with 2 ml portions of 1 mol l^{-1} hydrochloric acid into a 50 ml glass beaker. The eluted solution was evaporated nearly to dryness, dissolved in water and transferred to a 25 ml plastic volumetric flask. A 2-ml volume of acetone and 1 ml of 5 mol l^{-1} NaOH were added to the flask to raise its pH to 12; the desired amount of calconcarboxylic acid solution was added to it and the volume was made up with water. The absorbance was measured at 560 nm against reagent blank. The amount of calcium present in the sample solution was determined from a calibrated plot.

Procedure for the determination of calcium in glass. About 0.1 g of glass sample was taken in a PTFE basin and digested with 0.5 ml of perchloric acid and 5 ml of hydrofluoric acid. The digested mass was evaporated until it was nearly dry and then it was extracted in 0.5 mol l^{-1} hydrochloric acid. The solution was transferred into a 50 ml volumetric flask and the volume was completed with distilled water. The calcium content of this solution was determined according to the general procedure.

Determination of calcium in ceramic sample. About 0.1 g of sample was taken in a platinum crucible and fused with 0.5 g of sodium carbonate until the melt was clear. The molten mass was cooled and then dissolved in 0.5 mol l^{-1} hydrochloric acid. Finally, the solution was transferred to a 50 ml volumetric flask and the volume was made up with distilled water. A suitable aliquot of the stock solution was pipetted out for calcium determination by following the general procedure.

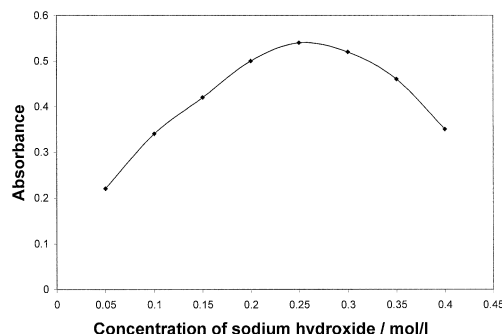


Fig. 1 Effect of sodium hydroxide concentration on the extraction: calcium, $2.0 \mu\text{g ml}^{-1}$; P & R, $1.36 \times 10^{-6} \text{ g ml}^{-1}$.

Results and Discussion

A series of investigations were conducted to optimize different parameters affecting quantitative sorption of calcium on foam, its elution and the stability of the calcium complex with calconcarboxylic acid.

Effect of NaOH concentration on the extraction of calcium

The effect of sodium hydroxide concentration on the extraction of calcium on TBP-loaded foam was studied. To establish the optimum sodium hydroxide concentration, we carried out a series of experiments by taking $2 \mu\text{g ml}^{-1}$ calcium and varying the sodium hydroxide concentration from 0.05 to 0.40 mol l^{-1} . It was observed (Fig. 1) that maximum sorption of calcium occurred at 0.25 mol l^{-1} NaOH. At higher sodium hydroxide concentrations, the sorption of calcium was decreased.

Effect of temperature

The effect of temperature on the extraction of $2 \mu\text{g ml}^{-1}$ calcium in a total volume of 40 ml of 0.25 mol l^{-1} sodium hydroxide was studied by varying the temperature from 10°C to 60°C . Figure 2 shows that the rate of extraction of calcium increases with the increase of temperature and reaches its maximum at $30 \pm 5^\circ\text{C}$, above which it tends to decrease. Therefore, the extraction temperature was maintained between 25 and 35°C for further experiments.

Effect of equilibration time

The effect of equilibration time for the quantitative sorption of calcium on PUF in batch operation technique, which is one of the most important parameters, was studied. Each calcium solution was equilibrated with TBP-plasticized foam in 0.25 mol l^{-1} NaOH for a different period of time at 30°C . It was clearly indicated by the absorbance value that equilibrium was attained within 30 min.

Effect of TBP concentration

The use of TBP for loading on foam has a dual effect.^{8,12} It may act as a solvent extractant as well as a plasticizer for the foam membrane. In TBP-plasticized foam, the polymer is considered as a support for TBP and it acts as a stationary phase. Due to the hydrophobic nature of PUF together with the high available surface area, immobilization of TBP takes place. TBP does not chemically react with the polymer but becomes physically immobilized on the foam matrix and modifies it through the reduction of van der Waals forces and increases the

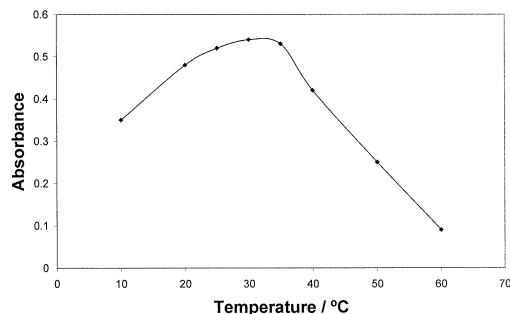


Fig. 2 Effect of temperature on the extraction: calcium, 2.0 $\mu\text{g ml}^{-1}$; sodium hydroxide, 0.25 mol l^{-1} .

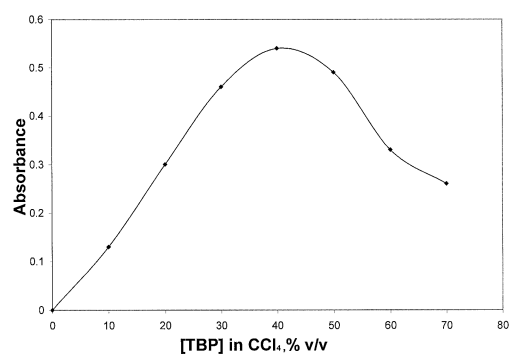


Fig. 3 Effect of TBP concentration on the extraction: calcium, 2.0 $\mu\text{g ml}^{-1}$; sodium hydroxide, 0.25 mol l^{-1} .

permeability of the foam material. Thus plasticization favorably affects the mobility of extractable species in the foam polymer and enhances the rate of sorption of the species by the immobilized solvent. Thus, retention of calcium on TBP from aqueous solution of NaOH is similar to the liquid-liquid extraction process. The extraction of calcium from 0.25 mol l^{-1} NaOH solution were performed on TBP-loaded foam having different concentrations of TBP in CCl_4 . The results (Fig. 3) indicate that calcium can best be extracted when PUF was plasticized with TBP in CCl_4 (40% v/v).

Effect of hydrochloric acid concentration for quantitative elution of calcium from PUF

Quantitative elution of the complex from the foam matrix is essential for spectrophotometric measurement of calcium. Several solutions were tested for elution of calcium from TBP-loaded foam. The results show that calcium can be effectively recovered using 1.0 mol l^{-1} hydrochloric acid.

Effect of calconcarboxylic acid concentration

In order to measure traces of calcium spectrophotometrically, calcium was complexed with calconcarboxylic acid, a chromogenic reagent. The concentration of the reagent was optimized. It has been found that a minimum concentration of $1.36 \times 10^{-6} \text{ g ml}^{-1}$ of the reagent is necessary for quantitative formation of the complex.

Effect of acetone

The effect of acetone on the stability of Ca-calconcarboxylic acid complex was studied. Initially it was found that the complex is unstable in alkaline medium and that the color concentration of the complex fades out rapidly so the complex

Table 1 Effect of diverse ions in the determination of calcium

Ion	Tolerance ratio	Ion	Tolerance ratio
Al^{3+}	1000	Zn^{2+}	1000
Mg^{2+}	1000	Zr^{4+}	1000
Fe^{2+}	1000	Mn^{2+}	1000
Fe^{3+}	1000	Ni^{2+}	1000
Ti^{4+}	1000	Co^{2+}	1000
K^+	1000	PO_4^{3-}	1000
Cu^{2+}	1000	SO_4^{2-}	1000
Cr^{3+}	1000	F^-	1000

becomes colorless. This problem was studied critically with a view to improve the stability of the complex as well as the sensitivity of the method, which was enhanced appreciably by the addition of acetone (8% v/v). The complex is stable up to 1 h in aqueous acetone medium.

Effect of pH

The formation of Ca-calconcarboxylic acid complex is selective for titrimetric determination of calcium between pH 12 to 14.²⁵ In the present study, it has been found that the characteristic wine red color of the complex is quite sensitive and stable at pH 12 in the acetone-water system.

Effect of foreign ions

The experiments were performed by extracting calcium on TBP-plasticized PUF from aqueous alkaline solution in the presence of various foreign ions that are normally present in glass and ceramic materials (Table 1). Solutions containing 2.00 μg of calcium and different amounts of several cations were prepared and the efficiency of the separation procedure was tested. The results show that, at NaOH concentration of 0.25 mol l^{-1} , 2.00 μg of calcium can perfectly be separated from 1.00 mg of the following ions: Al^{3+} , Mg^{2+} , Fe^{3+} , Fe^{2+} , Ti^{4+} , Si^{4+} , Na^+ , K^+ , Ba^{2+} , Cu^{2+} , Cr^{3+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Zr^{4+} , Pb^{2+} , SO_4^{2-} , F^- and PO_4^{3-} .

Validity of Beer's law, molar absorptivity, Sandell's sensitivity and correlation coefficient

A calibration graph was prepared for the determination of calcium under optimum conditions, *i.e.* sodium hydroxide, 0.25 mol l^{-1} ; hydrochloric acid, 1.0 mol l^{-1} ; calconcarboxylic acid, $1.36 \times 10^{-6} \text{ g ml}^{-1}$; acetone, 8% v/v. Beer's law was obeyed in the concentration range 0.10 to 5.00 μg of calcium. The molar absorptivity at the wavelength corresponding to the maximum absorbance at 560 nm was calculated by measuring the absorbance of solutions at different concentration levels of calcium. The mean value of the molar absorptivity was found to be $1.082 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$, which indicates that the method is sensitive. Sandell sensitivity was calculated for the method and was found to be $0.0037 \mu\text{g cm}^{-2}$. The correlation coefficient of Ca-calconcarboxylic acid complex, with concentration as an independent variable and absorbance as a dependent variable, is 0.9995. This indicates an exact linearity between the two variables. Thus, calcium content in real samples was determined by using the following straight line equation:

$$Y = 0.2466X + 0.0169.$$

Application of the method

The developed extractive spectrophotometric method for calcium is applied in glass and ceramic materials. After elution

Table 2 Determination of calcium in various samples

Sample	Certified value CaO, %	Proposed method, %			ICP method, %		
		CaO, found ^a	RSD	Rec.	CaO, found	RSD	Rec.
Lead barium Glass NIST SRM 89	0.21	0.208 ± 0.002	0.96	99.05	0.209 ± 0.001	0.48	99.5
Borosilicate Glass NIST SRM 1411	2.18	2.19 ± 0.02	0.91	100.4	2.19 ± 0.01	0.46	100.4
Multicomponent Glass NIST SRM 1412	4.53	4.51 ± 0.04	0.89	99.6	4.52 ± 0.03	0.67	99.8
Burnt refractory NIST SRM 78a	0.11	0.109 ± 0.001	0.92	99.1	0.109 ± 0.001	0.92	99.1
Sillimanite BCS CRM 309	0.22	0.218 ± 0.002	0.92	99.6	0.219 ± 0.002	0.91	99.5
Silica brick BCS CRM 267	1.75	1.74 ± 0.01	0.57	99.4	1.76 ± 0.01	0.57	100.5

a. Average of five determinations.

of calcium from foam, the solutions were tested for calcium in ICP-AES and the results (Table 2) were compared with those obtained in the present spectrophotometric measurements.

Conclusion

Traces of calcium can be selectively extracted by TBP-loaded PUF and can be recovered from foam matrix very easily using hydrochloric acid. The solid solvent extraction has two typical advantages over the liquid solvent extraction: use of organic solvents which are often toxic can be avoided and the common problem of emulsions can be eliminated. Polyurethane foam is also commercially available at a low price.

Acknowledgements

The authors are thankful to Dr. H. S. Maiti, Director of the institute, for his kind permission to publish this work.

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