



# Procedure for determination of trace ions in boric acid by matrix volatilization–ion chromatography

K. Dash, D. Karunasagar\*, S. Thangavel, S.C. Chaurasia

*National Centre for Compositional Characterisation of Materials, Bhabha Atomic Research Centre, ECIL (PO),  
Hyderabad 500062, India*

Received 6 November 2002; received in revised form 18 February 2003; accepted 16 April 2003

## Abstract

A method for determination of anions and cations in boric acid is proposed by matrix volatilization. The boric acid matrix was eliminated as trimethyl borate ester in a vapour phase matrix elimination (VPME) system using a mixture of glycerol–methanol. In this VPME system, in situ reagent purification, sample decomposition and digest evaporation were achieved in a single step. Trace anions were separated on an anion-exchange column (IonPac AS17) by an isocratic elution with 15 mM sodium hydroxide and the cations on a cation-exchange column (IonPac CS12) by 20 mM hydrochloric acid as eluents. Method detection limits ( $3\sigma$ ) for most ions ranged from 0.3 to 8 ng/g (ppb). Recovery experiments combined with comparison of data obtained by other methods were employed to verify the accuracy of the proposed method. Application of the method to determine trace levels of anions like acetate, oxalate, sulfate, phosphate and cations such as lithium, sodium, potassium, magnesium and calcium in two highly pure grades of boric acid using ion chromatography is demonstrated.

© 2003 Elsevier Science B.V. All rights reserved.

**Keywords:** Vapour phase matrix volatilization; Trace analysis; Boric acid; Methanol; Cations; Anions

## 1. Introduction

Boric acid is used in the primary water systems of pressurised water reactors (PWRs) [1] and as a precursor material to produce  $B_2O_3$  [2] (used as a network former in optical wave-guide [3]) where stringent purity levels are required. When HF (hydrofluoric acid) is used for digestion of samples especially in plasma based techniques [inductively coupled plasma atomic emission spectrometry/mass spectrometry (ICP-AES/MS)] the excess acid is

complexed with boric acid. Thus boric acid should be of highest purity to reduce the process blanks.

Determination of trace anions and cations in real samples containing large excess of matrix component is a fundamental analytical problem. For determination of a wide range of anions and cations, ion chromatography (IC) [4,5] with conductivity detection is a highly suitable method. Boric acid being a weak acid, on first inspection it appears that good separation of borate from analyte (anions) peaks is obtained through suppressed IC. However, due to limited solubility (50 g/l, i.e., 1 g/20 ml) of matrix at ambient temperature, concentrations of trace ions fall below the detection limits of IC. In such circumstances, trace enrichment techniques such as

\*Corresponding author. Fax: +91-40-712-5463.

E-mail address: [dks@cccm1.ernet.in](mailto:dks@cccm1.ernet.in) (D. Karunasagar).

precolumn concentration [6–10], Donnan dialysis across an ion-exchange membrane [11] or alternately large volume direct injection [12] is used. Precolumn enrichment and large volume direct injection are widely used for aqueous samples [13]. As determination of both groups of ions are required to assess the purity of different grades of boric acid, pre-concentration methods applied to such samples should permit the quantitative recovery of both anions and cations. Problems pertaining to analyte recovery (organic, inorganic ions) from the concentrator column and separation on an analytical column have been reported by Toofan et al. [8,14].

Generally, sample preparation before determination of ions by IC involves simple operations such as filtration, dilution or pH adjustment. Recently a range of sample treatment techniques [15] and pretreatment chemistries have been reported by Slingsby and Pohl [16] for matrix elimination in a wide range of matrices. The present work reports a novel VPME technique for determination of anions and cations through volatilization of matrix ( $H_3BO_3$ ). In trace metal analysis of boron materials by ICP-AES [17] or other spectroscopic techniques, preconcentration of analytes could be achieved through volatilization of matrix as  $BF_3$  using HF, where the detection limits are governed by the purity of acid used. However, addition of large quantities of such ionic solvent leads to high ionic strength that can overload the low-capacity ion chromatographic column. Thus the use of non-ionic solvent for the digestion and evaporation of the matrix, as has been done in the present method, offers the advantage of lower blanks and negligible background conductivity. To our knowledge, this is the first report where determination of trace ions in boric acid has been carried out after matrix volatilization (trimethyl borate ester) prior to ion chromatography. Use of a dual vessel VPME system (glycerol–methanol solution) also ensures contamination free elimination of matrix by carrying out the whole operation in closed condition, without the need for a clean room facility.

## 2. Experimental

### 2.1. Chemicals and reagents

All standards and eluents were prepared from

deionised water. High purity deionised water with specific resistance of  $18 M\Omega$  cm was obtained from a Milli-Q system (Millipore, Bedford, MA, USA). Sodium hydroxide, hydrochloric and hydrofluoric acid of suprapur grades (Merck, Germany) were used. Acetate, oxalate stock standards ( $1000 \mu\text{g/ml}$ ) were prepared from their sodium salts (AR grade, SD Fine Chemicals, India). A drop of chloroform was added to the stock standard of acetate to prevent bacterial decomposition. Standards of other anions and cations were prepared from their respective reagent grade salt (SD Fine Chemicals). Glycerol and methanol of AR grade were obtained from SD Fine Chemicals.

### 2.2. Apparatus

VPME of boric acid was carried out in a 175-ml capacity polypropylene vessel (Fig. 1). The vessel has an air-locking provision due to a rib in the lid and corresponding recess in the vessel. A PFA (polyfluoroalkoxy) vial (Cole Parmer, USA) was used as sample container. All necessary precautions were taken to minimize contamination during all phases of analysis because of the low concentrations of ions being determined. Insides of the polypropylene VPME chamber and PFA container were soaked for overnight in deionised (DI) water and rinsed several times before use. The VPME assembly was always kept in closed condition when not in use.

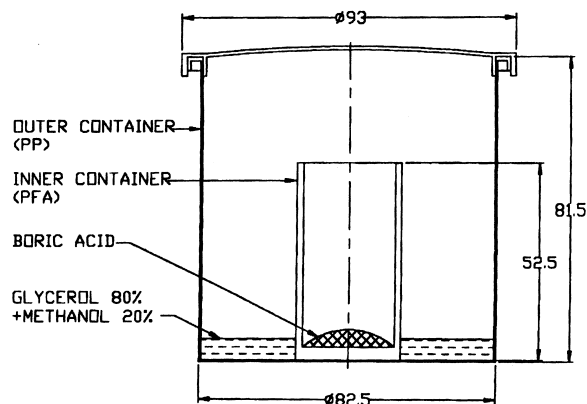


Fig. 1. Drawing of VPME assembly.

### 2.3. Instrumentation and chromatographic conditions

All separations were carried out with a DX-300 ion chromatograph (Dionex, Sunnyvale, CA, USA). The system consisted of an advanced gradient pump (AGP-1), a liquid chromatography module (LCM-3) and a conductivity detector (CDM-3). Data acquisition and processing was carried out using a personal computer equipped with chromatography software (Indtech, Mumbai, India). All columns used in this study were from Dionex. For the separation of anions an IonPac AG17 guard column (50×4 mm) and IonPac AS17 (250×4 mm) analytical column were used. The eluent was sodium hydroxide (15 mM) at a flow-rate of 1 ml/min. For cation separation an IonPac CG12 (50×4 mm) guard column and IonPac CS12 (250×4 mm) analytical column was utilized which provides a fast separation of monovalent and divalent cations. Hydrochloric acid (20 mM) was used as eluent at a flow-rate of 1 ml/min. The injection volumes for determination of anions and cations were 50 and 25 µl, respectively. Anion self regenerating suppressor (ASRS) and cation self regenerating suppressor (CSRS) from Dionex were used in the IC analyses for suppressing the conductivity due to eluents.

### 2.4. Sample digestion in VPME system

A 1-g amount of boric acid powder was accurately weighed into the PFA vial. Thoroughly mixed glycerol–methanol (80:20, v/v) solution (25 ml) was placed in the polypropylene vessel. The PFA sample vial without its cap was placed inside the polypropylene vessel, and the VPME assembly was capped (Fig. 1). The assembly was kept on water bath (operating at 90 °C) for 7 h for complete removal of matrix. Complete elimination of boric acid matrix from the PFA container could be visually monitored through the transparent polypropylene vessel. The VPME assembly was allowed to cool to room temperature, sample vial was taken out and capped immediately. The outer surface of the sample container that was in contact with the glycerol–methanol solution was wiped with tissue paper. The trace ion residues were dissolved in 1 ml of DI water using an Eppendorf micropipette (1 ml capacity). This solution was injected in to the IC for separation

and detection of ionic impurities. Quantification of trace analytes was carried out by an external calibration.

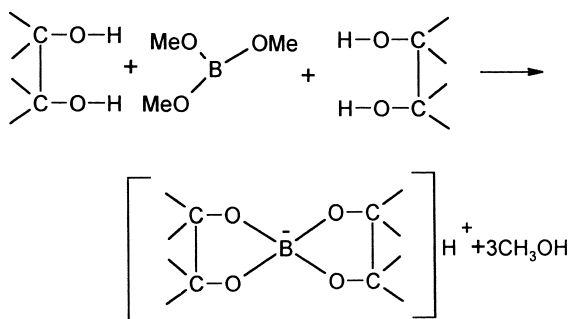
## 3. Results and discussion

### 3.1. Assessment of VPME system performance

On heating the VPME assembly, methanol vapours released from the glycerol–methanol solution (outer container) react with boric acid in the PFA vial (inner container) forming trimethyl borate as follows:



Since the reaction is reversible, the progress of the reaction depends upon the facility with which water or the trimethyl borate can be removed from the reaction zone. Vapours of trimethyl borate (b.p. 68.7 °C) or its condensate formed, react with glycerol (outer container) to form a polyolborate complex [18] which is a monobasic acid and again three molecules of CH<sub>3</sub>OH are released as shown in the following reaction:



The net effect of these two reactions is the migration of boron from boric acid in the inner container to the glycerol solution present in the outer container. Formation of the monobasic acid was confirmed by titration of the “glycerol–methanol” solution after VPME against standard sodium hydroxide to phenolphthalein end point. Titrimetric values obtained correspond exactly (within a titrimetric error of ±0.2%) to the amount of boric acid placed initially in the PFA container. This implies that more than 99% of the matrix is eliminated in the described procedure. Water molecules formed during

sample digestion (reaction 1) are simultaneously distilled off under the sub-boiling temperature ( $\approx 70^\circ\text{C}$ ) that normally exists inside the VPME assembly and thus gets absorbed in the glycerol solution present in outer container. As a result, inside of the PFA sample container was apparently dry after VPME procedure. This condition particularly makes it possible to leach the residual trace ions into 1 ml of deionised water accurately using a micropipette.

The use of the VPME system results in a controlled transport of methanol vapours from the outer vessel to the inner vessel, which in turn regulates the decomposition reaction. Impurities present in methanol remain in the glycerol solution. Therefore in situ purification of methanol, matrix elimination are accomplished in one step. After matrix elimination, the dilution factor is reduced by 20 times (when made up to 1 ml) as compared to the ambient solubility of boric acid in water (50 g/l, i.e., 1 g/20 ml). The glycerol (b.p.  $267^\circ\text{C}$ ) used serves many purposes. Methanol and water are soluble in glycerol, whereas trimethyl borate forms polyolborate complex with it. Thus large pressure build up inside the VPME assembly is prevented. Additionally methanol (toxic) is not released into the environment as its vapours are absorbed in glycerol during cooling of the VPME assembly. Thus, glycerol obviates the need for any pressure-regulating device and acts as a trapping medium for trimethyl borate ester. Multiple experimental observations indicated that glycerol–methanol (80:20, v/v) is ideal to carry out vapour phase matrix elimination. Increasing methanol content further, leaves residual liquid in sample vial, which is undesirable.

Fig. 2 shows chromatograms of alkali and alkaline earth metal ions present in a highly pure grade boric acid (sample 1, suprapur grade, Merck), (a) obtained after matrix volatilization (b) from a saturated solution (1 g/20 ml water). Chromatogram (c) in Fig. 2 is that of VPME process blank. Similarly Chromatograms of anions in boric acid (sample 2, Aristar grade, BDH, UK) with and without matrix elimination are presented in Fig. 3. As stated earlier it is clearly seen that acetate peak is lost in presence of 5% boric acid matrix (Fig. 3b), whereas after matrix elimination it is separated from water dip (Fig. 3a). A comparison of chromatograms obtained after matrix volatilization reveals the advantage of the

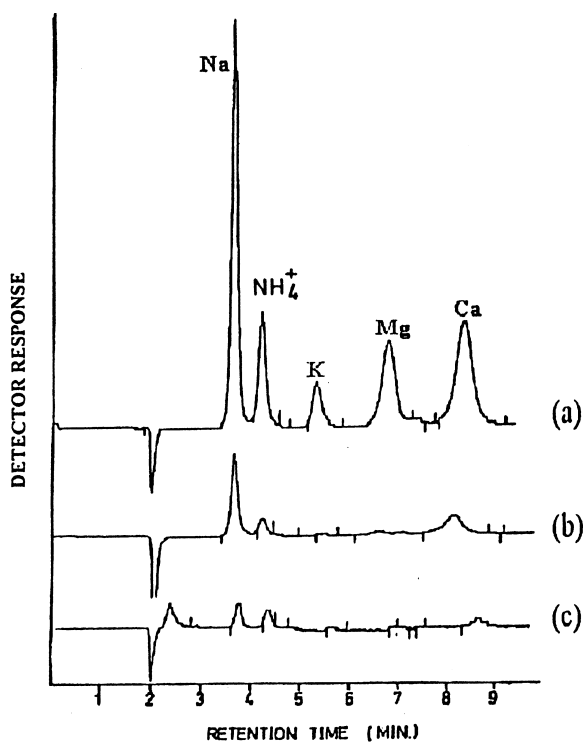


Fig. 2. Ion chromatograms of mono and divalent cations in (a) boric acid (1 g), suprapure grade, Merck, after matrix volatilization; (b) saturated solution (1 g/20 ml water) of the same sample; (c) VPME process blank.

described matrix elimination procedure for determination of both cations and anions.

### 3.2. Matrix effect on anions

The borate matrix complicates the quantification of anions. Sulfate and oxalate ions elute on the tail of borate peak, making peak integration difficult. Severe matrix effect was observed especially in case of acetate while phosphate was also affected to some extent. Up to a boric acid concentration of 1% (m/v), no reduction in peak height of acetate was observed. As the boric acid concentration increased to 5% (m/v), complete suppression of signal was noted (Fig. 3b). Acetate is a weakly retained anion that elutes close to the water dip and the presence of matrix tends to affect its retention time on the column. Similarly at 5% (m/v) boric acid concentration, the phosphate peak height was 23% less in

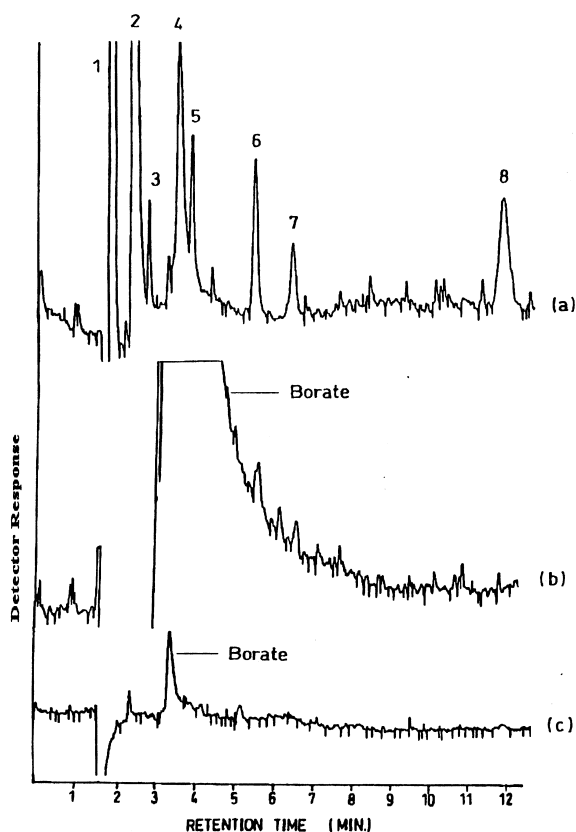


Fig. 3. Chromatograms of anions in boric acid (Aristar grade, BDH, UK) obtained after matrix elimination Water dip arrives before acetate. Peaks: 1=acetate, 2=chloride, 3=unknown, 4=borate, 5=nitrate, 6=sulfate, 7=oxalate, 8=phosphate. (b) Chromatograms of anions of the same sample from its saturated (1 g/20 ml) solution. (c) Chromatogram of the VPME process blank, the borate peak was due to contamination from a previous run.

comparison to the matrix-free standard. Thus, it was necessary to separate the matrix with simultaneous preconcentration of trace analytes.

### 3.3. Need for a closed VPME system

Boric acid has better solubility in methanol than water and a gram of it requires 8 ml of the reagent for complete dissolution of the matrix to form trimethyl borate. When this solution was passed through analytical column with NaOH eluent, trace analyte (anions) signals were swamped with high background conductivity. Trimethyl borate thus creates compatibility problems with the IC suppres-

sor-conductivity detection system. Further un-reacted methanol might reduce the capacity for cation exchange due to formation of esters with the carboxylic acid functional groups of the CS12 column. These factors further necessitate complete removal of trimethyl borate and unreacted methanol. Very often AR- and even HPLC-grade methanol contains traces of alkali and alkaline earth metal ions, which create problem when very low (ppb) levels of cationic impurities in boric acid are determined. Thus, direct addition of reagent and subsequent volatilization step increase the blank values to unacceptable levels.

In the case of the present VPME system, methanol is not directly added to sample, only its vapours come in contact with boric acid matrix. Thus the trace contaminants present in the reagent do not add to sample. As matrix evaporation occurs completely in closed conditions, the laboratory environment also does not influence the blank levels. Comparison of reagent with process blank values between VPME and open volatilization (Table 1) indicates that contamination is significantly reduced for these critical alkali and alkaline earth metal ions by VPME. For instance, blank value of sodium obtained by VPME is 120-times less than that of open volatilization.

### 3.4. Recovery study and detection limits

In the VPME process where more than 99% of the matrix is volatilised off, it was imperative to study the recovery behaviour of trace analytes. Boric acid (suprapur grade, 1 g) was spiked with 50–200 ng of trace analytes, digested through VPME and analysed

Table 1

Comparison of reagent with process blanks (ng) between open volatilization and VPME for 1 g of boric acid ( $n=2$ )

Ion	Open volatilization*	VPME
Na <sup>+</sup>	240	2
K <sup>+</sup>	25	n.d
Mg <sup>2+</sup>	32	n.d
Ca <sup>2+</sup>	68	3
SO <sub>4</sub> <sup>2-</sup>	24	n.d

\* Methanol 8 ml (AR grade, 99%) was placed in a PFA (polyfluoroalkoxy) vial and evaporated to dryness on a hot plate (surface temperature 70 °C.). Ionic impurities were leached into 1 ml DI water and determined by IC as described in the text.

n.d.=Not detected.

Table 2  
Recover study of analyte ions during matrix volatilization and LODs

Ion	Added (ng)	Found (ng)	Recovery (%)	LOD (ng/g)
CH <sub>3</sub> COO <sup>-</sup>	200	192 (6)	96	7
Cl <sup>-</sup>	100	40 (12)	40	–
SO <sub>4</sub> <sup>-</sup>	200	196 (5)	98	5
(COO) <sub>2</sub> <sup>2-</sup>	200	200 (5)	100	6
PO <sub>4</sub> <sup>3-</sup>	200	198 (5)	99	8
Li <sup>+</sup>	50	50 (7)	100	0.3
Na <sup>+</sup>	50	52 (8)	104	2
K <sup>+</sup>	50	49 (7)	98	1
Mg <sup>2+</sup>	50	50 (7)	100	2
Ca <sup>2+</sup>	50	51 (6)	102	2

Figures shown in parentheses are percentage relative standard deviations for three replicate measurements.

by IC. The recovery of spikes ranged from 96% for acetate to 103% for sodium (Table 2). The only exception was chloride, for which very inconsistent and low recovery (25–40%) was observed. The limits of detection (LODs) were determined by injecting VPME process blanks ( $n=5$ ) in to IC and the standard deviations were calculated for all the analytes. The LOD was defined by the protocol as the concentration of analyte that gives a peak (height) response of three times the standard deviation ( $3\sigma$ ) of the blank. Detection limits for different trace analyte ions are presented in Table 2. In the present case both solution and solid detection limits are same, as 1 g of boric acid after matrix removal is made up to 1 ml.

### 3.5. Sample analysis, accuracy and precision

The proposed matrix elimination procedure was applied for determination of trace ions in highly pure grades of boric acid. Quantification of analytes was carried out from calibration curves which were linear ( $R^2 > 0.991$ ) in concentrations ranging from 0.05 to 1 mg/l (anions) and between 0.01 and 1 mg/l for cations. The accuracy of this method was evaluated from recovery data and by cross validation with other methods where ever possible. Phosphate values obtained by IC were compared against a spectrophotometric method [19], developed in our laboratory. Similarly values of cations were cross validated by ICP-AES [17] after matrix volatilization using suprapur-grade HF. Analysis result of two different grades of boric acid samples by suppressed IC and those obtained by other methods along with the

specifications of the impurity levels provided by the manufacturer are presented in Table 3. The values obtained by the proposed volatilization–suppressed IC method agrees well with the values obtained by other methods. Further the impurities were found to be within the limits specified by the manufacturers. For low levels of Li (sample-2, Aristar grade, BDH) and K (both samples), suppressed IC after VPME offers superior sensitivity than ICP-AES. This may be partly attributed to the higher make up volume (5 ml) normally required for a sequential ICP-AES instrument with a common cross flow nebulizer. Additionally for preconcentration of trace cations by boron trifluoride volatilization, expensive suprapur/ultrapure grade HF and clean room are required. In this aspect one of the major advantages of the described VPME procedure is its cost effectiveness as a much cheaper (GR/AR) grade methanol is utilized. At the same time, these cost savings do not compromise the detection limits, because in situ purification and matrix elimination in closed system prevents contamination of the sample. The precision of the method, expressed as the relative standard deviation (RSD) of three independent analyses of the same sample, provided RSD values of less than 8% for most of the ions.

## 4. Conclusions

The VPME described in this work has demonstrated an effective use of matrix volatilization to determine trace ions (anions, cations) in boric acid by IC. Matrix elimination carried out in the closed

Table 3

Trace ion concentrations ( $\mu\text{g}/\text{g} \pm \sigma$ ) determined by suppressed IC ( $n=3$ ) and comparison with the results of other methods\*\* ( $n=2$ )

Sample	Method	$\text{CH}_3\text{COO}^-$	$\text{SO}_4^{2-}$	$(\text{COO})_2^{2-}$	$\text{PO}_4^{3-}$	$\text{Li}^+$	$\text{Na}^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$
1	IC	n.d.	$0.109 \pm 0.007$	n.d.	$0.092 \pm 0.008$	n.d.	$0.032 \pm 0.003$	$0.015 \pm 0.002$	$0.028 \pm 0.003$	$0.055 \pm 0.004$
	ICP-AES	–	–	0.11	n.d.	0.045	n.d.	0.035	0.063	
	A <sup>#</sup>	n.a	<5	n.a	<0.5	<0.01	<0.05	<0.1	<0.1	<0.05
2	IC	$0.56 \pm 0.03$	$0.114 \pm 0.006$	$0.068 \pm 0.005$	$0.213 \pm 0.015$	$0.018 \pm 0.002$	$0.223 \pm 0.010$	$0.018 \pm 0.002$	$0.053 \pm 0.004$	$0.130 \pm 0.008$
	ICP-AES	–	–	–	0.23**	n.d.	0.257	n.d.	0.062	0.151
	B <sup>#</sup>	n.a	<1.5	n.a	<1	<0.05	<5	<5	<0.3	<1

\* 1—Boric acid, Suprapur grade, Merck, Germany. 2—Boric acid, Aristar grade, BDH, UK.

\*\*  $\text{PO}_4^{3-}$  by spectrophotometry [19] and cations by ICP-AES [17].<sup>#</sup> Specifications for the impurity levels provided by the manufacturer, n.d.=not detected, n.a=not available.

condition controls the analytical blanks, which are often the limiting factors in accurate trace ion analysis. The VPME assembly used is simple and inexpensive, which requires only a low-cost commercially available polypropylene vessel. Though sample preparation time is long, it can be considerably reduced (when analyzing many samples) by digesting multiple samples simultaneously on a water bath. Among the limitations, chloride could not be determined by this method as significantly low recovery of it was observed.

### Acknowledgements

The authors thankfully acknowledge the support and suggestions of Dr. J. Arunachalam, Head, CCCM/BARC.

### References

- [1] J.I. Kroschwitz, in: 4th ed., Encyclopedia of Chemical Technology, Vol. 17, Wiley, 1996, p. 391.
- [2] W. Gerhartz, in: 5th ed., Ulman's Encyclopedia of Industrial Chemistry, Vol. A-4, VCH, 1985, p. 266.
- [3] H. Bernhard Pogge, in: Electronics Materials Chemistry, Marcel Dekker, 1996, p. 20.
- [4] D.T. Gjerde, J.S. Fritz, Ion Chromatography, 2nd ed., Hüthig, Heidelberg, 1987.
- [5] P.R. Haddad, P.E. Jackson, Ion Chromatography—Principles and Applications, Elsevier, Amsterdam, 1991.
- [6] P.E. Jackson, P.R. Haddad, J. Chromatogr. 439 (1988) 37.
- [7] A. Tapparo, G.G. Bombi, Anal. Chim. Acta 238 (1990) 279.
- [8] M. Toofan, J.R. Stillian, C.A. Pohl, P.E. Jackson, J. Chromatogr. A 761 (1997) 163.
- [9] P.R. Haddad, P.E. Jackson, J. Chromatogr. 447 (1988) 155.
- [10] D.L. Campbell, J. Stillian, S. Carson, R. Joyce, S. Heberling, J. Chromatogr. 546 (1991) 229.
- [11] J.A. Cox, N. Tanaka, Anal. Chem. 57 (1985) 2370.
- [12] E. Kaiser, J. Riviello, M. Rey, J. Statler, S. Heberling, J. Chromatogr. A 739 (1996) 71.
- [13] B. Lopez-Ruiz, J. Chromatogr. A 881 (2000) 607.
- [14] M. Toofan, C.A. Pohl, J.R. Stillian, P.E. Jackson, J. Chromatogr. A 775 (1997) 109.
- [15] R. Slingsby, R. Kiser, Trends Anal. Chem. 20 (2001) 288.
- [16] R.W. Slingsby, C.A. Pohl, J. Chromatogr. A 739 (1996) 49.
- [17] P. Hulmston, Anal. Chim. Acta 155 (1983) 247.
- [18] G. Wilkinson, in: 1st ed., Comprehensive Coordination Chemistry, The Synthesis, Reactions, Properties and Applications of Coordination Compounds, Vol. 3, Pergamon Press, 1987, p. 94.
- [19] S. Thangavel, K. Dash, S.C. Chaurasia, Talanta 55 (2001) 501.