



ELSEVIER

Journal of Chromatography A, 804 (1998) 193–200

JOURNAL OF
CHROMATOGRAPHY A

Cation analysis in electronics-grade organic solvents by ion chromatography

John K. Sanders

Eastman Chemical Company, P.O. Box 1972, B-167B, Kingsport, TN 37662-5150, USA

Abstract

Many organic solvents are used in the manufacture of semiconductor products, especially as components of the photoresist or as rinse solvents. Assessing the concentration of trace alkali and alkaline earth metal contaminants in these materials is important in order to control circuit defects brought about by the presence of ionic contaminants deposited on the surface during the manufacturing process. This paper describes an ion chromatographic (IC) procedure for the analysis of alkali and alkaline earth metals in the water-immiscible organic solvents methyl *n*-amyl ketone (2-heptanone, MAK), *n*-butyl acetate (NBA), and propylene glycol monomethyl ether acetate (PM acetate, PMA). The procedure consists of in-vial aqueous extraction of the organic solvent followed by on-line preconcentration of the extracted cations onto a Dionex CG-12A guard column and subsequent analysis by ion chromatography. The IC analysis uses a Dionex CS-12A column with isocratic sulfuric acid eluent at elevated temperature and rubidium cation added as internal standard. Data obtained using this method compares well with data from inductively coupled plasma MS analysis of the same materials. Reporting limits for the method are at the one part-per-billion (*w/w*) level for all cations (Li, Na, K, Ca, Mg). The method is simple to implement, automatable, and relatively free from the possibility of contamination during the analysis. © 1998 Eastman Chemical Company. Published by Elsevier Science B.V.

Keywords: Metal cations; Heptanone; Butyl acetate; Propylene glycol monomethyl ether acetate

1. Introduction

Many organic solvents are used in the manufacture of semiconductor devices and liquid crystal displays, especially as a component of the photoresist or as a rinse solvent. Assessing the concentration of trace alkali and alkaline earth metal contaminants in these materials is important in order to control circuit defects due to surface deposition of ions during the manufacturing process. Typically, a variety of spectroscopic techniques such as graphite furnace atomic absorption spectrophotometry and inductively coupled plasma mass spectrometry (ICP-MS) have seen utility in this application [1].

In 1994, Kaiser and Wojtusik reported on the use of ion chromatography (IC) for certification of ppb-

levels of anions in electronics-grade isopropanol [2]. They showed that IC can be a viable technique for measuring trace contaminants in water miscible solvents. In the present work, the utility of using IC to determine trace metal contaminants in the water-immiscible organic solvents methyl *n*-amyl ketone (2-heptanone, MAK), *n*-butyl acetate (NBA), and propylene glycol monomethyl ether acetate (PM Acetate, PMA) is evaluated.

Some of the desired characteristics of a method for the trace determination of cations in electronics-grade solvents may be summarized as; (1) the method should be sensitive down to $1 \mu\text{g kg}^{-1}$ (ppb); (2) it should be robust enough for control laboratory use by analysts without specific expertise in this area (and which also does not require a clean

room or hood); (3) it should be automatable to minimize the likelihood of sample contamination during processing; (4) the method should be inexpensive to implement; (5) it should use accepted technology for industry; and (6) it should be robust enough for application to a growing list of solvents without the need for major modification.

Ion chromatography is generally considered an aqueous analytical technique. Because the organic solvents under consideration in this paper are fully or partially immiscible with water, extraction of the cations from the sample before the IC analysis must be performed. This can be performed manually before the chromatographic analysis or in an on-column mode. The advantage of on-column extraction is that it is automatable and minimizes handling of the sample. However, to eliminate the organic solvent prior to the IC analysis step, a buffer solvent that is mutually miscible with the sample and water would have to be used. This buffer solvent would be under stringent purity requirements to avoid contamination of the system. In addition, most polymeric resins in use may still undergo swelling and other chemical and physical changes when exposed to organic solvents, causing complications such as increased column backpressure that must be dealt with. For these reasons, a pre-analysis extraction step was used in this application. To minimize sample handling, the extraction is performed in the sample vial before analysis in the IC system.

Conductivity detection, although a sensitive and universal detection technique for ions, cannot usually provide the required sensitivity for direct ion analysis at low ppb concentrations. Therefore, pre-concentration of the analyte cations before IC analysis is required. On-column pre-concentration has the advantage of being automatable and relatively free from contamination during analysis. Since the sample matrix after extraction is aqueous, no complications due to incompatibilities between the ion-exchange resin and the matrix would be expected.

2. Experimental

2.1. Reagents and materials

18 M Ω cm deionized (DI) water was obtained using a Millipore (Bedford, MA, USA) Milli-Q

water purification system. Trace metal grade acids were used for eluent and sample preparation. Ultrex II ultrapure reagent-grade sulfuric acid (H₂SO₄, CAS 7664-93-9), and Baker Analyzed Reagent Grade acetic acid (HOAc, CAS 64-19-7) were obtained from J.T. Baker (Phillipsburg, NJ, USA). A 1-ppm mixed cation standard solution (Li, Na, K, Mg, Ca) in water was obtained from High Purity Standards (Charleston, SC, USA). Rubidium chloride, 99.99% (RbCl, CAS 7791-11-9) was obtained from Aldrich (Milwaukee, WI, USA). Working standards were prepared by making an appropriate gravimetric dilution of the 1 ppm standard in an HDPE container (50-ml HDPE centrifuge tube, Evergreen Scientific, Los Angeles, CA, USA). The internal standard (I.S.)-containing extractant was prepared by dilution of a concentrated RbCl solution (ca. 760 ppm Rb) to 140 ppb Rb with 0.6 mM HOAc in deionised (DI) water. The I.S./extractant was stored in a 500-ml PTFE bottle prior to use. Actual production samples of the organic solvents were collected from product storage tanks or shipping containers in 250-ml brown HDPE bottles made by Nalgene (Nalge Nunc International, Pittsburgh, PA, USA) which were purchased pre-cleaned from the I-Chem subsidiary of Nalge.

2.2. In-vial sample extraction

Using a displacement-type pipette with polyethylene disposable tips, 3.5 ml of the organic sample were placed into an 8-ml Nalgene (HDPE) bottle which had been thoroughly rinsed with ultrapure water. Using a fresh pipette tip, 3.5 ml of the internal standard solution were then added to the vial. A silicone/PTFE septum closure was applied and the vial shaken for 10 min in a 180° horizontal shaker to extract any cations present in the organic (top) layer. The sample vial was then placed in the autosampler tray for further processing.

2.3. Chromatographic system

In-vial extraction and ion chromatographic analysis was performed using commercial equipment. System timing and control was programmed into a Spark-Holland (Emmen, Netherlands) Triathlon programmable autosampler. The Triathlon was equipped with a Rheodyne (Cotati, CA, USA) Model 9010-076 polyether ether ketone (PEEK) injection valve

and two optional Rheodyne Model 9010-076 PEEK switching valves built directly into the side of the autosampler. A 2-ml PTFE buffer tubing loop was connected to the 1-ml syringe on the autosampler. A 2-ml aliquot of sample was analyzed by overfilling the 2-ml PEEK sample loop on the injection valve as described in the System Operation section below. Connecting tubing in the chromatographic system was made from 0.02 or 0.01 in. I.D. PEEK tubing (1 in.=2.54 cm). Programmable TTL signal connections from the autosampler were used to control (run/idle) the PEEK DraChrom (Greensboro, NC, USA) Series IV pumps used to deliver the eluent and rinse solvents. Cannula washing, valve control, pump control, sample loading, and triggering of the Hewlett-Packard (Palo Alto, CA, USA) ChemStation data acquisition system were all controlled using the internal programming functionality of the autosampler. Extracts of the organic solvents were sampled directly from the 8-ml HDPE sample vial. The autosampler was fitted with optional trays which were designed to accommodate 23-mm O.D. 10-ml glass sample vials. Custom inserts were added to each vial position in the tray in order to accommodate the slightly smaller diameter of the 8-ml polymer vial. Autosampler wash, rinse solvent and eluent reservoir bottles were either HDPE or PTFE. The autosampler wash solvent and concentrator rinse solvent were ultra-pure water. However, to prevent the introduction of even trace amounts of cations via the rinse solvent, a Dionex (Sunnyvale, CA, USA) cation trap column (CTC) was placed between the outlet of the rinse solvent pump and the switching valve. The temperature of the analytical column was controlled by mounting the column inside a Spark-Holland Mistral column heater. The conductivity cell of the Dionex ED-40 detector and Dionex Model CSRS-1 self-regenerating suppressor were mounted outside of the column heater and remained at room temperature. The detector was operated in the conductivity mode at 20 μS FS (typical), while the suppressor was operated in the external water mode with a 300 mA current setting.

2.4. System operation

The concentration and analysis of trace cations using this system proceeds in three discrete steps: (a) sample loop loading, (b) concentrator column load-

ing, and (c) analysis. The configuration of the injection and switching valves during each of these steps is illustrated in Fig. 1. The sample loop loading step (Fig. 1A) includes a preliminary wash of the needle and buffer tubing with ultra-pure water, priming of the 1-ml loading syringe, and transport of the sample vial in the autosampler carousel to the needle carriage position. The autosampler carriage then lowers a stainless steel cannula that pierces the PTFE/silicone septum of the vial. The cannula is lowered to a depth in the sample vial just above the bottom of the vial and the 1-ml syringe withdraws sample from the bottom layer of material in the vial (i.e., the aqueous extract of the sample). A 3-ml volume of sample is withdrawn from the vial in order to overfill the sample loop and the rinse solvent pump is triggered to turn on at 1 ml min⁻¹ flow. During the concentrator column step (Fig. 1B), the injection valve is switched to direct the rinse solvent flow through the sample loop, pushing the sample extract onto the concentrator column where cations are deposited on the ion-exchange resin of a Dionex Ionpak CG-12A column. After an appropriate time interval that allows for the complete loading of the concentrator column, the analysis step (Fig. 1C) commences with the actuation of Switching Valve A. In this step, 11 mM sulfuric acid at a flow-rate of 1 ml min⁻¹ elutes the pre-concentrated cations (in a direction counter to the column loading step) and injects them into the flow path to a Dionex Ionpak CS-12A analysis column. The data acquisition program is triggered simultaneously with the valve actuation. After the analysis is complete, the rinse and eluent pumps are triggered to the idle state and both valves are reset to the sample loop loading configuration for the performance of a post-run cannula and system flow path washing operation before commencement of the next queued analysis.

3. Results and discussion

Since certification of materials destined for use in electronics applications involves determination of impurities at levels typically involving pre-concentration before analysis, the avoidance of contamination during sample processing is of highest concern. Use of powder-free latex gloves during the handling of consumables such as sample vials, septa, and

pipette tips was found to be useful in this respect. Strict avoidance of borosilicate glass was also important. Indeed, glass vials typically used for high-performance liquid chromatographic applications or head-space gas chromatography were tested and found to be virtually unusable due to high residual surface cation contamination. Either HDPE, LDPE, or PTFE containers were found to be most useful in this application. At the start of each sequence run, a sample of the eluent was analyzed followed by an ultrapure water 'blank' in order to initialize the system and ensure complete system clean-out. To minimize the likelihood of system carry-over between samples, ultra-pure water blanks were also inserted between each sample analysis. Typically, ultra-pure water runs showed the sodium peak only, with a peak area corresponding to less than 0.3 ppb sodium.

Extraction recoveries were found to depend on both the organic sample matrix as well as control of the pH of the extraction solvent. Presented in Table 1

are data which illustrate the recovery of lithium and rubidium from each of the three organic solvents. To generate these data, samples of the organic materials were first extracted with ultrapure water and the extracts analyzed by ion chromatography. Separate aliquots of the samples were then extracted with a multi-component standard containing lithium and rubidium (lithium and rubidium were chosen for this experiment due to their unlikely occurrence as a result of contamination from sample handling). The corrected peak areas corresponding to the recovered amounts of each ion were obtained by subtracting the contribution of lithium and rubidium originally in the sample as indicated in the chromatograms of the water extracts (if any) from the peak areas indicated in the chromatograms of the extracts obtained with the multi-component standard. The corrected peak areas of each ion obtained from the extraction were then compared to the peak areas obtained from chromatographic analysis of the multi-component standard alone to arrive at a measure of the recovery.

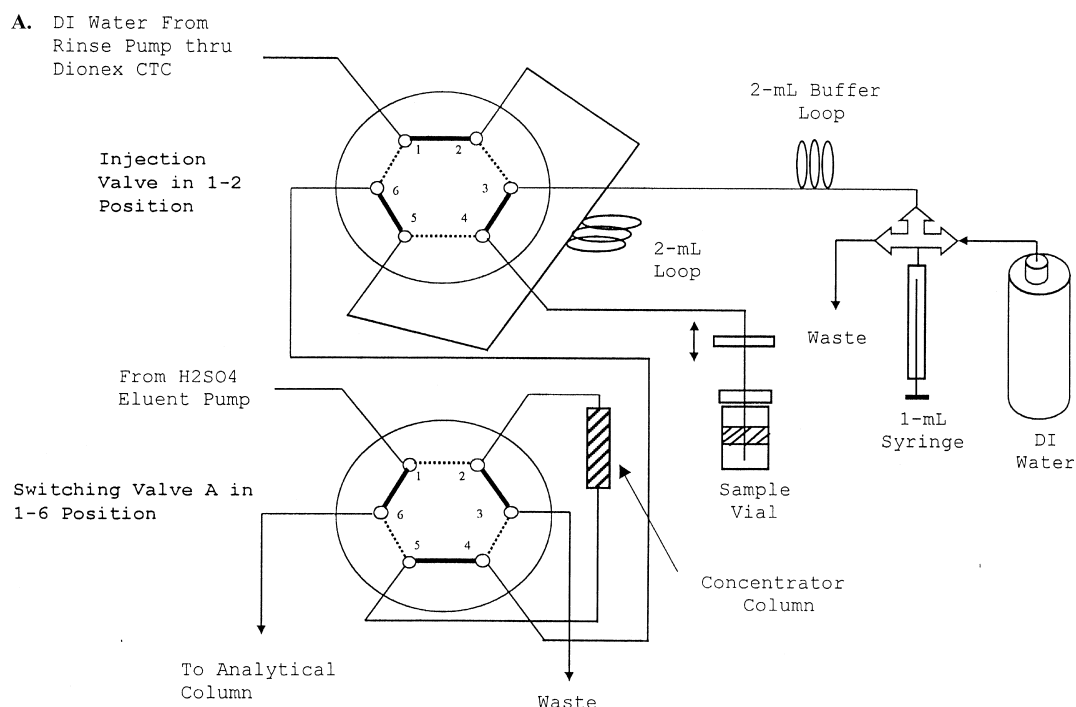
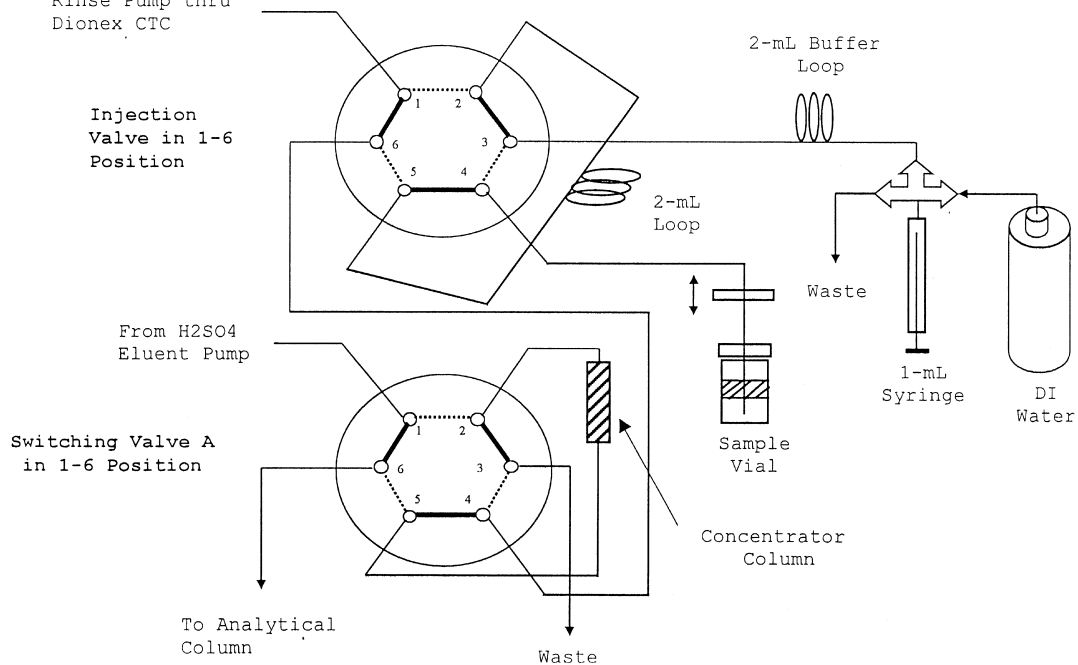


Fig. 1. Valve configuration diagram. (A) Sample loop loading step, (B) concentrator column loading step, (C) Analysis step.

B. DI Water From Rinse Pump thru Dionex CTC



C. DI Water From Rinse Pump thru Dionex CTC

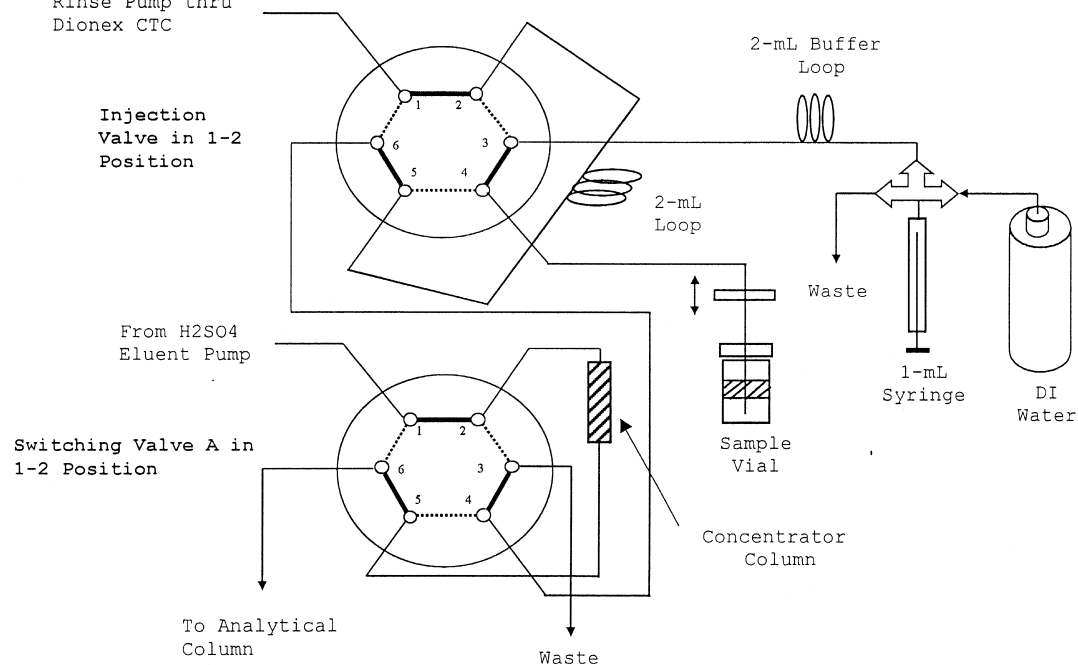


Fig. 1. (continued)

Table 1
Table of recovery data for lithium and rubidium

Solvent	Recovery (%) without pH adjustment		Recovery (%) with pH adjustment	
	Li	Rb	Li	Rb
PMA	83.8	77.7	84.0	84.9
NBA	99.2	104.2	100.3	100.2
MAK	100.5	115.2	101.0	101.6

PMA consistently gave a low recovery of both lithium and rubidium. Both MAK and NBA gave lithium recoveries consistent with complete extraction while also displaying consistently high recoveries of rubidium.

Also listed in Table 1 are data from a similar experiment after pH adjustment of the extract solutions and the standard by the addition of trace metal grade acetic acid (final concentration of acid ca. 0.6 M HOAc in DI water). As can be seen, by adjusting the pH of the extraction to slightly acidic conditions, recoveries of both lithium and rubidium fall into line for MAK and NBA. The high recovery of the ions under pH unadjusted extraction conditions is most likely a result of the presence of the masking of the metal ions in the standard at neutral pH which is not present under more acidic conditions. Since the organic solvents typically contain low levels of organic acid impurities which serve to acidify the aqueous phase during the extraction, comparison of the cations extracted from the organic solvent with those under the neutral conditions of the standard gives the appearance that a more complete extraction of the ions is obtained in the presence of the organic matrix. Addition of the acetic acid to both sample matrices eliminate the influence of pH on the recovery of the ions. In addition, after pH adjustment, PMA shows identical extraction efficiency for both Li and Rb. The reason that PMA differs in extraction efficiency from MAK and NBA is that water and PMA are to some extent miscible, resulting in a measurable change in volume of the aqueous layer upon extraction. For this reason, an internal standard method of quantitation is required for the analysis. Using Rb as an internal standard for quantifying the other cations will correct the analysis results for any change in volume as a result of the extraction step.

Chromatographic conditions were optimized for eluent strength, flow-rate, and analysis temperature. An eluent concentration of 11 mM sulfuric acid at a flow-rate of 1 ml per minute was found to give a good separation within 10 min, however the alkaline earth cations were found to elute at room temperature as broad peaks. Fig. 2 illustrates the improvement in separation efficiency for the Mg and Ca peaks as a function of the analytical column temperature. In comparison to room temperature, performing separations at a column temperature of 50°C dramatically improves the peak shape of the magnesium and calcium peaks and was therefore selected as the standard temperature for the analysis. No deterioration of column lifetime was observed due to the relatively high column temperature employed. An example chromatogram of a 5-ppb mixed cation standard obtained under these standard conditions is shown in Fig. 3.

Using the analysis conditions as discussed in the preceding paragraphs, the method was found to be linear over the range 1 to 20 ppb for each cation. Although this range could be extended to higher values, an upper limit of 10 ppb was established as a shipping quality criterion for the product, so extension of the linear range was unnecessary. Other performance criteria relating to precision and bias are summarized in Table 2. As shown in the table, precision at the 5 ppb level is acceptable for all cations, although the higher variance of the more common cations (Na, Mg, Ca) in comparison to those obtained for Li and K indicate that contamina-

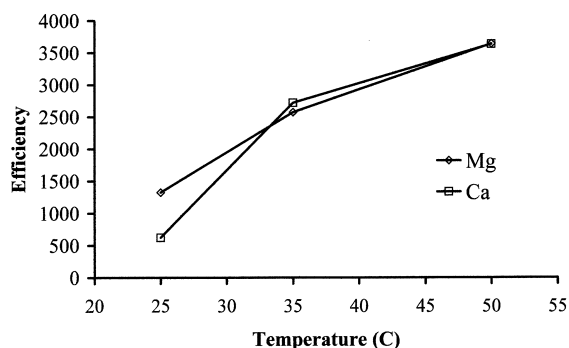


Fig. 2. Effect of temperature on the separation efficiency of the magnesium and calcium peaks, CS-12A column

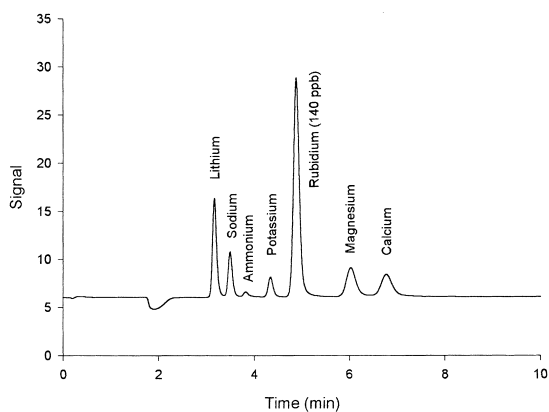


Fig. 3. Representative Chromatogram-trace cation analysis; 5 ppb each ion except 140 ppb Rb. Other conditions as noted in text.

tion due to sample handling may be a significant contributor to the variability of the method. Recovery of the cations averaged over all solvents is also excellent, well within the SEMI guidelines of 75–125% recovery at one-half the upper specification limit [1].

Finally, multiple samples of MAK were analyzed for sodium content using both the IC method and a referee ICP–MS method. The ICP–MS method involved evaporative reduction of the sample from ca. 33 ml to less than 1 ml in a class 100 clean hood (Nuair, Plymouth, MN, USA), heating to dryness, and digestion of the sample residue using nitric acid before dilution in ultrapure water and ICP–MS analysis using a Perkin–Elmer (Norwalk, CT, USA) Elan 5000 instrument. As shown in Table 3, excellent agreement between the techniques was obtained

Table 2
Method performance of the trace cation analysis

	Retention time (min)	R.S.D. (n=4)	DL ^a (ppb)	Average recovery (%) ^b
Lithium	3.4	1.27	0.2	99.7
Sodium	4.2	3.78	0.6	104.8
Potassium	4.7	1.80	0.3	114.1
Magnesium	5.7	3.42	0.5	102.6
Calcium	6.4	6.76	1.0	97.7

^a DL=detection limit= $3 \times$ S.D. at 5 ppb level.

^b Average Recovery for all solvents (n=9).

Table 3

Comparison of sodium in MAK using ICP–MS and IC methods

Sample No.	Result using ICP–MS method (ppb)	Result using IC method (ppb)
1	<1.0	<1.0
2	3.5	2.3
3	<1.0	<1.0
4	4.2	4.7
5	4.1	2.1
6	1.2	1.0
7	5.5	4.3
8	10.6	8.7
9	2.4	3.3
10	1.7	1.0
11	3.0	2.7
12	2.2	<1.0
13	11.2	5.8

for sodium. Similar behavior would be expected for the other cations as well.

4. Conclusions

This paper has shown that IC can be used for the analysis of cations in water immiscible solvents after extraction of the ions into an aqueous phase and on-line pre-concentration. Using automated (in-vial) extraction and on-column pre-concentration decreases likelihood of contamination during sample processing. Extraction of alkali and alkaline earth cations followed by IC analysis has been shown to be a sensitive, straightforward, and relatively inexpensive technique (compared to more traditional spectroscopic trace analysis techniques) that is suitable for control laboratory use.

Acknowledgements

I wish to thank Linda Jo Street of Eastman Chemical Company for performing many of the ion chromatographic analyses described in this report, as well as Dr. Joseph Dougherty of Eastman Chemical Company who assisted with this work by providing the spectroscopic comparison data described in the text. I would also like to thank Dr. Edward Kaiser of

Dionex for many helpful discussions dealing with the issues involved in the testing of electronics grade chemicals via ion chromatography. Finally, I acknowledge the assistance of Armin Sonnenshein of Sonntek in the programming and configuration of the autosampler used in this work.

References

- [1] Book of SEMI Standards (BOSS), Semiconductor Equipment and Materials International, Mountain View, CA, 1996.
- [2] E. Kaiser, M.J. Wojtusik, *J. Chromatogr. A* 671 (1994) 253–258.