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Determination of trace anions in isopropanol

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Abstract

Ion chromatography along with matrix elimination reliably determines low μg/l levels of anionic contaminants in isopropanol. The use of ion-exchange columns that are solvent compatible makes elimination of the isopropanol sample matrix possible and allows calibration standards to be prepared in deionized water. By concentrating a large amount of sample, detection limits for chloride, sulfate, phosphate and nitrate between 0.2 and 1.0 μg/l are achieved. The sample can be injected without sample pretreatment. The procedure is automated and yields a complete analysis in less than 1 h.

1. Introduction

In the manufacture of semiconductor materials, much attention is directed toward minimizing sources of contamination. Production yield and product reliability can be significantly compromised by contamination [1]. Of particular interest are those chemicals that contact the microelectronic circuitry. One such chemical is isopropanol (IPA), which is used to clean semiconductor surfaces [2,3].

Analysis of trace anions in IPA by wet chemical methods is laborious and time consuming. Procedures involve evaporation of a large volume of sample for several hours on a hot plate. Anions are determined by either colorimetric or turbidimetric methods, and each anion must be determined separately [4]. These techniques lack the sensitivity to detect trace concentrations (μg/l) as required by the semiconductor industry.

In the present study, ion chromatography (IC) is employed as an alternative approach for this analytical challenge. The Dionex IonPac ion-exchange columns used in this study are packed with highly cross-linked substrate resin. These columns can withstand up to 100% concentrations of organic solvents without damage to the resin [5]. This paper reports the results of evaluating IC as an analytical tool for detecting trace anions in IPA using matrix elimination on the IonPac AC10 ion-exchange column.

The determination of trace anions in IPA by IC must meet the following requirements; (1) the method must be sufficiently sensitive to detect low μg/l levels of chloride, sulfate, phosphate and nitrate; (2) direct injection of IPA without sample pretreatment is required to minimize sample contamination; (3) an automated analysis is necessary to provide cost effective sample turnaround time; and (4) a concentrator column must pre-concentrate anionic impurities while allowing uninhibited passage of IPA.

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2. Experimental

2.1. Chromatographic system

All chromatography is performed on a Dionex (Sunnyvale, CA, USA) DX-300 ion chromatograph. The system consists of an advanced gradient pump (AGP), a liquid chromatography module (LCM-3) and a conductivity detector (CDM-3). For sample loading a Rheodyne 9126-038 valve is fitted with a 5-ml loop made from 0.037 in I.D. (0.94 mm) I.D. Tefzel tubing supplied by Dionex. To deliver the sample to the concentrator column an inert double stack four-way slider valve (Dionex) is used. Two Dionex Quic Pump (DQP) single-piston pumps are utilized, one for pumping the deionized water rinse solution (rinse-DQP) and the other for drawing sample from the sample container into the sample loop (sample-DQP). A pressurizable reservoir chamber (Dionex) large enough to accommodate the sample container is maintained at 8 p.s.i. (55 kPa) with helium.

All columns used in this study are manufactured by Dionex. The separations are performed on an IonPac AS10 analytical column (250 × 4 mm) and a IonPac AG10 guard column (50 × 4 mm). To concentrate the anions and eliminate the sample matrix, an IonPac AC10 concentrator column (50 × 4 mm) is used. The packing material for AC10, AG10 and AS10 is anion-exchange macroporous resin with 2000-Å pores. The resin consists of polyethylvinylbenzene cross-linked with 55% divinylbenzene. To this substrate, a layer of latex particle beads are permanently bonded. This latex layer consists of 65-nm particles fully functionalized with alkanol quaternary ammonium groups. Sodium hydroxide (100 m*M*) is used to elute the analyte anions from the AC10, AG10 and AS10 columns. An anion self regenerating suppressor (ASRS) from Dionex is used [6]. To prevent contamination of the sample with anionic impurities in the rinse solution, an anion trap column (ATC-1) is used. This column contains a high-capacity anion-exchange resin in the hydroxide form. The ATC-1 is initially prepared for use by flushing (2 ml/min) with 200 ml of 200 m*M* sodium hydroxide followed by 100 ml of deionized water at the same flow-rate. The ATC is periodically regenerated using this procedure. Table 1 summarizes the chromatographic conditions.

2.2. Chemicals

Reagent-grade chemicals are used for standard and eluent preparation. Semiconductor-grade IPA is from Olin Hunt Specialty Products (West Patterson, NJ, USA). Sodium hydroxide, 50% (w/w) is from Fisher Scientific (Pittsburgh, PA, USA). Deionized water with a specific resistance of 17.8 MΩ cm or greater from a Millipore (Bedford, MA, USA) Milli-Q water purification system is used to prepare all reagents and standards.

Anion standards (1000 mg/l) for chloride, sulfate, phosphate and nitrate are prepared from the sodium and potassium salts obtained from Fisher Scientific. The salts are dried for 30 min at 105°C in an oven and then cooled in a desiccator prior to weighing. Working standards are prepared by further diluting the 1000-mg/l standards to the range expected for the anions of interest. Dilute working standards are prepared weekly. Polyethylene containers presoaked with deionized water that has a specific resistance of 17.8 MΩ cm or greater are used to store samples and standards.

2.3. System operation

The trace anion analysis of IPA is accomplished in four steps: (1) filling the sample loop, (2) loading the concentrator, (3) eliminating the IPA matrix and (4) chromatographing the retained ions. Fig. 1 illustrates how the system performs these tasks. In step 1 (Fig. 1A), the sample-DQP pump draws the sample from the pressurized reservoir into the 5-ml sample loop on the Rheodyne valve (valve 5). Use of the pressurized reservoir chamber ensures that the sample loop is consistently filled without bubbles. A 7-min loading time at 1.5 ml/min flushes the loop with approximately two and one-half times its volume with each sample, minimizing carryover from previous samples. After the sample loop has been filled, deionized water from

Table 1
Chromatographic conditions

Guard column	IonPac AG10 (50 × 4 mm)			
Analytical column	IonPac AS10 (250 × 4 mm)			
Concentrator column	IonPac AC10 (50 × 4 mm)			
Trap column	ATC-1			
Eluent	100 m*M* NaOH			
Eluent flow-rate	1.0 ml/min			
Rinsing reagent	Deionized water			
Rinsing flow-rate	1.7 ml/min			
Sample volume	5.0 ml			
Sample fill rate	1.5 ml/min			
Detection	Suppressed conductivity, AutoSuppression, recycle mode			
AGP Program				
Time (min)	Eluent (%)	Valve 5	Valve 6	Remarks
0.0	100	0	1	Fill sample loop
7.0	100	1	0	Sample to AC10
17.0	100	0	1	Begin sampling[a]

[a] Begin sampling refers to data collection.

the rinse-DQP transfers the sample from the loop and to the AC10 concentrator column on the four-way slider valve (valve 6). Anions are retained on the concentrator column while the IPA passes through unretained assisted by washing the AC10 with deionized water from the rinse-DQP at 1.7 ml/min for 10 min (Fig. 1B). Activating valve 6 switches the AC10 in line with the eluent stream and the analytical columns. The anions are then eluted from the AC10 in the reverse direction of the concentration step and separated on the AS10 (Fig. 1C).

Special care is taken to minimize contamination. The deionized water used for preparing rinse solution, eluent and standards is free of measurable levels of ionic impurities, organics, microorganisms and particulate matter (larger than 0.2 μm). Polyethylene containers are soaked for at least 24 h with deionized water and rinsed several times prior to use. Polyethylene is used as a sample container because the use of glass results in a low recovery of phosphate. Disposable gloves (for cleanroom electronics applications) are worn at all times when handling apparatus that come into contact with standards or samples.

3. Results and discussion

3.1. Method performance

To achieve the low detection limits required by the Semiconductor Equipment and Materials International (SEMI) guidelines, a 5-ml sample volume is concentrated on a solvent-compatible AC10 concentrator column. Analyte anions are retained as the IPA matrix is eliminated by rinsing the column with deionized water. The analyte anions are then eluted from the concentrator column and separated on the AS10. The use of an isocratic method results in lower baseline noise in comparison to gradient methods. With lower baseline noise, signal-to-noise ratios are improved and sensitivity enhanced.

An advantage of this matrix elimination method is that standards can be prepared in deionized water and external calibration is performed rather than standard addition to each sample. Calibration curves are prepared for the four anions of interest based on standards prepared in deionized water and 99% IPA. The coefficients of determination (r^2) are calculated for chloride at concentrations of 1–300 μg/l, and for sulfate,

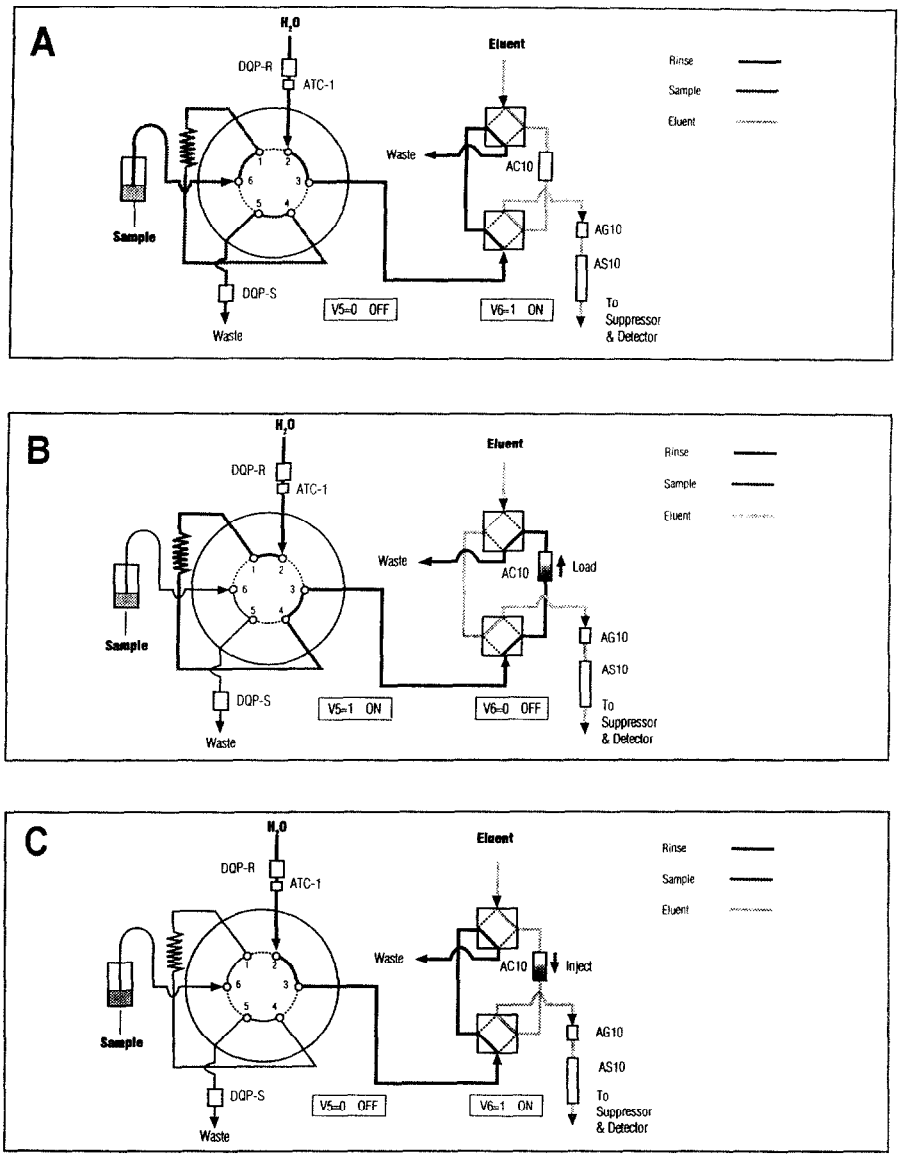

Fig. 1. IC matrix elimination instrument configuration. (A) Loading the sample loop, (B) loading the concentrator column and eliminating the matrix and (C) chromatographing the retained ions. V = Valve.

phosphate and nitrate at 5–500 μg/l. Results for both cases yield a linear response for the four anions with r^2 values greater than 0.9999.

Method detection limit (MDL) values are determined using the standard deviation for seven replicate analyses of IPA samples spiked with 10 μg/l of chloride, sulfate, phosphate and nitrate. A one-tailed Student's t test at the 99.5% confidence level for seven replicates is used for the statistical calculation. By concentrating a large sample volume and eliminating the IPA matrix, excellent retention time precision and low μg/l detection limits are achieved (Table 2). The stated detection limits are lower than the maximum limit of impurity specified by SEMI for ultra-high-purity IPA [7].

Table 2
Method performance of trace anions[a] in isopropanol

Anion	Retention time (min)	R.S.D. ($n = 7$) (%)		Method detection limit (μg/l)[b]	SEMI maximum limit of impurity (μg/l)[c]
		Retention time	Peak area		
Chloride	8.8	0.2	0.4	0.2	50
Sulfate	11.4	0.6	2.0	0.7	50
Phosphate	16.9	0.9	3.6	1.0	50
Nitrate	29.1	0.5	2.7	1.0	50

[a] For IPA spiked with 10 μg/l of each anion and number of samples analyzed, $n = 7$.
[b] Method detection limit = (S.D.) × $(t_s)_{99.5\%}$, where $(t_s) = 3.71$ for a single-sided Student's t test distribution at a 99.5% confidence.
[c] SEMI Guidelines for Isopropanol, Tier B [4].

A representative chromatogram of trace anions in semiconductor-grade IPA is shown in Fig. 2. Levels detected in this sample are well below the maximum limit of impurity: chloride 0.7 μg/l, sulfate 1.1 μg/l and nitrate 1.3 μg/l. The concentrations of these anions are calculated based on the calibration curve prepared in deionized water. An IPA sample spiked with 10 μg/l of the four anions of interest is shown in Fig. 3.

A system blank is determined by using 17.8 MΩ cm or greater deionized water as the sample. This blank consists of 22 ml of deionized water; 17 ml from the rinsing step and 5 ml from the sample loop The blank establishes baseline anion concentrations from such sources as the polyethylene sample container, the deionized water and the chromatograph. Any ionic contamination present in the deionized rinse water is magnified in proportion to the volume needed for the rinsing step. The importance of high-quality deionized water cannot be over-emphasized.

A chromatogram of a representative system blank is shown in Fig. 4. Sulfate is the only species of interest that is detected at 1.0 μg/l.

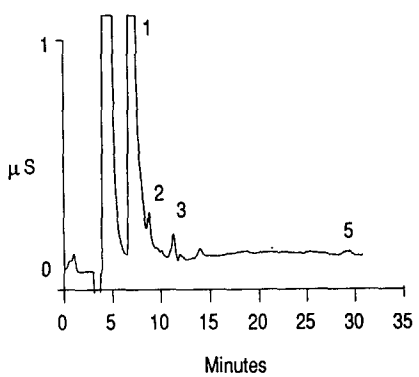

Fig. 2. Analysis of semiconductor-grade isopropanol by IC with matrix elimination. Sample: 100% isopropanol. Peaks: 1 = carbonate; 2 = chloride (0.7 μg/l); 3 = sulfate (1.1 μg/l); 5 = nitrate (1.3 μg/l). Sample volume: 5 ml; analytical column IonPac AS10 (250 × 4 mm); guard column IonPac AG10 (50 × 4 mm); concentrator column AC10 (50 × 4 mm); detection: suppressed conductivity, ASRS in recycle mode; eluent: 100 mM sodium hydroxide, isocratic; eluent flow-rate: 1.0 ml/min; rinsing reagent: deionized water; rinsing flow-rate: 1.7 ml/min.

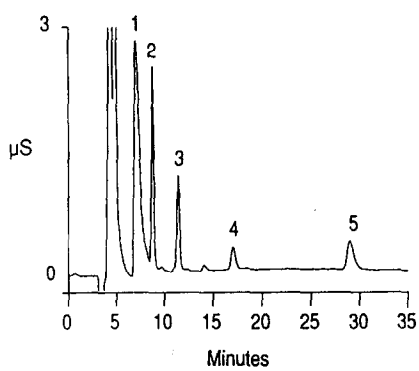

Fig. 3. Analysis of spiked isopropanol by IC with matrix elimination. Sample: 99% isopropanol and 1% aqueous standard; Peaks: 1 = carbonate; 2 = chloride; 3 = sulfate; 4 = phosphate; 5 = nitrate. IPA spiked with 10 μg/l of each of the analytes of interest. Chromatographic conditions as in Fig. 2.

Table 3
Spike/recovery of trace anions in 99% isopropanol

Anion	IPA blank (μg/l ± S.D., $n = 4$)	Spike in IPA (μg/l)	Found − blank (μg/l ± S.D., $n = 7$)	Recovery (%)
Chloride	0.7 ± 0.1	25	21.9 ± 0.2	88
Sulfate	Tr < 0.7	25	25.5 ± 3.2	102
Phosphate	ND < 1.0	25	25.1 ± 1.8	100
Nitrate	1.3 ± 0.2	25	26.3 ± 0.7	105

Tr = Trace; ND = not detected.

This is based on a one point calibration with a 5 μg/l sulfate standard which is corrected for the amount detected in the blank. The sample loop contributes 0.2 μg/l sulfate and the rinsing step contributes 0.7 μg/l sulfate to the total system blank. These values are meant to be approximations, since they are both below the detection limit. The contribution from the rinsing blank is common to all analyses. The peaks eluting before 5 min are fluoride and organic acids.

3.2. Method validation

Recovery of the four anions of interest is determined using a sample of IPA that was spiked with 25 μg/l of each anion. All concentrations are calculated using the aqueous calibration curve described earlier. After correction for the rinsing blank and the IPA blank, recovery values range from 88 to 105% for seven replicates are obtained. These results are summarized in Table 3. To meet the SEMI guidelines for method validation, a recovery of 75–125% must be demonstrated at 50% of the specified maximum limit of impurity [7].

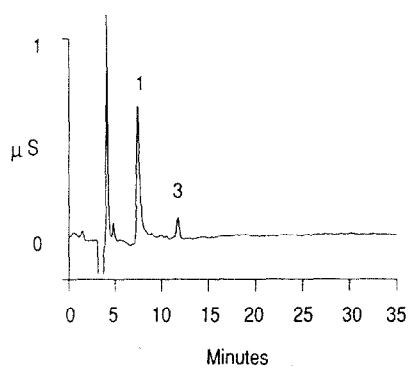

Fig. 4. System blank for IC with matrix elimination. Peaks: 1 = carbonate; 3 = sulfate (1.0 μg/l ≈ 0.7 μg/l for rinse step + 0.2 μg/l for loop volume). Chromatographic conditions as in Fig. 2.

4. Conclusions

Combined use of the IonPac AC10 concentrator column and matrix elimination provide an improved analysis of high-purity IPA for trace anionic contaminants. The success of this method is ensured by using high-purity deionized water for preparation of the rinse solution and standards. Chloride, sulfate, phosphate and nitrate are determined at low μg/l levels with excellent recovery. This technique can be useful as a quality control test in many high-purity applications.

5. References

[1] W. Kern, *J. Electrochem Soc.*, 137 (1990) 1887.
[2] R. Poliak, R. Matthews, P. Gupta, M. Frost and B. Triplett, *Microcontamination*, 10, No. 6 (1992) 45.
[3] W. Runyan and K. Bean, *Semiconductor Integrated Circuit Processing Technology*, Addison-Wesley, Redding, MA, 1990, p. 34.
[4] *Book of SEMI Standards 1993 Chemicals/Reagents Volume*, Semiconductor Equipment and Materials International, Mountain View, CA, 1993, p. 74.
[5] J.R. Stillian and C.A. Pohl, *J. Chromatogr.*, 499 (1990) 257.
[6] S. Rabin, J. Stillian, V. Barreto, K. Friedman and M. Toofan, *J. Chromatogr.*, 640 (1990) 105.
[7] *Book of SEMI Standards 1993 Chemicals/Reagents Volume*, Semiconductor Equipment and Materials International, Mountain View, CA, 1993, p. 145.