Quantitation of anions at parts-per-trillion levels in semiconductor pure water by means of a laboratory ion chromatograph

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Abstract

In the analysis of grab samples for parts-per-trillion (w/w) levels of anions, the most difficult challenge is eliminating contamination sources. This paper discusses the steps taken to identify and deal with these problems. Areas addressed include instrument configuration and assembly, preparation of standards, analysis of standards, and water purification. Precision and accuracy data from the system are given. A Dionex 4000i unit was utilized for all work.

Keywords: Inorganic anions; Anions

1. Introduction

In the semiconductor industry, device geometries are becoming more and more compact. Consequently, even the smallest amount of contamination can cause component failures. Since enormous amounts of water are used in the fabrication process, this liquid must be as pure as possible to ensure product cleanliness. To that end, maximum recommended levels in water of chloride, bromide, nitrate and sulfate range from 25 to 500 ppt (w/w) [1].

With the invention of suppressed ion chromatography [2] and the introduction of concentrator columns [3], quantitation became feasible at or below low-ppb (w/w) levels. On-line instrumentation exists for doing this type of work with minimum risk of contamination [4]. However, these units are quite expensive and do not allow the sampling flexibility that a laboratory unit provides. The latter instrument, though, is much more susceptible to contamination.

Several researchers have discussed laboratory analyses of these species at trace levels [5–10]. However, most were chromatographing standards that were at or above the low-ppb range, and none has thoroughly investigated all the steps needed to assure integrity of results. In addition, no one has evaluated two relatively new columns: the Dionex AS12A and the Dionex AS11. This paper looks at these two columns. Afterwards, it describes a protocol for building and operating a benchtop ion chromatograph that can quantify six anions (fluoride, chloride, bromide, nitrate, sulfate and phosphate) at ppt levels.

2. Experimental

2.1. Materials

The chemicals used in preparing the eluent of sodium carbonate/sodium bicarbonate were obtained from Fluka (Ronkonkoma, NY, USA). Carbonate-free sodium hydroxide was purchased from Fisher Scientific (Pittsburgh, PA, USA). Working solutions of fluoride, chloride, bromide, nitrate, sulfate and phosphate were prepared from 1000 ppm (w/w)

solutions from National Institute of Standards and Technology (Gaithersburg, MD, USA). All water was from the in-house system and was brought above 18 MΩ by a point-of-use polisher. Separate solutions of sodium hydroxide (200 and 5 mM), sodium carbonate (2.7 mM) and sodium bicarbonate (0.3 mM) were prepared for use as eluents. Water for eluents was sparged with helium before solutions were mixed; sparging continued for the life of the eluents. Working standards ranged in concentration from 25 to 100 ppt.

2.2. Apparatus and columns

A Dionex (Sunnyvale, CA, USA) Series 4000i ion chromatograph was utilized for all work. Unless otherwise noted, all instrument modules and consumables were from Dionex. Columns sets used were: (1) IonPac AG12A Guard (50 mm×4 mm) with AS12A Analytical (200 mm×4 mm) and (2) IonPac AG11 Guard (50 mm×4 mm) with AS11 Analytical (250 mm×4 mm). Eluent flow-rates were 1.5 ml/min for the first set and 2.0 ml/min for the second. Post-column eluent suppression was accomplished with an Anion Self-Regenerating Suppressor (ASRS-I, 4 mm); detection was via a CDM-3 conductivity detector at an output range of 1.0 μS. For concentrating standards and blanks, a TAC-LP1 (35 mm×4 mm) column was used. Instrument control and data collection were performed with a personal computer and Dionex AI-450 software.

3. Results and discussion

3.1. General precautions

The overriding concern in trace-level work is contamination of specimens. To that end, thoughts and efforts were centered continually on eliminating this problem. Vinyl gloves, such as those made for clean-room use, were worn when working either on systems or with standards and blanks. Even so, care was taken to minimize contact with solutions or critical surfaces, since even these gloves leach out some anions. All work was performed in a room in which airborne contaminants were minimized.

3.2. Plumbing a system

The trace-level system was configured basically the same as a corresponding high-concentration channel [11]. However, a TAC-LP1 concentrator column was used instead of a sample loop. To allow rinsing of the sampling tube between injections, a four-way slider was utilized in the Load/Inject valve. Eluent and waste lines were of ETFE tubing (0.063 inch I.D.×0.125 inch O.D.; 1 inch=2.54 cm); all other connections were of 0.062 inch O.D. PEEK (polyether ether ketone) (0.010 inch I.D. inside the chromatography path and 0.020 inch I.D. outside). Parts and modules were kept as clean as possible. If there was any doubt about critical pieces, they were either soaked in deionized water before use or replaced with new parts.

The conventional method of arranging the valve and conductivity cell is to mount them on the door of the chromatography module. However, this system was constructed so all pieces were free-standing (e.g., inside an empty module case). This arrangement had several advantages. First, every component was plainly visible at all times, allowing easy detection of leaks or other problems. Second, all tubing lengths (and total dead volume) could be kept to the bare minimum. Last, the entire system could be moved, if necessary, just by detaching the cell cables from the back of the detector; risk of contamination was minimized, since no liquid lines had to be broken. One drawback did arise with this configuration: there was no place to mount the cell, which must remain upright. The problem was solved by taping the block to a heavy object of appropriate height (an inverted 8-oz. (1 oz.≈28.35 g) specimen cup, filled with heavy beads, worked successfully).

3.3. Column selection

Two columns were evaluated for these analyses: the AS12A and the AS11. The AS12A had the advantage of requiring only a carbonate/bicarbonate eluent, which was used isocratically. However, as seen in Fig. 1, the 'water dip' was quite large, since a concentrator column was needed. Consequently, the fluoride peak was in that valley, making integration questionable at best. Also, the baseline for this column was fairly noisy and the sensitivity was poor.
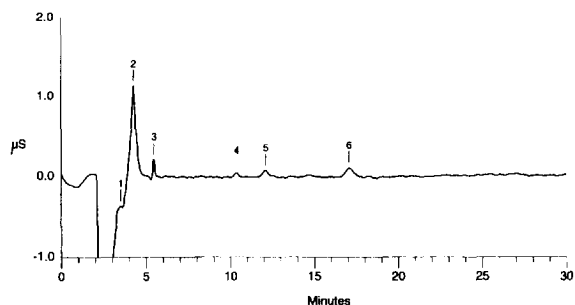
Fig. 1. Chromatogram of 100 ml of a six-anion standard (50 ppt each) on the AS12A column. Peak identities: 1=fluoride; 2= acetate and formate (contaminants); 3=chloride; 4=bromide; 5= nitrate; 6=sulfate. Phosphate was not detected. Experimental conditions are those given in the Experimental section.
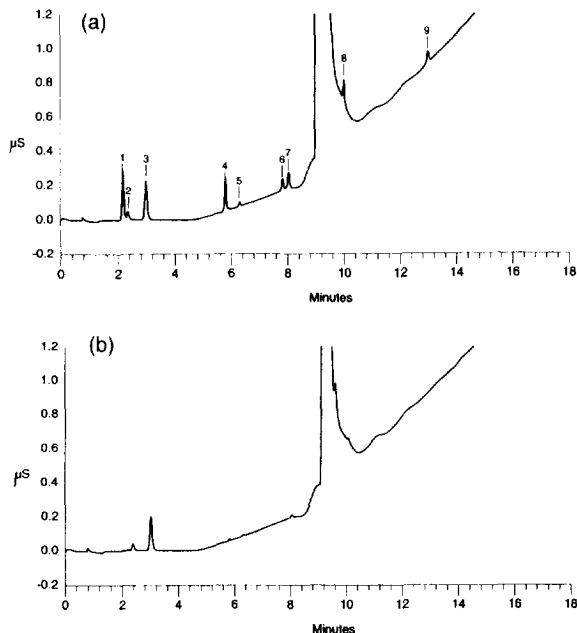

Fig. 2. (a) Chromatogram of 50 ml of a six-anion standard (50 ppt each) on the AS11 column. Peak identities: 1=fluoride; 2=acetate (contaminant); 3=formate (contaminant); 4=chloride; 5=nitrite (contaminant); 6=bromide; 7=nitrate; 8=sulfate; 9=phosphate. (b) Chromatogram of the accompanying blank. Experimental conditions for both tracings are those given in Table 1 and in the Experimental section.

The AS-11 was found to give much better chromatography. A representative chromatogram of a 50-ppt standard is shown in Fig. 2a and the accompanying blank in Fig. 2b. Here, only 50 ml gave quite adequate responses for all analytes. This column did demand the use of a sodium-hydroxide gradient, but all six anions of interest (F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-}, PO_4^{3-}) could be separated from each other and from the often-seen contaminants. All peaks eluted in 15 to 20 min. Over the course of the run, the baseline rose about 1 μS, but the program could be adjusted so that inflection points did not interfere with analyte responses. Because a concentrator was used, the carbonate peak was large and sulfate was on its back shoulder; however, the data-processing parameters could be adjusted so that integration of sulfate was reliable. Comparison of these results with those of the AS12A led to the selection of the AS11 for this research.

Concentrator columns considered were an AG11 and the columns specifically designed for this purpose. The TAC-LP1 was chosen because it is a low-back-pressure version that worked well in this application.

3.4. Eluent (NaOH) preparation for AS11

As with any NaOH eluent, the usual precautions were taken to keep carbonate out of the solution (carbonate in the eluent will shorten retention times

and may affect resolution adversely). Deionized water (18 MΩ or better) was degassed thoroughly before adding the NaOH. NaOH in solution (50% (w/w), carbonate-free) was used, since pellets readily absorb CO_2 from the air. To minimize introduction of carbonate, the bottle was not shaken or agitated before using, and pouring from the bottle was avoided. In addition, the open container always was purged with helium; a free line from the Eluent Degas Module worked well for this purpose. The 50% NaOH was transferred to the eluent reservoir by volume, using a disposable plastic syringe with a piece of plastic tubing on the end. The transfer was made as quickly as possible.

When the 50% solution became severely contaminated with white carbonate powder (usually after about 1/3 of the volume was gone or if the bottle had been in use for several months), new stock was obtained. These bottles were not bought in bulk,

since carbon dioxide was found to leach through the plastic over time.

3.5. Deionized (DI) water

The DI water used for standards (and blanks) was of the highest quality possible. The incoming feed to the IC lab was polished to 18.3 MΩ with a point-of-use unit ('perfect' blanks could be obtained by pumping high-quality water through an anion-exchange column (e.g., an ATC-1). However, this process was slow and recontamination usually occurred during collection).

3.6. Gradient program for AS11

Two concentrations of NaOH (200 and 5 mM) and DI water were needed to effect the gradient program used with the AS11 column. The program shown in Table 1 is from the AS11's Installation and Troubleshooting Guide [12] and worked well in this study (occasionally, some minor modifications may be needed to obtain the desired resolution on a particular column).

In between analyses, the program's strongest eluent was kept flowing through the column. The starting concentration was pumped only long enough to re-equilibrate the column properly before the next injection. Once this time was determined, it was used with each sample. Following this procedure kept contaminants flushed from the system and ensured reproducible chromatography.

Table 1
Gradient program for AS11 column

Time (min)	%1	%2	%3
0.0	90	10	0
0.2	90	10	0
2.5	90	10	0
6.0	0	100	0
18.0	0	83	17

Eluent 1: Deionized water.
Eluent 2: 5 mM NaOH.
Eluent 3: 200 mM NaOH.
Flow-rate = 2.0 ml/min.

3.7. Anion self-regenerating suppressor (ASRS)

The most stable baseline was achieved using the Anion Self-Regenerating Suppressor (ASRS-I), operated in the external-water mode. Deionized water was supplied to the suppressor via either a pump (e.g., an Iwaki pump, as used in the AutoRegen System) or pressurized plastic eluent bottles. When the former was used, it was set so that the Stroke Rate was 100% and the Stroke Length was 20–25%. Also, an ATC-1 anion-trap column was needed between the pump outlet and the ASRS; this addition suppressed the pulses of the pump. With the pressurized reservoirs, the air pressure was kept below 25 psi (the maximum recommended for these containers) (1 p.s.i.=6894.76 Pa). In either case, an adequate flow was found to be 6 or 7 ml/min when the suppressor was in operation. Power was supplied to the unit from either an SRS Controller Module or the CDM-3 Conductivity Detector. The current level was set at 3.

3.8. Containers for standards and blanks

The best container for anion standards and blanks was found to be a Corning polystyrene tissue-culture flask with plug seal. The straight-neck version accommodated the IC's sampling tube properly. To condition these flasks, the following procedure worked well. The vessels (and their lids) were rinsed out at least three to four times with the highest-quality DI water; each time, the container was filled to overflowing. Then the flask was filled totally, capped, and kept full until needed. During storage, the flasks were rinsed and refilled periodically.

When the above protocol was observed, low blanks were obtainable fairly quickly, even from new flasks that had not been soaking very long. There were two exceptions, though: acetate and formate. Significant amounts of both leached out, even after many rinsings. However, these anions were not of interest, so their presence in the blanks was not an issue.

3.9. Standards preparation

Working standards were prepared from NIST stock solutions (1000 ppm) and diluted in soaked-out

tissue-culture flasks that were dedicated to specific concentrations. The water for dilution was from the highest-purity source; the stream was allowed to run for at least 30 min before use. Prior to use, each flask (and cap) again was emptied and filled at least four times, always to overflowing. Then the final rinsing was discarded and the empty flask used for the standard in question.

Any standard in the range of 1 to 1000 ppb was remade every few days. Anything below 1 ppb was remade daily and analyzed within six h of its preparation. All standards were kept at moderate temperatures throughout their lifetimes. When all analyses had been completed, any remaining low-level standards were discarded and the flasks rinsed/soaked for reuse the next time.

Two other precautions were found to be necessary. First, the blanks for a given standard needed to be from the soaked-out flask that would contain that standard, and the water had to be from the same flowing stream as used for dilutions. Any positive blanks then could be subtracted from the standard's response. Second, trace-level standards were best prepared by weight, with transfer of solutions done by pouring (plastic transfer pipets were found to be a source of contamination). DI water for dilution then was added straight from the source and the flask reweighed. This procedure inevitably precluded the generation of exactly the desired concentration. However, as long as weighings were recorded accurately, the precise level could be calculated for use in the calibration curve.

3.10. Loading of concentrator column

For accurate and precise analyses, the DI water used for standards was of superior quality, and integrity of standards was maintained at all times. In addition, the technique used for loading the concentrator column was found to be extremely important. Actually, the task was quite simple: keep to a minimum the connections and components between the sample container and the Load/Inject valve. The following discussion addresses the possibilities.

From a practical standpoint, loading the concentrator with either a syringe or autosampler was ruled out. It took several syringefuls or vials to load enough water, and such a practice greatly increased

the possibility of contamination. Pulling the sample through the concentrator was tried, using a vacuum pump on the end of the waste line. However, even the Low Pressure concentrators exhibited too much back pressure for this method to succeed. Two viable alternatives were the use of a sample pump (e.g., a DQP) and a modified reagent delivery module (RDM).

When the pump was used, the tubing attached to the inlet was Tefzel (0.042 inch I.D.×0.125 inch O.D.) and on the outlet it was PEEK (0.020 inch I.D.×0.062 inch O.D.); the free end of the former was cut off at an angle to prevent any build-up of contaminants. Internal parts that were solvent-compatible were sonicated in methanol, followed by sonication of all internal pieces in DI water. After the pump head had been reassembled (wearing vinyl gloves throughout the procedure), strong NaOH (200 mM) was pumped through the module for at least 2 h, followed by overnight rinsing with DI water. Only then was the pump ready to be placed into service. These practices usually reduced the initial blanks substantially. It sometimes took several runs, though, before the blank was down to an acceptable level.

For actual analyses, the pump speed was set so that concentration occurred at 3 ml/min or less. For a specific time period, the delivery usually was not totally reproducible. Therefore, the effluent from the waste line was measured, and a specific volume or weight obtained for each analysis.

The second alternative, an RDM, could not be used with high-back-pressure concentrators, but worked extremely well with the TAC-LP1; flows of around 2 ml/min could be achieved with this latter column. As with the pump, effluent was collected and measured for accurate results.

The RDM is comprised of the Module itself (with pressure gauges and regulators) and a Pressurizable Reagent Reservoir. The lid to the latter has a hole to allow liquid to exit. A fitting ((1/4–28)×1/8 inch I.D.) plus attached tubing is supplied on the underside of the opening; a check valve comes on the top side [13]. These extra connections and their respective parts were seen as potential sources of contamination. Thus, the aperture was modified as follows. Both fittings were unscrewed from the lid and all check-valve parts removed from their housing. The 1/8 inch O.D. tubing was cut so that approximately

2 cm extended out of the fitting. A piece of PEEK tubing (0.020 inch I.D.×0.062 inch O.D.) was cut long enough to reach from the bottom of the Reagent Reservoir to the Load/Inject valve; the end going into the Reservoir was cut off at an angle. The PEEK tubing was guided through the fitting/tubing, the hole in the lid itself, and finally through the check-valve housing. The fitting/tubing and the housing then were screwed into their respective holes. This seal was secure enough to hold under pressure but loose enough to allow adjustment of the tubing's position.

Using the RDM in the above configuration was found to have two advantages over the DQP. First, the system usually rinsed down much more quickly, and the subsequent blanks were lower. Second, the RDM was virtually maintenance-free, since there were no moving parts to be replaced. However, one precaution had to be observed when removing the lid, which contains an O-ring. Care was taken to be sure the ring stayed either on the cylindrical housing or in the lid. Otherwise, this gasket could fall onto an open sample container.

3.11. Precision and accuracy data

Table 2 shows the precision data for replicate analyses of 50 ml of a mixed standard (the tissue-culture flasks hold a maximum of about 270 ml; thus, only five 50 ml injections were possible). An example chromatogram is shown in Fig. 2a. Table 3 contains the correlation coefficient and regression equation for each four-level calibration curve (only four levels were chosen, since this number was the

Table 2
AS11 precision

Anion	Concentration (ppt)	% R.S.D. (5 replicates)
Fluoride	48	4.8
Chloride	45	2.5
Bromide	48	8.1
Nitrate	40	8.8
Sulfate	39	6.8
Phosphate	72	5.2

Experimental conditions are those given in Table 1 and in the Experimental section. For each analysis, 50 ml of the standard was concentrated.

Table 3
AS11 calibration curves[a]

Anion	Correlation coefficient	K_0^b	K_1^b
Fluoride	0.999	3.04	0.0366
Chloride	0.999	−0.471	0.0618
Bromide	0.999	4.82	0.133
Nitrate	0.999	−15.6	0.117
Sulfate	0.997	−3.57	0.114
Phosphate	0.992	2.21	0.137

[a] Calibration levels were 25, 50, 75 and 100 ppt (2 injections/level). Experimental conditions are those given in Table 1 and in the Experimental section.
[b] Regression equation is: Amount $= K_0 + (K_1 \cdot$ Area).

maximum that could be analyzed in duplicate in one day).

4. Conclusions

The preceding data show that reliable anion analyses can be performed in the laboratory at the 50-ppt level. For each anion, the R.S.D. values for multiple injections were below the usually accepted value of 10%. In addition, four-point calibration curves resulted in correlation coefficients that were better than 0.99 for each anion.

To obtain such data, precautions (e.g., wearing vinyl gloves, preparing standards by pouring) must be observed consistently. Tissue-culture flasks should be used for samples as well as standards and blanks, with vessel preparation the same in all cases. Any stream that is to be sampled should be flowing for at least 30 min, and the resulting sample (or standard) analyzed within 6 h of collection or preparation. Most importantly, a connection-free length of tubing should be used to transfer the sample from its container to the Load/Inject valve; this procedure eliminates prime sources of contamination. If these measures are followed, precise and accurate data can be obtained at the 50-ppt level using a laboratory ion chromatograph.

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