Determination of Low-ppt Levels of Acetate, Propionate, and Formate in Semiconductor-Grade Deionized Water via Ion Chromatography

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Abstract

The goals of this research were the development of a method to determine acetate, propionate, and formate at low part-per-trillion (ppt; w/w) levels in deionized water, and the assessment of sources of variability and contamination associated with the method; both objectives were met. A calibration study involving six replicates of each of four standards (blank, 20, 50, and 80 ppt) resulted in straight-line (with ordinary-least-squares fitting) curves for all analytes. At 95% confidence, the half-widths of the prediction intervals were ± 30, 14, and 14 ppt for the three analytes, respectively. Much of the acetate and formate seen in blanks was found to originate in the deionized water system itself. For formate, peak heights increased with water temperature.

Introduction

Throughout its history, the semiconductor industry has been concerned with contamination control at all stages of the manufacturing process. Liquid chemicals have always been of prime concern. Because deionized water (DIW) is used in almost all stages of wafer and chip production, specifications for this chemical are some of the most rigid. In the area of ions, common inorganic anions, such as fluoride, chloride, nitrite, sulfate, bromide, nitrate, and phosphate, and ammonium have been held to no more than approximately 50 parts per trillion (ppt) for many years. In recent times, the levels of small organic acids, especially acetate, propionate, and formate, have become a concern as well, although the industry has not set specific levels (1). These three species are often found in city water (the starting point at most deionization plants), so these potentially could be found in the finished product as well.

Analysis of low-molecular-weight organic acids is possible by ion chromatography because the species are ionic in water. Column technologies have advanced to the stage where the early-eluting analytes, such as acetate, propionate, and formate, can now be resolved adequately both from themselves and from fluoride. Studies covering the range of 100 ppt to 10 parts-per-billion (ppb; w/w) have been conducted in high-purity waters (2,3). However, no one has investigated these organic acids at low-ppt concentrations.

Thus, the purpose of this work was three-fold: to develop a low-ppt-level ion chromatographic method for analyzing acetate, propionate, and formate in DIW and to evaluate a calibration study statistically; to determine the sample-handling techniques that would be necessary at these concentrations; and to investigate the source(s) of contamination seen in blanks (i.e., how much was from sample handling and how much was from the water itself).

Experimental

Instrumentation and columns

The ion chromatograph used was a Metrohm 850 Professional IC equipped with a pump, conductivity detector, 800 Dosino with 50-mL burette, and MSM chemical suppressor (Herisau, Switzerland). The columns employed were Metrosep A Supp 7 250/4.0 5-µm anion column and Metrosep A PPC 1HC concentrator column. The oven temperature for the analytical/guard column set was 45°C. Samples and standards were introduced onto the concentrator column at the rate of 1 mL/min until 20 mL had been concentrated. Chromatographic analysis time was 14 min. Instrument control and data collection were accomplished with MagIC Net 1.0 (Metrohm). JMP 7.0.1 (SAS Institute, Cary, NC) was used for statistical analysis of the results.

Consumables and chemicals

The eluent was 3.6 mM Na_2CO_3 used isocratically at a flow rate of 0.8 mL/min; the solution was prepared from 99%-pure dry chemical (Sigma Aldrich, St. Louis, MO). The suppressor was regenerated with 100 mM H_2SO_4 and then rinsed with DIW. The sulfuric-acid solution was made from 100% acid (Air Liquide, Dallas, TX). Individual preparations of each of the organic acids were obtained from Inorganic Ventures (Christiansburg, VA) at a concentration of 1000 parts-per-million (ppm) (w/v) each.

Bottles (250 mL, narrow-mouth HDPE) for blanks and standards were obtained from Wheaton (Millville, NJ). A 1000-mL

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plastic tub (Fisher Scientific, Pittsburgh, PA) was used as a secondary container in the off-line liquid-introduction system. The PEEK cross used in the work with on-line blanks was purchased from Upchurch Scientific (Oak Harbor, WA).

Calibration study standards and design

A mixed stock standard was prepared (from the individual 1000-ppm stocks) to contain each acid at 10 ppm (w/w). At the beginning of the calibration study, a 50-ppb (w/w) solution was prepared from the mixed stock and used throughout the research. Both the 10-ppm and 50-ppb standards were refrigerated when not in use. Each day calibration standards were needed, a 500-ppt standard was made from the 50-ppb preparation. This 500-ppt solution was then used to make the working standards for that day. Blanks were prepared using the same protocol as for the working standards, except that DIW was added instead of 500-ppt standard.

All working standards and blanks were prepared fresh (i.e., immediately before analysis). Each bottle had been well-leached previously and was kept full of DIW when not in use. Each bottle was dedicated to a specific concentration. Before use, containers were rinsed 12 times with DIW from the tap. Each rinse involved filling the emptied bottle completely with water, followed by emptying the container completely. Throughout the rinsing process, the cap was allowed to soak in DIW. All solutions were prepared by pouring, and to avoid contamination, no transfer pipettes were used. Immediately before dilution water was needed, it was collected quickly from the DIW tap. A bottle was dedicated to this purpose and kept full of DIW when not in use.

The study design was six replicates of each of a blank and three working standards, the latter of which had the target concentrations of 20, 50, and 80 ppt. Because all solutions were prepared by pouring, exact dilution volumes were not achieved. However, all masses were recorded accurately so that the exact concentrations could be calculated. Within each replicate, the concentrations were prepared and analyzed in random order.

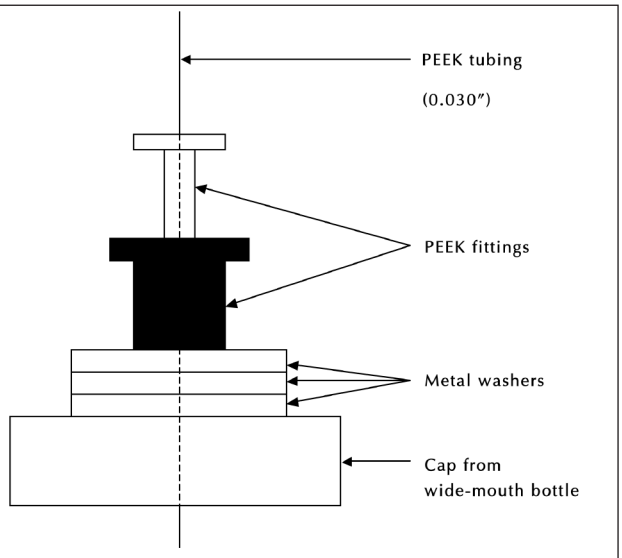

Figure 1. Diagram of off-line sample-introduction system. See text for details.

Results and Discussion

Off-line liquid-introduction system

In the analysis of these organic acids at the ppt level, the primary analytical challenge is controlling contamination, especially during off-line work. Typical ways of introducing liquid into the ion chromatograph (e.g., autosampler, syringe) do not perform well in this setting. In order to minimize problems, a special liquid-introduction system was designed to transfer the desired 20 mL from the bottle to the concentrator column.

The arrangement was as follows: When a bottle containing a blank or a standard was ready for analysis, the cap was removed, and the free end of a PEEK (0.030" i.d.) tube was inserted into the bottle (the other end of the line was attached to the sample-introduction port on the chromatograph's Fill/Inject valve). The tubing was held in place within the bottle via the design shown in Figure 1. The construction of this configuration was as follows: The PEEK line was first threaded through two PEEK fittings that screwed into each other and stayed in place on the tubing when they were tightened. The tubing then passed through three metal washers, which sat on top of a cap (from a wide-mouth HDPE bottle), thereby acting as weights on the cap. A small hole was punched in the cap to allow passage of the PEEK tubing. The position of the two PEEK fittings was as follows: When the bottom of the larger fitting was against the top washer, the free end of the PEEK tubing rested just above the bottom of the bottle. This arrangement ensured that the cap assembly stayed firmly against the mouth of the bottle and minimized any air exchange from the lab. When the system was not being used, the assembly was left intact, and the free length of PEEK tubing was kept in a 250-mL HDPE bottle that was full of DIW and dedicated to this soaking process.

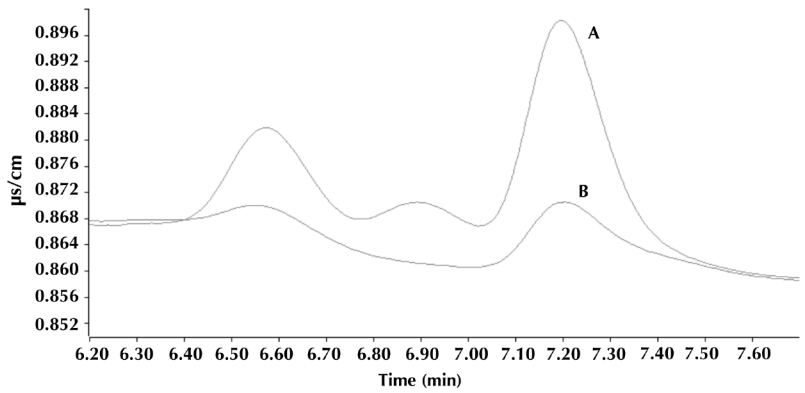

Figure 2. Overlay of chromatograms for a typical blank (B: lower tracing) and a typical 50-ppt standard (A: upper tracing). Elution order is acetate (first), propionate, and formate. See text for details.

Calibration study

Positive blanks were seen for acetate and formate. Figure 2 is an overlay plot of chromatograms for a typical blank and a typical 50-ppt standard.

After the study was completed, the data were analyzed statistically. A summary of the general approach to sound regression work can be found in another study (4). Because exact replicates were not available, the regression diagnostics used were those detailed previously (5). On one day, a 40-ppt standard was inadvertently prepared and analyzed instead of a 50-ppt solution. During regression diagnostics, the 40-ppt standard was considered to belong to a concentration group by itself. For each analyte, a straight line with ordinary-least-squares fitting was deemed adequate to explain the data. At 95% confidence, the uncertainties (determined by the half-width of the prediction intervals) in subsequent measurements estimated from this curve were ± 30, 14, and 14 ppt for acetate, propionate, and formate, respectively. At this level of instrumental sensitivity, these uncertainties were deemed acceptable.

Comparison of off-line with on-line blanks

This experiment compared DIW that was collected off-line with water that was fed directly into the Fill/Inject valve on the instrument. For this work, a DIW line (different from the one that fed the tap used to fill bottles) was connected to one port on a PEEK cross. The tee's second port was connected to a waste line. The third port held a line attached to the Fill/Inject valve's sample-introduction port during on-line work. The line was removed from the valve and capped off during off-line collections. The fourth port was plugged at all times. All transfer lines were PEEK tubing (0.030" i.d.). The flow rate was ~ 20 mL/min out the waste port. To minimize build-up of contamination within this DIW line, the water was allowed to run throughout the study, even when samples were not being collected.

For on-line work, the previously mentioned arrangement allowed the Dosino to concentrate water at the correct rate without exerting excess pressure on the Dosino itself. For off-line experiments, the waste line was removed from the waste port. This port then was held directly above the mouth of the well-rinsed collection bottle. Collection lasted 2 min (i.e., ~ 40 mL was obtained).

For these experiments, six blanks were collected and analyzed via the off-line arrangement. Then the system was reconfigured for on-line sampling, and six more blanks were analyzed. For acetate and formate, a *t*-test was used to compare the on-line peak areas with their off-line counterparts. For each analyte, there was no statistically significant difference (at the 95% cofidence level) between the two sets of responses. These results indicate that virtually all of the acetate and formate contamination is from the DIW system itself.

Sources of contamination and variability

In order to assess the ability of the off-line liquid-introduction system to control contamination, DIW blanks were analyzed in replicate periodically throughout this research. In these experiments, DIW was collected into a bottle directly from the tap. The container was rinsed 12 times before the final sample was obtained. Any time water was being collected, the mouth of the bottle was held as close as possible to the outlet of the tap, thereby minimizing contamination from the air.

Two "ages" of blanks were analyzed. The first was a blank that was collected and analyzed in replicate immediately thereafter. The second type was a blank that had been collected 1–4 days before replicate analyses were begun. In every case for both "ages", no response was seen for propionate; for acetate, only a small signal was seen, which varied little over the course of the replicates.

However, the formate peak behaved differently. The size of the initial peak was typically taller for the "held overnight" samples than for the "new" blanks, presumably due to factors such as longer residence time in the bottle for older samples. The changes of the peak heights (PHs) during replicate analyses, though, was not consistent. For the "new" blanks, the PHs trended downwards as the replicates analyses proceeded. For a given set of replicates, the ranges of peak heights varied from a minimum span of 0.005 to a maximum span of 0.008 PH units. For the "old" waters, the overall trend was up. The ranges of PHs within a given set of replicates were 0.006 to 0.023.

A possible explanation for the formate behavior was temperature. Differences were found in the author's laboratory, which consists of two rooms that are connected by an open doorway. Typically, the sample bottles are stored in one room, but the ion chromatograph is located in the second area, and the temperature of the instrument lab may be up to ~ 3°C higher than in the other room. The temperature of the DIW out of the tap can be up to ~ 5°C degrees higher than the reading in the lab areas. A possible explanation of the observed peak-area trends could be cooling/warming processes that occurred during a given set of replicate analyses.

To test this theory, the following experiment was conducted on two separate days. A DIW sample was collected directly from the tap via the typical protocol. Three replicate analyses were made. Immediately thereafter, the secondary container was filled to slightly below the liquid level in the bottle with hot water (~30°C), and replicate analyses were continued uninterrupted. The first "hot" analysis gave a formate peak that was taller than seen in the previous chromatogram. Two subsequent analyses gave peaks that were similar in size.

Immediately following the heated runs, the water bath was removed via a pipette. Ice was then introduced into the secondary container, followed by a continuation of the analyses for three additional injections. The height of the formate peak trended downward throughout these runs.

A final experiment was conducted on two separate days to assess the variability of replicate analyses performed on temperature-equilibrated blanks. On the day previous to an experimental run, two separate bottles were rinsed and filled with DIW in the late afternoon. These bottles were placed next to the off-line liquid-introduction system and left there overnight. The next morning, six or seven analyses were performed on each bottle. The variability in the peak heights was the least for this experimental protocol, and the ranges of peak heights within a bottle's replicates on a given day were 0.001, 0.003, 0.003, and 0.004.

Conclusions

Ion chromatography provides the sensitivity needed to ana-

lyze acetate, propionate, and formate at the low-ppt level. However, blank contamination during blank and standard preparation can be a problem. Although laboratory air is always a potential source of the problem, this research showed that the DIW system itself can be a major culprit as well. Whenever positive blanks are obtained for any analyte, the user must determine if the responses are low enough to meet the method's data-quality objectives, especially if the contamination can be traced to standard preparation.

The off-line liquid-introduction system performed well throughout the research. At 95% confidence, the calibration curves that were obtained for the three analytes had acceptable prediction-interval widths.

Temperature differences between the laboratory environment and the sample itself were found to have a significant effect on the response for formate. Responses from replicate analyses had the least noise when the temperatures of the water and the lab were well-equilibrated throughout the testing. However, accomplishing such conditions may be almost impossible to achieve from a practical and expedient point of view. Both room and water temperatures vary and are hard to control.

Acknowledgments

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