

Ultratrace Ion Analysis with Automated Multilevel Calibration

Bernard Sheldon
 Dionex Corporation, Sunnyvale, CA, USA

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INTRODUCTION

Trace analysis of anions and cations in ultrahigh-purity water samples is very important to many industries, including power generation facilities and semiconductor manufacturing facilities. Even very low levels of contaminants can lead to corrosion in the severe environments found in power plants. Control of contaminants in process waters used by semiconductor fabs is critical to the quality and yield of the microcircuits they make.

Trace analysis of ions is highly enhanced by using Reagent-Free™ Ion Chromatography (RFIC™) systems and techniques. RFIC systems with Eluent Generation (RFIC-EG™ systems) produce eluents with extremely low backgrounds for highest sensitivity analyses. Gradients are generated automatically from water with eluent generation. The newest extensions of RFIC technologies are the RFIC systems with Electrolytic Sample Preparation (RFIC-ESP™ systems). These systems extend the power of electrolytic devices to the realm of sample preparation, making preinjection sample processing easy, automatic, highly reproducible, and traceable.

Trace analysis of ions can be performed using an electrolytic water purifier (EWP) and multiport valve. The EWP produces very low background water for sample loading in ion chromatography, simplifying automatic sample loop loading and multilevel calibrations. Collecting analyte ions on a concentrator column before injection facilitates a calibrated dual sample loop approach. This approach simplifies standards preparation by allowing the use of standards at concentrations of 1000-fold higher than sample analyte concentrations.

The use of an EWP permits the performance of this type of application with moderately priced ion chromatographs equipped with only one pump for the chromatographic separation. The water purifier is part of a closed loop system and produces extremely pure water from eluent. This ultrapure water is used to transfer the sample from a loop to the concentrator column.

EXPERIMENTAL

An ICS-2100 integrated RFIC-ESP ion chromatography system was used. The instrument was equipped with a 2-position, 10-port valve in the auxiliary valve position (Valve_2) in addition to the standard 6-port injection valve. A UTAC-LP1 concentrator column was installed in place of the sample loop on the 6-port valve. The 10-port valve had a 10 µL (nominal volume) loop installed as one sample loop, and a loop of approximately 10 mL volume as the second sample loop.

Eluent was produced by eluent generation from a KOH cartridge. A hydroxide concentration gradient was used for the separation on a 4 mm i.d. IonPac® AS15 analytical column and AG15 guard column.

Table 1. Chromatographic Conditions

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System	ICS-2100
Injection Volume	14 µL (Standard) or 10 mL (Sample)
Column	IonPac AS15, 4 mm × 250 mm, and AG15 guard, 4 mm × 50 mm
Column Temperature	35 °C
Eluent	KOH gradient
	22 mM to 44 mM from 0 to 18 min
	44 mM to 65 mM from 18 to 27.9 min
	22 mM at 28 min, hold to end, 33 min
Eluent Source	EluGen II KOH cartridge on EGC-1
Eluent Flow Rate	1.2 mL/min
Detection	Suppressed conductivity (35 °C cell temp.)
Suppressor	ASRS® 300, 4 mm; operated at 180 mA

Setup

The approach was to use an experimental setup very similar to that used for Dionex AutoPrep—a 2-position, 10-port valve was used to select between either a 10 µL loop or a large loop of nominal 10 mL volume. The contents of these loops were sent to an anion concentrator column positioned in place of the sample loop on a standard 2-position, 6-port injection valve.

Electrolytic Water Purifier

An EWP was used to provide ultrapure loading water. The Auxiliary Power Supply of the ICS-2100 ion chromatograph was used to power the device at a constant current of 20 mA.

The EWP device used was a dual chamber device. The first chamber was filled with a mixture of anion- and cation-exchange resins. The second chamber is filled with a cation-exchange resin bed.

Plumbing to the EWP is illustrated in Figure 1. The suppressed eluent from the conductivity cell outlet enters port 1 and exits port 4 from which it is then directed to the ICS-2100 10-port valve. The processed water emerging from port 4 is the ultrapure water that is used for rinsing, sample loading, and standard preparation. Port 2 of the device is connected to the waste line from the 6-port valve (concentrator waste) and after an additional purification cycle it exits port 5 to the suppressor regenerant inlet. Ports 3 and 6 are the EWP regenerant inlet and outlet respectively, with flow emerging from port 6 being directed to waste.

The need for a second pump used for sample loading along with an anion trap column is eliminated when the EWP is plumbed in this manner.

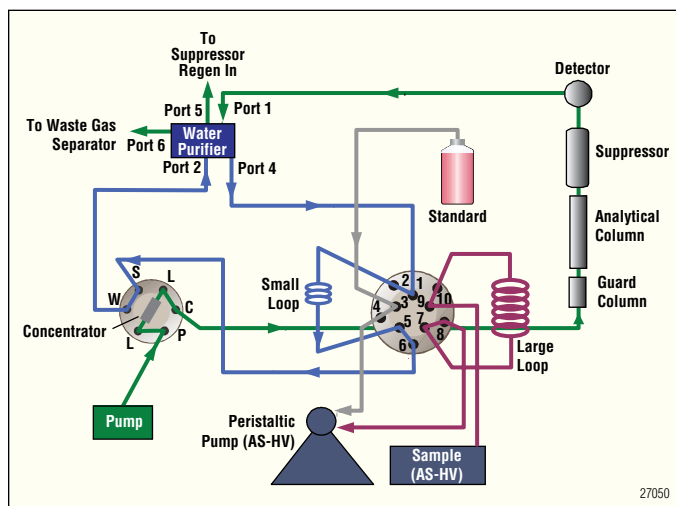


Figure 1. Plumbing schematic.

RESULTS

Calibration

Preparing ng/L standards is extremely difficult due to the need to maintain background levels of ions at levels significantly below the ng/L concentration range. Standards with concentrations in the $\mu\text{g/L}$ are much easier to prepare accurately, and are not affected as much by trace contaminants in the DI water used to prepare them. A dual loop approach to calibration permits easy automation of multilevel calibration at the ng/L level by using smaller injections of higher concentration standards.

The 10 μL loop is used to meter a precise volume of standards in the $\mu\text{g/L}$ range to a concentrator column. By repeatedly filling and dispensing the volume of the loop to the concentrator column, multiple concentration levels are simulated. Standard concentrations used are shown in the table below. When the standards injected in 10 μL volumes are compared to samples of 1000 times higher volumes, the result is the same as performing calibrations with ng/L standards injected at the higher volume.

A 1 to 1000 dilution of a 7 anion standard mix was used (anion concentrations of 20 $\mu\text{g/L}$ to 150 $\mu\text{g/L}$). Loading the concentrator column with 1, 2, 4, and 10 loop volumes produces standards of 1, 2, 4, and 10 times the concentration of the stock dilution. Concentrations emulated and example calibration curves and chromatograms are shown in Table 2, and Figures 2 and 3 below. Table 3 shows the calibration report from the Chromeleon[®] software.

Table 2. Standard Concentrations					
Peak	R. T. (min)	Standard 1/1000 ($\mu\text{g/L}$)	Standard 1/500 ($\mu\text{g/L}$)	Standard 1/250 ($\mu\text{g/L}$)	Standard 1/100 ($\mu\text{g/L}$)
Fluoride	4.01	20	40	80	200
Chloride	8.37	100	200	400	1000
Nitrite	10.37	100	200	400	1000
Bromide	15.67	100	200	400	1000
Sulfate	17.741	100	200	400	1000
Nitrate	19.90	100	200	400	1000
Phosphate	25.37	200	400	800	2000

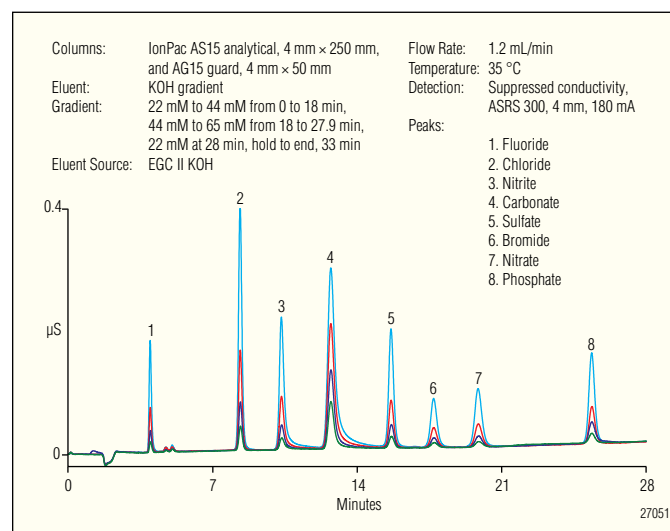


Figure 2. Standard levels overlaid.

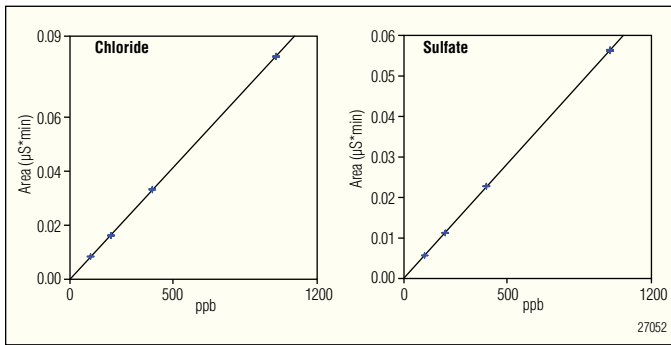


Figure 3. Calibration plots for chloride and sulfate.

Table 3. Calibration Report				
R. T. (min)	Peak Name	Cal.Type	Points	Coeff.Det. %
4.01	Fluoride	LOff	15	99.9717
8.37	Chloride	LOff	15	99.9914
10.37	Nitrite	LOff	15	99.9405
15.67	Sulfate	LOff	15	99.9948
17.741	Bromide	LOff	15	99.9831
19.90	Nitrate	LOff	15	99.9840
25.37	Phosphate	LOff	15	99.9556

Loop Calibration

Good quantitation requires that the exact relative volume of the two loops is established. A comparison of peak areas of two standards is used, using bromide for anions and lithium for cations, since these two ions are very uncommon contaminants in the systems and the water used for analysis. A standard of 10 mg/L was injected using the small loop and a 1 to 1000 dilution of the 10 mg/L standard was injected using the large loop. If the volume of the small loop was exactly 10 mL and the large loop exactly 10 µL, then the area ratios for two standards would be exactly 1 to 1. If the small loop volume were actually 12 µL and the large loop 10 mL, the relative area ratio of the two standards injections would be 1.2 to 1. In fact, the small loop volume is typically determined to be 12 µL to 14 µL, since port-to-port volumes in the injection valve are also included.

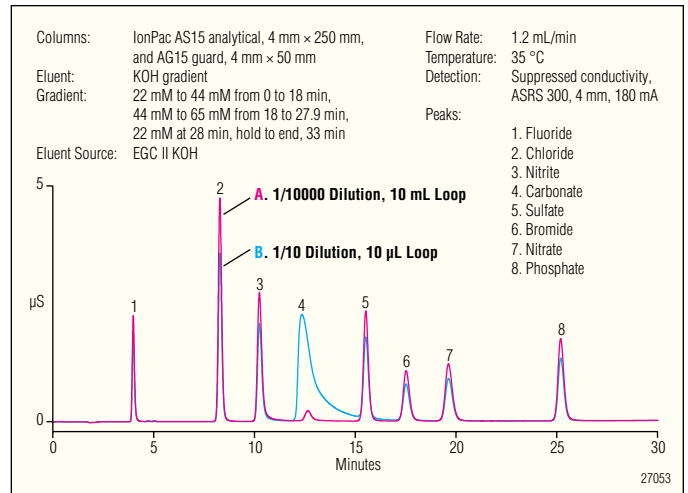


Figure 4. Comparison of results from 10 µL and 10 mL loop volume ratio calibration.

Water Purifier Validation

The capability of the water purifier was tested by comparing results with and without the electrolytic water purifier in the eluent stream (Figure 5). The water purifier was removed from the eluent stream and the effluent of the detector cell was directly concentrated on the concentrator column and injected. As can be seen, the EWP is effective at removing nearly all of the background ions.

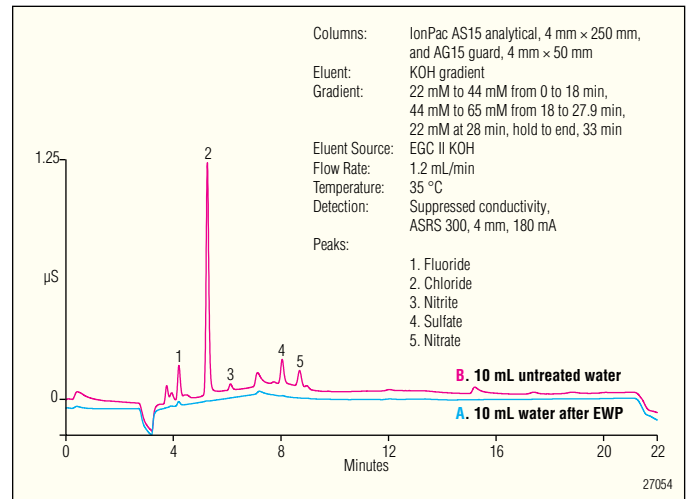


Figure 5. Untreated water compared to purified water.

Application Example

Semiconductor fabrication depends on water of the utmost purity for the highest yields of wafers. Impurity level monitoring to the low ng/L range is now possible. The chromatogram below shows that limits of detection for the anions in the standard are well below 1 ng/L in the sample. This level of sensitivity depends upon the availability of blank water that is at least that pure.

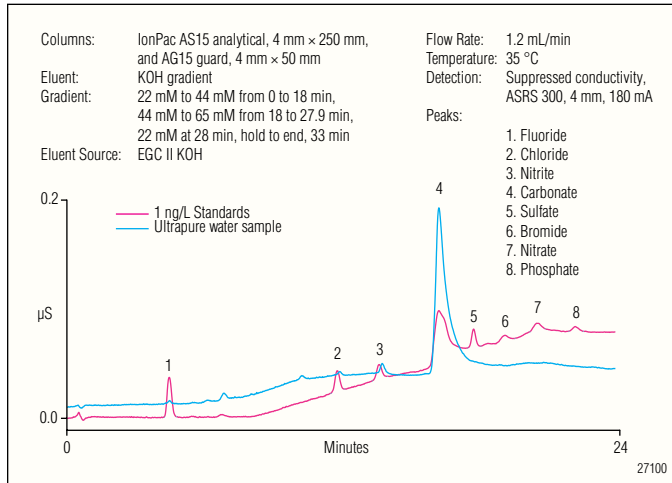


Figure 6. Semiconductor fabrication plant water compared to 1 ng/L standards.

CONCLUSION

The EWP device provides very low backgrounds of the common anions. Only fluoride, chloride, and sulfate could be detected at levels above the limit of quantification. Unquantified low levels of contaminants with retention times corresponding to formate and acetate were also detected.

Automated calibration reduces background ionic contamination, operator labor, and potential errors. Calibration of the small and large loops ensures accurate quantification of analytes down to ng/L levels.

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Dionex Corporation

1228 Titan Way
 P.O. Box 3603
 Sunnyvale, CA
 94088-3603
 (408) 737-0700

North America

U.S./Canada (847) 295-7500

South America

Brazil (55) 11 3731 5140

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Australia (61) 2 9420 5233 China (852) 2428 3282 India (91) 22 2764 2735
 Japan (81) 6 6885 1213 Korea (82) 2 2653 2580 Singapore (65) 6289 1190
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