

Ultrapure water blank for boron trace analysis

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Weakly charged elements, or elements that are not well dissociated in water, are not removed efficiently by conventional water-purification technologies. In the production of high-purity water, silica and boron are generally the first ions to breakthrough into purified water when the ion-exchange resin approaches depletion. In this study, the behavior of these two elements was studied through various steps in a water-purification chain. An optimized system configuration is proposed that combines reverse osmosis and electrodeionization technologies in the pre-treatment phase, and results in the efficient removal of boron. These initial purification steps produce high-resistivity water, presenting a low ionic challenge to ultrapure polishing resins. In addition, a specific chelating adsorbent enhances the retention capacity of boron. Typical values achieved for the most important parameters assessed while producing ultrapure water are described.

Introduction

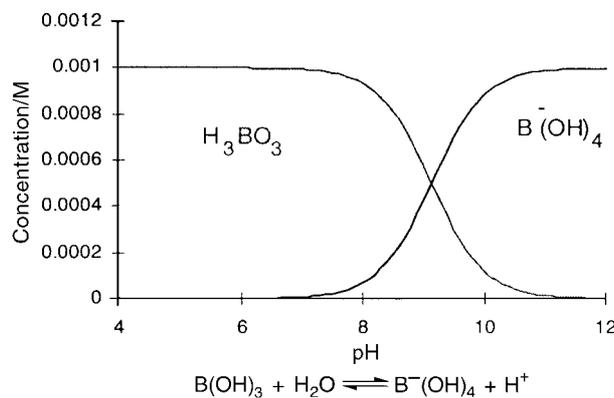
When performing trace analysis, two parameters are vital in order to attain the best possible quantification limits: the experimental environment and the reagents used, *i.e.* the ultrapure water used to perform blanks, dilute standards and wash glassware. An ultrapure water system has already been developed specifically for trace analysis and is described in a previous paper.¹

In addition to being detrimental to equipment, silica is also known to be the first ion to breakthrough when the ion-exchange resin approaches depletion. Much work has been done during the past decade in removing and measuring silica.^{2,3} Recently, boron breakthrough was correlated with dissolved silica and an associated resistivity drop.⁴

In the operation of some reverse osmosis/de-ionization systems, boron is used in addition to silica and resistivity to monitor ion-exchange resin performance. This is important because one of the dopants used in wafer fabrication is boron. It is known to affect electronic junctions. Consequently, a boron-free high-purity water rinse at the point of use is a necessity.⁵

Boric acid is a very weak acid with an equilibrium constant (pK_a) value of 9.2; it is only slightly stronger than silicic acid with a pK_a of 9.5. At a pH lower than 7, boron is present in its non-dissociated form and at a pH greater than 11.5, it is present in the dissociated borate form.

Boron, whose electronic configuration is $1s^2 2s^2 2p$, has three



Scheme 1

valence electrons and forms planar, trivalent derivatives that are electron deficient, which, similarly to Lewis acids, accept two electrons from bases to complete the boron outer-shell octet and give tetrahedral adducts.⁶ Boric acid exemplifies this behavior by ionizing, in aqueous solution, not by direct deprotonation, but by hydration and subsequent ionization, to give the symmetrical borate anion, as shown in Scheme 1.

Much attention has been given to the interaction of these ions with various chemicals such as carbohydrates.^{7,8} Negatively charged borate can be retained by anion-exchange resins. Various chemistries have been tried for chromatographic studies of boron.⁹ A synthetic polymer, which contains a hydrophobic styrene backbone as well as a tertiary amine group, is more suitable as a boron removal resin. This type of boron specific resin (whose use has already been described¹⁰⁻¹²), in combination with advanced water purification system materials and configuration, enables the production of boron-free ultrapure water suitable for ultratrace analyses. In this case, the removal of boron is not performed through an ion-exchange mechanism but more likely through an "affinity" type mechanism.

Experimental

Water-purification chain

The specific water-purification chain used for trace analytical applications consists of a combination of purification technologies.¹³ The initial purification system combines reverse osmosis (RO) and electrodeionization (EDI). This purified water is stored in a specially designed storage reservoir made of

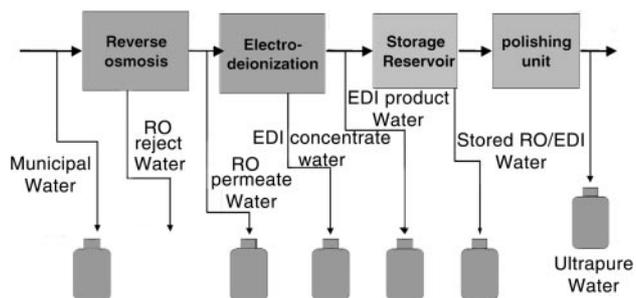


Fig. 1 Water-purification chain.

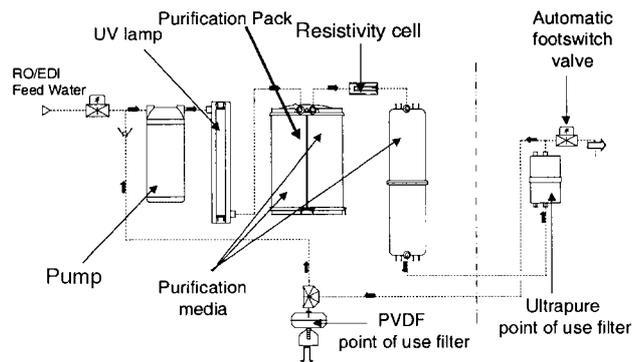


Fig. 2 Schematic diagram of the polishing unit.

polyethylene selected for its low leaching characteristics¹⁴ before further purification *via* a final polishing system. A schematic diagram of this purification chain, as well as the different sampling ports, is shown in Fig. 1. Samples were collected after each purification step in polyethylene bottles that were previously rinsed thoroughly in nitric acid and ultrapure water-baths.

For the EDI step flow rates of either purified (product) water or reject (concentrate) water were measured in order to calculate the mass balance.

In the final polishing step (Fig. 2), two types of purification packs were tested to check boron removal performance. The first contains mixed-bed ion-exchange resins and activated carbon. The second contains boron-specific ion-exchange resin and mixed bed ion exchange resins.

Boron breakthrough studies were performed under challenging conditions: the purification pack was fed with RO-treated well water, containing $10 \mu\text{g L}^{-1}$ of boron, 0.2 mg L^{-1} of silica and 30 mg L^{-1} of carbon dioxide, at $15 \mu\text{S cm}^{-1}$ conductivity. The flow rate was adjusted to 1500 ml min^{-1} to have the same kinetic performance as the normal operating conditions of the final polishing system. Samples of water purified by this pack were collected every 100 l and analyzed for boron and silica content. The resistivity of this purified water was also monitored simultaneously.

Finally, the water obtained through the various purification technologies was analyzed by trace analysis.

Analytical methods

Boron analysis. To evaluate medium-to-high range boron concentrations in tap and purified water, a spectrofluorimetric method was used. This method is based on the specific fluorescence of a complex between chromotropic acid and boron, following the protocol described by Lapid *et al.*¹⁵ and modified by Motomizu *et al.*¹⁶ for high sensitivity and flow injection methods. In this study, a new modified method was developed to adapt it to the analysis of purified water. To

Boron analysis ($>1 \mu\text{g L}^{-1}$) Spectrofluorometric determination

Sample water, 10 ml
 Add, 1 ml Chromotropic reagent solution
 1 M Sodium acetate
 100 mM EDTA-2Na
 0.4 mM Chromotropic acid
 pH adjusted to 6.0 with acetic acid
 Mix immediately
 Measure fluorescence within 15 min
 excitation at 313 nm
 emission at 360 nm.
 Band pass 10 nm
 1 cm cuvette
 Limit of detection $0.5 \mu\text{g L}^{-1}$
 Precision 4% at $10 \mu\text{g L}^{-1}$

Fig. 3 Medium-to-high range boron analysis.

maximize the sensitivity, the pH of the reagent was adjusted to 6 and the fluorescence studied with excitation at 313 nm and emission at 360 nm. The chromotropic reagent was prepared by dissolving disodium EDTA, sodium acetate and chromotropic acid; the pH was adjusted by adding acetic acid. The precise analytical procedure is described in Fig. 3. The limit of detection is $0.5 \mu\text{g L}^{-1}$.

For trace determination of boron, see the procedure described in the Trace elemental analysis section.

Silica analysis. Silica was determined by a spectrophotometric method with a silica–molybdate complex. Depending on the concentration range, a silica–molybdate complex determination at 450 nm ($>1 \text{ mg L}^{-1}$) or a heteropolyblue determination at 815 nm ($<1 \text{ mg L}^{-1}$) was selected. The reagents and spectrophotometer used were from HACH.

Trace elemental analysis. Trace elemental analysis was carried out using an HP4500 ICP-MS (Hewlett-Packard).

To perform multi-elemental measurements simultaneously, with the exception of boron, a cool plasma and shield torch were used to eliminate polyatomic interference. The ICP-MS was optimized with ^{59}Co signal intensity for sensitivity and with ^{39}K , ^{40}Ca and ^{56}Fe for background adjustment. The operating conditions are given in Table 1.

For boron-specific trace analysis, another tuning condition was developed. Higher rf energy up to 1200 W was applied to increase boron sensitivity (Table 2).

A 0.5 mm id PFA tube for sample introduction was connected directly to a coaxial nebulizer and the sample was loaded by self aspiration. While preparing standards and samples, it is essential to avoid contact between the solutions and the external environment. The use of a polyethylene cover to protect the sampling bottle prevents particulate contamination while loading the sample into the analyzer.

Table 1 HP 4500 ICP-MS conditions for multi-elemental analysis

Rf power/W	600	Drawing electrode 1/V	-80
PF matching/V	2.3	Drawing electrode 2/V	-19
Sampling position/mm	14.3	Einzel lens 1,3/V	-80
Torch horizontal position/mm	0	Einzel lens 2/V	-4
Torch vertical position/mm	0	Omega bias/V	-100
Carrier gas flow/L min ⁻¹	1.19	Omega lens (+)/V	-8
Blend gas flow/L min ⁻¹	0.4	u gain	-115
Peristaltic pump/rpm	0.3	u offset	175
Spray chamber temp./°C	0	Mass axis gain	0.999
		Mass axis offset	-0
Plasma torch	Quartz	Plate bias/V	-10
Spray chamber	Quartz	Pole bias/V	-10
Shield plate	Applied	Discriminator/mV	13
Nebulizer	Quartz, co-axial type	EM voltage/V	-1700
Sampling tube	PFA, id 0.15 mm	EM final stage/V	-278

Table 2 HP4500 ICP-MS conditions for boron analysis

Rf power/W	1100	Einzel lens 1,3/V	-80
PF matching/V	2.31	Einzel lens 2/V	-4
Sampling position/mm	12	Omega bias/V	-120
Torch horizontal position/mm	-0.3	Omega lens (+)/V	-3
Torch vertical position/mm	-0.3	Omega lens (-)/V	3
Carrier gas flow/L min ⁻¹	0.95	Quadrupole focus/V	-2
Blend gas flow/L min ⁻¹	0.65	Alternate electrode/V	20
Peristaltic pump/rpm	0.3	u gain	115
Spray chamber temp./°C	5	u offset	175
Plasma torch	Quartz	Mass axis gain	0.999
Spray chamber	Quartz	Mass axis offset	0
Shield plate	Applied	Plate bias/V	-10
Nebulizer	Quartz, co-axial type	Pole bias/V	-10
Sampling tube	PFA, id 0.5 mm	Discriminator/mV	13
Drawing electrode 1/V	-70	EM voltage/V	-1700
Drawing electrode 2/V	-18	EM final stage/V	-278
Plasma gas flow/L min ⁻¹	16		
Auxiliary gas flow/L min ⁻¹	1		

The multi-element solution used as a standard was from SPEX (Cat. No. XSTC-331). It contains 28 elements and was used to construct the different calibration graphs.

The boron standard solution was purchased from Kanto Kagaku.

Ultrapure-grade nitric acid (Kanto Kagaku) was used for the acidification of standard solutions and dilutions.

The calibration and determination was performed by the standard additions method. In each case, the limit of detection (DL) was taken as three times the standard deviation of ten replicates of a blank (Milli-Q SP ICP-MS water, Nihon Millipore, Japan), the limit of quantification (QL) being 3.33 times the limit of detection (or 10σ).

Boron is a difficult element to measure at trace concentration levels because of its memory effect. The injection of a hydrogen peroxide solution was efficient in removing "memorized" boron from the sample introduction device, nebulizer, spray chamber and plasma torch. Before tuning the setting of the ICP-MS, it is necessary to note its stability at designated *m/z*, ¹⁰B and ¹¹B. Samples were measured from low to high concentrations. It is recommended that the calibration graph be constructed at the end of the analysis: when performing ultratrace analysis on samples such as ultrapure water, dilute standard solutions might cause a memory effect.

Conductivity and resistivity measurement. The conductivity or resistivity of water is often used to express water purity, with respect to ionic impurities. Built-in conductivity and resistivity measurement equipment was used to monitor these values.

Results and discussion

Initial purification system and reservoir

Of the water treatment steps, the performance of the EDI technology was particularly analyzed. The conductivity of water and concentration of boron and silica during operation are shown in Fig. 4.

The vast majority of contaminants in the feed water are removed to yield good quality purified water. These removed impurities are concentrated in the waste water. The quality of EDI product water achieves <0.1 μS cm⁻¹ conductivity, <1 μg L⁻¹ boron and 0.01 mg L⁻¹ silica.

Fig. 5 shows the mass balance of contaminants during EDI treatment. A positive value indicates retention of elements and a negative value indicates the release of elements that have accumulated during the EDI purification. The results demonstrate that ionic rejection is well balanced. Electrical deionization is operated under steady state conditions. The

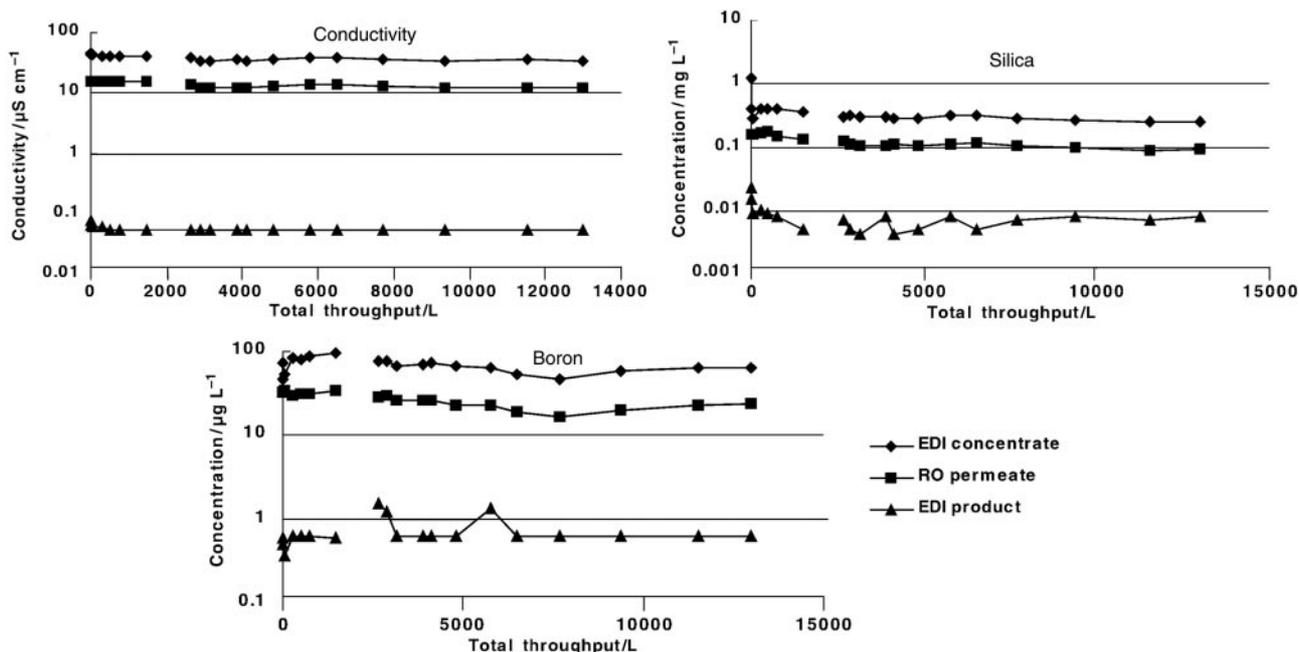


Fig. 4 EDI module performance.

Table 3 Water purification results prior to final polishing step

	Conductivity/ $\mu\text{S cm}^{-1}$	Silica/ mg L^{-1}	Boron/ $\mu\text{g L}^{-1}$
Municipal water	480	7.1	42.6
RO permeate	12.4	0.092	23.7
Rejection by RO	97%	99%	44%
EDI concentrate	33	0.26	65.1
EDI product	0.056	0.008	<0.5
Rejection by EDI	99%	91%	98%
Water in reservoir	0.13	0.009	<0.5

electrical current removes ionic contaminants, and at the same time, regenerates ion removal capability.

The improvement in water quality from municipal feed water to the reservoir is shown in Table 3. In the first step of the purification chain, the RO membrane removes more than 90% of ionic contaminants and silica. The efficiency of boron rejection is still only 44%. After EDI, the quality is again improved. The conductivity of EDI product water is around $0.06 \mu\text{S cm}^{-1}$, almost the theoretical conductivity of pure water. Silica concentration is less than 0.01 mg L^{-1} and boron is less than $1 \mu\text{g L}^{-1}$ or below detection limits. The rejection efficiency of total ions (as measured by conductivity), silica and boron is 99, 91 and 98%, respectively. The purified water is then stored in a reservoir. In some circumstances, storage may increase contamination due to extraction from the reservoir material or dissolution of gases from the atmosphere. Carbon dioxide is a major contaminant known to cause a rise in conductivity. In our experiment, a blow-molded reservoir equipped with a specific vent filter,¹³ is used. Only a slight conductivity increase is observed after overnight storage in the reservoir. Moreover, no significant increase in silica and boron is detected during storage.

Trace analysis is used to analyze EDI product water more

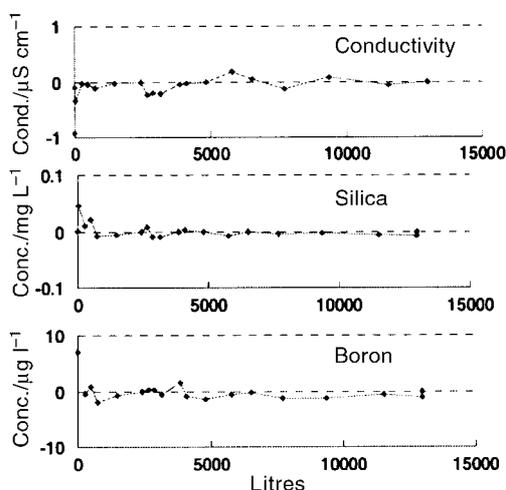


Fig. 5 EDI module mass balances.

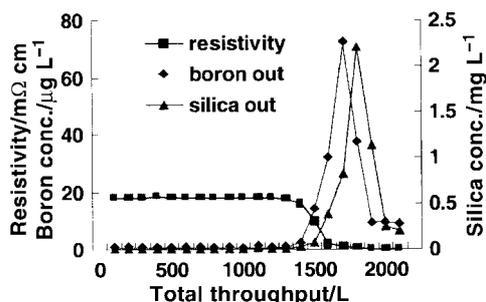


Fig. 6 Results with conventional purification pack fed with RO water containing $200 \mu\text{g L}^{-1}$ Si and $9 \mu\text{g L}^{-1}$ B.

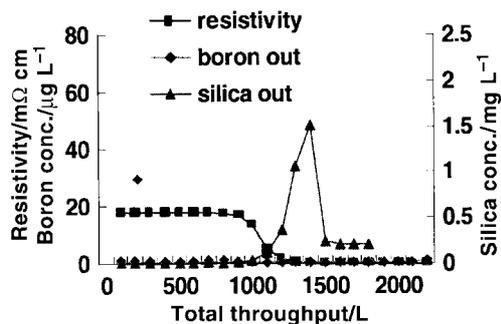


Fig. 7 Results with boron-specific purification pack fed with RO water containing $200 \mu\text{g L}^{-1}$ Si and $9 \mu\text{g L}^{-1}$ B.

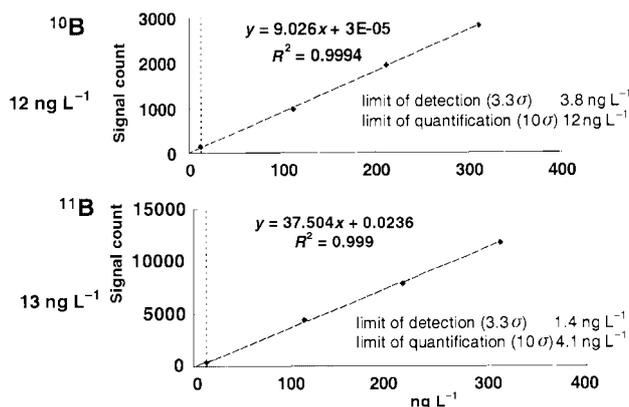


Fig. 8 Final polishing unit result: trace boron analysis.

precisely. Even though the conductivity of the purified water is fairly good, large amounts of contaminants are nevertheless detected, for example, 340 ng L^{-1} of sodium. Levels of impurities not monitored by conductivity meters are visualized by trace analysis. In addition, boron contamination can be quantified at 240 ppt, whereas its value determined by the fluorescence method was below detection limits ($0.5 \mu\text{g L}^{-1}$). It is necessary to polish this water further to meet the requirements for trace elemental analysis.

Purification pack in the final polishing unit

Performance comparison of the two packs described under Experimental is shown in Fig. 6 and 7.

Table 4 Trace elemental analyses of ultrapure water by ICP-MS. All values in ppt (ng L^{-1})

Element	DL ^a	QL ^b	RO/EDI	Ultrapure water
Li	0.026	0.079	0.08	<QL
B	1.4	4.1	240	12.9
Na	0.094	0.29	340	0.33
Mg	0.012	0.036	1.5	0.16
Al	0.075	0.23	5.8	<DL
K	2.8	8.6	22	9.6
Ca	3	9	16	9.1
Cr	0.22	0.67	0.9	<DL
Mn	0.25	0.77	<QL	0.8
Fe	0.048	0.15	1.5	0.5
Co	0.5	1.5	<QL	<DL
Ni	0.13	0.38	<QL	<DL
Cu	0.075	0.23	0.9	<QL
Zn	2.2	6.6	55	<DL
Sr	0.022	0.068	0.8	<DL
Ag	0.076	0.023	0.2	0.17
Cd	1.3	3.8	<DL	<DL
Ba	0.29	0.89	<QL	<DL
Pb	0.15	0.45	1.2	<DL

^aDL=limit of detection. ^bQL=limit of quantification.

With the standard pack configuration (Fig. 6), boron breakthrough is observed. At the end of the pack's life, a high level of boron is released into the purified water in a short time. The maximum concentration of boron at this time is much higher than that in the feed water. In this case, used in a water purification system, there is a high risk of purified water delivered with a high concentration of boron even though the water quality, as measured by resistivity, is acceptable. This early boron release occurs due to the low efficiency of the mixed-bed ion-exchange resin. Boron acid is removed by the anion-exchange resin in the mixed-bed resin bed. However, boric acid, the dominant form of boron in water, is not well dissociated (first dissociation constant is 7.3–10). The release takes place not only because of poor kinetics, due to the low dissociation, but also due to re-exchange of borate ions with other major contaminants in the water. It is assumed that, once captured in the ion-exchange resin, boron can be replaced by other anions, which have a higher concentration and affinity for the resin. This is why a specific affinity-type resin is required. Moreover, when feed water to ion-exchange resin is of higher conductivity, there is an earlier boron breakthrough due to this re-exchange of borate ions with other major ions in water. In this case, the water-purification system will deliver 18.2 M Ω cm containing significant boron concentrations.

With this specific configuration (Fig. 7), there is no further boron release during the pack lifetime. The special ion-exchange resin is designed for specific boron removal. The functional group, which can attach boron, is immobilized on the resin bed substrate. The adsorption of boron on the resin is specific and less competitive with other ions than conventional strongly basic ion-exchange resins. Boron breakthrough is not observed even after the resistivity drop. As the boron removal resin does not act as an ion exchanger, the capacity of the pack in terms of ionic retention is less than that of the conventional pack. This is why the resistivity drop occurs earlier during this experiment.

Final ultrapure water delivery system

Final ultrapure water is analyzed by ultratrace analytical techniques. The results in terms of boron analysis are shown in Fig. 8, and the concentrations of other elements are summarized in Table 4.

Boron concentration is expressed by a standard additions calibration graph. Boron measurement is performed on both ^{10}B and ^{11}B . The resulting concentration, as the blank equivalent concentration, is 12 ng L $^{-1}$. The final polishing unit contributes significantly to eliminating trace levels of boron, from 240 ng L $^{-1}$ in EDI feed water to 12 ng L $^{-1}$ in final ultrapure water. The calculated limits of detection/quantification show low enough values to execute ng L $^{-1}$ level analysis. For ^{11}B , a detection limit of 1.4 ng L $^{-1}$ and a quantification limit of 4.1 ng L $^{-1}$ are obtained.

Values for silica concentrations are under the 1 ppb spectrophotometric method detection limit.

Furthermore, this system achieves single ppt levels of water quality for most elements, with many values actually being below detection or quantification limits. For all elements tested in this study, the final polishing unit shows excellent impurity retention, achieving ppt level water quality.

Conclusion

When performing ultratrace analyses at ppt levels, the ultrapure water used to perform blanks, prepare standards and dilute samples should be of the highest purity. Specific features and configuration allow such detection limits to be achieved for most elements. However, weakly ionized ions, such as boron, do not impact resistivity measurement. Water quality is thus affected without the user being aware of the fact. Specific developments to reduce the breakthrough of this weakly bound ion are proposed. Additional research is still in progress to improve the sensitivity of silica determinations and the purification of trace levels of silica in ultrapure water. The water purification chain described in this paper ensures constant minimal elemental contamination. In the final water-purification unit, early boron breakthrough from the ion-exchange resin is eliminated by using a special adsorption device, and a combination of technologies can provide ultrapure water suitable for ppt and sub-ppt trace elemental analysis.

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