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RD003

Ultrapure Water for Boron-and Silica-Sensitive Laboratory Applications

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Abstract: 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 break through into purified water when the ion-exchange resin approaches depletion. In this study, the behavior of these two elements is studied through various steps in a water purification chain. An optimized system configuration is proposed that combines reverse osmosis and electrodeionization technologies in the pretreatment phase, and results in the efficient removal of boron and silica. 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. A water purification system producing ultrapure water suitable for trace analyses down to ppt levels, including boron sensitive laboratory applications, can be achieved providing specific system design and configuration are respected.

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, including the ultrapure water used to perform blanks, dilute standards and wash glassware.

In the production of high-purity water, dissolved silica is one of the most critical parameters used (in addition to resistivity measurement) to monitor ion-exchange resin efficiency.

Besides being detrimental to equipment, silica is also known to be the first ion to break through when the ion-exchange resin approaches depletion. Much work has been done during the past decade to remove and measure silica^{1,2}. Recently, boron breakthrough was correlated with dissolved silica

and an associated resistivity drop³. In the operation of some Reverse Osmosis/Deionization 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, boron-free high-purity water rinse at the point of use is a necessity⁴.

Boric acid is a very weak acid with an equilibrium constant (pKa) value of 9.2; it is only slightly stronger than silicic acid with a pKa of 9.5. At a lower pH 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 1s² 2s² 2p,

has 3 valence electrons and forms planar, trivalent derivatives that are electron deficient, which, similarly to Lewis acids, accept 2 electrons from bases to complete the boron outer-shell octet and give

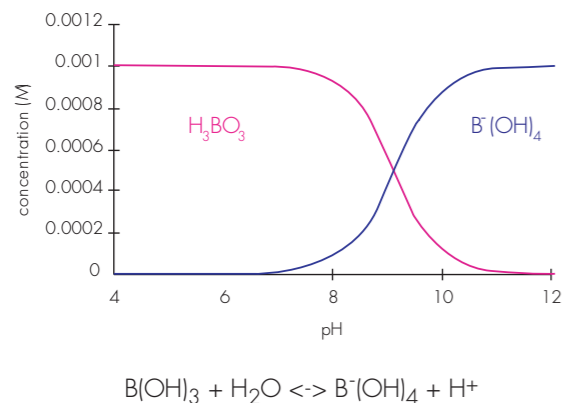


Figure 1: 1 mM boric acid behavior in aqueous solutions.

tetrahedral adducts⁵. 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 (figure 1).

Much attention has been given to the interaction of these ions with various chemicals such as carbohydrates^{6,7}. Negatively charged borate can be retained by anion-exchange resin. Various chemistries were tried for chromatographic studies of boron⁸. A synthetic polymer which contains a hydrophobic styrene backbone as well as a tertiary amine group, is more suitable as boron removal resin. This type of boron-specific resin, (whose use has already been described^{9,10}), in combination with advanced water purification system materials and configuration, enable the production of boron-free ultrapure water suitable for ultratrace analyses.

Materials and Methods

Water purification chain

The specific water purification chain used for trace analytical applications consists of a combination of purification technologies¹¹. The initial purification system, the Elix[®] 10 system, is an advanced water purification system that is made up of a pretreatment filter, a reverse osmosis membrane and an electrodeionization module. It delivers 10 liters per hour of purified water from tap or well water. This purified water is then stored in a specially designed storage reservoir made of polyethylene selected for its low leaching characteristics¹². The water in the reservoir will be distributed to a final polishing system, the Milli-Q[®] Element System, to remove any remaining trace contaminants. The flow schematic of this purification chain, as well as the different sampling ports, are shown in figure 2. Samples are collected after each purification step. They are collected 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 are measured in order to calculate mass balance.

In the final polishing step, (figure 3), two types of purification packs are tested to check boron removal performance. One is a standard Q-Gard[®], purification pack containing mixed-bed ion-exchange resin and activated carbon. The second one, Q-Gard B1, contains boron-specific ion

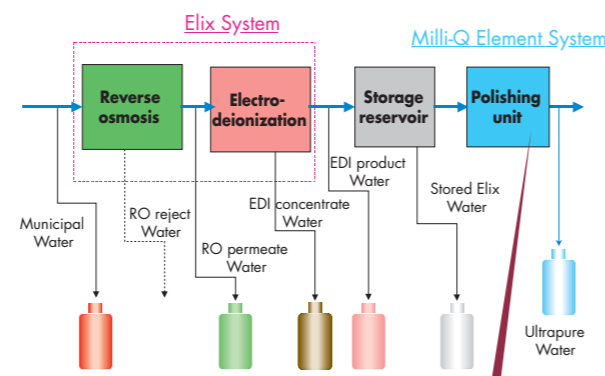


Figure 2: Water purification chain.

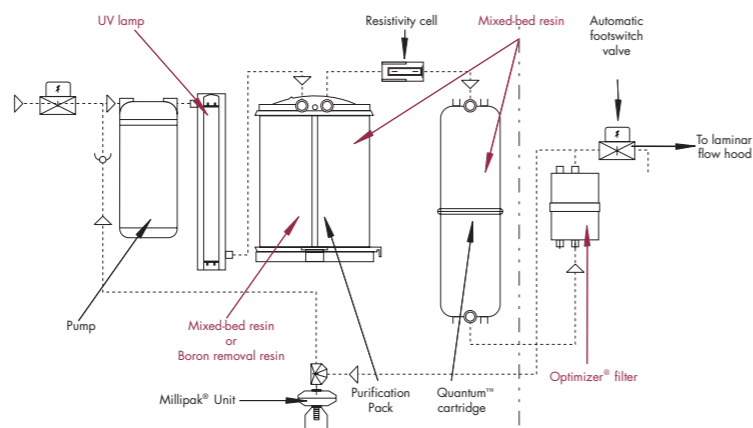


Figure 3: Flow schematic of polishing unit (Milli-Q[®] Element).

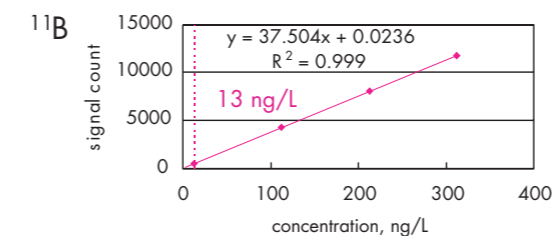
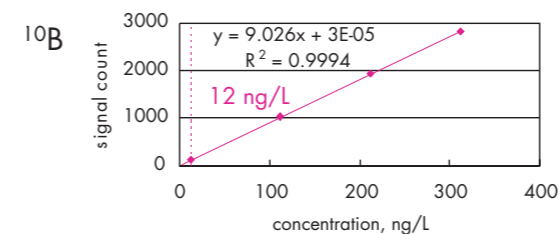


Figure 10: Final polishing unit result: Trace boron analysis.

Element	DL	QL	Milli-Q Element System water
Li	0.026	0.079	0.028
B	1.4	4.1	12.9
Na	0.094	0.29	0.33
Mg	0.012	0.036	0.16
Al	0.075	0.23	< DL (0.033)
K	2.8	8.6	9.6
Ca	3	9	9.1
Cr	0.22	0.67	< DL (0.096)
Mn	0.25	0.77	0.8
Fe	0.048	0.15	0.5
Co	0.5	1.5	< DL (0.42)
Ni	0.13	0.38	< DL (0.063)
Cu	0.075	0.23	< QL (0.13)
Zn	2.2	6.6	< DL (1.4)
Sr	0.022	0.068	< DL (0.004)
Ag	0.076	0.023	0.17
Cd	1.3	3.8	< DL (0.67)
Ba	0.29	0.89	< DL (0.13)
Pb	0.15	0.45	< DL (0.1)

Table 5: Trace elemental analyses by ICP-MS on Milli-Q Element system water – All values in ppt (ng/l).

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 and silica, 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 these weakly-bound ions 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. The EDI module shows good ionic balance for extended periods of time without the need for resin regeneration.

The combination of reverse osmosis and electrodeionization shows good efficiency and stability of ionic reduction, for all ionic substances including boron. In the final water purification unit, early boron breakthrough from ion-exchange resin is eliminated by using a special adsorption device. As a result, the combination of these technologies can provide ultrapure water suitable for ppt and sub ppt trace elemental analysis.

RF power [W]	1100
RF matching [V]	2.31
sampling position [mm]	1.2
torch horizontal position [mm]	-0.3
torch vertical position [mm]	-0.3
plasma gas flow [L/min]	1.6
auxiliary gas flow [L/min]	1
carrier gas flow [L/min]	0.95
blend gas flow [L/min]	0.65
peristaltic pump [rpm]	0.3
spray chamber temp. [°C]	5
plasma torch	quartz
spray chamber	quartz
shield plate	applied
nebulizer	quartz, co-axial type
sampling tube	PFA, id 0.5mm
drawing electrode 1[V]	-70
drawing electrode 2 [V]	-18
plasma gas flow [L/min]	1.6
auxiliary gas flow [L/min]	1
einzel lens 1,3 [V]	-80
einzel lens 2 [V]	-4
omega bias [V]	-120
omega lens (+) [V]	-3
omega lens (-) [V]	3
quadrupole focus [V]	-2
alternate electrode [V]	20
AMU gain	115
AMU offset	175
mass axis gain	0.999
mass axis offset	0
plate bias [V]	-10
pole bias [V]	-10
discriminator [mV]	13
EM voltage [V]	-1700
EM final stage [V]	-278

Table 2: HP4500 ICP-MS conditions for Boron analysis.

A 0.5 mm id PFA tube for sample introduction is connected directly to a coaxial nebulizer and the sample is 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.

The multi-element solution used as a standard was

from SPEX (Cat. No. XSTC-331). It contains 28 elements and was used to perform the different calibration curves.

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 done by standard addition method. In each case, the limit of detection (DL) is taken as 3 times the standard deviation of ten replicates of a blank (Milli-Q SP ICP-MS water, Nihon Millipore Ltd., 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 is 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 , ^{10}B and ^{11}B . Samples are measured from low concentrations to high concentrations. It is recommended that the calibration curve be performed at the end of the analysis: when performing ultratrace analysis on samples such as ultrapure water, diluted 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 is used to monitor these values.

Results and discussion

Initial purification system and reservoir

Of the water treatment steps, special attention was given to analyzing the performance of electrodeionization technology.

The conductivity of water and concentration of boron and silica during operation are shown in figure 6.

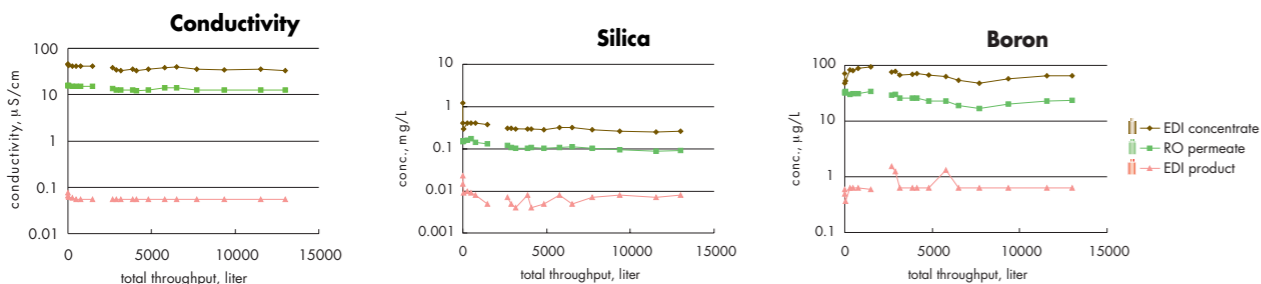


Figure 6: EDI module performance.

The vast majority of contaminants in the feedwater (RO permeate) are removed to yield good quality purified water (EDI product). These removed impurities are concentrated in the wastewater (EDI concentrate). The quality of EDI product water achieves $<0.1 \mu\text{S/cm}$ conductivity, $<1 \mu\text{g/L}$ boron and 0.01 mg/L silica.

Figure 7 shows 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 electrical current removes ionic contaminants, and at the same time, regenerates ion removal capability.

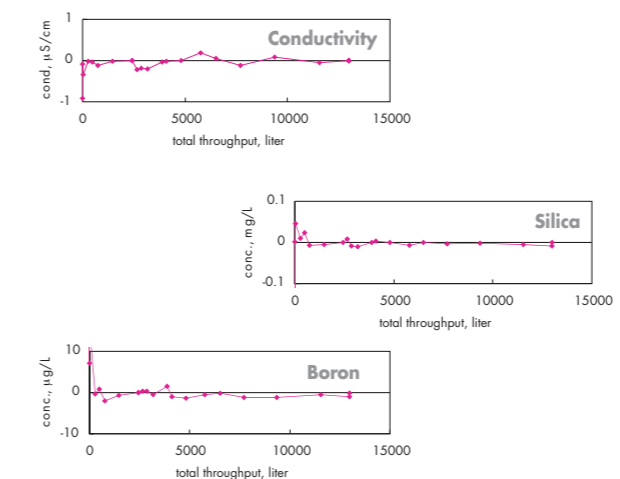


Figure 7: EDI module mass balances.

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 reverse osmosis membrane removes more than 95% 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 $0.06 \mu\text{S/cm}$, almost the theoretical conductivity of pure water. Silica concentration is less than 0.01 mg/L and boron is less than $0.5 \mu\text{g/L}$ 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

	Conductivity $\mu\text{S/cm}$	Silica mg/L	Boron $\mu\text{g/L}$
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

Table 3: Water purification results prior to final polishing step.

filter⁽¹²⁾, 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 precisely. The results are shown in table 4. Even though the conductivity of the purified water is fairly good, large amounts of contaminants are nevertheless detected, for example 340 ng/L of sodium. Levels of impurities not monitored by conductivity meters, are visualized by trace analysis. In addition, boron contamination can be quantified (240 ppt), whereas its value determined by the fluorescence method was below detection limits ($0.5 \mu\text{g/L}$).

Element	EDI product water
Li	0.08
B	240
Na	340
Mg	1.5
Al	5.8
K	22
Ca	16
Cr	0.9
Mn	0.7
Fe	1.5
Co	0.7
Ni	0.3
Cu	0.9
Zn	55
Sr	0.8
Ag	0.2
Cd	0.8
Ba	0.4
Pb	1.2

Table 4: ICP-MS analyses on RO/EDI purified water (ng/l).

This water quality is acceptable for many applications such as chemical analysis and glassware rinsing. It is, however, necessary to further polish this water to meet the requirements for trace elemental analysis.

Final polishing unit purification pack

Performance comparison of the two packs described in the "Materials and Methods" section is shown in figures 8 and 9.

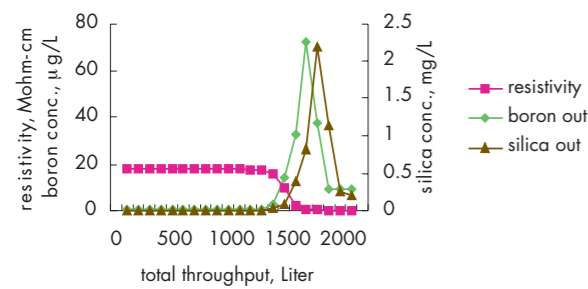


Figure 8: Results with conventional purification pack fed with RO water containing 200 µg/L Si and 10 µg/L B.

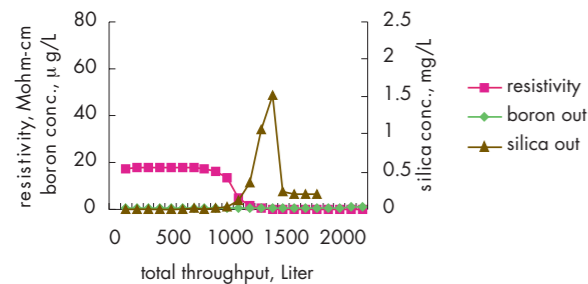


Figure 9: Results with boron-specific purification pack fed with RO water containing 200 µg/L Si and 10 µg/L B.

With the standard pack configuration (figure 8), boron breakthrough is observed just before the dramatic drop in resistivity. 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 feedwater.

In this case, purified water is delivered containing 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 mixed-bed ion-exchange resin. Boric acid is removed by the anion-exchange resin in mixed-bed resin bed. However, boric acid, the dominant form of boron in water, is not well dissociated (first dissociation constant is $7.3 \cdot 10^{-10}$). The release takes place not only because of poor kinetics, due to the low dissociation, but also due to re-exchange of borate ions by 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 to resin.

With the specific boron configuration (figure 9), there is no more 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 structure of this functional group is illustrated in figure 4. The adsorption of boron on the resin is specific and less competitive with other ions than conventional strong basic ion-exchange resin. Boron breakthrough is not observed even after the resistivity drop.

Final ultrapure water delivery system

Final ultrapure water is analyzed by ultra trace analytical techniques. The results in terms of boron analysis are shown in figure 10, and the concentrations of other elements are summarized in table 5.

Boron concentration is expressed by a standard addition calibration curve. Boron measurement is done on both ^{10}B and ^{11}B .

The resulting concentration, as blank equivalent concentration, is 13 ng/L.

The final polishing unit contributes significantly to eliminating trace levels of boron, from 240 ng/L in EDI feedwater to 13 ng/L in final ultrapure water.

Calculated limits of detection/quantification show low enough values to execute ng/L level analysis. For ^{11}B , a detection limit of 1.4 ng/L and a quantification limit of 4.1 ng/L 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; 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.

This final purification system developed specifically for trace analysis is fully described in a previous paper¹⁵.

exchange resin and mixed-bed ion-exchange resin. This pack configuration is illustrated in figure 4.

Boron breakthrough studies are performed under challenging conditions: the purification pack is fed with RO-treated well water, containing 10 µg/L of boron, 0.2 mg/L of silica and 30 mg/L of carbon dioxide, at 15 µS/cm conductivity. The flow rate is adjusted to 1500 ml/min to have the same kinetic performance as normal operating conditions of the final polishing system. Samples of water purified by this pack are collected every 100 liters and analyzed for boron and silica content. The resistivity of this purified water is also monitored simultaneously. Finally, the water obtained through the various purification technologies is analyzed by trace analysis.

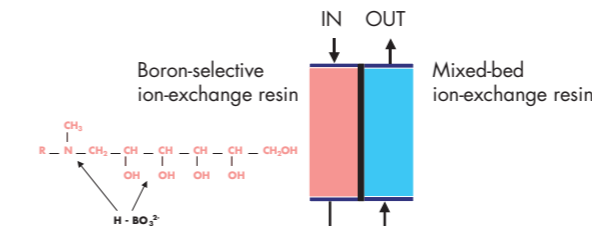


Figure 4: Configuration of special pack for boron removal.

Analytical Methods

Boron analysis

To evaluate medium-to high-range boron concentrations in tap and purified water, a spectrofluorometric method is 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.¹³ and modified by Motomizu et al.¹⁴ for high sensitivity and flow injection methods. In this study, a new modified method is developed to adapt it to the analysis of purified water. To maximize the sensitivity, the pH of the reagent is adjusted to 6 with excitation at 313 nm and emission at 360 nm. The chromotropic

Boron analysis (> 1 µg/L)
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 minutes

excitation at 313 nm
emission at 360 nm
band pass 10 nm
1 cm cuvette

Limit of detection 0.5 µg/L
Precision 4% at 10 µg/L

Figure 5: Medium-to high-range boron analysis.

reagent is prepared by dissolving EDTA 2Na, sodium acetate and chromotropic acid; pH is adjusted by adding acetic acid. The precise analytical procedure is described in figure 5. For trace determination of boron, see the procedure described in the trace elemental analysis section below.

Silica analysis

Silica is determined by a spectrophotometric method with a silica-molybdate complex. Depending on the concentration range, a silica molybdate complex determination at 450 nm (>1mg/L) and a hetero poly blue determination at 815 nm (<1mg/L) are selected. The reagents and spectrophotometer used are from the Hach Company.

Trace elemental analysis

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

- To perform multi-elemental measurement simultaneously, with the exception of boron, cool plasma and shield torch mode are used to eliminate poly atomic interference. The ICP-MS is 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.

RF power [W]	600
RF matching [V]	2.3
sampling position [mm]	14.3
torch horizontal position [mm]	0
torch vertical position [mm]	0
plasma gas flow [L/min]	16
auxiliary gas flow [L/min]	1
carrier gas flow [L/min]	1.19
blend gas flow [L/min]	0.4
peristaltic pump [rpm]	0.3
spray chamber temp. [°C]	0
plasma torch	quartz
spray chamber	quartz
shield plate	applied
nebulizer	quartz, co-axial type
sampling tube	PFA, id 0.15mm
drawing electrode 1[V]	-80
drawing electrode 2 [V]	-19
einzel lens 1.3 [V]	-80
einzel lens 2 [V]	-4
omega vias [V]	-100
omega lens (+) [V]	-8
AMU gain	115
AMU offset	175
mass axis gain	0.999
mass axis offset	0
plate vias [V]	-10
pole vias [V]	-10
discriminator [mV]	13
EM voltage [V]	-1700
EM final stage [V]	-278

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

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