

Using ultrapure water in ion chromatography to run analyses at the ng/L level

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Abstract

Thanks to enhanced capabilities, ion chromatography (IC) occupies an increasing position in many types of applications. Achieving ideal performances for an extended life-time can only be reached, however, if the IC system is operated in optimum experimental conditions. Among the various parameters that need to be controlled, water is particularly important, because it is used throughout the analysis, from sample preparation to column rinsing, elution, and mobile phase preparation. More and more, devices are included in IC systems to generate the eluent in situ, and ultrapure water becomes the major reagent. Data of pre-concentration of high purity water show that detection limits at the ng/L level can be expected with water purified using the right combination of technologies.

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Keywords: Water, ultrapure; Inorganic cations; Inorganic anions

1. Introduction

Due to the increased sophistication of instrumentation, analytical detection limits have reached ng/L levels on a routine basis, and even pg/L levels under certain conditions. Among the various methods available to analyze ions, ion chromatography (IC) combined with conductivity measurement has become a solid and popular method for analyzing a large variety of anions and cations in dilute samples [1–3]. This method has been developed in several research areas, such as the study of Antarctic ice [4], in the semi-conductor industry [5], and in analytical research domains, such as environmental analyses of air [6], soil [7], and water [8,9]. The need for qualification and validation of drinking water, and for meeting new standards and regulations has also encouraged more widespread use of IC, as well as the development of novel analytical methods and techniques. Beside technical performances of the instruments, careful sample handling and reagent purity are the main parameters that can be controlled to record trace analysis data with confidence [10]. In IC, water is one of the most important reagent, because it is used in so many areas: for rinsing of

chromatography chains, for dilution and preparation of blanks, standards and samples, and for mobile phase preparation. Because of this broad range of applications and the volumes required, extreme care must be taken with water quality. In particular, in trace ion analysis, using high purity water of constant quality and free of residual ions is essential.

There is a real challenge involved in developing water purification systems that can produce a quality of water suitable for trace analysis, and that can monitor this water quality on demand, in compliance with Good Laboratory Practices. Concentrations of the major ions detected in tap water were studied by IC at various stages of a water purification chain, from the ppm to the ppt level. The benefits of purification technologies utilized to achieve such detection limits are reviewed.

2. Materials and methods

2.1. General

Standard solutions for trace analysis were prepared by mixing and diluting standard solutions (from SpexCertiprep, ca. 1000 ppm) for each ion. Ultrapure water from the Milli-Q Element system (Millipore, Billerica, MA, USA) was used for dilution. Standard linear regressions were forced through

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the origin and had the following slopes and correlation coefficients: Li (0.2482, correlation coefficient 99.99, concentrations 0.25, 0.375, 0.50 and 1 $\mu\text{g/L}$); Na (0.0877, correlation coefficient 99.75, concentrations 0.50, 0.75, 1 and 2 $\mu\text{g/L}$); K (0.0583, correlation coefficient 99.76, concentrations 1, 1.5, 2 and 4 $\mu\text{g/L}$); Mg (0.1348, correlation coefficient 99.81, concentrations 1, 1.5, 2 and 4 $\mu\text{g/L}$); Ca (0.0997, correlation coefficient 99.96, concentrations 2, 3, 4 and 8 $\mu\text{g/L}$). Verification of the standard curves was performed with mixed standard 0.5 $\mu\text{g/L}$.

Ion chromatography was performed using a Dionex (Sunnyvale, CA, USA) DX 500 apparatus with a GP50 pump and an AS40 autosampler, connected to a CD20 conductivity meter with Peaknet software. An ASRS Ultra suppressor, at 100 mA, with an external water feed, was used for anion chromatography, and a CSRS Ultra suppressor, with a 50 mA recycle mode, was used for cations. Quantification limit was taken as 10 times S/N.

The pretreatment water purification system was an Elix 10 system (Millipore), combining reverse osmosis and electrodeionization, and delivering 10 L/h of 5 $\text{M}\Omega\cdot\text{cm}$ water. A 60 L polyethylene reservoir (Millipore) equipped with an air-vent filter was used to store water. The polishing unit was a Milli-Q Element ultrapure water purification system (Millipore), with QGard01 and Quantum IX cartridges. These cartridges contain high quality Jetpore (Rohm&Haas, Philadelphia, PA, USA) mixed-bed ion-exchange resins. Resistivity of the high purity water delivered was consistently 18.2 $\text{M}\Omega\cdot\text{cm}$, compensated at 25 °C.

2.2. Column ion chromatography

For anion chromatography, an IonPac AS12A/AG12A column (250 mm \times 4 mm) with a 2.7 mM Na_2CO_3 –0.3 mM NaHCO_3 eluent at a 1.5 mL/min flow rate, was used. For cation analysis, an IonPac CS12A/CG12A column (250 mm \times 4 mm), with a 20 mM methanesulfonic acid eluent at a 1.0 mL/min flow rate was used. Samples were injected by the AS40 automated sampler to sample loops of 25 and 200 μL .

2.3. Sample preparation

Polyethylene (PE) bottles were rinsed three times before sample collection, and 1 L of water was flushed through the system before collecting samples. Samples of 50 mL were collected. Volumes of 25 μL were injected for the 50–5000 $\mu\text{g/L}$ range and 200 μL for the 5–1000 $\mu\text{g/L}$ range.

2.4. Trace analysis

For trace analysis, the same columns and suppressors were used, but the injection loop was replaced by a Dionex TAC-2 pre-concentration column for trace anion analysis, and by a Dionex TCC-2 for cation trace analysis. Samples in PE bottles were placed inside a chamber pressurized (2 bar) by

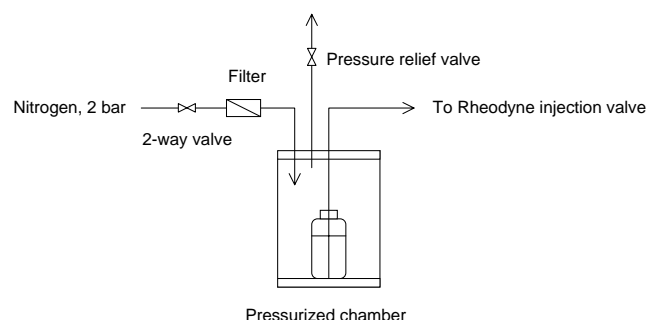


Fig. 1. Pressurized injection line used for trace analysis.

filtered N_2 (Fig. 1). Samples of 7 mL were pneumatically loaded onto the pre-concentration column at a 1 mL/min rate.

The pressurized chamber was a mini-reservoir RC800, Amicon/Millipore (Billerica, MA, USA) and the sampling tubes used were made of PFA, with outside diameter of 1/8 in. (1 in. = 2.54 cm) pierced through the chamber. The gas filter employed was the Wafergard F II from Mykrolis (Billerica, MA, USA). Before pre-concentration loading, the injection line (tube–chamber–up to the rheodyne injection valve) was flushed for 10 min with the water sample. The sample went directly to drain from the rheodyne valve, and the pre-concentration column was in the eluent line during this 10 min period. This period of time served also to stabilize the pressure of the chamber and the flow rate.

3. Water purification chain

A water purification chain designed to produce high purity water for analytical applications requires a combination of several technologies. The chain can be formally divided into two basic parts: (1) the pretreatment, that involves an initial purification system and which produces pure water that is stored in a reservoir; and (2) the final purification system, so-called polishing unit, which delivers ultrapure water (Fig. 2). The intermediary storage is a necessary step, because flow rates are very different between the two purification systems. Water stored in the reservoir, however, can be used for purposes such as glassware washing.

The pretreatment system described in this study combined reverse osmosis (RO) and electrodeionization (EDI) technologies. Following a protective pretreatment pack, water was processed through a spiral thin film composite (polyamide and polysulfone) semi-permeable RO membrane. Reverse osmosis is a widely used technology that removes the bulk of the contaminants, including ions, present in the tap feedwater [11]. The RO permeate water was then directed to an EDI module, which combines ion-exchange membranes, ion-exchange resins, and an electrical current (dc) [12–15]. The current also continuously regenerates the ion-exchange resins, avoiding the need for resin replacement. The RO/EDI unit used in these experiments delivered 10 L/h of purified water to the storage reservoir. The conical

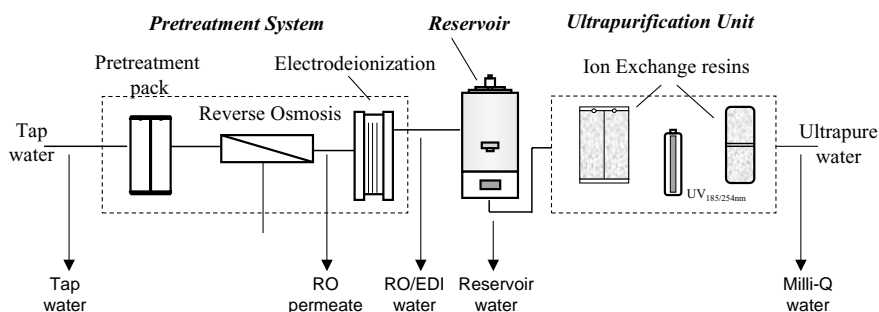


Fig. 2. Water purification chain and sampling ports.

bottom storage reservoir is made of blow-molded polyethylene, selected for its high grade quality (low release of extractable from the polymers) [16]. Water was then fed to the final polishing unit to remove traces of residual ions.

The Milli-Q Element system was selected here as a final ultra-purification system, and delivered ultrapure water treated by photooxidation and ion exchange (Fig. 2) [17]. The photooxidation process employs a dual wavelength ($\lambda = 185$ and 254 nm) low pressure mercury UV lamp, causing organic chelating molecules to break up, and inducing a release of chelated ions. Breaking up the organics also helps to avoid organic fouling of the chromatography media. Ions are then removed by mixed-bed ion-exchange resins made of low leaching materials. The anion resin is based on polymer grafted with quaternary ammonium groups, while benzenesulfonates are the active functional groups of the cation resin.

The flow schematic depicted in Fig. 2 shows the various sampling ports along the purification chain. Samples were collected in PE bottles [18] that were previously rinsed thoroughly with ultrapure water. Sampling ports were selected to monitor the efficiency of each purification step: tap water, RO permeate water, EDI product water, reservoir water, and final ultrapure water.

4. Results

4.1. Pretreatment RO/EDI purification unit: to the $\mu\text{g/L}$ level

In the water purification configuration selected, reverse osmosis was the first process (Fig. 2) employed to eliminate the bulk of the ions. Concentrations of the major ions present in tap water (Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , F^- , Cl^- , NO_3^- , and SO_4^{2-}) and the respective concentrations in the RO permeate are reported in Table 1. Also mentioned are the percentages of rejection, i.e. the percentage of each ion eliminated by RO ($(\text{total ion} - \text{remaining ion})/\text{total ion} \times 100$). The RO process is clearly a very efficient technology to remove a very large proportion (87–99%, depending on ion) of ions present in tap water. The selective permeability of a particular ion across the RO membrane is a function of

its charge, the size, and the solvation. Thus, divalent ions are removed more efficiently (>99% for Mg^{2+} and Ca^{2+}) than monovalent ions (87–93%), due to the charge and the resulting interaction with the hydrophilic RO membrane. Higher valence ions have less affinity for the polysulfone membrane and they do not diffuse well through the RO semi-permeable membrane, remaining in the waste side of the RO membrane. In parallel with ion concentrations, the conductivity decreased from $569 \mu\text{S/cm}$ in tap water to $12.3 \mu\text{S/cm}$ in RO permeate, corresponding to an overall ionic rejection of 97.8%. Because the ion rejection is a percentage of the incoming total ion concentration, it is clear that the ion concentration in the RO permeate is feedwater related.

Monitoring of ion concentrations over a 20 min period (ca. 3.3 L) showed that the system reached the final concentration within 5 min, or after 0.8 L (Fig. 3A and B). More importantly, the ion concentration remained stable for all ions studied, as long as the feedwater quality remained stable. As could be anticipated, the conductivity readings paralleled those results and reached a stable value within 5 min. So, RO process is efficient in consistently removing all types of ions, which makes it particularly suitable as the initial purification step in a complete water purification chain. In addition to removing ions, one the major advantages in using RO is the ability of the process to eliminate above 99% of organic molecules ($M_r > 200$), bacteria, and particulates, thus preventing fouling and spoilage of further parts of the water purification system.

Table 1
Effect of RO and EDI process on ion concentration

Ion	Tap water ^a	RO permeate ^a	Rejection (%)	EDI water ^a
Li^+	2.9	0.19	93.4	<1
Na^+	14599	1868	87.2	<1
K^+	3138	371	88.2	<1
Mg^{2+}	6438	20	99.7	<1
Ca^{2+}	106502	584	99.5	<1
F^-	578	6	99.0	<1
Cl^-	45477	831	98.2	<1
NO_3^-	13843	1756	87.3	<1
SO_4^{2-}	117546	232	99.8	<1

^a Ion concentrations in ppb ($\mu\text{g/L}$).

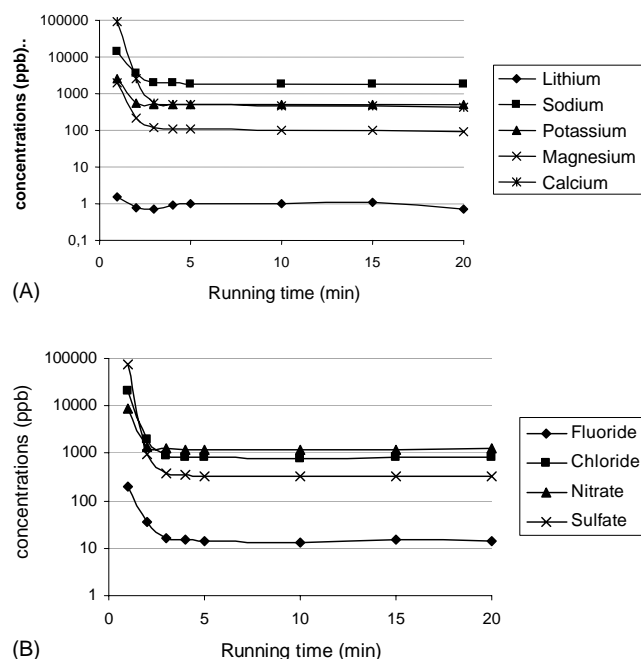


Fig. 3. Reverse osmosis performance for cation (A) and anion (B) elimination (ppb = $\mu\text{g/L}$).

Following the initial bulk removal of ions by RO, EDI [12] was applied, and the results reported in Table 1 showed a clear decrease in all ion concentrations from the RO permeate water to the EDI product water. Concentrations obtained in the product water were $<1 \mu\text{g/L}$ for every ion studied, and the conductivity was $0.2 \mu\text{S/cm}$ (resistivity = $5 \text{ M}\Omega\cdot\text{cm}$). To the difference of RO purification, removal of ions by EDI is much less dependent on the nature of the ions. The process of electrodeionization is based on the mobility of the ions, on their affinity for ion-exchange resins and on the current applied across the EDI module. The current also serves for resin regeneration. Indeed, current induces electrolysis of water, and the protons (H^+) exchange with cations at the binding sites of the resins, while the hydroxide ions (OH^-) exchange with anions.

Chromatograms (Fig. 4A and B) showed the decrease in ion concentrations from tap water to RO water to RO/EDI water. Under the experimental conditions described here, no more ions were detected at the $\mu\text{g/L}$ level. Estimate of the remaining ionic contamination was obtained in a separate study using inductively coupled plasma (ICP) MS analysis, ranging from 0.3 ng/L for Cr to 545 ng/L for Na [17].

4.2. Ultra-purification unit: to ng/L levels

While an EDI system fed by RO permeate water delivers water with ionic concentrations at the ppb level, a higher water purity is needed for ion chromatography. To reach ng/L and sub-ng/L purification levels, a water ultra-purification system, which employs purification technologies and range of materials [17] designed for trace ion removal, was set up

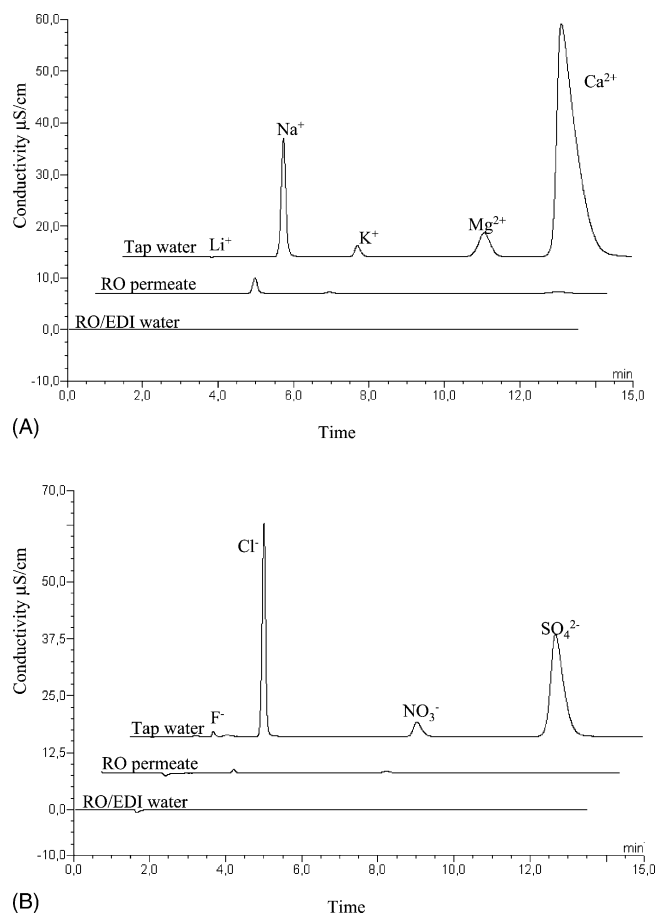


Fig. 4. Ion chromatograms showing the concentration of cations (A) and anions (B) in tap water, RO permeate, and EDI dilute.

for the ultratrace analysis. Water delivered by the system was consistently at $18.2 \text{ M}\Omega\cdot\text{cm}$. The IC system was fitted with an ion-exchange pre-concentration column to allow for the measurement of lower concentrations of ions. The RO/EDI-fed reservoir water (Fig. 2) and ultrapure (Milli-Q) water were compared to standard solutions. Solutions of cations, Li^+ , Na^+ , K^+ , Mg^{2+} and Ca^{2+} , and anions, F^- , Cl^- , Br^- , NO_2^- , NO_3^- , SO_4^{2-} and PO_4^{3-} , were prepared, with concentrations of 1000 ng/L for each ion. Results were reported in Fig. 5A (cations) and Fig. 5B (anions). Chro-

Table 2
Concentrations (ng/L) of ions in reservoir water and in water from Milli-Q

Ion	Reservoir	Milli-Q
Li^+	<1	<1
Na^+	286	5
K^+	50	<2
Mg^{2+}	6	2
Ca^{2+}	64	35
F^-	<1	<1
Cl^-	254	<1
NO_3^-	369	<1
SO_4^{2-}	238	<1

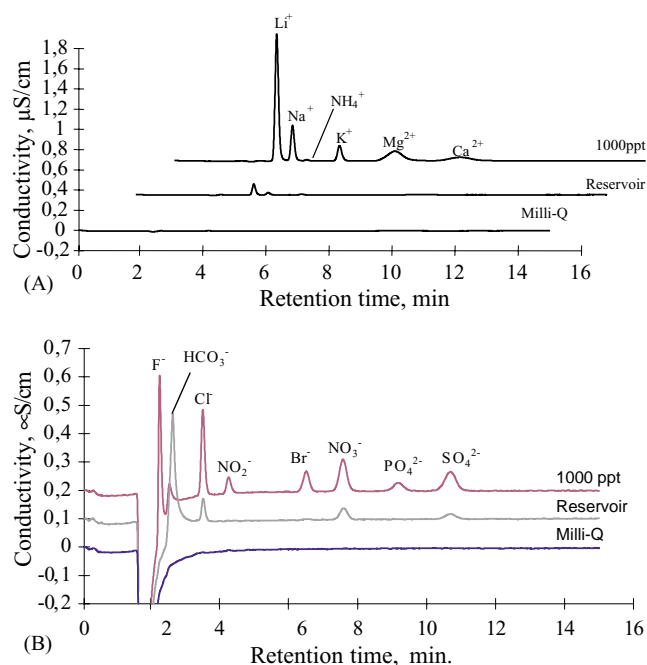


Fig. 5. Ion chromatography of RO-EDI-fed reservoir water, water from Milli-Q and standard (1000 ng/L) cation (A) and anion (B) solutions.

matograms were superimposed for comparison purposes. Comparison of the IC traces indicated a reduction of ion concentrations from reservoir water to Milli-Q water. Integrated peak values were reported in Table 2. Anion concentrations in Milli-Q water were all below detection limits (<1 ng/L). Experiments are currently in progress to improve detection limits for early eluting ions, using KOH as an eluent, an eluent generator, and a CO_2 trap column to reduce baseline drift and improve quantification limits. Cation concentrations also were very low (<1 ng/L), with the exception of Ca^{2+} and NH_4^+ . While the presence of NH_4^+ , most likely arose from airborne NH_3 contamination, the Ca^{2+} contamination probably originated from the tubing and the PE bottle.

Based on these results, Milli-Q water used in standard IC conditions is a suitable water for dilution and blanks. Specific ion concentrations could be improved by using specially designed purification media, by carrying out particular

rinses of the tubing (such as HNO_3 for cation analysis), or by special chromatographic designs and columns.

5. Conclusion

Water delivered by an ultrapure water system, such as the Milli-Q Element, is suitable for IC analysis. It is important, however, that the feedwater for the polishing system is already of a very good quality, to ensure optimum efficiency of the polishing technologies. As sampling techniques and instrumentation constantly improve, detection limits are pushed increasingly lower, and high quality ultrapure water delivered by water purification systems such as the Milli-Q is necessary to meet all the requirements of ultratrace analysis, such as critical cleaning and the preparation of blanks and standard solutions.

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