Importance of pure water in modern ion chromatography

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Ion chromatography (IC) is evolving to meet the analytical demands for more rapid analyses using significantly smaller sample volumes. Sub-5 minute analysis times and sub-µl sample volumes are now becoming available for some applications, along with a number of improved detectors (1). To take full advantage of these changes it is essential that sensitivity and reproducibility are maintained. The purity of the water used has a key role to play.

Introduction

IC has seen a continuing increase in popularity over recent years due to its relative simplicity and improved reliability and utility. A form of liquid chromatography, it uses ion-exchange based stationary phase materials to separate atomic or molecular ions for qualitative or quantitative analysis. When the sample is injected onto the IC column, in the presence of eluent, sample ions are attracted to the stationary phase of the column to differing extents and are eluted sequentially by the eluent. A suppressor module is typically used to remove the eluent and sample counter-ions before the sample is detected (most commonly by conductivity). The different modes of chromatography (anion exchange, cation exchange and ion exclusion) simply relate to the different types of columns used to achieve the separation of the ions, but anion exchange chromatography forms the largest group of IC methods due mainly to the lack of alternatives methods to analyze trace levels of anions. Common applications include testing for common anions (US EPA Method 314.1, perchlorate (US EPA Method 332.0, 314.2) and haloacetic acids (US EPA Method 557) in drinking water.

Using pre-concentration techniques in which ions are initially concentrated on a small ion-exchange column prior to elution into the eluent stream, IC is capable of providing detection limits down to the ng/L scale and for a sample in a homogeneous, ionic form, very little sample preparation is required; quantified results can often be obtained within a matter of minutes. As such, the technique finds application in a diverse range of industries, from pharmaceuticals, bio-analytics and petrochemicals, to the determination of ionic contamination on the surfaces of wafers, chips and packages.

Use of pure water in Ion Chromatography

When analyzing samples at such trace levels, the only way to ensure confidence in the data is to have a reliable IC instrument, high-quality reagents and, especially, pure water. Water is used in all aspects of IC, including the dilution of samples, sample preparation or pre-treatment, preparing blanks and standards, the rinsing of equipment and as an eluent. In reagent-free ion chromatography (RFIC) systems the only flow stream is water, therefore, any impurities present in the water can interfere with the analysis in a number of ways and a reliable source of water free of contamination is essential for reproducible results.

So what type of water impurities is a chromatographer at risk of encountering and what effects could they have?

Types of water impurities

Ultrapure (type I) water is usually produced by the multi-stage treatment of potable mains water but the unique ability of water to dissolve to some extent or other virtually every chemical compound and support practically every form of life means that natural waters inevitably contain a wide range of impurities and contaminants (see Table 1). As the water is rendered potable, many of the contaminants are removed, but some others may be introduced, such as plasticizers from pipe-work systems or bituminous coatings from tanks. The natural water supply, and potable water produced from it, also varies significantly in purity both from one geographical region to another and from season to season.

Type of contaminant	Example source
Ions	Calcium and magnesium dissolved from rock formations (make water hard), ferrous and ferric iron compounds from minerals and rusty pipes, phosphates from detergents, nitrates from fertilizers, silicates leached from sandy river beds
Dissolved organics	Pesticides, herbicides, decayed plant and animal tissues, plasticizers leached from fittings and storage tanks
Suspended particles	Silt, pipe-work debris, colloids
Microorganisms	Amoebae, bacteria, paramecia, diatoms, algae, rotifers, pyrogens
Dissolved gases	Oxygen, carbon dioxide (dissolved in water to give weakly acidic carbonic acid)

Table 1. *Types of water impurities in natural water and their common sources.*

Effects of contamination

With a sensitive technique such as IC, the effects of contamination of the water could have serious consequences, with the potential to negate experimental results.

But what impact can impurities really have on the reliability and reproducibility of an IC analysis?

As summarized in Figure 1, the effects of contamination from ions, organics, colloids, bacteria and gases can all impact on sensitivity and reproducibility to some degree. Contaminating ions tend to have a significant but short-term effect, producing high blanks, high background and chemical interferences that directly degrade results and reduce sensitivity. Varying levels of contaminating ions would result in higher variances in the observed results. While organics, colloids and bacteria will also affect background/blanks, they also tend to have a longer-term impact through media fouling and surface coating that can affect parts of the instrumentation, such as the chromatography column, the detector or inner surfaces of the system itself. The net effect of this type of fouling is anomalous baseline shifts, unknown peaks on the baseline, high noise etc.

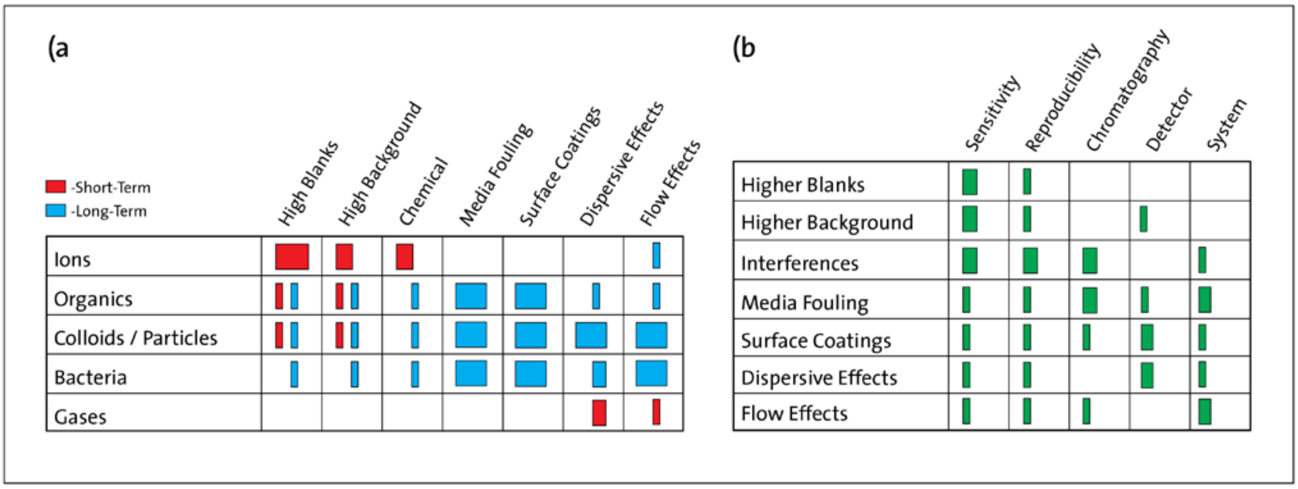


Figure 1. *The effects of water impurities on the ion chromatography technique: (a) effects on the system and (b) the subsequent potential impact on experimental results. The size of the area in each box indices the significance of each effect (qualitative).*

In addition various contaminants can interfere indirectly, but equally seriously; for example, by reacting with reagents or analytes during sample pre-treatment, by contamination of columns or detectors, or by reducing the lifetime of standards. The general objective is not only to reduce the concentrations of specific impurities in the water used, but to minimize the overall contamination levels to facilitate reliable operation of the ion chromatograph.

Figure 2 and Figure 3 demonstrate two examples of interference from poor water quality in the eluent encountered during ion chromatography. Data in Figure 2 shows the effects on trace cation analysis, while data in Figure 3 compares poorer water quality with Type I (18.2 MΩ-cm) water.

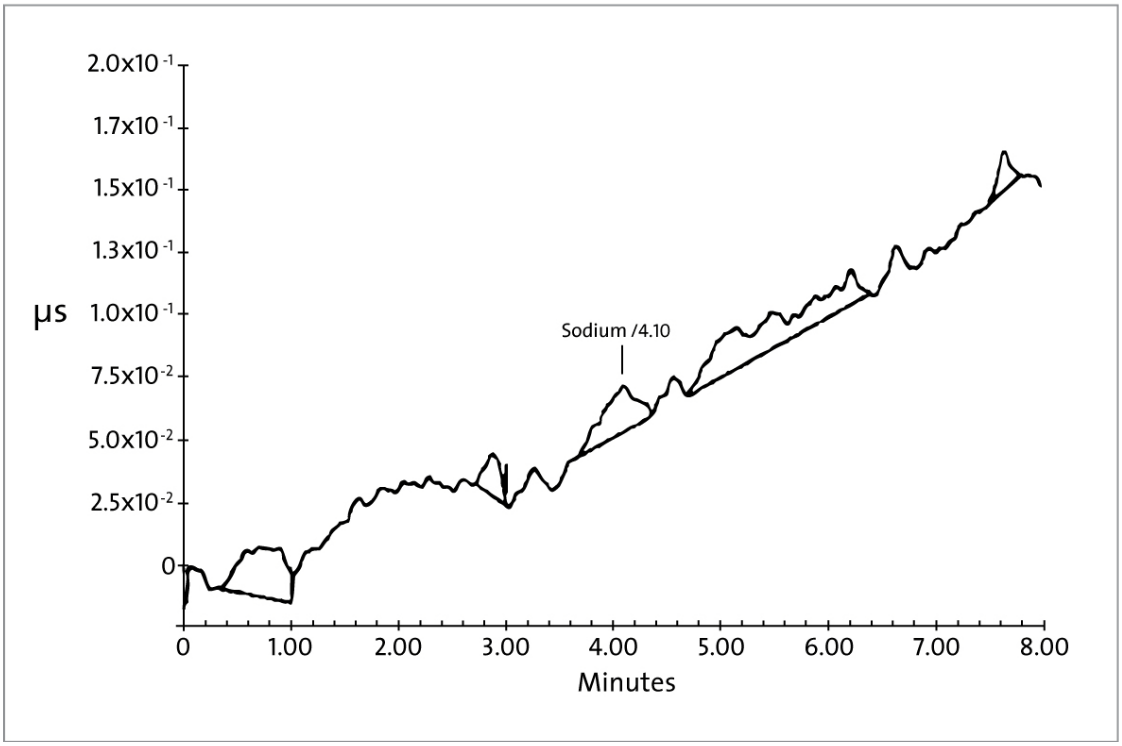


Figure 2 *Trace cation analysis of eluent from ion chromatography performed using water of poor quality.*

Figure 3 *Ionic contaminants from the water affect baseline, integration and resolution. Poor water quality (chromatogram A) and Type I (18.2 MΩ-cm) water (chromatogram B).*

Typical water purity required

For basic isocratic IC applications, good quality general laboratory grade water (Type II pure water) may be adequate with a typical specification shown in Table 2. However, even a “basic measurement” will only benefit from using water purified to Type I ultrapure standards. Extremely low limits of detection (down to ppt levels) can be achieved using IC by pre-concentrating the ions to be measured on a short ion exchange column and then eluting into the eluent stream for separation and analysis. In this case, extremely pure water is essential, requiring a water purification system to deliver 18.2 MΩ-cm resistivity and low TOC. The requirements for water purity are more stringent for ultratrace IC, with ng/L levels of ions and low organics (Table 2).

Impurity	Routine IC	Trace and Ultra-trace IC
Ions	Low ppb (µg/L)	Low ppt (ng/L)
Organics	< 200 ppb	< 10 ppb
Bacteria	< 10 CFU/mL	< 1 CFU/mL
Particles	0.2 µm filter	0.2 µm filter
Gases	<< saturation	<< saturation

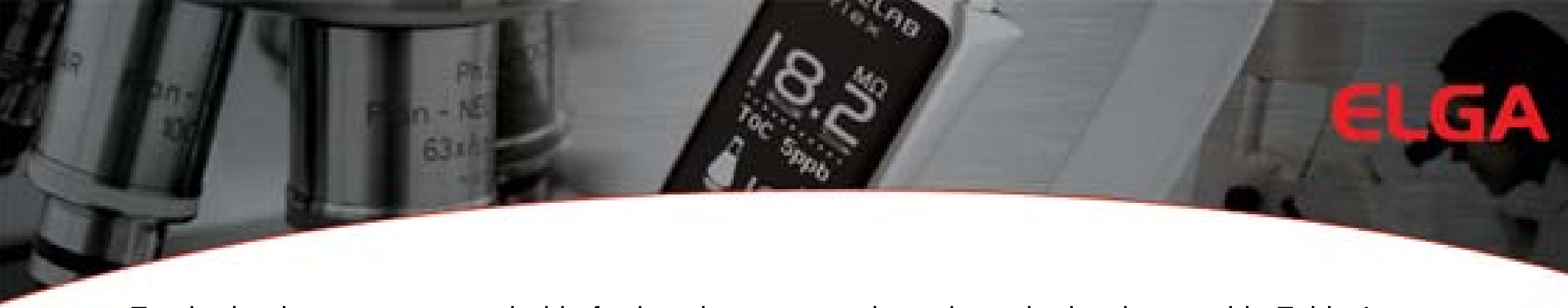
Table 2: *Water purity required for ion chromatography.*

Many water purification systems are required to conform to industry standards set by Pharmacopoeia, ASTM, ISO and CLSI. These international authorities have established water quality standards for general types of application with the water graded according to the level of purity required.

Purification technologies

Water purification can be performed using a range of technologies:

- Distillation
- Ion exchange
- Adsorption
- Micro-filtration
- Ultra-filtration
- Reverse osmosis
- Electrical deionization
- Ultraviolet irradiation



To obtain ultrapure water suitable for ion chromatography to impurity levels stated in Table 1, a combination of technologies are required. Although it is possible to combine all of these technologies in one unit, in practice it can prove more flexible and effective to separate the technologies into two or more stages (except for low-volume applications). The optimum approach to providing ultrapure water has proved to be a combination of a primary-grade purifier based on reverse osmosis followed by a polishing unit (Figure 4).

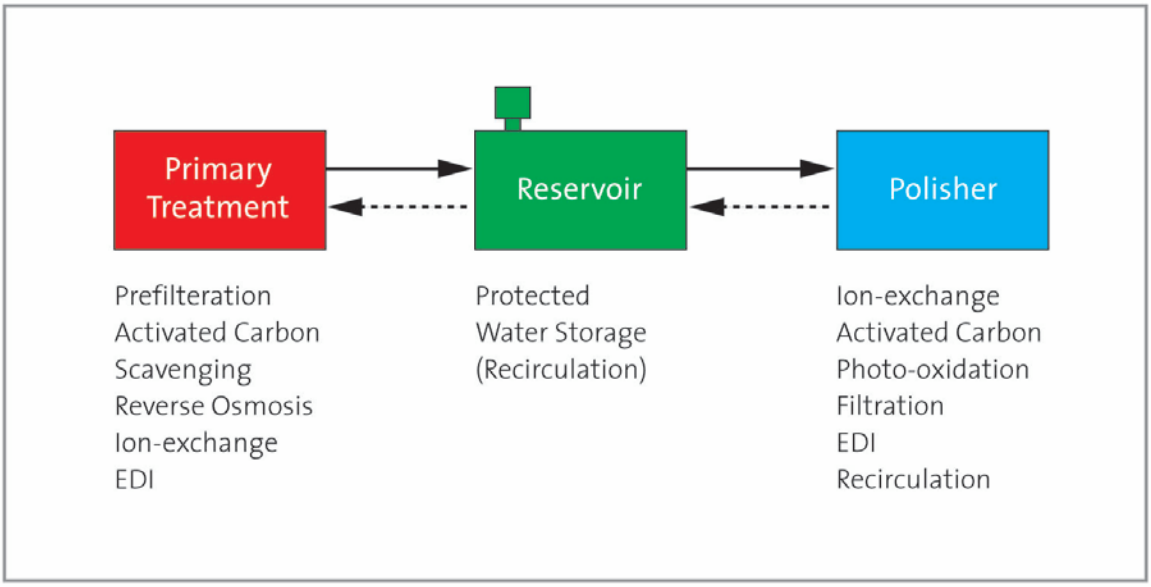


Figure 4: *Typical laboratory water purification system*

Primary treatment may include ion exchange, electro-deionization (EDI) as well as reverse osmosis, pre-filtration and activated carbon technologies. Reverse osmosis is the single most effective method for removing a range of impurities, able to reject up to 98% of all the dissolved salts in water and particles and organic compounds with molecular weight over about 200 Daltons (Figure 5). However, low-molecular weight organics, such as trihalo-methanes and solvents, can pass through into the treated permeate. Removal of these small organic molecules can only be achieved by adsorption onto activated carbon or a similar adsorbent, or by enhanced photo-oxidation using short-wavelength ultraviolet irradiation.

Ultraviolet treatment has the added benefit of controlling bacterial growth and, in combination with microfiltration, can produce totally sterile water to meet the requirements of immunocytochemistry and similar applications. Recirculation through the purification technologies is also recommended (3) as this will help to minimize bacterial build-up in standing water and maintain consistent peak purity.

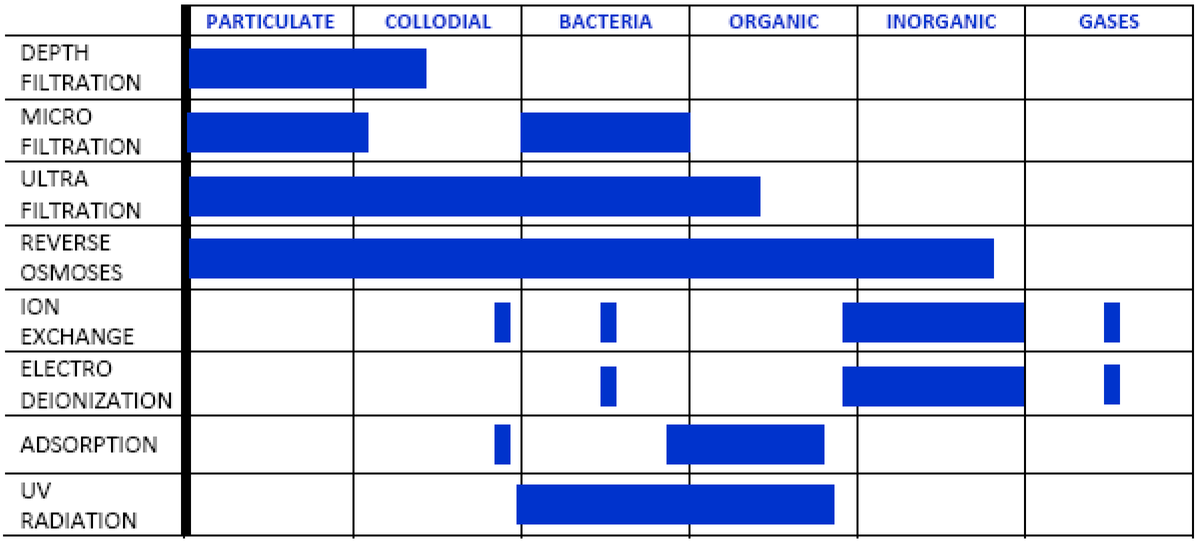
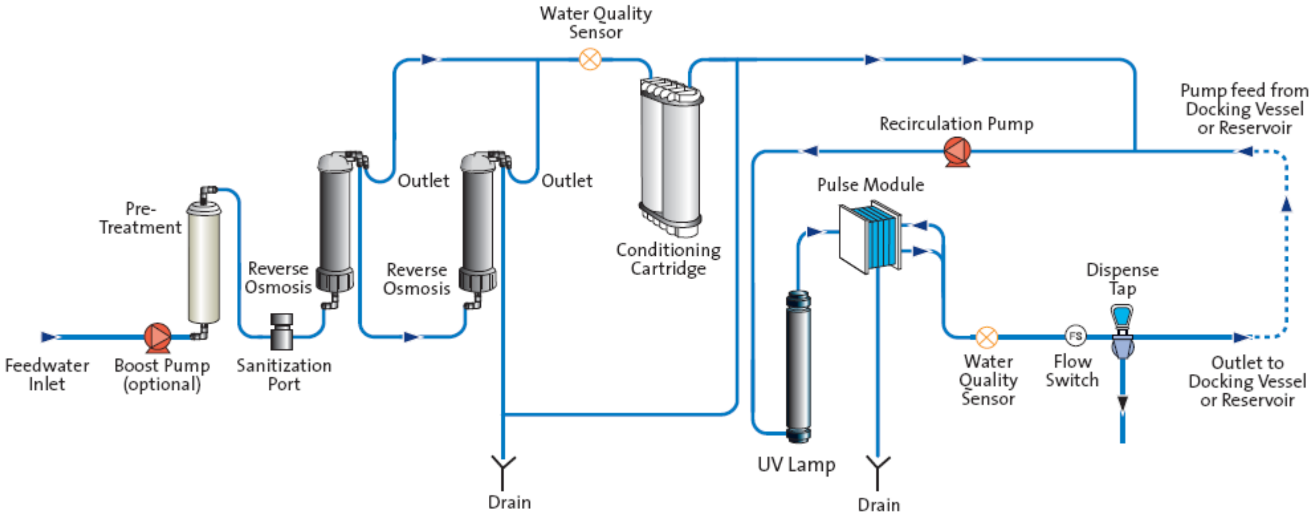


Figure 5: *A combination of purification technologies provides assurance of complete contaminant removal.*

Purification chain at work: an example system

This two-stage purification process has been adopted by many laboratories as an efficient means of providing high-quality pure and ultrapure water for a range of applications. The PURELAB Pulse (**ELGA LabWater**, High Wycombe, Bucks, UK), is an example of a treatment system producing Type II pure water from a potable source using a primary treatment cartridge incorporating fine filtration and granular activated carbon to adsorb organics and remove chlorine, followed by reverse osmosis to remove up to 98% of dissolved salts and 99% of organic and particulate contaminants (including bacteria and viruses) and recirculation through ultraviolet (UV) and electro-deionization (EDI) modules to control bacteria and reduce ionic levels to ppb concentrations . The water produced is ideal for feeding ultrapure water systems and for many laboratory applications including basic IC and general analysis (meeting ASTM type 3, CLSI CLRW and pharmacopeia standards).

Process Flow **PURELAB Pulse**



The pure water is then purified to Type I ultrapure standard using a PURELAB flex or PURELAB Ultra Analytic. These systems both combine absorbents, ion exchange resins, 185nm UV and membrane processes to purify the water to 18.2 MΩ-cm in order to meet ASTM Type I specifications. The resulting water has a total concentration of ions of less than 0.1 µg/L, less than 5 µg/L TOC and bacterial counts below 1 CFU/ml, ideal for ultra-trace IC applications and other critical analytical techniques such as ICP-MS. Both polishers include real-time resistivity and TOC monitoring.

Conclusion

For IC applications, especially at trace levels, contaminants of all types (organic, particulate, bacterial, and gaseous as well as ionic) can seriously affect the quality of the data produced. A Type I ultrapure water system is required that can guarantee the ionic purity of the water and ensure consistent organic purity. Water suitable for such applications can only be produced by a combination of technologies removing all contaminants. When choosing a laboratory water purification system for analytical applications such as IC, it is essential to consider systems that combine such technologies and incorporate real-time monitoring of water purity in order to have confidence in the water and confidence in the experimental results.

All unattributed experimental data was produced at ELGA's R&D facilities.

1) Ion Chromatography: an Overview and Recent Developments", Swartz M. Chromatography Online, 1st July 2010
2) Dionex (UK) private communication.
3) Clinical and Laboratory Standards Institute. Preparation and Testing of Reagent Water in the Clinical laboratory; Approved Guideline – 4th Edition. CLSI document C3-A4 (2006)
4) "Ultrapure Water for Ion Chromatography" Whitehead P. Journal Of Chromatography A 770(1997) 115-118

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