High Purity Water for Inorganic Analysis

VARIOUS POSSIBILITIES EXIST TO ADDRESS THE SPECIFIC WATER PURITY REQUIREMENTS OF EACH LABORATORY AND FIELD. SOME OF THESE SOLUTIONS ARE IN RELATIONSHIP TO THE NEEDS OF VARIOUS LABORATORIES.

Environmental analysis, microelectronics, material chemistry, and clinical analysis all involve or rely on metal and ion analyses. However, the analytical laboratories in these fields are not all equipped with the same instruments and do not pursue the same analyses. Therefore, a variety of analytical tools and techniques are utilized for measuring various matrices at different concentrations and throughput. Due to the diversity of sample types, the analytical methods differ by the required sensitivity and sample preparation steps.

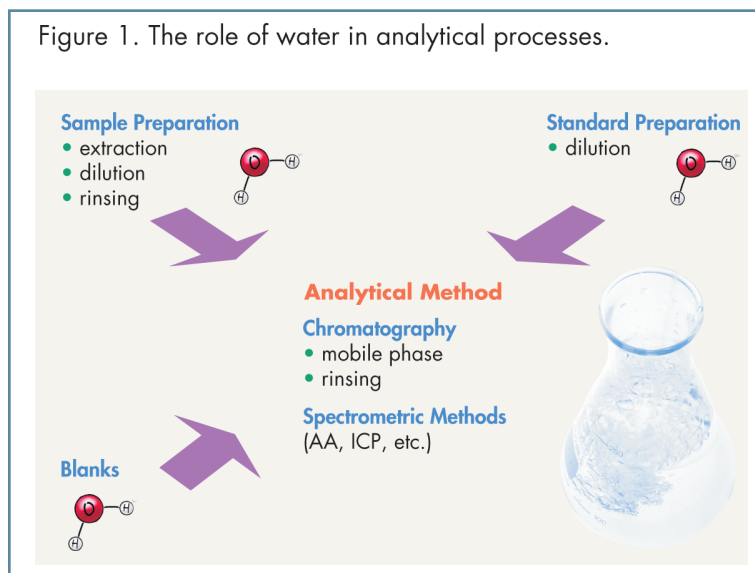## PURIFIED WATER IN THE ANALYTICAL PROCESS

Analytical methods may be divided into those employing water during the actual analysis phase (liquid chromatography-based techniques) and those without water during the analysis step (spectrometric and spectrophotometric techniques – ICP-OES, ICP-MS, and AA). In both cases, water is, or can be, used for sample preparation, standard dilution, blanking, and instrument rinsing (Figure 1). The amount of water added is so important that the presence of any water contaminants may generate interference in the detection range of the sample. In addition, water is the major component of mobile phases and buffers for liquid chromatography techniques (e.g., IC, IC-MS, and CE).

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Figure 1. The role of water in analytical processes.

Sample Preparation
- extraction
- dilution
- rinsing

Standard Preparation
- dilution

Analytical Method

Chromatography
- mobile phase
- rinsing

Spectrometric Methods
(AA, ICP, etc.)

Blanks

WATER QUALITY REQUIREMENTS

Since all the aforementioned techniques measure levels of inorganic analytes, it is important to select water with a high ionic purity. Resistivity has traditionally been a useful parameter to monitor the overall ionic purity of the water and is the basis to distinguish various water quality grades in norms, standards, and guidelines. The resistivity value is based on the sum of the contribution (concentration, valence, and mobility) of each ion present in the water. As the mobility is temperature-dependent, the resistivity value usually is given together with a temperature value. The maximum resistivity value of pure water, arising from water dissociation, is 18.2 MΩ·cm at

Stéphane Mabic,* Beatrice Gerion, Elodie Castillo, and Ichiro Kano

Table 1. Concentrations (ppt) of various elements measured using ICP-MS. The water was produced by a purification chain combining an Elix 5 and a Milli-Q Gradient system. ICP-MS data ware obtained on Perkin Elmer DRC and Agilent 7500 instruments.

Element	Concentration (ppt)
Li	0.01
Na	1.10
Mg	0.16
Al	0.31
K	6.90
Ca	19.00
Ti	3.90
Cr	0.54
Mn	0.13
Fe	2.40
Co	1.40
Ni	0.32
Cu	0.08
Zn	4.40
Cd	0.13
Pb	0.22

Table 2. Blank equivalent concentrations (ppt) of various elements measured using ICP-MS. The water was produced by a purification chain combining an Elix 5 system and a Milli-Q Element system operated in a clean room.

Element	Concentration (ppt)
Li	0.01
Na	0.22
Mg	0.18
Al	0.09
K	2.60
Ca	0.10
Ti	1.70
Cr	0.12
Mn	0.54
Fe	0.40
Co	0.04
Ni	0.20
Cu	0.10
Zn	1.20
Cd	0.11
Pb	0.09

25 °C.[1] This value ensures that the overall concentration of ions is below 1 ppb (1µg/L), in Type-I water.

Other parameters also are important to monitor. Bacteria, which can release ions and behave as particulates, should be minimized because they can spoil the nebulizers and ionization chambers. The organic contamination also needs to be controlled for avoiding spoilage of the instruments. Additionally, organics can make complexes with metals.

Water degrades very rapidly on storage not only due to carbonic acid formation but also because ions and organics from air and containers readily dissolve in high purity water. Bacteria quickly start growing when water remains stagnant in a container and bring additional contamination and issues. Therefore, it is crucial to use freshly produced, high purity water and minimize the storage time.

OPTIONS FOR SELECTING TYPE-I WATER

No unified solution exists for water consumption, utilized techniques, selected methods, required purity and methods for sample preparation. Various possibilities exist to address the specific requirements of each laboratory and field. Some of these solutions are discussed in relationship to the needs of various laboratories.

LOW WATER VOLUME NEED AND MID DETECTION RANGE

Some laboratories require a few liters of water per week only or use water sporadically for sample preparation and analyses campaigns. Others perform analyses at the ppm levels and focus more on flexibility and reliability of the analysis than on the sensitivity of the detection methods. For all these cases, there are simple water purification solutions. Compact and easy-to-operate systems that produce high resistivity water from tap water can be selected. Type-I water is always available and there is no need for water storage over extended periods of time. The purification process from tap to Type-I water may combine reverse osmosis, activated carbon, and ion exchange resins. Other possibilities exist to finalize the water purification only when pure water is available already in the laboratory or facility. These solutions are suitable for environmental laboratories using AA or ICP-OES.

HIGH WATER VOLUME NEEDS AND LOW DETECTION RANGE

For higher sample numbers or higher purity, other combinations of purification technologies can be selected to deliver higher volumes per hour and consistent purity

for analysis in the low detection range. In addition to the resistivity, other parameters, such as the organic level (total organic carbon – TOC), become significant when water is used for chromatography purposes. The overall purity of the water (particulates, organics, ions, and bacteria) may affect the performances of IC and CE for example, and even more so if the chromatography instrument is hyphenated to MS. These contaminants also would affect ICP instruments by spoiling nebulizers, generating deposits on CCD imaging systems, or creating interferences.

The selection of purification technologies requiring low maintenance over a long period of time is recommended for laboratories requiring large volumes, whether it is for sample preparation, dilution of standards, or instrument rinsing. Expected levels of some elements in water produced by a purification chain combining reverse osmosis and electrodeionization followed by ion exchange resins are reported in Table 1.
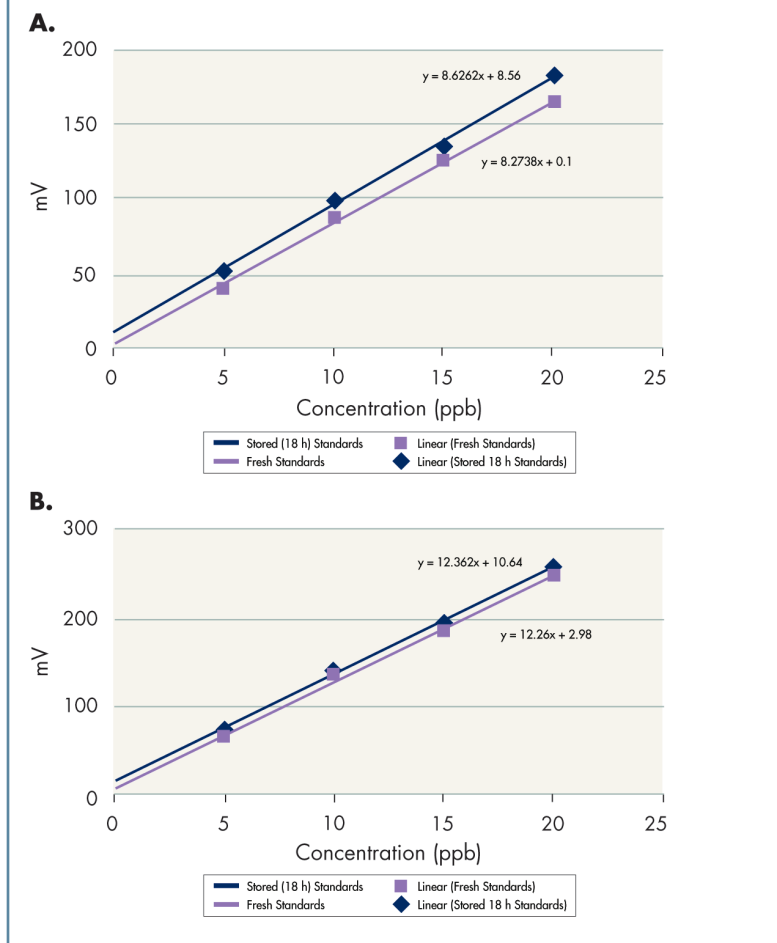
ULTRA LOW DETECTION RANGE (PPT OR SUB-PPT)

Some fields require ultra low ion levels in the water at any time. ICP-MS instruments usually are operated in cleanrooms. A specific water purification system dedicated to trace elemental analysis was developed.[2,3] Design and material selection are important for optimizing the performance of the purification process and reducing water contamination with tubing and filters. The water system can be operated in clean environments (cleanrooms and clean hoods) using a foot-switched pedal to consistently deliver water with extremely low levels of ions. Typical concentrations of some elements are reported in Table 2. Most elements are present at a level below the ppt concentration.[4,5] This water is adapted for analyses in microelectronics, pure metals, as well as in certain research areas, such as glaciology and geochemistry.

UTILIZING HIGH PURITY WATER

Selecting a purification chain and using high purity water is important. The analytical method, including the selection and the cleaning of filters and sampling containers as well as the water handling and usage are just as crucial.

Figure 2. Sodium (A) and Calcium (B) calibration curves obtained with fresh standards (magenta) and standards kept for 18 hours (blue).

A.

$y = 8.6262x + 8.56$

$y = 8.2738x + 0.1$

Legend: Stored (18 h) Standards | Linear (Fresh Standards) | Fresh Standards | Linear (Stored 18 h Standards)

B.

$y = 12.362x + 10.64$

$y = 12.26x + 2.98$

Legend: Stored (18 h) Standards | Linear (Fresh Standards) | Fresh Standards | Linear (Stored 18 h Standards)

These examples highlight the opportunities to add contamination in the analysis.

SAMPLE PREPARATION

The selection and the rinsing of good filters used to clean the samples are particularly important. All filters need to be cleaned with a few milliliters of water. Elements typically released by plastic filters include sulfate, chloride, calcium, potassium, and sodium.

STORAGE OF STANDARDS

In an experiment, Ca and Na standards were prepared using freshly produced Type-I water. The plastic vials containing the standards were installed onto an automatic sampler and IC was run. Standard curves were obtained (5–20 ppb) with high correlation coefficient for both elements. In both cases, the line goes through the

Figure 3. Superimposition of preconcentration chromatograms of Milli-Q water (blue) and two buffers prepared with methanesulfonic acid from two different suppliers (magenta and green).
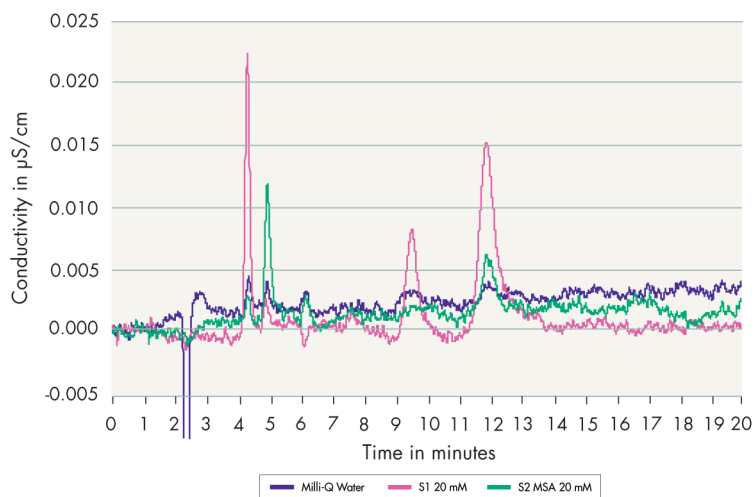
origin. The vials containing the standards were left as is, and 18 h later, the calibration curve was built again (Figure 2). As one can see, very straight standard lines were obtained with high correlation coefficients. However, both the Ca and Na standard curves were off and no longer going through the origin anymore. Overnight, Na and Ca from air had dissolved in the vials (it was checked independently that the vials were not the source of the contamination). The concentrations measured are off. This is a common phenomenon that usually is hidden when an autozero is applied on the IC before starting the measurements. Concentrations measured are not accurate, yet frequent. Reducing water storage, the standards, and samples after preparations should be a constant focus in the analytical process.

REAGENT SELECTION

In the course of IC experiments, we have been confronted with the presence of extraneous peaks on the chromatograms. In searching for the source of the contamination, it appeared that the ACS-grade methane-sulfonic acids used to prepare the mobile phase were not as clean as expected. Two well known brands of acids were compared (Figure 3). It is clear that the reagents will contaminate the mobile phase.

SAMPLING PROTOCOLS

When trace or ultratrace levels of ions are being measured, it is recommended to have well defined protocols to prepare the containers receiving the samples and standards. Ultrapure water becomes an extremely powerful solvent and it can extract elements from any material it touches. Plastic

containers should always be used to collect samples for ionic analysis, because glass releases silica, calcium, and sodium. Protocols have been developed in our application laboratories and can be provided.

DETECTING ISSUES

Recognizing and identifying the source of issues in an analytical process is not always an easy task. While water may sometimes be the cause, the few examples mentioned above show that other sources of contamination may impair the analysis. Water storage is certainly a major source of contamination. Using freshly produced water with a resistivity at 18.2 MΩ·cm at 25 °C ensures that the overall ionic contamination of the water is below 1 ppb. Consequently, ICP levels of Na at 35 ppb or an IC peak of Cl at 20 ppb are unlikely to originate from the water and other sources of contamination should be investigated.

CONCLUSIONS

The opportunity to have high purity water on demand is certainly one of the major assets of a purification system. There are various alternatives to having Type-I water in a laboratory and the selection of a purification chain is based on the needs and requirements of each laboratory. Good practices include reducing the storage times of standards and samples as well as carefully selecting the reagents and rinsing protocols. These are an inherent part of the analytical process and must be optimized to take full advantage of analytical instrumentation. In the laboratory, water is a chemical reagent and should be treated as such.

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Stéphane Mabic, Ph.D. *is the worldwide applications support manager for Millipore's Bioscience Division. Millipore Corporation, Boîte Postale 307, F-78094 St. Quentin en Yvelines, France; Phone: +33 1-30-12-71-40; stephane_mabic@millipore.com; www. millipore.com.*

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