

Ultrapure Water for Elemental Analysis Down to ppt Levels

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Recent enhancements in modern analytical instrumentation have dramatically improved the sensitivity of analysis. Trace elements are now measured at ppt and sub-ppt levels. These levels can be achieved if careful control of the analytical protocol is maintained. Contamination can result from anything that comes into contact with the sample; the laboratory environment, the air, and anything used during sample preparation. Limits of detection down to ppt levels can be achieved if special care is taken with the experimental environment as well as with the quality of the reagents. This includes the ultrapure water used to run blanks, dilute samples or prepare standards. Part of this paper looks at the most sensitive multi-elemental analytical tool, i.e. inductively coupled plasma mass spectrometry (ICP-MS). Some of the most common causes of interference will be reviewed, as well as ways of reducing this interference by specific instrument developments and particular care taken during inductively coupled plasma mass spectrometry analysis. Sub-ppt values for limits of quantification are achievable when the ultrapure water used is produced by a system for which all parts have been carefully selected and whose configuration has been specifically developed for ultratrace purposes. This specific water purification system is described and typical values that can be achieved for blanks with inductively coupled plasma mass spectrometry technology are shown.

1. Introduction

Due to newly developed instrumentation, limits of detection reached by trace analysis are becoming lower and lower. Hyphenated techniques currently used for sample studies and element detection can now reach ng/L levels and even pg/L levels when specific clean conditions and careful experimental handling are ensured. Consequently, instruments and reagents used for blank analysis, standard dilutions and sample preparations need to be of the highest quality. Depending on the elements studied and the environmental conditions of the analytical laboratory, various instrument configurations are possible. Flame or electrothermal atomic absorption spectroscopy (FAAS or ETAAS) and inductively coupled

plasma — optical emission spectroscopy or mass spectrometry (ICP-OES or ICP-MS) are the main technologies employed by trace analysis scientists [1].

2. Materials and methods

2.1. The analytical instrument

ICP-MS is a choice tool for ultratrace analysis. Although technical advances are improving the sensitivity and detection limits of most analytical techniques, instrumental limitations, such as difficulties in performing multi-elemental simultaneous studies, still remain in advanced analytical technologies [2]. This is why, in many applications, ICP-MS is often considered as the ideal instrument to perform fast, multi trace-elemental analyses [3]. This technology allows fast, qualitative analysis of unknown samples, and quantitative, multi-elemental analysis down to ppt (ng/L) and even ppq (pg/L) levels. Application fields where this instrument is a key tool are quite varied: they include the medical area [4], where heavy metals have a significant impact on health; the environmental field, with metal traceability [5]; the nuclear world, with the ability to perform isotope ratio screenings and detect speciation; and the microelectronics industry, with ultratrace analysis in various high purity chemicals, including ultrapure water [6]. Major software development comes with ICP-MS instruments. However, this method still requires skill and specific experimental conditions in acquiring and interpreting data. The actual detection limits depend on the element, the matrix, the sample preparation and the condition of the instrument. Precise method protocols and experimental conditions are developed to perform some specific element determinations.

2.2. The water purification system

Blank levels of a given element are affected by such factors as the purity of sample-treating solutions, container purity, and the general analytical environment. Among the various reagents used during the key steps of blank, standards and sample preparation, is ultrapure water. Investigations are often performed on the background obtained while aspirating air, pure acid or ultrapure water. Ultrapure water such as that produced by a Milli-Q[®] system, causes less spectral interference than high quality nitric acid. Although this acid is purified by sub-boiling, the trace element concentrations are still

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above those of ultrapure water. It is clear that 18.2 M Ω cm is no longer a “quality certification” value. Studies concerning ultratrace analysis show that blank optimization is only achievable when ultrapure water with sub-ppt level contamination for most of the elements is used. Contamination risks are greatly increased when the ultrapure water is stored. Results clearly indicate that the quality of high purity water degrades with storage time. In addition to clean air, the laboratory needs an ultrapure water supply, and the analytical instrument, or at least the sample preparation station, should be located close to the water outlet.

2.3. The pretreatment system

Production of high quality ultrapure water requires a combination of technologies to process tap water to ultrapure water. Water is first purified through a system including reverse osmosis and electrodeionization (EDI). This EDI technology is a key step in the production of ion-free water. The EDI module, where a direct current voltage is applied to the resin-containing cells, maintains consistent water quality with no significant fluctuations due to changes in feed water ion concentration. The high resistivity water produced, presents a low ionic challenge to ultrapure polishing resins. The hydrolysis and ion removal in the EDI module result in a steady-state operation of the resin without exhaustion or the need for regeneration. A more complete description of this RO/EDI treatment, performed in a system called Elix[®], has been previously published. This purified water is then processed in a polishing system where additional technologies produce the ultrapure water suited to ultratrace analysis. Elix water is stored in an intermediate reservoir to provide an adequate flow rate to feed ultrapure water systems. Numerous tests were performed to select the right materials of construction, to define the reservoir design and finally to limit water degradation during storage. As a result of these tests, polyethylene with low extractable levels was selected for the container; a blowmolding process was chosen to ensure smooth and regular inner surfaces for the conical reservoir and a vent filter containing activated carbon and soda lime was developed.

2.4. The ultrapure water polishing system

The ultrapure water system uses high quality ion-exchange mixed bed resin in a pure natural polypropylene housing selected for its low leaching characteristics. The best ultrapure water to optimize blanks and prepare standards is obtained by adding UV photo-oxidation technology within the water system. A 185/254 nm UV lamp placed upstream of the polishing packs ensures the destruction of organics, including those with trapped metals. The released elements can then be retained by the ion exchange resins. A resin for the specific removal of boron is included in the first purification pack. Additionally, an accurate resistivity meter is placed upstream of the final polishing cartridge that contains mixed-bed

resins (Quantum IX) in order to monitor the very first ionic release from the first purification pack (Q-Gard B1). Final filtration is ensured through a 0.1 μ m filter, containing a membrane specifically designed for critical ultratrace applications. This membrane is made of ultra-high molecular weight polyethylene (UHMWPE filter). The specific membrane charged structure removes colloidal traces. The flow schematic of this water purification system called Milli-Q Element is shown in Fig. 1. To be able to collect the ultrapure water directly under a laminar hood, with ease and limited contamination risks, a three meter distance can separate the main system cabinet and the point of use. The delivery of water is ensured via an automatic footswitch solenoid valve.

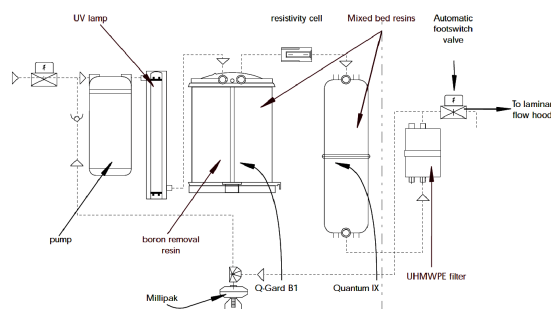


Fig. 1. Flow schematic of the Milli-Q Element water purification system for ultratrace analysis.

3. Experimental requirements

Sample and/or laboratory contamination can affect the accuracy of trace metal analysis. Special care must be taken with the experimental environment, this includes the quality of the reagent used. Moreover, most of the contamination can result from anything that comes into contact with the sample, including glassware, the laboratory environment, the air, and anything used during sample preparation. Even cleanroom gloves can present significant metal contamination. Precise washing protocols are thus established in order to remove any contamination coming from the various containers used to prepare samples and standards. High quality plastic bottles, mainly polyethylene (PE), perfluoroalkoxy (PFA) or fluorinated ethylenepropylene (FEP) are used throughout all sampling and analysis procedures. Several acid and ultrapure water washing steps should be performed prior to running the experiment in order to avoid further leaching from the vials. The impact of contamination coming from the various vials, or sample adsorption on the walls of such containers, have led scientists performing ultratrace analysis to develop cleaning steps for materials. The procedure followed by scientists working in the glaciology field is given hereafter as an example. “Low density PE (LDPE) bottles for storage of samples and plastic tools were acid cleaned in the class 100 environment. Briefly, items were cleaned as follows: rough rinse

with tap water to remove dust; degrease with chloroform and rinsing with ultrapure water; immersion in a first acid bath (HNO₃/ultrapure water 1/3, 50 °C, 2 weeks), and rinsing with ultrapure water; immersion in a second acid bath (HNO₃/ultrapure water 1/1000, 50 °C, two weeks) and rinsing with ultrapure water; immersion in a third acid bath (HNO₃/ultrapure water 1/1000, 50 °C, two weeks); finally, bottles are rinsed several times with ultrapure water, filled with a diluted ultrapure HNO₃ fresh solution and stored inside double polyethylene acid clean bags". Washing steps are even more important in the microelectronics industry, where efficient rinsing protocols should be employed after wafer-cleaning steps.

4. Results and discussion

4.1. Preliminary study

ICP-MS analysis with no element-specific optimization is performed on ultrapure water and counts are recorded to get an idea of the achievable blanks. The addition of 10 ppt standards of the studied elements gives information on the achievable quantification limits. The high counts generated for ⁴⁰Ca clearly show the interference due to ⁴⁰Ar and confirm that specific conditions must be applied to the ICP-MS instrument in order to perform sensitive and accurate calcium determinations.

4.2. Elemental analysis of Milli-Q[®] Element water

A significant number of experiments were performed with a Milli-Q[®] Element system fed by an Elix[®] system. 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

this limit of detection. Values are given for ultrapure water samples, even when these are under limits of quantification. BEC corresponds to the blank equivalent concentration calculated using linear calibration curves obtained with 0.50 and 100 ppt standard solutions for each element (Fig. 2).

Extrapolation to the *x*-axis (*y* = 0) gives the BEC value and is a good curve obtained for Ca, which clearly shows the limitation for this ion (due to instrumentation and experimental conditions). On the other hand, the good Fe results confirm the interference elimination with the chosen ICP-MS conditions as indicated in Sect. 2.

5. Conclusion and perspectives

Taking the environmental field as an example, over the past 10 years, reported background dissolved trace element concentrations have declined from tens of ppb (μg/L) through single digit ppb, to the ppt (ng/L) range. This in fact does not reflect improved water quality, but rather, reduction in contamination introduced during sampling, processing, and analysis. These improved instrumental and experimental procedures highlight the impact of minute contamination. Consequently, the use of very high quality ultrapure water is required to prepare blanks and standards, perform critical cleaning and run high sensitivity analyses. Being able to modulate the polishing cartridge composition according to the application allows blank optimization for trace analysis of a specific element such as boron. Other developments can also be geared to specific needs, such as the focus on silica 25 for example. Additional added features, such as the ability to operate the system with a footswitch, ensure minimum cross contamination by other users and facilitate operation under a laminar hood. The combination of these different advancements in instrumental and purification technologies has resulted in a system that produces ultrapure water suitable or ultratrace analysis at the sub-ppt levels.

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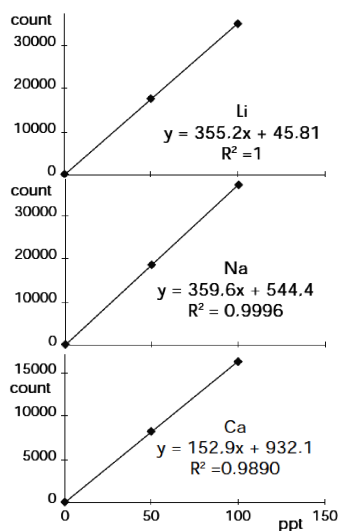


Fig. 2. Selected calibration curves.