

AVAILABLE OPTIONS FOR THE DETERMINATION OF ULTRA TRACE ELEMENTS IN PRISTINE ENVIRONMENTS

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ABSTRACT

There are many key factors that require consideration when trying to successfully determine elemental concentrations at ultra-low levels. Some of these processes include: sample collection, preservation, preparation and the consideration of the choice of instrumental technique for analysis. These all must be taken into account in order to ensure the highest quality and accuracy of the resulting data. This paper will discuss some of the options available for advanced contamination control as well as analytical techniques available for reporting extremely low detection limits. Instrumentation such as high resolution inductively coupled plasma mass spectrometry (HR-ICPMS) and hydride generation atomic fluorescence spectrometry (HG-AFS) will be discussed.

High resolution ICPMS coupled with a clean working environment and procedures has shown through experimental data that for baseline monitoring work, where samples are relatively free of interferences, that extremely low detection limits are accurately achievable to the low parts per trillion levels for many elements including, cadmium, arsenic and selenium. The versatility of high resolution ICPMS has also been extended to biological and seawater testing along with numerous other applications.

Hydride generation AFS has also been demonstrated to be capable of accurate measurements to the low parts per trillion levels for selenium and arsenic. This technology also has the added benefit of being able to measure to these levels in the presence of high chloride concentrations.

INTRODUCTION

The science of environmental testing for elemental determination at ultra-low concentrations involves many complex and interdependent processes, all contributing inherent factors towards the end results. All aspects of this procedure, from sample collection and preservation to sample analysis require careful consideration in order to maintain the integrity of the outcome. This paper describes some of these aspects as well as a general overview of some of the types of instrumentation currently available for the determination of trace metals. A brief discussion on more challenging applications such as seawater and tissue biopsy work is also included.

OVERVIEW OF INSTRUMENTAL OPTIONS

The choice of instrumental analysis will depend on the unique objectives of each project. Since every analytical technique has advantages and limitations, certain techniques will be more suitable than others depending upon the requirements for the work at hand. Some of the considerations that could influence these decisions may include one or several of the following:

- What are the metals of interest?
- What are the detection limit requirements?
- What is the matrix or nature of the samples?
- What are the objectives or reasons for the analysis (baseline monitoring work, regulatory guidelines, etc.)?

Information related to these factors will always be beneficial to testing laboratories, especially to instrument operators. Prior knowledge of sample make-up and any specific reporting limit requirements will enhance the overall efficiency of sample analysis and will ultimately decrease turnaround time. For samples of unknown background, the initial use of an inductively coupled plasma optical emission spectrometry (ICPOES) scan for either qualitative and/or quantitative purposes is common practice in many environmental laboratories.

Inductively Coupled Plasma – Optical Emission Spectrometry (ICPOES)

For decades, this technique has been widely used in many laboratories for the purpose of multi-elemental determination. By measuring the various wavelengths of the emitted light from a given sample, this technology can provide analytical results for more than 30 elements within 3-4 minutes or significantly less, depending on the application. One of the main advantages of ICPOES is an ability to handle matrices high in mineralogical salts such as sludges, industrial wastewaters and seawaters. ICPOES can also offer excellent performance at higher concentration levels. However, one of the major limitations of this technique is its relatively limited sensitivity. For applications requiring lower detection limits, more sensitive techniques such as ICPMS are needed. However, the use of ICPOES as an efficient ‘pre-screening’ mechanism for these other technologies when dealing with samples potentially high in metals can be highly beneficial.

Inductively Coupled Plasma – Mass Spectrometry (ICPMS)

This section will focus on three types of ICPMS technology: quadrupole, reaction/collision cell and sector field.

Both the conventional quadrupole and reaction/collision cell-based ICPMS technology are now readily available technologies used by many environmental testing laboratories. These instruments are also multi-element determination techniques with analysis times comparable to that of ICPOES. The principle of ICP mass spectrometry incorporates the direct measurement of the mass-to-charge ratio of the ions produced from a given sample and is capable of providing much lower detection limits than those achievable by optical emission for many metals. For broad suites of elements, where reporting limits in the low parts per billion (ppb) or parts per trillion (ppt) levels are required, the employment of ICPMS technology is essential. Compared to ICPOES, one of the most significant drawbacks of this technology is its susceptibility to matrix interferences from samples which contain high concentrations of metals. The high salt content from these samples causes depositions surrounding the orifice of the cones in the interface region of the instrument. The effects of this are reflected in the rapid decrease of instrument sensitivity and the suppression of most analyte signals over time.

The advent of reaction/collision cell technology has vastly improved the ability of ICPMS to handle spectral interferences in which atomic or polyatomic species overlap or share the same nominal mass-to-charge ratio as those of the element of interest. To minimize these interferences, the process may involve the introduction of various types of reactive or non-reactive gases, such as ammonia, helium, hydrogen or oxygen into the cell chamber of the instrument. Through a series of different reactions and/or collision processes between ions and molecules, many polyatomic interfering species such as $^{40}\text{Ar}^+$, $^{40}\text{Ar}^{16}\text{O}^+$ and others, are converted to non-interfering species, or in some cases the actual ion of interest is converted into another ion that is free of interferences (Thomas, 2008). However, a consequence of these complex interactions between ions and molecules can be secondary reactions and/or collisions that may result in the generation of other undesirable interfering species and the creation of additional spectral interferences (Thomas, 2008). In spite of this, cell-based ICPMS technology is capable of addressing many spectral interferences in difficult matrices given sufficient analysis time, the appropriate gases and tuning conditions.

High Resolution - Inductively Coupled Plasma Mass Spectrometry (HR-ICPMS)

High resolution-ICPMS or sector field mass spectrometry has been well recognized by some specialists as the premier technology for multi-elemental determination of ultra-trace metals. Although HR-ICPMS is routinely used in many scientific settings such as clinical laboratories, universities and other government agencies, the availability of this service for commercial environmental testing services has been extremely limited. The reason for this is partially related to the high purchasing cost per instrument; approximately three times higher than most low resolution ICPMS instruments. However, for certain applications requiring the lowest possible reporting limits, such as baseline monitoring of pristine waters, some of the advantages offered by Sector Field-ICPMS cannot be duplicated by quadrupole or reaction/collision cell technology.

This technology is uniquely different from the standard quadrupole and cell-based ICPMS instrument in that it employs the use of both a magnetic and electrostatic sector field to separate analyte ions according to their momentum ($p=mv$) and kinetic energy ($k=mv^2/2$) respectively. Depending upon the specificity of the method, this combined ‘double-focusing’ mechanism can permit peak resolutions ($R=m/|\Delta m|$) of $>12,000$ (Table 1). By comparison, peak resolution on a standard quadrupole ICPMS is approximately 300 (Thomas, 2008). This capability to efficiently resolve spectral interferences and vastly reduce the potential for reporting false positives coupled with superior sensitivity are the major advantages of HR-ICPMS (Figure 1).

Table 1: Resolution Requirements for certain Polyatomic Interferences

Analyte and Mass*	Interference and Mass*	M	$ \Delta m $	R**
$^{52}\text{Cr} = 51.94051$	$^{40}\text{Ar}^{12}\text{C} = 51.96238$	51.94051	0.02187	2375
$^{56}\text{Fe} = 55.93494$	$^{40}\text{Ar}^{16}\text{O} = 55.95729$	55.93494	0.02235	2503
$^{51}\text{V} = 50.94396$	$^{35}\text{Cl}^{16}\text{O} = 50.96376$	50.94396	0.01980	2573
$^{75}\text{As} = 74.92160$	$^{40}\text{Ar}^{35}\text{Cl} = 74.93123$	74.92160	0.00963	7780

* Mass values taken from (Audi and Wapstra 1993)

** Resolution is expressed using 10% valley definition

Figure 1: Spectral Interferences

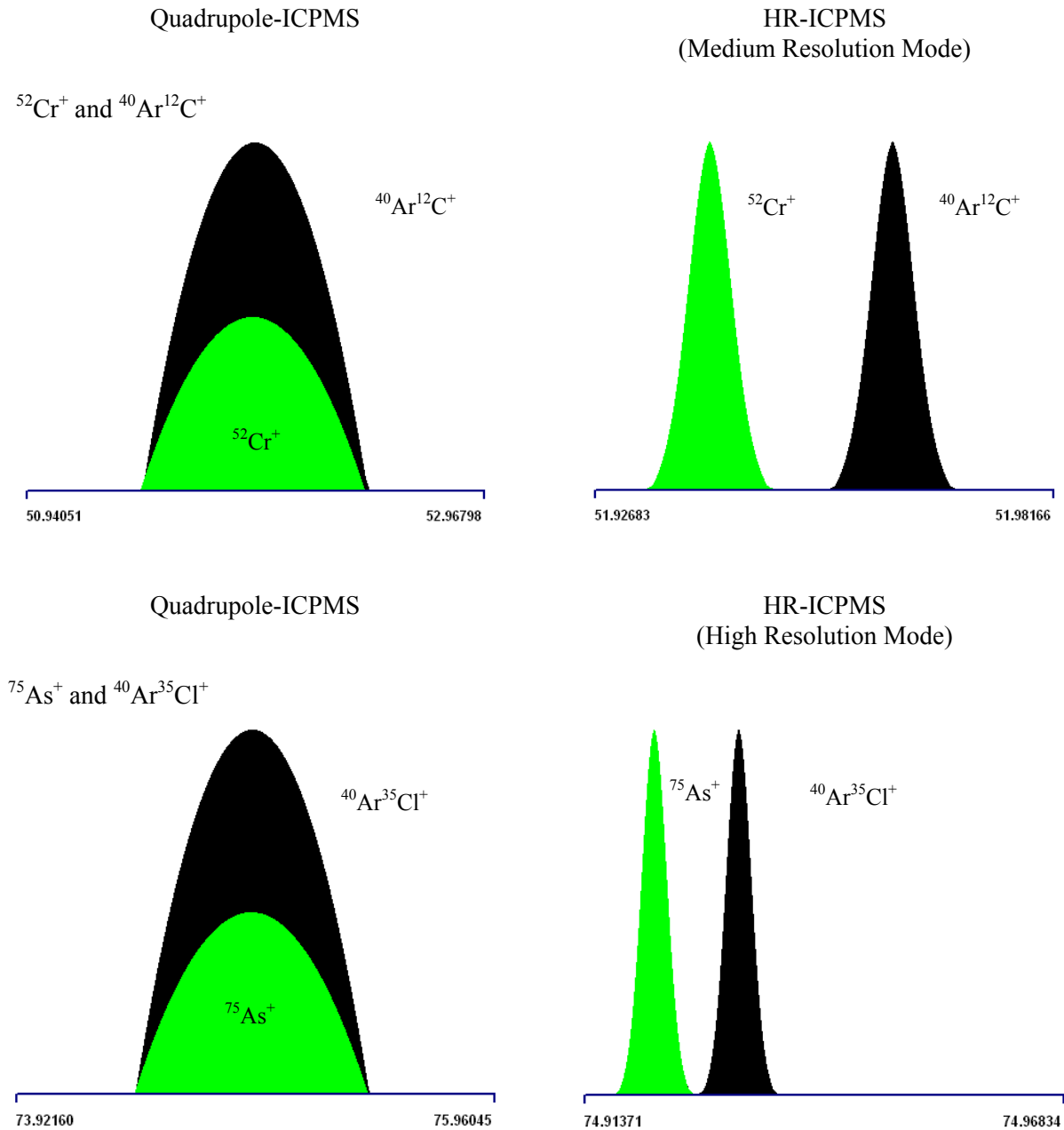
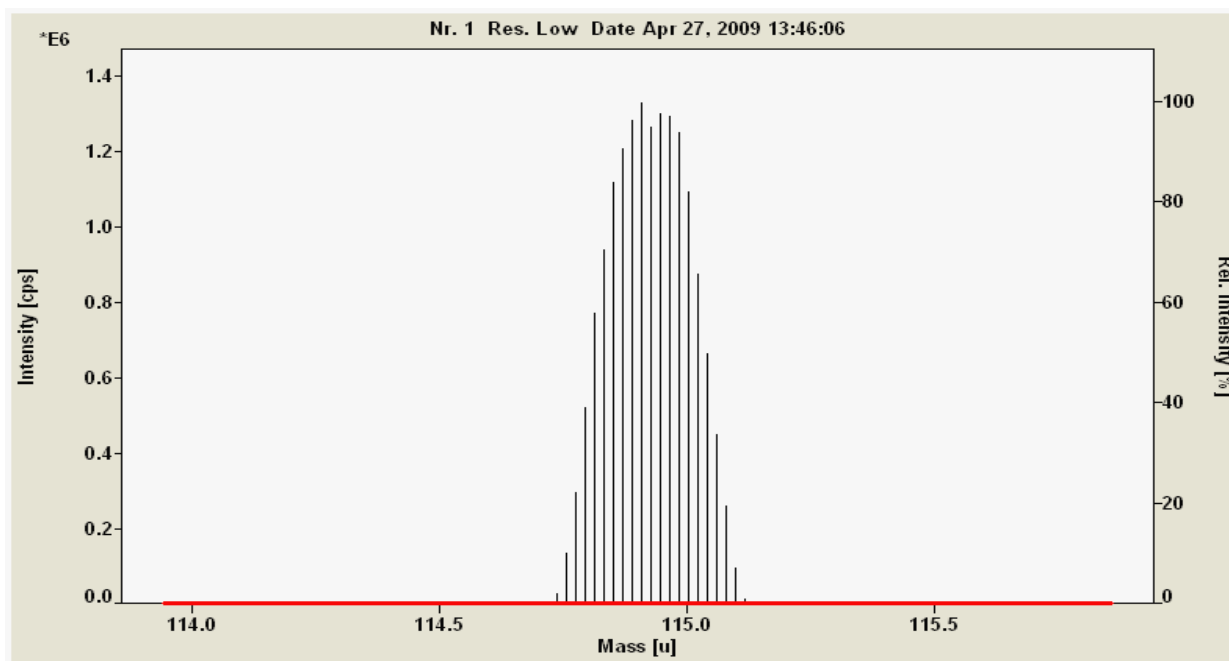


Figure 1: Courtesy of Element 2 Demo Version 3.2 Thermo Electron (Bremen) GmbH, 1997, 2003 Bremen, Germany

The sensitivity offered by HR-ICPMS is unparalleled by any other ICP technology because of its ability to extract ions from the plasma stream at an extraordinary high transmission rate. For instance, a 1 ug/L In^{115} standard under normal operating conditions could readily provide more than a million counts per second (cps) (Figure 2).

Figure 2: Measured intensity of 1 ppb In¹¹⁵ standard



For samples relatively free of matrix interferences, the high signal-to-noise ratio (dark noise <0.2 cps) of sector field ICPMS has resulted in limits of quantitation (Table 2) for many elements that are at least ten-fold lower than those obtainable by either the standard quadrupole or cell technology.

Table 2: Examples of Limits of Quantitation* (LOQ) by HR-ICPMS for elements in high purity water (reported in nanograms per Litre = parts per trillion)

Isotope	LOQ (ng/L)	Isotope	LOQ (ng/L)	Isotope	LOQ (ng/L)
107Ag	0.6	39K***	30	118Sn	2
27Al**	20	7Li	2	88Sr**	2
75As***	4	24Mg**	20	125Te	0.4
11B	30	55Mn**	4	232Th	0.02
138Ba	0.7	98Mo	0.3	47Ti**	9
9Be	0.6	23Na**	200	205Tl	0.08
209Bi	0.04	60Ni**	50	238U	0.06
44Ca**	300	206Pb	0.3	51V**	1
111Cd	0.4	85Rb	0.3	184W	0.05
52Cr**	3	187Re	0.01	89Y	0.04
133Cs	0.2	121Sb	0.5	64Zn**	50
63Cu**	6	77Se***	10	90Zr	0.1
56Fe**	20				

* Calculated as ten times the standard deviation for twenty separate, sequentially analyzed, acidified aliquots. Mass resolution was ~300 unless otherwise indicated: ** ~4000; *** ~10,000.

Hydride Generation - Atomic Fluorescence Spectrometry (HG-AFS)

For situations involving the need for ultra low arsenic or selenium detection limits in matrices high in chloride, such as seawater samples (Table 3) or sediment samples digested with hydrochloric acid, the use of hydride generation atomic fluorescence spectrometry is an available analytical option. Analysis of these sample types by either ICPOES or by non cell- based ICPMS technology can prove to be challenging due to limitations with sensitivity, matrix or spectral interferences from chloride ions.

Table 3: Arsenic in seawater by HG-AFS

Element	NRC CASS-4 (ug/L)		NRC NASS-5 (ug/L)	
	Found	Certified*	Found	Certified*
Arsenic	1.19	1.11 (0.16)	1.25	1.27 (0.12)

CASS-4: National Research Council Canada (NRC) Nearshore Seawater Reference Material

NASS-5: National Research Council Canada (NRC) Seawater Reference Material

** Certified uncertainty values in brackets (95% confidence intervals)*

With the continuing demands for lower and lower reporting limits, coupled with increasingly stringent regulatory guidelines and complex matrices, it is unlikely that any single technique can efficiently meet all the needs of most projects. Because of this, many commercial laboratories will in practice employ between two to four analytical methods per given sample in order to meet all the metals testing needs of their clients.

CONTAMINATION CONTROL

As previously mentioned, in order to preserve the integrity of the resulting data, particular focus and care must be extended to all stages of the testing process. Contamination control during sample handling and treatment is a challenging task, the importance of which is often underestimated. The capability to report detection limits at parts per trillion (ppt) levels or below is often limited not by the sensitivity of many instrumentation, but rather by the introduction of trace contaminants into the sample of interest. Many precautions must be taken to prevent exposure of samples to contaminants. The following are some of the most commonly encountered sources of trace element contaminants:

Airborne Dust

Of all the sources of contamination, household dust is the most prevalent, containing many contaminants that interfere with elemental determinations at low concentrations. The chemical composition of dust has been shown to contain a host of metals but those of most significance include Al, Ca, Mg, Cr, As, Cu, Zn and K (Ayoko et al., 2005). Although airborne dust particles can never be completely eliminated, measures can be taken to reduce their presence inside the laboratory. The following options have shown to be successful in limiting contamination from dust:

- For sample preparation, the use of a laminar flow hood.
- For sample analysis, the use of a positive pressurized room coupled with a high efficiency particulate air (HEPA) filter for input air.
- For instrument auto-sampler, the use of a cover or enclosure unit. Ultra low particulate air (ULPA) filter units can also be mounted onto certain auto-sampler enclosure units for ultra trace analysis.

Sample Container and Acid Preservative

It is recommended that all field sampling be conducted using bottle containers supplied by the laboratory that will analyze the samples. These bottles along with the accompanying acid preservatives are routinely checked and monitored for metal contaminants to verify their cleanliness and fitness for use. For sampling of ultra clean samples such as pristine surface waters or open-ocean seawater samples, acid-cleaned bottles and high purity distilled acid preservatives supplied in sealed plastic bags are highly recommended.

Sample Handling

Field sampler or laboratory analyst contact can be another source of sample contamination. Items such as personal jewelry, cosmetics, deodorants and hair products can be significant sources of many trace elements. Human sweat is known to contain trace levels of Zn, Cu, Fe, Ni, Pb, Mn and high levels of Na (Guy et al. 1999). Therefore, the uses of ‘metal free’ gloves are essential when handling samples, both for contamination control and to protect laboratory staff from exposure to acids. The type of glove used depends on the application and analytical requirements.

APPLICATIONS

Analysis of Ultra Trace Metals in Tissue Biopsy

The use of biopsy needles or dermal punches as a non-lethal method for sampling tissue continues to gain recognition with environmental practitioners. There are several distinct advantages to this approach versus traditional methods. Sampling permits may be more easily obtained from regulatory authorities for sites with low fish densities when non-destructive techniques are used (Baker et al., 2004). Tissue biopsy sampling also allows for repeat sampling and monitoring of the same fish at later dates, normally without lethal consequences to the specimen (Baker et al., 2004). Although studies have been performed for the determination of mercury in lake fish by this sampling technique, less data is available for the other metals. This is in part because higher instrument sensitivity is required to compensate for the reduced sample amounts available for analysis (approximately 150 mg). In-house studies by ALS Laboratory Group employing HR-ICPMS for the determination of multi-elements in various biological reference materials have shown promising results as shown in Table 4.

Table 4: Recoveries in selected tissue certified reference materials

Element	NIST 2976 (mg/Kg)*		NRC TORT-2 (mg/Kg)*	
	Found	Certified**	Found	Certified**
Arsenic	14.1	13.3 (1.8)	21.5	21.6 (1.8)
Cobalt	0.60	0.61 (0.02)	0.51	0.51 (0.09)
Mercury	0.057	0.061 (0.0036)	0.29	0.27 (0.06)
Molybdenum	0.47	***	1.02	0.95 (0.10)
Nickel	0.87	0.93 (0.12)	2.36	2.50 (0.19)
Lead	1.20	1.19 (0.18)	0.45	0.35 (0.13)
Selenium	1.93	1.80 (0.15)	5.98	5.63 (0.67)
Tin	0.099	0.096 (0.039)	0.047	0.04 ***
Vanadium	0.71	***	1.71	1.64 (0.19)
Zinc	137	137 (13)	178	180 (6)

2976: National Institute of Standard & Technology (NIST) Mussel Tissue
Tort-2: National Research Council Canada (NRC) Loster Hepatopancreas
100 mg digestion weight used

* Dry mass basis

** Certified uncertainty values in brackets (95% confidence intervals)

*** Not certified or Informational values only

Analysis of Ultra Trace Metals in Seawaters

Baseline monitoring of metals in marine and estuarine environments can be crucial to determine whether anthropogenic activities could impact pristine environments. However, the analysis of trace metals in seawater samples poses many difficult challenges due to their high salt content, coupled with the low background concentrations of most trace elements in seawater. To sufficiently resolve the matrix interferences caused by the high salinity of seawaters while maintaining extremely low reporting limits, a chelation extraction procedure using chelating resins can be employed for several metallic elements of environmental significance. Within a very narrow pH range, the chelating resins bind to specific metals, without binding to the predominant ionic species found in seawaters (Na^+ , Mg^{2+} , Ca^{2+} , K^+ , or anions like Cl^- or SO_4^{2-}). Once chelated onto the resin, metals of interest can be physically separated from the salt water matrix. With the salt matrix removed, the samples can be analyzed in a concentrated state by standard ICPMS techniques for these metals. HR-ICPMS can also be used for low level determinations of broad suites of elements in dilute seawater without the need for chelation (Rodushkin and Ruth, 1997).

SUMMARY

The science of environmental testing for elemental determination at ultra-low concentrations is an ever-changing and ever-challenging science. There are many instrument techniques available in commercial environmental laboratories to meet the requirements of analysis for standard levels of detection. However, the levels of detection in the ppt range for waters and the ppb range for tissues requires a different approach to traditional sample handling, processing and analysis. For this reason, it is highly recommended that the laboratory conducting the analysis of the samples be contacted prior to sample collection in order to ensure a successful project.

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