Guide for environmental sample analysis by ICP-MS:

Recommendations for getting started and best practices to streamline workflow

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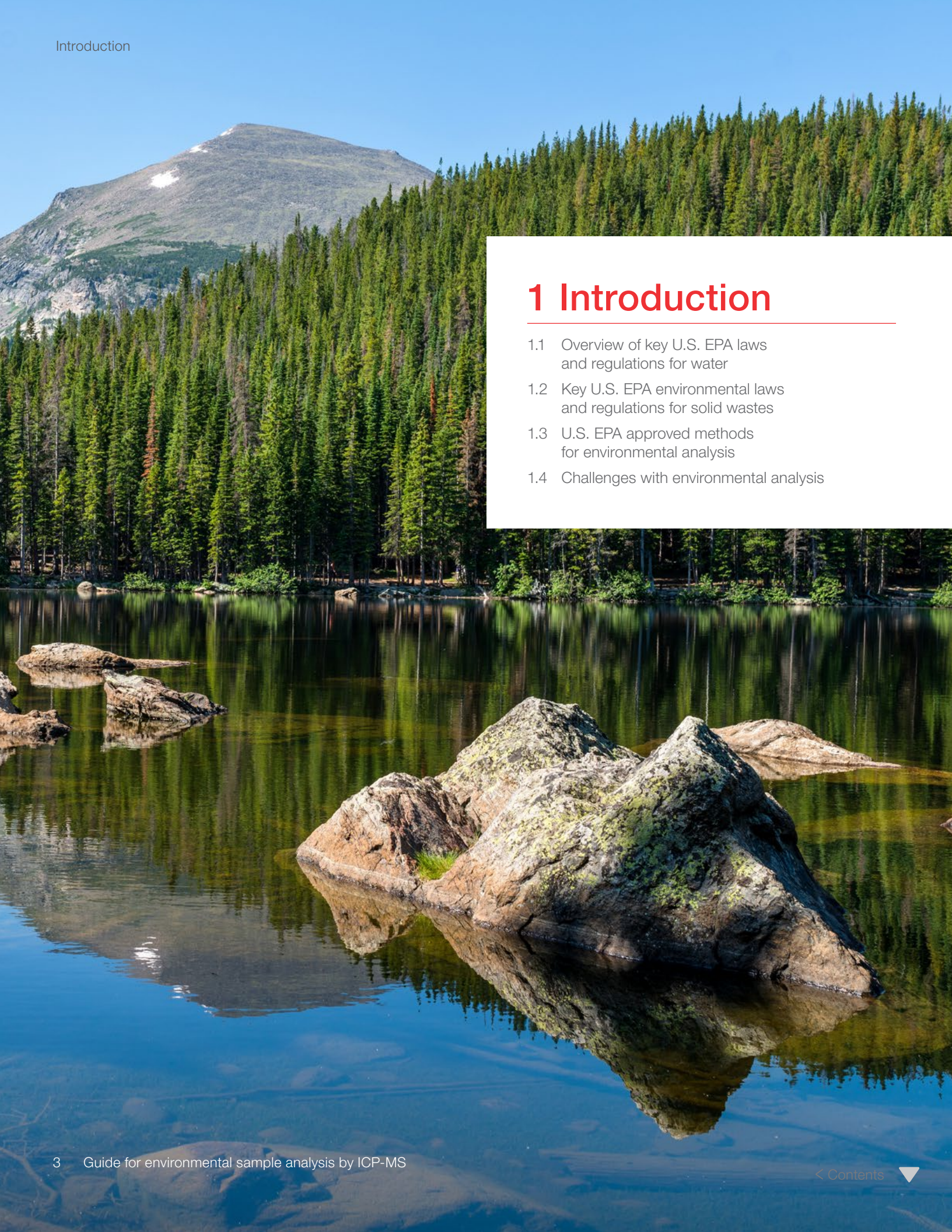


1 Introduction

Environmental analysis essentially encompasses the application of various analytical techniques to obtain information about the environment for pollution and toxicity assessment. It goes beyond the testing of drinking water, wastewater, and ground and surface waters to ensure public protection and compliance with the standards set by the United States Environmental Protection Agency (U.S. EPA) under the authority of the Safe Drinking Water Act (SDWA). It also entails a broad range of testing and applications:

- The assessment of pollution levels in soil prior to building, farming, or other urban development.
- The analyses of industrial wastes using a procedure that simulates leaching through a landfill {Toxicity Characteristic Leaching Procedure (TCLP)} for hazard identification and appropriate management, transport, and disposal.
- Wastewater discharge monitoring to ensure compliance with effluent limits set in a National Pollutant Discharge Elimination System (NPDES) permit.
- Preliminary Assessment/Site Inspection stage of the Superfund cleanup program where water or soil samples are tested to determine the presence of hazardous substances.

Water compliance monitoring

Environmental remediation

Power generation

Industrial waste disposal

Oil and gas industry

Agricultural testing

Figure 1.1 Environmental testing is required for water compliance monitoring, toxicity assessment, agricultural testing and field mapping, disposal of industrial wastes, and throughout various industries such as oil and gas.

The testing of water, soil, air, and industrial wastes for pollution and hazard assessment is driven by federal, state, and local environmental laws and regulations. Some of the federal laws enacted for solid waste management, the preservation of waters of the United States, and for public, aquatic, and wildlife protection are summarized in the following sections. Associated regulations, programs, and federal offices responsible for working with state agencies, local governments, local health departments, and public utilities for the implementation of these laws are also summarized for additional context.

1.1 Overview of key U.S. EPA laws and regulations for water

Clean Water Act (CWA)

The CWA, originally known as the Federal Water Pollution Control Act, passed in 1948, was restructured and expanded in 1972 to the CWA.[1] It established the structure for regulating the discharge of pollutants into the waters of the United States[2] and for regulating surface water quality standards. Under the CWA, industrial wastewater standards were set, prohibiting the discharge of pollutants by industries from a point source into a river, lake, stream, etc. without an NPDES permit.

National Pollutant Discharge Elimination System (NPDES)

The EPA gives most of the states the authority to enforce and administer the NPDES permit program and to issue permits. The permit includes effluent limits, monitoring and reporting requirements, and other stipulations to ensure water quality and public health are not compromised due to pollutant discharge by industrial plants and other facilities.[3]

Figure 1.2 The discharge of wastewater by industries into navigable waters requires an NPDES permit.

Safe Drinking Water Act (SDWA)

The SDWA, passed by Congress in 1974, is the law that protects public health by regulating the public drinking water supply. In 1986 and 1996 the law was amended, requiring additional actions to protect drinking water and its sources: rivers, lakes, reservoirs, springs, and ground water wells. The EPA set standards for drinking water under the SDWA and oversees the implementation of these standards by states, municipalities, and water suppliers. The SDWA applies to all public water systems (PWS).[4] Note, the SDWA does not apply to bottled water which is regulated by the Food and Drug Administration (FDA).[5]

Figure 1.3 Surface and ground waters, such as rivers and lakes, used as drinking water supplies are regulated by the U.S. EPA under the SDWA.

National Primary Drinking Water Regulations (NPDWR)

The EPA established the NPDWR under the SDWA as legally enforceable standards that limit the levels of contaminants in drinking water to ensure quality and protect the public. The NPDWR standards and treatment techniques are applicable to all PWS. The standard is organized into six groups of pollutants, one of which is Inorganic Chemicals, where metals (e.g., Pb, As, Hg, Cd) are covered.[6]

Figure 1.4 Springs, often used as domestic and drinking water supplies, are also regulated by the U.S. EPA under the SDWA.

National Secondary Drinking Water Regulations (NSDWR)

The EPA established the NSDWR to set standards for contaminants that affect the aesthetic quality (e.g., color, odor, taste) of drinking water. These standards are not federally enforceable since the contaminant levels do not present a risk to public health.[7]

Lead and Copper Rule (LCR)

In accordance with the SDWA, the U.S. EPA issued the LCR in 1991 to minimize lead and copper in drinking water primarily from plumbing material. The LCR requires water suppliers to monitor drinking water at consumer taps by sampling. If greater than 10% of the sampled taps exceed the action levels for lead (15 ppb) and copper (1.3 ppm), specific actions are to be taken by water suppliers, such as, the implementation of treatment techniques, removal of lead plumbing, corrosion control, inspecting and eliminating the source water, replacement of lead service lines, and informing and educating the public on measures to protect against lead exposure.[8]

Since this LCR was issued in 1991, it has undergone several revisions. For the long-term revision, on December 16, 2021, the U.S. EPA announced its intent to strengthen the LCR by developing a new regulation, the Lead and Copper Rule Improvements (LCRI), with plans for promulgation prior to October 16, 2024. Focus areas for the LCRI include inventory, removal, and replacement of lead service lines, strengthening compliance tap sampling, evaluation of action and trigger levels, and prioritizing underserved communities. A trigger level of 10 ppb was introduced requiring more proactive planning in communities with lead service lines. The overall goals are to reduce lead in drinking water, 100% removal of lead service lines, and more equitable public protection.[9]

1.2 Key U.S. EPA environmental laws and regulations for solid wastes

Figure 1.5 Proper onsite management of industrial wastes include labelling and hazard identification, containment, and daily documented inspection.

Resource Conservation and Recovery Act (RCRA)

The RCRA, enacted in 1976, is the federal law establishing the structure for the proper disposal and management of industrial and municipal hazardous and non-hazardous solid wastes. Under RCRA, the EPA has the authority to control hazardous wastes from *cradle-to-grave* and developed regulations, guidelines, and policies for environmentally safe management, storage, transportation, disposal, remediation, and recycling.[10]

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)

The CERCLA, known as Superfund, passed by Congress in 1980 established a tax on chemical and petroleum industries and a Federal trust fund, or *Superfund,* for the cleanup of identified hazardous wastes sites, or *Superfund Sites,* spills, accidents, and emergency releases of contaminants that are harmful to the public and the environment. Under CERCLA, the EPA has the authority to pursue responsible parties for the cleanup of sites contaminated by hazardous substances.[11] There are thousands of designated Superfund Sites in the U.S. and over 1,000 are on a National Priorities List (NPL) which are considered highly contaminated.[12]

Superfund Amendments and Reauthorization Act (SARA)

The SARA amended the CERCLA in 1986 by making changes to the complicated Superfund program. Such changes included increasing the amount of the trust fund, the addition of advanced treatment technologies for remediation, increasing state involvement and decision making in site cleanup, and bringing more attention towards public health issues due to hazardous wastes sites.[13]

Contract Laboratory Program (CLP)

The CLP supports the Superfund program, created under CERCLA, and currently under the SARA, by providing analytical testing services by EPA-approved contract testing laboratories

who have met very stringent requirements and standards to be part of the program. The sample analysis produced by the CLP is of documented quality and can be used in support of enforcement proceedings. The CLP consists of a network of EPA personnel and regional managers, quality assurance and technical support contractors, and contracted laboratories that conduct various tests on samples from Superfund Sites.[14]

Figure 1.6 As part of the Preliminary Assessment stage of the Superfund cleanup program, samples are collected to test the presence and levels of toxic substances.

Table 1.1 U.S. EPA offices with oversight of key environmental laws

EPA office	Overview
Office of Water (OW)	The OW ensures the safety of drinking water and protects oceans and watersheds to maintain a healthy environment for fish, plants, and wildlife. The OW is responsible for implementing the CWA, SDWA, portions of RCRA, and other acts that protect oceans and coastlines.[15]
Office of Ground Water and Drinking Water (OGWDW)	The OGWDW, part of the OW, oversees the SDWA and works with the states to ensure the safety of drinking and ground water.[16]
Office of Wastewater Management (OWM)	The OWM, part of the OW, supports the CWA and provides regulatory standards and effective wastewater treatment, disposal, and management.[17]
Office of Land and Emergency Management (OLEM)	The OLEM provides guidance and direction for the U.S. EPA's waste programs and emergency response: providing technical support to state and local governments for safe waste management, responding to abandoned and active hazardous waste sites through Superfund, developing guidelines for land disposal and underground storage tanks, and managing numerous related programs and projects.[18]
Office of Superfund Remediation and Technology Innovation (OSRTI) Analytical Services Brand (ASB)	The ASB manages the CLP which consists of a network of regional U.S. EPA CLP project officers, regional sample coordinators, commercial laboratories, and support contractors.[19]

1.3 U.S. EPA approved methods for environmental analysis

The analyses of drinking water, ground water, surface water, wastewater, and other environmental samples, under the regulations of the CWA, are performed by U.S. EPA approved CWA analytical or test methods. These methods, promulgated under the CWA, are prescribed in 40 CFR Part 136.[20]

Maximum levels, and level goals, for most inorganic contaminants (e.g., metals, metalloids, cyanide, fluoride) regulated under the CWA are at trace (ppm to ppb) or ultra-trace (ppb to ppt) concentrations to ensure public health against toxicity at higher levels. Because of these levels, the approved CWA test methods entail the use of sensitive analytical techniques for analysis, such as, Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), and ICP Mass Spectrometry (ICP-MS). The AAS techniques capable of meeting sub-ppb detection requirements are Graphite Furnace AAS (GFAAS), Cold Vapor AAS (CVAAS) for mercury and Hydride Generation AAS (HGAAS) for hydride forming metals (e.g., Se, As, Sb, Pb). Table 1.2 lists some of the most common U.S. EPA approved CWA analytical methods used by government and environmental contract testing laboratories for metals analysis.

Table 1.2 Most common U.S. EPA CWA test methods for metals analysis

Method number	Method title
200.2	Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements. Revision 2.8
200.7	Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry. Revision 4.4
200.8	Trace Elements in Water and Wastes by Inductively Coupled Plasma-Mass Spectrometry. Revision 5.4
200.9	Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry. Revision 2.2
245.1	Mercury in Water by Cold Vapor Atomic Absorption Spectrometry. Revision 3.0
245.2	Mercury (Automated Cold Vapor) by Atomic Absorption

Table 1.3 The SW-846 compendium ICP and AAS inorganic determinative methods

Method number	Method title
6010D	Inductively Coupled Plasma Atomic Emission Spectrometry
6020B	Inductively Coupled Plasma Mass Spectrometry
7000B	Flame Atomic Absorption Spectrophotometry
7010	Graphite Furnace Atomic Absorption Spectrophotometry
7470A	Mercury in Liquid Waste (Manual Cold-Vapor Technique)
7471B	Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)
1311	Toxicity Characteristic Leaching Procedure (TCLP)

For solid wastes, the RCRA oversees its management, giving the U.S. EPA the authority to control the generation, storage, transportation, treatment, and disposal of hazardous wastes. To test solid wastes for compliance with RCRA regulations, the EPA developed methods assembled in the publication, *Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods Compendium*, also known as the SW-846 Compendium.[21] This compendium includes quality assurance and quality control protocols, guidance for selecting the appropriate analytical method, sample preparation methods, and a collection of over 200 analytical methods for the sampling and analysis of wastes. The methods are divided into series according to type of method, analyte, and technique. The 6000 and 7000 series contain numerous methods for the determination of inorganic analytes; examples of these methods are provided in Table 1.3.

1.4 Challenges with environmental analysis

A major challenge in the analyses of environmental samples is the requirement to measure trace and ultra-trace concentrations of metals in a variety of matrices, from simple (e.g., drinking water) to complex (e.g., soils, wastewater, sludge). The SDWA authorized the EPA to establish the NPDWR, which set legally enforceable standards for inorganic contaminants in drinking water for protection against levels that present risks to human health. Table 1.4 summarizes the national standards for inorganic chemicals in drinking water.

The Maximum Contaminant Level (MCL) is the highest level of a contaminant allowed in drinking water while the Maximum Contaminant Level Goal (MCLG) is the level of a contaminant in drinking water below which there are no known or expected health risks. The MCLs are legally enforceable standards while MCLGs are non-enforceable public health goals.

The EPA also established the NSDWR to set water quality standards for 15 contaminants, each with a Secondary Maximum Contaminant Level (SMCL). The SMCLs are not enforceable, rather, they serve as guidelines for public water systems to manage the aesthetics (e.g., color, odor) of drinking water. At levels higher than the SMCLs, drinking water may become cloudy or have an unpleasant taste and smell, creating a public perception of unsafe for use and drinking. Table 1.5 summarizes the NSDWR standards for inorganic contaminants.

Table 1.4 National primary drinking water regulations for inorganic contaminants[22]

Contaminant	MCL (mg/L)	MCLG (mg/L)
Antimony	0.006	0.006
Arsenic	0.010	0
Barium	2	2
Beryllium	0.004	0.004
Cadmium	0.005	0.005
Chromium (total)	0.1	0.1
Copper	1.3	1.3
Cyanide (as free cyanide)	0.2	0.2
Fluoride	4.0	4.0
Lead	0.015	0
Mercury (inorganic)	0.002	0.002
Nitrate (measured as Nitrogen)	10	10
Nitrite (measured as Nitrogen)	1	1
Selenium	0.05	0.05
Thallium	0.002	0.0005

*Regulation for asbestos not included in Table 1.4

Table 1.5 National secondary drinking water regulations for inorganic contaminants[23]

Contaminant	SMCL (mg/L)	Effects above SMCL
Aluminium	0.05 to 0.20	Coloring of water
Chloride	250	Salty taste
Copper	1.0	Metallic taste; blue-green staining
Fluoride	2.0	Tooth discoloration
Iron	0.3	Rusty color, metallic taste, reddish/orange staining
Manganese	0.05	Black to brown color and staining; bitter metallic taste
Silver	0.10	Skin discoloration
Sulfate	250	Salty taste
Zinc	5	Metallic taste

As part of the SDWA amendments of 1996, the EPA is required to issue a list of no more than 30 contaminants every five years that are to be monitored by public water systems and to collect data to determine whether new regulations are needed for these emerging contaminants. This is known as the Unregulated Contaminant Monitoring Rule (UCMR). The contaminants listed are known or suspect to be present in drinking water, selected based on health risk factors but not regulated by the SDWA. The UCMR requires large public water systems and a sample of smaller public water systems, serving fewer than 10,000 people, to sample drinking water sources (e.g., groundwater, surface water, mixed water) during a twelve-month period.[24] Since the 1996 amendment, there have been five UCMRs. Table 1.6 summarizes the inorganic contaminants listed in previous and current UCMRs.

Table 1.6 Inorganic contaminants listed in UCMRs

Rule	Contaminant	Minimum reporting level (µg/L)
UCMR 3[25] (2012 - 2016)	0.05 to 0.20	Coloring of water
	Vanadium	0.2
	Molybdenum	1.0
	Cobalt	1.0
	Strontium	0.3
	Chromium (total)	0.2
	Chromium - 6	0.03
UCMR 4[26] (2017 - 2021)	Germanium	0.3
	Manganese	0.4
UCMR 5[27] (2022 - 2026)	Lithium	9.0

State specific water quality regulations may require contaminants to be lower than the federal levels. In California, the MCL for chromium in drinking water is 0.05 mg/L,[28] while the NPDWR MCL is 0.1 mg/L. For surface waters in New York, the standard for mercury in fresh surface waters used as a source for drinking is 0.7 µg/L,[29] lower than the NPDWR standard of 2 µg/L. The U.S. EPA has compiled state specific water quality control standards that have been approved by the EPA or are in effect for CWA purposes.[30]

With federal, state, and municipal water quality standards set at ultra-trace levels for toxic inorganic contaminants, ICP-MS is the technique that offers the sensitivity to meet detection requirements with the benefits of wide linear dynamic range, analytical speed, and robustness for routine analysis. Furthermore, most environmental samples must be converted to a solution suitable for introduction to the ICP-MS instrument, resulting in a diluted sample solution with analytes at lowered concentrations (i.e., trace concentrations of analytes become ultra-trace after preparation and dilution). Hence, with regulations becoming more stringent and the need for flexibility to analyze from trace to ultra-trace concentrations of analytes in a variety of matrices, ICP-MS has grown in demand with continuous advancements in instrumentation to enhance robustness and performance.

The EPA methods for the analysis of environmental samples by ICP-MS are Methods 200.8, Revision 5.4, and Method 6020B (SW-846). Table 1.7 summarizes some of the important aspects of these methods and their differences. For complete method guidelines and procedures, refer to EPA Method 200.8, Revision 5.4,[31] SW-846 Compendium,[32] Chapter One, “Project Quality Assurance and Quality Control,” Chapter Two, “Choosing the Correct Procedure,” and Chapter Three, “Inorganic Analytes,” and to Method 6020B (SW-846).[33]

Table 1.7 Overview of U.S. EPA Method 200.8, Revision 5.4, and Method 6020B (SW-846)

	Method 200.8, Revision 5.4	Method 6020B (SW-846)
Sample preparation	• Sample preparation procedures are also given in Method 200.2 – Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements. • Sample preparation by hot plate acid digestion (hot block optional). • Direct analysis of drinking water with a turbidity of <1 Nephelometric Turbidity Unit (NTU) for total recoverable analytes.	• For the analysis of dissolved constituents in groundwater, acid digestion is not necessary if samples are filtered and preserved at collection. • Guidance for the selection of the appropriate sample preparation method is detailed in the SW-846 Compendium, Chapter Two, "Choosing the Correct Procedure."
Interference correction	• The use of Collision/Reaction Cell (CRC) technology is prohibited from use in drinking water compliance monitoring under the CWA; only mathematical correction equations may be used to correct for spectral interferences that affect the accuracy of analysis.	• Collision/Reaction Cell may be used for interference correction with demonstration of the freedom of interference using the analysis of the Spectral Interference Check (SIC) solution. Guidance on the preparation of the SIC solution is provided in Section 7.23 and for quality control in Section 9.9.
Quality control	• Refer to Section 9.0 for quality control requirements including initial demonstration of laboratory capability, periodic analysis of QC standards, and maintenance of data quality records.	• Refer to the SW-846 Compendium, Chapter One, "Project Quality Assurance and Quality Control," for QC guidelines, and to Method 6020B (SW-846) Section 9.0 for method specific QC standards and criteria.
Method scope	• Used for drinking water and wastewater compliance monitoring programs under the SDWA and CWA. • Applies to the analysis of dissolved elements in groundwaters, surface waters, and drinking water. • Applies to the analysis of total recoverable elements in groundwaters, surface waters, wastewaters, sludges, and soils.	• In support of RCRA, SW-846 Method 6020B was developed for the ICP-MS analysis of various environmental samples: soils, sediments, sludges, groundwater, surface water, aqueous samples with suspended solids, and industrial wastes requiring a measure of the total leachable elements. • This is a performance-based method, used for guidance, not for compliance testing.
Analytes	• 21 Elements – Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Hg, Mo, Ni, Se, Ag, Tl, Th, U, V, and Zn **Note:** Minerals (e.g., Ca, Fe, Mg, K and Na) are not included.	• 23 Elements – Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, K, Se, Ag, Na, Tl, V, and Zn **Note:** Other elements may be analyzed using this method provided their performance is demonstrated in the same manner as the listed elements.
Sample preparation	• Sample preparation procedures are given in Sections 11.1, 11.2, and 11.3 and include preparations for total dissolved and total recoverable analytes in aqueous samples, and total recoverable analytes in solid samples.	Sample preparation methods are given in the SW-846 Compendium, Chapter Three, "Inorganic Analytes." The following methods are specified for the digestion of samples prior to ICP-MS analysis: Methods 3005A, 3010A, 3015A, 3020A, 3050B, 3051A, and 3052.

It is imperative that data obtained from the analyses of environmental samples be of high quality. For this reason, the quality control protocols of Method 200.8, Revision 5.4, and Method 6020B (SW-846) are comprehensive and designed to help ensure accurate results. In addition, measures outlined within these methods to prevent contamination will help to preserve sample and standard integrity. Furthermore, due to the high sensitivity of ICP-MS, extra precautions, and best practices to streamline the analytical workflow are needed for optimal performance and accurate results.

This document is intended to assist laboratories getting started with the analyses of environmental samples by ICP-MS and to recommend best practices and tips for preventing contamination, streamlining standard and sample preparation processes, and preventing analytical issues that lead to inaccurate results and poor data quality. Considerations and recommendations for the selection and use of laboratory apparatus and equipment, reagents, stock standards, ICP-MS instrument components, and other workflow items along with online links to access relevant literature and additional information will be provided.

This document offers information complementary to the procedures and guidelines specified in Method 200.8, Revision 5.4, and Method 6020B (SW-846) with a scope that includes the following:

- Recommended best practices for the use and selection of laboratory apparatus and equipment, standard solutions, reagents, and ICP-MS instrument components.
- Recommended best practices to streamline analytical workflow, prevent contamination, and reduce handling and transfer steps to improve overall efficiency.
- An overview of the most common chemical dissolutions methods for environmental analysis by ICP-MS with an evaluation of their benefits and suggested systems for acid digestion.
- Recommended best practices for the inspection and maintenance of ICP-MS instrument parts to prevent analytical issues.
- Considerations for the selection of ICP-MS instrument parts and consumables.
- Lists of recommended items for the analytical workflow along with links to access product information and specifications for convenience.
- Lists of helpful resources, applications and technical notes, product, and application webpages.

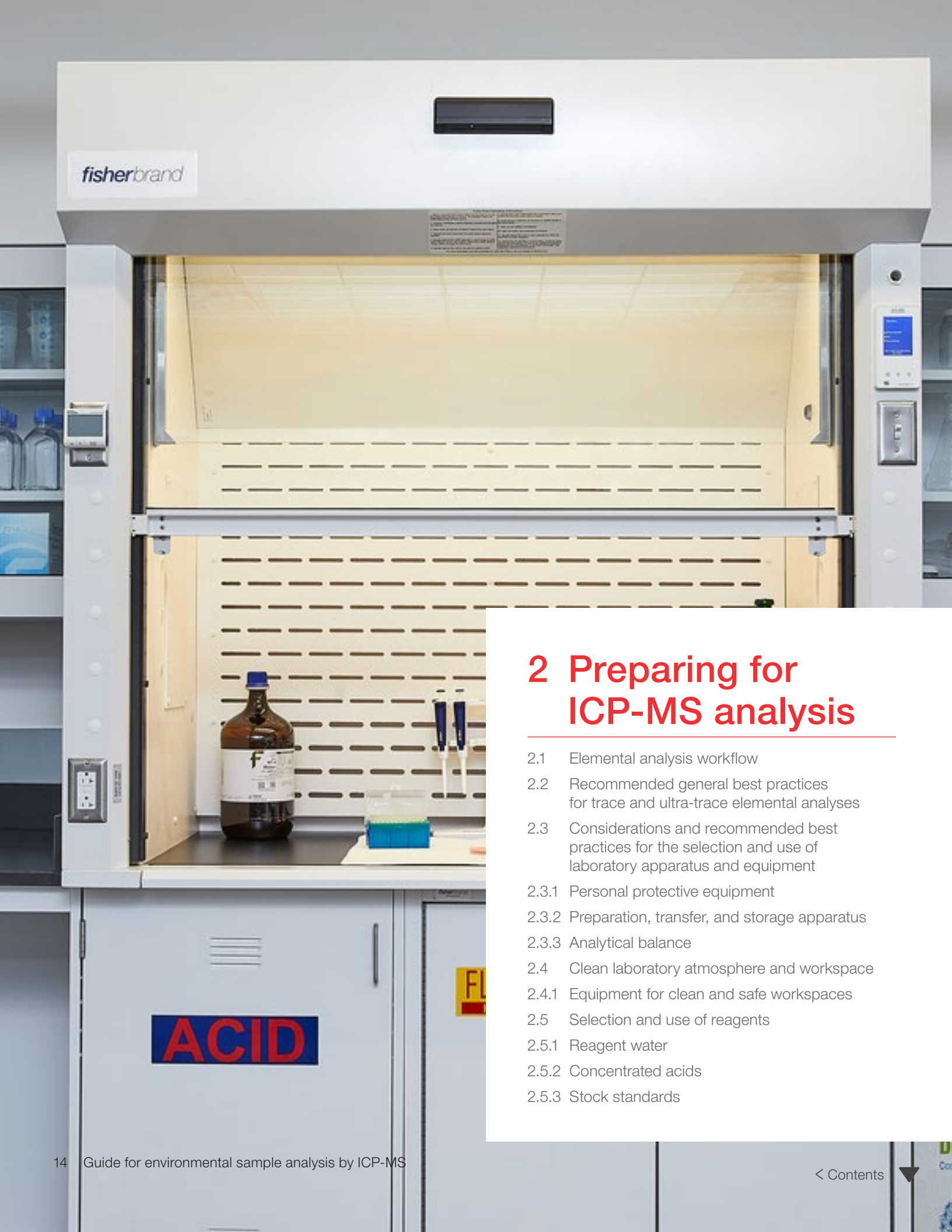
In addition to laboratories getting started with the analysis of environmental samples according to EPA Method 200.8, Revision 5.4, and Method 6020B (SW-846), this document is also helpful for:

- Industrial laboratories getting started with ICP-MS analysis using EPA methods as a starting point to develop their own analytical methods and Standard Operation Procedures (SOPs).
- Established laboratories looking for tips and best practices to improve existing workflows for sample and standard preparation and pre-analysis routines.
- Laboratories with new analysts that need a training tool which provides a general overview of environmental analysis by ICP-MS and recommended best practices and tips for success with this technique.

The following topics are out of scope for this document:

- Pre-treatment of samples (e.g., drying, sieving, grinding) prior to chemical dissolution.
- In-depth discussion of the different types of chemical dissolution methods (e.g., extraction, fusion) that can be employed for sample preparation.
- In-depth discussion of autosamplers and autodilution systems available on the market.
- In-depth discussion on instrument tuning, operation, method development, sample analysis, and interference removal technology as many aspects of these topics are instrumentation and software specific. However, general discussions of these topics are included in this document where appropriate.
- Instrument and method troubleshooting to address analytical issues and erroneous sample results. However, a discussion of measures to prevent analytical issues and recommended actions for troubleshooting a poor calibration curve are included.

In the next chapters, Method 200.8, Revision 5.4, will be referred to as Method 200.8 and Method 6020B (SW-846) will be referred to as Method 6020B.



2 Preparing for ICP-MS analysis

2.1 Elemental analysis workflow

In the context of this document, the elemental analysis workflow consists of all processes, and steps within these processes, involved to get from sample to data. These processes include sample and standard preparation; instrument set-up; sample introduction; instrument calibration; sample analysis; data evaluation; troubleshooting and corrective action; and reporting results.

Due to the physical and chemical properties of samples, standards, and reagents handled throughout these processes and the high sensitivity of ICP-MS, general best practices and considerations will be recommended to avoid systematic errors that lead to poor data quality. Systematic errors will refer to repeated errors due to faulty equipment or apparatus, incorrect and inconsistent measurements, contamination, spectral interferences, performing procedures incorrectly, and errors in calculation.

Figure 2.1 Processes within a typical element analysis workflow.

2.2 Recommended general best practices for trace and ultra-trace elemental analyses

Trace and ultra-trace elemental analyses extend beyond their uses in determining the safety of drinking water or the toxicity of an environment. They are instrumental in ensuring the quality and safety of consumer products, in screening programs by public health departments, in the research and development of new products and emerging technologies, etc. Such applications drove the increase in demand for ICP-MS analysis. Over a broad range of industries and applications, ICP-MS has become a reliable technique for fast, sensitive, multi-element analysis.

Due to method and industry protocols required to meet federal, state, or local regulations or industry quality and safety standards for consumer products, general analytical best practices will be emphasized throughout this document.

The following general best practices are recommended to help achieve reliable, accurate results and overall success with trace and ultra-trace elemental analyses by ICP-MS.

Be aware of contamination sources.

Contamination from the laboratory air, environment and workspace, instrument components, and all materials that come into contact with standards and samples needs to be prevented or minimized as much as possible. Contamination compromises the integrity of samples and standards and causes systematic errors impacting the accuracy of trace and ultra-trace elemental analysis. Contamination can be introduced at any point in the elemental analysis workflow and can come from unapparent sources, such as, paint chipped from walls and ceilings; corroded faucets and piping; and the analysts themselves (e.g., hair, moisturizers, sunscreen, cosmetics, jewelry). Furthermore, elements that are ubiquitous in nature (e.g., Na, Fe, Zn) are prone to contamination and are problematic for ICP-MS analysis.

Minimize handling and transfer steps.

Streamlining sample and standard preparation processes saves time and resources, prevents systematic errors and additional exposure to contamination, and improves the overall efficiency of the elemental analysis workflow, thereby increasing sample throughput and laboratory productivity. Remember, every handling and transfer step is an opportunity for error and introduction of contamination.

Use high-purity reagents.

Quality stock standards and reagents that are certified and of ultra-high purity grade are essential for all sample and standard preparations for trace and ultra-trace analyses. Be aware of trace impurities present in the different grades of reagents available as their levels may not be suitable for the detection required.

Use ultrapure water.

For the preparation of all standards, samples, diluents, and rinse solutions for ICP-MS analysis, ultrapure water is specified by the U.S. EPA approved analytical methods and is necessary for achieving trace and ultra-trace detection limits. Using ultrapure water to clean laboratory apparatus and instrument components as part of a comprehensive cleaning procedure is also best practice.

Measure weights and volumes with accuracy.

Use the appropriate apparatus and equipment to measure and deliver accurate volumes and weights and ensure their accuracy and proper functioning with documented periodic calibration, weekly checks, and spot checks prior to use.

Apply proper skill, technique, and attention to detail.

Standard and sample preparation steps need to be performed with proper skill, technique, and attention to detail to avoid systematic errors, exposure to contamination, and inconsistencies between preparations. Aside from instrument performance and the maintenance of components, precision and accuracy of the measurement also depend on how well standards and samples are prepared. With the high sensitivity of ICP-MS, minor errors will be apparent and reflected in the instrument calibration, affecting the accuracy of the sample analysis.

2.3 Considerations and recommended best practices for the selection and use of laboratory apparatus and equipment

The laboratory apparatus, equipment, and supplies selected must meet specific performance criteria as only certain materials are appropriate for the elemental analysis workflow that requires the use of corrosive concentrated acids, ultra-high purity stock standards and reagents, processes involving heat, processes that generate fumes and vapors, etc. Materials should be compatible, thermally durable, inert, robust, and should not contribute contamination. This section will discuss some recommended best practices for the use and selection of laboratory apparatus, reagents, and supplies for ICP-MS sample and standard preparation processes.

Note

- **The products mentioned in this document are from reputable vendors with years of experience in elemental analysis. Thermo Fisher Scientific does not receive endorsements from any of the vendors listed, nor is an endorsement implied. Recommended items and products are underlined with a link to either the Fisher Scientific or Thermo Fisher Scientific web pages for convenient access to further details and specifications.**
- **It is the responsibility of the laboratory to maintain a safe work environment and handle all chemicals and samples with utmost caution and in accordance with local, state, and federal {Occupational Safety and Health Administration (OSHA)} regulations in addition to their own established procedures for safety and chemical hygiene.**
- **It is the responsibility of the laboratory to ensure that all protective equipment, materials, reagents, standards, and apparatus selected are appropriate for present and future hazards in the laboratory, compatible with the chemicals and samples being handled, and meet the analytical requirements of U.S. EPA methods and procedures for trace and ultra-trace elemental analyses.**
- **Recommended best practices, tips, and considerations provided in this document should only be used as a guide for getting started and preparing for ICP-MS analysis and to improve or complement existing laboratory workflows, methodologies, and procedures.**

2.3.1 Personal protective equipment

Safety and personal protection are first and foremost in the laboratory due to the presence of hazards (e.g., chemical, physical, mechanical, electrical) and risk of exposure. Examples of common chemical hazards in an elemental analysis laboratory include flammable gases, corrosive acids, reactive chemicals, and toxic metals. Safety Data Sheets (SDSs) for all chemicals must be accessible, well organized, and kept on file for personnel hazard awareness and communication as required by state, local, and federal Right-to-Know laws. Safety Data Sheets contain important information about a material: chemical properties; the physical, health and environmental hazards present; protective measures; and precautions for safe handling, storage, and transport. Aside from the known hazards, samples are considered unknown and should be treated as potentially hazardous and handled with caution.

Personal Protective Equipment (PPE) must be worn to minimize exposure to the different hazards present in the laboratory or workplace and prevent injury and illness. The Occupational Safety and Health Administration (OSHA) requires employers to provide PPE and ensure proper use through training and implementation of a PPE program.[34] The OSHA standards for PPE are given in 29 CFR Part 1910 Subpart I – PPE, and require that categories of PPE meet or be equivalent to the standards by the American National Standards Institute (ANSI).[35]

For general information and to view a comprehensive inventory of PPE and types of protection available for different types of hazards, please refer to the **PPE** and **Gloves, glasses, and safety** pages.

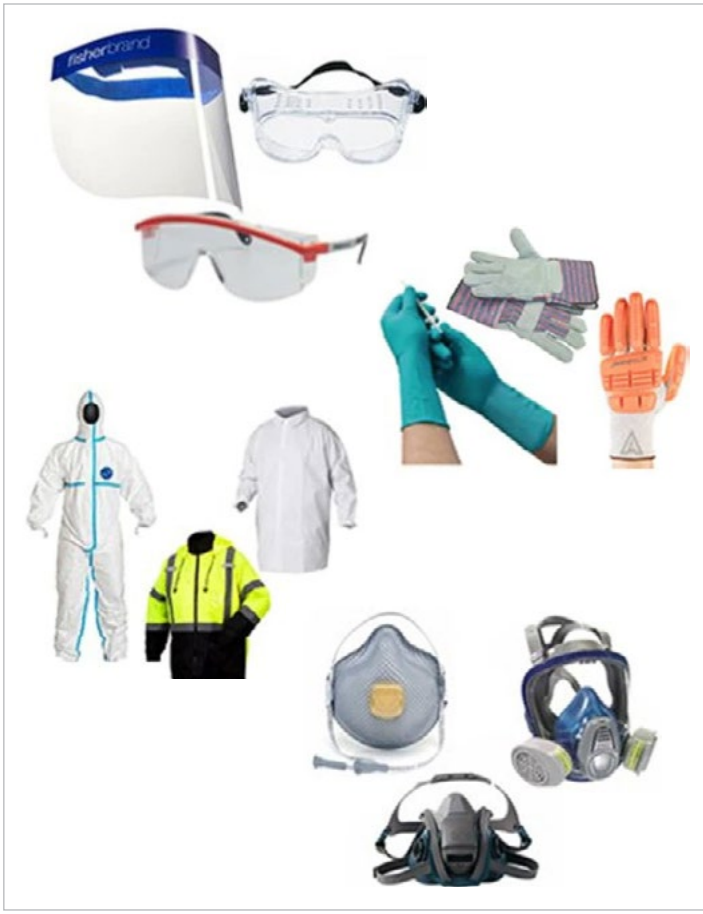


Figure 2.2 Various types of PPE products and specifications can be viewed on the PPE page.

Tip

This section includes recommended best practices for some of the PPE used in a laboratory where chemicals are handled. Always consult your laboratory safety advisor or officer to determine the appropriate PPE and engineering controls to protect against analytical processes, chemicals, and hazards present in your laboratory.

Laboratory coat

Wearing a laboratory coat is a basic personal protection requirement for laboratories handling chemicals and where exposure to hazards is possible. However, criteria to consider when selecting a laboratory coat may not be known, with the only consideration being that it is long sleeves and knee length. However, material, fit, and ease of removal are key considerations. At a minimum, for laboratories handling chemicals, it is recommended that a laboratory coat be:

- Front buttoned, preferably with snap closures for quick removal in case of chemical exposure, spills, accidents, and other emergencies.
- Appropriately fitted and not too loose, allowing comfortable movement without getting caught on laboratory equipment or instruments.
- Cuffed at the end of the sleeves for a snug fit, protecting the wrist, and preventing sleeves from hanging loosely into reagent or sample containers or getting caught on laboratory apparatus.
- Made from a material appropriate for the samples and chemicals being handled and hazards present in the laboratory.
- Heat resistant and made from material that will not readily burn when working near open flames.
- Cleaned regularly by an industrial laundering service.

Laboratory coats should not be worn outside the laboratory. The removal of laboratory coats can easily be overlooked when multi-tasking or going from the laboratory to the office, breakroom, restroom, and other areas in the workplace. Laboratory coats should not be taken home for laundering. To avoid laundering and possible cross-contamination, disposable laboratory coats are an option.

To assist in selecting the appropriate laboratory coat, please refer to the **Lab coats** page to view products with the specific features that fit the needs of your laboratory safety requirements. To learn about other protective apparel, please refer to the **Safety clothing** page.

Figure 2.3 Examples of laboratory coats typically used in a chemical laboratory with cuffed sleeves and snapped closures. Disposable coats (right) may be an option for some laboratories.

Safety glasses

Safety glasses are essential for preventing exposure of the eyes to hazards that can cause temporary irritation or severe and permanent damage. The OSHA standard for eye and face protection is 29 CFR 1910.133 and requires employers to have eye protection available for all employees exposed to hazardous chemicals and reagents, gases and vapors, harmful light, dust and particles in the air, splashing liquid, etc.

Safety glasses provide protection against UV radiation, dust, and airborne particulates. For work in a chemical laboratory, safety glasses should also be scratch resistant and not prone to fogging. The lens material for most laboratory safety glasses is polycarbonate with an anti-fog coating.

Safety glasses should properly fit for full protection. If possible, select safety glasses that can be adjusted and that fit close to the face for minimal gaps. Safety glasses should not fall or slip down the bridge of the nose. If prescription glasses are worn, safety glasses must be worn over them since prescription glasses alone do not provide adequate protection from the hazards in the laboratory.

The ANSI / International Safety Equipment Association (ISEA) Z87.1-2020 Occupational and Educational Personal Eye and Face Protection Devices is the standard that sets the criteria for general requirements, testing, permanent marking, selection, care, and use of safety glasses to minimize injuries due to hazard exposure in occupational and educational work environments.[36] When selecting safety glasses from the numerous products available, check the product specifications to ensure they are ANSI Z87.1 compliant.

Goggles protect against chemical splashes as well as airborne contaminates. A face shield over the goggles must be worn for secondary protection of the eyes and face from splashes.

Figure 2.4 Safety glasses come in many types that differ in look and feel. Goggles (right) offer protection against chemical splashes and come in anti-fog and scratch resistant.

Preparing and soaking laboratory apparatus in an acid bath are examples of procedures that are part of the elemental analysis workflow that require extra protection to the eyes and face.

The **General purpose safety glasses** page is a helpful resource for further information and to view different types of safety glasses, with specifications. In addition to safety glasses, other types of eye and face protection can be viewed on the **Eye protection and face protection** page.

Laboratory gloves

Laboratory gloves are worn to protect the hands from hazardous chemicals and samples and to prevent moisture and oil on the hands from contaminating sample, standards, laboratory apparatus, and instrument components.

Laboratory chemical resistant gloves come in different types of material: latex, nitrile, polyvinyl chloride (PVC), butyl, neoprene, etc. Select the glove material resistant to the chemicals, samples, and hazards present in your laboratory. Chemical resistance charts for glove materials are available by manufacturers to assist with the selection of appropriate and compatible glove material. These charts also provide important performance information, such as, glove degradation, breakthrough time, and permeation rate. A chemical resistance chart to assist with the selection of chemical resistant gloves is also available by OSHA.[37]

Nitrile is a common glove material used by chemical laboratories. It is flexible, abrasion resistant, and has good resistance to many chemicals. However, nitrile does not provide sufficient chemical resistance to concentrated acids. When handling concentrated acids, especially in large volumes (e.g., preparing an acid bath), consult the glove manufacturers for the appropriate material.

Latex is a well-known glove material. When considering nitrile and latex, nitrile gloves have been rated with higher chemical resistance and outperform latex, due to the acrylonitrile copolymers it is made from. In a chemical exposure test conducted with 71 chemicals, both nitrile and latex were rated with nitrile outperforming latex by protecting against 44 chemicals while latex only protected against 24 chemicals on the list.[38] Hence, latex is generally not recommended for handling chemicals. Also, since latex is a natural rubber, it is known to cause allergic reactions from its proteins. For additional information on nitrile gloves, please refer to the **Nitrile exam gloves** page.

It is also recommended to avoid the use of powdered gloves as they can also introduce contamination in the elemental analysis workflow.

For additional information on different glove materials and their applications, and glove products, please refer to the **Chemical, temperature, and cut resistant gloves** and the **Chemical resistant gloves** pages.

Figure 2.5 Nitrile gloves (right) are a commonly used, chemical-resistant glove. Latex gloves (left) are suitable for general purpose industrial applications but not recommended for chemical resistance.

2.3.2 Preparation, transfer, and storage apparatus

The high sensitivity of ICP-MS and the trace or ultra-trace detection requirements of environmental regulations and many industrial applications require the use of preparation, transfer, and storage apparatus (e.g., flasks, beakers, graduated cylinders, bottles) for all elemental analysis workflow processes to be of high quality, constructed and tested according to industry standards, and made from compatible material that does not contribute to contamination and result in the loss of analytes through adsorption.

Class A and Class B volumetric apparatus

There are two classes of volumetric ware for laboratory use: Class A and Class B. These are American Society for Testing and Materials (ASTM) designations specifying the qualified accuracy and tolerance of volumetric glassware, as specified in ASTM E694-18, Standard Specification for Laboratory Glass Volumetric Apparatus.[39] They are indicated by markings and serial numbers for traceability, as shown in Figure 2.6.

Class A volumetric glassware are:

- Typically made from borosilicate glass.
- A higher quality than Class B glassware.
- Best for use when accurate volume measurements are required.
- Compliant with the construction and accuracy requirements of ASTM standards.
- Superior in thermal and chemical resistance.
- Suitable for use as a storage container.

Class B volumetric glassware are typically made from soda lime glass and are of a lower standard, mainly used for general purpose work and not intended for long-term storage of chemicals and standard solutions.

In addition to accuracy and tolerance, two designations are used for volumetric apparatus: *To Deliver* (TD) and *To Contain* (TC). A volumetric apparatus designated *To Deliver* has been calibrated to deliver the exact volume of liquid measured when poured out. A volumetric apparatus calibrated *To Contain* will hold the volume designated; however, when poured out, some of the liquid will remain on the walls inside the cylinder and the volume poured out will be less than that measured.

Figure 2.6 Laboratory apparatus with associated markings for Class A and Class B. On the right, a volumetric flask with markings designating both To Contain and To Deliver.

Apparatus materials

Laboratory apparatus used for preparation, transfer, and storage available on the market are mostly made from glass. It is resistant to many chemicals, easy to produce and form into different shapes and sizes, withstands very high temperatures, can be tinted to block ultraviolet radiation, and is inexpensive. Laboratory glassware is largely made from either borosilicate glass or soda lime glass.

Glass is suitable for general laboratory use; however, it is not recommended for the elemental analysis workflow when trace and ultra-trace detection are required. The main concerns when using glass are:

- Contamination from major and minor elemental components in glassware (e.g., Si, Na, B, Ca, Mg) that may leach out into the solution being stored.
- The loss of analytes through adsorption onto the walls of glassware. This effect has a greater impact when storing standard solutions with analyte concentrations at ultra-trace levels.

High purity quartz is a better alternative to borosilicate glass. Its high purity and resistance to high temperatures make it suitable for ICP-MS sample introduction components (e.g., torch, injector) and as an acid digestion vessel. Quartz also has a very low coefficient of thermal expansion compared to borosilicate glass; under high temperatures, borosilicate is more likely to expand and crack than quartz. Quartz has many attractive properties for use in the laboratory. However, quartz laboratory apparatus is limited in availability.

Figure 2.7 Quartz beaker (left) and borosilicate glass beaker (right). Quartz beakers, and other quartz apparatus, typically do not have graduated markings.

Plastics are the preferred material for laboratory apparatus used for the elemental analysis workflow as they do not exhibit the same contamination and adsorption issues associated with glass. Plastics are chemically inert, lightweight, durable, and shatterproof. Furthermore, a meniscus is not formed by liquids in a plastic volumetric apparatus, hence, the liquid is level to the volume graduation, simplifying volume readings and reducing errors associated when filling glass volumetrics to volume according to the meniscus.

There are many types of plastics used for laboratory apparatus; the most common are polyolefins and fluoropolymers.

- **Polyolefins –** are derived from olefins which are hydrocarbons with carbon atoms linked by a double bond (alkenes). They are durable, heat resistant, able to withstand most chemicals, non-toxic, lightweight, and flexible. The two most widely used types in industry are polypropylene (PP) and polyethylene (PE). The following are common types used for laboratory apparatus**:**
  - Polypropylene (PP)
  - Low Density Polyethylene (LDPE)
  - High Density Polyethylene (HDPE)
  - Polymethylpentene (PMP)

Figure 2.8 Various polyolefin plastic apparatus: (from top) PP graduated cylinders, container, holder, and LDPE unitary wash bottle; (bottom left) HDPE narrow mouth bottles; and (bottom right) LDPE top dispensing wash bottles.

Figure 2.9 Various fluoropolymer laboratory apparatus: FEP bottles (left); PFA beaker, Erlenmeyer flasks, and graduated cylinder (center); and Teflon™ top dispensing wash bottle (right).

- **Fluoropolymers –** fluorocarbon polymers with high chemical resistance, wide working temperature ranges, and low coefficient of friction. They are non-contaminating, flexible, and translucent.
  - Perfluoroalkoxy (PFA)
  - Polytetrafluoroethylene (PTFE)
  - Fluorinated Ethylene Propylene (FEP)

Of these plastics, fluoropolymers are higher in cost due to their exceptional chemical and physical properties. Their high purity makes them best suited for analyses requiring ultra-trace detection limits. Since PTFE has a high working temperature up to 260°C,[40] it can be used as a digestion vessel material for hot plate acid digestion. For the storage of standard solutions (e.g., calibration, quality control, internal standard), Method 200.8, Revision 5.4, Section 6.10.7, specifies the use of narrow mouth FEP bottles. The maximum working temperature for FEP is around 190°C, which is not suitable for acid digestion.

For the preparation of standard solutions, either PMP or PP volumetric flasks can be used, but, PMP is recommended; it has better chemical resistance and higher clarity, which is important for accurate and precise preparation of standard solutions. For a comparison between PMP and PP, please refer to the **Reusable plasticware – volumetric flask** page. For additional information regarding recommended materials for sample containers, please refer to the *SW-846 Compendium,* Chapter Three, "Inorganic Analytes," Table 3-7.

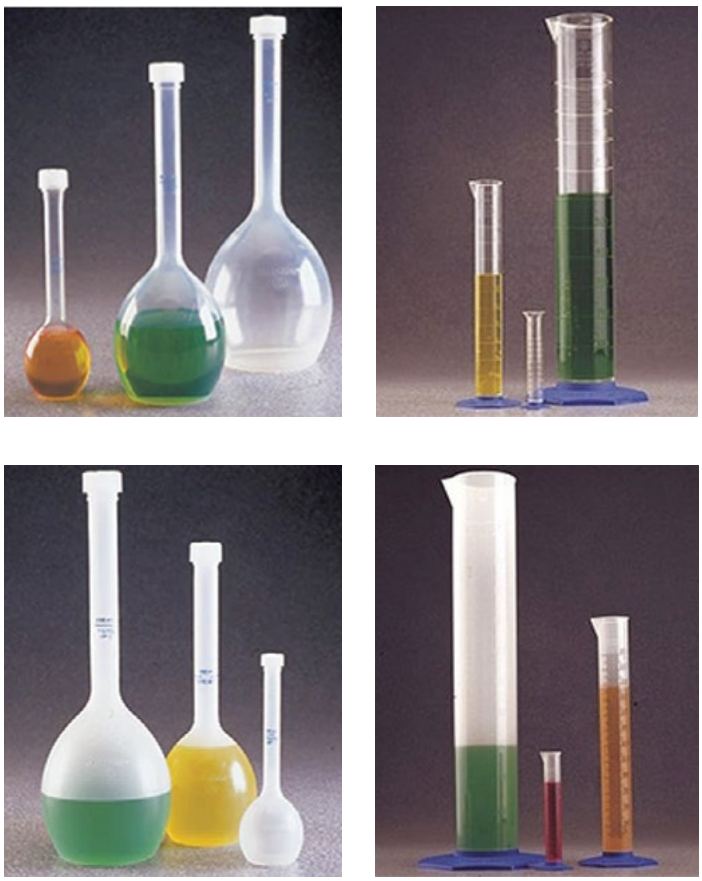


Figure 2.10 PMP volumetric flasks and graduated cylinders (left) have higher clarity compared to PP volumetrics (right) making PMP more suitable for accurate and precise preparation of standard solutions.

Transfer apparatus made from plastic is also preferred. Wash bottles made from Teflon™ with the screw cap, stem, and draw tube as one piece are recommended for storing and dispensing the acid diluent used to prepare standard solutions at trace and ultra-trace concentrations. Unitary wash bottles made from LDPE are appropriate for general purpose laboratory work. Disposable plastic transfer pipettes have numerous uses in the laboratory, including the preparation of standard solutions by dispensing small volumes of acid diluent precisely to the volume mark of a volumetric flask.

Additional information on the different types of plastics used for laboratory apparatus, including their structure and properties, can be found in the **Plastic material selection** page. This page includes resources such as **Plastic chemical resistance guides** and brochures for plastic laboratory ware. The **Lab plasticware and supplies** and **Thermo Scientific™ Nalgene™ labware** pages are additional helpful resources providing information and specifications on a comprehensive list of plastic laboratory apparatus and products.

An instance where the use of glass is advised over plastics is for preparations involving mercury. Mercury is very volatile and can be lost during preparation processes, acid digestion, and storage. Mercury tends to adhere to plastics, causing memory effects and cross-contamination. Mercury analyses require the addition of gold to stabilize mercury in solution and help wash it out of the ICP-MS sample introduction system and peristaltic pump tubing within a reasonable time. Method 200.8, Section 4.1.5, specifies a concentration of 100 µg/L of gold in all final dilutions of samples and calibration, quality control, and internal standard solutions for the analysis of mercury at 5 µg/L or less.

Note

All laboratory apparatus used for sample and standard preparation should be thoroughly cleaned according to a comprehensive cleaning procedure. The procedure specified in Method 200.8, Section 6.10, involves soaking apparatus in an acid bath for several hours. The procedure specified in the *SW-846 Compendium*, Chapter Three, "Inorganic Analytes," Section 3.3.3, entails a cleaning sequence starting with a phosphate-free detergent followed by tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, rinsing with tap water, and then reagent water. Apparatus should also be cleaned prior to use even if they are brand new. Clean all apparatus immediately after use to avoid the formation and sticking of residue which will make it more difficult to clean and may cause damage to the apparatus.

If higher concentrations of mercury are expected in the samples, a higher concentration of gold should be added. The instrument rinse solution should also contain gold at this concentration.

Pipettes and pipette tips

A very important tool in the laboratory for accurate dispensing and preparation of samples and standards is the pipette. A pipette can be fixed or variable volume. Almost all sample and standard preparation steps involve dilution and the quality of the prepared solution greatly depends on the accuracy of the pipettes and the skill and technique of the analyst using the pipette.

Variable volume pipettes, either mechanical or digital, with disposable plastic tips offer more convenience and a lower risk of contamination exposure over glass pipettes, hence, they are recommended for all sample and standard preparation steps within the elemental analysis workflow.

To cover the typical range of volumes dispensed for the preparation of dilute acid solutions, standard solutions, and samples for trace and ultra-trace concentrations, mechanical pipettes in the following volume ranges are recommended: 1 µL to 10 µL, 10 µL to 100 µL, 100 µL to 1000 µL, and 1 mL to 10 mL.

Figure 2.11 Mechanical, variable volume pipettes come in different models with features ranging from lightweight, ergonomic design, to lock in place tips, to the ability to withstand harsh chemicals and resistance to UV light.

Figure 2.12 Pipetting kits that include pipettes in different volume ranges, associated pipette tips, and pipette stand are available to help laboratories get started.

Pipettes should be calibrated by a third-party service at least annually and re-calibrated as necessary. To help ensure the accuracy of weights and volumes measured, documented weekly checks and daily spot checks are recommended. Weekly checks are performed by measuring a range of volumes, from the smallest to the largest, the pipette can dispense. Daily spot checks are done by checking the volume required for dilution prior to using the pipette for the preparation step.

Pipettes can be checked by measuring a volume of reagent water dispensed on a tared weighing dish placed on top of an analytical balance. For more accurate measurement, use the density of water at the ambient temperature to calculate the exact weight of the water dispensed by the pipette. The weight of water measured on the tared weighing dish should be within the tolerance level set by your laboratory's quality assurance protocol. All checks should be documented in a laboratory notebook for record and auditing purposes.

For additional information on pipettes and best practices, please refer to the **Single channel pipettes** page. On this page, different types of pipettes and pipetting kits can be viewed in addition to the **Good laboratory pipetting guide**.

Table 2.1 provides links to webpages where information and specifications regarding preparation, transfer, and storage apparatus can be accessed.

Figure 2.13 Best practices for using a mechanical pipette include the use of colorless tips, depressing the plunger slowly and smoothly, and using the pipette in an upright position.

Best practices

Recommended best practices for using mechanical pipettes:

- **Use one plastic pipette tip per stock standard, sample, or solution being prepared and dispose right after use to avoid cross contamination.**
- **Use colorless disposable tips. Colored tips may have trace impurities that can contribute contamination.**
- **Wet or wash the pipette tip several times by pulling and dispensing the acid diluent, stock standard, or sample, discarding after each wash.**
- **Pull liquid up slowly and smoothly to avoid air bubbles and inaccurate volumes.**
- **Do not immerse the pipette tip too deep into the liquid.**
- **Use the pipette in an upright position, as shown in Figure 2.13, to avoid liquid going up to the pipette causing damage. For most pipette models, pull liquid up until the first stop of the plunger is reached; this is the volume the pipette is set at.**
- **Dispense liquid slowly and smoothly, pressing the plunger to the second stop to release the set volume of liquid.**
- **Do not allow the pipette tip to touch the surface of laboratory countertops, fume hoods, and other workspaces to avoid contamination from dust, dirt, chemicals, etc., on these surfaces. Always clean and clear workspaces and lay an absorbent, lint free cloth over surfaces prior to use.**

Table 2.1 Common preparation, transfer, and storage apparatus for the elemental analysis workflow

Preparation, transfer, and storage apparatus		
Preparation	**Transfer**	**Storage**
Volumetric flasks • Plastic • Glass Variable volume pipettes Variable volume pipette tips Surface protector	Wash bottles • Teflon™ • LDPE Disposable plastic transfer pipettes Plastic graduated cylinders Plastic beakers	Plastic narrow mouth bottles Plastic wide mouth bottles Disposable plastic beakers Centrifuge tubes Carboys

2.3.3. Analytical balance

The analytical balance is used for accurate measurement of the small weight amounts (e.g., sub-milligram to gram) often measured for sample and standard preparations for ICP-MS analysis. A balance with readability to 0.1 mg, accuracy to 4 decimal places, and an enclosure to isolate the weighing pan and sample from fluctuations caused by the laboratory environment is required for precise and accurate measurements. An analytical balance that is certified (e.g., GLP) or manufactured in an International Organization for Standardization (ISO) 9001 quality management system should be selected.

The analytical balance must be calibrated periodically based on manufacturer's recommendation, how often it is used, its condition, and storage environment. Calibration should be performed and certified by a third-party service, accompanied by a certificate. The calibration should be done where the balance is stored and repeated if it is moved to a new storage location. Routine checking of the balance should be done in-house using certified standard test weights, traceable to national or international standards, to ensure validity of balance calibration and the accuracy, precision, and reproducibility of the weight measured. Standard test weights must also be recertified annually or sooner if they have been damaged by corrosion, scratches, chips, etc. which may affect their weight.

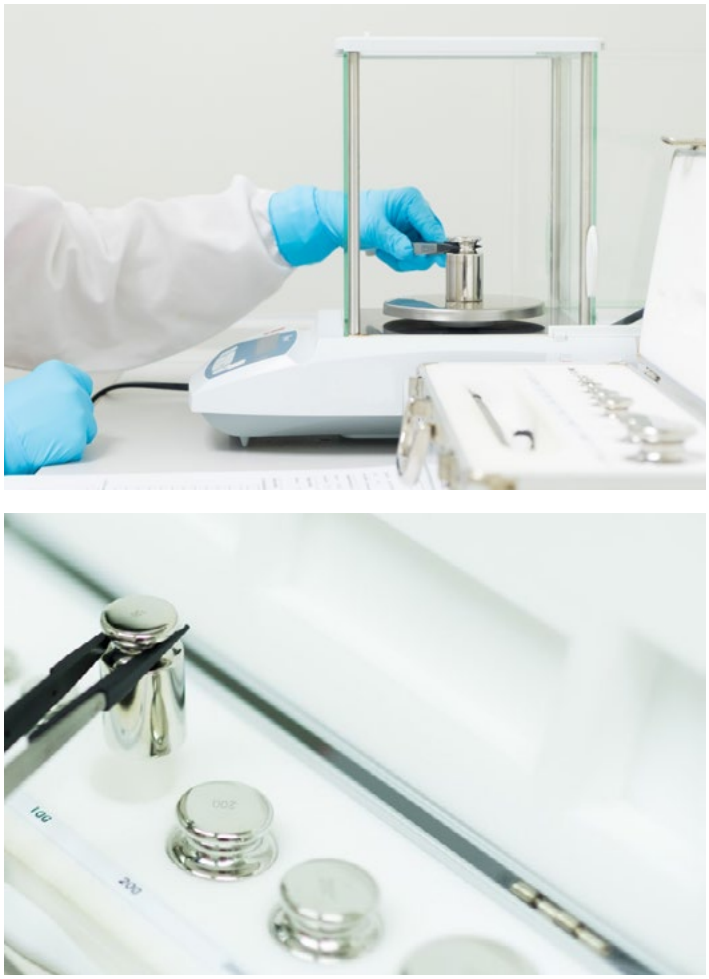


Figure 2.14 Documented periodic or daily inspections of analytical balances using certified test weights is a way to ensure the accuracy of weights measured.

Best practices

Recommended best practices for analytical balances

- Store the analytical balance on a stable countertop or on a sturdy, secure table away from windows and direct sunlight, HVAC vents, high traffic areas, doorways, and sources of vibration, as shown in Figure 2.15. Movement, variations in temperature, and vibrations will affect the weight measured and the precision of the analytical balance.
- The analytical balance should be operated at or near room temperature with the material to be measured also at room temperature prior to measurement.
- Remember to always level the analytical balance and place the sample in the center of the weighing pan.
- Clean any spilled chemicals, dust, dirt, and particulates on the weighing pan with reagent water and a soft cloth or a light brush.
- Before taking a measurement, close the enclosure door, tare the balance, and allow the reading to stabilize for a few seconds. Keep the enclosure door closed when the balance is not in use.
- Do not weigh sample, standards, or chemicals directly on the weighing pan, use a disposable weighing dish, as shown in Figure 2.16, weighing paper, or other weighing containers.
- A sample or standard may also be weighed in the container (e.g., hot block digestion vessel, autosampler tube) it will be used or prepared in. This helps to minimize transfer and handling steps that can introduce contamination.
- Glass and plastic weighing containers can become electrostatically charged causing drift and instability in the measurement. A way to avoid this affect is by using an ionizer to neutralize the charge on glass or plastic containers or using antistatic plastic weighing dishes.
- Disposable plastic weighing dishes and spatulas are recommended to avoid cross contamination.

Figure 2.15 Storing analytical balances in the corner of a room away from sources of vibration, movement, direct sunlight, and ventilation help to ensure accurate measurements.

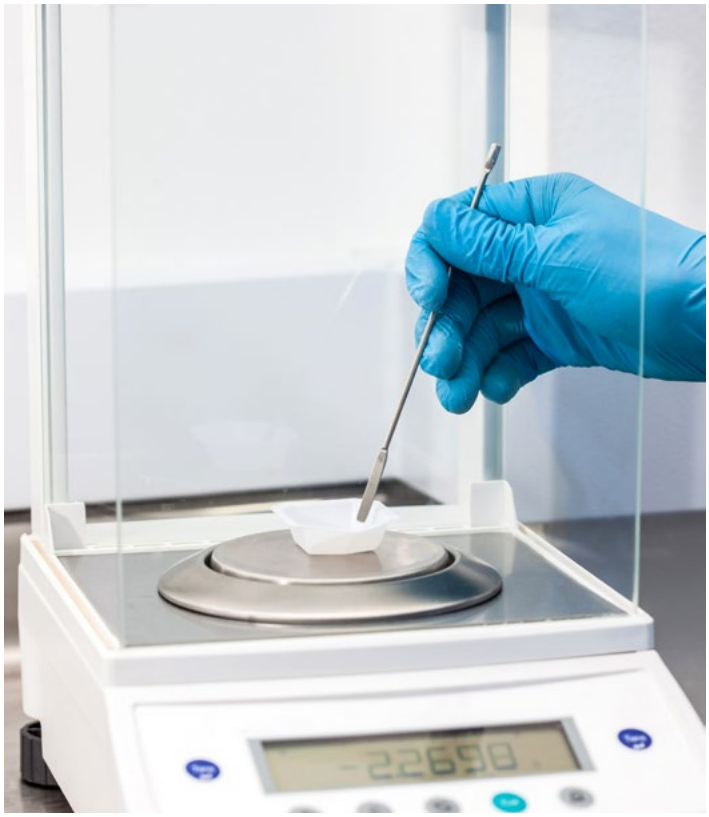


Figure 2.16 Weighing a sample on a disposable dish placed in the center of the balance pan helps to ensure accurate measurement and prevents damage to the pan and balance.

For more information and to view analytical balance products and specifications, please refer to the Analytical balances and Calibration weights pages. For analytical balance accessories, please refer to the Weighing dishes and paper and the Laboratory spatulas pages.

2.4 Clean laboratory atmosphere and workspace

The laboratory air can be a source of contamination with dust, dirt, and other particulate matter that can deposit on samples and standards at any step of the elemental analysis workflow. Dust particles can contain high levels of elements ubiquitous in nature (e.g., Na, K, Ca, Mg, Al, Si) and elements resulting from industrial pollution (e.g., Pb, Zn, Cu, Ni, Mn). Samples are susceptible to airborne contamination during open vessel acid digestion. Standards and samples are also vulnerable to airborne contamination prior to analysis while loaded on an autosampler for minutes or hours prior to introduction to the instrument.

To help prevent particulates in air from contaminating standards and samples, it is recommended to perform processes within the elemental analysis workflow in a *clean laboratory or cleanroom*. A cleanroom is specifically designed to have very low levels of particulates quantified by the number of particles per cubic meter or cubic foot in the atmosphere.

Outside air supplied to the laboratory is typically filtered and conditioned using building air handlers with very fine filters to remove particulate matter. The pre-filtered, pre-conditioned air is introduced to the clean laboratory, or cleanroom, through special filtering units containing High Efficiency Particulate Air (HEPA) filters. A HEPA filter has a standard efficiency of 99.97% {American Society of Mechanical Engineers (ASME) standard} removal of airborne particulates, dust, and other contaminants with a diameter size of 0.3 µm.[42] A higher performing filter used for cleanrooms is the Ultra-Low Particulate Air (ULPA) filter, capable of removing at least 99.999% of dust, pollen, bacteria, etc., with a size range of 1.2 µm. There are some similarities between HEPA and ULPA filters such as their construction and design and the way they trap contaminants. Their differences are not only in efficiency, but also in airflow, cost, and lifetime.[43]

Many cleanrooms are designed with laminar air flow and are called Unidirectional Airflow cleanrooms. Laminar air flow is the movement of air in a uniform direction and speed. The flow of a Unidirectional Airflow cleanroom is shown in Figure 2.17 with the HEPA filters in the ceiling. Laminar flow hoods, which will be discussed later in this chapter, maintain the unidirectional flow of a cleanroom.

The ISO standard for cleanrooms and controlled environments is ISO 146441-1:2015, it defines the cleanliness of air as a maximum number of specifically sized particles from 0.1 µm to 5 µm per cubic meter of air.[44] The ISO standard was developed from

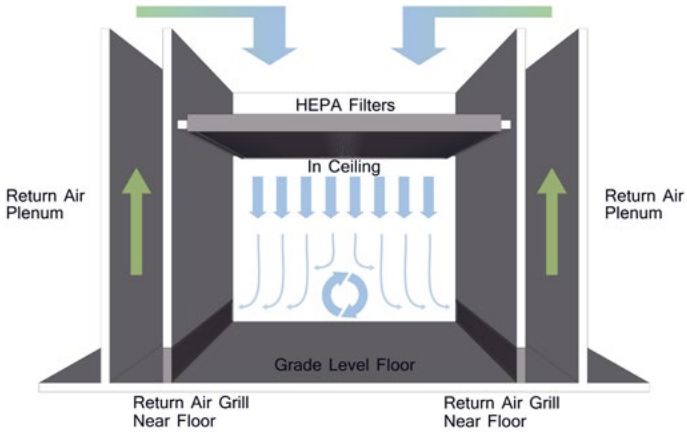


Figure 2.17 Schematic of unidirectional airflow with HEPA filters.

the U.S. Federal Standard, FED-STD-209E Airborne Particulate Cleanliness Classes in Cleanrooms and Clean Zones, which was globally applied.

The FED-STD-209E standard classifies cleanrooms by the maximum number of particles, from 0.1 µm to 5 µm, permitted per cubic foot of air. The name of the class in U.S. units is taken from the maximum allowable number of particles 0.5 µm or larger per cubic foot. For instance, a Class 100 cleanroom has less than 100 particles of 0.5 µm or large per cubic foot of air. There are six classifications, from Class 1 to 100,000.[45]

The ISO standard superseded the U.S. Federal Standard which was cancelled by the General Services Administration (GSA) in November 2001 due to the need for international standardization and a wider range of standards.[46] Compared with the Federal Standard that defines a cleanroom as one where the concentration of airborne particles is controlled, the ISO 14644-1:2015 standard defines a cleanroom as a room with the concentration of airborne particles controlled, in addition to being designed, constructed, and operated in a way to control the introduction, generation, and retention of particles.

The ISO standard classification for cleanrooms is designated by the ISO Class number, N, which defines the air cleanliness by particle concentration. The N indicates the decimal logarithm of the number of 0.1 µm particles. For example, an ISO 5 cleanroom has at most 100,000 particles sized 0.1 µm or larger per cubic meter of air. There are nine ISO classes for cleanroom with Class 1 being the cleanest.

Best practices

As a best practice for maintaining sample and standard integrity and preventing airborne contamination, it is recommended that the workflow for trace and ultra-trace elemental analysis be done in an ISO 5 (FED-STD-209E Class 100) clean laboratory or cleanroom.[47] An ISO Class 5 cleanroom has a maximum of 3,520 particles with a size > 0.5 µm per cubic meter of air. For environmental and industrial laboratories that do not have an ISO 5 cleanroom, preventing airborne contamination may be accomplished more conveniently using a laminar flow hood configured to meet ISO 5 requirements.

For additional information on clean working environments and the ISO 14644-1 maximum concentration limits for particles in air for each ISO classification (from Class 1 to Class 9), please refer to the SW-846 Compendium, Chapter Three, *Inorganic Analytes,* Section 3.4.2.1 and Table 3-5, Cleanliness Levels in International Standard ISO 14644-1.

2.4.1 Equipment for clean and safe workspaces

Fume hoods and laminar flow hoods are laboratory equipment designed to protect personnel from exposure to hazardous substances.[48] They are similar in appearance and provide a separate, enclosed workspace for the safe handling of chemicals, reagents, and samples. However, there are key differences in how they operate, hazard and sample protection, air flow, and their application in the laboratory or in the elemental analysis workflow that require a discussion to avoid confusion and improper application.

Fume hood

A fume hood is a ventilated enclosure specifically designed for safety and containment while working with hazardous chemicals. It protects the analyst and the laboratory environment from toxic fumes and volatile vapors by pulling air up through the hood for release outside the laboratory. It also provides a means for containing spills in case of an accident. Preparation processes within the elemental analysis workflow that use concentrated acids and toxic chemicals or emit gases should be performed under a fume hood (e.g., the preparation of dilute acid solutions from concentrated acids) as shown in Figure 2.18. However, a fume hood does not provide an ISO Class 5 workspace and prevent airborne particulates, hence, certain processes within the elemental analysis workflow (e.g., preparation of standard solutions at trace and ultra-trace concentrations) should not be performed in a fume hood.

Industry best practices for laboratory ventilation systems and guidelines for developing a Laboratory Ventilation Management Plan (LVMP) can be found in the document, ANSI/AIHA/ASSE Z9.5-2012 – Laboratory Ventilation. This document includes guidelines for design and specifications that can be used to achieve acceptable air contaminant concentrations, performance tests, air cleaning, and preventive maintenance.[49]

While a fume hood is an important part of an LVMP, there are additional industry standards that address laboratory ventilation and fume hood requirements: OSHA 1910.1450, Occupational exposure to hazardous chemicals in laboratories, and ANSI/ASHRAE Standard 110-2016 – Methods of Testing and Performance of Laboratory Fume Hoods. For instance, the OSHA standard requires fume hoods to function properly with measures taken to ensure proper, adequate performance.

There are two types of fumes hoods: ducted and ductless. A ducted fume hood, the more common among the two types, pulls conditioned laboratory air through the front sash into and up the fume hood. The air is then vented through ducts that go outside of the laboratory. Fumes are completely removed from the laboratory and are typically treated by a building's HVAC system before release to the environment. In many environmental, industrial, and university laboratories, ducted fume hoods are the only type permitted for use in maintaining personnel and workplace safety.

Figure 2.18 Fume hoods provide a safe, contained space for preparing solutions with concentrated, corrosive acids and other toxic chemicals. Always keep the fume hood workspace clean, clear, and organized when working with hazardous reagents.

A ductless fume hood works in a similar manner, the difference is in the presence of a series of filters and a fan contained in the fume hood to treat the contaminated air and recirculate it back to the laboratory environment. The hazards associated with all laboratory activities and chemicals being handled must be known to select the appropriate filter medium. If the hazards in the laboratory change due to the preparation of a new type of sample or addition of a new application, the filter medium must also be changed. This is one of the drawbacks of ductless fume hoods and the reason they are inappropriate for laboratories (e.g., environmental, contract testing, academic, research) that perform different applications or analyze a variety of samples; flexibility in fume hood operation is required for removing all types of known and future hazards. Some of the advantages and disadvantages of both types of fume hoods are summarized in Table 2.2.

Table 2.2 Comparison of ducted and ductless fume hoods[50]

Fume hood	Advantages	Disadvantages
Ducted 	• Safer for the analyst and laboratory environment as fumes are removed and vented outside. • Flexibility to handle a variety of samples and applications since the contaminated air is removed and not filtered and recirculated back to the laboratory. • Easy to operate and low maintenance. • Low noise since the exhaust fan is located away from the laboratory.	• More expensive and complicated installation as the fume hood must operate within the building's infrastructure and HVAC system. • Energy inefficient as conditioned, temperature-controlled laboratory air is removed and vented outside. • Contaminated air or fumes are vented to the outside environment and may not be appropriately treated prior to release.
Ductless 	• Less expensive and easier to install compared to ducted fume hoods. • Flexibility to relocate the hood within the laboratory. • Temperature controlled, conditioned air is not removed from the laboratory. Air is circulated back offering more efficient use of air. • Suitable when samples are known, chemical handling is light, and when hazards are known and will not change.	• More maintenance required due to the replacement of filters to ensure constant removal of hazardous substances from laboratory air. • More risk of chemical exposure compared to ducted fume hoods. • Not recommended for laboratories analyzing various or changing sample types or performing different applications.

Laminar flow hood

Laminar flow hoods, also referred to as clean benches or Biological Safety Cabinets (BSC), provide a controlled workspace for processes that require a clean and sterile environment. They protect samples and standards from airborne contamination by providing a constant, laminar flow of HEPA or ULPA filtered air vertically or horizontally over the workspace. They are available in configurations that meet ISO standards for cleanrooms which are suitable for trace and ultra-trace elemental analysis preparations {e.g., ISO Class 4 (Class 10), ISO Class 5 (Class 100)}.

There are two types of configurations for laminar flow hoods based on filtered air flow:

- **Horizontal –** Air flow is parallel to the workspace, flowing from the back of the hood, where the filters are located, towards the front where the analyst works. Since the air flow is towards the analyst, a horizontal laminar flow hood should not be used when handling or working with hazardous, toxic chemicals.
- **Vertical –** Air is filtered from the top of the hood and then flows down towards the workspace. Vertical laminar flow hoods provide a higher, or taller, workspace which allows the use of larger equipment inside the hood.

For the preparation of ultra-trace concentration standard solutions, a vertical laminar flow hood is more appropriate compared to a horizontal laminar flow hood. Figure 2.19 shows the air flow in a vertical laminar flow hood.

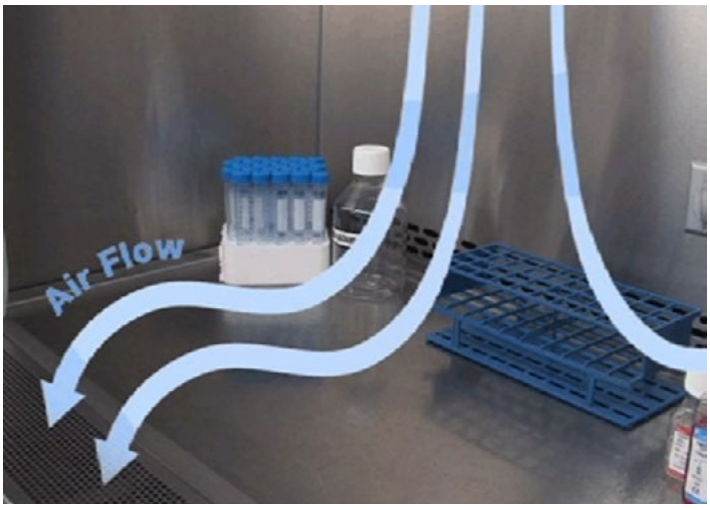


Figure 2.19 Air flow in a vertical laminar flow hood.

Laminar flow hoods protect the sample from airborne contamination, however, not all types also provide protection for the analyst from toxic, hazardous substances. Biological Safety Cabinets (BSC) are a type of laminar flow hood that provides protection to the analyst from harmful substances being handled in the cabinet, protection to sample from contamination, and protection of the environment (laboratory and external environment) from aerosols generated or contaminants inside the cabinet. Such protections are accomplished by engineered controls built in each BSC. The main uses of BSCs are for cell culture, pharmaceutical, clinical, and microbiological work. They can also be used when handling radioisotopes, carcinogenic and toxic chemicals. Due to these critical applications, BSCs are regulated and must comply with the NSF International/ANSI 49 standard. There are three classes of BSCs:

- **Class I –** Provide protection to the analyst and the environment but not to the sample. They are similar in design to a fume hood. These BSCs are generally used to contain equipment (e.g., centrifuges) or perform procedures that generate aerosols.
- **Class II –** They are designed with an inward airflow drawn in the front opening that instantly gets captured into the front intake grille (analyst protection) and with a smooth downward flow of HEPA filtered air that gets split. Half goes to the front intake grille (sample protection from airborne contamination and cross contamination) and the other half goes to the back grill as exhaust airflow that is HEPA filtered (laboratory and external environmental protection). Class II BSCs are further classified as A1, A2, B1, B2, and C1. Among the five types, B2 should be used when working with biological hazards; volatile, toxic chemicals; and radionuclides. The B2 BSC is designed in such a way that the air pulled in from the front and the air flowing down from the top of the cabinet are pulled up, passing through a HEPA filter before being exhausted outside the building. The air does not get recirculated back to the cabinet or returned to the laboratory environment. For this reason, B2 BSCs are also referred to as 100% Exhaust or Total Exhaust cabinets.[51] Compared to an A2 BSC, a portion of the inflow air is recycled back into the cabinet and the rest is exhausted outside; approximately 70% of the air is recycled and 30% passes through a HEPA filter before exhaust. Although both BSCs can be used when working with volatile, toxic chemicals and radionuclides, the B2 BSC dilutes volatile, toxic chemicals to a greater extent than an A2. However, the B2, and A2, cannot be used when handling or working with flammable, corrosive, and explosive materials. Figure 2.20 compares the air flow within the A2 and B2 BSCs.

Figure 2.20 Flow of air within the A2 (left) and B2 (right) BSCs; most of the total air flow in an A2 gets recirculated back to the cabinet while 100% of the air flow in a B2 gets exhausted.

- **Class III –** These BSCs are also called glove boxes. They are completely enclosed, ventilated, gas-tight with rubber gloves attached for performing work inside the cabinet. They provide the highest level of protection to the analyst and the environment and are typically used when working with pathogens.

For additional information and to view types of fume hoods and accessories, please refer to the **General purpose fume hoods** page. For additional information on BSCs, please refer to the **Laminar flow hoods**, **Class II biosafety cabinets**, **Class II, Type A2 biosafety cabinets**, and **Class II, Type B2 biosafety cabinets** pages.

Key takeaways for fume hoods and laminar flow hoods

- Fume hoods protect the analyst and the laboratory environment from toxic fumes, vapors, hazardous substances, and dust. It also provides an enclosed workspace to prevent widespread chemical spills.
- Processes within the elemental analysis workflow that involve handling concentrated acids, toxic chemicals, and the generation of fumes and vapors must be done in a fume hood (e.g., open vessel acid digestion, preparation of acid diluents).
- Laminar flow hoods provide a clean, sterile workspace that protects samples and standards from contamination.
- A laminar flow hood configured for ISO Class 5 cleanliness requirements, at a minimum, should be used for the preparation of standard solutions at trace and ultra-trace concentrations.
- A vertical laminar flow hood should be used over a horizontal laminar flow hood for the preparation of standard solutions.
- Always keep the fume hood and laminar flow hood workspaces and surface clean and clear.
- For protection of samples and standards from airborne contaminants and protection of the analyst and laboratory environment from toxic fumes, vapors, and hazardous chemicals, a Class II Type B2 BSC should be used.
- BSCs must not be used when handling corrosive, flammable, or explosive materials.
- Always consult your laboratory safety adviser and a manufacturer's representative to determine the fume hood, laminar flow hood/BSC that provides the protection required for the analytical workflows, applications, and hazards present in your laboratory.

2.5 Selection and use of reagents

2.5.1 Reagent water

Reagent water is copiously used throughout the elemental analysis workflow and can be a major source of contamination. For preparations, dilutions, and cleaning laboratory apparatus and instrument components, it is essential that the reagent water is at a high level of purity appropriate for trace and ultra-trace analyses. Method 200.8, Section 7.2, states that all references to reagent water in the method refer to ASTM Type 1 water (ASTM D1193, Standard Specifications for Reagent Water). This type of water is also known as ultrapure water and in the context of this document, reagent water will refer to this. The use of ultrapure water is imperative as the presence of dissolved and suspended particulates, organic and inorganic compounds, high levels of salts, and other impurities present in untreated water will contaminate samples, standards, acid diluent, and rinse solutions and cause an elevated calibration blank. The quality and purity of water is measured by its conductance (reciprocal of resistivity). Ultrapure water has a resistivity of 18.2 MΩ-cm, or a conductivity of 0.05501 µS/cm. Inability to obtain ultra-trace detection limits may be due to an elevated calibration blank prepared from water that is not at this standard level.

Ultrapure water is often confused with or used to refer to deionized (DI) water and vice versa. They are not the same and these terms should not be used interchangeably. Ultrapure water has gone through a more comprehensive treatment process that entails passing feed water through a combination of filters, ion exchange cartridges, reverse osmosis systems, etc. to remove trace metals, organic material, dissolved gases, and suspended particles to achieve a resistivity of 18.2 MΩ-cm. While deionized water has almost all of the mineral ions (e.g., sodium, calcium, iron, chloride, sulfates) removed using mixed-bed cartridges with cation-exchange and anion-exchange resins. However, organic material, viruses, and bacteria are not typically removed.

For further information on water purification systems and to view available products and accessories (e.g., replacement cartridges, consumables), please refer to the **Water purification** page. Also, consult a water purification system manufacturer for the system that meets the applications and needs of your laboratory.

2.5.2 Concentrated acids

Concentrated acids can be another source of contamination. Like the reagent water used for preparations and dilutions of samples and standards, the use of ultra-high purity acids is necessary to achieve trace and ultra-trace detection limits and avoid an elevated calibration blank.

Different grades of acid are available on the market, such as, ultrapure, analytical grade, extra pure grade, etc. Lower purity acids contain trace levels of elemental impurities that can interfere with the analytical measurement and cause inaccurate results, especially for trace and ultra-trace analyses. These acids are generally suitable for applications involving analysis by FAAS or ICP-OES for high ppm to percentage levels of detection and higher. For detection limits in the sub-ppb to ppt range, ultrapure acids, such as Fisher Chemical™ Optima™ Nitric Acid 67-69% for Ultra Trace Elemental Analysis and double distilled grades are required.

Concentrated nitric and hydrochloric acids are the two most predominantly used for the preparation of standard solutions and sample preparation. Nitric acid is preferred due to the solubility of nitrates, its oxidizing ability, and commercial availability. From an analysis standpoint, nitric acid does not contribute as many spectral interferences for ICP-MS analysis as hydrochloric acid, sulfuric acid, and phosphoric acid. When comparing between double distilled grades, nitric acid is the cleanest in terms of trace elemental impurities. However, to maintain the stability of certain elements (e.g., silver, antimony), hydrochloric acid is required to prevent the formation of insoluble precipitates and photoreduction.

Best practices

Recommended best practices for handling concentrated acids

- Prior to handling concentrated acids, review their Safety Data Sheets and know where the nearest eyewash, shower station, and acid spill kits are in the laboratory. Know the hazards associated with each acid: nitric and hydrochloric acids are corrosive and highly irritating to skin; hydrofluoric acid is extremely corrosive and penetrates the skin and tissues deeply; and sulfuric acid is viscous, highly corrosive, and reacts vigorously with water releasing a lot of heat. More information on concentrated acids will be provided in Chapter 5.
- Always consult your laboratory safety officer for the appropriate PPE to use when handling concentrated acids.
- When preparing solutions from concentrated acids, always work in a fume hood.
- Open vessel acid digestions using a hot plate or a hot block must be performed under a fume hood.
- Prior to use, prepare the fume hood workspace by removing unnecessary chemicals, apparatus, and equipment that can interfere with preparations and lead to spills and accidents. Clean or wipe the fume hood surface prior to and after use.
- Make sure the fume hood is functioning properly and adjust the fume hood sash to cover the face and body prior to use and handling concentrated acids.
- Handle all concentrated acids slowly and with extra caution.
- Always add acid to water, never the other way around. If water is added to acid, a reaction will occur releasing heat. The concentrated acid solution can boil and splatter as shown in Figure 2.21. Conversely, when acid is added to water slowly, the acid solution formed is dilute, the amount of heat released is smaller, and the solution is not as likely to splatter and boil.

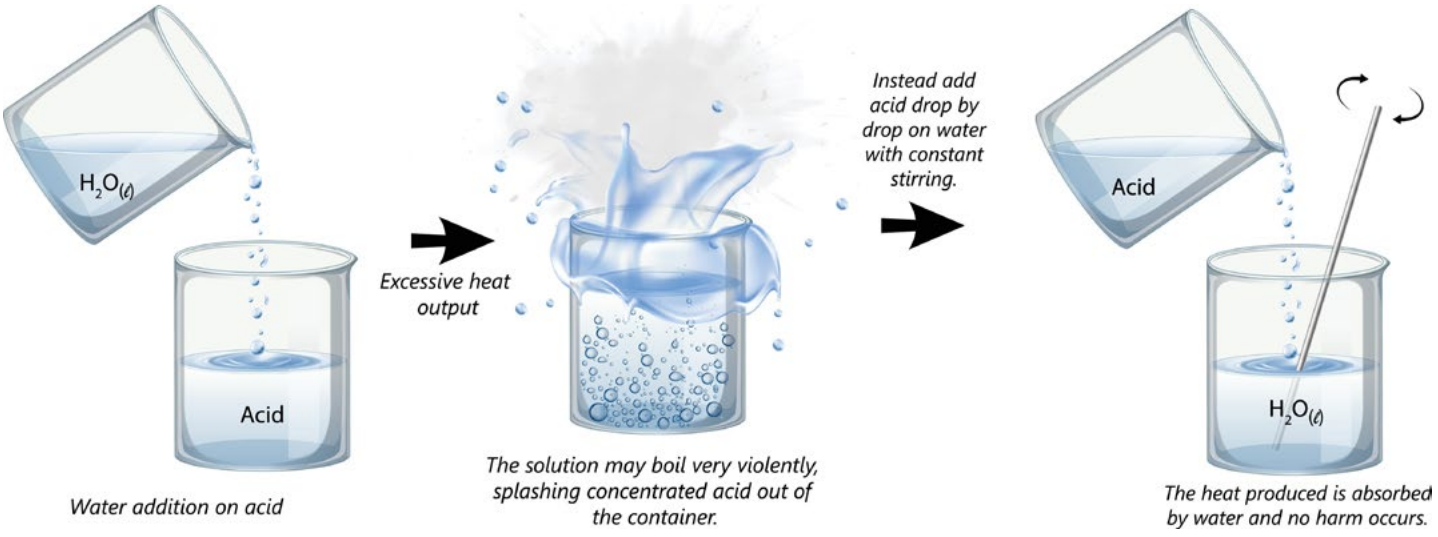


Figure 2.21 Schematic showing what happens when water is added to acid. Always add acid slowly to water to dilute the acid and avoid splattering, boiling, and generation of a high amount of heat.

Figure 2.22 Concentrated acids used for trace elemental analysis by Fisher Chemical™ TraceMetal™ Grade (left), Optima™ Grade (center), and ACS Plus grade.

Table 2.3 Common concentrated acids for trace and ultra-trace elemental analysis

Concentrated acid products	Volume
Nitric Acid, 67-69% (Optima™), Fisher Chemical™	1L
Hydrochloric Acid, 32-35% (Optima™), Fisher Chemical™	1L
Hydrofluoric Acid, 47%-51%, (Optima™), Fisher Chemical™	500 mL
Sulfuric Acid (Optima™), Fisher Chemical™	1L
o-Phosphoric Acid, 85% (Certified ACS), Fisher Chemical™	500 mL

2.5.3 Stock standards

Stock standards used for the preparation of intermediate, calibration, quality control, and internal standard solutions should be certified and of the highest purity possible (99.99 – 99.999%). Stock standards specified for ICP-MS analysis should be used and be National Institute of Standards and Technology (NIST) traceable, manufactured under a quality system that complies with ISO 9001, ISO 17025, and ISO 17034 requirements, and come with a certificate of analysis that provides information on trace impurities. Sections 7.1 of Method 200.8 and Method 6020B specify the use of certified, ultra-high purity stock standards and reagents for calibration and standard solution preparations. It is also recommended to select stock standards from reputable commercial sources with a history of manufacturing proven stock standards.

Stock standards can either be purchased or prepared from individual metal salts or solids. For trace and ultra-trace analyses, it is highly recommended to purchase stock standards as preparation from individual metal salts involve additional steps (e.g., weighing, pickling, drying) that can introduce contamination. It is also best practice to prepare calibration standard solutions from multi-element stock standards rather than preparing from single element stock standards. Using multi-element stock standards saves time, streamlines the preparation process, and minimizes exposure to contamination by eliminating numerous handling and transfer steps.

Tip

Custom standards at the concentrations required for calibration may be purchased from standard manufacturers. Custom standards offer convenience and streamline the standard preparation process, saving time and resources. Furthermore, they can be analyzed directly, without further processing or dilution steps which can introduce contamination. Consult a standard manufacturer for custom standard options available.

Although the use of multi-element stock standards is recommended, single element stock standards are preferred for the preparation of certain standards or analytes. As specified in Section 7.4, the concentration of Hg should be kept at < 5 µg/L due to its tendency to adhere to plastic and memory effects. Mercury standard solutions should be prepared in a borosilicate glass volumetric flask, not in a plastic flask with other analytes. Another instance where preparation from single element stock standards is preferred is for the preparation of the internal standard solution. It is recommended to use a single element stock standard of each internal standard element to allow preparation of each element at a different concentration. More information on the preparation of the internal standard solution will be discussed in Chapter 3.

Standards for Method 200.8 analysis

Calibration standards

Multi-element calibration standard solutions must contain elements that are compatible and stable and prepared in the appropriate acid matrix. Two suggested combinations of multi-element calibration standard solutions are given in Section 7.4 of Method 200.8. A concentration range of 10 to 200 µg/L depending on the sensitivity of the instrument is suggested. Method 200.8 also specifies that the concentration of Hg be limited to < 5 µg/L and for the concentration of Se to be a factor of 5 greater than the other analytes in the calibration standard.

Additional information regarding compatibility and stability of calibration standard solutions will be provided in Chapter 3.

Quality Control Sample (QCS)

The QCS is used to verify the calibration and performance of the instrument. The QCS should be obtained from a source outside the laboratory, or, from a source or vendor different than the stock standards used to prepare the calibration standards. Section 7.8 specifies that the concentration of all elements in the QCS be at 100 µg/L except for Se which should be at 500 µg/L and Hg limited to a concentration of 5 µg/L.

Tuning solution

The instrument tuning solution is used for performance verification and mass calibration. Method 200.8 specifies a tuning solution of 100 µg/L of Be, Mg, Co, In, and Pb in a 1% nitric acid. This solution may be diluted depending on the sensitivity of the instrument. The tuning solution that comes with the instrument may include different elements in a different acid matrix (e.g., nitric acid and hydrochloric acid). It is common practice to use the tuning solution that comes with the instrument and then add method specified elements that were not included. However, consult your laboratory Quality Assurance Manager or regulatory auditors to confirm whether this practice is acceptable in meeting audit requirements.

The requirements and preparation procedures for the tuning solution and calibration, quality control, and blank {e.g., Laboratory Reagent Blank (LRB), Laboratory Fortified Blank (LFB)} standards are given in Section 7.0. of Method 200.8.

Recommended stock standards

A list of recommended stock standards from reputable commercial sources is provided in Table 2.4. At least two manufacturers are provided as options. Please take note of the concentration of each element in the multi-element calibration and QCS stock standards. Some of these stock standards were prepared according to the specifications in Section 7.4 with Se at a concentration five times higher than other elements while other

Note

Method 200.8 specified multi-element stock standards prepared according to the specifications for Hg and Se in Section 7.4 are available on the market. However, other Method 200.8 specified multi-element stock standards with all elements at the same concentration are also available. Please take note of the concentration of each element in a multi-element stock standard and select the standard with the combinations of analytes and concentrations appropriate for the analysis and application.

stock standards have all elements at the same concentration. Also, note that the concentrations of the multi-element stock standards were optimized for the preparation of standard solutions from ultra-trace to the high-level ppm range. Method 200.8, Section 7.8 specifies that the QCS be obtained from a source outside the laboratory. In other words, from a source other than that used to prepare the calibration standard solutions. Hence, two manufacturer options were provided in the table.

Single element Hg and Au stock standards were also included. It is recommended to prepare Hg separate from other elements due to stability and compatibility issues. To address the memory effects associated with Hg, single element Au stock standards were also included for preparation of an Au solution to add to all standards and samples in the analytical run sequence, including the rinse solution.

Table 2.4 Stock standards recommended for Method 200.8 analysis

Manufacturer	Stock standard description	Volume (mL)
Method 200.8 calibration standards according to Section 7.4		
Thermo Scientific™	ICP-MS Stock Standard Solution A for 200.8, Revision 5.4, Specpure™ Al, As, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Th, Tl, U, V – 10 µg/mL; Se – 50 µg/mL	100
	ICP-MS Stock Standard Solution B for 200.8, Specpure™ Ag and Ba – 10 µg/mL	100
	Mercury Plasma Standard Solution, Specpure™ Hg – 10 µg/mL	100
Inorganic Ventures	200.8 Calibration Solution 2A Al, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Ag, Tl, Th, U, V, Zn – 20 µg/mL; Se – 100 µg/mL	125
	200.8 Calibration Solution 1 Sb, Mo – 20 µg/mL	125
	200.8 Calibration Standard 3 Hg – 5 µg/mL	125
SPEX CertiPrep™	Claritas PPT™ Grade ICP-MS Instrument Calibration Standard 1A Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Ag, Tl, Th, U, V, Zn – 10 µg/mL Se – 50 µg/L	125
	ICP-MS Mercury Single Element Standard Hg – 10 µg/mL	125
Other calibration standards for Method 200.8		
Inorganic Ventures	200.8 Calibration Solution 2 Al, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Ag, Tl, Th, U, V, Zn – 20 µg/mL	125
SPEX CertiPrep™	Instrument Calibration Standard 2 for ICP-MS Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Ag, Tl, Th, U, V, Zn – 100 µg/mL	125

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Table 2.4 Stock standards recommended for Method 200.8 analysis *(continued)*

Manufacturer	Stock standard description	Volume (mL)
Quality control standards		
Inorganic Ventures	200.8 Quality Control Standard 3 Al, Sb, As, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Ag, Na, Tl, Th, U, V, Zn, Ba – 10 µg/mL Se – 50 µg/mL	125
	200.8 Quality Control Standard Hg Hg – 5 µg/mL	125
SPEX CertiPrep™	Claritas PPT™ Grade ICP-MS Initial Calibration Verification Standard 3 Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Ag, Tl, V, Zn – 10 µg/mL Se – 50 µg/mL; Ca, Fe, K, Mg – 100 µg/mL	125
	Instrument Check Standard 4 Mo, Th, U – 10 µg/mL	125
Tuning solutions		
Thermo Scientific	For the Tune Solution used with Thermo Scientific ICP-MS instrumentation, refer to Chapter 6 of this document.	
Inorganic Ventures	200.8 Tuning Solution Be, Co, In, Pb, Mg – 10 µg/mL	125
SPEX CertiPrep™	Tuning Solution 2 Ba, Be, Ce, Co, In, Pb, Mg, Rh, U – 10 µg/mL	125
Single element standards		
Inorganic Ventures	Gold Single Element Standard for ICP-MS Au – 100 µg/mL	125
SPEX CertiPrep™	Gold Standard 1 for ICP-MS Au – 100 µg/mL	125

Standards for Method 6020B analysis

Calibration standards

Prepare calibration standards by diluting multi-element stock standards to concentrations that cover the range of analyte concentrations in the sample but within the linear dynamic range of the instrument. This is an important note as samples analyzed according to Method 6020B often contain analytes at concentrations higher than the linear dynamic range. To help in optimizing the calibration range, perform a semi-quantitative anlaysis to determine the range of analyte concentrations present in the samples.

Quality control standards

Requirements for initial and continuing calibration verification are given in Sections 7.24 and 7.25 of Method 6020B. For the Initial Calibration Verification (ICV) standard, the method specifies that this be prepared from a source different from that used to prepare the calibration standards with analyte concentrations near, but not equal to, the midpoint of the calibartion curve. The Continuing Calibration Verification (CCV) standard is to be prepared from the same stock standard used to prepare the calibration standards with the analyte concentrations equal or nearly equivalent to the midpoint of the calibration curve.

Tuning solution

The tuning solution should be prepared to cover the entire mass range of the analytes. Section 7.26 specifies a tune solution consisting of Li, Co, In, and Tl at 10 µg/L. It is common practice to add these elements if they are missing from the tuning solution that accompanies the instrument. As previously mentioned, it is recommended to consult your laboratory or regulatory auditors to confirm whether this practice is acceptable in meeting audit requirements.

Interference check standards

The purpose of the Spectral Interference Check (SIC) solutions are to test the effectiveness of the interference correction technique (e.g., mathematical equations, collision/reaction cell technology) applied during the anlaysis. Method 6020B specifies that the SIC solutions contain the commonly known interferents in environmental samples: Al, Ca, Fe, Mg, Na, K, P, S, and C. The addition of Chloride in the SIC solution is intended to evaluate software corrections on common polyatomic interferences containing chloride (e.g., ArCl, ClO). The requirements and preparation procedures for the SIC solution are given in Section 7.23. The working SIC solution should contain these interferents in addition to Ti and Mo as specified in Section 7.23.2. If other inteferents are suspected to be present in the sample, it is the responsibility of the laboratory to confirm their presence and then modify or prepare another SIC solution accordingly.

A standard analyzed by many enviromental and contract testing laboratories to test the performance of the interference correction applied is the Interference Check Sample (ICS), which consists of two solutions: ICS Solution A (ISCA) and ICS Solution AB (ICSAB). The ICSA consists of the interferents at specific concentrations while the ICSAB consists of the interferents and the analytes also at specific concentrations. The analyses of the ICSA and ICSAB are required in every analytical run sequence according to the Quality Assurance and Quality Control (QA/QC) protocol of the CLP. As previously discussed, the CLP was established under RCRA and one of its functions is to manage the analyses of samples under the EPA Superfund program. Laboratories contracted under the CLP must comply with comprehensive QA/QC protocols and analytical requirements to ensure data produced is of known and documented quality. With the QA/QC protocols of the CLP being recognized as comprehensive and stringent, laboratories integrate parts of this protocol into their analytical methods and SOPs; the addition of the ICSA and ICSAB solutions to every analytical run sequence is an example.

The requirements and preparation of the SIC solutions and calibration and QC standards are detailed in Section 7.0 of Method 6020B.

Stock standards

A list of stock standards for Method 6020B analysis is provided in Table 2.5. The calibration stock standards listed should also be used to prepare the CCV standard. The ICV standard is to be prepared from a stock standard different than that used to prepare the calibration standards, hence, at least two manufacturers are listed. For the interference check standard, multi-element stock standards prepared according to Method 6020B and CLP requirements are both provided. Multi-element spike standards for soil and water analyses are also provided.

Table 2.5 Recommended stock standards for Method 6020B analysis

Manufacturer	Stock standard description	Volume (mL)
Stock standards for calibration, ICV, and CCV		
Thermo Scientific™	ICP-MS Calibration Standard Solution 6020, Specpure™ Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Tl, V, and Zn – 10 µg/mL	100
	Mercury, Plasma Standard Solution, Specpure™ Hg – 10 µg/mL	100
	Gold, Plasma Standard Solution, Specpure™ Au – 1000 µg/mL	100
Inorganic Ventures	6020 Calibration Solution Al, Sb, As, Be, Ba, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, Na, Tl, V, and Zn – 20 µg/mL	125
	ICP-MS Calibration Standard 33 Ca, Fe, Mg, K, and Na – 500 µg/mL	125
	Aluminum Standard Al – 1000 µg/mL	125
SPEX CertiPrep™	Instrument Calibration Standard 1 for ICP-MS Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Ag, Tl, Th, U, V, and Zn – 20 µg/mL	125
	Calibration Standard 3 for ICP-MS Ca, Fe, Mg, K, and Na – 1000 µg/mL	125
	Mercury Standard for ICP-MS Hg – 10 µg/mL	30
	Initial Calibration Verification Standard 1 for ICP-MS Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Ag, Tl, Th, U, V, Zn – 10 µg/mL Ca, Fe, Mg, K, Na, Sr – 1000 µg/mL	125
Interference check standards		
Thermo Scientific™	ICP-MS Interference for 6020 ICS, Specpure™ Al, Mg, P, K, S – 1000 µg/mL; Ca – 3000 µg/mL Fe, Na – 2500 µg/mL; C – 2000 µg/mL; Cl – 20000 µg/mL Mo, Ti – 20 µg/mL	500
	Interference Check Standard A (ICS-A) Solution, Specpure™ Al, Ca, Mg – 5,000 µg/mL; Fe – 2,000 µg/mL	500
	Interference Check Standard B (ICS-B) Solution, Specpure™ Ag, Al, As, Cd, Co, Cr, Cu, Mn, Ni, Se, V, Zn – 10 µg/mL	100

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Table 2.5 Recommended stock standards for Method 6020B analysis *(continued)*

Manufacturer	Stock standard description	Volume (mL)
Interference check standards *(continued)*		
Inorganic Ventures	6020 Interference Check Solution A Al, K, Mg,P, S – 1000 µg/mL; Ca – 3000 µg/mL; C – 2000 µg/mL; Cl – 18000 µg/mL Fe, Na – 2500 µg/mL; Mo, Ti – 20 µg/mL	500
	6020 Interference Check Solution A (high chloride) Al, Mg, P, K, S – 1000 µg/mL; Ca – 3000 µg/mL; C – 2000 µg/mL; Cl- - 21215 µg/mL; Fe, Na – 2500 µg/mL; Mo, Ti – 20 µg/mL	500
	6020 Interference Check Solution B (Analytes) As, Cd, Se, Zn – 10 µg/mL; Cr, Co, Cu, Mn, Ni, V – 20 µg/mL; Ag – 5 µg/mL	125
	6020 Interference Check Solution A (CLP concentrations) Al, Ca, Fe, Mg, P, K, Na, S – 1000 µg/mL; C – 2000 µg/mL; Cl – 10,000 µg/mL; Mo and Ti – 20 µg/mL	500
	6020 Interference Check Solution B (CLP concentrations, note: some CLP analytes missing) As, Cd, Cr, Co, Cu, Mn, Ni, Ag, and Zn – 2 µg/mL	125
SPEX CertiPrep™	ICP-MS 6020 Interferents A Al, Mg, P, K, S – 1000 µg/mL; Ca – 3000 µg/mL; C – 2000 µg/mL; Cl- - 21215 µg/mL; Fe, Na – 2500 µg/mL; Mo, Ti – 20 µg/mL	125
	ICP-MS 6020 Interferents B As, Cd, Se, Zn – 10 µg/mL; Cr, Co, Cu, Mn, Ni, V – 20 µg/mL; Ag – 5 µg/mL	125
Tuning solutions		
Thermo Scientific	For the Thermo Scientific ICP-MS instrument tuning solution, refer to the Chapter 6 of this document.	
Inorganic Ventures	6020 Tuning Solution Co, Li, Tl, In – 10 µg/mL	125
SPEX CertiPrep™	ICP-MS Tuning Solution 4 Co, Li, Tl, In – 10 µg/mL	125

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Table 2.5 Recommended stock standards for Method 6020B analysis *(continued)*

Manufacturer	Stock standard description	Volume (mL)
Spike standards		
Inorganic Ventures	6020 Water Spike Solution As, Pb, - 10 µg/mL; Sb, Cr, Co, Cu, Mn, Ni, V – 20 µg/mL; Cd, Be, Se, Ag, Tl – 5 µg/mL; Fe – 100 µg/mL; Ba, Zn – 50 µg/mL	125
	6020 Soil Spike Solution As, Cd, Ag – 10 µg/mL; Sb, Co, Pb – 20 µg/mL; Be, Se, Tl – 5 µg/mL; Ni – 25 µg/mL; V – 30 µg/mL; Ba, Cr, Cu, Zn – 50 µg/mL	125
SPEX CertiPrep™	ICP-MS Spike Sample 1 (Water) Sb, Cr, Co, Mn, Ni, V – 100 µg/mL; As, Pb – 50 µg/mL; Be, Cd, Se, Ag, Tl – 25 µg/mL; Fe – 500 µg/mL; Ba, Zn – 250 µg/L	125
	ICP-MS Spike Sample 2 (Soil) As, Cd – 50 µg/mL; Be, Se, Ag, Tl – 25 µg/mL; Sb, Co, Pb – 100 µg/mL; V – 150 µg/mL; Ni – 125 µg/mL; Ba, Cr, Cu, Zn – 250 µg/mL	125

3 Calibration and standardization routines

Instrument calibration is fundamental for a broad range of analytical chemistry techniques. For ICP-MS, several calibration strategies can be employed: external calibration, matrix-matched calibration, standard additions, and isotope dilution.[52] The most common strategy is external calibration as it is the most straightforward to implement and required for analysis by the EPA methods. Hence, it will be the only strategy discussed in this chapter.

After warming up the instrument, a pre-calibration routine that consists of tuning specific instrument parameters is necessary to ensure manufacturer's performance specifications are met prior to calibration and sample analysis. Tuning is essential for optimization, ensuring consistent daily performance and accurate results. Requirements for instrument tuning are given in Section 10.0 of Method 200.8 and Method 6020B.

3.1 Pre-calibration routine

Tuning an ICP-MS instrument can be performed manually or automatically through an instrument software tuning procedure or an *Autotuning* feature. Manual tuning is typically done by an experienced ICP-MS analyst or for diagnostic purposes. For routine applications, automatic tuning is recommended.

Although the tuning procedure can vary between instruments and applications, the basic principles are essentially the same and involve tuning important parameters such as the torch position, flow rates (e.g., nebulizer flow), lens voltages (e.g., extraction lens, Collision/Reaction Cell) and other parameters. The solution used to tune the ICP-MS is the tuning solution which consists of elements that cover the mass range, from low to high mass, in a dilute acid matrix. The tuning solution is also used for mass calibration and checking instrument resolution. For Method 200.8, the tuning solution consists of Be, Mg, Co, In, and Pb at 100 µg/L in 1% nitric acid, while for Method 6020B, the tuning solution should contain 10 µg/L Li, Co, In, and Tl.

After tuning, a Performance Report is generated to document proper tuning and the optimization of operating parameters to meet manufacturer's and method performance specifications. It provides a documentation of system performance, which is required for auditing and helpful for troubleshooting purposes. A Performance Report typically includes tests on sensitivity, stability, mass calibration, resolution, oxides, and the level of interferences.

Methods 200.8 and Method 6020B each have specific requirements for mass calibration and resolution. Method 200.8, Section 10.2.1, specifies a resolution of 0.75 amu peak width at 5% of the peak height while Method 6020B, Section 10.1, specifies a resolution of 0.9 amu peak width at 10% peak height. For both methods, if the mass calibration is greater than 0.1 amu of the true value, then the mass calibration requires adjustment. Method 200.8 further requires that the stability of the instrument be tested by analyzing the tuning solution at least five times with the relative standard deviation (%RSD) of all elements in the tuning solution being less than 5%. If one of the tests in the Performance Report fails, troubleshooting to resolve the issue must be initiated. The instrument is ready for calibration and analysis of samples when all tests within the Performance Report pass.

3.2 External calibration

External calibration entails the use of standard solutions that are external to the samples. A calibration curve is generated from the analyses of a series of standards with known analyte concentrations and a calibration blank. The concentration of the calibration standards should be within the linear dynamic range of the instrument and cover the range of expected analyte concentrations in the samples in the analytical run sequence. Plotting the instrument response {i.e., intensity in counts per second (cps)} on the y-axis against the analyte concentration in each calibration standard on the x-axis should result in a linear relationship (i.e., the instrument response is directly proportional to the concentration of the analyte).

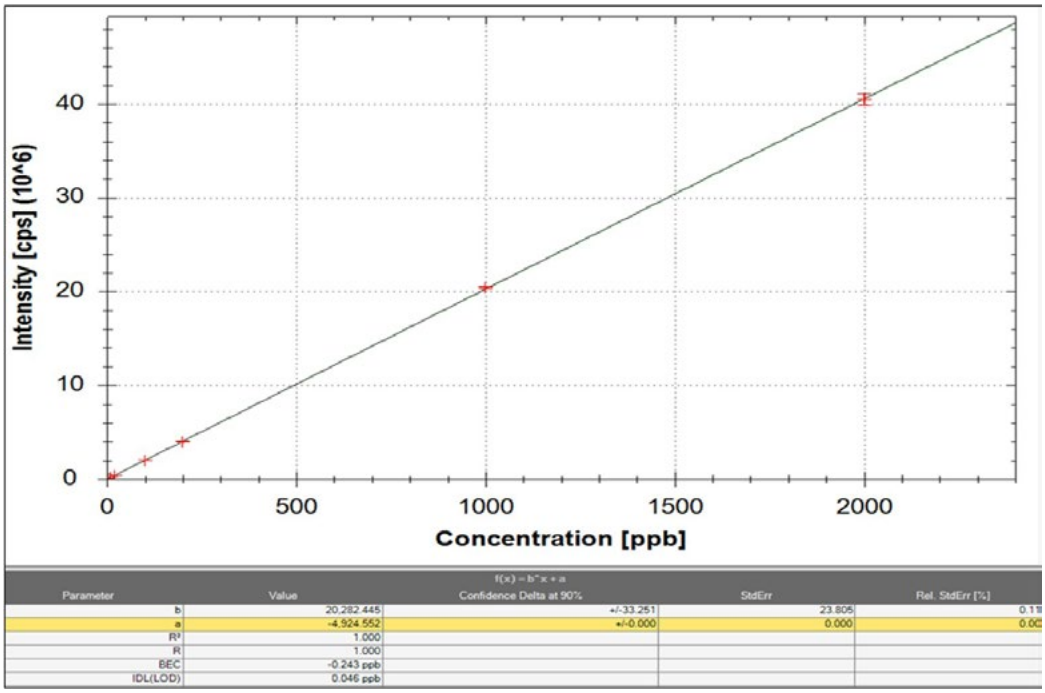
The concentration of the analyte in the calibration standards and the instrument responses of the analyte from the analyses of the calibration standards are fit to a straight line using linear regression analysis. The analyte concentration in the sample is then calculated using the equation:

$$y = mx + b$$

Where the concentration of the analyte is calculated by solving for (x) where (m) is the slope representing the sensitivity, (b) is the y-intercept, and (y) is the instrument response of the analyte in the sample.

The correlation coefficient (R) of a calibration curve is a measure of the linear relationship between the instrument response and the concentration. A correlation coefficient of 1.0 indicates a perfect, directly proportional relationship; for every increase in concentration there is an increase in the instrument response in a fixed proportion. An acceptable calibration correlation coefficient for most environmental analyses is > 0.995, as specified in Method 6020B, Section 10.4, for a multipoint curve consisting of a minimum of three calibration standards. However, it is always best to achieve a correlation coefficient as close to 1.0 as possible as lower values may indicate calibration standard preparation errors, contamination, analyte instability in the calibration standards, issues with sample introduction system components, issues with instrument interface components, etc.

As ICP-MS is a linear technique with a linear dynamic range of > 10 orders of magnitude, it is a misconception that an excellent calibration curve with a correlation coefficient of 1.0, or close to 1.0, over a wide range of concentrations (e.g., from 1 ppb to 100 ppm) can easily be obtained with accurate sample results calculated from it. Standard and sample failures can occur despite an excellent calibration curve and determining the root cause through troubleshooting measures can be perplexing and time consuming. The following sections will discuss recommended best practices and considerations for achieving a good instrument calibration to help avoid a poor calibration curve.



f(x) = b*x + a

Parameter	Value	Confidence Delta at 90%	StdErr	Rel. StdErr [%]
b	20,282.445	+/-33.251	23.805	0.11
a	-4,924.552	+/-0.000	0.000	0.00
R^2	1.000			
R	1.000			
BEC	-0.243 ppb			
IDL(LOD)	0.046 ppb			

Figure 3.1 In this calibration curve, (b) is the slope or the sensitivity, (a) is the y-intercept, (R) is the correlation coefficient, (BEC) is the Background Equivalent Concentration, and (IDL) is the Instrument Detection Limit.

3.2.1 Considerations and recommended best practices for calibration

Instrument calibration is the foundation of all analytical measurements. When an excellent instrument calibration is obtained, it is generally not viewed as the root cause of erroneous results and failures; the instrument and its components or the standard or sample preparation processes are often the areas examined when troubleshooting. A calibration curve with an excellent correlation coefficient is not an indication of a calibration scheme that is optimized for the application and range of sample concentrations. Furthermore, systematic errors in the calibration standard preparation process may not affect the linearity of the calibration curve but can influence the accuracy of sample results.

Preventing analytical issues is key for productivity, efficient use of time and resources, and obtaining accurate results. In addition to the general best practices recommended for the overall elemental analysis workflow, the following considerations and best practices for instrument calibration are recommended to achieve a calibration curve that meets the requirements of U.S. EPA or other method and application requirements.

Optimize the calibration range.

Prevent contamination to the blank.

Use a multi-point calibration curve.

Calibration affects detection limits.

Apply skill, attention to detail, and consistency.

Test the accuracy of the calibration curve.

Optimize the calibration range.

Calibrate the instrument to cover the range of analyte concentrations in the sample, stay within the linear dynamic range of the instrument, and do not calibrate higher than necessary. If the concentration range is unknown or when analyzing new sample matrices, it is recommended to conduct a semi-quantitative analysis to scan the sample and screen for high concentration elements.

A semi-quantitative analysis feature within the instrument software provides a rapid assessment of the sample including elemental and isotopic information and knowledge of potential interferences. It can help to prevent damage to the ICP-MS detector by identifying elements outside the linear dynamic range. Furthermore, it can help to identify the presence of internal standard elements, therefore assisting in the selection of appropriate internal standard elements that are not present in the sample and preventing bias in the calculation of analyte concentrations.

Calibrating over a wide range of concentrations (e.g., 1 ppb to 100 ppm) affects the accuracy on the low end of the calibration curve due to the influence of the high concentration calibration standards on the fit of the points on the calibration curve. It is recommended to calibrate only to the range necessary to cover analyte concentrations. As an example, for the analysis of toxic metals at ultra-trace concentrations in a sample, calibration to high ppm levels is not recommended. Calibrate within the ultra-trace range (e.g., from 1 ppb to 10 ppb) and take the necessary measures to prepare calibration standard solutions as precisely and accurately as possible especially at ultra-trace concentrations.

Method 200.8, Section 7.4.1, suggests a calibration range from 10 µg/L to 200 µg/L, while in Method 6020B, calibration ranges up to 100 mg/L, or higher, may be required as high concentration samples are typically analyzed by this method. Sample dilution is necessary to keep measurements within the linear dynamic range and to preserve the lifetime of the instrument detector.

Prevent contamination to the calibration blank.

While it is nearly impossible for a calibration blank to be completely free of contamination and any amount of analyte, especially those that are ubiquitous in nature, the recommended best practices and measures to minimize an elevated calibration blank should be carried out to produce a good calibration curve, accurate results, and detection limits that meet regulatory requirements. The calibration blank must be prepared from ASTM Type 1 and ultra-high purity reagents for trace and ultra-trace analyses. It is recommended to use plastic laboratory apparatus and mechanical pipettes with disposable plastic pipette tips for all preparation and dilutions. Store the calibration blank solution in Teflon, FEP, or PFA storage containers or wash bottles. These types of plastic materials are high purity and less contaminating than borosilicate glass and other types of plastics.

Use a multi-point calibration curve.

For better precision and accuracy, a multi-point calibration curve is recommended over a single point curve generated from one calibration standard and a calibration blank. A minimum of three calibration standards is recommended, and specified in Method 6020B, Section 10.4, for a multi-point calibration curve. As mentioned, the concentration of the calibration standards must be optimized and bracket the range of sample concentrations.

A poor calibration curve affects detection limit calculations.

Almost all environmental and industrial methods and standards require the determination of Instrument Detection Limits (IDLs) and Method Detection Limits (MDLs) prior to the analysis of samples. Both require the analyses of a series of solutions—reagent water (blank) for the IDL and spiked method blank and spiked sample for the MDL (U.S. EPA CWA requirement).[53] The IDLs and MDLs are both calculated by multiplying the standard deviation from these replicate analyses by the Student's t value. If the blank analyses are inaccurate due to contamination or if there are errors in the calibration standards resulting to a poor calibration curve, then the calculated detection limit will not be accurate or as low as required to meet regulatory or application requirements.

Prepare calibration standards with skill, consistency, and attention to detail.

Proper skill, technique, and attention to detail are imperative when preparing calibration standards, especially at trace and ultra-trace concentrations. Because of the high sensitivity of ICP-MS, even small inconsistencies between the preparation of each calibration standard will introduce variation to the calibration curve which also includes variation from noise, background, and the calibration blank. A detailed discussion of recommended best practices and measures to avoid systematic errors in the preparation of standard solutions will be provided in Chapter 4.

Test the accuracy of the calibration with an independent standard.

Test the accuracy of the instrument calibration with the analysis of an independent standard of certified concentration right after calibration and prior to sample analysis. For Method 6020B and CLP analyses, this standard is the ICV and for Method 200.8, this standard is the QCS. The ICV and QCS must be obtained from a source outside the laboratory. For best practice, it is recommended that these standards be custom made at method specified analyte concentrations (e.g., near midpoint of the calibration curve) to allow direct analysis and avoid further processing that can introduce error and affect the certified concentration. In addition to the ICV and QCS, Standard Reference Materials (SRMs) are available for a variety of sample types and may be used to test the accuracy of the calibration and the sample preparation method.

3.3 Internal standardization

External calibration entails the use of calibration standards external to the sample that are usually prepared in a dilute acid matrix. When the sample matrix is different from that of the calibration standards, there will be variability in the response of the analyte in the sample compared to the response in the calibration standards. The variability can either be a suppression or enhancement of the analyte response caused by the sample matrix (e.g., high salts, suspended solids) or the physical properties of the sample (e.g., viscosity, volatility). This effect of the sample matrix is a physical interference and must be corrected for accurate analyte concentrations. For instance, when a sample contains high total dissolved solids (TDS), its nebulization and transport efficiency will not be as efficient as a calibration standard prepared in 1% nitric acid. This inefficiency causes a variability, in this instance a suppression, of the analyte response in the sample compared to the same concentration in the calibration standard. To correct this variability in response, a technique called internal standardization can be applied.

Internal standardization monitors and corrects for the effect of physical interferences and instrument drift on analyte concentrations. It involves the addition of one or more reference elements, or internal standards, to all measured solutions (e.g., calibration blank, calibration and QC standards, samples) in the analytical run sequence and then applying a correction to the analyte concentration based on the internal standard recovery.

For internal standardization to work accurately, the internal standard element must be added precisely in the same amount to all standards and samples in the analytical run sequence. The response of the internal standard is monitored throughout the run and should be affected the same way as the analyte. The response of the internal standard in the calibration blank is used as the reference point for calculation and correction of the analyte concentration.

Internal standardization and matrix matching are two common approaches to address the variability of the analyte response due to physical interferences. When different types of samples (e.g., drinking water, wastewater, soils) are analyzed in the same analytical run sequence, it is almost impossible to matrix match the calibration standards for every type of sample. For this reason, internal standardization is the most practical and common approach. Some level of matching is often applied in addition to internal standardization by preparing the calibration standards in the same acid matrix used to digest the samples.

In addition to the precise addition of the internal standard elements, the following are requirements for optimal application of internal standardization:

- Use at least three internal standard elements representing the low, middle, and high end of the mass range for a multi-element analysis covering a wide range of masses.
- The internal standard elements must not be present in the sample as this will cause bias in the calculation of the sample results.
- Select internal standard elements that do not cause spectral interferences with the analytes.
- Select internal standard elements that are close in mass, approximately 50 amu, to the analytes.
- The internal standard and the analyte should behave in an identical manner in the plasma for an effective correction. It is therefore recommended that the ionization potential of the internal standard element be close to the ionization potential of the analyte it is correcting.

3.3.1 Preparing the internal standard solution

The concentration of the internal standard elements should be high enough for good measurement precision which in turn allows more accurate correction of the analyte concentrations. However, the concentration of the internal standard elements should not be too high as this may lead to a shortened service life of the ICP-MS detector. Since the internal standard is added to all measured solutions in the analytical run sequence, the presence of high concentration internal standard elements will generate a continuous flux of ions or high ion count to the detector. High internal standard concentration combined with high sample volume consisting of high matrix samples will result in more frequent detector cross-calibration or detector replacement.

A preparation procedure for an internal standard stock solution containing Sc, Y, In, Tb, and Bi at 100 µg/mL is given in Section 7.5 of Method 200.8. Depending on the sensitivity of the instrument, this stock solution should be diluted to a concentration range of 20 to 200 µg/L, as specified in Section 10.3. If the internal standard solution contained all elements at the same concentration, the higher mass elements will generate higher responses, or ion count, compared to the low mass elements which may not generate a high enough response for good precision. It is therefore recommended to prepare the internal standard solution with each element at a concentration optimized for good measurement precision while preserving the detector lifetime.

Tip

It is recommended to prepare the internal standard solution from single element stock standards. This allows each element to be prepared at a concentration that will deliver a response within an optimal range for good measurement precision while preserving the lifetime of the detector. Preparing the internal standard solution from a commercially available multi-element internal standard stock containing all elements at the same concentration is convenient. However, it is not recommended for highly sensitive ICP-MS instruments due to the high flux of ions that will be generated by the more sensitive elements present in the stock standard.

Method 6020B, Section 7.21, recommends the following internal standards: Li, Sc, Y, Rh, In, Tb, Ho, and Bi to be added to the calibration standards at suitable concentrations.

Note

Consult the ICP-MS instrument manufacturer for the optimal response range for the internal standard elements or for the recommended concentration of each element in the internal standard solution.

Table 3.1 is a list of recommended single element stock standards from different manufacturers that can be used to prepare the internal standard solution. Included in the list are multi-element stock internal standards for convenience of preparation if the sensitivity of the ICP-MS instrument is not a factor. Custom internal standard stock solutions with each element at the optimized concentration may also be used; please consult a stock standard manufacturer for custom options available.

Table 3.1 Stock standards for internal standard solution preparation

Vendor	Product description	Volume (mL)
Thermo Scientific™	Single Element Standard, 6Li – 100 µg/mL, Specpure™	100
	Single Element Standard, Sc – 1000 µg/mL, Specpure™	100
	Single Element Standard, Y – 10 µg/mL, Specpure™	100
	Single Element Standard, In – 10 µg/mL, Specpure™	100
	Single Element Standard, Tb – 10 µg/mL, Specpure™	100
	Single Element Standard, Ho – 10 µg/mL, Specpure™	100
	Single Element Standard, Bi – 10 µg/mL, Specpure™	100
Inorganic Ventures	Single Element Standard, Y – 10 µg/mL	125
	Single Element Standard, In – 10 µg/mL	125
	Single Element Standard, Tb – 10 µg/mL	125
	Single Element Standard, Ho – 10 µg/mL	125
	Single Element Standard, Bi – 10 µg/mL	125
	200.8 Multi-element Internal Standard Bi, In, Sc, Tb, Y – 20 µg/mL	125
	6020 Multi-element Internal Standard Bi, Ho, In, 6Li, Rh, Sc, Tb, Y – 10 µg/mL	125
SPEX CertiPrep™	Lithium 6 Single Element Standard, 6Li – 100 µg/mL	125
	Scandium Single Element Standard, Sc – 10 µg/mL	125
	ICP-MS Multi-element Internal Standard 1 Bi, Ge, In, 6Li, Sc, Tb, Y – 10 µg/mL	125
	ICP-MS Multi-element Internal Standard 2 Bi, Ge, In, 6Li, Lu, Rh, Sc, Tb – 100 µg/mL	125

3.3.2 Adding the internal standard

Internal standardization requires the accurate and precise addition of the internal standard solution to all standard and samples in the analytical run sequence. The internal standard solution can be added manually or automatically using an online internal standard kit.

Manual addition of the internal standard solution is inefficient, time-consuming, and can be another source of contamination and other systematic errors. Manual addition may be appropriate when only a few samples are to be analyzed and for troubleshooting.

Automatic addition of the internal standard is highly recommended. There are many internal standard kits available on the market. A kit typically consists of a connector, in the shape of a Y or T, that combines the sample and internal standard prior to introduction to the nebulizer. The combination of the sample with the internal standard also serves to dilute the sample, with the ratio of dilution depending on the size or inner diameter of the peristaltic pump tubing used to transport the internal standard solution and the inner diameter of the sample pump tubing. Figure 3.2 shows the addition of the internal standard solution online using a Y-connector.

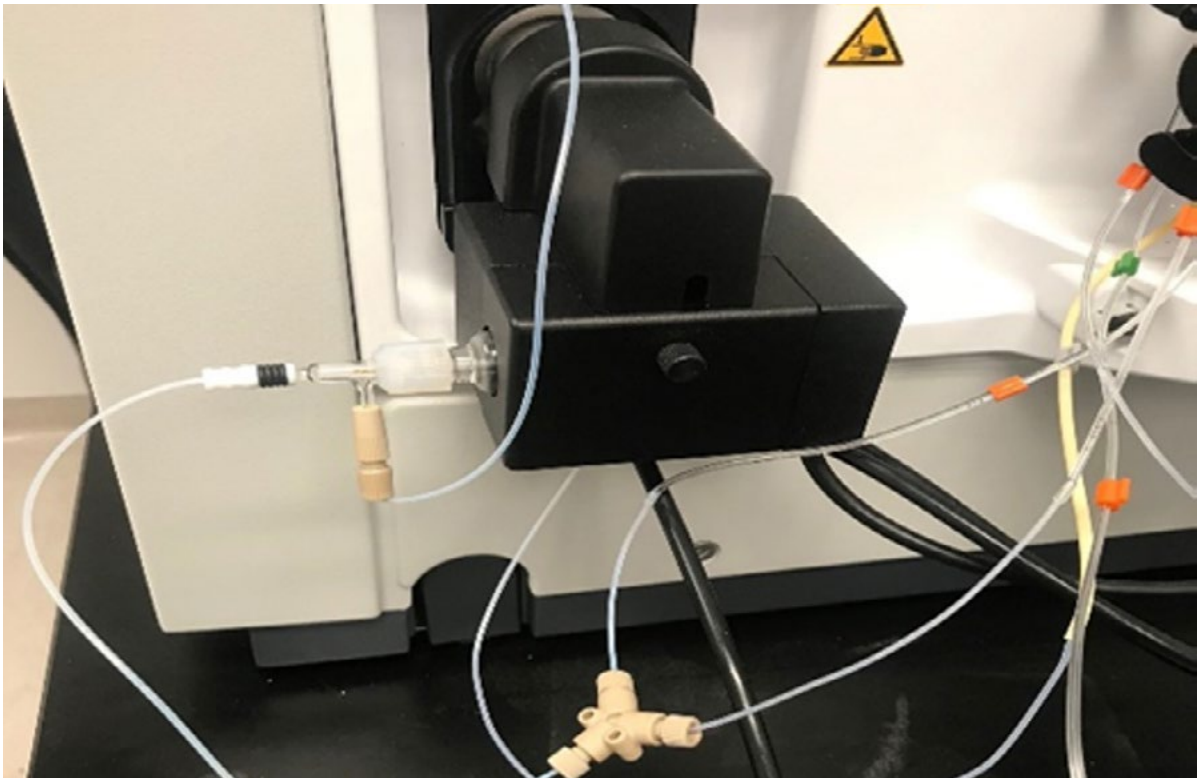


Figure 3.2 Addition of the internal standard solution online using an internal standard kit consisting of a Y-connector combining the sample and internal standard lines prior to introduction to the nebulizer.

4 Preparation of standard solutions

The preparation of standard solutions (e.g., calibration, intermediate, quality control, internal standard) requires extra discussion. With many steps involved in the standard preparation process come many opportunities for error and exposure to contamination. Even the slightest error in the preparation of each calibration standard solution can have a negative impact on the instrument calibration, especially when calibrating at an ultra-trace concentration range.

Furthermore, the analyst may be unaware of the contamination being introduced at each step of the preparation process or how imperative proper skill, attention to detail, and consistency are to the overall success of the calibration and sample analysis.

As previously mentioned, multi-element calibration standard solutions should be prepared to contain elements that are compatible and stable and in the appropriate acid matrix (e.g., the acids used to digest the samples). Prior to discussing the steps in the standard preparation process, an overview of compatibility and stability is needed.

4.1 Compatibility and stability

As discussed in the previous chapter, standard solutions and acid diluents must be prepared and stored using compatible laboratory apparatus and storage containers. The material must be compatible to the analytes and the acid matrix and should not leach elemental impurities. For trace and ultra-trace analyses, plastics are recommended for the ICP-MS analytical workflow. If sub-ppb and ppt detection limits are required, plastics such as PTFE, PFA, FEP, and PMP are recommended. Most acid matrices are compatible with plastics. Hydrofluoric acid requires the use of plastic and resistant sample introduction components. For acid digestion, quartz is preferred over borosilicate glass while specific plastic materials can be used as digestion vessels. This topic will be further covered in Chapter 5.

Certain elements are known to be problematic for analysis by spectroscopic techniques due to stability, evaporation, precipitation, photoreduction, or contamination issues. Some of the elements that exhibit one or more of these issues are Hg, As, Pb, Ag, Ba, Na, and Zn.

Mercury is problematic due its volatility and adsorption to plastics. As discussed in Chapter 2, the addition of gold resulting to a concentration of 100 µg/L (Method 200.8) is required to be added to all samples and standards to stabilize Hg in solution and assist in washing it out from the ICP-MS sample introduction system. The preparation procedures in Methods 200.8 and 6020B result to a 1000 µg/mL Hg stock standard solution in 5% nitric acid that must be further diluted for instrument calibration. Borosilicate glass containers should be used to store Hg solutions in a 5% nitric acid matrix. It is also recommended to prepare Hg calibration standards separate from other analytes.
It should be noted that high concentration single element Hg stock standards prepared in a 10% hydrochloric acid matrix stored in LDPE containers are commercially available. However, for ICP-MS analysis at ultra-trace concentrations, borosilicate glass containers should be used to avoid stability issues.

Silver can be another problematic element. In the presence of trace amounts of hydrochloric acid, AgCl precipitation will form. At higher concentrations of hydrochloric acid, a soluble chloride complex will form; solutions containing this complex are photosensitive and need to be kept away from light to avoid photo-reduction to elemental Ag. Another problem with silver is that it forms insoluble salts with sulfate, phosphate, arsenate, fluoride, and other inorganic ions. Hence, it is recommended

to prepare Ag separate from other analytes and in a nitric acid matrix. Method 200.8 suggests the preparation of Ag and Ba in a calibration standard solution separate from all other method analytes. If hydrochloric acid was used in the sample digestion process and as a result, required for matrix matching calibration standards to digested samples, it is recommended to prepare Ag calibration standards at low concentrations in a high hydrochloric acid matrix (e.g., 10%) and to minimize exposure of the calibration standards to light to avoid photoreduction that will lead to erroneous results.

Like Ag, Ba instability is due to the formation of insoluble precipitates. If sulfur compounds are present in the sample or if sulfuric acid was used in sample preparation, insoluble BaSO4 precipitate may form. Furthermore, the sample preparation procedure specified in Method 200.8 for total recoverable analytes is suitable for solubilizing and retaining only low concentrations of barium if sulfate is present. Therefore, the analysis of the samples must be performed right after preparation.

Lead and As are significant for environmental analyses; Pb has been identified as a probable human carcinogen while As is classified as a human carcinogen by the U.S. EPA. Therefore, accurate detection is required. The challenge associated with arsenic in sample and standard preparation is its volatility, while the challenges with lead are compatibility with sulfates, sulfides, chromate, etc., and contamination. Lead is present in the atmosphere, in airborne particulates and dust. Lead also has many uses throughout industry (e.g., pipes, batteries, solder, gasoline, pigments, roofing, glass). Lead-based paint was widely used and is still present in many buildings, causing contamination for analysis when paint chips or dust from lead-based paint on walls and ceilings deposit onto samples. Like Na, Mg, Zn, and Ca, measures need to be taken to avoid contamination from lead.

In addition to the method analytes, the internal standard elements must also be taken into consideration. The internal standard solution must be prepared with elements that will not cause spectral interferences with the analytes (e.g., rare earth elements) and that are compatible with the acid matrix and the storage container. The internal standard must also be prepared from high purity single element stock standards. Check the Certificate of Analysis for each internal standard element for trace concentrations of the analytes.

4.2 General best practices when preparing standard solutions

The following best practices are recommended for preparing standard solutions. Examples of common analytical issues, which are often thought to be due to instrument performance but are due to errors in the standard preparation process, are provided to demonstrate the importance of proper standard solution preparation. In the context of this document, standard solutions refer to calibration, quality control (e.g., CCV), spike, internal standard, and intermediate solutions prepared from stock standards as well as blank standards (e.g., ICB, CCB).
The instrument rinse solution is often the same solution as the blank standards and should therefore be prepared with same best practices.

Apply clean practices, use clean reagents, and be aware of contamination in every step of the standard preparation process.

Figure 4.1 A clean laboratory environment and apparatus are imperative for the preparation of standard solutions.

The use of ultrapure water, ultra-high purity stock standards and reagents, and thoroughly cleansed apparatus are essential for preparing standard solutions for trace and ultra-trace analyses. Preparation should be done in a laminar flow hood to avoid or minimize the introduction of airborne contamination to the stock standards as well as the solutions being prepared. Minimize transfer and handling steps; if possible, prepare a standard or sample in the container it will be used in. Finally, maintaining a clean and clear workspace cannot be emphasized enough for both safety and contamination prevention.

Contamination of the calibration blank and calibration standard solutions will affect the calibration curve and accuracy of results. The intensity of the calibration blank is subtracted from the intensities of all measured solutions in the analytical run sequence. If the intensity of an analyte in the calibration blank is higher than that in a sample, the net sample result will be negative. Contamination of the calibration blank will also affect the linear relationship of all calibration standards. Furthermore, contamination of a quality control standard, such as the CCV, may result in high analyte recoveries requiring the re-analyses of the ten samples prior to the CCV, causing delays and impacting productivity and reporting of results.

Apply proper skill, consistency, and attention to detail when preparing standard solutions.

As reiterated throughout this document, accuracy depends on many factors, many of which relate to contamination and how to prevent it. However, a factor often overlooked as the cause for erroneous results is the skill, technique, and consistency applied in the preparation of standard solutions. Steps from weighing to pipetting to bringing solutions up to volume, must be performed with precision and consistency for accurate analyte concentrations in the standards, especially for trace and ultra-trace concentrations. Attention to detail is necessary to avoid systematic errors, such as the introduction of contamination and incorrect dilutions.

To demonstrate the importance of these points, consider the following scenarios:

- An excellent calibration curve with a correlation coefficient of close to 1.0 indicates a nearly perfect linear relationship between the instrument response and the analyte concentrations in the calibration standards. However, when a low concentration SRM was analyzed against the calibration curve, the result was out of the certified range.
- An instrument calibration in the low ppb range is unacceptable with a correlation coefficient of < 0.995 despite correct dilutions calculated and applied when preparing the calibration standard solutions.

An excellent calibration curve can still be achieved if systematic errors are made. In the first scenario, the cause may be due to an issue with the stock standard: it may be contaminated or old with the loss of analytes. Calibration standards prepared from a contaminated stock standard may result in instrument responses that are proportionately high, while with an old stock standard, the responses are proportionately low. Both will still result in a good linear relationship and correlation coefficient. However, when samples are analyzed against this calibration, the results can be erroneous, such as the failure of the SRM.

With the high sensitivity of ICP-MS, slight inconsistencies (e.g., pipetting errors, diluting standard solutions slightly off from volume) in preparation from standard to standard, especially when preparing ultra-trace concentrations, will be apparent in the calibration curve. This will affect the ability to establish a good linear relationship, as in the second scenario. For environmental analysis according to regulated methods, a poor calibration curve will require the analysis to be stopped and for corrective actions to take place prior to resuming analysis.

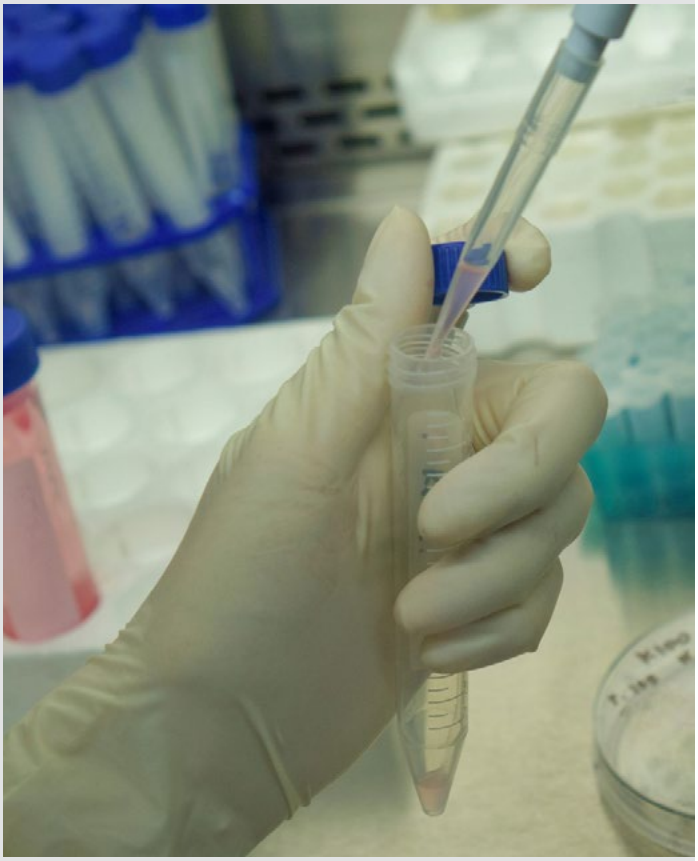


Figure 4.2 When filling an autosampler tube with a standard, it is best practice to use a calibrated and inspected mechanical pipette.

4.3 Steps in the standard solution preparation process

Figure 4.3 The work surface of laminar flow hoods should be cleaned prior to and after use.

Each step of the standard preparation process can be a source of error. The following is a recommended list of steps for the standard preparation process. A detailed discussion of measures for accurate preparation and contamination prevention are included for each step.

a) Maintain a clean workspace.

Maintaining a clean workspace is imperative to ensure a safe working environment, prevent contamination, and preserve the service life of equipment, apparatus, countertops, and workbenches. Recommended measures for maintaining workspaces and countertops are:

- Remove all unnecessary items or apparatus that can get in the way of the preparation process.
- Clean the surfaces of laboratory countertops, benches, and fume and laminar flow hood workspaces. Remove dust, dirt, and chemicals from these surfaces, as in Figure 4.3.
- Place an absorbent, lint free cover over work surfaces to absorb spills and prevent direct contact of chemicals causing stains, roughness, cracks, etc., that lead to shortened service life of the work surface.

Most laboratory countertops are constructed from epoxy resin, which is sturdy, durable, non-porous, and resistant to most chemicals, heat, moisture, and flame. However, periodic cleaning is required to maintain its shine, resistance, and service life. Daily or weekly cleaning with a soft cloth, water, and mild laboratory soap is recommended; abrasive sponges and polishes with wax should not be used as they may damage the surface.

Figure 4.4 Laboratory with instrumentation organized and work surface clean and clear.

b) Organize all laboratory apparatus, stock standards, and other required items prior to the preparation process.

Gathering and organizing all items required for the preparation process saves time and avoids extended delays between preparation steps when standard solutions are left unattended and exposed to contamination from the atmosphere. Items required for the standard preparation process are:

- Multi-element calibration and QC standards and single element stock standards.
- Acid diluent stored in a plastic wash bottle.
- Laboratory apparatus, such as, mechanical pipettes and disposable pipette tips, volumetric flasks with stoppers, disposable beakers, small waste container, autosampler tubes and racks, and lint free wipes.
- Laboratory notebooks and writing utensils to document standard preparations for traceability and audit purposes and to properly label standard solution storage containers.
- Adsorbent cloth to cover the countertop or workbench protecting it from potential damage caused by the acids, standards, and other chemicals.

Have all stock standards, volumetric flasks, pipettes, autosampler tubes, etc., at room temperature to avoid errors in volumetric transfers. Aqueous standard solutions that were stored at lower temperatures have a higher density; this will affect the accuracy of volumetric measurements.

Figure 4.5 All necessary items for standard and sample preparation should be gathered and organized prior, including logbooks and forms to document preparations (top). Work surface should also be covered (bottom) to protect the surface and to prevent contamination from direct contact of apparatus to dust, dirt, etc., on the surface.

c) Check analytical balances and mechanical pipettes prior to use.

Spot checks of analytical balances and mechanical pipettes, as described in sections 2.2.2 and 2.2.3, should be done daily or before use to ensure:

- The accuracy of weights and volumes measured for all dilution steps in the standard preparation process.
- Proper functioning. If mechanical issues are observed, actions to re-calibrate, service, or replace can be taken.

Documentation of spot checks, in addition to weekly comprehensive checks, in a laboratory notebook should be done as part of the standard preparation steps and for traceability and audit purposes.

Figure 4.6 Analytical balances should be spot checked prior to use when preparing standard solutions.

d) Prepare acid solutions safely and accurately.

Dilute acid solutions (e.g., 1% nitric acid) are often used for the preparation of standard solutions to retain analytes in solution and prevent precipitation and adsorption of analytes onto container walls. Dilute acid solutions are also used as blank QC standards (e.g., ICB, CCB), instrument rinse, and as the matrix for the instrument tuning solution.

Calibration standards should be prepared in the same acid matrix used for sample digestion to minimize physical interferences that can result when the nebulization or transport efficiency differs between samples and calibration standards. For ICP-MS standard preparation, nitric acid at less than 2% is advised to prevent damage to the instrument interface (e.g., sample and skimmer cones). Methods 200.8 and Method 6020B specify 1% nitric acid for all standard preparations.

The following best practices are recommended when preparing dilute acid solutions:

- Always prepare acid solutions from concentrated acids under a fume hood. Clean and clear the hood workspace of any unnecessary items that can get in the way of preparation. Lay an absorbent, lint free cloth on the hood surface to absorb any acid spills and protect the surface.
- Use a plastic volumetric flask to prepare the acid solution. Since the acid solution will be used as the diluent for all standard preparations and as the calibration and QC blanks, it should be prepared as carefully as possible avoiding contamination.
- Rinse the volumetric flask with reagent water several times to remove any dust or dirt that may have settled inside the flask. Fill the flask approximately halfway with reagent water.
- As an important reminder, always add acid to water, never the other way around.
- Use ultra-high purity acids (e.g., Optima™) for trace and ultra-trace detection requirements.
- Never place a pipette tip directly into the container of concentrated acid. Always pour an aliquot of concentrated acid into a disposable plastic (e.g., polypropylene) beaker. Use this aliquot to pipette the required volume of acid. This measure avoids cross-contamination to the entire container of ultra-high purity concentrated acid.
- After preparation, transfer the acid solution from the volumetric flask to a plastic wash bottle for storage and convenient dispensing when preparing standard solutions. The preferred plastic materials for ultra-trace analyses are Teflon™, PFA, and FEP.
- Label the wash bottle with the contents (e.g., 1% nitric acid), any specific laboratory identifiers, date of preparation, initials of preparer, etc., for proper identification, safety, and traceability.

Figure 4.7 Preparations involving concentrated acids and other hazardous reagents must done in a fume hood to protect the analyst and laboratory environment.

Figure 4.8 For ultra-trace analysis, Teflon™ (left) wash bottles are recommended for storing and dispensing acid diluents used to prepare standard solutions. For general purpose work or higher detection limit analyses, LDPE wash bottles (right) are appropriate.

e) Calculate dilution factors.

As previously recommended, it is best practice to prepare calibration and quality control standard solutions using commercially available multi-element stock standards to save time and resources, minimize preparation steps and contamination exposure, and to prevent systematic errors. To calculate the amount of stock standard required to prepare a calibration, quality control, or internal standard solution, use the following formula:

$$C_iV_i = C_fV_f$$

Where C_i is the concentration of the stock standard and V_i is the volume of the stock standard; C_f is the concentration of the calibration standard and V_f is the volume of the calibration standard.

As an example, to prepare a 200 µg/L calibration standard solution in a 50 mL Class A volumetric flask using a 20 µg/mL stock standard, use the following steps and calculation.

Stock Standard: 20 µg/mL, Inorganic Ventures Multi-Element Calibration Standard 2A (manufacturer's part number: WW-MSCAL-2-125ML, Fisher Scientific part number: 50-723-867)

Note

Use the same units on both sides of the formula for the calculation. For this example, convert the stock standard concentration unit from µg/mL to µg/L, this results to a concentration of 20,000 µg/L of the stock standard.

Using the formula, determine the volume of stock standard **(V_i)** needed to prepare a 200 µg/L calibration standard solution:

$$V_i = C_fV_f / C_i$$

$$V_i = \frac{(200\ \mu g/L)\ (50\ mL)}{(20{,}000\ \mu g/L)} = 0.5\ mL\ of\ stock\ standard$$

Hence, 0.5 mL of stock standard into 50 mL, or a 100-fold dilution of the stock standard.

f) Streamline the preparation process by minimizing handling and transfer steps.

- Keep the preparation process as simple as possible. The more steps involved, the more chance for exposure to contamination and systematic errors leading to inaccurate results.
- Purchase stock standards with the elements at concentrations sufficient for the analysis, but not too high to require multiple dilutions and preparation of intermediate standards. For instance, if calibration at trace concentrations is required (e.g., 1 µg/L to 25 µg/L), it is not ideal to purchase stock standards at 10,000 mg/L as this will require multiple dilutions resulting in multiple transfer and handling steps with each being a potential source of error and contamination.
- Intermediate and calibration standard solutions may also be prepared in centrifuge or autosampler tubes to:
  - Minimize the transfer between multiple containers (e.g., from the volumetric flask to a storage bottle and then to the autosampler tube for analysis).
  - Minimize the use and cleaning of glassware.

When using a centrifuge/autosampler tube for preparation, check that they are ASTM Class A. If not, use a mechanical pipette that has been spot checked for each volume to be delivered to fill the centrifuge/autosampler tube with the required volume of acid diluent and stock standard to prepare the standard solution.

g) Prepare standard solutions in a laminar flow hood.

A laminar flow hood or BSC provides a clean, dust free environment for the preparation of standard solutions, which is especially important for low concentration standards in the sub-ppb to ppt range. As previously mentioned, if a designated cleanroom is not available in the laboratory, a laminar flow hood configured to meet ISO 5 requirements is an appropriate and convenient alternative.

h) Use clean apparatus and prevent cross-contamination.

The following measures are recommended to prevent cross-contamination:

- Rinse volumetric flasks, autosampler tubes, storage containers, etc., at least 3 times with reagent water before use. Even if the apparatus has already gone through a comprehensive cleaning routine, rinsing removes any dust that may have collected inside the apparatus during storage or while sitting out on the laboratory countertop.
- Rinse volumetric flask stoppers and autosampler caps at least 3 times with reagent water. Never place the end of the stopper or cap that faces inside the volumetric flask or autosampler tube down directly onto the surface of the laboratory countertop.
- Never place pipette tips directly into stock and intermediate standard solutions.
- Pour an aliquot of the stock or intermediate standard into a suitable separate container (e.g., 5 mL disposable polystyrene beaker) and from this aliquot, pipette the required volume to prepare the calibration, quality control, or internal standard solution.
- After pouring an aliquot, quickly cap the stock or intermediate standard. Do not leave the stock standard uncapped for longer than necessary to avoid contamination and accidental spills.
- Pre-wet the pipette tip at least once with the stock standard solution from the polystyrene beaker. Dispose of this rinse, do not place it back into the beaker.

i) Add acid diluent and stock standards carefully.

The addition of acid diluent and stock standard should be done carefully, with proper technique and consistency. This is to help ensure that the required volumes are precisely dispensed to obtain the correct analyte concentrations. The following steps are recommended:

- Add the acid diluent (e.g., 1% nitric acid) from a Teflon™ wash bottle to the volumetric flask, wetting the walls of the flasks. Add the diluent to approximately half the volume of the flask to prevent the analytes from adhering to the surface of the volumetric flask, as shown in Figure 4.9.
- Using a mechanical, variable volume pipette, dispense the required volume of stock standard into the volumetric flask by carefully placing the pipette tip in the center of the neck of the flask, as shown in Figure 4.10. Do not touch the walls of the flask. Slowly dispense the stock standard to avoid splattering the acid diluent in the flask. Refer to Section 2.3.2 for recommended best practices when using mechanical pipettes.

Figure 4.9 The addition of acid diluent using a wash bottle, wetting the walls of a container (left). Acid diluent should be filled to approximately half the volume of the flask prior to adding the stock standard to prevent analytes from adhering to the wall of the flask (right).

- When filling a glass volumetric flask to volume, add the acid diluent using the wash bottle to just below the volume line or mark. Then using a small volume disposable plastic pipette, dispense the acid diluent precisely until the bottom of the solution meniscus (for clear, colorless solutions) touches the volumetric line at eye level.
  - For dark colored solutions, fill the flask until the top of the meniscus touches the volume line.
  - Note: When using plastic volumetrics, liquids do not form a meniscus, as shown in Figure 4.11, resulting in easier volume readings and more consistent preparations.
- Cap the volumetric flask and carefully invert until the standard solution is thoroughly mixed. Watch for any spillage of the standard solution from the flask.
- Transfer the intermediate or calibration standard to an autosampler tube for analysis or to an FEP bottle for storage. Label the autosampler tube or FEP bottle with the content or description of the standard solution, date of preparation, initials of the preparer, any laboratory specific identifier, etc., for traceability, safety, and audit purposes as shown in Figure 4.12.

Figure 4.10 Pipette dispensing liquid into a flask with the tip in the center of the neck of the flask.

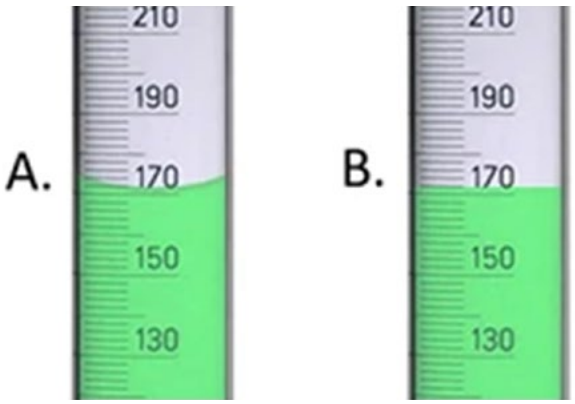


Figure 4.11 A meniscus forms in glass volumetrics (A) while in plastic (B), a meniscus does not form. The liquid level in B can be read clearly across the graduation indicating the exact volume, avoiding error and inconsistency in preparations.

Figure 4.12 Autosampler tubes must also be labelled with the contents (e.g., standard solution, sample) for proper identification, safety, and traceability. All preparations must be documented for traceability and audit purposes.

j) Prepare calibration standard solutions fresh with each sample preparation and analysis.

Low concentration calibration standards at ppb and ppt concentrations will not stay stable for long, hence, preparation with each batch of digested samples or daily with each analytical run is preferred for a more accurate measure of sensitivity and a good calibration. For intermediate standards at ppm levels, weekly preparation is recommended, or sooner depending on frequency of use.

k) Document all preparations in a laboratory notebook.

Preparation of all standard solutions should be fully documented in laboratory notebooks or by other means, such as on laboratory log sheets or forms. Information on the stock standards, such as, lot numbers, expiration date, contents, and concentration, etc., should be included along with the amounts of stock standard used, the volume of the final solution, any specific laboratory identifiers or laboratory name, identification of the preparer, and the date of preparation, at a minimum. This measure is to ensure proper identification for safety and traceability for audit purposes.

Note

In addition to the preparation of standard solutions, document all instrument maintenance and troubleshooting actions and inspections of equipment and apparatus in a designated laboratory notebook. Documentation is not only important for traceability and audit purposes, but for keeping track of issues and corrective actions for future reference and for training new analysts.

5 Sample preparation

Sample preparation is the central part of the elemental analysis workflow. Selecting the appropriate sample dissolution method, reagents, apparatus, and executing all preparation steps to avoid contamination and loss of analyte are essential. The sample preparation process can be the most time-consuming part of the elemental analysis workflow, hence, measures to reduce digestion time and improve efficiency are needed and will be discussed.

For elemental analysis by atomic spectroscopy techniques, dissolution of the sample is required prior to introduction to the instrument. Several chemical methods can be employed to accomplish dissolution: hot plate acid digestion, hot block acid digestion, high-pressure microwave assisted acid digestion, ashing, fusion, extraction, leaching, etc. Among these methods, acid digestion using a hot plate, hot block, or microwave are commonly employed by environmental and contract testing laboratories, hence, they will be the only methods covered in this document.

Acid digestion involves the dissolution of a sample by the addition of concentrated acids and heat until the matrix is completely or partially decomposed and the analytes are released into solution. For some applications, acid digestion is not required, such as the analysis of total recoverable analytes in drinking water with a turbidity of <1 NTU as specified in Method 200.8, Section 11.2. Another example is the analysis of aqueous samples with detection limit requirements at ppm levels where sample dilution to fit the calibration range may be the only preparation necessary. Many environmental samples have complex matrices containing high dissolved solids, salts, organic matter, siliceous material, oils, suspended solids, etc., requiring acid digestion prior to elemental analysis. Acid digestion not only converts the sample into a solution suitable for introduction to the instrument, it also helps to minimize physical, chemical, and spectral interferences.

The solution remaining after acid digestion is the digestate and is of high acid concentration requiring dilution with reagent water prior to analysis by ICP-MS. Incomplete or partial decomposition of samples such as soils, sludges, wastewaters, etc., may result in solids in the digestate. To avoid blockage or clogging of the instrument sample introduction (e.g., nebulizer, injector) and interface (e.g., sample and skimmer cones) components, samples must be filtered, centrifuged, or the solids allowed to settle prior to analysis. Blockage of instrument components will cause drift, sensitivity, and precision issues during analysis affecting the accuracy of results. Plus, more frequent maintenance of sample introduction and interface components will be required due to blockages.

Figure 5.1 Samples from wastewater treatment plants (above) that contain suspended solids, high TDS, and organic material (below) require acid digestion.

Figure 5.2 Sample solution after partial digestion containing suspended solids needs to be filtered prior to analysis.

In the context of this document, sample preparation refers to all steps involved to convert the sample to a solution suitable for ICP-MS analysis: weighing, measuring, dissolution of the sample by a chemical method, filtering, dilution, and all transfer and handling steps in between. The sample dissolution process will be referred to by the specific method, either hot plate acid digestion, hot block acid digestion, or microwave assisted acid digestion. This is important to specify as sample preparation is often used in other literature to refer to just the sample dissolution process.

Note

To avoid reiteration, the same considerations and recommended best practices for safety and the selection and use of apparatus and reagents for standard preparation (e.g., compatibility, suitability, purity) must be applied for the sample preparation process. Preventing contamination in all sample transfers; ensuring the accuracy of all measurements; and proper skill, technique, and attention to detail must also be applied throughout all steps to maintain sample integrity and achieve data quality.

5.1 Sample preparation methods

For environmental analysis under the CWA, the analysis of trace metals is performed according to the requirements and procedures specified in Method 200.8, which includes sample preparation procedures for dissolved and total recoverable analytes in aqueous and solid samples in Sections 11.1, 11.2, and 11.3. The procedures in Method 200.2, Revision 2.8: Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements, can also be used to prepare samples prior to analysis by Method 200.8.

For analysis according to Method 6020B, standard procedures for hot plate, hot block, and microwave assisted acid digestion are summarized in the *SW-846 Compendium*, Chapter Three, "Inorganic Analytes," Section 3.6, Sample Digestion Methods. Table 5.1 summarizes these sample preparation methods with a brief description. Please refer to Method 200.8, Revision 5.4, Method 200.2, Revision 2.8, and the individual SW-846 methods for details on each sample preparation procedure.

Table 5.1 Overview of sample preparation methods

Analytical method	Sample preparation procedure	Sample preparation overview
Method 200.8	Section 11.1 – Aqueous Sample Preparation – Dissolved Analytes	• For filtered, acid preserved ground and surface waters. • Adjust acid concentration of sample to approximate a 1% nitric acid solution, sample is ready for analysis by ICP-MS. • Note: This preparation should not be used for the determination of silver; samples should be acid digested.
	Section 11.2 – Aqueous Sample Preparation – Total Recoverable Analytes	• For direct analysis of total recoverable analytes in drinking water with a turbidity of <1 NTU, process the unfiltered sample as in Section 11.1. • For total recoverable analytes in all other aqueous samples or preconcentrating drinking water samples, prepare samples by acid digestion on a hot plate/hot block with nitric and hydrochloric acids.
	Section 11.3 – Solid Sample Preparation – Total Recoverable Analytes	• Solid samples are dried at 60°C, sieved and ground for homogeneity then digested in nitric and hydrochloric acids on a hot plate/hot block.
Method 6020B	Method 3005A – Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy	• Acid digestion of filtered and unfiltered ground and surface waters using nitric and hydrochloric acids and heating on a hot plate, or equivalent, prior to analysis by FLAA, ICP-OES or ICP-MS.
	Method 3010A – Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy	• Acid digestion of aqueous samples, extraction procedure and mobility-procedure extracts and wastes that contain suspended solids using nitric and hydrochloric acids and heating on a hot plate, or equivalent, prior to analysis by FLAA, ICP-OES or ICP-MS.
	Method 3015A – Microwave Assisted Acid Digestion of Aqueous Samples and Extracts	• Preparation of aqueous samples, drinking water, mobility-procedure extracts and wastes containing suspended solids using microwave heating with nitric and/or nitric and hydrochloric acids.
	Method 3050B – Acid Digestion of Sediments, Sludges and Soils	• This method consists of two separate preparation procedures for total recoverable metals: one for GFAA or ICP-MS analysis and one for FLAA and ICP-OES. • For analysis by GFAA or ICP-MS, samples are prepared by hot plate or microwave digestion in nitric acid and hydrogen peroxide.
	Method 3051A – Microwave Assisted Acid Digestion of Sediments, Sludges, Soils and Oils	• This preparation is an alternative to Method 3050 for improving performance for analytes antimony, iron, aluminium, and silver with the addition of hydrochloric acid prior to FLAA, GFAA, ICP-OES and ICP-MS analysis.
	Method 3052 – Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices	• For microwave digestion of siliceous and organically based samples such as ash, biological tissue, oil, oil contaminated soil, sediment, and sludge for total metals analysis by FLAA, CVAA, GFAA, ICP-OES and ICP-MS.

5.2 Sample dissolution

The sample preparation process can be the most time-consuming part of the elemental analysis workflow and a source of systematic errors if it is not optimized.

In this section, sample dissolution methods will be discussed as an integral part of the sample preparation process. Each dissolution method has benefits and limitations, which will be assessed to assist a laboratory in the selection of the most appropriate method for their applications, unique needs, and budget. For all sample preparations, the general goals are to obtain a sample solution suitable for introduction to the instrument and to enable the accurate analysis of the sample. Accurate analysis of the sample can be affected by the loss of analyte during acid digestion leading to poor recoveries; exposure to contamination from the atmosphere, digestion vessels and apparatus and through handling and transfer steps; and the addition of contamination from trace metal impurities present in digestion reagents (e.g., concentrated acids). Hence, to the extent possible, the sample dissolution method should be optimized to:

- Convert a sample into an aqueous solution suitable for ICP-MS analysis.
- Decompose the sample matrix, completely or partially, depending on the method or application requirements.
- Enable complete solution and retention of the analytes at measurable concentrations.
- Prevent the loss of analytes.
- Minimize sample contamination.
- Minimize sample handling.
- Reduce digestion time to meet sample workload and productivity requirements.

The considerations and best practices recommended in this section are not intended to replace the standardized sample preparation procedures in Method 200.8 or the individual SW-846 sample preparation methods; rather, they are provided to complement existing procedures and to outline differences to assist laboratories in the selection of an appropriate sample dissolution method.

5.3 Dissolution methods

The most common dissolution methods used by environmental and contract testing laboratories are hot plate acid digestion, hot block acid digestion, and microwave assisted acid digestion. These methods are also referred to as wet digestion methods. In general, they involve the use of concentrated mineral acids (e.g., nitric, hydrochloric, hydrofluoric, sulfuric, phosphoric) and heat for partial or complete decomposition of the sample matrix and solution of the analytes.[54] The type and amount of acid needed depends on the matrix and the sample size. The sample size may also depend on the sensitivity of the analytical technique. The sensitivity of ICP-MS enables extra dilutions to reduce the acid concentration or TDS content to acceptable levels for introduction to the instrument without compromising the detection of the analyte in the diluted sample solution.

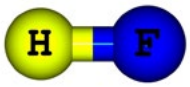
5.3.1 Concentrated acids

Acid digestion methods involve the use of a combination of concentrated acids, with most methods requiring the use of nitric acid. Table 5.2 summarizes properties and key information for some of the concentrated mineral acids used for the digestion of samples prior to analysis by spectroscopic techniques.

Table 5.2 Overview of most common concentrated acids for acid digestion

Physical properties	Applications for elemental analysis[56]
HNO_3 *Aqua Fortis* **Nitric Acid**[55] Concentration: 67-69% (w/w) Boiling point: 120.5°C Density: 1.40 g/mL Molecular weight: 63.01 g/mol Notes: Corrosive, strong oxidizing agent reacts with most metals except precious metals and some alloys.	Nitric acid is commonly used for sample and standard preparation for analysis by ICP-MS. It is an oxidizing acid capable of decomposing organic matter but does not form insoluble compounds with inorganic analytes or cause major polyatomic interferences for ICP-MS analysis. It is used in standard preparation for stabilization of the analytes. Other advantages include its purity, commercial availability, and low cost. The main limitation for sample preparation is the inability to decompose all organic material alone, other strong acids (e.g., hydrochloric acid) and oxidant reagents are required to improve decomposition.
HCL *Muriatic Acid* **Hydrochloric Acid**[57] Concentration: 35% (w/w) Boiling point: 57°C Density: 1.18 g/mL Molecular weight: 36.46 g/mol Notes: Strong, corrosive, non-oxidizing acid; least hazardous to handle among other acids.	Hydrochloric acid can dissolve many metals (e.g., precious metals – Au, Pt, Ag, Pd) and certain metal alloys (e.g., steel). It is often used with nitric acid and an oxidant reagent (e.g., hydrogen peroxide) in the digestion of environmental samples for enhanced decomposition of organic material. It is specifically used in environmental methods to stabilize Ag and Sb. The main disadvantage of hydrochloric acid for ICP-MS analysis is the formation of polyatomic interferences. For instance, a major interferent for As, a key environmental analyte having only one isotope, is $ArCl^+$ formed by the presence of chloride from the acid digestion process.

Table 5.2 Overview of most common concentrated acids for acid digestion *(continued)*

Physical properties	Applications for elemental analysis[56]
HF *Hydrogen Fluoride Solution*  **Hydrofluoric Acid**[58] Concentration: 47 - 51% (w/w) Boiling point: 105ºC Density: 1.15 - 1.20 g/mL Molecular weight: 20.01 g/mol Notes: Weak, Non-oxidizing, extremely corrosive acid; considered a poison due to its attack on skin, tissue, and bones.	Hydrofluoric acid is a highly corrosive acid, attacking glass and other silica-containing material. Complete decomposition of environmental samples containing silicates (e.g., soils, rocks/stones) can be achieved with the addition of hydrofluoric acid in the digestion process. It is used for the digestion of plants, cement, ceramics, quartz, metals, and metal alloys containing Ti, Si, W, Sn, Al, Sb, etc., that cannot be attacked by other mineral acids. Plastic, preferably PFA or PTFE, apparatus, digestion vessels, and sample introduction components are required when handling samples containing hydrofluoric acid. Utmost caution and use of appropriate PPE must be exercised when handling this highly hazardous acid.
H_2SO_4 *Oil of Vitriol*  **Sulfuric Acid**[59] Concentration: 90% - 98% (w/w) Boiling point: 290ºC - 338ºC Density: 1.84 g/mL Molecular weight: 98.07 g/mol Notes: Strong, oxidizing, highly corrosive, viscous acid; highly dehydrating and hygroscopic; colorless and odorless.	Sulfuric acid is strong and reactive, with a viscosity similar to oil, hence called the Oil of Vitriol, making handling and transfers challenging. It has a strong dehydrating property; it removes water from any material it encounters. It is often used for the dehydration of organic materials and in combination with other acids in the digestion of plastics, ores, minerals, oils, fats, etc. Preparation of dilute sulfuric acid solutions must also be done carefully due to the amount of heat released upon addition to water. Sulfuric acid must be handled with extra caution due to severe burns that may be caused upon exposure.

5.3.2 Open and closed vessel acid digestion systems

There are two general types of acid digestion systems: open and closed vessel systems.

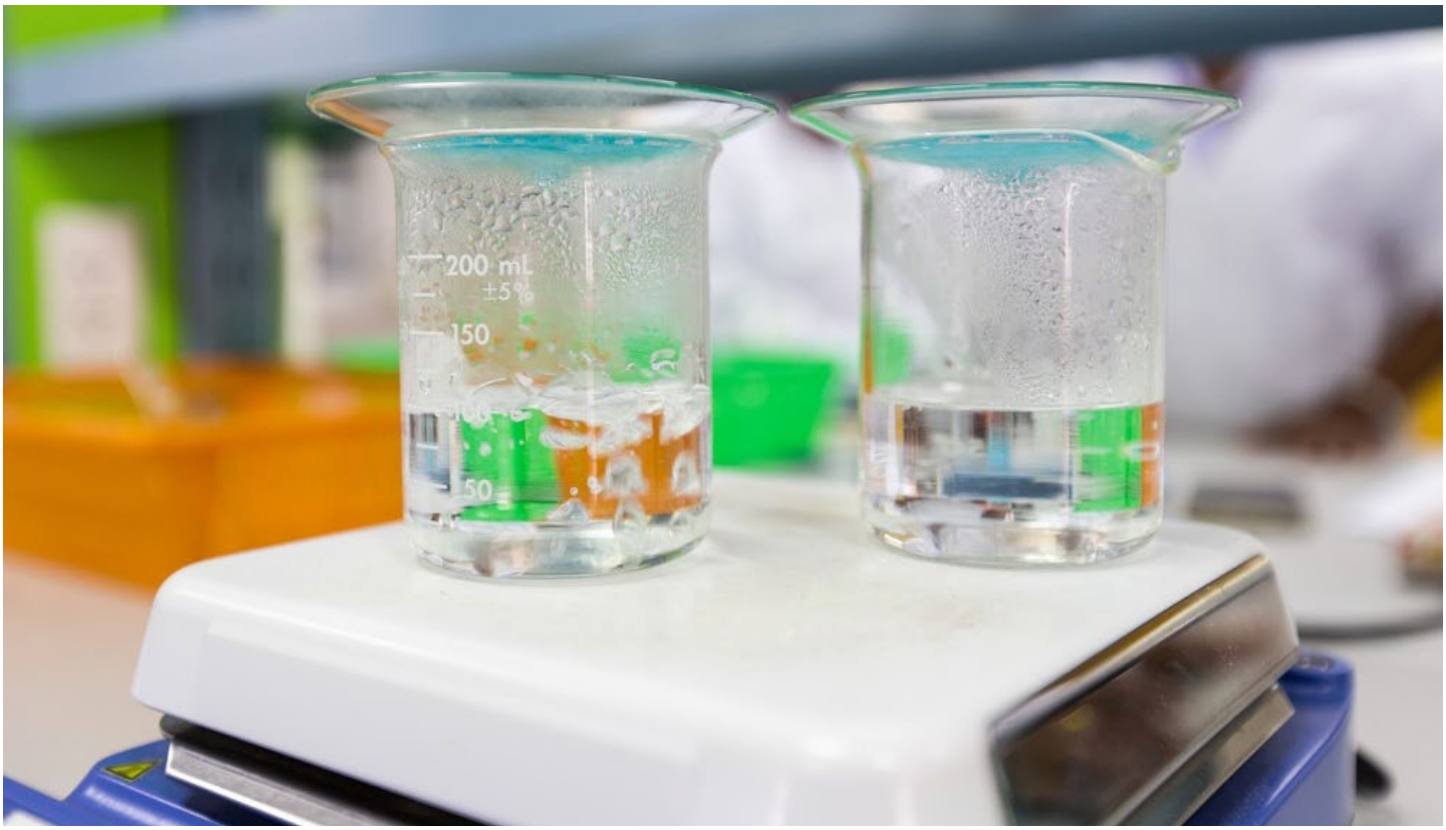
- **Open vessel system**
  Acid digestion methods using a beaker on a hot plate or a digestion vessel in a hot block are open vessel systems because digestion is conducted in an open environment at atmospheric pressure.
- **Closed vessel system**
  Microwave assisted acid digestion is a closed vessel system that allows the acid and sample to be heated above the boiling point of the acid, achieving more complete decomposition of the sample matrix and an overall higher quality digestion.

Each of these methods has advantages and disadvantages that will be discussed. Selection of an acid digestion method typically depends on the regulated method to be used for analysis, the sample matrix, the analytes, detection requirements, and the laboratory's unique needs and factors, such as, budget, sample load, turnaround of results, simplicity of parts, set-up and maintenance, cost per analysis, and overall return on investment.

Hot plate acid digestion

Acid digestion on a hot plate is the oldest and traditional method still widely used by many environmental and industrial laboratories for the following advantages:

- Simple and inexpensive set-up involving the use of commonplace laboratory apparatus and a hot plate.
- Procedures are standardized and uncomplicated.
- Higher sample sizes (e.g., > 1 gram) are possible, which may be required for multiphasic, heterogeneous samples.



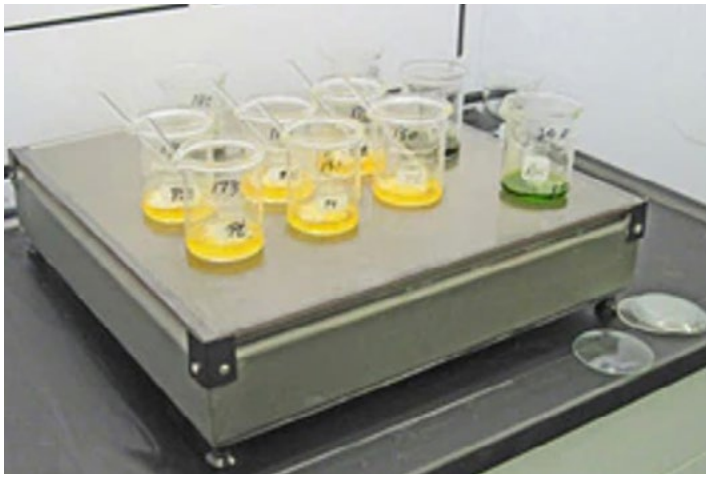


Figure 5.3 The traditional method for sample dissolution is hot plate acid digestion with the advantages of flexibility in sample weight and configurations to accommodate sample load.

Disadvantages of hot plate digestion

When determining improvements to a current sample preparation process that includes hot plate acid digestion or deciding whether hot plate acid digestion is a suitable dissolution method for the range of samples, applications, and analytical requirements in the laboratory, the following disadvantages should be considered.

Long digestion time.

The duration of the hot plate acid digestion process can be several hours. For context, the hot plate digestion procedures in Method 200.8, Section 11.2 for total recoverable analytes in aqueous samples and in Method 3050B for sediments, sludges, and soils, require well over two hours. The digestion time depends on the sample matrix, sample size, and the degree of decomposition required. The long digestion time is also due to the digestion temperature in an open vessel system being limited to the boiling point of the acid solution.

Incomplete digestion.

With the digestion temperature being limited to the boiling point of the acid solution, it may be insufficient to achieve complete decomposition of the sample matrix. To address this issue, additional acids and reagents must be added to facilitate decomposition. However, despite the addition and the extensive digestion time, decomposition may still be incomplete resulting in poor analyte recoveries and inaccurate results.

Exposure to contamination.

Samples are at risk of contamination from dust and other airborne particulates in the atmosphere throughout the duration of the digestion process. Contamination may also be contributed from impurities that leached into the sample from the digestion vessel and trace impurities in the digestion reagents. Furthermore, open vessel digestion often requires the continuous addition of reagents with each addition being a potential source of contamination.

Loss of analytes.

Loss of analyte is due to volatilization, chemical reactions, and adsorption to the digestion vessel. The high temperature required for acid digestion combined with an open vessel system may result in the loss of the more volatile elements, such as Hg, As, and Pb, resulting to poor recoveries and inaccurate results for these key elements in environmental analysis.

High reagent consumption.

The constant addition of concentrated acids and reagents during the digestion process increases the cost per analysis, especially when using expensive ultra-high purity acids to meet trace and ultra-trace detection requirements. Furthermore, safety is a concern each time concentrated acids are handled.

Constant monitoring and addition of acids.

Throughout the duration of the digestion process in an open system, acids and reagents are continuously added and the samples must be monitored to prevent them from going to dryness. If the samples are unattended and allowed to go to dryness, low recoveries will result, requiring the digestion to be repeated.

Numerous sample handling and transfer steps.

Sample preparation using hot plate acid digestion involves numerous handling and transfer steps: weighing and measuring the sample, transferring to the digestion vessel, filtering the sample to another container, diluting the sample to volume, and then transferring the sample to an autosampler tube.

Overall inefficiency.

The lengthy duration of the digestion process (e.g., at least two hours for Method 200.2), the high consumption of acids and reagents and constant monitoring of sample, with transfer and handling steps requiring the use of numerous laboratory apparatus, contribute to the overall inefficiency of the hot plate acid digestion process. Furthermore, the potential for contamination, systematic errors, and loss of analytes are challenges that lead to poor recoveries, inaccurate results, and the reprocessing of samples.

Hot block acid digestion

To address some of the disadvantages associated with hot plate acid digestion, hot block acid digestion systems are recommended. These systems streamline the sample preparation process by eliminating many of the sample handling and transfer steps involved with hot plate acid digestion.

Current hot block acid digestion systems consist of blocks made from graphite coated in PTFE for corrosion and chemical resistance. The non-metallic construction prevents contamination from the system when handling samples. The blocks contain several wells where the digestion vessels are placed. The digestion vessels are single use and made from a high grade, high temperature polypropylene and have graduation marks equivalent to ASTM Class A specifications.[60] Shown in Figure 5.4 is the Cole-Parmer™ Environmental Express™ HotBlock™ SC151 Digestion System. It streamlines the sample preparation process by reducing handling and transfer steps; samples are weighed, digested, filtered, and diluted in disposable polypropylene digestion cups.

Figure 5.4 Cole-Parmer Environmental Express HotBlock SC151 Digestion System.

Hot block acid digestion systems offer the following advantages:

- **Reduced sample handling and transfers.**
  The sample is weighed directly in the digestion vessel on a tared analytical balance. Digestion acids are added, then the digestion vessel is placed in the hot block ready for digestion. After digestion, the sample is filtered and diluted to volume inside the vessel and ready for analysis. Hence, handling and transfers of the sample between multiple containers and vessels are eliminated as the digestion vessel acts as a weighing container, storage container, and autosampler tube.
- **Exposure to contamination is reduced.**
  With less transfer and handling steps and the use of non-metallic block material and all plastic digestion tubes and apparatus, exposure of the sample to contamination is reduced.
- **Elimination of issues associated with glassware.**
  The issues associated with the use of glassware, such as adsorption of analytes to container walls or leaching of elemental impurities to the sample solution, are eliminated. Plus, cleaning of glass apparatus typically used in sample preparation involving hot plate acid digestion (e.g., beakers, watch glasses, funnels, flasks) is also eliminated.

  Hot block digestion systems mainly address the sample handling, transfer, and some of the contamination issues associated with hot plate acid digestion. However, the duration of the digestion process is still extensive, reagent consumption is high, and exposure to contamination from the atmosphere may be possible since it is an open system.

Microwave assisted acid digestion

To overcome many of the limitations associated with open vessel digestion systems, microwave assisted acid digestion is recommended. It saves time, yields a higher quality digestion, retains the analyte, and reduces exposure to contamination.

Microwave assisted acid digestion is a closed vessel system and has become widely used and known as the best solution for *clean chemistry* when preparing samples for trace and ultra-trace elemental analyses. This dissolution method involves raising the pressure and temperature of a sample, to which concentrated acids have been added, in a closed vessel through microwave irradiation. In this way, the digestion temperature is not limited to the boiling point of the solution, resulting in higher temperatures that increase the speed of matrix decomposition and the solubility of the analytes in solution. Shown in Figure 5.5 is the CEM Corporation MARS 6™ Microwave Digestion System.[61] Microwave systems further streamline the sample preparation process by dramatically reducing sample digestion time from hours using a hot plate or hot block to minutes.

Figure 5.5 The CEM Corporation MARS 6 Microwave Digestion System.

Figure 5.6 With microwave assisted acid digestion, the quality of decomposition is improved due to higher pressure and higher digestion temperature, often yielding a clean and clear digestate.

The advantages of microwave assisted acid digestion for the sample preparation process are:

- **Speed of digestion.**
  For the digestion of solid environmental samples according to Method 3051a, the microwave digestion process can take approximately 10 minutes[62] compared to over two hours[63] using a hot plate or hot block, thereby greatly reducing digestion time, improving overall efficiency, and allowing an increase in sample throughput and laboratory productivity.
- **Quality digestion.**
  Since digestion takes place at an elevated temperature and pressure, the acid can be heated above its boiling point, resulting in more complete decomposition of the matrix, a cleaner digestate, and better analyte recoveries.
- **Reduced exposure to contamination.**
  Exposure to contamination is reduced as digestion takes place in a closed system where the sample is not exposed to the atmosphere susceptible to the deposition of dust or other airborne particulates. Additionally, digestion vessels and vessel liners made from chemically inert, thermally robust, high purity fluoropolymers (e.g., PFA, PTFE) are available to further reduce the contamination and leaching issues associated with the use of glass digestion vessels.
- **Reduced reagent consumption.**
  The quantity of reagents used for the microwave digestion process is lower compared to open vessel acid digestion where reagents are continuously added after evaporation of the sample; the cycle of evaporation and adding acid continues until partial or satisfactory decomposition of the matrix is achieved. With microwave digestion, reagents are added only once prior to the digestion process; contamination from any impurities present in the reagents is minimized due to the lower quantity used.
- **Retention of analyte.**
  Loss of analytes is prevented as the digestion vessels are sealed and digestion takes place in a closed system, unlike a hot plate or hot block where evaporation of the reagents and analyte loss are more likely to occur.
- **Overall efficiency.**
  The dramatically reduced digestion time combined with the quality of digestion, better analyte recoveries, reduced contamination, and use of less reagents result in savings in time and resources. Overall efficiency of the elemental analysis workflow is improved with more accurate sample results and data quality.

Table 5.3 is a comparison of the three sample dissolution methods based on key items to consider when selecting the most appropriate method for the applications, sample throughput, budget requirements, etc. of the laboratory.

Table 5.3 Comparison between open and closed vessel acid digestion systems

Key considerations	Open vessel acid digestion		Closed vessel acid digestion
	Hot plate	Hot block	Microwave
Initial investment	$	$$	$$$
Ease of set-up	Easiest	Easier	Easy
Consumables	N/A	Required	Optional
Maintenance and cleaning	High	Low	Medium
Sample handling	Highest handling	Lowest handling	Medium handling
Contamination exposure	Highest risk	Medium risk	Lowest risk
Reagent consumption	High	High	Low
Retention of analyte	Lowest	Medium	Highest
Digestion quality	Low	Medium	High
Batch size	Lowest	Highest	Medium
Digestion time	Hours	Hours	Minutes
Sample throughput	Lowest	Medium	High
Recommended for ultra-trace elemental analysis	Not recommended	Recommended	Highly recommended
Overall efficiency	Low	Medium	High

Note: Comparisons between the dissolution methods were based on years of practical experience and collective feedback from laboratories within various industries. Comparisons reflect majority of feedback received.

5.3.3 Apparatus and equipment for acid digestion

Hot plate acid digestion

The following are considerations and recommended best practices for the selection of material and apparatus for hot plate digestion and for the filtration of the sample solution after digestion.

- For ultra-trace elemental analysis, borosilicate glass digestion vessels and associated apparatus (e.g., watch glasses) are not recommended due to the presence of major and minor elemental components (e.g., B, Si, Na, K, Al). Plastic and high purity quartz are recommended as they are not as contaminating as borosilicate glass and can withstand the high temperatures required for acid digestion. Fluoropolymers are the most appropriate plastic material for acid digestion due to their high working temperatures of over 200°C. High purity quartz can withstand even higher temperatures over 300°C, necessary when digesting samples using sulfuric acid. For digestions requiring hydrofluoric acid, quartz is not compatible. Fluoropolymers are preferred over quartz for most digestion applications for their high chemical resistance, durability, lower cost, and availability.

  There are many types of plastic material used for laboratory apparatus. As an overview, fluoropolymers (e.g., PFA, PTFE, FEP) are used in many industrial applications for their wide working temperature ranges, chemical resistance, and other important properties. Polytetrafluoroethylene (PTFE) has a high working temperature of up to 260°C and has non-stick, non-wetting, and friction reducing properties. The most well-known fluoropolymer is Teflon™ which is a PTFE formulation.[64] Perfluoroalkoxy alkanes (PFA) have similar properties to PTFE except more flexible. They are also highly chemical resistant and transparent and are often used for laboratory equipment and ICP-MS sample introduction components (e.g., spray chambers, nebulizers). Method 200.8 specifies the use of FEP storage containers for standard solutions and PTFE digestion vessels with PTFE covers; FEP has a lower working temperature of 200°C, hence, it is not suitable for acid digestion. Polypropylene and PE are appropriate for storage and transfer apparatus but not for acid digestion.

- Filtration apparatus and materials may also introduce contamination to the sample solution. For best practice, the use of disposable plastic (e.g., polypropylene) syringes and syringe filters, shown in Figure 5.8, is recommended for trace and ultra-trace elemental analyses over a traditional filtration set-up consisting of filter paper, funnel, and Erlenmeyer flask, which is more labor intensive and inefficient. The traditional set-up is more labor intensive, inefficient, and contamination is more susceptible through numerous handling and transfer steps involved with this set-up.

Figure 5.7 Griffin beakers made from different materials. PTFE (left) is best for ultra-trace detection limits, high purity quartz (center) is a better alternative to borosilicate glass (right). Borosilicate glass is suitable for higher detection limit applications or general laboratory work.

Figure 5.8 Disposable plastic syringes and syringe filters are recommended for filtration of samples prior to ICP-MS analysis. Pictured are Luer lock syringes (top) and a PTFE syringe filter (bottom).

- Different types of syringe filter membranes are available on the market: Polyethersulfone (PES), glass fiber, PTFE, polyvinylidiene difluoride (PVDF), polypropylene, cellulose nitrate, cellulose acetate, nylon, etc. Some membranes are hydrophilic while others are hydrophobic, some are best suited for organic solvents prior to analysis by chromatography techniques (e.g., HPLC) and others are best for aqueous samples only. For trace elemental analysis, PES, Nylon, and PTFE are suitable.[65] Hydrophobic filters (e.g., PTFE, PP) need to be pre-wetted with a water-miscible organic solvent prior to use for aqueous solutions.

- As a similar step recommended prior to the use of any laboratory apparatus, rinse syringe filters several times with either reagent water or 1% nitric acid. This measure can help to reduce contamination from the syringe filter to the sample. As an extra step, discard the first few mL of sample and use the rest of the sample in the syringe for analysis.
- To clear the syringe filter of any remaining sample or rinse solution, pull or draw up about 1–2 mL of air into the syringe prior to drawing or pulling the sample up. Once the sample is pushed through the syringe filter, the air at the end of the syringe will help to eject any rinse solution or sample remaining in the syringe filter.
- For applications where higher levels of detection are acceptable, filtration by the traditional set-up consisting of filter paper placed in a funnel mounted above an Erlenmeyer flask, as shown in Figure 5.9, can be used. Otherwise, the sample can be centrifuged or allowed to sit until the solids settle to the bottom of the container.

Tip

It is recommended to determine the presence of impurities that may pass from the syringe and syringe filter onto the sample solution. This can be done by analyzing blank solutions that have been pushed through just the syringe and then another set of blank solutions that have been pushed through the syringe and syringe filter. This can help to isolate the source of contamination. Compare these results with the result from the analysis of a blank solution that has not been filtered. If the level of impurities is high enough to affect detection requirements, then another syringe filter membrane should be selected and tested.

Figure 5.9 Traditional method of filtering samples involves pouring samples into a funnel lined with filter paper and collecting the filtered sample into an Erlenmeyer flask (left) or beaker (right).

Table 5.4 provides links to webpages where products for hot plate acid digestion can be viewed.

Table 5.4 Apparatus for hot plate acid digestion and filtration

Equipment/apparatus links
Hot plates
Hot plates and stirrers
Hot plate digestion accessories
Ultra-trace detection limits
Quartz beaker
Glass Griffin beaker
PTFE beaker
Higher detection limits
Glass watch glass/beaker cover
PTFE watch glass/beaker cover
Filtration apparatus – syringe and syringe filters
Disposable plastic syringe and syringe filters
Filtration apparatus – funnels, filter paper, iron stand
Quantitative filter paper: Grade 42
Funnels
Erlenmeyer flask
Iron ring with clamp and cast iron stand with tripod-base support

Hot block acid digestion

The hot block digestion systems are listed in Table 5.5, including associated consumables like the digestion vessels, watch glasses, and filters. These systems are commonly used throughout environmental and contract testing laboratories. Links to the product pages are provided for convenience in accessing further information and product specifications.

Microwave assisted acid digestion

For the analysis of environmental samples according to the requirements of Methods 200.8 and Method 6020B, the CEM MARS 6 Microwave Digestion System with IR temperature control and MARSXpress™ vessels is recommended. The MARS 6 system is simple to use with onboard video tutorials to help labs maintain consistency in training new technicians.

The system is also loaded with pre-programmed methods which include US EPA 3015A, 3051A, 3052, NPDES, and TCLP to make sample preparation of both aqueous and solid environmental samples simple and efficient. The digestion times range from 10 to 30 minutes total, giving high throughput labs the ability to process more samples per hour than any other sample preparation technique. The MARSXpress vessel is a closed PFA vessel that allows for heating of samples above the boiling point of reagents to achieve the most complete sample decomposition. The simple to assemble 3-piece vessels are easily hand tightened with the manual torque block prior to loading into the cavity.

Table 5.5 Hot block acid digestion systems and accessories

Product description
SCP Science DigiPREP MS Digestion Block
SCP Science DigiPREP Keypad Controller (for use with DigiPREP Digestion Block)
SCP Science DigiTUBEs
SCP Science Watch Glasses
Cole-Parmer Environmental Express Hot Block SC154 Digestion System
Cole-Parmer Environmental Express FilterMate SC0407 Digestion Cup Filter, PVDF with PTFE Prefilter
Cole-Parmer Environmental Express UC475-GN Ultimate Digestion Cups

Figure 5.10 Turntable of the CEM MARS 6 Microwave Digestion System.

The process for using microwave digestion is very simple. As shown in the illustration below, sample is placed into the clean and empty liner along with the acid(s) being used for the method. When digesting soil samples that contain oils or solvents, allow the samples to predigest in the hood for 15 minutes prior to capping the vessel. After pre-digestion, place plug and cap onto vessel and hand tighten. Use MARSXpress Manual Torque Block to tighten vessels to specification. Place liners all the way into the turntable and place the turntable into the MARS 6 system. Select the appropriate method and press Start. After the method has completed, remove vessels from turntable and place into rack to cool. After they have cooled to room temperature, vent vessels in a hood and remove cap and plug. Transfer sample into appropriate volumetric vial and dilute with DI water. Wash and dry liner and begin the next batch.

To learn more about the CEM MARS 6 microwave digestion system and other systems, please visit **cem.com/en/microwave-digestion**. For microwave digestion system accessories for environmental analysis, please visit **cem.com/MARS-Enviro**.

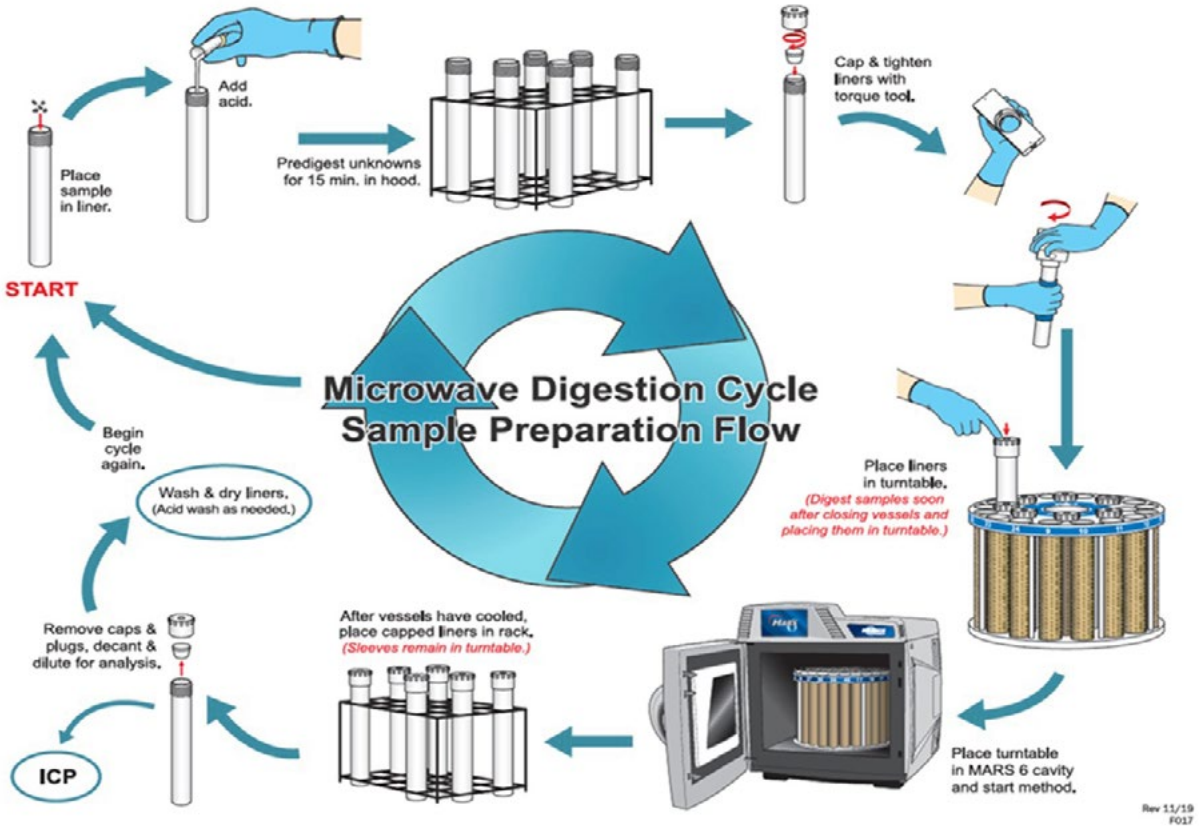


Figure 5.11 The streamlined sample preparation flow using the Mars 6 Microwave Digestion System.

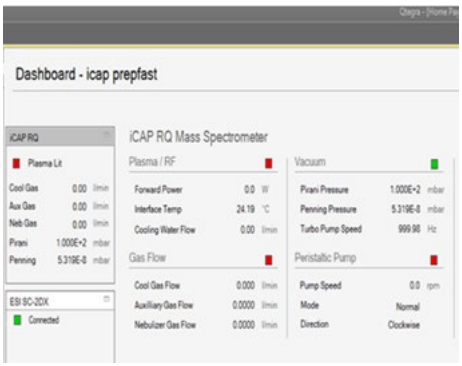
6 ICP-MS instrumentation

Today's ICP-MS instruments are not only capable of providing the required sensitivity, detection limits, and wide linear dynamic range for the quantitative analysis of the majority of elements in the periodic table. They are more robust, capable of handling a variety of samples and are used for advanced applications, including, speciation, laser ablation, and nanoparticle analysis. Instrument features and peripherals to improve high matrix tolerance, a limitation of ICP-MS that was a barrier for many applications, have been developed to allow undiluted analysis of more challenging samples.

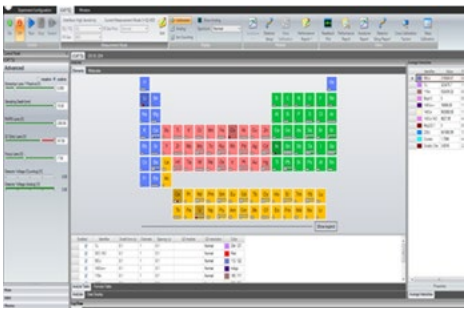
For the analysis of environmental samples according to Method 200.8 and Method 6020B, the Thermo Scientific™ iCAP™ RQ ICP-MS, part of the **Thermo Scientific portfolio of ICP-MS instruments**, is a powerful yet compact and easy to use instrument for single quadrupole ICP-MS (SQ-ICP-MS) analysis.[66] Environmental and contract testing laboratories are often challenged with high throughput and fast turnaround of results for a wide range of samples, from drinking water to soils to wastewater; hence, performance, speed, and robustness are essential for instrumentation.

Figure 6.1 Following over 35 years of experience in ICP-MS, the compact and innovative design of the iCAP RQ ICP-MS combines high performance with robustness and ease of use to meet challenging analytical requirements over a broad range of industries and applications.

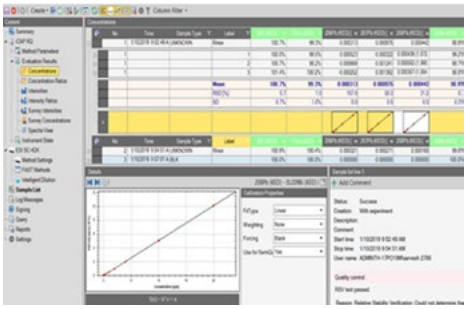
Comprehensive quality control protocols within the EPA-approved analytical methods, which include specified actions upon standard and sample failures, must be applied in every analytical run sequence. All method parameters, data files, and reports must be kept on file and readily available for records, traceability, and audit purposes. **The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) software**, designed for streamlined workflow, scalability, and data management, is a common platform across ICP-MS, ICP-OES, and isotope ratio analysis techniques {e.g., Multi-collector ICP-MS (MC-ICP-MS), Isotope Ratio Mass Spectrometry (IRMS)}.[67] It comprises a Dashboard and Control Panel for easy operation, tuning, and view of all instrument parameters and interlocks, tools for 21 CFR Part 11 compliance, report templates and data export to LIMS, and Quality Control features for automatic implementation of EPA method specified protocols. Method development is done using a top down approach with all method parameters and results conveniently stored in one file called a *LabBook*.



Dashboard



Control panel



LabBook

Figure 6.2 The iCAP RQ ICP-MS (below) is the first bench top, vertical ICP-MS instrument. The Qtegra ISDS software (left) consists of three workspaces called the Dashboard, Control Panel, and the LabBook where method and operating parameters are stored.

Instrumentation for ICP-MS has greatly evolved since its introduction in 1983. The size of the instrumentation has dramatically decreased from floor to bench top models. Features for advanced interference removal, easy installation, set-up, operation, and maintenance have been implemented to make this technique more accessible and easier to use across different applications and industries. The main parts of the iCAP RQ ICP-MS are shown in Figure 6.3. The unique Right Angle Positive Ion Deflection (RAPID) Lens focuses the ion beam upward resulting in compact size and vertical design.

The instrument sample introduction system and interface are the main areas that the analyst will handle and maintain. It is important to note that all parts under vacuum {(e.g., ion optics, Collision/Reaction Cell (CRC), quadrupole, and SEM detector)} are not maintenance items for the iCAP RQ ICP-MS. The following sections of this document will focus on the sample introduction system and the interface, two very important parts of the instrument that require attention and routine maintenance to ensure best instrument performance and prevention of the issues that cause standard and sample failures, downtime for troubleshooting and maintenance, and re-analyses of samples impacting overall laboratory productivity. Parts and consumables, along with tips and best practices for their use prior to analysis, will also be provided.

Figure 6.3 Main areas of the innovative iCAP RQ ICP-MS. The compact design results from shifting the ion beam upward with the RAPID Lens. The two areas routinely handled are the Sample Introduction System and the Interface, both at bench height and easily accessible.

6.1 ICP-MS instrument parts and consumables

6.1.1 Sample introduction system

The sample introduction system is the part of the instrument that is handled routinely and can be a major source of random and systematic error if not inspected prior to analysis and maintained properly. Although the standard sample introduction system included with the instrument is streamlined, easy to set-up, and fit for most samples matrices and routine applications, it is an important area requiring attention prior to analysis to ensure smooth instrument operation, best analytical performance, and overall data quality. For more aggressive samples matrices (e.g., highly corrosive acids, organic solvents), the sample introduction system will require further optimization of components for compatibility and prevention of analytical issues.

Best practices

As a best practice, inspect sample introduction components (e.g., torch, injector, nebulizer, spray chamber, peristaltic pump, peristaltic pump tubing, capillary tubing, autosampler probe, internal standard connector and associated tubing) prior to analysis for contamination, blockage, deposits, and any defects to avoid analytical issues, such as, signal instability and loss of sensitivity, that affect the precision and accuracy of the measurement. General industry best practices for maintaining sample introduction components will be discussed in this document, however, always refer to the product or instrument manufacturer's operating manual for instructions on specific cleaning and maintenance procedures.

The main components of the sample introduction system are the torch assembly, nebulizer, spray chamber, and peristaltic pump. The sample introduction system on the iCAP RQ ICP-MS is located at bench height and open for easy access and peripheral connectivity (e.g., autosampler, discrete sampling valves, autodilution systems). The components are *quick connect* since they do not require any tools, extra O-rings, or washers for assembly; all parts are push-fit connected for easy installation.

Torch assembly

The torch assembly, shown in Figure 6.4, is streamlined in design with minimal parts, simple set-up, and automatic connection to the argon gas flows for plasma ignition. The torch assembly consists of the following components:

- **Quartz torch**
  The quartz torch is demountable, single piece, and tulip design. It was made for easy push-in connection to the torch holder.
- **Torch holder**
  The torch holder is made from Teflon™ and has built-in gas inlets for automatic connection to the argon gas supply upon installation to the instrument.
- **Quartz injector**
  The quartz injector is of proprietary design and self-aligning. The injector is pushed into a Teflon™ injector holder which screws into the torch holder for quick connection to the torch assembly.

Figure 6.4 The streamlined design of the torch assembly allows fast and easy connection between components and installation to the instrument; no extra parts or tools required.

Best practices

Best practices for the torch assembly

- **Prior to analysis, inspect the injector and torch for matrix build-up, blockages, fractures, and devitrification. These will affect instrument performance, sensitivity, precision, accuracy, and cause drift throughout the analysis.**
- **The torch and injector can be cleaned by soaking them in a solution of 5% nitric acid and 2% hydrochloric acid for 20 minutes or longer if build-up persists. Afterwards, rinse thoroughly with reagent water and allow to air dry completely.**
- **Do not sonicate the torch and injector or use a wire brush or scraping tools for cleaning and removing deposits.**
- **Handle the injector and torch with care; do not use excessive force when pushing into the injector and torch holders. When not in use, always store them in a cushioned box or their original packaging.**
- **Do not touch the injector or torch with bare hands. Always wear gloves to prevent oil and moisture on the hands from contaminating and damaging the surfaces.**
- **Ensure that the argon flow rates are optimized for the application and are correctly set prior to plasma ignition. Incorrect settings may cause damage such as melting of the torch.**
- **At the end of analysis, run the blank solution (e.g., 1% nitric acid) followed by reagent water for several minutes to prevent the formation of matrix deposits or salts inside the injector.**

Table 6.1 lists the torch assembly components that come standard with the iCAP RQ ICP-MS and are used for most environmental and industrial applications.

Table 6.1 Torch assembly components

	Parts
Torch assembly	2.5 mm ID quartz injector
	iCAP Qnova quartz torch
	iCAP Qnova torch holder

Nebulizer

The nebulizer converts the sample solution into a fine aerosol for introduction into the plasma. The nebulizer that comes with the iCAP RQ ICP-MS is a low-flow, borosilicate glass, self-aspirating, concentric nebulizer with a flow rate of 400 µL/min. The concentric nebulizer is widely used for its easy installation, stability, and high sensitivity required for most ICP-MS applications.

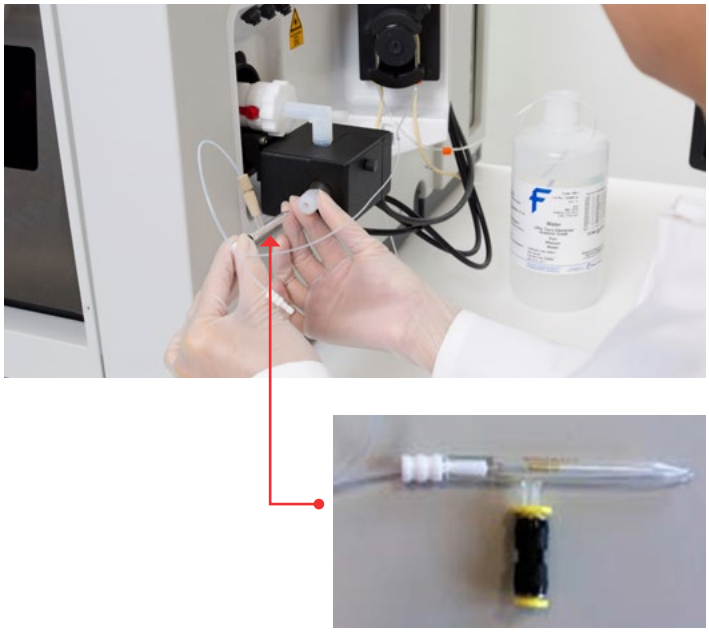


Figure 6.5 The glass concentric nebulizer comes with the iCAP RQ ICP-MS. It produces a fine mist, delivering the sensitivity required for most applications. It is push-fit connected to the spray chamber for quick and easy installation.

A concentric nebulizer has a central capillary for the sample and an outer capillary for the argon gas flow. The argon gas draws the sample into the gas stream through induction and breaks it up into a very fine aerosol consisting of micrometer sized droplets. The concentric nebulizer generally produces a stable aerosol and is easy to set up; the main limitation is its inability to handle high TDS and particulates in the sample. Dissolved solids and particulates can block the tiny central capillary resulting in poor performance and signal drift. In general, low-flow concentric nebulizers can handle up to 1% TDS; however, due to the interface of the ICP-MS, consisting of sample and skimmer cones with very small orifice diameters, a commonly recommended limit or industry standard for TDS is <0.2%. This limit is also specified in Method 6020B, Section 4.6.

Best practices

Best practices for glass concentric nebulizers

- Prior to analysis, inspect the nebulizer for blockage, damage, and deposits at the tip that restrict aerosol formation, decrease sensitivity, cause signal drift, and affect analytical precision.
- Prevent nebulizer blockage by filtering particulates and suspended solids from the sample solution prior to analysis. Use an autosampler enclosure to prevent dust and airborne contamination from depositing onto samples and standards loaded on the autosampler awaiting analysis.
- Clean the nebulizer by soaking in 10% nitric acid; this should be sufficient for removing crystalline deposits at the tip. Otherwise, soak in aqua regia (1:3 nitric acid and hydrochloric acid). Afterwards, rinse the nebulizer thoroughly with reagent water.
- Note: Do not sonicate the nebulizer and do not insert a wire through the tip of the nebulizer to remove blockage. Also, do not touch the delicate tip of the nebulizer. These actions will cause permanent damage to the central capillary requiring replacement of the nebulizer.
- Blockages in the nebulizer can be dislodged by backflushing using a specific tool or cleaning kit. Consult the instrument or nebulizer manufacturer for cleaning kits or backflushing tools available.
- Monitor the nebulizer back pressure to detect blockages and other issues. Record the back pressure in an instrument log daily to track any upward or downward trends.
- After analysis, rinse the nebulizer by running the blank solution followed by reagent water for a few minutes to prevent sample matrix, salts, etc., from forming inside the nebulizer capillary. Allow the nebulizer to run dry before shutting off the argon gas supply. Disconnect the uptake line to prevent liquid from being drawn up to the nebulizer when the instrument is not in operation.

Spray chamber

The spray chamber included with the iCAP RQ ICP-MS is a Peltier cooled, high purity quartz, baffled cyclonic spray chamber with a small volume for fast washout and reduced memory effects. The sample aerosol produced by the nebulizer is not uniform in droplet size. For suitable ionization and stability of the plasma, a fine sample aerosol with an average droplet size of < 10 µm is optimal. The cyclonic spray chamber uses centrifugal force to filter out larger sized droplets that go down the drain, while the smaller sized droplets are carried with the gas stream into the plasma. The center baffle further refines the aerosol so that only the smallest droplets go into the plasma. The nebulizer is push-fit connected to the spray chamber which is attached to the torch assembly with a PTFE elbow connector.

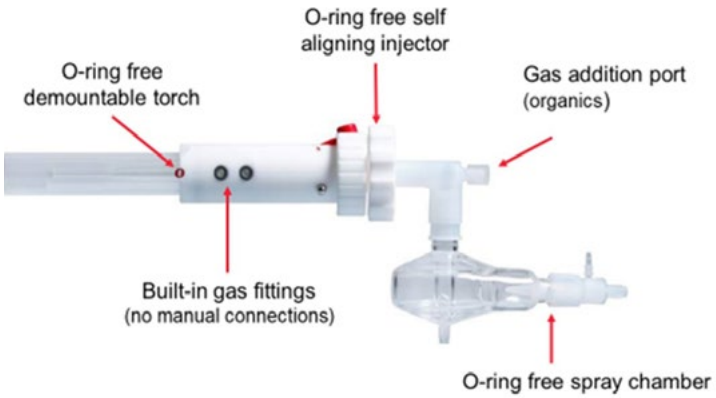


Figure 6.6 The small volume cyclonic spray chamber of the iCAP RQ ICP-MS allows fast wash out and reduced memory effects. It is push-fit connected to the torch assembly using a Teflon™ elbow connector and is housed inside a Peltier cooler for temperature stability, solvent removal, and reduction of oxides.

Best practices

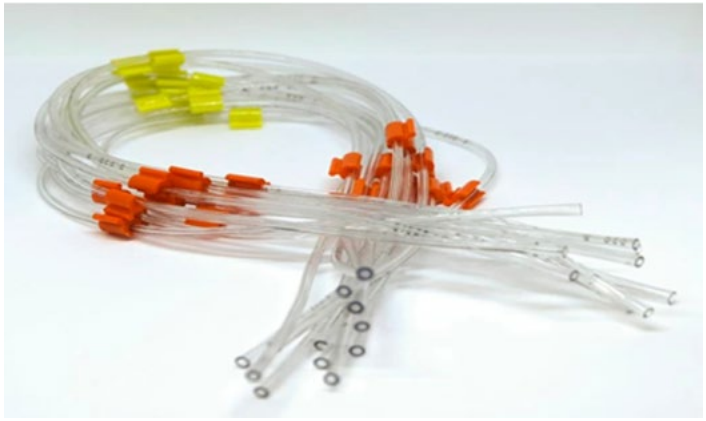
Best practices for the cyclonic spray chamber

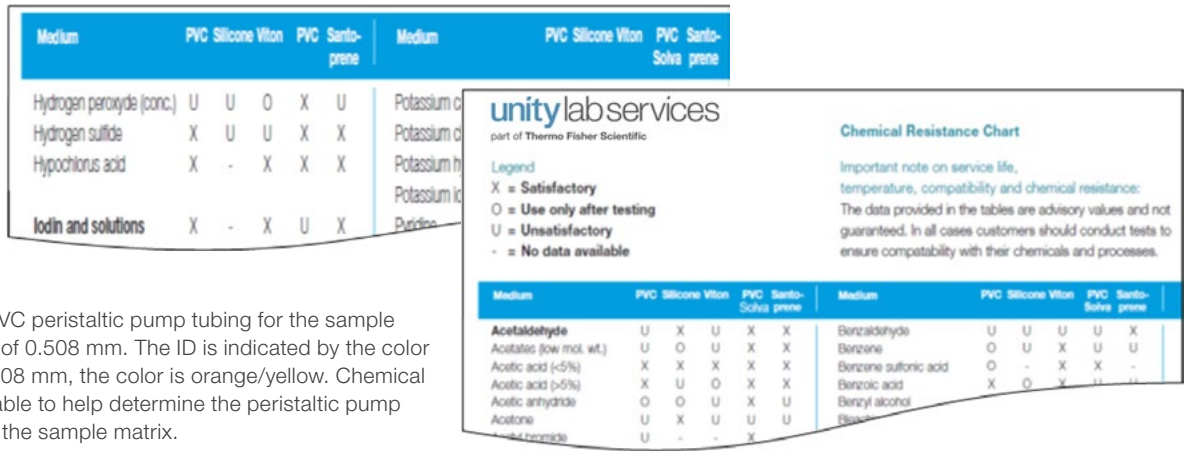
- **Signal instability and the formation of droplets along the walls of the spray chamber are indications that the spray chamber requires cleaning.**
- **The spray chamber can be cleaned by soaking it in 5% nitric acid and 2% hydrochloric acid for at least 20 minutes or overnight for tough deposits. Rinse the spray chamber with reagent water and allow it to air dry.**
- **Exercise the same care when handling the glass cyclonic spray chamber as described for the torch, injector, and nebulizer; do not sonicate, touch with bare hands, or use a wire brush for cleaning.**
- **Do not use a glass cyclonic spray chamber when analyzing samples containing hydrofluoric acid. A spray chamber made of a compatible, resistant material such as PFA must be used.**
- **After analysis, rinse the spray chamber by running the blank solution for several minutes followed by reagent water to prevent sample deposits from forming inside the spray chamber when the solvent dries out.**

Peristaltic pump and pump tubing

The peristaltic pump of the iCAP RQ ICP-MS is a compact, mini-pump that is metal free and consists of 12 rollers and 4-channels, shown in Figure 6.8. The pump settings are software controlled and should be optimized for the application. The peristaltic pump tubing for the sample and drain must be of material compatible and resistant to the samples being analyzed otherwise degradation of the tubing will occur. The standard sample peristaltic pump tubing is made from Polyvinyl Chloride (PVC) while the drain tubing is Santoprene™, a high-performance plastic which looks and feels like rubber. Chemical resistance charts, such as the one shown in Figure 6.7, are available to assist with the selection of the appropriate pump tubing material for different sample types, from organic solvents to concentrated acids. The following are some common pump tubing material for trace elemental analysis:

- PVC – for aqueous samples of low to medium acid concentrations, suitable for most routine aqueous applications
- Viton™ – for strong acids (e.g., hydrofluoric acid), alkalis, and solvents
- Solvent Flex – for organic solvents
- Santoprene™ – for medium to high concentrated acids and some organic solvents





Medium	PVC	Silicone	Viton	PVC	Santo-prene
Hydrogen peroxyde (conc.)	U	U	O	X	U
Hydrogen sulfide	X	U	U	X	X
Hypochlorus acid	X	-	X	X	X
Iodin and solutions	X	-	X	U	X

Medium	PVC	Silicone	Viton	PVC Solva	Santo-prene
Potassium c					
Potassium c					
Potassium h					
Potassium io					
Pyridine					

unity lab services
part of Thermo Fisher Scientific

Chemical Resistance Chart

Legend
X = Satisfactory
O = Use only after testing
U = Unsatisfactory
- = No data available

Important note on service life, temperature, compatibility and chemical resistance:
The data provided in the tables are advisory values and not guaranteed. In all cases customers should conduct tests to ensure compatability with their chemicals and processes.

Medium	PVC	Silicone	Viton	PVC Solva	Santo-prene
Acetaldehyde	U	X	U	X	X
Acetates (low mol. wt.)	U	O	U	X	X
Acetic acid (<5%)	X	X	X	X	X
Acetic acid (>5%)	X	U	O	X	X
Acetic anhydride	O	O	U	X	U
Acetone	U	X	U	U	U
Acid bromide	U	-	-	X	

Medium	PVC	Silicone	Viton	PVC Solva	Santo-prene
Benzaldehyde	U	U	U	U	X
Benzene	O	U	X	U	U
Benzene sulfonic acid	O	-	X	X	-
Benzoic acid	X	O	X	U	U
Benzyl alcohol					
Bleach					

Figure 6.7 The standard PVC peristaltic pump tubing for the sample has an inside diameter (ID) of 0.508 mm. The ID is indicated by the color coding of the stops, for 0.508 mm, the color is orange/yellow. Chemical resistance charts are available to help determine the peristaltic pump tubing material suitable for the sample matrix.

The peristaltic pump is a major contributor to signal variation, causing precision and stability issues during the analytical run which is indicated by an elevated %RSD between replicates. A %RSD of higher than 1% for dilute aqueous solutions aspirated by the standard glass, concentric nebulizer is usually a sign that the pump tubing needs replacement. The constant motion of the peristaltic pump and pressure from the rollers cause the pump tubing to wear and become less rounded and elastic, affecting the smooth flow of the solution to the nebulizer. Also, depending on the sample throughput and variation of the sample matrices, the peristaltic pump tubing may require more frequent replacement.

Figure 6.8 The sample introduction system and mini peristaltic pump of the iCAP RQ ICP-MS are located on the right side of the instrument at bench height. The mini pump has 12 rollers, 4 channels and inert rollers.

Best practices

Best practices for peristaltic pump and peristaltic pump tubing

- **Prior to analysis, inspect the peristaltic pump and clean the surface, rollers, and tension arms to remove any dust or dirt.**
- **Prior to analysis, inspect the peristaltic pump tubing for wear and tear, discoloration, flatness, blockage, and contamination. Replace the pump tubing if any of these defects are observed. Worn or defective pump tubing will disrupt the smooth, continuous flow of solutions to the nebulizer, resulting in signal instability and poor precision.**
- **Replace the peristaltic pump tubing if the %RSD between replicates begins to increase higher than 1% for dilute aqueous solutions aspirated using a standard glass, concentric nebulizer.**
- **The autosampler wash station pump tubing should also be inspected for wear and tear and replaced as needed to avoid leakage of acidic wastes in the laboratory.**
- **Ensure the peristaltic pump tubings are correctly installed by checking the sample and drain flow direction when the pump is in operation.**
- **Adjust the tension on the peristaltic pump tubing using the thumbscrews; they should not be over tightened as this will lead to faster wear and tear. Adjust the tension enough to allow smooth and even sample and drain flows.**
- **After analysis, rinse the peristaltic pump tubing by running the blank solution followed by reagent water. Disconnect the peristalic pump tubing from the sample and allow the peristaltic pump to run until the sample and drain tubings are dry. Lift the collar and release the tubings from the brackets to prevent premature wear and tear.**

Table 6.2 lists the sample introduction components that come standard with the iCAP RQ ICP-MS and are suitable for typical aqueous samples in environmental and routine applications. For high matrix samples or samples containing hydrofluoric acid or organic solvents, other types of nebulizers, spray chamber, injectors, and pump tubing are available and must be used for optimization.

Table 6.2 Sample introduction system components

	Parts
iCAP RQ ICP-MS sample introduction system	High purity quartz baffled cyclonic spray chamber
	PFA adapter elbow (for spray chamber)
	Glass concentric MicroMist nebulizer, 400 µL/min flow rate
	Peltier cooler, software controlled, -10ºC to 20ºC
	PVC peristaltic pump sample tubing 0.508 mm ID, orange/yellow, 3 bridges, flared ends
	Santoprene™ peristaltic pump drain tubing 1.295 mm ID, grey/grey, 3 bridges, straight ends

Argon Gas Dilution (AGD)

The analysis of high matrix samples has been a challenge for ICP-MS mainly due to the susceptibility to blockage of the sample and skimmer cone orifices by solids, salts, and high TDS present in the samples. High levels of salts and TDS cause physical interferences that result in a suppression of signal or response which must be corrected for accurate results. Samples can be diluted to reduce the TDS level to less than 0.2% either manually or online using an autosampler with an autodilution feature. Both options have their limitations:

- Manual dilution requires extra time and resources with the possibility of introducing contamination and systematic error with each dilution and handling step.
- Autosamplers with an autodilution feature are costly compared to standard autosamplers, require extra set-up and parts, extra method development, and more maintenance.

The demand to analyze high matrix samples (e.g., sea water, brackish water) undiluted to measure ultra-trace levels of toxic contaminants for water compliance monitoring, research, etc., has increased resulting in the need for more robust ICP-MS instrumentation. A widely accepted approach to overcoming these challenges is AGD. This entails the reduction of the nebulizer gas flow and the addition of a make-up flow of argon gas to dilute the sample aerosol prior to entering the plasma. Since the nebulizer gas flow is reduced, the amount of matrix going to the plasma and depositing onto the sample and skimmer cones is also reduced. The robustness is improved allowing the analyses of undiluted, high matrix samples throughout an analytical run. There are several limitations, however, when using AGD:

- All samples within the analytical run are diluted the same; there is no flexibility to dilute different samples at different levels.
- Sensitivity is reduced since the amount of sample is reduced, affecting elements with high ionization potentials, such as As, Se, and Cd, which are key analytes for environmental analysis and research.
- Additional method development and instrument tuning are required for optimization of the analysis.
- Measures to address sensitivity issues, such as, using humidified argon, adding an alcohol to the internal standard, and adding CH4 may be necessary depending on detection limit requirements.

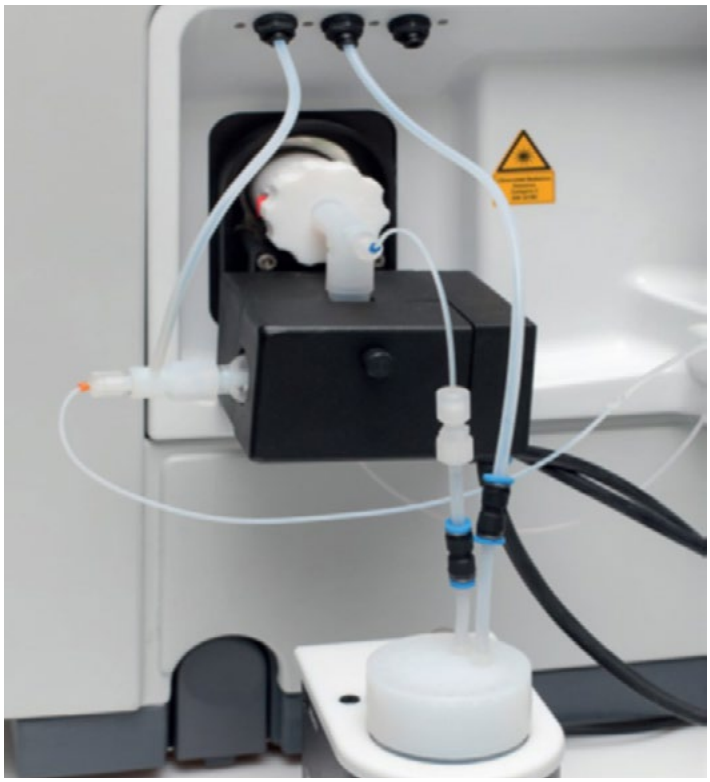


Figure 6.9 The Argon Gas Dilution set-up on the iCAP RQ ICP-MS. In this set-up, an argon humidifier is used to humidify an additional supply of argon added to the sample aerosol.

Despite these limitations, AGD remains a viable approach to addressing issues associated with the routine analysis of high matrix samples, mainly due to its lower cost and easier implementation compared to autodilution or automatic preconcentration systems. Argon Gas Dilution is a better option to avoid the inefficiency and systematic errors associated with manual dilution. However, if only a few samples within the analytical run sequence require dilution and at different dilution levels, then careful manual dilution may be the best approach to take.

6.1.2 Interface

The interface is where ion extraction from the plasma occurs. In the iCAP RQ ICP-MS, the interface is conveniently located behind the front drop-down door, as shown in Figure 6.10, and consists of the sample cone, skimmer cone, and extraction lens. Ions generated in the plasma, at atmospheric pressure, are extracted first through the sample cone and then through the skimmer cone. The area between the sample cone and skimmer cone is the first vacuum stage maintained at < 2 mbar by an external rotary vacuum pump. The ions are then pulled through the skimmer cone by the extraction lens for acceleration and focus into the ion optics inside the high vacuum area of the instrument.

Figure 6.10 The interface drop-down door of the iCAP RQ ICP-MS allows fast and easy access to the sample and skimmer cones, without breaking vacuum, reducing downtime due to maintenance.

The limitation on robustness for ICP-MS is mainly due to the sizes of the sample and skimmer cone orifices and their susceptibility to blockage by high matrix components in the sample. The sample cone, typically made of solid nickel, has an orifice diameter of 1.1 mm, while the skimmer cone, also constructed of nickel, has an even smaller orifice diameter of 0.5 mm. Advances in ICP-MS instruments include the design of the sample and skimmer cones for reduced matrix deposition with the skimmer cone tip operated at an optimized temperature. However, over time and routine analyses of high matrix samples, the build-up of salts, oxides, and dissolved matrix in and around the cone orifices will lead to inefficient ion extraction, signal instability, and reduced sensitivity.

To enhance the robustness of the interface, while maintaining sensitivity, a proprietary skimmer cone insert was designed and fitted inside the tip of the skimmer cone, as shown in Figure 6.12, to allow the signal to be tailored for the application. The size of the central channel of the insert allows the instrument response to be modified across the mass range. There are three types of inserts available for the iCAP RQ ICP-MS: high matrix, high sensitivity, and robust. They are made from stainless steel and are available in three sizes to enhance either robustness, sensitivity, or to provide a balance of both.

Note

Inspect the sample and skimmer cones prior to analysis for blockage in and around the orifices, corrosion, and heavy deposits as these will affect the sensitivity, precision, and stability of the analysis. The sample and skimmer cones should be cleaned gently if these are observed. Aggressive cleaning procedures should not be applied as these will damage the surface and delicate tips of the cones, reducing the service life and resulting in replacement.

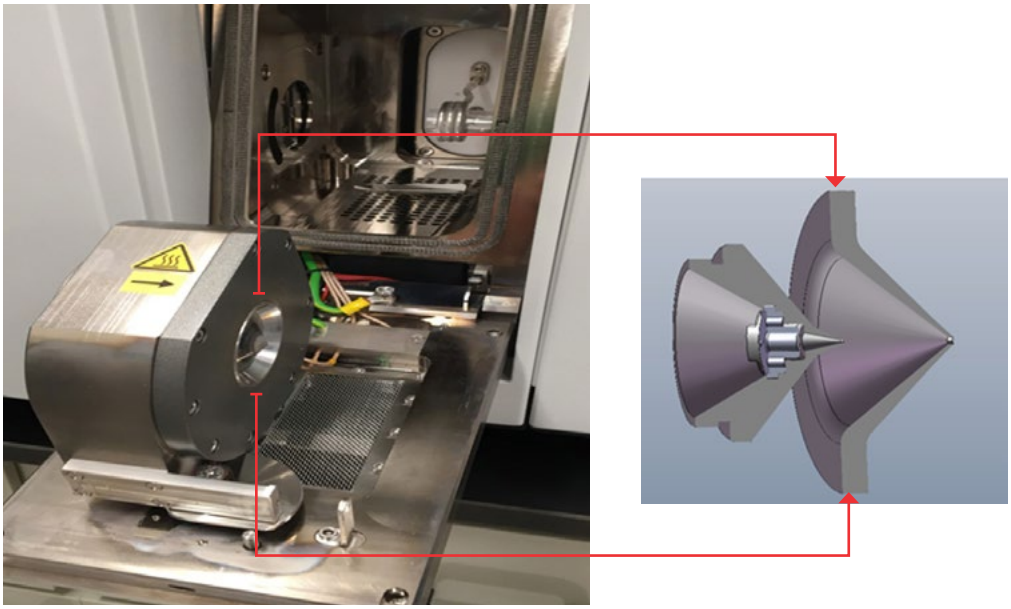


Figure 6.11 An up-close look at the interface and torch area of the iCAP RQ ICP-MS. The sample and skimmer cone and extraction lens are mounted behind the drop-door for easy access when maintenance is needed.

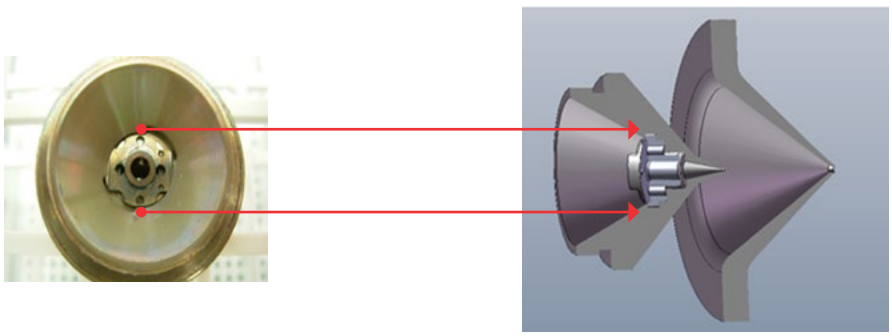


Figure 6.12 Proprietary skimmer cone insert is fitted behind the tip of the skimmer cone.

Table 6.3 summarizes the types of skimmer cone inserts available for the iCAP RQ ICP-MS including their applications and benefits. Increasing the length of central channel enhances matrix tolerance and robustness. The high matrix insert is suitable for most routine environmental and industrial applications while the robust insert enables prolonged analysis of high matrix samples with minimal signal drift.

Table 6.3 Skimmer cone insert types and applications

			
Insert	**High sensitivity**	**High matrix**	**Robust**
Channel size	2.8 mm	3.5 mm	4.5 mm
TDS tolerance	Below 0.1%	Up to 0.2%	Up to 0.5%
Benefit	Best detection and signal to noise ratio	Optimum balance between matrix tolerance and sensitivity	Minimal drift and reduced maintenance for high matrix samples
Applications	Ultra-trace analysis (e.g., semiconductor, UHPC) and advanced applications (e.g., laser ablation, nanoparticles)	Routine applications (e.g., environmental, food and beverage, pharmaceutical, general industrial)	Long term analysis of high matrix samples (e.g., sea waters, brackish waters)

In earlier designs of ICP-MS instrumentation, the interface was in the vacuum area, making it difficult to access for maintenance. Furthermore, breaking vacuum was required to access the sample and skimmer cones, taking hours to bring the instrument back to vacuum and ready for analysis. With the innovative design of the iCAP RQ ICP-MS, the interface is located outside the high vacuum area, mounted behind the unique drop-down door for quick access to the sample and skimmer cones. For added convenience, a dedicated mounting tool is available for easy removal of the sample and skimmer cones. The mounting tool has a magnetic surface on both sides to hold the cones in place during removal. One side of the mounting tool is dedicated to removing the sample cone while the other side is for removal of the skimmer cone, as shown in Figure 6.13.

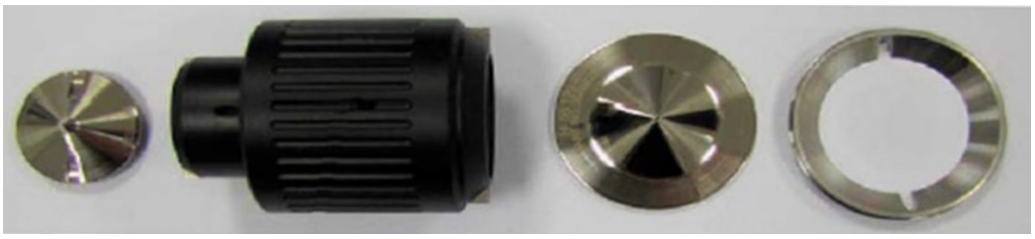
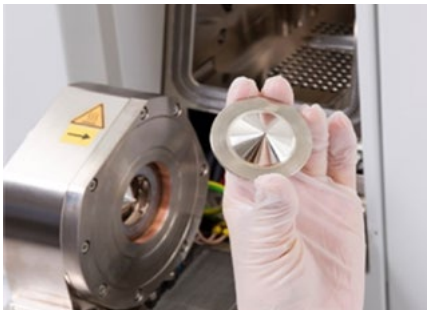


Figure 6.13 The sample and skimmer cones are easily removed using the magnetic mounting tool shown at left. The left side of the tool removes the skimmer cone while the right side is used to remove the sample cone.


The high matrix skimmer cone insert comes standard with the iCAP RQ ICP-MS and is fit for most applications. If enhanced robustness or extra sensitivity is required for a particular application, the skimmer cone insert can easily be switched using the dedicated skimmer cone insert tool. The tool has two nodes on one end that fit into the small apertures of the skimmer cone insert for easy removal. The use of the skimmer cone insert tool is shown in Figure 6.14.

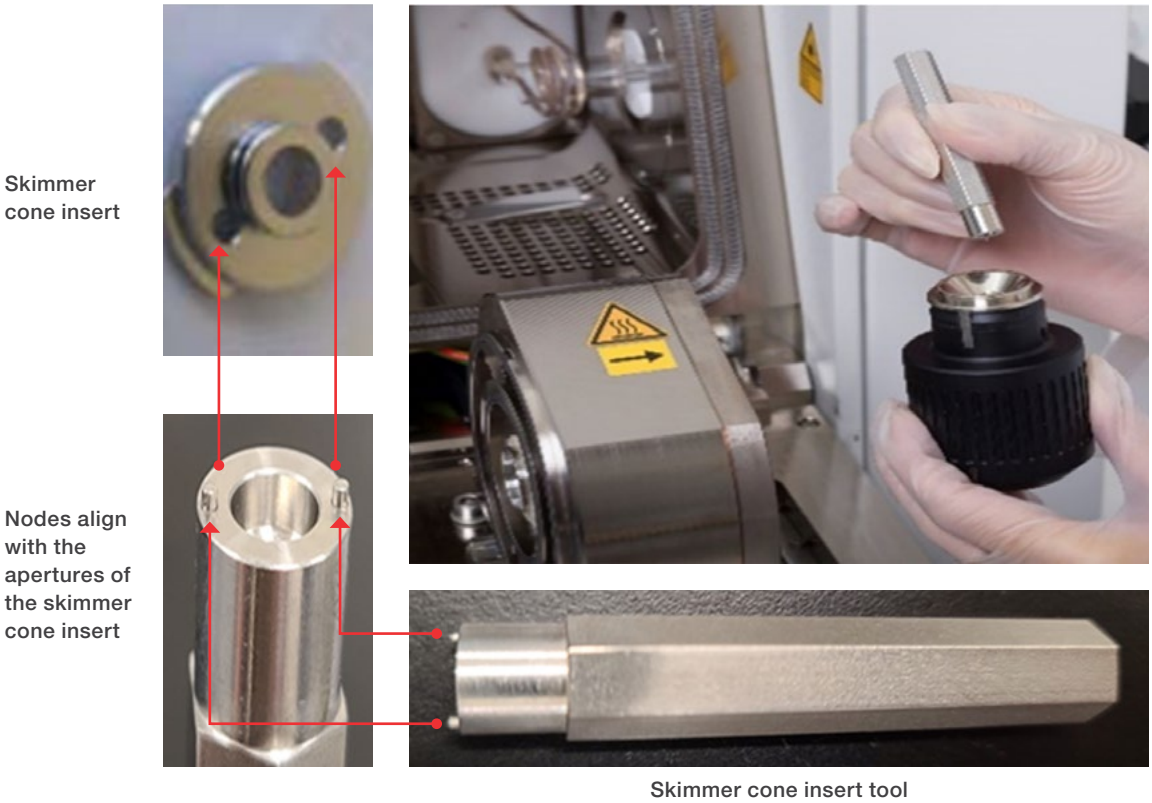


Figure 6.14 The skimmer cone insert is easily removed using the dedicated skimmer cone insert tool as shown.

The extraction lens is bayonet mounted and located after the skimmer cone before the slide valve, as shown in Figure 6.15, for easy access without breaking vacuum. The extraction lens typically does not require maintenance unless ultra-high matrix samples were analyzed, affecting ion extraction. If the extraction lens does require cleaning, it can easily be removed by turning the extraction lens assembly counterclockwise and carefully pulling it out; no tools are required.

If the extraction lens requires cleaning, take apart the extraction lens assembly, consisting of three parts: holder, washer, and the extraction lens cone. Place the extraction lens cone in an ultrasonic bath with reagent water and sonicate for 5 to 10 minutes. For tough deposits, use 2% nitric acid and rinse thoroughly with reagent water. Allow the cone lens to air dry or carefully dry with a lint-free laboratory wipe or cloth. When completely dry, insert the extraction lens assembly into the housing and turn clockwise to fix it into position.

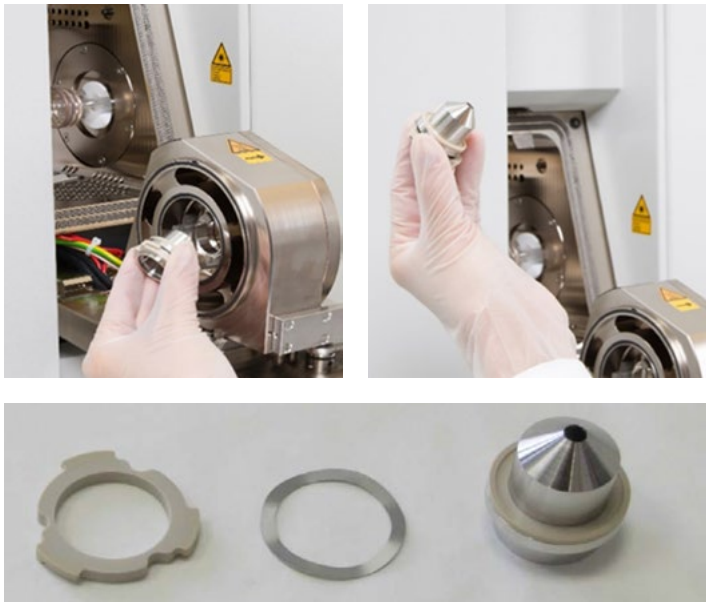


Figure 6.15 The extraction lens is located behind the drop-down door, bayonet mounted for easy removal.

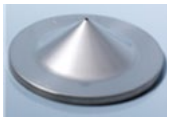
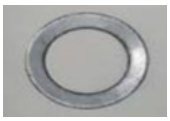
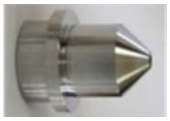
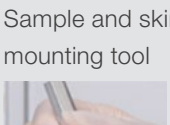
Best practices

Best practices for sample and skimmer cones

- New cones, and cones that have been thoroughly cleaned, must be conditioned prior to use. Conditioning is done to coat the cones with oxides, promoting long-term stability and preserving their service lifetime. Cones can be conditioned by:
  - Aspirating a solution of 500 ppm calcium in 2% nitric acid and 0.5% hydrochloric acid for an hour.
  - Aspirating the highest matrix sample for an hour followed by the blank solution for 5 to 10 minutes.
- Prior to analysis, inspect the sample and skimmer cones for heavy deposits, blockage, damage, and corrosion. These defects will cause performance issues, such as, increased background, memory effects, decreased sensitivity, signal drift, and poor precision.
- It is recommended to clean the cones if deposits and blockage are visible or if the sensitivity does not pass instrument performance specifications or sensitivity specifications defined by the laboratory or application, and after troubleshooting sample introduction components. However, the cones should not be cleaned aggressively or more often than necessary. To clean the cones, the following steps can be followed:
  - Sonicate the cones with reagent water for 5 to 10 minutes. This step should be adequate to clean the cones and restore performance. Re-conditioning may not be needed as the coating of oxides should still be intact after this step. However, if oxides are not intact, then proceed with the conditioning step prior to analysis.
  - If performance issues persist or for tough deposits, sonicate the cones in 2% nitric acid or 2% Citranox™ (a phosphate free cleaner for removal of metal oxides, scale, salts, etc., that can be applied manually or by ultrasonic cleaning, Fisher Scientific catalog number P/N 16-000137). Rinse the cones with reagent water and allow them to air dry or dry with a lint-free cloth.
- Damage to the sample and skimmer cone tips (e.g., chipped, enlarged orifice) is irreparable, requiring replacement of the cones. The skimmer cone tip is especially delicate. Always handle cones with care; do not place them tip side down on any laboratory surface.

Table 6.4 lists the interface components, with their part numbers, that come with the iCAP RQ ICP-MS and fit for most environmental and routine applications. For samples containing aggressive acids (e.g., hydrofluoric acid, sulfuric acid) or organic solvents, platinum tipped sample and skimmer cones are appropriate.

Table 6.4 iCAP RQ ICP-MS interface components

Interface Parts	Part Description
Sample cone	Sample cone  Sample cone gasket 
Skimmer cone and inserts	Skimmer cone  High matrix insert, high sensitivity insert, robust insert 
Extraction lens	Extraction lens 2 
Tools	Skimmer cone insert tool  Sample and skimmer cone mounting tool 

6.1.3 Detector

The detector of the iCAP RQ ICP-MS is an SEM detector. It is a discrete dynode detector with a linear dynamic range of > 10 orders of magnitude allowing detection from major to ultra-trace concentrations of analytes in one sample. As ions exit the quadrupole mass analyzer, they strike the first dynode of the SEM detector, releasing a cloud of electrons; as they strike the next dynode, more electrons are released. A cascade of electrons is generated and counted as a single pulse at the end of the detector.

Although the SEM detector is not considered a maintenance item, it has a finite lifetime. The detector is cradle mounted and can be easily replaced by the analyst; no tools required and no cable connections to be moved or replaced.

Best practices

Best practices for the SEM detector

- **Perform a detector cross calibration weekly, at a minimum. Depending on the sample throughput, types of matrices, and range of analyte concentrations routinely analyzed, a more frequent schedule may be necessary. A detector cross calibration is automatically done through the Qtegra ISDS software using Detector Setup Wizard in the Instrument Control Panel.**
- **It is recommended to perform a High Voltage (HV) set-up at least monthly. Doing this will optimize sensitivity by setting the voltages applied to the detector to optimum values. This is also done through the Qtegra ISDS software using the Detector Setup Wizard. After an HV set-up is performed, a Cross Calibration will be done automatically.**
- **Order a new SEM detector when it is close to replacement. The SEM detector has a shelf life. Do not order a detector and keep it in storage as a spare item.**

Table 6.5 iCAP RQ ICP-MS detector

Part description
Secondary Electron Multiplier (SEM) detector
iCAP RQ ICP-MS detector, cradle design for easy exchange, linear dynamic range of > 10 orders of magnitude, dwell times of 100 µs in both pulse counting and analog modes, automated optimization of operating voltages and cross-calibration.

6.1.4 Other parts and consumables

Online internal standard kit

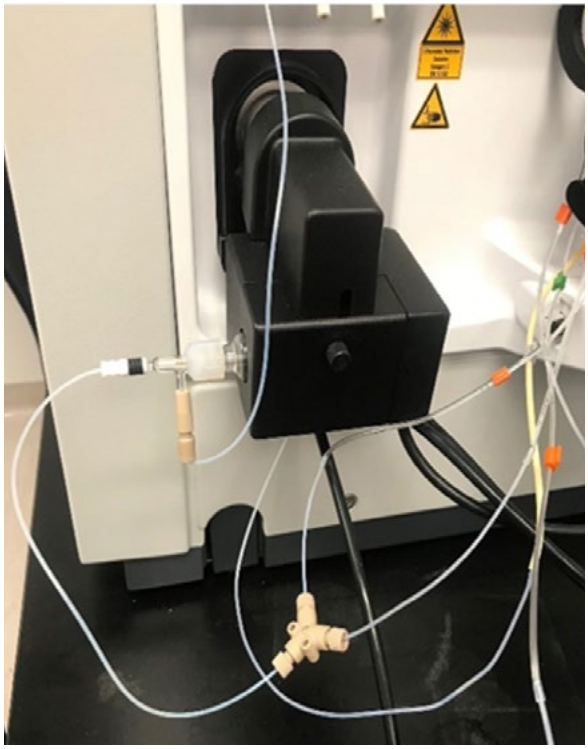
An internal standard improves the accuracy of the analysis by correcting signal drift and instability throughout the analytical run sequence. For best precision and accuracy, the internal standard must be added at the same amount to all standards and samples. The internal standard may be added manually; however, this is inefficient and can be a source of systematic error and contamination. For best practice, it is recommended to add the internal standard online using a kit that includes a connector that combines the sample and internal standard lines prior to delivery to the nebulizer. Table 6.6 lists the parts that are included in the iCAP RQ ICP-MS online internal standard kit.

Table 6.6 iCAP RQ ICP-MS online internal standard kit

Part description and components

Online internal standard kit iCAP RQ

- Y-connector, PEEK, 0.5 mm
- Autosampler probe, carbon fiber, 0.5 mm ID
- 1 Liter HDPE bottle (to contain the internal standard solution)
- Pour-out spout
- Peristaltic pump tubing, PVC, 0.381 mm ID, orange/green
- Peristaltic pump tubing, PVC, 0.254 mm ID, orange/blue
- Peristaltic pump tubing, PVC, 0.508 mm ID, orange/yellow
- Peristaltic pump tubing, PVC, 0.762 mm ID, black/black
- Peristaltic pump tubing, Santoprene™, 1.295 mm ID, grey/grey
- Adapters and fittings



Parts for hydrofluoric acid or aggressive sample matrices

For sample solutions containing hydrofluoric acid or when ultra-trace detection in strict cleanrooms (ISO Class 5 or lower) or sterile working environments (e.g., semiconductor, ultra-high purity chemicals) are required, the sample introduction system must be optimized, consisting of a nebulizer, spray chamber, and injector constructed of high-purity and chemically inert materials. Hydrofluoric acid is highly corrosive and incompatible with the standard glass sample introduction system components. The PFA-ST microflow nebulizer manufactured by Meinhard™, an Elemental Science (ESI) company, is appropriate for HF applications, is constructed of high purity PFA, produces a fine aerosol, provides high sensitivity, and is compatible with aggressive acids, alkalis, organics, and high salt solutions.[68] The instrument interface should also be robust, set up with sample and skimmer cones with platinum tips that can withstand HF and other aggressive matrices. Table 6.7 provides a list of sample introduction and interface parts for samples containing hydrofluoric acid and other aggressive matrices.

Table 6.7 Parts for hydrofluoric acid containing samples

Part description	
PFA-ST nebulizer (tubing included) • All PFA construction • 400 µL/min flowrate • High performance and sensitivity • Self-aspirating	
PFA cyclonic spray chamber kit • PFA cyclonic spray chamber • PFA adapter (connecting the spray chamber to the torch)	
Injector, sapphire, 2.0 mm ID	
Injector, platinum, 2.0 mm ID	
Sample cone, platinum tip	
Skimmer cone, platinum tip	

Nebulizer for high matrix samples

The nebulizer that comes with the iCAP RQ ICP-MS is the glass, concentric nebulizer. It is widely used due to its sensitivity, ease of set up, and suitability for most environmental and routine applications. However, the central capillary may easily become blocked or clogged by TDS, suspended solids, particulates, salts, etc., often present in environmental samples. Hence, a more robust nebulizer that will not clog as easily and require maintenance is recommended for routine analysis of high matrix samples. The Burgener Mira Mist nebulizer, shown in Table 6.8, is recommended for high matrix samples. Its unique Parallel Path design tolerates higher matrix samples compared to the concentric glass nebulizer. For additional information and specifications, please refer to the manufacturer's website.

Table 6.8 Nebulizer for high matrix samples

Part description
PEEK Mira Mist nebulizer **Burgener Research, Inc.** • Polyetherketone (PEEK) construction • Appropriate for most aqueous samples, not for concentrated acids and some organic solvents.[69] • Enhanced patented Parallel Path design– the sample and gas flows are parallel with the sample being drawn into the gas stream by induction, the opening of the liquid path is larger preventing solids, particulates, etc., from clogging the sample path.[70] • 0.2–2.5 mL/min flowrate. • Delivers an excellent mist while handling high levels of particulates. • Not self-aspirating 

Table 6.9 Instrument tune and calibration solutions

Part description
iCAP RQ ICP-MS tune solution Ba, Bi, Ce, Co, In, Li, and U – 1 µg/L matrix: 2% HNO_3 and 0.5% HCl
iCAP RQ calibration solution 25 elements at 3 – 35 µg/L matrix: 2% HNO_3

6.1.5 Autosamplers

Autosamplers are required for the continuous and automatic delivery of all measured solutions in the analytical run sequence to the sample introduction system of the instrument. Autosampler technology has evolved to include features to further streamline the elemental analysis workflow. Available on some autosampler models are discrete sampling valves that improve the overall sample analysis time by greatly reducing the uptake and rinse times between samples in the analytical run. Advanced autosampler models include two discrete sampling valves where autodilution can be accomplished allowing automatic preparation of calibration standards from a stock standard and the automatic dilution of samples that are out of the calibration range during the analysis. These features are advantageous for high throughput laboratories challenged with quick turnaround of results. To demonstrate, for the analysis of 21 elements in environmental samples according to Method 200.8, typical analysis time per sample, with three replicates, ranges between 3 to 4 minutes. However, when using an autodilution system, analysis time can be reduced to 66 seconds.[71]

The Qtegra ISDS software includes plug-ins for automatic connectivity to basic autosamplers and some autosampler models with discrete sampling valves and autodilution systems manufactured by Teledyne CETAC Technologies and Elemental Scientific (ESI). The plug-ins allow seamless control of the instrument and the autosampler. Figures 6.16 and 6.17 show the iCAP RQ ICP-MS connected to autosamplers and autodilution systems from Teledyne CETAC Technologies and ESI. With many advances in autosampler technology over the past decade, a detailed discussion of autosampler models with their features and accessories is beyond scope of this document. Please refer to the Teledyne CETAC Technologies and ESI websites for additional information on the wide range of autosampler products and accessories available.

Figure 6.16 The iCAP RQ ICP-MS with a Teledyne CETAC ASX 560 autosampler is used for many routine applications. When higher throughput is required, sample uptake and washout times can be reduced using the Teledyne CETAC ASXpress™ PLUS Accessory shown on the right for rapid sampling and reduction in sample analysis time.

Figure 6.17 The iCAP RQ ICP-MS with the ESI prep*FAST* autodilution system. The prep*FAST* performs inline dilution of samples and standards. Benefits include elimination of manual dilutions, improving the elemental analysis workflow, and increasing overall productivity.

6.1.6 Speciation

For many industries and applications, it is necessary to conduct a further evaluation of elemental constituents in a sample for assessment of actual toxicity. Pollution and hazard identification, remediation, product quality control, consumer safety, process control, brand protection, regulatory compliance, etc., are general concerns for all industries. However, for some industries such as, environmental, food and beverage, and pharmaceutical, it is necessary to determine the different chemical forms, or species, of some elements since the total concentration of the element alone is not a measure of the true toxicity of an environment or product. Hence, speciation is required for the identification and quantitation of individual chemical species in a sample.

Arsenic is an important element in environmental analyses and exists in organic and inorganic forms with different toxicities between each. The inorganic forms of arsenic–arsenate {As(III)} and arsenite {As(V)}, are the most toxic forms and are classified by the U.S. EPA as human carcinogens.[72] However, the organic forms, such as dimethylearsinic acid (DMA) and monomethylarsonic acid (MMA) are much less toxic while arsenobetaine has been identified as non-toxic. Another well-known element requiring speciation analysis is chromium–Cr(III) is essential for human metabolism while Cr(VI) is carcinogenic.[73]

Analysis by atomic spectroscopy techniques gives the total elemental concentration. Speciation analysis is needed to separate and quantify the different chemical forms of an element using a chromatographic technique for the separation of individual species and ICP-MS for trace elemental determination and quantification. The combinations of ICP-MS with chromatographic techniques, such as ion chromatography (IC), high performance liquid chromatography (HPLC), gas chromatography (GC), and laser ablation are called *hyphenated techniques.*

Another feature and advantage of the Qtegra ISDS software is the ability to fully control the chromatography system and the ICP-MS with the addition of the ChromControl Plug-in, offering seamless integration and simplified method development.[74] Please refer to the **Speciation analysis by IC-ICP-MS** page for additional information on this technique and systems.

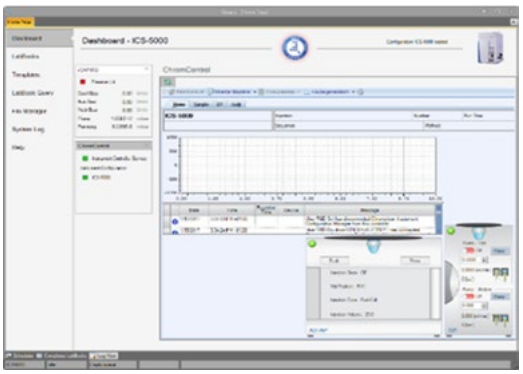


Figure 6.18 The Qtegra ISDS software can control chromatography instrumentation and the iCAP RQ ICP-MS for speciation applications using the ChromControl Plug-in.

6.1.7 Other instrumentation for elemental analysis

Thermo Fisher Scientific offers the widest portfolio of elemental analysis instrumentation from the atomic spectroscopy techniques of AAS, ICP-OES, and ICP-MS to advanced techniques such as Triple Quadrupole ICP-MS (TQ-ICP-MS) and high resolution ICP-MS (HR-ICP-MS) and isotope ratio analysis using multi-collector ICP-MS (MC-ICP-MS).

With over 60 years of history and expertise in elemental analysis, Thermo Scientific has been in the forefront of innovation, advancing elemental analysis as the first manufacturer to produce many highly relevant, ground-breaking technologies: solid state array detectors for ICP-OES, axial plasma technology for *trace* ICP-OES analysis, anti-blooming Charge Injection Device (CID) detectors for ICP-OES, first ICP-MS paper, first commercialized ICP-MS, high resolution ICP-MS (HR-ICP-MS), a compact benchtop ICP-OES, first *vertical* benchtop ICP-MS, and many more unique innovations and technological advancements in the fields of atomic spectroscopy and mass spectrometry.

The evolution of trace elemental analysis technology entailed the design and development of unique hardware and intuitive software features for streamlined, high performing, powerful, yet easy-to-use instrumentation that meets the analytical requirements of a wide variety of fields including environmental compliance monitoring, food safety, pharmaceutical QA/QC, petrochemical, clinical, geological, agricultural, metallurgy, semiconductor, and many other industries and applications.

To further facilitate training and a seamless transition in operation between atomic spectroscopy techniques, minimized downtime and learning curves, Thermo Fisher Scientific developed the Qtegra ISDS software as a common platform between ICP-MS and ICP-OES instrumentation. Furthermore, the Qtegra ISDS software has recently been implemented for advanced inorganic mass spectrometry instrumentation for isotope ratio analysis.

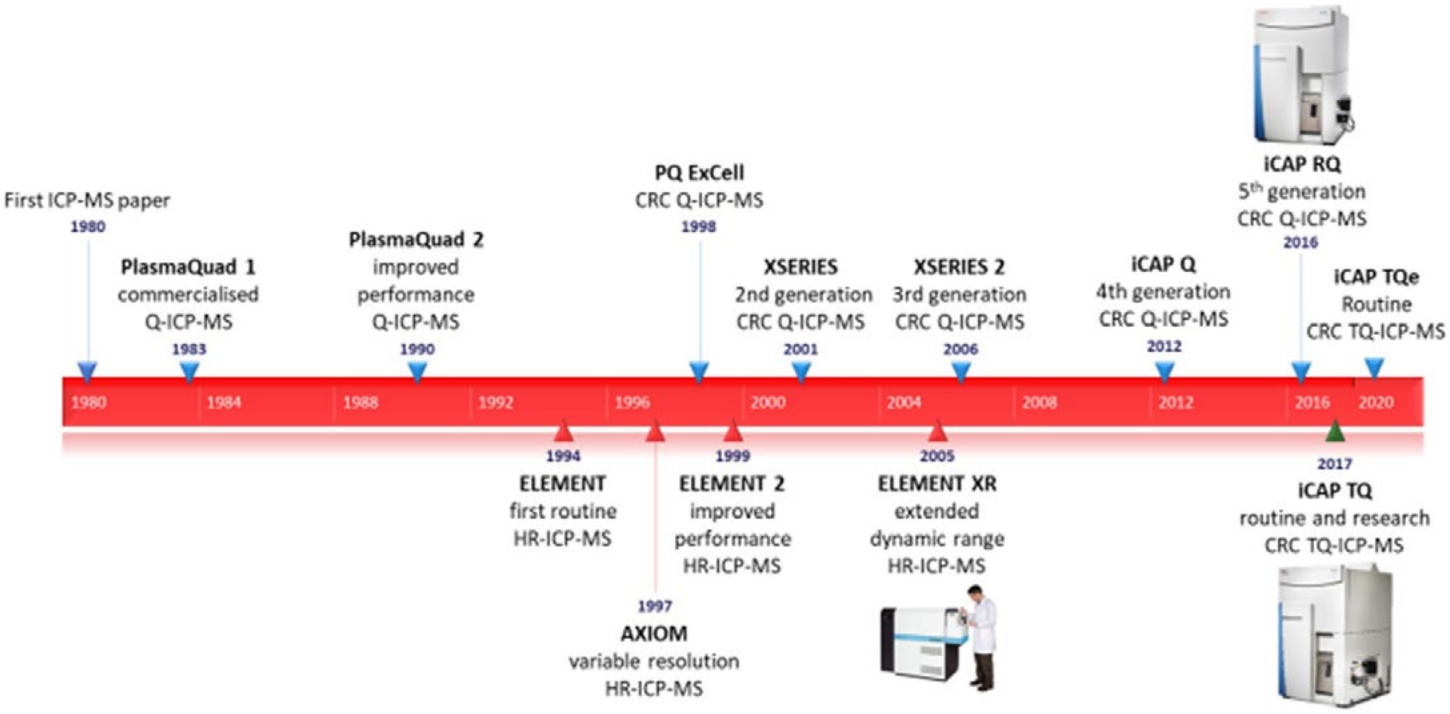


Figure 6.19 Timeline of the evolution of ICP-MS instrumentation.

The streamlined design refers not only to the compact size of the instrumentation, but, also to the ease of installation, accessibility to gas and electrical connections, and the ability to place the instrumentation flush against the wall, optimizing laboratory bench space. For the iCAP RQ ICP-MS, the sample introduction system is located on the right side of the instrument, the gas and electrical connections are located on the left, and no connections are on the rear of the instrument. The same streamlined design also applies to ICP-OES instrumentation. A similar look and feel across the Thermo Scientific atomic spectroscopy and ICP-MS instrumentation is shown in Figure 6.20.

For further information on the Thermo Scientific elemental analysis portfolio, please visit the **Trace elemental analysis** page.

AAS	ICP-OES	SQ-ICP-MS	TQ-ICP-MS
Thermo Scientific™ iCE™ 3000 Series AAS	**Thermo Scientific™ iCAP™ PRO Series ICP-OES**	**Thermo Scientific iCAP RQ ICP-MS**	**Thermo Scientific™ iCAP™ TQ ICP-MS**
• FAAS for fast, single element analysis • GFAAS offers high sensitivity for key analytes, Method 200.9 analysis	• Fast, sensitive, multi-element analysis • Highly robust for the toughest samples • Methods 200.7/6010D • Industry *workhorse*	• Single quadrupole • Highest sensitivity • Wide dynamic range • Methods 200.8/6020B • Hyphenated techniques, speciation, laser ablation	• Triple quadrupole • Advanced interference removal • Research applications • Laboratory futureproofing

Figure 6.20 The Thermo Fisher Scientific trace elemental analysis instrumentation portfolio.

7 Troubleshooting

Prior to the analysis of samples, pre-calibration routines (i.e., instrument warm up and tuning) are necessary for optimizing operating conditions and ensuring the instrument meets manufacturer's and method required performance specifications. As discussed in Chapter 3, the instrument is ready for analysis when all the tests (e.g., sensitivity, precision, mass calibration, resolution) in the Performance Report pass.

The analytical run sequence begins with the analysis of calibration standards followed by the ICV or QCS standard, to test the calibration curve, and then the SIC or ICSA/ICSAB standards, to check the effectiveness of the spectral interference correction technique applied. Specific protocols and control limit criteria for the calibration curve and these QC standards must be met prior to analyzing samples. If the calibration curve or one of these QC standards fail, the analysis must be discontinued. Troubleshooting and corrective actions are required prior to re-starting the analysis.

7.1 Troubleshooting a poor calibration curve

If the correlation coefficient of the calibration curve is less than U.S. EPA method (e.g., < 0.995) or other application acceptance criteria, or, if the results of the ICV or QCS standard are not within QC control limits (e.g., ± 10% of the true value) even if the correlation coefficient of the calibration curve meets acceptance criteria, the analysis must be stopped and corrective action must take place prior to re-calibration and resuming analysis.

Possible causes for a poor instrument calibration curve and/or failed ICV and QCS analyses are:

- Expired stock standards used to prepare the calibration standard solutions.
- Calibration and intermediate standard solutions no longer stable. Instability may be due to evaporation, adsorption to container walls, precipitation, photoreduction, etc.
- Errors in dilution and preparation.
- Inaccurate volumes and weights measured.
- Inconsistency in technique between the preparation of each calibration standard solution.
- Incompatibility of the analytes with the acid matrix, the container, and sample introduction components.
- Contamination of the calibration blank, acid diluent used for standard preparation, reagent water, calibration stock standards, calibration standard solutions, and internal standard solution. The instrument rinse solution may also be a source of contamination.
- Contamination from containers (e.g., autosampler vials), sample introduction system components, and autosampler components (e.g., autosampler probe, capillary tubing or transfer lines connected to peristaltic pump tubing). If the internal standard is added online, contamination from parts and associated pump tubing can also be a source.
- Calibration ranges were not optimized for the range of analyte concentrations in the samples.
- Analytes calibrated outside the linear dynamic range of the instrument.
- Issues (e.g., blockage, deposits) with instrument components, such as, the nebulizer, spray chamber, peristaltic pump tubing, torch, injector, and sample and skimmer cones.
- Memory effects.
- Spectral interferences.

Troubleshooting a poor calibration curve can be somewhat straightforward if the cause is apparent (e.g., elevated calibration blank). However, troubleshooting a failed ICV or QCS standard with an acceptable calibration curve can be difficult and time consuming as the causes are not apparent and may entail the process of elimination. The following are areas to consider for troubleshooting along with recommended actions.

Calibration blank

Troubleshooting a poor calibration curve should start by checking the response or signals of the analytes in the calibration blank. An elevated calibration blank is usually an indication of contamination. Check the responses for Na, Zn, Ca, Fe, and Mg as these elements are ubiquitous in nature. Contamination can be from the laboratory environment, the acid used to prepare the calibration blank, laboratory apparatus used for preparation, or containers.

To help determine the source of contamination in the calibration blank, the following actions are recommended:

- Analyze the reagent water. Avoid additional handling or transfers of the reagent water by sampling directly from the source into an autosampler tube (rinse the tube several times with reagent water) and analyze right away.
- Analyze the instrument rinse solution to check for contamination.
- Analyze the internal standard solution to check for analyte contributions. Check the Certificate of Analysis of each internal standard element stock standard for trace impurities.
- Directly aspirate the calibration blank, reagent water, and instrument rinse solution using a self-aspirating nebulizer (e.g., concentric nebulizer). This isolates the sample introduction system to help determine the source of contamination; if the analyses of each of these solutions show low analyte responses or very little to no contribution to contamination, then the source of contamination may be from the peristaltic pump tubing, capillary tubing, autosampler probe, online internal standard addition parts and associated tubing.
- Check the type of acid used to prepare the calibration blank; is it trace metal or a lower grade? Check the Certificate of Analysis for levels of trace elements or impurities.
- Check the instrument and autosampler surfaces for dust, dirt, or other airborne particulates. Use an autosampler cover to protect samples from airborne contamination while awaiting analysis. Always clean these surfaces prior to analysis.
- Contamination may be from the autosampler tube, any container used to store the calibration blank (e.g., wash bottles), or preparation and transfer apparatus. Always acid soak or thoroughly clean all containers (including lids and autosampler tube caps) and apparatus according to a comprehensive cleaning procedure prior to use.

Calibration standards

Issues with the stock standards used to prepare calibration standard solutions may be the cause of a poor calibration curve or failed ICV or QCS analyses. The stocks standards may be expired, contaminated, or of a lower grade.

- Check the expiration date and the Certificate of Analysis of the stock standard for trace elements.
- Use standards that are designated for ICP-MS analysis. Stock standards designated for AAS or ICP-OES may contain trace elements at concentrations unacceptable for ultra-trace analysis by ICP-MS.
- It may be helpful to look at data generated in the past or recently generated, specifically at the responses from calibration standards at the same concentration, preferably prepared from the same stock or intermediate standard and acid diluent.
  - If the responses from Na, Ca, Mg, Zn, and Fe are higher compared to past analyses, this could be an indication of a stock or intermediate standard that became contaminated (if the acid diluent is not contaminated). Although the responses will vary from day to day due to instrument noise, random error, etc., contamination can contribute significantly to the analyte responses and are more apparent.
  - If the response from Ag, As, or Hg is lower, this could be an indication of instability due to volatilization, adsorption, photoreduction, or incompatibility with the acid matrix.
  - If there is a difference in the responses of all analytes compared to previous data of the same calibration standard, a dilution error may be the cause.
- Issues with the ICV or QSC standard may also be the cause. These standards must be from an independent source and should be analyzed directly with no preparation or dilution by the laboratory. If the responses from some of the analytes are higher, contamination of the ICS or QCS standard or from autosampler tube, sample introduction system, etc., could be the cause.

Internal standard

The internal standard is added to all standards and samples, hence, should also be examined when troubleshooting. The internal standard solution should be added at precisely the same amount for it to be effective for monitoring and correcting drift or physical interferences. Since the calibration blank and calibration standards are in a similar matrix, there should be little variation between their nebulization efficiencies resulting in consistent internal standard responses. If the response of the internal standard drops or varies during calibration, check the online internal standard addition kit, consisting of a plastic Y-connector, that combines the calibration standard and internal standard lines and associated peristaltic pump tubing, capillary tubing, the internal standard probe, etc. Issues with these components will affect the precision of the measurement and the amount of calibration standard solution entering the plasma will be inconsistent from standard to standard, affecting the calibration.

As discussed in Chapter 3, the concentration of each element in the internal standard solution must be of sufficiently high concentration for good measurement precision throughout the analytical run sequence while not being too high to decrease the service life of the ICP-MS detector. It is also recommended to prepare the internal standard solution from single element standards to enable the concentration of each internal standard element to be optimized with the lower mass elements at higher concentrations and the high mass elements at lower concentrations. The concentration range suggested in Method 200.8 is 20–200 µg/L depending on the sensitivity of the instrument. Consult the instrument manufacturer for the optimum range of concentration or signal/response of the internal standard solution. Also, for high matrix samples, a higher concentration range for the internal standard solution may be required for good measurement precision and to meet method required internal standard recoveries.

If the internal standard elements do not pass method required recovery or control limits (internal standard recovery of 60–125% for Method 200.8, and for Method 6020B the intensities of each internal standard element must not decrease to below 30% of the intensity during initial calibration), the following troubleshooting actions are recommended:

- Determine if the instrument has drifted by checking the recovery of the internal standard elements in the next blank solution (e.g., ICB or CCB). If the responses are low and out of the control limits, then the instrument has drifted and the analytical run sequence must be terminated to determine the cause and correct the issue. Possible causes are blockage in sample introduction and/or interface components (e.g., nebulizer, injector, sample and skimmer cones) or change in the tuning or operating parameters since the start of the analytical run sequence. After correcting the issue, the instrument must be recalibrated with the calibration passing method specific acceptance criteria prior to re-analyzing affected samples.
- If the internal standard recovery fails in a sample, the sample must be diluted to reduce the effect of the matrix causing variability of the signal or response. It is recommended to dilute the sample five-fold; if the internal standard recovery remains out of control limit criteria, apply a further dilution. Document the dilution applied to the samples in the sample or analysis report.

Memory effects

Memory effects result when analytes from a previous standard or sample affect or contribute to the response of the analytes in the next standard or sample. Memory effects are indicated by a consecutive drop in analyte response between replicate measurements (i.e., the first replicate measurement is higher than the second and the second is higher than the third). This will affect the precision of the analysis resulting to elevated %RSDs and a poor calibration. The following are recommended actions to address memory effects:

- Optimize the rinse time between the analysis of each standard to allow complete wash out of high concentration analytes. Instrument software may have a feature to assist in determining the optimized rinse time for high concentration analytes. A procedure for determining rinse times is described in Method 200.8, Section 4.1.5.
- Mercury is known to suffer from memory effects due to its tendency to stick to the plastic peristaltic pump tubing, therefore, a longer rinse time between samples is required to rinse mercury out. As previously discussed, gold at a concentration of 100 µg/L for analyses at < 5 µg/L, must be added to all standards and samples, including the rinse solution, to wash out mercury from the sample introduction system within a reasonable amount of time. For the analysis of higher amounts of mercury, a higher concentration of gold is required.
- Memory effects are also caused by sample or standard deposition on the sample and skimmer cones, torch, injector, nebulizer, and spray chamber. It is recommended to inspect these parts prior to instrument operation to avoid analytical issues and memory effects.

Low sensitivity

A decrease in sensitivity would be known while tuning or after conducting a Performance Report and one or more analytes fail to meet manufacturer's, or method required, sensitivity specifications. To prevent a failure in sensitivity, inspect the nebulizer, torch, injector, sample and skimmer cones for blockage and deposits and clean as needed. Blockage or deposits on these sample introduction and interface components will cause a drop in sensitivity. Ensure all operating conditions and plasma gas flow rates are correct prior to operating the instrument.

A decrease in sensitivity may be due to old, expired, or unstable tuning solution or calibration stock standard, intermediate standard, or calibration standard solutions. Calibration standard solutions at ultra-trace concentrations do not remain stable in solution for a long time. Some elements, such as Ag and Hg, are not as stable as other elements in solution. It is recommended to prepare calibration standard solutions daily or fresh with each batch of samples prepared and analyzed in the same analytical run sequence. Always check the expiration date of the stock calibration standard solution prior to preparation. Also, ensure mechanical pipettes are delivering the required volumes for dilution by conducting spot checks of the pipettes as described in Chapter 2.

If sensitivity issues remain after troubleshooting the sample introduction system, interface, and calibration standards, an Autotune or advanced tuning procedure may be needed. With differences in instrument design and operation, consult the instrument manufacturer for specific measures to troubleshoot issues with sensitivity.

Precision

Poor precision is another cause for a poor calibration curve. If the relative standard deviation (%RSD) between replicate measurements of the calibration standard is greater than 1%, the following actions are recommended:

- Check the peristaltic pump tubing (sample, drain, and internal standard) for wear and tear, flatness, contamination, deposits, blockages, etc. Issues with the peristaltic pump tubing are the likely cause of poor precision.
- Check the tension applied to the peristaltic pump tubing to ensure a smooth flow of solution.
- Replace worn peristaltic pump rollers. If the flow is still not smooth, the peristaltic pump may need to be replaced.
- Check the uptake time and ensure it is appropriate to allow the calibration standard solutions to enter the plasma and stabilize prior to measurement. An insufficient uptake time is indicated by a consecutive increase in response between replicate measurements, opposite of the memory effect. This also affects the %RSDs and precision of the analysis.

7.2 Spectral interferences

As ICP-MS is a matrix dependent, comparative technique, calibration standard solutions are often prepared by matrix matching with the samples to minimize variations in their nebulization efficiencies that cause inaccurate results. Calibration standards are commonly prepared in the same acids used to digest the samples; nitric acid or a mix of nitric acid and hydrochloric acid are the most common. Since it is difficult to matrix match standards completely and precisely to that of the samples, internal standardization combined with external calibration is the most common approach for correcting physical interferences caused by differences in matrix between standards and samples. However, sample matrix constituents and the acids used for digestion cause spectral interferences that also affect the accuracy of sample results.

Nitric acid is preferred and widely used for digestion due to its oxidizing ability and commercial availability. Another advantage of nitric acid is that it does not contribute significantly to spectral interferences in ICP-MS analysis compared to acids containing chlorine, sulfur, phosphorus, and fluorine.[75] If calibration standards are prepared with these acids, an interference correction technique must be included when developing the analytical method and applied during analysis to mitigate spectral interferences caused by these acids on particular analytes. A well-known instance is the spectral interference on As caused by the combination of Cl from hydrochloric acid in the standard or sample, with argon from the plasma, forming the ArCl+ having the same mass-to-charge as arsenic.

As part of the QA/QC protocol when analyzing environmental samples, the SIC or ICSA and ICSAB standards are analyzed after the ICV/ICB pair prior to the analysis of samples to test the effectiveness of the interference correction applied in mitigating spectral interferences. If these standards do not meet acceptance criteria, the analysis must be stopped and corrective actions must be taken prior to re-calibrating the instrument and continuing the analysis.

There are two classifications of spectral interferences: polyatomic and isobaric. Polyatomic interferences are molecular ions having the same mass-to-charge ratio as an analyte. They form in the plasma or the interface by the reaction of sample constituents with the plasma, reaction gases, and other sample components. Some of the most known polyatomic interference are: $ArCl^+$, $ArAr^+$, ArC^+, ArO^+, ClO^+, and $ArNa^+$ which interfere with As, Se, Cr, Fe, V, and Cu respectively. Isobaric interferences are elemental interferences with the same mass-to-charge ratio as

the analytes. An example is ^{87}Rb and ^{87}Sr. For environmental analysis by Method 200.8, two analytes with known isobaric interferences are ^{82}Se and ^{98}Mo, which are interfered by krypton and ruthenium respectively. Doubly-charged interferences are another type of isobaric interference that cause problems for ICP-MS analysis; examples are the doubly-charged Rare Earth Elements (REEs) $Nd2^+$ and $Gd2^+$ that interfere with As and Se respectively.

Correcting the effects of polyatomic spectral interferences on the analysis can be accomplished by:

- Applying mathematical correction equations.
- Selecting an alternative isotope (if available).
- Removal using Collision/Reaction cell technology
  - Kinetic Energy Discrimination (KED)
  - Reaction gases

Advancements in ICP-MS instruments include the development of Collision/Reaction cell technology for removal of spectral interferences. Collision/Reaction cells operate in two modes, KED or Reaction mode.

- In KED mode, a flow of an inert gas (typically helium) in the Collision/Reaction cell collides with polyatomic ion interferences and analyte ions causing a loss of kinetic energy. Since the polyatomic ion interference has a larger cross-sectional area than the analyte ion with the same mass, it will experience more collisions, becoming attenuated as it makes its way through the cell. An energy or voltage barrier is placed at the end of the Collision/Reaction cell preventing the low energy polyatomic ion from exiting while allowing the analyte ion to go through to the quadrupole and detector to be measured interference free.
- In Reaction mode, a specific reaction gas flows through the Collision/Reaction cell reacting with the analyte or the interferent shifting their mass away from each other. When reacting with the analyte, a product is formed with a mass-to-charge ratio different from the interferent, allowing measurement of the analyte free from the interference. Conversely, the reaction gas can react with the interferent forming a product with a different mass-to-charge than the analyte. Implementing an analytical method with reaction gases, or reaction chemistry, to resolve polyatomic interferences can be challenging, requiring knowledge of the reaction type, appropriate reaction gas (e.g., O_2, H_2, NH_3) gas flow rates, etc. Furthermore, other interferents may be created if the product ions from the reaction have the same mass-to-charge as other analytes.

The spectral interference correction technique to apply depends on regulatory or method requirements, detection limits, the analyte, the type of interference, the amount or intensity of interferences, etc.

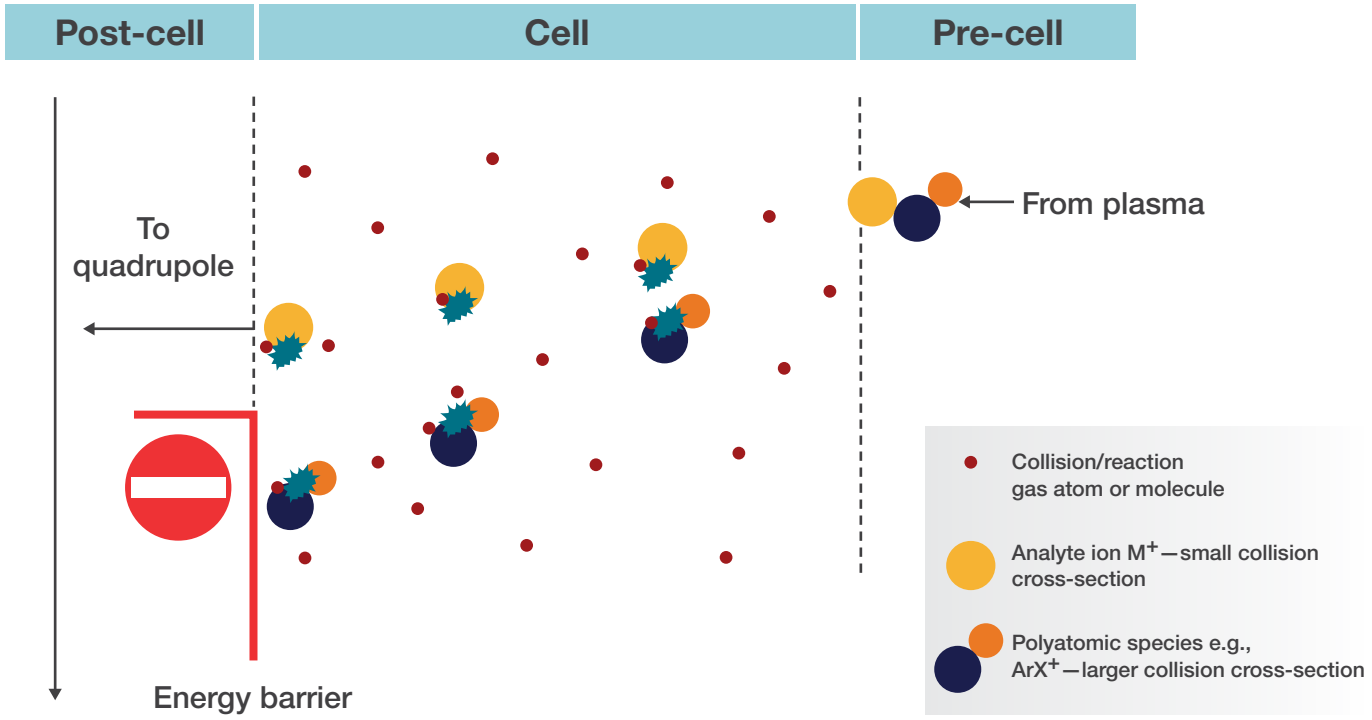


Figure 7.1 Schematic of the Kinetic Energy Discrimination process in the Collision/Reaction cell.

For environmental sample analysis, the spectral interference correction technique to use depends on what is permitted by the U.S. EPA. For drinking water compliance monitoring using Method 200.8, collision/reaction cell technology is not permitted by the U.S. EPA. Polyatomic interferences can be avoided by using an alternative isotope or mathematical correction equations. However, for the analysis of wastewater under the CWA using Method 200.8, collision/reaction cell technology is permitted. For the analysis of solids wastes, Method 6020B, Section 4.3, acknowledges collision/reaction cell technology as a modification to ICP-MS that can reduce or remove common interferences, eliminating the reliance on most mathematical correction equations. However, instruments must be able to demonstrate freedom from interference with the analysis of the SIC solution, or for some laboratories, the analysis of the ICSA and ICSAB standards.

The **ICP-MS systems and technologies** page provides an overview on the functions of an ICP-MS including collision/reaction cell technology. Additional information on the use of collision/reaction cell for trace element analysis is provided on the **Analyzing trace elements with EPA Method 200.8** page.

The type of spectral interference also determines the appropriate correction technique. Polyatomic interferences can be corrected using KED, reaction gases, and mathematical correction equations. However, isobaric interferences, single and doubly charged, cannot be resolved using KED. Furthermore, doubly charged interferences are enhanced in KED mode. Reaction gases can be used to resolve isobaric interferences; however, new interferences may be created when applying reaction chemistry in single quadrupole ICP-MS.

To resolve isobaric interferences and intense polyatomic interferences present in high matrix samples (e.g., metal alloys), the advanced interference removal technology of triple quadrupole ICP-MS meets these challenges. As a brief overview, triple quadrupole ICP-MS instruments use reaction chemistry to resolve these advanced interferences. A quadrupole is placed before the collision/reaction cell to filter or “clean” the ion beam allowing only the target isotope and its interference to enter the collision/reaction cell. The cell is filled with a gas that reacts with the interference, allowing the unreacted target isotope to be transmitted to a quadrupole, set to the target isotope mass, and then to the detector. Otherwise, the cell gas can react with the target isotope forming a product ion which is then transmitted to a quadrupole, set to the product ion mass, and detected free from the interferent. Further information and literature on how triple quadrupole ICP-MS technology works and its applications in industry can be accessed on the **Triple Quadrupole Inductively Coupled Plasma Mass Spectrometry (TQ-ICP-MS)** page.

8 Helpful resources

Table 8.1 includes a list of iCAP RQ ICP-MS literature including applications for environmental analysis and technical notes and product spotlights highlighting key instrument features and software.

Table 8.1 A select list of iCAP RQ ICP-MS product and environmental literature

Number	Literature type	Title
BR 43317	Brochure	Thermo Scientific iCAP RQ ICP-MS - Robust ICP-MS with ease of use and high productivity for routine laboratories
AN 43323	Application note	Fully automated, intelligent, high-throughput elemental analysis of drinking waters using SQ-ICP-MS
AN 44358	Application note	US EPA SW-846 Method 6020B using the iCAP RQ ICP-MS
AN 44448	Application note	Direct analysis of environmental samples using ICP-MS with argon gas dilution (AGD)
AN 43132	Application note	Drinking water compliance monitoring using US EPA Method 200.8 with the Thermo Scientific iCAP Q ICP-MS
TN 43202	Technical note	Analysis of high matrix samples using argon gas dilution with the Thermo Scientific iCAP RQ ICP-MS
TN 43427	Technical note	Thermo Scientific iCAP RQ ICP-MS: Typical Limits of Detection
TN 43400	Technical note	iCAP Qnova Series ICP-MS – Mass Stability
TN 43399	Technical note	Linear dynamic range performance of the Thermo Scientific iCAP Qnova Series ICP-MS
AB 43327	Application brief	Direct analysis of a 25% sodium chloride sample matrix using the Thermo Scientific iCAP RQ ICP-MS with argon gas dilution
SP 43397	Product spotlight	Qtegra Intelligent Scientific Data Solution Software – Integrated Autodilution Solutions for ICP-OES and ICP-MS
SP 43398	Product spotlight	Sample Introduction Systems for the iCAP Qnova Series ICP-MS
SP 43395	Product spotlight	Performance and Flexibility with the iCAP Qnova Series ICP-MS Interface
SN 44415	Smart note	Trace Elements in Routine Sample Matrices Using Single Quadrupole iCAP RQ ICP-MS
SN 43380	Smart note	Why should I add analytical capabilities to perform speciation in my laboratory?

Table 8.2 provides links webpages for trace elemental analysis (AAS, ICP-OES, and ICP-MS) instrumentation for access to product overviews, application notes for environmental and many other industries, videos, and other educational resources.

Table 8.2 Trace elemental analysis instrument webpages

Technique	Webpage and description
Trace elemental analysis	Trace elemental analysis – Analytical solutions for applied science and research laboratories Overview of technologies for AAS (FAAS and GFAAS), ICP-OES, ICP-MS, Glow Discharge ICP-MS (GD-ICP-MS), Organic Elemental Analysis (OEA)
ICP-MS	Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Overview of technologies for SQ-ICP-MS, TQ-ICP-MS, MC-ICP-MS, HR-ICP-MS, Qtegra ISDS Software
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) iCAP PRO Series ICP-OES systems – robust and advanced, high-throughput systems
AAS	Atomic Absorption Spectroscopy (AAS) Overview of AAS instruments: iCE 3000 series AAS for flame, graphite furnace and combination flame and graphite furnace systems

Table 8.3 Provides links to the thermo fisher scientific environmental learning center and other relevant webpages concerning environmental analysis.

Table 8.3 Environmental webpages

Webpage	Webpage description
Industrial & applied sciences – environmental	Thermo Fisher Scientific main page for accessing information on technologies and workflows for environmental analysis. Subtopics include: Water analysis Soil analysis Environmental contaminant analysis Metal analysis Chromium measurement Hydraulic fracturing
Environmental Learning Center	Connects the reader to Thermo Fisher Scientific resources for learning about environmental analytical methods and solutions, providing key points of entry to access vast environmental content. Subtopics include: Contaminant analysis information Soil contaminant analysis information Water quality analysis information
Water quality analysis information	Access to information on techniques for the analysis of drinking water, surface and ground waters, and wastewater. An overview of water regulations is also provided. Water regulations Analysis of drinking water contaminants Wastewater testing
Soil contaminant analysis	Information on the routine testing of soil for research and agricultural purposes, with emphasis on organic contaminants, heavy metals, and nutrients. Nutrient analysis Heavy metal analysis
Elemental speciation analysis	Overview of elemental speciation, its relevance for environmental analysis, and techniques and instrument solutions for speciation analysis. Tools for elemental speciation Chromium speciation for drinking water samples Arsenic speciation in drinking water Bromine speciation in drinking water Mercury and tin speciation using gc-icp-ms
Environmental resource library	Access a collection of application notes, case studies, videos, webinars and white papers for contaminant and water quality analysis. U.S. EPA methods Environmental webinars and podcasts

To speak with a technical support representative or to get in touch with a sales representative, call 1-800-955-6288 or go to **thermofisher.com/us/en/home/technical-resources/contact-us.html**

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9 Conclusion

The extent of environmental analysis goes well beyond water compliance monitoring to a broad range of applications performed by almost every industry where solid and liquid wastes are generated.

Federal, state, and local agencies, public utilities, local health departments, academia, national laboratories, etc., all perform environmental analyses in some capacity. Each application has its unique challenges; however, the general challenges for the analysis of trace metals in environmental samples are:

- Trace and ultra-trace detection limit requirements due to stringent regulations for inorganic contaminants set by federal, state, and local agencies for drinking water, groundwater, wastewater, and surface water for public, aquatic, and wildlife protection.
- The variety of sample types, from simple (e.g., drinking water) to complex (e.g., soils, sludges, solid industrial wastes), that are typically analyzed by environmental, industrial, and contract testing laboratories with quick turnaround of results.
- Obtaining quality, reliable data as accurate sample results are crucial for making important decisions, such as the proper disposal of industrial wastes, designation of hazardous sites for the Superfund cleanup program, screening of soil for farming and agricultural development, and many other decisions resulting in actions applied on a large scale.

The need for fast, multi-element, and sensitive analysis to meet detection limit requirements led to the increasing demand for ICP-MS. The two EPA-approved methods for the analysis of inorganic contaminants in aqueous and solid samples by ICP-MS are U.S. EPA Method 200.8, Revision 5.4, and Method 6020B (SW-846). Included within these methods are specific procedures for sample and standard preparation and quality control protocols to ensure the accuracy, precision, reproducibility, and overall reliability of sample results.

The superior sensitivity and wide linear dynamic range have made ICP-MS the technique of choice for ultra-trace environmental sample analysis. High sensitivity is a major benefit of ICP-MS but it also causes challenges in its use and application for laboratories. Detection limits in the ppt range are possible for many elements. With this level of sensitivity comes the need for extra precautions to avoid contamination which will compromise the integrity of samples and standards and affect the accuracy of results. Contamination to samples and standards can come from obvious sources, such as, dust and particulate matter from the atmosphere and work surfaces, dirty laboratory apparatus, lower grade reagents with trace metal impurities, low purity water, etc. There are unapparent sources of contamination that the analyst should be aware of, including, ceiling tiles, paint chips, corroded faucets and piping and the analysts themselves (e.g., hair, sweat, sunscreen, makeup, jewelry). The use of borosilicate glass, which is the traditional and commonly used material for laboratory apparatus, is another source of contamination. Hence, knowledge of contamination sources and measures to avoid them should be taken for success with trace and ultra-trace analysis by ICP-MS.

In addition to contamination from the mentioned sources, other causes of sample and standard failures are:

- Excessive handling and transfer steps that may introduce systematic error.
- Inaccurate preparation of samples and standards due to incorrect dilutions or the use of pipettes or analytical balances that are damaged or out of calibration.
- Improper skill and technique when performing preparation steps (e.g., dilutions) that require precision and accuracy.
- Inconsistencies between the preparation of calibration standards.
- The use of expired or unstable standard solutions.
- The use of damaged, blocked, and dirty instrument sample introduction and interface components.
- An instrument set-up that has not been optimized for the types of samples to be analyzed in the run sequence.

With the superior sensitivity of ICP-MS, trace and ultra-trace detection limits will not be achieved if these issue are not addressed and if measures are not taken to optimize and streamline the elemental analysis workflow, especially the sample and standard preparation processes. Most of the errors introduced to the analysis are from sample and standard preparation steps that were not performed with attention to detail and consideration for all sources of contamination. The following general best practices to avoid analytical issues and sample and standard failures, causing re-runs and affecting overall productivity, were emphasized throughout this document:

- Be aware of all sources of contamination.
- Use ultrapure reagent water.
- Use quality, high-purity reagents.

- Use compatible laboratory apparatus for preparation, handling, transfers, and storage.
- Ensure the accuracy of weights and volumes measured.
- Minimize transfer and handling steps.
- Inspect instrument sample introduction and interface components prior to analysis.

Considerations and best practices for the selection and use of laboratory apparatus, materials, reagents, and equipment were also provided. Safety is first and foremost in the laboratory; designated personnel responsible for safety and chemical hygiene should always be consulted. The physical and chemical properties of standards, reagents, and samples and the known and unknown hazards present require extra care and consideration to be applied.

Additional best practices and tips for performing various steps within the sample and standard preparation processes were provided to help streamline and minimize the risk of contamination and other systematic errors. A bad calibration resulting in erroneous sample results may be caused by slight systematic errors that become apparent due to the high sensitivity of ICP-MS.

Sample preparation is the central part of the elemental analysis workflow and can be the most time-consuming part and major source of error if not optimized. An overview of the three most common sample dissolution methods used in environmental and industrial laboratories was provided: hot plate acid digestion, hot block acid digestion, and microwave assisted acid digestion. An assessment of the benefits and limitations, including an overall comparison based on key considerations, of each digestion method was provided to assist a laboratory in the selection of the appropriate method for their applications and unique needs. For the best overall efficiency, recovery of analytes, minimal exposure to contamination, and dramatic reduction in digestion time, microwave assisted acid digestion is the recommended method.

Finally, with the trace and ultra-trace detection requirements and the variety and complexity of environmental samples routinely analyzed by many laboratories, sensitivity, robustness, and interference removal are essential for ICP-MS. Instrumentation has come a long way since its introduction over 35 years ago, from floor models to compact benchtop models. In addition to innovations in hardware design, features to improve robustness and the mitigation of polyatomic interferences were also developed and implemented, allowing long-term analysis of high matrix samples while maintaining the sensitivity and performance needed for trace and ultra-trace detection limits.

The iCAP RQ ICP-MS delivers the high sensitivity, speed, robustness, and exceptional interference removal required for routine environmental and industrial sample analyses while being easy to use and maintain. The sample introduction system is streamlined, consisting of compact components that are push-fit connected for quick and easy assembly and installation. The sample and skimmer cones are located outside the high vacuum region, behind the unique, bench height, drop-down door, allowing fast, easy access for maintenance. Vacuum does not need to be broken to access the sample and skimmer cones for maintenance, hence also reducing downtime.

The Qtegra ISDS software further facilitates ease of use with an intuitive design, simplified top down method development, and all instrument parameters and data located in one file called a LabBook. Important for environmental and regulated laboratories are built-in Quality Control features and 21 CFR Part 11 compliance features that include audit trails, electronic signatures, and the ability to control access to various areas within the software. Advanced environmental analysis to further investigate the exact toxicity present in an environment or product can be accomplished with speciation using the iCAP RQ ICP-MS coupled with an IC, GC, or HPLC. The combination of ICP-MS with these chromatography techniques are known as hyphenated techniques. Both ICP-MS and chromatography systems are seamlessly controlled using the ChromControl Plug-in.

In general, the goal of this document is to serve as a practical resource guide for:

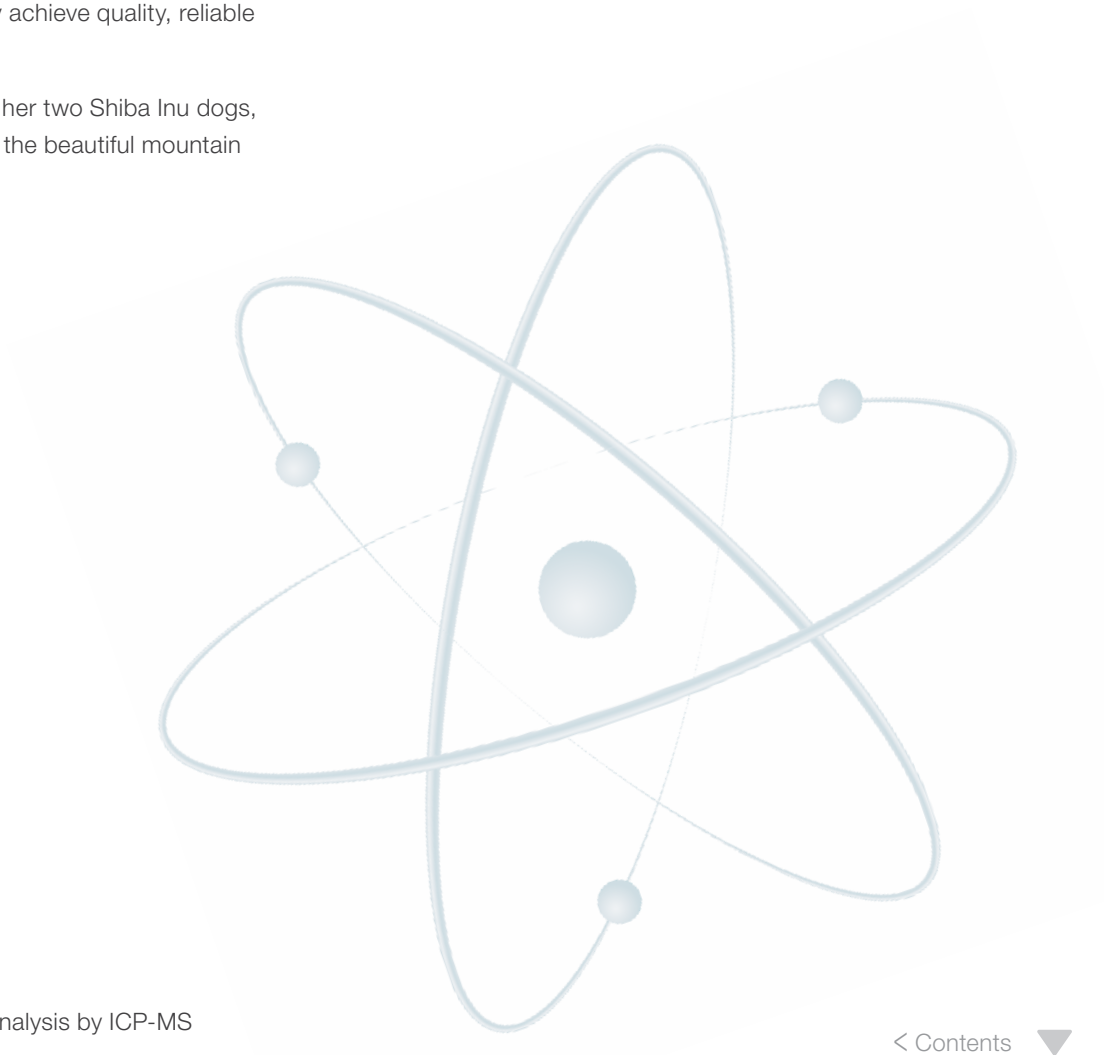
- Helping environmental, contract testing, and industrial laboratories get started with sample analysis by ICP-MS.
- Providing context around the importance of environmental analysis with overviews of relevant environmental laws, regulations, and analytical methods.
- Providing recommended best practices, tips, and considerations to streamline sample and standard preparation processes and help prevent analytical issues and inaccurate results.
- Connecting the analyst to online resources for laboratory apparatus, stock standard solutions, instrumentation, and environmental analysis information.
- Bringing awareness to the importance of knowing contamination sources and applying skill, consistency, and attention to detail when performing all steps within the elemental analysis workflow.

About the author

Sabrina Antonio is a chemical engineer and chemist with a penchant for thinking outside the box, as exemplified by her diverse industry experience. She led onsite laboratory audits as an inorganic data and Quality Assurance auditor for the U.S. EPA Contract Laboratory Program (CLP) focused on the inorganic Statement of Work; supported analysts across the U.S. as a Product and Application Specialist of atomic spectroscopy instrumentation; designed and implemented green projects as an Energy Conservation Engineer and Construction Project Manager at the New York Power Authority; worked in Environmental, Health, and Safety (EH&S) as a Senior Chemical Engineer at Consolidated Edison (Coned) of New York, Steam Operations; and designed cooling towers for power plants in Asia as an Application Engineer for an engineering and construction firm.

She is currently the Trace Elemental Analysis and Inorganic Mass Spectrometry Regional Marketing Manager at Thermo Fisher Scientific. Her innovation focus is to develop and implement awareness programs and creative tools that assist laboratories throughout industry achieve quality, reliable data and optimized workflows.

Sabrina lives in Denver, Colorado with her two Shiba Inu dogs, Beanie and Shogun, where they enjoy the beautiful mountain scenery and unpredictable weather.



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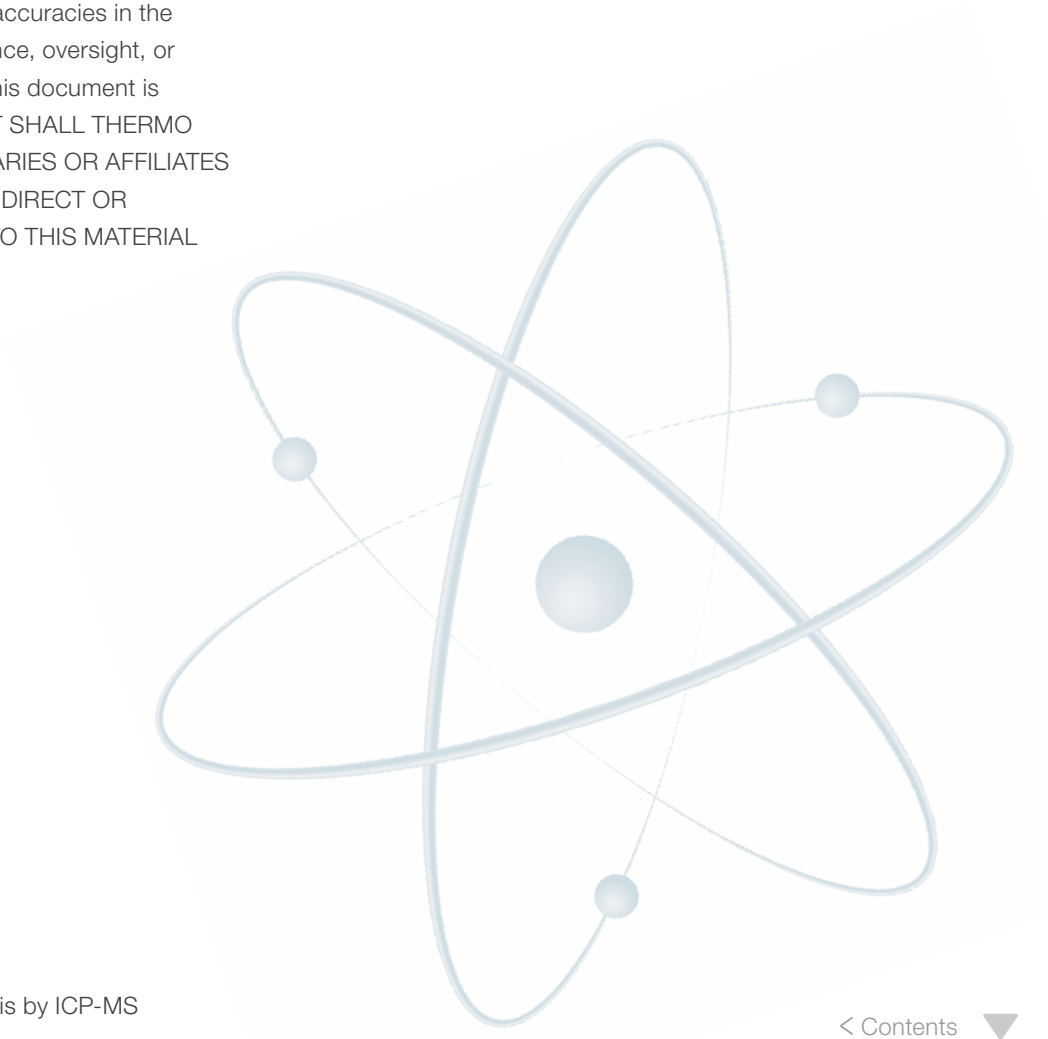

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