

An Executive
Summary

Trace Element Analysis Using ICP-MS for Environmental Samples, Part One

Regulations and Routine Monitoring



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Environmental regulations and best practices
for trace element analysis.

Overview

Inductively coupled plasma-mass spectrometry (ICP-MS) is one of the most powerful techniques used for elemental analysis in environmental applications. It provides the advantage of low detection limits, easy quantification and high throughput. However, experience and best practices are necessary to achieve optimum results. This manuscript focuses on environmental regulations for trace elements, instruments, and analytical methods for elemental analysis in the United States and Europe, and provides practical advice for successful trace element analysis.



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Environmental Regulations in the United States

There are five major environmental regulation laws in the United States that relate to air, surface water, drinking water, wastewater, soil, and solid waste.

Air. The Clean Air Act (CAA) is the primary law for controlling air pollution in the United States. This act requires the Environmental Protection Agency (EPA) to establish and periodically review emissions standards for new sources of six common air pollutants, 187 hazardous air pollutants, volatile organic compounds (VOCs), and other pollutants. The EPA must also conduct Residual Risk Assessments and Technology Reviews, as well as update the existing standards when necessary. In addition, the Mercury and Air Toxics Standards limit emissions of mercury, arsenic, and other metal pollutants into the air.



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Water. The Clean Water Act (CWA) regulates the discharge of pollutants into surface water, while the Safe Drinking Water Act (SDWA) ensures safe drinking water for Americans. Wastewater regulations govern direct and indirect discharge sources, and use 115 “priority pollutants” for water quality criteria.

Regulations dictate that before wastewater can be discharged, sewage treatment plants must have National Pollutant Discharge Elimination System (NPDES) permits issued by the individual state or the EPA to treat the wastewater. This system ensures that regulated contaminants are discharged at levels that are lower than those permitted. NPDES permits are different than those for industrial wastewater.

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For drinking water, the EPA must review existing standards every six years. The agency also must monitor a list of selected and unregulated contaminants every five years, which is a requirement of the Unregulated Contaminant Monitoring Rule. If a contaminant is added to the list, the EPA will propose and finalize the rule for the maximum contaminant level goal and maximum contaminant level.

Eleven metals are on the National Primary Drinking Water Regulations list and six metals are on the secondary drinking water standards list.

For trace elemental analysis in drinking water and wastewater, EPA Methods 200.7, 200.8, or 200.9 should be used. Detailed analytical methods for compliance with CWA and SDWA are provided on the EPA website.

Soil. For soil, the EPA uses the Soil Screening Guidance (SSG) to monitor contaminant levels and compare them with soil screening levels (SSLs) for 110 chemicals. If contaminant levels exceed the standards, full monitoring is triggered. The SSG includes SSLs for particulate metals as well.

Solid waste. The treatment and disposal of solid waste and hazardous waste are regulated by the Resource Conservation and Recovery Act (RCRA).

For environmental cleanup after contamination from hazardous waste, the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA)/Superfund Amendments and Reauthorization Act (SARA) laws are used. The EPA establishes minimum criteria, and local state officials oversee the program through permits to ensure compliance. EPA regulations for solid waste and hazardous waste can

be found under Title 40 of the *Code of Federal Regulations* 239 through 282. RCRA and CERCLA/SARA use the SW846 compendium for analytical methods, which can be found on the EPA website. EPA SW846 Methods 6010 and 6020 are recommended for trace elemental analysis in solid and hazardous waste. Analytical chemists should note that some states and local governments have stricter environmental regulations for air, water, and soil than the EPA. The eight toxic metals required to be measured in soil are known as the “RCRA 8.”

Environmental Regulations in Europe

In August 2013, the European Union Water Framework Directive (WFD) 2013/39/EU was introduced to provide a strategy to monitor river and surface water pollution and biota contamination for European Union member states. The WFD also lists a set of priority hazardous substances that pose a significant risk to the aquatic environment.

Based on river basin districts, the WFD established a legal framework to protect and restore clean water across Europe and ensure its long-term, sustainable use. For individual water bodies, the Directive defines good ecological status, as well as good chemical status, which is defined by Environmental Quality Standards (EQSs).

There are three different EQSs set by the WFD: annual average concentrations (AA-EQS); maximum allowable concentrations (MAC-EQS); and biota-EQS, which is set primarily in fish, although some are in crustaceans and molluscs.

Figure 1 shows what trace element levels need to be measured and in what samples as well as the annual average threshold in rivers, fresh water lakes, transitional waters,

Figure 1: Trace element levels measured in samples.

Element	Hardness as CaCO ₃ (where applicable)	Annual Average (AA)		Maximum Allowable Concentration (MAC) (µg/l)
		All inland surface waters (µg/l)	All other surface waters (µg/l)	
Cd (PHS)	0 – 40	<0.08	0.2	<0.45
	40 – 50	0.08		0.45
	50 – 100	0.09		0.6
	100 – 200	0.15		0.9
	>200	0.25		1.5
Hg (PHS)	n/a	0.05		0.07
Ni	n/a	4	8.6	34
Pb	n/a	1.2	1.3	14

Element	Hardness as CaCO ₃ (where applicable)	Annual Average (AA)	
		Rivers and fresh water lakes (µg/l)	Transitional and coastal waters (µg/l)
As	n/a	50	25
Cr III	n/a	4.7	n/a
Cr VI	n/a	3.4	0.6
Cu	0-50	1	5
	50-100	6	
	100-250	10	
	>250	28	
Fe	n/a	1000	1000
Zn	0-50	8	40
	50-100	50	
	100-250	75	
	>250	125	

and coastal waters. The latest EU Trace Elements in Water Legislation (ISO 17294-2:2016) specifies an ICP-MS method for the determination of 63 elements in water (e.g., drinking water, surface water, ground water, and waste water).

Analysis of Trace Elements in Environmental Samples

The diverse array of analytes in environmental testing requires multiple methods for sample preparation, different analytical techniques and a variety of instrumentation.

Figure 2 indicates which EPA-approved methods are appropriate for atomic absorption spectrometry (AAS), ICP-optical emission spectrometry (ICP-OES), and ICP-MS for trace elemental analysis in compliance with U.S. regulations. The levels of regulatory standards will determine which technique is most appropriate.

The choice of which technique to use for metal analysis is mainly based on the detection that is required, the concentration range to be measured and the analysis speed required, as well as the instrument purchase cost and the range of analytes to be measured (see **Figure 3**).

- **Flame AAS** is inexpensive and fast, and is suitable when only a few elements need to be measured. It lacks the sensitivity and range of applicable

elements to meet all the US and EU environmental legislation requirements, however.

- **Furnace AAS** provides lower detection limits to key elements such as cadmium and lead, but is slow and more expensive. This technique is best applied when relatively few elements need to be measured in a small to medium number of samples.
- **ICP-OES** is more sensitive than Flame AAS and is a multi-element technique. It performs rapid analysis for environmental samples at ppb to ppm detection levels, but is more expensive than AA instrumentation. ICP-OES is ideal for

Figure 2: Trace elemental analysis in the United States.

- Toxicity of heavy metals leads to regulations and testing
- Different levels of regulatory standards determine the different tools

Application Notes

AN43157 (EPA Method 200.7)
AN43376 (EPA Method 200.7)
AN43323 (EPA Method 200.8)
AN40849 (EPA Method 200.9)
AN40851 (EPA Method 200.9)

Single-Element Techniques Lower Sample Throughput

FAA and GFAA



Thermo Scientific™ ICE™ 3300 AAS Atomic Absorption Spectrometer and ICE 3500 AAS Atomic Absorption Spectrometer

Drinking water
Wastewater
Soil/solid waste

Trace Elemental Products

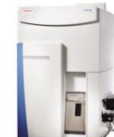
ICP-OES



Thermo Scientific™ iCAP™ 7000 Plus Series ICP-OES ICP-OES Systems

EPA Method 200.9
EPA Method 200.9

Q-ICP-MS

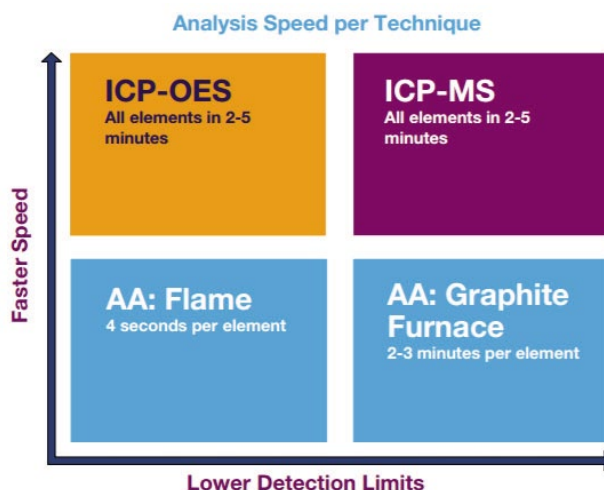
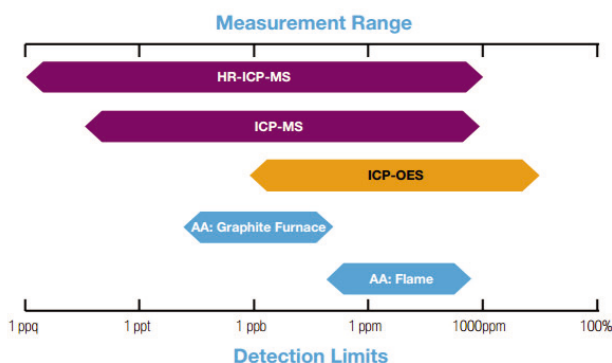


Thermo Scientific™ iCAP™ RQ ICP-MS

EPA Method 200.7
EPA Method 200.7
EPA SW846 Method 6010
EPA Method 200.8
EPA Method 200.8
EPA SW846 Method 6020

Figure 3: Selecting a technique used for metal analysis.

- Detection limit and measurement range
- Analysis speed



medium to high sample throughput where ultra-low detection limits are not required.

- **Single-quadrupole ICP-MS** is a fast, sensitive, multi-element technique well suited for low-level elemental analysis. It is more expensive than ICP-OES, but is essential for meeting the lowest concentration requirements of the US and EU environmental legislation.
- Finally, **triple-quadrupole ICP-MS** is the technique of choice when challenging interferences cannot be fully eliminated by a single-quadrupole ICP-MS system. Triple-quadrupole ICP-MS is a larger investment for laboratories, but has extended capabilities. For instance, the Thermo Scientific™ iCAP™ TQ ICP-MS system offers flexibility in both single- and triple-quadrupole operating modes.

EPA Methods 200.8 and 6020A

Two EPA methods are recommended for ICP-MS environmental analyses in the United States:

- 200.8—ground water, surface water, drinking water, waste water, and, less commonly, sludges and soils
- 6020A—ground water, aqueous samples, industrial wastes, soils, sludges and sediments

Both methods are similar, and they cover many—though not all—of the same analytes. EPA 200.8 is a prescriptive method, meaning there is very little room for a customized setup. In contrast, EPA 6020A is a performance-based method, so it has more flexibility. Clients often require runs of both methods for their quality assurance projects.

Advanced Environmental Laboratories (AEL), a Florida-based environmental testing laboratory network, created a universal method by combining EPA Methods 200.8 and 6020A into one. The new method satisfies the most stringent requirements of both methods, covers all the analytes and requires only one calibration. The only major challenge with the combination method is drinking water compliance for Method 200.8; use of a collision cell is not yet approved for this method.

To address this issue, AEL creates a duplicate analyte in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ platform software, running it in both standard (STD) and kinetic energy discrimination (KED) modes. This enables analysts to generate the most usable data from a single calibration run.

The hardware used by AEL for the universal method consists of the iCAP Q ICP-MS system with a Peltier-cooled cyclonic spray chamber, the ESI PolyPro-ST nebulizer, and a CETAC ASX-520 autosampler. A “high matrix” tune is utilized for each analysis using this method. More information about finding solutions on improving matrix tolerance for complex samples can be found online in Thermo Fisher Scientific’s [technical notes TN43202](#) and [TN43208](#).

With well-established methods, AEL endorses the use of custom-mixed standards to save time. However, when developing a new method, mixing one’s own standards is recommended until the ranges of interest are locked in. Although individually bottled single-element standards offer the greatest flexibility, they are very time consuming and tedious to make into mixed standards. Analysts must also be mindful of the accumulation of trace contamination amounts contributed by each standard.

It can be difficult to combine samples into a single sample preparation method. There are many similar procedures, but AEL recommends keeping the samples in separate batches for each type. The one exception is dissolved analysis by EPA 3005/200.8, because it does not involve sample digestion.

In addition, many laboratory information management system (LIMS) software packages are not configured to handle combining two different preparations in the same batch.

Best Practices

Tip 1: Sample preparation. There are several best practices for sample preparation. Good attention and skills are necessary; a good result begins with good preparation.

- Before digestion, analysts are advised to be cautious with unknown samples (e.g., odd color or texture) because they may exhibit unexpected behavior.
- Acids should be added slowly to avoid splashing and the vessel should be angled away from the eyes.
- Proper protection equipment is essential for the protection of eyes, hands and body.
- If it is not possible to avoid using hydrofluoric acid, analysts should have a safety plan in place, a colleague nearby and an antidote ready.
- Ample time should be allowed for the reaction to run to completeness in a hood before putting samples onto a hot plate. Hot samples must then be monitored in case of strong reactions.

Tip 2: Dilution before sample digestion. Dilution of difficult samples should be done at the digestion stage. Otherwise, it may result in incomplete digestion of the sample before loading on the instrument. This does not produce good analytical results.

Tip 3: After sample preparation. Oily (non-water miscible) samples tend to overheat and resist volume reduction. Placing a disposable glass pasteur pipette in the digestion vessel helps reduce the chance of boil over.

Tip 4: Unknown TDS. For most samples, the total dissolved solids (TDS) is unknown. A quick measurement of conductivity will yield a rough estimate of TDS in water. This will indicate whether sample dilution is needed. However, time is usually too critical to allow for this measurement. Experience and observations should be used to decide if

dilution is necessary. For example, AEL currently has a standard practice of diluting sea water, since it has invariably been necessary in the past. Similarly, a standard 10–50X dilution is performed on soil samples. All samples are examined for signs of high viscosity, bubbling or other abnormalities before being placed in the autosampler, as these are signs that dilution is necessary.

Tip 5: Arrange your samples. In the autosampler, the cleanest samples should be placed at the beginning of the sequence and the most difficult samples positioned at the end of the run and in their own calibration bracket. With this sequence order, if a problem arises with the difficult samples, the other samples will already be analyzed and only the difficult samples would need to be rerun.

Tip 6: Peristaltic pump tubing change. Preparing the instrument before an analytical run is as critical as sample preparation. Operators should change the peristaltic pump tubing regularly. It is inexpensive and can help avoid delays caused by unacceptable data acquisition. The overwhelming majority of poorly running instruments is related to sample introduction.

Tip 7: Check cones and sample introduction system.

Cones should always be examined before running samples. Look for deposits on the cones and check for leaks or moisture around the sample introduction system. If the cones have obvious deposits visible on them, clean them in deionized water in an ultrasonic bath for five minutes, then dry and replace them in the instrument.

Tip 8: Watch the run. During the run, the instrument should be checked to ensure the analyses are running properly. If necessary, it is better to do reruns the same day and avoid lengthy retuning and recalibration.

Conclusion

Proper analysis of water, soil, and air are a requirement of environmental regulations in the United States and Europe. Specific analytical methods should be used for each type of analysis, as stipulated by regulating bodies. ICP-MS instrumentation has proven to be a useful tool for monitoring trace elements in environmental water and soil samples. For the acquisition of acceptable data, best practices for both sample and instrument preparation should be followed.