EXECUTIVE SUMMARY

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Discover the Simple Way to Develop an ICP-OES Method

New ICP-OES methods for elemental analysis can be developed seamlessly by using EPA Method 6010D as a starting point.

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INTRODUCTION

While inductively coupled plasma optical emission spectroscopy (ICP-OES) can provide comprehensive detection of trace elements, interferences may negatively impact analytical results. Chemical, physical, and spectral interferences can introduce substantial errors, these are even more noticeable from a complex matrix such as soil, sludge, solid waste, and ground and surfaces waters. A key approach to minimize the impact of interferences is to employ a robust, established procedure for ICP-OES that was designed specifically for the intended class of samples. The US EPA Method 6010D (SW-846) is a proven approach for analyzing environmental samples and can also serve as a foundation for developing methods adapted to a wide range of other sample types. Adaptations of EPA Method 6010D can be readily validated through straightforward procedures and quality control protocols, thereby minimizing false positives, false negatives, or other analytical issues.

BASICS OF WATER, SOIL, AND WASTE ANALYSIS WITH ICP-OES

Testing water, solid, and waste materials from a region or city offers valuable information pertaining to the environment and human health. As population centers grow, new areas of land are sought for use, but each expansion requires environmental and safety assessments. These analyses often pertain to monitoring greenfield or pristine environmental sites, soil

> *Most ICP-OES systems obtain an entire optical emission spectrum from a single measurement, which means ICP-OES offers short analysis times for the fast pace of an environmental laboratory.*

nutrients from agricultural sites for fertilization, and other related applications. With an increase in pressure to restore former industrial and commercial locations to their original states, there is a need to determine the extent of contamination and identify any pollutants for environmental remediation.

These types of analyses were introduced in the United States with the passage of the 1976 Resource Conservation and Recovery Act (RCRA). The RCRA governs the disposal of solid and hazardous wastes with the intent to protect human health and the environment from hazardous substances. Additionally, the RCRA promotes the conservation of energy and natural resources, reduces the amount of waste generated, and ensures that waste is managed in an environmentally sound manner. Analytical method guidelines developed under the impetus of the RCRA are gathered in a collection known as "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," or by the shorter moniker the SW-846 Compendium. A method within this collection for ICP-OES applied to elemental analysis of waste, waters, soils, sludges, and sediments is known as EPA Method 6010D. The EPA Method 6010D is a versatile analytical workflow that can be adapted to a wide range of sample types and target analytes. The SW-846 Compendium also includes sample preparation procedures, in Chapter 3, Inorganic Analytes, notably the acid digestion approaches using Methods 3005A, 3010A, 3015A, 3031, 3050B, 3051A, and 3052. Regarding the actual analysis, use of ICP-OES instrumentation permits multi-element detection while the 6010D procedures have strict quality control requirements for ensuring consistent and accurate results.

Additional EPA methods have been based upon ICP-OES systems, such as Method 200.7 for water analysis. EPA Method 200.7 was developed for drinking water and wastewater compliance monitoring but can also be applied to elemental analysis in matrices such as wastewater, groundwater, sludges, and soils. While the EPA Methods 6010D and 200.7 both involve ICP-OES for trace elemental analysis, the two methods were created for different purposes and have distinct procedures and requirements. It should be noted that the EPA Method 6010D was developed for RCRA regulations, which pertain to solid waste analysis, and therefore cannot be used for Safe Drinking Water Act and Clean Water Act regulatory compliance monitoring.

With respect to the suitability of approaches to multi-elemental analysis, ICP-OES systems are ideal by offering a valuable combination of speed, economy, sensitivity, and robustness for waste, water, and solid analysis. Most ICP-OES systems obtain an entire optical emission spectrum from a single measurement, which means ICP-OES offers short analysis times for the fast pace of an environmental laboratory. This same analytical speed makes the ICP-OES method an economical choice by minimizing the use of system consumables such as argon. ICP-OES can overcome matrix effects in complex samples, so the systems are ideal even for analysis of solid waste. Additionally, the broad dynamic range afforded by ICP-OES is crucial for the large possible variation in trace element concentrations, even down to the parts-per-billion level of sensitivity.

The Thermo Scientific™ iCAP™ PRO Series ICP-OES platforms are an example of systems that have these attributes as well as proprietary features for streamlining analytical workflows. Four different ICP-OES configurations are available in the series and tailored to specific laboratory needs in a small footprint, including the iCAP PRO ICP-OES, iCAP PRO X ICP-OES, iCAP PRO XP ICP-OES, and iCAP PRO XPS ICP-OES. Each instrument is designed with high throughput optics, improved detection, and shortened warmup time to get started faster, while the unique vertical torch and purged optical path contribute to system robustness. With optimized preset settings, the iCAP PRO ICP-OES is appropriate for simplified manual usage and small sample loads. The iCAP PRO X ICP-OES has options for automation and handling of up to 50–100 samples per day, while the iCAP PRO XP ICP-OES and iCAP PRO XPS ICP-OES can manage 300–400 and 1,000+ samples per day, respectively. The iCAP PRO X ICP-OES, iCAP PRO XPICP-OES, and iCAP PRO XPS ICP-OES are all applicable for both organic and inorganic analysis, with the iCAP PRO XP ICP-OES and iCAP PRO XPS ICP-OES providing enhanced performance in the UV emission range.

APPROACHES TO PREPARATION OF ENVIRONMENTAL SAMPLES

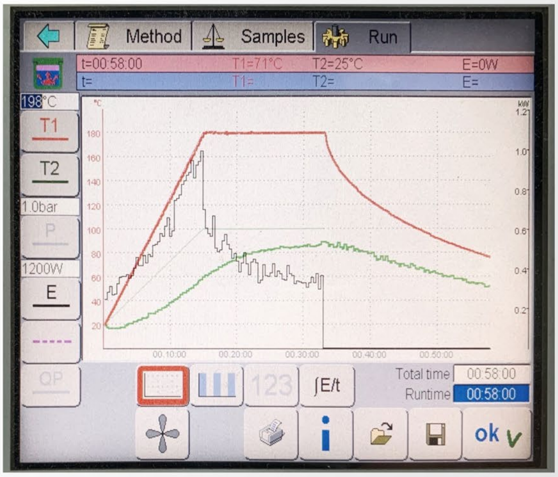
The classes of environmental samples targeted for analysis herein typically involve acid digestion techniques using a hot plate, hot block, or microwave, before ICP-OES analysis. The hot plate or hot block methods include EPA Methods 3010A and 3050B, where 3010A is for aqueous samples and 3050B is for the digestion of soils, sludges, and sediments. Digestion of water samples via 3010A and soil via 3050B both require nitric acid and hydrochloric acid to be added to the solutions. However, the 3050B soil digestion procedures require hydrogen peroxide in addition to the acid solutions to aid in the breakdown of organic matter.

Methods 3010A and 3050B both require the acid digestion processes to be performed in vessels with vapor recovery to minimize sample loss. This hot plate or hotblock digestion process may require digestion to take place for multiple hours with direct monitoring to prevent the sample from reaching dryness.

For microwave-assisted digestion, the two EPA methods available include 3015A for aqueous samples and 3051A for soils, sludges, sediments, and oils. A microwave digestion system such as the Milestone Ethos EZ SK 10 can be used for both the 3015A and 3051A approaches. Microwave digestion vessels are sealed to prevent loss of volatile elements, notably mercury, arsenic, and selenium. Nitric acid and hydrochloric acid are the only

Figure 1: EPA Methods 3015A and 3051A.

- EPA 3015A: Microwave Assisted Acid Digestion of Aqueous Samples and Extracts
- EPA 3051A: Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils
- Microwave digestion system (Ethos EZ SK10, Milestone®)
- Soil samples
  - 0.2 ± 0.001 g of sample
  - 9 ml HNO_3 + 3 ml HCl
  - Final volume – 50 ml



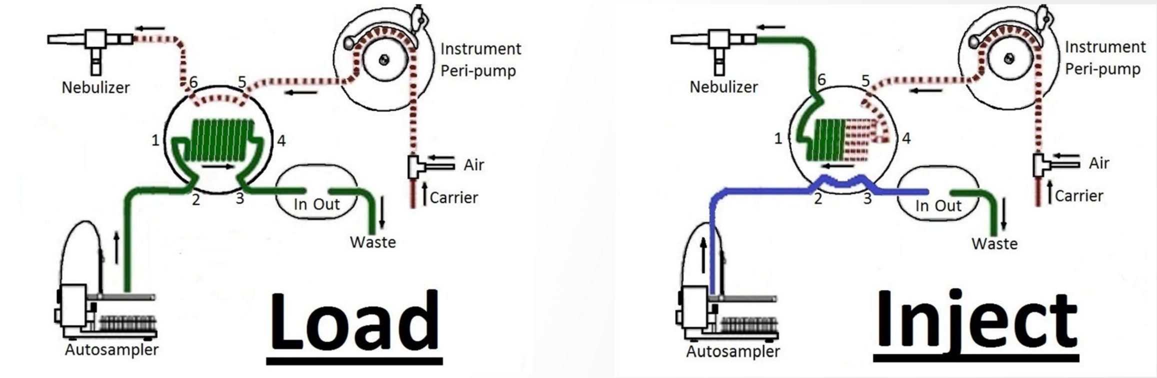
Ethos EZ SK10 is a product of Milestone Inc.

additives required for both 3015A and 3051A because the high pressure generated within the vessels negate the need for hydrogen peroxide to degrade any organics. Unlike hot block digestion, the microwave-assisted digestion process can be completed in under an hour because the vessel is pressurized (FIGURE 1). Nonetheless, microwave digestion vessels have limited sample capacity and a high initial cost of equipment relative to the simple arrangement needed for hot plate or hot block digestion.

Whether the digestion is performed on a hot plate or hot block or in a microwave vessel, all containers and glassware should be prepared appropriately, and the purity of reagents verified, to prevent contamination. Before starting sample preparation, any vessels, containers, stirring apparatus, or any devices that will be in contact with the sample should be scrupulously cleaned. For the microwave digestion vessels, this can be achieved by simply running the vessel through a cleaning cycle with nitric acid. The vessels should then be assessed for proper sealing so that loss of volatile analytes can be avoided. All solvents and other reagents used in the digestion process should be of trace metal grade, or better, and ≥18.2 MΩ-cm water should be used to prevent contamination.

With these methods as a general guide, the approaches can be applied to a broad range of analytes such as food, beverages, and pharmaceuticals, among others. The methods for aqueous samples are suitable for some beverages, while the techniques for solids are applicable for food and pharmaceuticals. Whenever samples have insoluble components, as can occur with some excipients, the acids may need to be altered. Aqua regia is a common option for metal analysis in addition to sulfuric acid, hydrofluoric acid, and perchloric acid. However, sulfuric acid, hydrofluoric acid, and perchloric acid should be avoided when

Figure 2: Rapid sample introduction system.



possible due to potential interferences and critical safety issues.

INSTRUMENTAL PARAMETERS AND METHOD DEVELOPMENT

The instrumental parameters and hardware for ICP-OES analysis of waste, water, and soil are straightforward for use with a variety of samples. With respect to the Thermo Scientific iCAP PRO ICP-OES systems, the operating mode known as intelligent Full Range (iFR) mode can capture a full emission spectrum for wavelengths in the range of 167 nm to 852 nm during a single measurement. Catching a full spectrum in one measurement not only improves analytical speed, but also simplifies standardization by enabling the use of a single internal standard for all elements. A standard glass concentric nebulizer is used for sample introduction as it provides good sensitivity while a low volume, glass cyclonic spray chamber is used for minimal carryover. When combined with a Teledyne CETAC™ ASX-560 autosampler and the ASXpress™ PLUS rapid sample introduction system, a sample analysis time of just 1 minute 28 seconds can be achieved. The loop and valve system shown in FIGURE 2 demonstrates how samples are loaded on to the sample loop. Solutions are injected in close proximity to the nebulizer resulting to a reduced sample introduction time of 10 seconds compared to 50 seconds in other ICP-OES systems.

Under select circumstances, slight adjustments to ICP-OES operating conditions and hardware may be needed for method adaptation. For most acidic solutions, the Saint-Gobain Tygon™ peristaltic pump tubing that is standard on iCAP PRO ICP-OES systems is sufficient, but chemical compatibility should be verified and peristaltic pump tubing material replaced if necessary. If Group I and Group II elements will be present in samples frequently, a ceramic torch will be needed for more robustness as it offers a long torch lifetime compared to a quartz torch. Furthermore, samples containing hydrofluoric acid also require compatible sample introduction components such as a ceramic torch, alumina center tube, and HF-resistant spray chambers, nebulizers, and pump tubing.

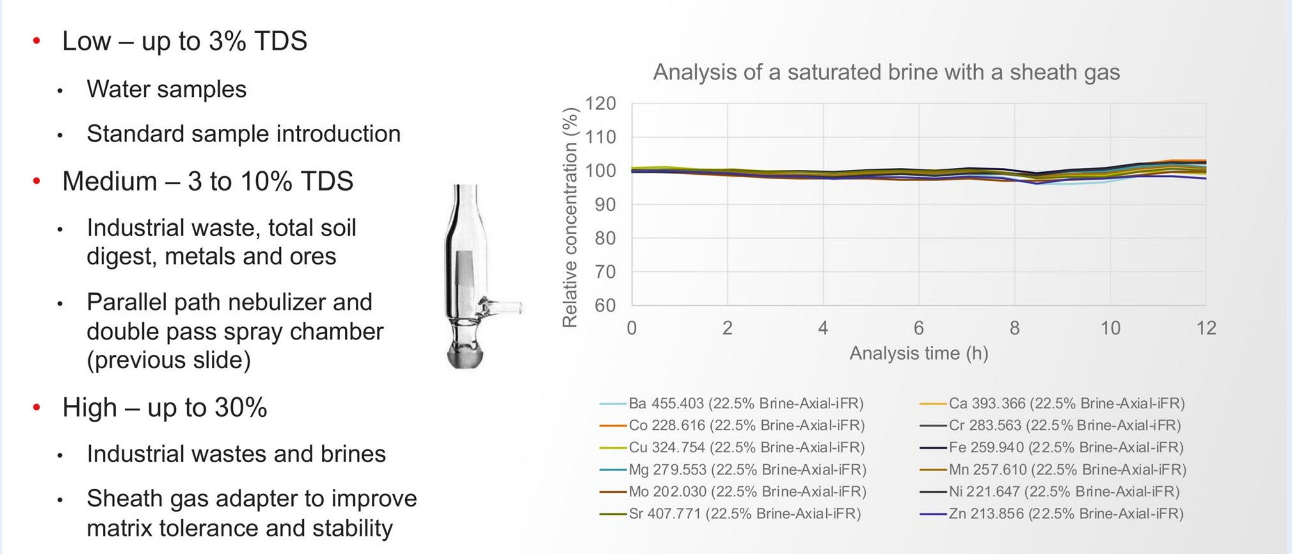


Figure 3: Total dissolved solids.

- Low – up to 3% TDS
  - Water samples
  - Standard sample introduction
- Medium – 3 to 10% TDS
  - Industrial waste, total soil digest, metals and ores
  - Parallel path nebulizer and double pass spray chamber (previous slide)
- High – up to 30%
  - Industrial wastes and brines
  - Sheath gas adapter to improve matrix tolerance and stability

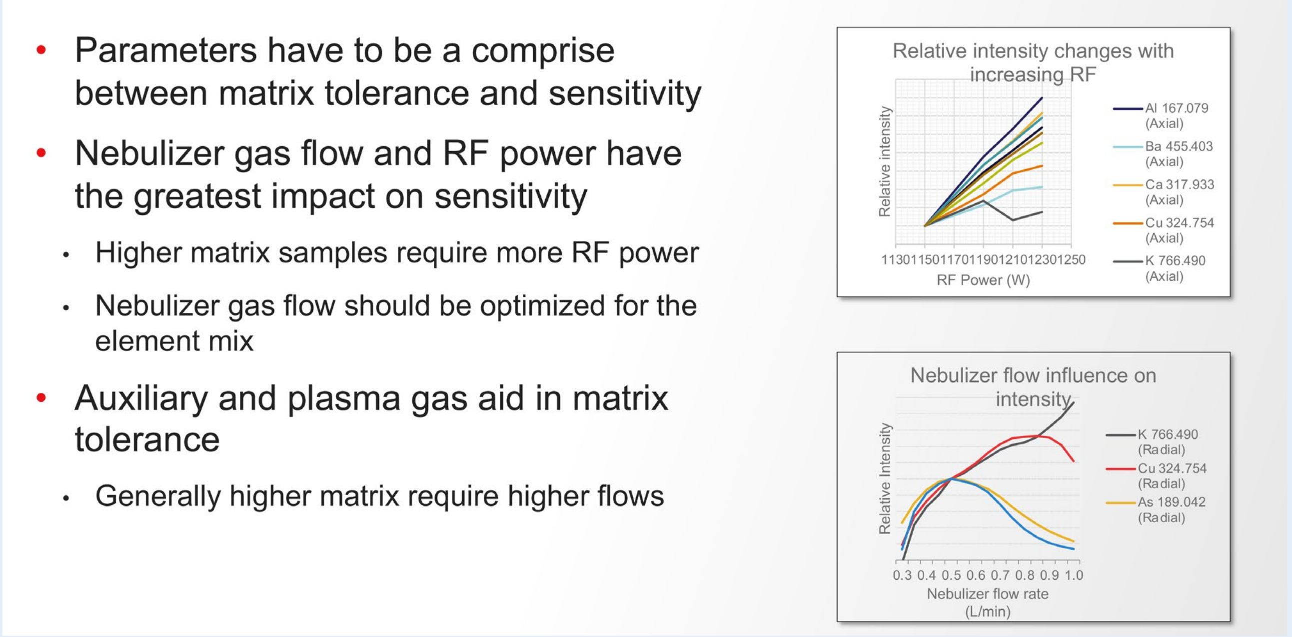


Figure 4: Adjusting parameters for different matrix.

- Parameters have to be a comprise between matrix tolerance and sensitivity
- Nebulizer gas flow and RF power have the greatest impact on sensitivity
  - Higher matrix samples require more RF power
  - Nebulizer gas flow should be optimized for the element mix
- Auxiliary and plasma gas aid in matrix tolerance
  - Generally higher matrix require higher flows

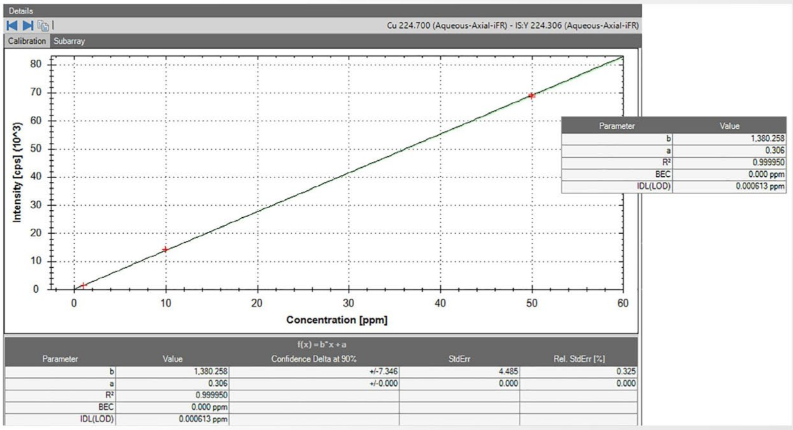
Sample solutions containing a high solids content may require hardware alterations to accommodate the solids. As shown in **FIGURE 3**, a total dissolved solids (TDS) content of up to 3% can be accommodated with the standard sample introduction system, but samples in the range of 3% to 10% TDS, from samples like industrial waste and soil digests, will require a parallel path nebulizer and double-pass spray chamber. For solutions containing more than 10% TDS and as much as 30% TDS, a sheath gas adaptor is needed for matrix tolerance and sample aerosol stability. In addition to combatting the impact of TDS, other matrix effects may be countered by optimizing flow rates and the RF power of the plasma according to the target analytes (**FIGURE 4**).

PROCESS FOR ANALYTICAL METHOD AND WORKFLOW VALIDATION

Validation of methods can be accomplished through straightforward workflows as outlined by EPA Method 6010D. A four-point calibration curve such as the plot in **FIGURE 5** demonstrates the high degree of linearity achievable with ICP-OES. From a series of reagent blanks, the instrument detection limits (IDLs) can be obtained for assessing instrumental noise and changes in response. Elemental emission spectroscopy can suffer from spectral interferences due to overlaps and, therefore, requiring calculation of interelement correction (IEC) factors to be applied to each sample. In iCAP PRO ICP-OES systems, the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ software includes an IEC feature for automatic calculation and application of IEC factors. Quality Control (QC) checks, including an Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB) are required for monitoring contamination and carryover, while matrix spike samples offer insight into the effects of the matrix on the sample, such as the influence of high salt concentrations. Overall method performance can be validated against known samples such as Standard Reference Materials (SRMs) 2781 and 2709a from NIST. System responses

Figure 5: 6010D linear dynamic range.

- The linearity demonstrated using a four-point calibration curve for all target analytes
- A linear range study to establish the highest concentration that can be reported without dilution of a sample
- If your calibration starts to curve, select a less sensitive wavelength



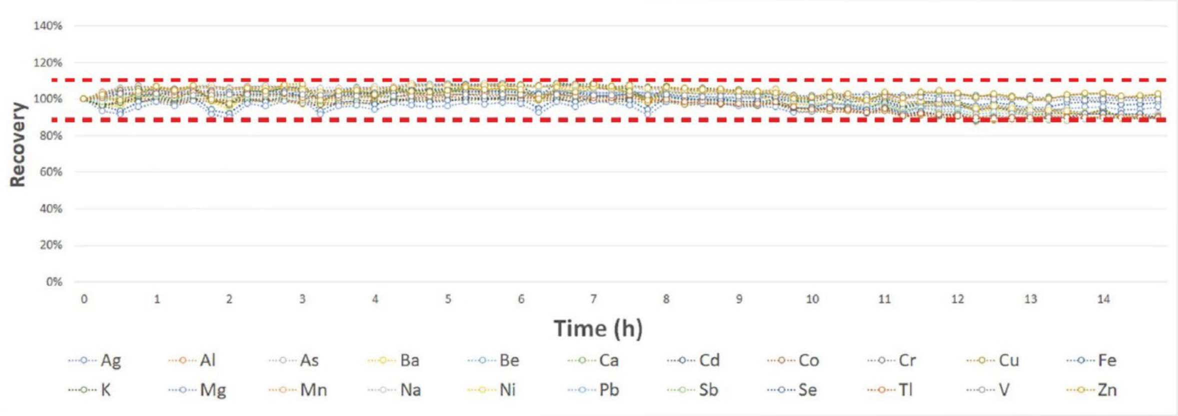
Parameter	Value
b	1,380.258
a	0.306
R²	0.999950
BEC	0.000 ppm
IDL(LOD)	0.000613 ppm

f(x) = b*x + a

Parameter	Value	Confidence Delta at 90%	StdErr	Rel. StdErr [%]
b	1,380.258	+/-7.346	4.485	0.325
a	0.306	+/-0.000	0.000	0.000
R²	0.999950			
BEC	0.000 ppm			
IDL(LOD)	0.000613 ppm			

Figure 6: Stability.

The monitoring of the CCV solution over many hours of analysis can provide a good indication of stability



Stability data from application note: AN 74146 Fast, accurate, and robust analysis of environmental samples according to US EPA Method 6010D

to Continuing Calibration Verification (CCV) standards over the course of 15 hours were monitored and the recoveries within ±10% acceptance criteria, thereby demonstrating stability and robustness of the ICP-OES instrument (FIGURE 6).

CONCLUSIONS

ICP-OES instrumental platforms offer sensitive and robust elemental analysis capabilities for water, soil, and beyond. Using the EPA Method 6010D as a template, ICP-OES methods can be developed for a broad range of sample types. This can be accomplished through optimization of the sample introduction system and operating parameters according to the sample matrices and detection limit requirements. Method validation and ensuring the accuracy of results can be achieved by following the strict QC protocol specified in Method 6010D, taking measures to avoid contamination, and by using compatible apparatus and high purity standards, acids, and reagent water.

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