

Overcoming interferences in challenging sample matrices using ICP-OES

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ABSTRACT

Purpose: Prove the performance of the Thermo Scientific™ iCAP™ PRO Series ICP-OES for the analysis of environmental samples by following the US Environmental Protection Agency (EPA) Method 6010D (SW-846).

Methods: EPA Method 6010D (SW-846) with Inter Element Correction.

Results: Different kind of environmental samples can be analyzed accurately, precisely, and quickly using a Thermo Scientific™ iCAP™ PRO XP ICP-OES Duo system, meet all requirements of the EPA 6010D (SW-846) protocol.

INTRODUCTION

In response to growing environmental issues, the EPA has developed various methods to test the contaminants in environmental samples. On October 21st, 1976, the United States Congress enacted the Resource Conservation and Recovery Act (RCRA), which governs the disposal of solid and hazardous waste. Guideline methods for the analysis of these types of samples are collated under “Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,” more commonly known as SW-846. One of the specified methods is EPA Method 6010D (SW-846) “Inductively Coupled Plasma – Atomic Emission Spectrometry.” This method prescribes the use of inductively coupled plasma optical emission spectrometry (ICP-OES) instrumentation for the determination of target elements in groundwaters, industrial and organic wastes, soils, sludges, and sediments. Although EPA Method 6010D (SW-846) is used mainly within the US for the analysis of environmental samples, variants of this method are widely used in other regions and for other sample types. Therefore, the ability to undertake the analysis of samples using this method represents an important benchmark for any ICP-OES instrument.

MATERIALS AND METHODS

Sample Preparation

Water and soil samples: Twenty water samples and 12 soil samples, provided by Pace Analytical Services, LLC (US), were digested using the hot plate acid digestion procedures according to EPA Methods 3010A and 3050B, respectively.

Standard Reference Materials: SRM® 2781 – Domestic Sludge, NIST; SRM® 2709a – San Joaquin Soil, NIST. NIST were digested according to EPA Method 3015A and 3051A using the ETHOS™ EZ SK10 (Milestone, Italy) microwave system.

Calibration standards: Prepared in 2% HNO₃ with analyte concentrations covering the range expected in the samples.

Internal standard: A 10 mg L⁻¹ yttrium internal standard was introduced online via the ASXpress® P/U liquid sample introduction system.

Individual element Spectral-Interference Check (SIC) solutions: These solutions are used to evaluate possible spectral interferences and to set interelement corrections if necessary. Individual element SIC solutions for each of the major and trace elements were prepared using 1,000 mg L⁻¹ and 10,000 mg L⁻¹ single element standards (SPEX CertiPrep®), Metuchen, NJ, US) to meet the requirements of different concentration ranges.

Mixed element SIC solution: This solution is used as an ongoing daily check of freedom from spectral interferences. The mixed element SIC solution contains aluminum, 500 mg L⁻¹; calcium, 500 mg L⁻¹; iron, 200 mg L⁻¹; and magnesium, 500 mg L⁻¹ and is made up in an acid solution equivalent to the calibration standards.

Initial Calibration Verification (ICV) Standard: An already-prepared, second-source reference material from VHQ (PN 16005990).

Test Method(s)

A LabBook was set up using the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software for the analysis. Wavelength selection within the Qtegra ISDS Software is simple. The wavelength with the least interferences and the strongest signal is automatically recognized and ranked by the software for the analyst to select.

Data Analysis

The Qtegra ISDS Software includes an automatic feature for the correction of interferences based on concentration was used for this work. Single element solutions for each of the major interferences were analyzed as SIC solutions to check for interferences on each analyte. Once identified, the Inter-Element Correction (IEC) function was used to calculate the interference correction factors based on concentration.

Inter Element Correction (IEC)

Achieving effective interference correction

Inductively coupled plasma optical emission spectrometry (ICP-OES) is a robust and efficient analytical technique for measuring trace elements in a wide variety of sample types. However, the presence of interferences on some of the elements of interest from wavelengths emitted from other elements in the sample is a well-known challenge. With the Thermo Scientific™ iCAP™ PRO Series ICP-OES instruments, these interferences can easily and accurately be corrected by using the interelement correction (IEC) protocol included with the Qtegra ISDS Software.

The key requirements for IEC are the ability to correct the interfered element signals based on either the interfering wavelength’s signal intensity or its equivalent concentration relative to the concentration of the element to be measured. Correcting based on concentration, as stipulated in regulatory protocols such as US EPA Method 200.7 and US EPA Method 6010D (SW-846), is more demanding.

The principal steps for correction based on concentration in the IEC workflow are summarized in the example shown in Figure 1.

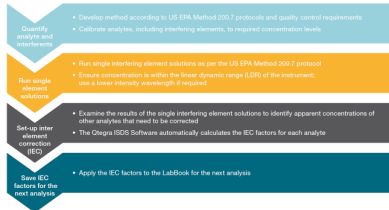


Figure 1. Example workflow for interelement correction (IEC) in Qtegra ISDS Software for the iCAP™ PRO Series ICP-OES for the analysis of samples according to US EPA Method 200.7

In addition to a comprehensive, yet simple to follow IEC workflow within a LabBook, the Qtegra ISDS Software allows the user to set pre-defined concentration limits, with color-coded flagging functionality to enable data affected by interelement interference in an analysis to be easily identified in the results table (Figure 2).

Figure 2. Main results table with data affected by interelement interference highlighted (blue = below the pre-defined lower limit, red = above the pre-defined higher limit). Only Al data is shown in this example, for clarity.

IEC correction on the target wavelength is then subsequently applied by first importing the set of single element solution data into the IEC tab, and then selecting each element interference in turn for those results where interference has been highlighted by color-coded flags (Figure 3) and finally applying the corrections to produce the interference corrected results for the single interference check solutions (Figure 4). At the same time, the interference corrections are automatically applied to all the other samples in the analysis, as illustrated in Figure 5.

Figure 3. Application of interference correction to results that are highlighted as being interfered (using the single element solution data)

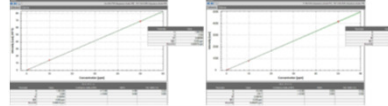
Figure 4. Results after IEC correction applied

Figure 5. Example of interference corrected data in the main results table. Only Al data is shown in this example, for clarity.

RESULTS

Linearity

The linearity of the target analytes was demonstrated using a four-point calibration curve. Calibration curves for all analytes were established in the same run.



Instrument detection limits

Table 1. IDLs achieved by iCAP PRO XP ICP-OES Duo system under typical laboratory conditions.

Element	Wavelength (nm)	View	IDL (mg L ⁻¹)	Element	Wavelength (nm)	View	IDL (mg L ⁻¹)
Ag	328.068	Axial	0.00037	Mn	253.044	Axial	0.00196
Al	396.152	Radial	0.01965	Nb	589.592	Radial	0.00653
As	189.042	Axial	0.00170	Ni	231.504	Axial	0.00086
B	248.729	Axial	0.00016	P	178.284	Axial	0.00078
Ba	485.453	Radial	0.00025	Pb	320.353	Axial	0.00228
Be	234.861	Axial	0.00012	S	182.034	Axial	0.00629
Bi	220.051	Axial	0.00248	Sc	226.833	Axial	0.00148
Ca	318.887	Radial	0.00248	Se	196.590	Axial	0.00318
Cd	226.502	Axial	0.00004	Si	251.811	Radial	0.00438
Co	228.616	Axial	0.00025	Sr	189.989	Axial	0.00207
Cr	284.325	Axial	0.00092	Sr	421.552	Axial	0.00004
Cu	254.700	Axial	0.00061	Tb	283.730	Axial	0.00190
Cu	255.340	Radial	0.00014	Ti	334.341	Radial	0.00096
K	766.490	Radial	0.01515	Tl	190.856	Axial	0.00331
Li	670.791	Radial	0.00165	V	292.402	Axial	0.00037
Mg	279.079	Radial	0.00012	Zn	213.856	Radial	0.00050
Mn	257.610	Radial	0.00025	Zr	343.823	Axial	0.00009

Method validation check – NIST SRM recoveries

Method performance was also verified by analyzing two NIST Standard Reference Materials: SRM 2781 – Domestic Sludge and SRM 2709a – San Joaquin Soil, which were digested using microwave assisted acid digestion according to EPA Method 3051A. Table 2 shows the results for both materials. All results were within ± 10% of the certified values.

Table 2. Method validation: NIST SRM recoveries. Please note that the SRM samples did not contain all of the elements required by EPA Method 6010D (SW-846).

Element	SRM 2781 – Domestic Sludge			SRM 2709a – San Joaquin Soil		
	Measured (mg kg ⁻¹)	Certified value (mg kg ⁻¹)	Recovery (%)	Measured (mg kg ⁻¹)	Certified value (mg kg ⁻¹)	Recovery (%)
Al	16253	16000	102	79036	73700	96
As	8.1	7.81	104	11.2	10.5	107
Ba	-	-	-	892	978	101
Be	0.5820	0.6130	95	-	-	-
Ca	20523	39000	101	18945	19100	99
Cd	11.83	12.78	93	0.348	0.371	94
Co	-	-	-	12.2	12.8	95
Cr	208	202	103	129	135	96
Cu	607.3	627.8	97	32.0	33.9	94
Fe	23537	28000	101	23559	38600	97
K	4962	4900	101	20649	21100	98
Mg	5953	5900	101	14825	14600	102
Mn	45.9	46.6	98	535	525	101
Nb	2215	2100	105	11979	12200	98
Ni	79.2	80.2	98	83	85	98
P	24722	24300	102	704	895	102
Pb	266	200.8	133	16.4	17.5	94
Se	17	16	106	0.559	0.58	96
Ti	-	-	-	108	110	98
Zn	-	-	-	98	103	95

Robustness

The iCAP PRO XP ICP-OES Duo instrument includes highly precise mass flow controllers for gas control and effective temperature control of the optic and CID detection system. This advanced temperature control technology ensures that the spectrum remains constant with fluctuations in the laboratory conditions. This ensures that the long-term signal stability of the instrument is exceptional and that CV samples are within acceptable levels for extended periods. To demonstrate the long-term stability of the system, more than 500 environmental samples were analyzed continuously over a 15-hour period. During this analysis a CVV validation was analyzed after every five samples. Figure 6 shows the recoveries of the CVV solution plotted against time (h). All results of the CVV were within the acceptance criteria of ± 10%.

The recovery of the yttrium internal standard is shown in Figure 7. The recovery of the internal standard was consistent throughout the analysis and demonstrates stability and accuracy. No detectable carryover or other effects from sample matrices (e.g., signal suppression or enhancement) were observed.

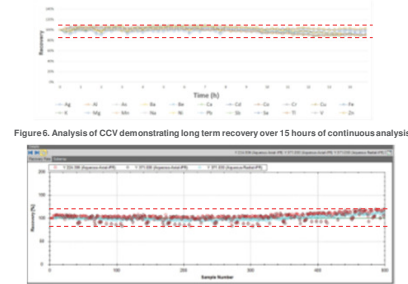


Figure 6. Analysis of CVV demonstrating long term recovery over 15 hours of continuous analysis

Figure 7. Recoveries of the internal standard wavelengths from the analysis of more than 500 samples over 15 hours showing recoveries within the acceptance criteria

CONCLUSIONS

The iCAP PRO XP ICP-OES Duo system is well suited for the analysis of environmental samples according to the EPA Method 6010D (SW-846) protocol and exceeds the requirements needed.

- High sensitivity achieved the detection limits of all target elements in the low ppb level, for several elements even at sub-ppb levels
- Spectral interferences were easily corrected, as required by the EPA Method 6010D (SW-846), using the IEC function within the Qtegra ISDS Software
- Fast analysis (1 minute and 28 seconds per sample) for all target analytes utilizing both Axial and Radial modes due to simultaneous acquisition over the full wavelength range.
- Robust and stable analytical performance was demonstrated throughout 15 hours of continuous sample analyses

REFERENCES

- US EPA, July, 2018, Method 6010D (SW-846 Update VII) – “INDUCTIVELY COUPLED PLASMA – OPTICAL EMISSION SPECTROMETRY”, Revision 6.
- Application Note 74146, Fast, accurate, and robust analysis of environmental samples according to US EPA Method 6010D, Thermo Fisher Scientific

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TRADEMARKS/LICENSES

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