



US EPA SW-846 Method 6010D using the Thermo Scientific iCAP 7400 ICP-OES Duo

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Goal

This application note describes the performance of the Thermo Scientific iCAP 7400 ICP-OES Duo for the analysis of environmental sample types by the US EPA Method 6010D. The iCAP 7400 ICP-OES Duo achieves short analysis times per sample whilst maintaining compliance with the protocol.

Introduction

On 21 October 1976, the United States (US) 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' Solid Wastes (SW)-846. One of the specified methods is US Environmental Protection Agency (EPA) Method 6010D 'Inductively Coupled Plasma-Optical Emission Spectrometry'. This method prescribes the use of Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) instrumentation for the determination of 31 elements in groundwaters, industrial and organic wastes, soils, sludges and sediments. All samples, except filtered groundwater, must be digested prior to analysis using either US EPA Method 3050B 'Acid Digestion of Sediments, Sludges, and Soils' or US EPA Method 3051A 'Microwave Assisted Digestion of Sediments, Sludges, Soils, and Oils'. US EPA Method 6010D is used within the USA and its variants are widely used in other regions, therefore the ability to undertake this type of analysis using US EPA Method 6010D represents an important benchmark for any ICP-OES instrument.

Instrumentation

The Thermo Scientific™ iCAP™ 7400 ICP-OES Duo was used to analyze a selection of environmental sample types within the quality control framework of the US EPA Method 6010D. A duo instrument was selected as it enables elements expected at low concentrations to be measured axially for maximum sensitivity whilst elements expected at high concentrations can be measured radially. This allows the dynamic range of the instrument to be extended compared to that of an axial view only instrument. The instrument parameters used for this analysis are shown in Table 1.

Table 1. Instrument parameters.

Parameter	Setting
Pump Tubing (Standard Pump)	Sample Tygon® orange/white Drain Tygon® white/white Internal Standard Tygon® orange/blue
Pump Speed	50 rpm
Spray Chamber	Glass cyclonic
Center Tube	2 mm
Nebulizer	Glass concentric
Nebulizer Gas Flow	0.7 L·min ⁻¹
Auxiliary Gas Flow	0.5 L·min ⁻¹
Coolant Gas Flow	12 L·min ⁻¹
RF Power	1250 W
Exposure Time	UV 15 s, Vis 5 s

Sample and standard preparation

Solid samples were digested according to US EPA Method 3051A. A microwave digestion system (Ethos EZ SK10, Milestone) was used to digest 1 ± 0.005 g of sample in 2 ml of concentrated nitric acid ($\geq 68\%$ TraceMetal™ grade, Fisher Scientific, Loughborough, UK) and 6 ml of concentrated hydrochloric acid (34 – 37% TraceMetal grade, Fisher Scientific), this digestion extract was then made up to a final volume of 100 ml with ultra-pure deionized water (18.2 MΩ).

Calibration standards were prepared in 6% hydrochloric acid v/v and 2% nitric acid v/v, and their element concentrations were selected to cover the required measurement range of each analyte. A 5 mg·L⁻¹ yttrium internal standard was automatically introduced online with the internal standard mixing kit. The internal standard wavelengths were appropriately matched to analyte wavelengths for each of the viewing modes, Axial/Radial and UV/Vis range. Details of the analyte wavelengths, plasma views and internal standard wavelengths selected are presented in Table 2.

Method development and analysis

A LabBook was setup using the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software for the analysis of a selection of elements covered by the US EPA Method 6010D (Table 2).

Table 2. Acquisition parameters.

Element	Wavelength (nm)	Plasma view	Internal standard (nm)	Interfering elements
Al	396.152	Radial	Y 371.030	Ca
As	189.042	Axial	Y 224.306	N/A
Ba	493.409	Axial	Y 324.228	N/A
Be	234.861	Axial	Y 324.228	N/A
Ca	422.673	Radial	Y 371.030	N/A
Cd	214.438	Axial	Y 224.306	N/A
Co	238.892	Axial	Y 324.228	N/A
Cr	357.869	Axial	Y 324.228	N/A
Cu	224.700	Axial	Y 224.306	N/A
Fe	259.940	Radial	Y 371.030	N/A
K	766.490	Radial	Y 371.030	N/A
Mg	202.582	Radial	Y 371.030	Co, Na
Mn	257.610	Axial	Y 324.228	N/A
Na	589.592	Radial	Y 371.030	K
Ni	341.476	Axial	Y 324.228	N/A
P	177.495	Axial	Y 224.306	N/A
Pb	261.418	Axial	Y 324.228	Co, Fe
Sb	206.833	Axial	Y 224.306	N/A
Se	196.090	Axial	Y 224.306	N/A
Tl	377.572	Axial	Y 324.228	N/A
V	292.402	Axial	Y 324.228	N/A
Zn	213.856	Axial	Y 224.306	N/A

*N/A not available

Due to the unknown and potentially highly contaminated nature of waste and soil samples, significant spectral overlaps may be observed and therefore will need to be identified and either removed or compensated for. Single element solutions for each of the major and trace elements were analyzed as spectral interference checks (SIC) to check for their spectral contributions on other analytical elements. For concentrations of SIC solutions, see Table 3. Once identified, the Inter-Element Correction (IEC) function was used to calculate interference correction factors. The interferences observed with these solutions are detailed in Table 2.

Table 3. Single element SIC solutions.

Element	Concentration (mg·L ⁻¹)
Na	1000
Al, Ca, Mg	500
Fe, Si	200
B, Ba, Cu, Mn	50
Other trace elements	20

Results and discussion

Method detection limits (MDLs) were established by measuring a blank solution (6% HCl, 2% HNO₃ v/v). This solution was analyzed three times with each analysis having seven replicates; the standard deviation of the repeats for each of these analyses was multiplied by 3 and a mean value calculated to provide the MDL. These calculated MDLs can be seen in Table 4.

Table 4. Method detection limits achieved.

Element	Wavelength (nm)	View	MDL (µg·L ⁻¹)
Al	396.152	Radial	6.91
As	189.042	Axial	1.74
Ba	493.409	Axial	0.13
Be	234.861	Axial	0.12
Ca	422.673	Radial	14.0
Cd	214.438	Axial	0.17
Co	238.892	Axial	0.93
Cr	357.869	Axial	0.68
Cu	224.700	Axial	0.85
Fe	259.940	Radial	3.92
K	766.490	Radial	31.8
Mg	202.582	Radial	28.0
Mn	257.610	Axial	0.15
Na	589.592	Radial	6.87
Ni	341.476	Axial	0.56
P	177.495	Radial	0.32
Pb	261.418	Axial	0.61
Sb	206.833	Axial	2.7
Se	196.090	Axial	0.82
Tl	377.572	Axial	0.30
V	292.402	Axial	0.79
Zn	213.856	Axial	0.23

The US EPA Method 6010D requires that a very strict quality control procedure should be followed to ensure the validity of sample data. Quality control checks should be carried out following instrument calibration, during sample analysis and at the end of the analytical run. All checks must meet the required US EPA Method criteria for the sample data to be valid. The instrument was set up using the parameters shown in Table 1. Immediately after calibration, an Initial Calibration Verification (ICV) solution and an Initial Calibration Blank (ICB) were analyzed. The validity of the calibration was verified through the analysis of a Continuing Calibration Verification (CCV) solution and Continuing Calibration Blank (CCB) after every 10 samples, and at the end of each analysis batch run. The ICB must return a result less than 0.5 times the Lower Limit of Quantification (LLOQ) for each element, while the ICV and CCV solutions must be within ±10% of the true values. The CCB must not contain target analytes above the LLOQ. Analysis of the CCV and CCB was then repeated every 10 samples and at the end of the analysis run to ensure the instrument remained in calibration, the results for the ICV and the first CCV are shown in Table 5.

Table 5. Initial and continuing calibration verification checks (ICV & CCV).

Element	ICV		CCV	
	Measured (mg·L ⁻¹)	Recovery (%)	Measured (mg·L ⁻¹)	Recovery (%)
Al	0.504	100.9	2.463	98.5
As	0.496	99.1	2.508	100.3
Ba	0.515	103	2.55	102
Be	0.482	96.5	2.524	101
Ca	0.488	97.7	2.542	101.7
Cd	0.53	106	2.503	100.1
Co	0.496	99.3	2.412	96.5
Cr	0.492	98.3	2.493	99.7
Cu	0.501	100.2	2.436	97.4
Fe	0.47	93.9	2.379	95.2
K	0.461	92.2	2.453	98.1
Mg	0.509	101.9	2.453	98.1
Mn	0.469	93.8	2.476	99
Na	0.544	108.8	2.538	101.5
Ni	0.469	93.8	2.455	98.2
P	0.474	94.8	2.513	100.5
Pb	0.501	100.2	2.615	104.6
Sb	0.501	100.2	2.443	97.7
Se	0.523	104.7	2.578	103.1
Tl	0.518	103.5	2.521	100.8
V	0.496	99.2	2.41	96.4
Zn	0.499	99.9	2.522	100.9

The iCAP 7400 ICP-OES Duo includes a highly regulated temperature control system. This advanced temperature control technology ensures that the spectrum position remains constant with fluctuations in the laboratory conditions. This ensures that the long-term signal stability of the instrument is exceptional and that CCV samples are within acceptable levels for extended periods, resulting in fewer sample re-runs. Interference check solutions were analyzed prior to the start of the sample analysis in order to verify the accuracy of the IEC factors and the background correction points. A mixed SIC solution (SIC-A) was prepared containing 500 mg·L⁻¹ each of Al, Ca, Mg and 200 mg·L⁻¹ of Fe. Then, a spiked SIC solution (SIC-B) was prepared by spiking the SIC-A solution with concentrations of 0.1 to 1 mg·L⁻¹ for the analyte elements. The values measured for SIC-B must be within 20% of the true value for the data to be acceptable. The obtained data is shown in Table 6.

Method performance was verified by analyzing two samples, a soil certified reference material (CRM) (#SQC001, lot 017309, RTC, Laramie, WY, USA) and a locally collected soil sample spiked with the equivalent of 100 mg·kg⁻¹ for each of the trace analytes and 1000 mg·kg⁻¹ for the major elements. The results of the spiked local soil and CRM samples as well as recoveries are shown in Table 7.

Table 6. Interference check solutions and recoveries.

Element	SIC-A (mg·L ⁻¹)	SIC-B (mg·L ⁻¹)	Target value (mg·L ⁻¹)	Recovery (%)
As	<DL	0.299	0.30	99.8
Ba	<DL	0.154	0.15	102.7
Be	<DL	0.562	0.55	102.2
Cd	<DL	0.763	0.80	95.4
Co	<DL	0.476	0.50	95.2
Cr	<DL	0.765	0.70	109.2
Cu	<DL	0.424	0.45	94.1
K	<DL	0.633	0.65	97.4
Mn	<DL	0.867	0.90	96.4
Na	<DL	0.427	0.40	106.7
Ni	<DL	0.602	0.60	100.4
P	<DL	0.883	0.85	103.9
Pb	<DL	0.366	0.35	104.7
Sb	<DL	0.102	0.10	102.2
Se	<DL	0.741	0.75	98.7
Tl	<DL	1.030	0.95	108.4
V	<DL	0.183	0.20	91.3
Zn	<DL	0.273	0.25	109.0

Table 7. Method validation check samples and recoveries.

Element	Soil sample			Soil CRM #SQC001		
	Unspiked sample (mg·kg ⁻¹)	Spiked sample (mg·kg ⁻¹)	Recovery (%)	Measured (mg·kg ⁻¹)	Certified value (mg·kg ⁻¹)	Recovery (%)
Al	9948	10965	101.8	11346	11100	102.2
As	2.20	107.9	105.7	219.4	202.0	108.6
Ba	62.56	169.0	106.4	669.0	662.0	101.0
Be	0.613	108.4	107.7	326.8	328.0	99.6
Ca	1964	2943	97.9	3239	3090	104.8
Cd	0.084	104.1	104.0	241.8	265.0	91.2
Co	6.16	105.5	99.3	286.1	314.0	91.1
Cr	17.76	127.5	109.7	244.3	232.0	105.3
Cu	8.369	105.4	97.0	80.30	88.40	90.8
Fe	16005	17040	103.5	8718	8850	98.5
K	1854	2881	102.8	9745	8890	109.6
Mg	1945	2913	96.8	2043	1890	108.1
Mn	214.3	307.6	93.2	1355	1370	98.9
Na	63.61	1008	94.4	4953	4890	101.3
Ni	12.51	118.6	106.0	81.29	76.50	106.3
P	320.6	426.6	106.0	340.0	371.0	91.6
Pb	86.16	194.3	108.1	57.26	55.90	102.4
Sb	0.914	104.8	103.9	133.4	125.0	106.7
Se	<DL	107.8	107.8	155.4	144.0	107.9
Tl	<DL	97.54	97.5	115.1	118.0	97.5
V	15.13	117.2	102.0	239.8	220.0	109.0
Zn	33.70	127.0	93.3	254.3	258.0	98.6

Conclusion

The Thermo Scientific iCAP 7400 ICP-OES Duo exceeds the requirements needed to meet the US EPA Method 6010D protocol. The instrument includes a high resolution optical system which minimizes spectral interferences and reduces stray light. In addition, the advanced Charged Injection Device (CID) detector results in higher sensitivity and lower noise, which produces a high signal to background ratio.

The simplified work flows of the Qtegra ISDS Software enable complex procedures to be easily adhered to using the automatic interference correction and quality control protocols. Using the method described, the time taken for each sample analysis was 2 minutes 35 seconds. This short analysis time leads to a low quantity of waste being produced and low consumable requirements, minimizing both the cost of analysis and its environmental impact.

Find out more at thermofisher.com/ICP-OES

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