

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

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Key Words

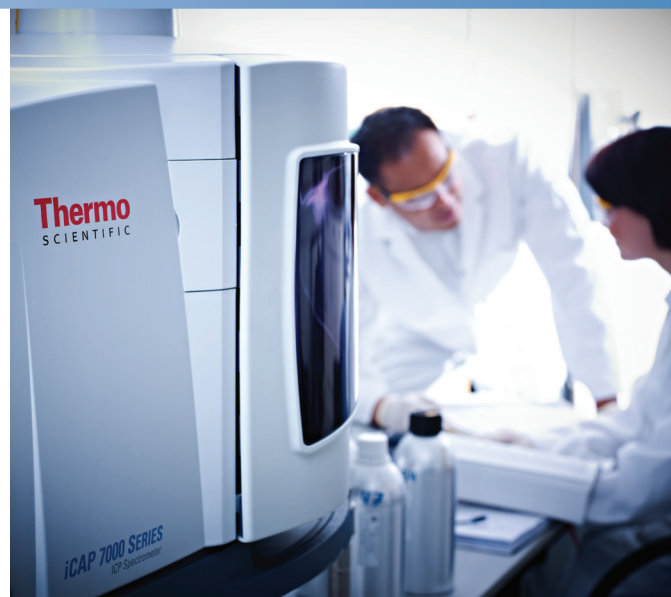
Environmental analysis, SW-846 method 6010c, US EPA

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 6010c. The iCAP 7400 ICP-OES Duo achieves short analysis times per sample whilst maintaining compliance with the protocol.

Introduction

On October 21st 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 6010c ‘Inductively Coupled Plasma-Atomic Emission Spectrometry’. This method prescribes the use of Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) instrumentation for the determination of 31 elements in ground waters, industrial and organic wastes, soils, sludges and sediments, using the Toxicity Characteristic Leaching Procedure (TCLP) or the Extraction Procedure (EP). 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 6010c 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 6010c represents an important benchmark for any ICP-OES instrument.



Instrument configuration

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 6010c. 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 below in table 1.

Table 1. Method modes and instrument parameters

Parameter		Setting
Nebulizer		Glass concentric
Spray Chamber		Glass cyclonic
Injector tube		2mm
Pump tubing (Tygon®)	Sample	1.016 mm
	Drain	1.524 mm
Nebulizer gas flow		0.7 l/min
Auxiliary gas flow		0.5 l/min
Coolant gas flow		12 l/min
RF power		1250 w
Flush time		20 secs
Pump speed		50 rpm
Exposure time	Low (166-230 nm)	15 seconds
	High (230-847 nm)	5 seconds

Sample preparation and methodology

A LabBook was setup using the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) for the analysis of a selection of elements covered by the US EPA method 6010c (table 2). Calibration standards were prepared in 6% hydrochloric acid v/v and 2% nitric acid v/v, trace metal grade (Fisher Chemicals™, Loughborough, UK) and their element concentrations were selected to cover the required measurement range of each analyte. Solid samples were digested according to US EPA method 3051a; A microwave digestion system (Ethos EZ SK10, Milestone) was used to digest $1 \text{ g} \pm 0.005 \text{ g}$ of sample in 2 ml of nitric acid and 6 ml of hydrochloric acid, this digestion extract was then made up to a final volume of 100 ml with ultra pure deionised water (18.2 MΩ).

A 5 mg/l yttrium internal standard was automatically introduced online with the mixing kit. The internal standard wavelengths were appropriately matched to analyte wavelengths for each of the viewing modes, Axial / Radial and Low range / High range. Details of the analyte wavelengths, plasma views and internal standard wavelengths selected are presented in 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	
Ba	493.409	Axial	Y 324.228	
Be	234.861	Axial	Y 324.228	
Ca	422.673	Radial	Y 371.030	
Cd	214.438	Axial	Y 224.306	
Co	238.892	Axial	Y 324.228	
Cr	357.869	Axial	Y 324.228	
Cu	224.700	Axial	Y 224.306	
Fe	259.940	Radial	Y 371.030	
K	766.490	Radial	Y 371.030	
Mg	202.582	Radial	Y 371.030	Co, Na
Mn	257.610	Axial	Y 324.228	
Na	589.592	Radial	Y 371.030	K
Ni	341.476	Axial	Y 324.228	
P	177.495	Axial	Y 224.306	
Pb	261.418	Axial	Y 324.228	Co, Fe
Sb	206.833	Axial	Y 224.306	
Se	196.090	Axial	Y 224.306	
Tl	377.572	Axial	Y 324.228	
V	292.402	Axial	Y 324.228	
Zn	213.856	Axial	Y 224.306	

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 at 200 mg/l of each of the major elements present in the samples (Al, Ca, Fe, K, Mg, Na) and 20 mg/l solutions for each of the trace elements; were analysed to check for their spectral contributions on other analytical elements. 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.

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 3.

Table 3. Method detection limits achieved

Element	Wavelength (nm)	Plasma View	MDL (µg/l)
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	0.30
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 6010c 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, calibration blank and Continuing Calibration Verification (CCV) solution were analyzed. The calibration blank readback must return a result less than 3 times the method detection limit for each element, while the calibration verification solutions must be within 10 % of the actual values. For each verification solution, the relative standard deviation of a minimum of 2 consecutive analyses must be less than 5% for the data to be acceptable. Analysis of the CCV solution and calibration blank was then repeated every 10 samples to ensure the instrument remained in calibration, the results for the first CCV are shown in table 4.

Table 4. Initial and continuing calibration verification checks (ICV & CCV)

Element	Initial Calibration Verification (ICV)		Continuing Calibration verification (CCV)	
	Measured (mg/l)	Recovery (%)	Measured (mg/l)	Recovery (%)
Al	0.504	100.9	2.463	98.5
As	0.496	99.1	2.508	100.3
Ba	0.515	103.0	2.550	102.0
Be	0.482	96.5	2.524	101.0
Ca	0.488	97.7	2.542	101.7
Cd	0.530	106.0	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	0.470	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	99.0
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	2.410	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. Interference Check Sample A (ICSA) was prepared containing 250 mg/l each of Al, Ca, Mg and 100 mg/l of Fe. Interference Check Solution AB (ICSAB) was then prepared by spiking the ICSA solution with concentrations of 0.1 to 1 mg/l for the analyte elements. The values measured for ICSAB must be within 20% of the true value for the data to be acceptable. Data is shown in table 5.

Table 5. Interference check solutions

Element	ICSA (mg/l)	ICSAB (mg/l)	Target Value (mg/l)	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

Method performance was verified by analysing two samples, a soil Certificate Reference Material (CRM) (#SQC001, lot 017309, RTC, Laramie, WY, USA) and a locally collected soil sample spiked with the equivalent of 100mg/kg for each of the trace analytes and 1000mg/kg for the major elements. The results from unspiked/spiked samples and recoveries are shown in table 6.

Table 6. Method validation checks

Element	Soil Sample			Soil CRM #SQC001		
	Unspiked Sample (mg/kg)	Spiked Sample (mg/kg)	Recovery (%)	Measured (mg/kg)	Certified value (mg/kg)	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

Conclusions

The Thermo Scientific iCAP 7400 ICP-OES Duo exceeds the requirements needed to meet the US EPA method 6010c 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 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, minimising both the cost of analysis and its environmental impact.

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