

US EPA Method 200.7 using the Thermo Scientific iCAP PRO XPS Duo ICP-OES

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Goal

This note describes the use of the Thermo Scientific iCAP PRO XPS Duo ICP-OES for the analysis of water samples using the US EPA Method 200.7.

Introduction

The analysis and monitoring of natural, produced and drinking waters is essential to ensure both human and environmental health. Levels of permissible contamination are controlled by local, national and international regulations. In the United States of America the Environmental Protection Agency (EPA) is the body responsible to set and regulate national standards for the quality of supplied drinking water and drinking water resources, such as ground waters. The EPA Office of Ground Water and Drinking Water (OGWDW) administers control under the Federal Regulation 40 CFR part 141 & 143. This regulation states that all supplied waters must comply with the Maximum Contaminant Levels (MCL) for the contaminants specified in the National Primary Drinking Water Regulations (NPDWR). Table 1 lists the MCL and Maximum Contaminant Level Goals (MCLG) that the EPA defines as the maximum level of an element in drinking water at which no known or anticipated adverse effect on the health of persons would occur. Further contaminants are given suggested maximum values in the National Secondary Drinking Water Regulations (NSDWR) as these elements will affect water properties such as taste and color (Table 2). The Unregulated Contaminant Monitoring Rule 3 (UCMR-3) requires that measurements are taken and recorded for two areas at every water treatment plant; the metals to be tested and their Maximum Reporting Limits (MRL) are shown in Table 3.

Table 1. MCLs and MCLG for the national drinking water regulations.

National primary drinking water regulations		
Contaminant	MCL (mg·L ⁻¹)	MCLG (mg·L ⁻¹)
Antimony	0.006	0.006
Arsenic	0.01	0
Barium	2.0	2.0
Beryllium	0.004	0.004
Cadmium	0.005	0.005
Chromium (total)	0.1	0.1
Copper	1.3	1.3
Lead	0.015	0
Mercury	0.002	0.002
Selenium	0.05	0.05
Thallium	0.002	0.002
Uranium	0.03	0

Table 2. MCLs for the national secondary drinking water regulations.

National secondary drinking water regulations	
Contaminant	MCL (mg·L ⁻¹)
Aluminium	0.05 - 0.2
Copper	1
Iron	0.3
Manganese	0.05
Silver	0.1
Sulphate	250
Zinc	5

Table 3. MRLs for Unregulated Contaminant Monitoring Rule 3.

Unregulated Contaminant Monitoring Rule 3 (UCMR-3)	
Contaminant	MRL (mg·L ⁻¹)
Chromium (total)	0.0002
Cobalt	0.001
Molybdenum	0.001
Strontium	0.0003
Vanadium	0.0002

The EPA Method 200.7 “Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry” is used extensively for the analysis and monitoring of a range of waters including, ground, river, drinking and waste water. The results of the analysis are used for a variety of purposes, in the case of drinking water the results are

used to ensure consumer safety and in the case of waste waters the results are to determine compliance with the permits issued within the National Pollutant Discharge Elimination System (NPDES) under the Clean Water Act (CWA) (40 CFR part 136).

Large numbers of water samples are analyzed using this method, including supplied waters, natural waters and waste waters. The method is commonly used in US States that require well water on private property to be analyzed prior to the purchase of real estate. Method 200.7 is used globally as the basis of water analysis methods by ICP-OES, particularly in regions where environmental monitoring developed later than in the US.

Method 200.7 summary

Method 200.7 describes the determination of 31 elements in water samples and suggests preferred wavelengths, calibration and quality control procedures in addition to specifying procedures for determining method performance characteristics, such as detection limits and linear ranges. A brief overview of the method procedures follows below.

Method detection limit

The method provides a protocol for determining the method detection limit (MDL). The instrument hardware and method are set up as intended for the analysis. A reagent blank solution spiked at 2-3 times the estimated instrument detection limit is subjected to seven replicate analyses. The standard deviation (SD) of the measured concentrations is determined and multiplied by 3.14 (the Student’s t value for a 99% confidence interval for 6 degrees of freedom) to calculate the MDL. It is important that contamination is kept under control, especially for environmentally abundant elements such as Al and Zn, since any contamination will degrade the MDL. Interference corrections also affect the MDL, since they employ the monitoring of additional wavelengths and propagate the measurement errors accordingly.

Linear dynamic range

The upper linear range limit of a calibration is termed the linear dynamic range (LDR). Method 200.7 defines the upper LDR to be the highest concentration at which an observed signal deviates by less than 10% from that extrapolated from lower standards. Sample dilution can facilitate the measurement of high concentrations, but with additional effort, cost and error. Therefore, a wide LDR is desirable.

Quality control

Method 200.7 specifies a variety of quality control (QC) standards. These are summarized in Table 4.

Table 4. Summary of Method 200.7 QC requirements.

Check name	Check code	Purpose	Frequency	Limits
QCS	Quality Control Standard	Checks the accuracy of the calibration with a second source standard	Post calibration	95-105% recovery
SIC	Spectral Interference Check Solution(s)	Checks for the presence of spectral interference and the effectiveness of inter-element corrections	Periodically	No specific requirements
IPC	Instrument Performance Check	A continuing check of accuracy and drift normally done by re-measuring a standard as a sample	Every 10 analyses and at the end of the run	95-105% recovery immediately following calibration; 90-110% recovery thereafter
Blank	Check Blank	A continuing check of the blank level by re-measuring the calibration blank as a sample	Every 10 analyses and at the end of the run	< IDL
LRB	Laboratory Reagent Blank	Checks the laboratory reagents and sample preparation process for contamination	1 per batch of 20 or fewer samples	< 2.2 x MDL
LFB	Laboratory Fortified Blank	Checks the recovery of analytes by spiking a known quantity into a blank	1 per batch of samples	85-115% recovery or within ± 3 standard deviations of the mean recovery
LFM	Laboratory Fortified Matrix	Checks the recovery of analytes in a matrix by spiking a known quantity into a batch sample	1 in 10 samples	85-115% recovery or within ± 3 standard deviations of the mean recovery

*<IDL: below instrument detection limit.

Instrumentation

A Thermo Scientific™ iCAP™ PRO XPS Duo ICP-OES was used for this analysis. The duo view plasma allows for elements expected at trace levels to be analyzed axially, for best sensitivity and for elements expected at high concentrations to be measured radially, for best dynamic range. In conjunction with this instrument, a Teledyne CETAC ASX-560 Autosampler was used. An internal standard mixing kit was also used to introduce a 5 mg·L⁻¹ yttrium internal standard solution online. Sample introduction details and instrument parameters are given in Table 5.

Method

A LabBook was set up using the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software for all 31 elements covered by Method 200.7. Sulfur, which is not part of Method 200.7 but is often required in this type of analysis, was also added to the method. Additionally, yttrium wavelengths were added, to be used as an internal standard. The acquisition parameters used are shown in Table 5.

Table 5. Instrument parameters.

Parameter	Setting	
Pump tubing	Sample Tygon® orange/white	
	Drain Tygon® white/white	
Pump speed	45 rpm	
Spray chamber	Glass cyclonic	
Nebulizer	Glass concentric	
Nebulizer gas flow	0.5 L·min ⁻¹	
Auxiliary gas flow	0.5 L·min ⁻¹	
Coolant gas flow	12 L·min ⁻¹	
Center tube	2 mm	
RR power	1150 W	
Repeats	3	
Radial viewing height	10 mm	
Exposure time	Axial	Radial
	10 sec	10 sec

All samples were preserved in 1.5% TraceMetal™ grade nitric acid (Fisher Chemicals, Loughborough, UK). Calibration standards and QC solutions were prepared using 1000 mg·L⁻¹ standard solutions (Fisher Chemicals, Loughborough, UK); acid matched to the samples and made up to volume with ultra-pure deionized water (≥18.2 mΩ).

Analytical procedure

A linear dynamic range (LDR) and method detection limit (MDL) study was performed as described in Method 200.7. The MDL study was performed with a reagent blank spiked with low concentrations of each element. An interference study was performed using single element SIC solutions as described in Method 200.7. To demonstrate the performance of the iCAP PRO XPS Duo ICP-OES for typical routine analysis of a variety of water samples with Method 200.7, a sequence was set up as follows:



The 10 samples analyzed between each IPC and blank pair consisted of a variety of aqueous matrices. Three sample types were analyzed, a drinking water, a trench water and a well water; each was spiked for analysis as a laboratory fortified matrix (LFM). The samples were analyzed multiple times throughout the process, replicating a run consisting of a total number of 114 samples (152 samples, including QC and calibration solutions).

Interference study

A comprehensive interference evaluation was performed using single element SIC solutions of the following concentrations: 300 mg·L⁻¹ Fe, 200 mg·L⁻¹ Al and 50 mg·L⁻¹ of each, Ba, Be, Cd, Ce, Co, Cr, Cu, Mn, Mo, Ni, Sn, Si, Ti, Tl, and V. If the apparent concentration of an interferent was above the quantification limit of the method, an inter-element correction (IEC) factor was established and applied. During this study, a few minor and only 9 significant (contribution of up to 1 mg·L⁻¹) interferences were identified in accordance with Table 2 of the annex of method 200.7, showing that the selected wavelengths are relatively interference free. The interferences observed (shown in Table 6) can easily be corrected for by applying the automatically calculated interference correction factors when necessary.

Results

Table 6. Comprehensive interference evaluation results.

Element and wavelength (nm)	SIC solution	Contribution (mg·L ⁻¹)	Element and wavelength (nm)	SIC solution	Contribution (mg·L ⁻¹)
Al 308.215	Ce	0.212	S 182.034	Mo	0.085
Al 308.215	Mo	1.314	S 182.034	Sn	0.074
Al 308.215	V	0.539	Sb 206.833	Ce	-0.111
As 193.759	Al	0.123	Sb 206.833	Cr	0.905
B 249.678	Co	0.066	Se 196.090	Fe	-0.031
Ba 455.403	Mo	-0.014	Se 196.090	Mn	0.021
Ca 315.887	Mo	0.14	Si 251.611	Mo	0.434
Co 228.616	Ti	0.109	Sn 189.989	Ce	0.009
Cu 224.700	Mo	0.058	Ti 334.941	Cr	0.01
Cu 224.700	Ti	0.015	TI 190.856	Ce	0.025
Hg 194.227	V	0.027	TI 190.856	Co	0.055
Hg 194.227	Mn	0.022	TI 190.856	V	0.040
P 177.495	Cu	0.131	V 292.402	Mo	-0.02
P 177.495	Ni	0.044	V 292.402	Ti	0.027
S 182.034	Mn	0.201	Zn 213.856	Ni	0.041

LDR

The high standards analyzed for the linear dynamic range check showed little deviation from their expected values, indicating linearity up to at least the levels indicated in Table 7. These levels are normally more than sufficient for the analysis of typical water samples.

Table 7. Analytical wavelengths, plasma views used, LDR and MDL achieved.

Analyte	Wavelength (nm)	Plasma view	LDR (mg·L ⁻¹)	MDL (µg·L ⁻¹)	Level of interest (µg·L ⁻¹)
Ag	328.608	Axial	>10	0.84	100
Al	308.215	Radial	>1000	21	50-200
As	193.759	Axial	>100	2.1	10
B	249.678	Axial	>100	1.2	N/A
Ba	455.403	Axial	>2	0.47	2000
Be	234.861	Axial	>10	0.08	4
Ca	315.887	Radial	>100	6.0	N/A
Cd	226.502	Axial	>10	0.25	5
Co	228.616	Axial	>10	0.75	1*
Cr	284.325	Axial	>10	0.29	100 / 0.2*
Cu	224.700	Axial	>10	0.51	1300
Fe	258.940	Radial	>1000	3.7	300
Hg	194.227	Axial	>100	1.0	2
K	766.490	Radial	>1000	42	N/A
Li	670.784	Radial	>100	3.3	N/A
Mg	279.079	Radial	>1000	21	N/A
Mn	257.610	Axial	>10	0.06	50
Mo	203.844	Axial	>10	0.90	1*
Na	589.592	Radial	>100	20	N/A
Ni	231.604	Axial	>10	0.85	N/A
P	177.495	Axial	>10	2.5	N/A
Pb	220.353	Axial	>100	3.2	15
SO ₄	182.034	Axial	>300	16.5	250000
Sb	206.833	Axial	>100	3.3	5
Se	196.090	Axial	>10	4.8	50
SiO ₂	251.611	Radial	>2000	11.8	N/A
Sn	189.989	Axial	>10	0.73	N/A
Sr	421.552	Axial	>1	0.02	0.3*
Ti	334.941	Axial	>10	0.61	N/A
Tl	190.856	Axial	>10	1.8	2
V	292.402	Axial	>10	0.50	0.2*
Zn	213.856	Axial	>2	0.02	5000

*Maximum report limit required for UMCR-3.

N/A: value not available

MDL

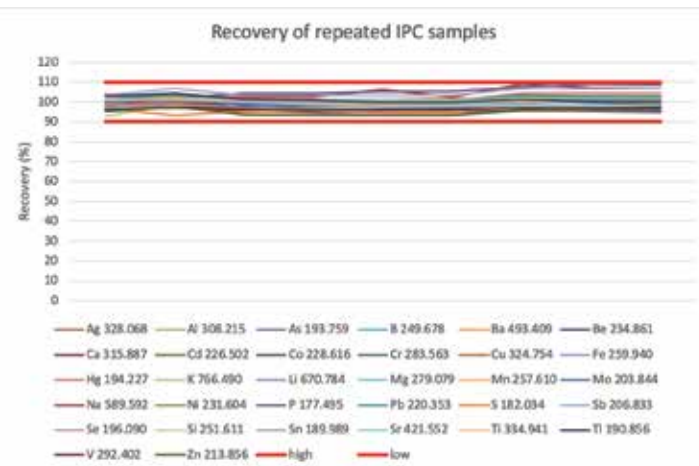
The method detection limits calculated from analysis of the MDL solution were generally in the low and sub $\mu\text{g}\cdot\text{L}^{-1}$ range for the majority of elements. All MDLs were sufficiently below the typical levels of interest for drinking water analysis according to National Primary and Secondary Drinking Water Regulations, with the exception of aluminium, antimony, mercury and thallium. The MDLs for these elements were of the same magnitude as the level of interest. For this reason ICP-MS, such as delivered by the Thermo Scientific™ iCAP™ RQ ICP-MS may be a more appropriate alternative for the regulatory drinking water measurements for these elements.

Accuracy, precision and stability

The iCAP PRO XPS Duo ICP-OES produced consistently accurate results with minimal intensity drift, as shown by the results for the QCS and IPC solutions (see Table 8). The ongoing IPC results were consistently within the allowed range of 90-110% of the known value, as shown in Figure 1. The precision of the 9 IPC measurements across the 150 sample run were also shown to be very good. Table 8 indicates that the relative standard deviations (RSDs) of these measurements were within 5% across the duration of the run.

Table 8. QCS and IPC results.

Analyte	QCS			IPC (n=9)			
	Measured ($\text{mg}\cdot\text{L}^{-1}$)	Known ($\text{mg}\cdot\text{L}^{-1}$)	Recovery (%)	Measured ($\text{mg}\cdot\text{L}^{-1}$)	Known ($\text{mg}\cdot\text{L}^{-1}$)	Recovery (%)	RSD (%)
Ag	0.207	0.2	103.5	0.201	0.2	100.5	1.7
Al	0.998	1	99.8	1.989	2	99.5	1.1
As	9.828	10	98.3	1.917	2	95.9	1.8
B	9.869	10	98.7	2.009	2	100.5	0.7
Ba	0.980	1	98.0	2.009	2	100.5	1.5
Be	1.473	1.5	98.2	1.964	2	98.2	0.7
Ca	97.964	100	98.0	1.914	2	95.7	0.9
Cd	0.957	1	95.7	2.011	2	100.6	1.3
Co	0.967	1	96.7	2.014	2	100.7	1.0
Cr	1.012	1	101.2	2.039	2	102.0	0.8
Cu	0.998	1	99.8	1.981	2	99.1	0.5
Fe	9.803	10	98.0	2.001	2	100.1	0.5
Hg	0.976	1	97.6	2.052	2	102.6	1.8
K	5.029	5	100.6	9.598	10	96.0	2.3
Li	2.088	2	104.4	2.004	2	100.2	2.7
Mg	0.971	1	97.1	2.019	2	101.0	1.2
Mn	0.985	1	98.5	1.996	2	99.8	0.8
Mo	0.989	1	98.9	1.963	2	98.2	1.6
Na	1.001	1	100.1	2.085	2	104.3	3.4
Ni	0.980	1	98.0	2.035	2	101.8	1.1
P	5.071	5	101.4	2.106	2	105.3	2.7
Pb	0.976	1	97.6	2.044	2	102.2	1.3
SO ₄	61.84	60	103.1	5.78	6	96.3	2.2
Sb	0.986	1	98.6	1.984	2	99.2	1.1
Se	9.664	10	96.6	1.923	2	96.2	1.8
SiO ₂	2.14	2.14	100.0	21.68	21.4	101.3	0.5
Sn	0.950	1	95.0	2.099	2	105.0	1.6
Sr	1.983	2	99.2	1.953	2	97.7	0.7
Ti	0.983	1	98.3	2.008	2	100.4	0.7
Tl	1.009	1	100.9	2.023	2	101.2	1.6
V	0.983	1	98.3	1.935	2	96.8	0.6
Zn	1.022	1	102.2	1.898	2	94.9	1.5



The accurate results for the LFM samples (shown in Table 9) show that quantitative recovery can be achieved in a variety of real environmental matrices. All spike recoveries were well within the allowable range of 85-115%.

Figure 1. Recovery graph of successive IPC measurements for all analyzed elements during the 114 sample analyses with the accuracy interval of 90-110% indicated as high and low.

Table 9. Laboratory fortified matrix results.

Analyte	Drinking water			Trench water			Well water			Laboratory fortified blank		
	Unspiked (mg·L ⁻¹)	Spiked (mg·L ⁻¹)	Recovery (%)	Unspiked (mg·L ⁻¹)	Spiked (mg·L ⁻¹)	Recovery (%)	Unspiked (mg·L ⁻¹)	Spiked (mg·L ⁻¹)	Recovery (%)	Unspiked (mg·L ⁻¹)	Spiked (mg·L ⁻¹)	Recovery (%)
Ag	<MQL	0.097	97.0	<MQL	0.087	87.0	<MQL	0.107	107.0	<MQL	0.104	104.0
Al	<MQL	1.999	100.0	<MQL	1.999	100.0	<MQL	1.958	97.9	<MQL	2.085	104.3
As	<MQL	0.200	100.0	<MQL	0.203	101.5	<MQL	0.203	101.5	<MQL	0.195	97.5
B	<MQL	0.224	112.0	0.167	0.364	98.5	0.116	0.314	99.0	<MQL	0.198	99.0
Ba	0.017	0.215	99.0	0.066	0.255	94.5	0.246	0.440	97.0	<MQL	0.209	104.5
Be	<MQL	0.206	103.0	<MQL	0.206	103.0	<MQL	0.215	107.5	<MQL	0.206	103.0
Ca	40.52	42.43	95.5	49.92	57.39	99.6	46.20	53.66	99.5	<MQL	1.950	97.5
Cd	<MQL	0.199	99.5	<MQL	0.196	98.0	0.001	0.199	99.0	<MQL	0.203	101.5
Co	<MQL	0.195	97.5	<MQL	0.191	95.5	<MQL	0.193	96.5	<MQL	0.199	99.5
Cr	<MQL	0.202	101.0	<MQL	0.200	100.0	<MQL	0.199	99.5	<MQL	0.207	103.5
Cu	0.024	0.319	98.3	<MQL	0.291	97.0	0.007	0.296	96.3	<MQL	0.301	100.3
Fe	0.045	0.239	97.0	1.360	8.701	97.9	27.40	34.82	98.9	<MQL	0.202	101.0
Hg	<MQL	0.196	98.0	<MQL	0.196	98.1	<MQL	0.197	98.5	<MQL	0.198	99.0
K	2.747	7.795	101.0	12.56	15.31	110.0	1.401	4.116	108.6	<MQL	4.311	86.2
Li	<MQL	0.231	115.5	0.018	0.225	103.5	0.013	0.226	106.5	<MQL	0.207	103.5
Mg	4.271	11.60	97.7	7.863	14.95	94.5	6.953	14.02	94.2	<MQL	7.777	103.7
Mn	0.003	0.201	99.0	0.065	0.256	95.5	2.583	2.790	103.5	<MQL	0.204	102.0
Mo	<MQL	0.194	97.0	<MQL	0.194	97.0	<MQL	0.194	97.0	<MQL	0.193	96.5
Na	14.24	19.67	108.6	145.31	170.8	102.0	92.85	118.3	101.8	<MQL	1.535	102.3
Ni	<MQL	0.197	98.5	<MQL	0.194	97.0	<MQL	0.195	97.5	<MQL	0.203	101.5
P	0.015	1.644	108.6	0.102	1.730	108.5	1.185	2.742	103.8	<MQL	1.696	113.1
Pb	<MQL	0.197	98.5	<MQL	0.192	96.0	0.077	0.266	94.5	<MQL	0.204	102.0
SO ₄	40.43	43.82	113.2	77.69	93.13	103.1	1.295	16.80	103.5	<MQL	2.864	95.6
Sb	<MQL	0.200	100.0	<MQL	0.195	97.5	<MQL	0.197	98.5	<MQL	0.194	97.0
Se	<MQL	0.193	96.5	<MQL	0.193	96.5	<MQL	0.194	97.0	<MQL	0.189	94.5
SiO ₂	20.05	22.39	109.4	15.82	21.88	113.3	26.14	32.07	110.9	<MQL	0.412	100.1
Sn	<MQL	0.201	100.5	<MQL	0.196	98.0	<MQL	0.200	100.0	<MQL	0.206	103.0
Sr	0.129	0.324	97.5	0.362	0.539	88.5	0.466	0.645	89.5	<MQL	0.211	105.5
Ti	<MQL	0.193	96.5	<MQL	0.193	96.5	<MQL	0.193	96.5	<MQL	0.205	102.5
Tl	<MQL	0.294	98.0	<MQL	0.281	93.7	<MQL	0.283	94.3	<MQL	0.301	100.3
V	<MQL	0.198	99.0	<MQL	0.198	99.0	<MQL	0.197	98.5	<MQL	0.201	100.5
Zn	0.0009	0.22	109.6	0.0013	0.22	109.4	0.282	0.48	99.0	<MQL	0.218	109.0

*<MQL: measured concentration below method quantification limit (MQL = 3 x MDL).

Conclusion

The Thermo Scientific iCAP PRO XPS Duo ICP-OES demonstrated compliance with the requirements of EPA Method 200.7 for a wide range of water sample types. The instrument was successfully used to follow stringent analytical quality control requirements of the method, these were easily implemented in the LabBook by the built-in QC checking capability of the Qtegra ISDS Software which is designed to meet the requirements of EPA methods.

In this study, the full wavelength range was covered for both, axial and radial view, keeping analysis time to a minimum. For trace elements, ideal detection limits are established in the axial view while matrix elements are analyzed in radial view so that the full potential of the linear dynamic range is used. This reduces the need for sample reruns and dilution and improves overall productivity of high throughput laboratories. Detection limits may even be further improved utilizing eUV (enhanced UV) capabilities of the iCAP PRO XPS ICP-OES, which improves detection limits in the UV region by up to 20%.

The compact high transmission optical design and non-blooming CID detector produce optimum performance, as indicated by the excellent method detection limits obtained. The optimized vertical torch interface combined with the high resolution optics minimizing physical and spectral interferences as demonstrated by the interference study, making the iCAP PRO Series ICP-OES ideal for analyzing waters and other environmental sample types.

The productivity tools of Qtegra ISDS Software combined with the speed of the iCAP PRO XPS ICP-OES drive rapid analysis times. Samples in this study were processed at a speed of 1 sample every 1 minutes and 58 seconds, or 30 samples per hour. In addition, an external discrete sampling valve could be used to speed up the sample uptake time even further and therefore increase sample throughput. The system also incorporates fast start up ensuring the system is purged and stable within minutes to allow for maximum instrument utilization during a working day. These combined features make the iCAP PRO XPS ICP-OES the ultimate instrument for cost-effective elemental analysis.

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