



EU water analysis using the Thermo Scientific iCAP 7400 ICP-OES Duo

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Goal

This application note describes the trace elemental water analysis requirements of laboratories within the European Union (EU) and how the Thermo Scientific iCAP 7400 ICP-OES Duo can be used to perform this analysis simply but to high quality standards.

Introduction

Within the EU, there are 3 types of water samples that require analysis; drinking waters, natural waters and waste waters. Each of these water types is regulated by different legislations under both European and national laws. These regulations are summarized below.

Drinking water

Drinking water analysis is performed under the guidelines of EU directive (98/83/EC) which provides maximum contaminant levels (MCL) for water to be deemed as safe for human consumption. The required MCL limits are shown in Table 1. This legislation is EU wide and requires individual member states to make provision for the required analysis. The regulation mandates for two groups of analytes; chemical parameters which are deemed toxic or hazardous to health, and indicator parameters which affect the taste, smell or quality of water.



Table 1. MCL of chemical parameters in drinking water under EU Directive 98/83/EC.

Chemical parameters	
Element	Limit (mg·L ⁻¹)
Arsenic	0.01
Antimony	0.005
Boron	1
Cadmium	0.005
Chromium	0.05
Copper	2
Lead	0.01
Mercury	0.001
Nickel	0.02
Selenium	0.01

Table 2. MCL of indicator parameters in drinking water under EU Directive 98/83/EC.

Indicator parameters	
Element	Limit (mg·L ⁻¹)
Aluminium	0.2
Iron	0.2
Manganese	0.05
Sulfate	250
Sodium	200

Natural waters

Natural waters cover samples from any body of water including, lakes, rivers, reservoirs and coastal waters. The requirement for analysis of these bodies of water falls under the EU Water Framework Directive (WFD) (2000/60/EC), whereby individual member states are responsible for the analysis, maintenance and cleaning of these waters, as required. The WFD demands that all bodies of water within the EU be classified as either 'good' or 'high' by 2015 (some bodies of water are exempt from the 2015 deadline). If this first deadline is not met, extra time can be given to take additional measures in order to reach the objectives at the latest in 2027. The directive lists 20 specific pollutants and 33 priority substances shown to be of major concern for European Waters; 11 of the priority substances were identified as priority hazardous substances and therefore subject to cessation or phasing out of discharges, emissions and losses. 4 of the priority substances and 6 of the specific pollutants are suitable for analysis by trace elemental analysis techniques, for which the requirement for 'good' or 'high' classification status are the same. 'High' status is derived by other analytes, such as alkalinity, biological oxygen demand (BOD) and temperature.

Environmental quality standards (EQS) for waters to be classed as 'good' or 'high', including annual averages (AA) and maximum contaminant concentrations (MAC) are stated in Directive 2008/105/EC. The AA is the mean value of all samples taken over a 12 month period and the MAC is the upper allowable limit for any individual sample. The established EQS for priority substances and specific pollutants are shown in Table 3.

Table 3. EQS for priority substances listed under EU Directive 2000/60/EC.

Element	Hardness as CaCO ₃ mg·L ⁻¹	Annual Average (AA)		Maximum Allowable Concentration (MAC) (µg·L ⁻¹)
		All inland surface waters (µg·L ⁻¹)	All other surface waters (µg·L ⁻¹)	
Cd (PHS)	0 – 40	<0.08		<0.45
	40 – 50	0.08		0.45
	50 – 100	0.09	0.2	0.6
	100 – 200	0.15		0.9
	>200	0.25		1.5
Hg (PHS)	n/a	0.05		0.07
Ni	n/a	4	8.6	34
Pb	n/a	1.2	1.3	14

* Priority Hazardous Substance (PHS)

Table 4. EQS for specific pollutants listed under EU Directive 2000/60/EC.

Element	Hardness as CaCO ₃ mg·L ⁻¹	Annual Average (AA)	
		Rivers and fresh water lakes (µg·L ⁻¹)	Transitional and coastal waters (µg·L ⁻¹)
As	n/a	50	25
Cr III	n/a	4.7	n/a
Cr IV	n/a	3.4	0.6
Cu	0-50	1	
	50-100	6	5
	100-250	10	
	>250	28	
Fe	n/a	1000	1000
Zn	0-50	8	
	50-100	50	40
	100-250	75	
	>250	125	

Waste waters

There are currently no European wide guidelines or legislation concerning the disposal and cleaning of waste waters. The environmental agencies and departments of each member state e.g. Environment Agency (EA) in the UK, Agence de l'Environnement et de la Maîtrise de l'Energie (ADEME) in France, Umweltbundesamt (UBA) in Germany etc., are responsible for the legislation, regulation and governance of domestic, commercial and industrial waste waters. Due to the wide and varying range of legislation, the elements selected for analysis in this application note are those covered by the Environment Agency's Monitoring Certification Scheme (MCERTS) certification required in the United Kingdom.

Instrumentation

The Thermo Scientific™ iCAP™ 7400 ICP-OES Duo instrument was used for this mixed analysis of water samples. The Duo instrument was selected as the axial plasma view allows for best sensitivity and detection limits, while the radial plasma view can be used for an increased linearity. A standard aqueous sample introduction kit was used, the components can be seen in Table 6.

Sample preparation

Three water samples were sourced locally to represent each of the sample types, a drinking water, natural (river) water and waste water. These samples were passed through a 0.45 µm filter and preserved with concentrated nitric acid (TraceMetal™ grade, Fisher Chemicals, Loughborough, UK) to contain a final concentration of 2% v/v. Calibration standards were prepared using single element 1000 mg·L⁻¹ stock solutions (Fisher Chemicals, Loughborough, UK), in order to match the required range of analysis. Quality control standards were prepared from independently sourced 1000 mg·L⁻¹ solutions (SPEX CertiPrep®). These solutions were acid matched to the preserved samples and their final concentrations can be seen in Table 5.

Table 5. Calibration standards and quality control solution concentrations.

Solution name	STD 0	STD 1	STD 2	STD 3	STD 4	STD 5	STD 6	Initial Calibration Verification (ICV)	Continuing Calibration Verification (CCV)
Concentration (mg·L ⁻¹)	0	0.001	0.01	0.1	1	10	100	1	5
Elements	n/a	As, Cd, Hg, Pb, Sb, Se	Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, S, Sr, Ti				Ca, Fe, K, Mg, Na, S	Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, S, Sr, Ti, Tl, V, Zn	

Method development

Method development is an easy step when using the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software. A LabBook was set up using the acquisition parameters also given in Table 6.

Table 6. Instrument and acquisition parameters.

Parameter	Setting
Pump Tubing (Standard Pump)	Sample Tygon® orange/white Drain Tygon® white/white
Spray Chamber	Glass cyclonic
Nebulizer	Glass concentric
Center Tube	2.0 mm
Pump Speed	50 rpm
Nebulizer Gas Flow	0.5 L·min ⁻¹
Auxiliary Gas Flow	0.5 L·min ⁻¹
Coolant Gas Flow	12 L·min ⁻¹
RF Power	1150 W
Exposure Time	UV 10 s, Vis 5 s

The analytical wavelengths, plasma views and internal standard wavelengths used can be seen in Table 7, along with the method detection limits (MDL) achieved. The MDLs were calculated by analyzing a blank with seven replicates and multiplying the standard deviation by 3, this was performed over 3 days and an average taken. Internal standard wavelengths were matched to analyte wavelengths by viewing mode (axial/radial view and ultraviolet/visible emissions).

Table 7. Acquisition parameters and MDL.

Element	Wavelength (nm)	Plasma view	Internal standard (nm)	MDL ($\mu\text{g}\cdot\text{L}^{-1}$)
Ag	328.068	Axial	Y 371.030	0.85
Al	396.152	Radial	Y 371.030	15
As	189.042	Axial	Y 224.306	2
B	208.959	Axial	Y 224.306	0.69
Ba	455.403	Radial	Y 371.030	0.38
Be	313.042	Axial	Y 371.030	0.038
Ca	422.673	Radial	Y 371.030	19
Cd	226.502	Axial	Y 224.306	0.18
Co	228.616	Axial	Y 224.306	0.34
Cr	267.716	Axial	Y 371.030	0.57
Cu	324.754	Axial	Y 371.030	0.69
Fe	259.940	Radial	Y 371.030	4.7
Hg	194.227	Axial	Y 224.306	0.8
K	766.490	Radial	Y 371.030	60
Mg	279.553	Radial	Y 371.030	0.16
Mn	259.373	Axial	Y 371.030	0.094
Mo	202.030	Axial	Y 224.306	0.41
Na	589.592	Radial	Y 371.030	17
Ni	221.647	Axial	Y 224.306	0.34
Pb	220.353	Axial	Y 224.306	0.7
Sb	206.833	Axial	Y 224.306	2.7
Se	196.090	Axial	Y 224.306	6.6
Sn	189.989	Axial	Y 224.306	0.81
S as SO ₄	180.731	Axial	Y 224.306	9.7
Sr	407.771	Radial	Y 371.030	0.16
Ti	334.941	Axial	Y 371.030	0.39
Tl	190.856	Axial	Y 224.306	2.4
V	309.311	Axial	Y 371.030	0.27
Zn	213.856	Axial	Y 224.306	0.19

When comparing these detection limits with the regulated limits for drinking and natural water, this method is appropriate for all elements, with the exception of Cd and Hg in natural waters, under the WFD (2000/60/EC). For this analysis an alternative technique should be used, such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS), as provided by the Thermo Scientific™ iCAP™ RQ ICP-MS.

Results

A batch of samples was created to analyze each of the sample types in duplicate. Each of the samples was spiked at 20% of the highest concentration standard and was analyzed beside quality control standards. This analytical sequence was analyzed seven times over a period of 4 days, as required by international standard ISO/IEC 17025:2005 (general requirements for the competence of testing and calibration laboratories). The sample list is detailed in Table 8.

Table 8. Analytical sequence of sample list.

Initial Calibration Blank (ICB)
Initial Calibration Verification (ICV)
Drinking water A
Drinking water B
Drinking water spike A
Drinking water spike B
River water A
River water B
River water spike A
River water spike B
Waste water A
Waste water B
Waste water spike A
Waste water spike B
Continuing Calibration Blank (CCB)
Continuing Calibration Verification (CCV)

The calculated mean results for the ICV and CCV quality control samples are shown in Table 9. The precision, expressed as relative standard deviation and the bias, expressed in percentage terms, are also shown. All elements displayed a precision of less than 5% and a bias within 10%, which is well within the requirements of ISO/IEC 17025:2005 and MCERTS accreditation.

Table 10 shows the mean results of each sample and spike, along with the element recoveries. The spike recoveries were within 10% for all elements and sample types.

Table 9. Mean, precision and bias of quality control samples.

Element	Mean ICV n=7 (mg·L ⁻¹)	Precision (%)	Bias (%)	Mean CCV n=7 (mg·L ⁻¹)	Precision (%)	Bias (%)
Ag	1.001	4.6	0.1	4.771	3.1	-4.6
Al	0.955	3.4	-4.5	4.675	2.4	-6.5
As	0.983	2.8	-1.7	4.722	2.8	-5.6
B	1.025	3.2	2.5	4.797	4.1	-4.1
Ba	0.966	4.2	-3.4	4.673	2.3	-6.5
Be	1.082	3.4	8.2	4.963	3.9	-0.7
Ca	0.998	2.6	-0.2	5.1	4.8	2
Cd	1.022	2	2.2	4.809	2.5	-3.8
Co	1.013	2.2	1.3	4.769	2.2	-4.6
Cr	0.985	3.2	-1.5	4.711	1.8	-5.8
Cu	0.99	2.7	-1	4.841	3.8	-3.2
Fe	1.001	1.6	0.1	4.869	3.2	-2.6
Hg	1.067	4.3	6.7	5.34	3.3	6.8
K	1.004	4.1	0.4	4.825	3.5	-3.5
Mg	1.02	3	2	5.34	3.7	6.8
Mn	1.039	2.2	3.9	4.865	1.3	-2.7
Mo	0.994	1.4	-0.6	4.74	3.7	-5.2
Na	1.031	2.9	3.1	4.93	3.9	-1.4
Ni	1.021	1.9	2.1	4.783	4.4	-4.3
Pb	1.039	1.7	3.9	4.807	0.4	-3.9
Sb	0.985	0.7	-1.5	4.756	2.6	-4.9
Se	0.999	3.3	-0.1	4.751	4	-5
Sn	1.016	0.3	1.6	4.775	1.7	-4.5
SO ₄	3.005	2.3	0.2	14.55	1.1	-3
Sr	0.997	0.8	-0.3	4.832	3.5	-3.4
Ti	1.001	0.6	0.1	4.817	2.5	-3.7
Tl	1.059	1.3	5.9	4.891	2.7	-2.2
V	0.974	0.7	-2.6	4.79	1.1	-4.2
Zn	1.041	1.1	4.1	4.884	4.3	-2.3

Table 10. Mean, spike and recovery of samples.

Element	Drinking water (n=14)			River water (n=14)			Waste water (n=14)		
	Neat (mg·L ⁻¹)	Spiked (mg·L ⁻¹)	Recovery (%)	Neat (mg·L ⁻¹)	Spiked (mg·L ⁻¹)	Recovery (%)	Neat (mg·L ⁻¹)	Spiked (mg·L ⁻¹)	Recovery (%)
Ag	-0.001	1.868	93.4	0	1.866	93.3	0.001	1.872	93.5
Al	-0.005	1.907	95.6	0.007	1.888	94.1	0.43	2.422	99.6
As	0.003	2.058	102.8	0.002	2.09	104.4	0.008	2.015	100.4
B	0.015	2.079	103.2	0.053	2.044	99.6	0.034	1.92	94.3
Ba	0.068	1.903	91.8	0.049	1.936	94.4	0.06	1.868	90.4
Be	0	2.169	108.4	0	2.16	108	0	2.159	107.9
Ca	96.4	115.9	97.4	119.6	139.3	98.3	104.7	123.6	94.8
Cd	0	2.039	102	0	2.002	100.1	0	1.883	94.2
Co	0	1.956	97.8	0	1.929	96.5	0.002	1.829	91.3
Cr	-0.001	1.935	96.8	-0.001	1.949	97.5	0.001	1.839	91.9
Cu	0.448	2.275	91.3	0.005	1.95	97.3	0.054	1.861	90.3
Fe	0.012	19.68	98.4	0.01	19.78	98.9	0.307	18.98	93.4
Hg	0	1.86	93	0	1.916	95.8	0	1.941	97
K	2.15	23.77	108.1	7.092	28.55	107.3	15.99	35.36	96.9
Mg	3.981	23.39	97	6.786	25.63	94.2	5.174	24.7	97.6
Mn	0	2.043	102.2	0.002	2.061	103	0.508	2.392	94.2
Mo	0	1.999	100	0.001	1.977	98.8	0	1.919	95.9
Na	11.36	32.93	107.9	33.54	53.12	97.9	140.7	161.2	102.3
Ni	0.009	1.971	98.1	0.004	1.94	96.8	0.015	1.837	91.1
Pb	0.004	1.97	98.3	0.001	1.916	95.8	0.007	1.891	94.2
Sb	0	2.014	100.7	-0.001	1.989	99.5	-0.001	1.889	94.5
Se	-0.003	2.182	109.3	0.003	2.168	108.2	0.007	2.192	109.2
Sn	-0.001	1.999	100	-0.001	1.955	97.8	0.003	1.807	90.2
SO ₄	30.01	88.62	97.7	79.03	136	95	279.3	337.1	96.2
Sr	0.312	2.328	100.8	0.548	2.485	96.8	0.235	2.378	107.2
Ti	-0.002	2.011	100.6	-0.002	2.028	101.5	0.015	1.908	94.7
Tl	0	1.975	98.7	0	1.915	95.8	-0.009	1.86	93.5
V	0.008	2.023	100.7	0.015	2.047	101.6	0.012	1.939	96.3
Zn	0.232	2.253	101.1	0.002	2.122	106	0.04	2.014	98.7

Conclusion

The data acquired from this method demonstrate the performance of the Thermo Scientific iCAP 7000 Plus Series ICP-OES instruments in analyzing water samples within the required regulations, with the exception of cadmium and mercury in natural waters under the EU Water Framework Directive (2000/60/EC). Both cadmium and mercury would typically be analyzed by ICP-MS.

The high resolution spectrometer along with the user-friendly Inter-Element Correction (IEC) function of Qtegra ISDS Software means that all interferences are either removed or compensated for automatically. This allows for simplified routine analysis and high confidence in results. The intelligent uptake and rinse function can be used to optimize uptake and washout times on a sample to sample basis, minimizing both analysis time and carryover effects.

The spike recovery data demonstrates that this method can be used to perform the analysis of all water sample types in a single sequence, without the need to optimize individual methods. The precision and bias requirements, for laboratory accreditation, can be met easily with the minimum of method development time. Qtegra ISDS Software can automatically control and perform the QC procedures required for compliance with ISO/IEC 17025:2005 and Good Laboratory Practice (GLP).

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