APPLICATION NOTE

U. S. EPA Method 200.7 - Wastewater Analysis for Trace Metals Using an Auto-Dilution System Coupled to the Thermo Scientific iCAP 7000 Plus Series ICP-OES

Sanja Asendorf, Application Specialist,
Thermo Fisher Scientific,
Bremen, Germany

Key Words

Auto-dilution, Calibration Range, Effluent Guidelines, EPA Method 200.7, Wastewater Analysis, Wastewater Regulations

Goal

To demonstrate the ability of the Thermo Scientific iCAP 7000 Plus Series ICP-OES to analyze high concentrated wastewater samples and the coupling of an auto-dilution system for intelligent dilution of samples that are outside the calibration range.

Wastewater Regulations

In addition to drinking water analysis, U. S. EPA method 200.7 is also used extensively for wastewater analysis for regulatory compliance required by the Clean Water Act (CWA) (40 CFR part 136). Wastewater regulations are much more complex compared to drinking water regulations, as the sources of wastewater depend upon the type of industry and municipality. After proper treatment, industrial wastewater is either directly discharged to surface waters with permits from National Pollutant Discharge Elimination System (NPDES) (direct discharge), or is discharged to a publicly owned treatment works (POTW) regulated under the National Pretreatment Program (indirect discharge). To regulate wastewater discharge, the EPA set daily maximum and monthly average discharge amounts for contaminants in Effluent Guidelines, based on industries and treatment types. Other countries have different wastewater regulations, but with the same goal: reduction of pollutants discharge into surface waters.

EU wastewater regulations are regulated in the Urban Wastewater Treatment Directive (UWTD) and Integrated Pollution and Control (IPC) Directive, both under EU Water Framework Directive (WFD). The German wastewater regulation (Abwasserverordnung – AbwV) incorporates various EU directives concerning discharge limits for pollutants to reduce environmental pollution. Unlike wastewater discharge regulations required by CWA in the U.S., the German AbwV does not differentiate between direct and indirect discharge. Both have to comply with the set requirements for the individual industry branch or communal wastewater.

In this application note, the Effluent Limitation Guidelines for Centralized Waste Treatment (40 CFR Part 437) were chosen as a baseline because of its wide applicability for different wastewaters polluted with elemental contaminants. It applies to wastewater discharges coming from centralized waste treatment facilities which accept hazardous or non-hazardous industrial wastes. As wastewaters can contain a high concentration and a wide range of elemental contaminants, intelligent auto-dilution offers a cost-effective and time-saving alternative to tedious manual redilutions of samples outside the calibration range. In Table 1 the combined maximum concentrations of 15 elements allowed for daily direct discharge are outlined.

Table 1. Maximum concentration of 15 elements allowed for daily direct discharge according to 40 CFR Part 437.

Analyte	Maximum Concentration mg·L⁻¹	Analyte	Maximum Concentration mg·L⁻¹
Ag	0.0122	Pb	0.16
As	0.0199	Sb	0.0312
Cd	0.0102	Se	0.0351
Co	0.0703	Sn	0.0367
Cr	0.0522	Ti	0.00612
Cu	0.216	V	0.0518
Hg	0.000246	Zn	0.252
Ni	0.309		

ICP-OES and Auto-dilution
For the sample analysis, the Thermo Scientific™ iCAP™ 7400 ICP-OES Duo was used with an aqueous sample introduction kit, consisting of a concentric glass nebulizer and a cyclonic glass spray chamber as well as a 2 mm injector tube.

The duo configuration was chosen for its ability to detect trace elements in the axial view and for its wide dynamic range which can be extended with the radial view. A Teledyne CETAC SDX High Performance Liquid Dilution System (HPLD) (Figure 1) was used to transfer the sample to the introduction system of the ICP-OES and to carry out automatic prescriptive and intelligent dilutions, respectively. The Thermo Scientific Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software was used for data acquisition and provides easy options for post-analysis data manipulation.

Figure 1. Teledyne CETAC SDX High Performance Liquid Dilution (HPLD) system.

Sample Preparation
All calibration and spike solutions were prepared from 1000 µg·g⁻¹ single element solutions provided by Spex CertiPREP (SPEX CertiPrep Group, Metuchen, US). The individual solutions were made up with 18 MΩ ultra-pure water and trace metal grade HNO_3 (67-69%, Fisher Chemical, Loughborough, UK) to a final concentration of 1% HNO_3 for each solution. To account for physical interferences due to differing contents of matrix components, an internal standard solution of yttrium (10 µg·g⁻¹) was added online to all solutions via a Y-piece. A certified reference material (EnviroMAT™ Wastewater EU-H, SPC Science, Baie D'Urfé, Canada) was analyzed to validate the accuracy of the method. To obtain the accuracy for the missing elements Ag, Sn, and Ti as well, the reference material was spiked with 1 µg·g⁻¹ of each of these three elements.

A multi element stock calibration solution was prepared according to the concentrations shown in Table 2 and diluted via the SDX HPLD auto-dilution system.

Table 2. Auto-dilution factors and concentrations of calibration standards in µg·g^{-1}.

Element	Stock solution	Standard 1	Standard 2	Standard 3	Standard 4
Auto-dilution factor		100	10	5	1
Ag	50	0.5	5	10	50
Al	100	1	10	20	100
As	50	0.5	5	10	50
B	50	0.5	5	10	50
Ba	100	1	10	20	100
Cd	50	0.5	5	10	50
Co	50	0.5	5	10	50
Cr	50	0.5	5	10	50
Cu	50	0.5	5	10	50
Fe	100	1	10	20	100
Ni	50	0.5	5	10	50
P	500	5	50	100	500
Pb	50	0.5	5	10	50
Sb	50	0.5	5	10	50
Se	50	0.5	5	10	50
Sn	50	0.5	5	10	50
Ti	50	0.5	5	10	50
Tl	50	0.5	5	10	50
V	50	0.5	5	10	50
Zn	50	0.5	5	10	50

Method Development and Analysis

A method was created in Qtegra ISDS Software. The wavelengths used for analysis are shown in Table 4, these were selected as they were free from interferences and provided the sensitivity to quantify the elements of interest in the expected concentration range. Additionally, yttrium wavelengths were added to be used as an internal standard. The parameters used for the method can be found in Table 3. The plasma was ignited and the instrument allowed to warm up for a period of 15 minutes. A spectrometer optimization was performed directly before analysis.

A linear dynamic range (LDR) and method detection limit (MDL) study was performed for elements combined from the Effluent Guidelines and those present in the reference material as described in EPA method 200.7. For the MDL seven replicates of a reagent blank spiked with matrix elements were measured. No major spectral interferences were found during analysis.

Table 3. Method parameters.

Parameter	Setting	
Pump tubing	Sample Tygon™ white/white Drain Tygon™ blue/yellow Internal standard Tygon™ orange/green	
Pump speed	50 rpm	
Spray chamber	Glass cyclonic	
Nebulizer	Glass concentric	
Nebulizer gas flow	0.5 L·min^{-1}	
Coolant gas flow	12 L·min^{-1}	
Auxiliary gas flow	0.5 L·min^{-1}	
Center tube	2 mm	
RF Power	1150 W	
Wash time	60 s	
Exposure time	Axial view	Radial view
	UV 15 s, Vis 5 s	Vis 5 s

Table 4. Analytical wavelength, plasma view and internal standard used for the analysis, as well as linear dynamic range (LDR) and achieved versus required method detection limit (MDL) for each element.

Element and wavelength (nm)	View	Internal standard wavelength (nm)	LDR ($\mu g \cdot g^{-1}$)	MDL ($ng \cdot g^{-1}$)	Required MDL ($ng \cdot g^{-1}$)
Ag 328.068	Axial	Y 377.433	> 10	0.7	4
Al 396.152	Radial	-	> 100	57	667
As 189.042	Axial	Y 224.306	> 50	0.3	7
B 208.959	Axial	Y 360.073	> 10	2.1	1000
Ba 455.403	Radial	Y 377.433	> 100	2.3	667
Cd 228.802	Axial	Y 224.306	> 10	1.1	3
Co 228.616	Axial	Y 360.073	> 50	0.6	23
Cr 284.325	Axial	Y 371.030	> 50	3.8	17
Cu 324.754	Axial	Y 224.306	> 50	3.2	33
Fe 259.940	Radial	-	> 100	16	1000
Ni 231.604	Axial	Y 224.306	> 10	0.9	17
P 177.495	Axial	Y 224.306	> 50	4.4	333
Pb 220.353	Axial	Y 377.433	> 10	1.9	17
Sb 206.833	Axial	Y 224.306	> 10	6.9	10
Se 196.090	Axial	Y 324.228	> 10	4.7	12
Sn 189.989	Axial	-	> 50	2.8	12
Ti 334.941	Axial	-	> 10	0.6	2
Tl 190.856	Axial	Y 224.306	> 10	4.4	17
V 309.311	Axial	Y 360.073	> 50	1.6	17
Zn 213.856	Radial	Y 224.306	> 50	4.8	67

To show the capability of the SDX HPLD system for dilution of samples that are outside the calibration range when analyzing wastewater samples according to EPA 200.7, the following sequence of samples was run:

Calibration
Quality Control Sample (QCS)
Initial Performance Check (IPC)
Check Blank (CB)
Calibration Range Sample (CR)

The certified reference material was used as the quality control sample (QCS) and was spiked with some elements above the LDR to initialize an intelligent auto-dilution (CR). As the reference value for the material was given for the 1:50 dilution, all concentrations were determined in a dilution of the reference material of 1 mL in 50 mL of acidified reagent water.

Auto-Dilution Speeds up EPA 200.7 Analysis without Manual Interruption

Due to the complex matrix and variable nature of wastewaters, the concentration range of the analytes of interest is hard to predict. Following EPA 200.7, the use of an auto-dilution system to speed up the sample analysis process for samples with analyte concentrations outside the calibration range while still achieving low detection limits was demonstrated.

The acquired method detection limits for elements of interest in the wastewater sample matrix were all below what is required in EPA 200.7, indicating suitability of all analytic wavelengths for this analysis (see Table 4).

For the determination of mercury at lower concentrations required for Centralized Waste Treatment Effluent Guidelines, a hydride generation technique should be applied. The detection limits of mercury with the standard sample introduction are 1.4 $\mu g \cdot g^{-1}$ in 18 MΩ ultra-pure water while they can be improved by a factor of 2 to 10 when using a basic or enhanced hydride generation accessory (see the Thermo Scientific application note: Analysis of Hydride Forming Elements with the Thermo Scientific iCAP 7000 Plus Series ICP-OES and the Basic Hydride Generator Kit AN43374).

In the first run, the QCS showed low recoveries below 90% for some elements (Co, Cu, Ni, Pb, Se, Tl) indicating bad performance of the method (Table 5). However, in a second run the QCS was spiked with these and additional elements (Ag, Sn, Ti) at a concentration of 1 µg·g⁻¹ and the recoveries were determined again. The spike recoveries were all within 94 to 104% suggesting that rather the reference material had somehow been adulterated. The IPC was done with the second calibration standard and showed very good recoveries within 100 to 105%.

After calibration and initial performance checks, a sample with a concentration higher than the highest calibration point was analyzed. According to EPA 200.7, samples with analyte concentrations of 90% or more of the upper limit of the LDR have to be diluted and reanalyzed. The Qtegra ISDS Software can be set to detect automatically, if the analyte concentration is above a certain percentage of the highest point of the calibration and also allows to enter a percentage for the target concentration (Figure 2). According to the detected concentration and the target percentage, an intelligent dilution factor is calculated and applied to the automatic dilution of the sample.

For this analysis, the reference material was spiked with 100 µg·g⁻¹ of Cu and Fe. The parameters for intelligent dilution were set according to Figure 2. The detected concentration was approximately two times above the upper limit of the calibration of copper and directly at the limit of iron (see Figure 3).

Figure 2. Settings within Qtegra ISDS Software for intelligent dilution of samples outside the calibration range.

Table 5. Known and measured concentrations of the QCS and IPC as well as recoveries before and after spiking.

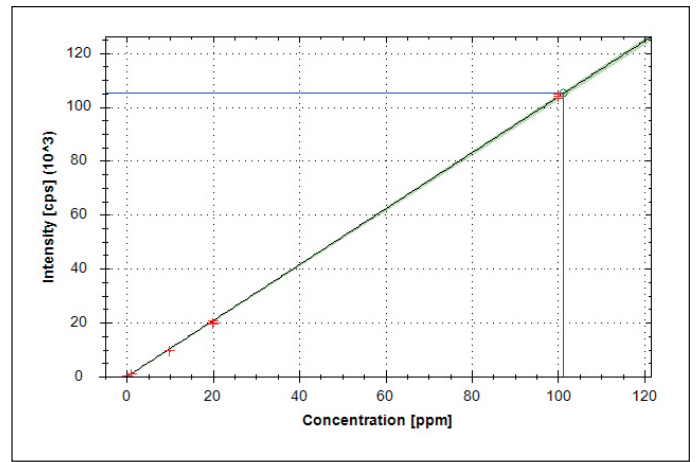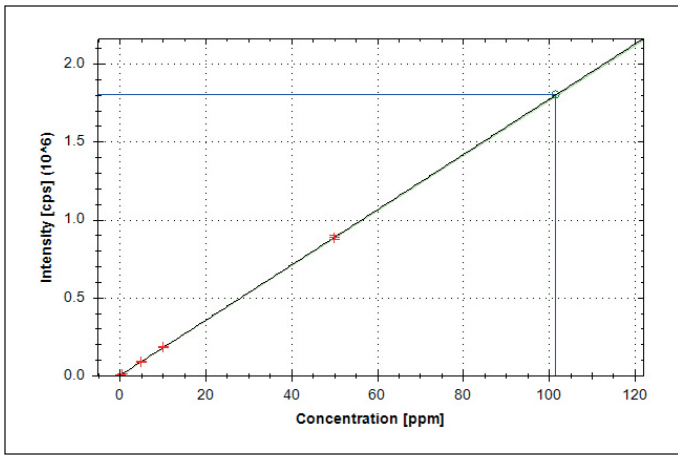| Element and wavelength (nm)	QCS known (µg·g⁻¹)	QCS measured (µg·g⁻¹)	QCS recovery (%)	QCS spike recovery (%)	IPC known (µg·g⁻¹)	IPC measured (µg·g⁻¹)	IPC recovery (%)
Ag 328.068	-	0.00	-	100.6	5	5.08	101.6
Al 396.152	0.43 – 0.47	0.46	98.0	-	10	10.01	100.1
As 189.042	0.81 – 0.91	0.88	103.6	-	5	5.22	104.4
B 208.959	0.78 – 0.96	0.79	92.3	-	5	5.05	101.0
Ba 455.403	1.23 – 1.29	1.23	92.9	-	10	10.10	101.0
Cd 228.802	0.30 – 0.32	0.29	94.1	-	5	5.23	104.5
Co 228.616	0.72 – 0.76	0.54	72.4	100.9	5	5.25	104.9
Cr 284.325	0.45 – 0.47	0.44	94.8	-	5	5.11	102.3
Cu 324.754	0.91 – 0.95	0.79	83.5	95.8	5	5.20	104.0
Fe 259.940	0.62 – 0.68	0.63	94.2	-	10	10.15	101.5
Ni 231.604	0.86 – 0.90	0.77	86.9	94.6	5	5.09	101.9
P 177.495	12.1 – 13.3	11.95	94.9	-	50	50.22	100.4
Pb 220.353	0.72 – 0.74	0.62	84.8	94.8	5	5.00	100.1
Sb 206.833	0.60 – 0.66	0.60	95.7	-	5	5.18	103.6
Se 196.090	0.16 – 0.18	0.14	85.0	102.0	5	5.07	101.5
Sn 189.989	-	0.00	-	103.7	5	5.14	102.7
Ti 334.941	-	0.00	-	99.8	5	5.18	103.7
Tl 190.856	0.46 – 0.50	0.39	82.3	100.1	5	5.15	103.0
V 309.311	0.94 – 0.98	0.95	97.7	-	5	5.09	101.9
Zn 213.856	0.97 – 1.03	0.98	94.2	-	5	5.10	102.1

Figure 3. Sample concentration on the calibration graphs for Cu 324.754 and Fe 259.940.

After analysis, the software intelligently added a sample to the sample list with an auto-dilution factor of 3.537, indicated by a green plus symbol in the status column (Figure 4).

The auto-dilution factor is calculated for the analyte that is highest above its upper limit of calibration but applied to all analytes that have had higher concentrations than the specified limit. In the diluted sample, concentrations for both analytes are about 30 µg·g^{-1} (see Figure 5).

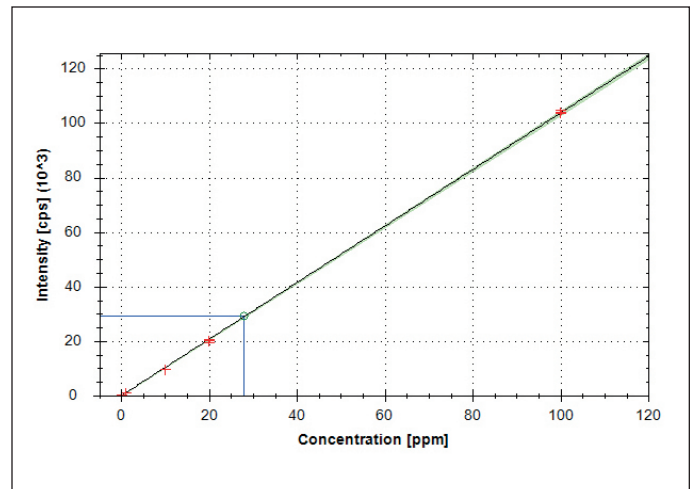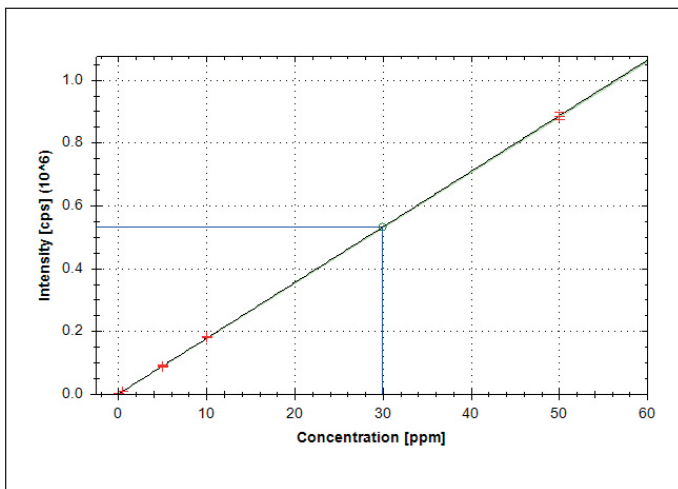Figure 4. Intelligent addition of a sample to the sample list.

Figure 5. Sample concentration on the calibration graphs for Cu 324.754 and Fe 259.940 after intelligent auto-dilution with a factor of 3.537.

iCAP 7000 Plus Series ICP-OES Delivers Performance that Meets the Regulatory Requirements of 40 CFR Part 437

The study shows that the Thermo Scientific iCAP 7000 Plus Series ICP-OES delivers very good accuracy and sensitivity for the analysis of elements in conformity with 40 CFR Part 437 using EPA method 200.7 (see AN43157 for further analytical data on EPA method 200.7 using the iCAP 7000 Plus Series ICP-OES).

A careful selection of internal standard wavelengths allows for correct quantification, even with increasing matrix element concentrations. Furthermore, for samples outside the calibration range, the SDX HPLD auto-dilution system allows for automated intelligent dilution that avoids false quantification due to signal saturation at a particular wavelength when sample concentrations are high. Apart from the advantage of correct quantification, the auto-dilution also saves time and manual labor to a great extent and therefore improves productivity for a routine environmental laboratory.

Find out more at **thermofisher.com/ICP-OES**

Thermo Fisher
SCIENTIFIC