

ICP-Optical Emission Spectroscopy

Authors

Praveen Sarojam, Ph.D.

PerkinElmer, Inc.

Shelton, CT 06484 USA

Analysis of Wastewater for Metals using ICP-OES

Introduction

The analysis of wastewater for trace metal contamination is an important step in ensuring human and environmental health. Wastewater is regulated differently in different countries, but the goal is to minimize the pollution introduced into natural waterways. In the U.S., the Environmental Protection Agency (EPA), in conjunction with the states, negotiates a discharge permit through the National Pollutant Discharge Elimination System (NPDES) which takes into account the federal guidelines for the industrial category (40 CFR, Parts 405-471)¹ and the sensitivity of the waterway receiving the discharge. Therefore, wastewater may need to be measured for a variety of metals at different concentrations, in different wastewater matrices.

A variety of inorganic techniques can be used to measure trace elements in waste water including atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectroscopy (ICP-OES) and ICP mass spectrometry (ICP-MS). Depending upon the number of elements that need to be determined and the number of samples that need to be run, the most suitable technique for business requirements can be chosen. ICP-OES is a good match with the productivity requirements of many laboratories and requires only a moderate investment.

The U.S. EPA has developed two methods for wastewater analysis using ICP-OES, Method 200.7 and Method 200.5.^{2,3} Method 200.5 was developed after the initial introduction of axial technology and gives more specific guidance for axial use. The methods have numerous quality control requirements (Table 1) to ensure proper instrument and methodology operation during the analysis of wastewater samples. The full suite of analytes listed in the method will be measured and quality control applied although the list of metals regulated in the effluent measured here, from the automobile industry, would be a subset. For example, elements specified for measurement in 40 CFR, Part 433, metal finishing point source category, include cadmium, chromium, copper, lead, nickel, silver, and zinc and may cover some automobile manufacturing processes.

Experimental

Instrumentation

The measurements were performed using the PerkinElmer® Optima™ 7300 DV ICP-OES instrument (PerkinElmer, Inc. Shelton, CT, USA) equipped with WinLab32™ for ICP Version 4.0 software for simultaneous measurement of all analyte wavelengths of interest (Figure 1). The Optima 7300 DV has been optimized to provide high speed analysis. By combining an SCD detector and an echelle optical system, the Optima 7300 DV can measure all elements simultaneously. Its wavelength flexibility allows the end users to easily add new elements as their program needs change.

The ICP torch is physically mounted in an axial orientation in the instrument's shielded torch box, but can be viewed either axially or radially. The view mode is user-selectable on an element-by-element basis. A shear gas flow (compressed air) provides elimination of the cool plasma tail to allow direct observation of the plasma's normal analytical zone, thus minimizing chemical matrix effects when the axial-view mode is employed.

The sample introduction unit consisted of a cyclonic spray chamber and a low flow GemCone™ nebulizer. The cyclonic spray chamber ensures high sample transfer to the plasma and fast rinse in and out times, which improves productivity. The low flow GemCone nebulizer permits lower nebulizer gas flow rates, useful for spectral lines with high excitation energies and for providing more robust plasma, which is essential for waste water samples.

The read time was set for a variable range from 2 s to 5 s using the auto-integration mode. This feature will take a snapshot of the intensities of various lines to be measured before the actual reading begins. For high intensities, the short read time will be used, while for low intensities, the larger time will be used and thereby increasing the sample throughput. Long read times reduce the effects of shot noise and are beneficial in obtaining lower detection limits (See Table 2 for detailed optimized instrument parameters).

Table 1. U.S. EPA Method 200.7 Requirements.

Check Code	Check Name	Purpose	Frequency of Check	Specified Limits
CCB	Continuing Calibration Blank	Checks calibration validity	After calibration, after every 10 analyses and at the end of analyses	<IDL
LRB	Laboratory Reagent Blank	Checks the laboratory reagents and apparatus for possible contamination	1 per batch	<2.2 *MDL
LFB	Laboratory Fortified Blank	Checks the analyte recovery of a spiked blank	1 per batch	85-115% recovery
LFM	Laboratory Fortified Matrix	Checks the analyte recovery in sample matrix	10 % of total samples	85-115% recovery
QCS	Quality Control Standard	Checks the accuracy of the calibration by analyzing a second source standard	Post calibration	95-105% recovery
IPC	Instrument Performance Check	To check the accuracy and drift by analyzing a standard as sample	Every 10 analyses and at the end of analyses	95-105% immediately after calibration, 90-110% thereafter
SIC	Spectral Interference Check	Checks the presence of spectral interferences	Periodically	No criteria specified
CRM	Certified Reference Material	Checks the accuracy of the developed method	Immediately after calibration	Should be analyzed whenever available

Table 2. Optima 7300 DV Operating Conditions.

Plasma gas flow	15 L/min
Auxillary gas flow	0.2 L/min
Nebulizer gas flow	0.6 L/min
RF power	1450 watts
Plasma view	Axial or Radial
Read delay	90 sec
Read parameters (s)	2.0 min, 5.0 max
Peristaltic pump flow rate	1.8 mL/min
Spray chamber	Cyclonic
Nebulizer	Low flow GemCone
Injector	Alumina, 2.0 mm i.d
Sample tubing	Standard 0.76 mm i.d
Drain tubing	Standard 1.14 mm i.d.
Quartz torch	Single slot
Sample capillary	Teflon® 1 mm i.d
Replicates	3
Resolution	Normal

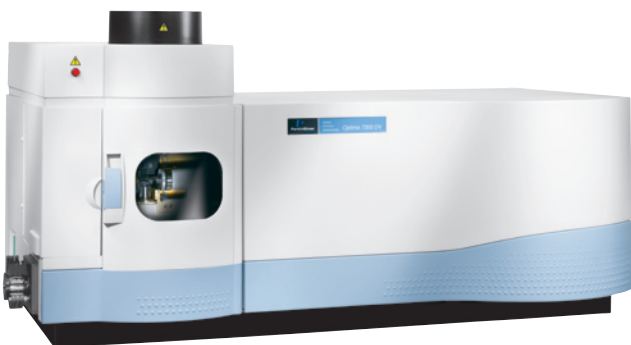


Figure 1. PerkinElmer Optima 7300 DV ICP-OES.

The PerkinElmer S10 Autosampler was used for high throughput and automated analysis. The autosampler automates standard and sample introduction for instrument calibration and sample analysis.

Standards, Chemicals and Certified Reference Material

PerkinElmer NIST® traceable quality control standards for ICP or ICP-MS (N9300233, N9300234 and N9300235) were used as the stock standards for preparing working standards. A total of three standards were used for calibration with each metal ion represented by one standard (Tables 3 and 4).

Table 3. Calibration Standards and Spike Concentration.

Element	Calibrated up to (mg/L)	Spike Concentration (mg/L)
Aluminum	1.0	1.0
Antimony	1.0	1.0
Arsenic	1.0	1.0
Barium	1.0	1.0
Beryllium	1.0	1.0
Boron	5.0	1.0
Cadmium	1.0	1.0
Calcium	1.0	1.0
Chromium	1.0	1.0
Cobalt	1.0	1.0
Copper	1.0	1.0
Iron	1.0	1.0
Lead	1.0	1.0
Lithium	1.0	1.0
Magnesium	1.0	1.0
Manganese	1.0	1.0
Molybdenum	5.0	1.0
Nickel	1.0	1.0
Phosphorus	5.0	1.0
Potassium	1.0	1.0
Selenium	1.0	1.0
Silicon	5.0	1.0
Silver	1.0	1.0
Sodium	1.0	1.0
Strontium	1.0	1.0
Thallium	1.0	1.0
Tin	1.0	1.0
Titanium	5.0	1.0
Vanadium	1.0	1.0
Zinc	1.0	1.0

Table 4. Combinations of Multi-element Standards Used.

Standard	Elements
STD 1	Al, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Ni, K, Se, Ag, Na, Sr, Tl, V, Zn
STD 2	B, Mo, P, Si, Ti
STD 3	Sb, Sn

ASTM® type I water acidified with nitric acid was used as the calibration blank. After constructing the calibration curves, two QC samples (one being a CCB, Continuing Calibration Blank), prepared at the midpoint of each calibration, were run to monitor the long term stability of the instrument. All standards were prepared in ASTM® type I water and were acidified with Suprapur® nitric acid (Merck®, Germany). Quality Control Check standard solutions were prepared from PerkinElmer Quality Control Check standards for ICP/ICP-MS (N9300233, N9300234 & N9300235). Working standards were prepared daily in polypropylene vials (Sarstedt®, Germany) and were prepared on volume-by-volume dilution basis. Micropipettes (Eppendorf®, Germany) with disposable tips were used for pipetting solutions. Several certified wastewater reference materials from High Purity Standards (Table 5) were used for validating the developed method.

Table 5. List of Reference Materials and Samples Analyzed.

Sample	Supplier
Certified wastewater-Trace metals solution H (CWW-TM-H)	High Purity standards
Certified wastewater-Trace metals solution G (CWW-TM-G)	High Purity standards
Certified wastewater-Trace metals solution F (CWW-TM-F)	High Purity standards
Certified Reference Material-River sediment A (Lot #0800230)	High Purity standards
Certified Reference Material-Soil solution A (Lot #0733733)	High Purity standards
Tap water	From the lab
Industrial effluent-Inlet	Automobile Industry
Industrial effluent-Outlet	Automobile Industry

Internal Standards

All solutions were spiked with 2.5 ppm Y. The spiking solution was made from a single element stock solution of Y 1000 ppm.

Sample Preparation

Two automobile industry wastewater samples (treated and untreated) and one tap water sample were collected and preserved in accordance with the procedure detailed in the method. For the determination of total recoverable analytes in aqueous samples, a 100-mL aliquot from a well mixed, acid-preserved sample was transferred to a 250 mL beaker and 2.0 mL (1+1) nitric acid and 1.0 mL of (1+1) hydrochloric acid was added. The beaker was placed on a hot plate for solution evaporation. The hot plate was located in a fume hood and was previously adjusted to provide evaporation at a temperature of approximately but no higher than 85 °C. The beaker was covered with an elevated watch glass to

prevent sample contamination from the fume hood environment. The volume of the sample aliquot was reduced to about 20 mL by gentle heating at 85 °C without boiling. Then the lip of the beaker was covered with a watch glass to reduce additional evaporation and gently refluxed for 30 minutes and cooled. The sample solution was quantitatively transferred to a 50-mL volumetric flask and made up to the mark with ASTM® type I water and allowed to settle overnight. The wastewater reference materials were taken through the entire analytical protocol to ensure that the method developed was accurate. The soil solution and river sediment reference materials were analyzed as such.

Results and Discussion

Wavelength selection followed U.S. EPA Method 200.7 which took into consideration, (a) the freedom from spectral interferences; (b) the different sensitivities and expected concentration in the samples. The selected analytical wavelengths are compiled in Table 6.

Table 6. Wavelengths Used and Plasma View Selected.

Element	Wavelength (nm)	View
Aluminum	308.215	Radial
Antimony	206.833	Axial
Arsenic	193.691	Axial
Barium	493.390	Radial
Beryllium	313.042	Radial
Boron	249.672	Radial
Cadmium	226.499	Axial
Calcium	315.880	Radial
Chromium	205.557	Axial
Cobalt	228.612	Axial
Copper	324.747	Radial
Iron	259.933	Radial
Lead	220.350	Axial
Lithium	670.750	Radial
Magnesium	279.071	Radial
Manganese	257.604	Radial
Molybdenum	203.843	Axial
Nickel	231.602	Axial
Phosphorus	214.912	Axial
Potassium	766.455	Radial
Selenium	196.022	Axial
Silicon	251.607	Radial
Silver	328.066	Radial
Sodium	588.983	Radial
Strontium	421.534	Radial
Thallium	190.802	Axial
Tin	189.924	Axial
Titanium	334.936	Radial
Vanadium	292.399	Radial
Zinc	213.855	Axial
Yttrium (Internal standard)	371.024, 324.221	Radial, Axial

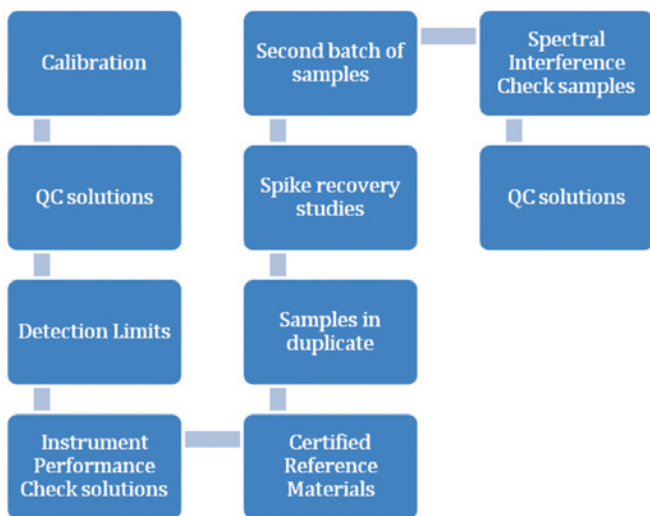


Figure 2. Analytical sequence followed for analysis of wastewater effluents.

Note that not always the most sensitive line was used in order to avoid spectral interferences. The resolution of the system is sufficient to warrant undisturbed measurements for typical analysis of wastewater samples. In unknown samples, unexpected spectral interferences may be observed. In order to safeguard against this event, all spectra generated during an analysis run were stored for post-analysis review. Observed interferences were compensated for by modifying the processing parameters (e.g., adjusting the background correction points). The analytical sequence followed in this analysis is given in Figure 2.

Initial Performance Demonstration

An Initial Performance Solution (IPC) was run (for all analytes at the levels of their respective standards used) immediately following calibration and the recoveries fell within the EPA limits of 95-105% (Table 7). This is an important parameter used to evaluate the performance of the instrument system with respect to a defined set of method criteria. Precision (%RSD) was also monitored to ensure the short term stability of emission signals.

Table 7. Analysis of Instrument Performance Check Solutions.

Analyte	IPC Avg. Conc. (mg/L)	% Recovery	% RSD
Aluminum	0.98	98	1.6
Antimony	1.0	102	1.2
Arsenic	1.0	100	2.3
Barium	0.97	97	0.1
Beryllium	1.0	100	0.6
Boron	5.4	105	0.2
Cadmium	1.0	102	1.6
Calcium	0.99	99	1.0
Chromium	1.0	101	1.6
Cobalt	1.0	100	1.7
Copper	0.98	97	0.9
Iron	0.99	99	1.6
Lead	1.0	102	1.6
Lithium	1.0	101	0.9
Magnesium	0.95	95	1.6
Manganese	0.99	99	0.7
Molybdenum	5.2	103	2.0
Nickel	0.97	97	1.7
Phosphorus	0.99	99	1.8
Potassium	5.7	105	0.8
Selenium	0.99	99	3.1
Silicon	1.2	105	4.2
Silver	1.0	100	0.8
Sodium	1.0	100	1.9
Strontium	1.0	101	0.1
Thallium	5.4	105	2.2
Tin	0.99	99	0.9
Titanium	1.0	101	0.1
Vanadium	0.95	95	1.0
Zinc	0.95	95	1.6

IDLs

Instrument detection limits (IDLs) were estimated by taking 10 replicate measurements of the calibration blank (1% nitric acid). The IDL was calculated to be the concentration equal to three times the standard deviation of those replicate measurements, and the exercise was repeated on three non-consecutive days, as specified in Method 200.7. The results are shown in Table 8.

Table 8. Instrument Detection Limits and Method Detection Limits.

Analyte	IDL (µg/L)	MDL (µg/L)
Aluminum	1.1	1.2
Antimony	3.8	5.5
Arsenic	5.7	6.3
Barium	0.04	0.04
Beryllium	0.02	0.02
Boron	1.1	1.5
Cadmium	0.1	0.1
Calcium	0.5	0.5
Chromium	0.3	0.4
Cobalt	0.4	0.5
Copper	0.3	0.4
Iron	0.3	0.3
Lead	1.5	1.7
Lithium	0.01	0.01
Magnesium	0.1	0.1
Manganese	0.04	0.04
Molybdenum	0.7	0.6
Nickel	0.5	0.5
Phosphorus	2.9	2.9
Potassium	0.3	0.3
Selenium	8.8	13
Silicon	0.9	0.9
Silver	0.3	0.4
Sodium	0.1	0.2
Strontium	0.01	0.01
Thallium	0.2	0.3
Tin	1.8	2.4
Titanium	0.1	0.1
Vanadium	0.2	0.3
Zinc	0.2	0.2
Yttrium	Int Std	

MDLs

Method detection limits (MDLs) were based upon seven replicate measurements of a series of spiked calibration blanks. Each blank solution was spiked with analytes at concentrations between 2 and 5 times the estimated IDL. The MDL was calculated by multiplying the standard deviation of the seven replicate measurements by the appropriate Student's t test value according to:

$$\text{MDL} = (S) \times (t)$$

where s is the standard deviation and t is the Student's t-value, based on a 99% confidence level. Both the Student's t-value and the standard deviation are based on n-1 degrees of freedom (t = 3.14 for six degrees of freedom).

In order to establish the system performance, wastewater samples were measured along with appropriate standard certified reference materials (CRM). The accuracy was calculated as the difference between measured and certified concentrations for the CRM. The results are presented in Tables 9-13. The accuracy and precision showed the developed method to perform well. The method detection limits calculated were generally in the low µg/L (ppb) range for a majority of elements. The reproducibility of the measurement was generally better than 2%. The analysis of spectral interference check solutions did not show any interference with any of the analytical lines selected.

Table 9. Analysis of Soil Solution A Reference Material.

Analyte	Certified Value (mg/L)	% Recovery
Aluminum	500	94
Barium	5.0	95
Calcium	350	99
Iron	200	97
Lead	0.40	98
Magnesium	70	99
Manganese	0.10	100
Phosphorus	10	96
Potassium	200	99
Silicon	3000	94
Sodium	70	103
Vanadium	0.10	104
Zinc	1.0	105

Table 10. Analysis of River Sediment Reference Material.

Analyte	Certified Value (mg/L)	% Recovery
Aluminum	250	93
Calcium	300	97
Chromium	300	102
Copper	1.0	96
Iron	1200	96
Lead	7.0	98
Magnesium	70	99
Manganese	8.0	98
Nickel	0.5	97
Potassium	150	98
Sodium	50	108
Zinc	15	96

Table 11. Analysis of Wastewater G Reference Material.

Analyte	Certified Value (mg/L)	% Recovery
Aluminum	100 ±1.0	96
Antimony	0.5 ±0.01	
Arsenic	25.0 ±0.5	100
Barium	2.5 ±0.03	97
Beryllium	25.0 ±0.3	100
Boron	2.5 ±0.03	100
Cadmium	25.0 ±0.2	100
Calcium	*	
Chromium	2.5 ±0.03	97
Cobalt	100 ±1.0	99
Copper	2.5 ±0.03	100
Iron	100 ±1.0	98
Lead	2.5 ±0.03	101
Lithium	*	
Magnesium	*	
Manganese	100 ±1.0	98
Molybdenum	100 ±1.0	97
Nickel	25.0 ±0.3	100
Phosphorus	*	
Potassium	*	
Selenium	25.0 ±0.5	100
Silicon	*	
Silver	*	–
Sodium	*	
Strontium	100 ±1.0	100
Thallium	0.5 ±0.01	98
Tin	*	
Titanium	*	
Vanadium	100 ±1.0	100
Zinc	25.0 ±0.03	97

*Not a specific element in the CRM

Table 12. Analysis of Wastewater F Reference Material.

Analyte	Certified Value (mg/L)	% Recovery
Antimony	25 ±0.5	105
Arsenic	0.5 ±0.01	105
Barium	100 ±1.0	100
Beryllium	0.50 ±0.01	104
Boron	100 ±1.0	94
Cadmium	*	–
Calcium	*	–
Chromium	100 ±1.0	106
Cobalt	2.5 ±0.03	100
Copper	100 ±1.0	105
Iron	*	
Lead	100 ±1.0	100
Lithium	*	
Magnesium	*	
Manganese	2.5 ±0.03	96
Molybdenum	2.5 ±0.03	96
Nickel	100 ±1.0	100
Phosphorus	*	
Potassium	*	
Selenium	0.50 ±0.01	96
Silicon	*	
Silver	25.0 ±0.3	100
Sodium	*	
Strontium	2.5 ±0.03	97
Thallium	2.5 ±0.05	104
Tin	*	
Titanium	*	
Vanadium	2.5 ±0.03	99
Zinc	100 ±1.0	100

*Not a specific element in the CRM

Table 13. Analysis of Wastewater H Reference Material.

Analyte	Certified Value (mg/L)	% Recovery
Aluminum	10.0 ±0.1	93
Antimony	20 ±0.4	100
Arsenic	10 ±0.2	99
Barium	10.0 ±0.1	95
Beryllium	2.0 ±0.02	106
Boron	25 ±0.3	100
Cadmium	10.0 ±0.1	99
Calcium	*	
Chromium	50.0 ±0.5	100
Cobalt	50.0 ±0.5	99
Copper	50 ±0.5	104
Iron	25 ±0.2	100
Lead	50.0 ±0.5	100
Lithium	*	
Magnesium	*	
Manganese	10.0 ±0.1	99
Molybdenum	10.0 ±0.1	98
Nickel	50.0 ±0.5	100
Phosphorus	*	
Potassium	*	
Selenium	5.0 ±0.1	101
Silicon	*	
Silver	2.0 ±0.02	103
Sodium	*	
Strontium	10.0 ±0.1	100
Thallium	*	
Tin	*	
Titanium	*	
Vanadium	50.0 ±0.5	100
Zinc	50.0 ±0.5	96

*Not a specific element in the CRM

The Continuing Calibration Verification standards were run at selected intervals in an unattended automatic analysis run, to ensure that the instrument performance is not degrading over the period of analysis. The results were consistently within the allowed range of 90-110% as shown in Table 14. The time difference between given CCV (first) and CCV (last) is more than 8 hours.

Table 14. Analysis of Continuing Calibration Verification Solutions (CCV).

Analyte	CCV First (%)	CCV Last (%)
Aluminum	97	96
Antimony	103	106
Arsenic	100	105
Barium	96	97
Beryllium	102	103
Boron	99	99
Cadmium	105	104
Calcium	97	97
Chromium	102	105
Cobalt	102	104
Copper	100	93
Iron	95	97
Lead	103	106
Lithium	97	96
Magnesium	99	96
Manganese	99	100
Molybdenum	99	99
Nickel	102	104
Phosphorus	100	102
Potassium	97	102
Selenium	103	105
Silicon	102	104
Silver	98	104
Sodium	103	97
Strontium	100	100
Thallium	105	104
Tin	101	104
Titanium	100	100
Vanadium	99	101
Zinc	102	103
Yttrium	Int . Std.	-

In order to further validate the method developed, post digestion spike recovery studies were performed at 1 ppm analyte concentration for all analytes in a tap water sample (Table 15) and a pre-digestion recovery study was performed with the Certified Wastewater Reference Material H (Table 16) to monitor the accuracy of the digestion procedure used. Both the pre- and post-digestion recoveries were well within the respective EPA set limits.

Table 15. Analysis of Tap Water.

Analyte	Avg. Conc. (mg/L)	Spike Recovery %
Aluminum	BDL	100
Antimony	BDL	106
Arsenic	BDL	103
Barium	BDL	101
Beryllium	0.00	102
Boron	0.03	100
Cadmium	BDL	104
Calcium	9.8	95
Chromium	BDL	103
Cobalt	BDL	102
Copper	BDL	106
Iron	BDL	100
Lead	0.01	105
Lithium	BDL	103
Magnesium	3.6	94
Manganese	BDL	100
Molybdenum	BDL	101
Nickel	BDL	103
Phosphorus	BDL	100
Potassium	0.54	105
Selenium	BDL	104
Silicon	18	87
Silver	BDL	70
Sodium	4.2	104
Strontium	0.03	105
Thallium	BDL	103
Tin	BDL	93
Titanium	BDL	106
Vanadium	BDL	101
Zinc	0.71	102

Table 16. Pre-digestion Analyte Recovery with Effluent (Wastewater CRM H).

Analyte	% Recovery
Aluminum	90
Antimony	97
Arsenic	98
Barium	107
Beryllium	109
Boron	91
Cadmium	92
Calcium	*
Chromium	96
Cobalt	92
Copper	102
Iron	91
Lead	92
Lithium	*
Magnesium	*
Manganese	94
Molybdenum	*
Nickel	96
Phosphorus	92
Potassium	*
Selenium	*
Silicon	85
Silver	*
Sodium	85
Strontium	*
Thallium	97
Tin	84
Titanium	*
Vanadium	*
Zinc	98

**Not a specific element in the CRM*

The wastewater reference materials were taken through the entire analytical protocol to make sure that the method developed was accurate and this resulted in an overall dilution of 1:10. The recoveries were well within the EPA set limits of 85-115%. After the initial instrument performance checks, the automobile industry effluents (both treated and untreated) were analyzed and the results are summarized in Tables 17 and 18.

Table 17. Analysis of Wastewater Inlet Samples.

Analyte	Inlet I (mg/L)	Inlet II (mg/L)
Aluminum	1.5	1.5
Antimony	BDL	BDL
Arsenic	BDL	BDL
Barium	0.40	0.39
Beryllium	BDL	BDL
Boron	0.16	0.17
Cadmium	BDL	BDL
Calcium	48	49
Chromium	0.51	0.52
Cobalt	0.01	0.01
Copper	0.02	0.03
Iron	7.9	8.0
Lead	0.04	0.04
Lithium	0.01	0.01
Magnesium	38	39
Manganese	6.3	6.5
Molybdenum	0.01	0.01
Nickel	7.4	7.5
Phosphorus	244	247
Potassium	4.9	4.3
Selenium	0.04	0.11
Silicon	174	176
Silver	BDL	BDL
Sodium	579	570
Strontium	0.23	0.23
Thallium	BDL	BDL
Tin	BDL	BDL
Titanium	0.08	0.07
Vanadium	0.01	0.01
Zinc	6.8	6.9

Table 18. Analysis of Treated Effluent and Recovery Studies.

Analyte	Avg. Conc. (mg/L)	% Recovery
Aluminum	BDL	104
Antimony	BDL	103
Arsenic	BDL	99
Barium	BDL	107
Beryllium	BDL	99
Boron	BDL	106
Cadmium	BDL	103
Calcium	43	101
Chromium	BDL	104
Cobalt	BDL	101
Copper	BDL	105
Iron	BDL	87
Lead	0.01	103
Lithium	0.01	100
Magnesium	5.8	99
Manganese	0.03	100
Molybdenum	BDL	103
Nickel	0.06	104
Phosphorus	60	96
Potassium	0.2	98
Selenium	0.03	96
Silicon	126	*
Sodium	345	*
Strontium	BDL	109
Thallium	BDL	96
Tin	BDL	108
Titanium	BDL	109
Vanadium	BDL	99
Zinc	0.13	106
Yttrium	Int.Std	

*Native concentration too high for spike recovery, BDL means below the detection limit.

Further post digestion spike recovery studies were performed for treated samples and the results are summarized in Table 18. The results show that there is marked difference between the concentration of most of the metal ions in the inlet and outlet discharges and the treatment process is removing a significant amount of the metals measured.

Conclusions

The simultaneous ICP-OES (Optima 7300 DV) used in this study has the analytical capabilities to perform the analysis of wastewater with EPA Method 200.7/200.5 with good accuracy, precision, analysis speed and robustness and fulfills the requirements normally set for the analysis of high matrix wastewater samples such as automobile industrial effluents. Long term stability (evident from QC recoveries) ensures that the calibration will be monitored during the analysis run requiring fewer QC actions and possible reruns. Trace metal constituents were measured at low and high concentrations in a variety of wastewater reference materials, demonstrating good accuracy. The Optima 7300 DV ICP-OES has been demonstrated in compliance with the requirements of EPA Method 200.7 for a wide range of wastewater reference materials and real industrial wastewater samples.

References

1. 40 CFR, Parts 405-471, U.S. Code of Federal Regulations, http://ecfr.gpoaccess.gov/cgi/t/text/text-idx?sid=ea0ee2727394bec6c2d8fc94e7cd5017&c=ecfr&tpl=/ecfrbrowse/Title40/40tab_02.tpl
2. EPA Method 200.7, "Determination of Metals and Trace Metals in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry," http://www.epa.gov/waterscience/methods/method/files/200_7.pdf
3. EPA Method 200.5, Determination of Trace Elements in Drinking Water by Axially Viewed Inductively Coupled Plasma-Atomic Emission Spectrometry, <http://www.epa.gov/nerlcwww/ordmeth.htm>