Modern Flame Atomic Absorption Analysis of Wastewater

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ABSTRACT

Wastewater analysis using a modern flame atomic absorption spectrometer (FLAA) is demonstrated. Samples are prepared using U.S. EPA methodology and method detection limits estimated. Method accuracy is verified using spiked blanks and reference materials. The method is used for the analysis of an independent standard and mixed sludge sample from a wastewater treatment facility. The results are compared to a confirmational ICP-OES analysis.

INTRODUCTION

Wastewater analysis is an important component of environmental monitoring to ensure clean water for natural ecosystems and for recreational use. Wastewater can be monitored at an industrial point source, at a wastewater treatment plant, or general monitoring of a natural water body can be performed to minimize degradation. In the United States, discharges from industrial sources are regulated through the National Pollution Discharge Elimination System (NPDES), a system of permits based on the industrial category, receiving water body, and Federal guidelines for acceptable limits. Recent advances in monitoring technology and modeling have allowed more sophisticated permits to be written based on the actual effects of each pollutant on the watershed. This represents a shift from best available technology (BAT), specifying a comprehensive cleanup to a water quality criteria (WQC) approach where the impact of the discharge is more completely evaluated. Although ultratrace techniques may be required for modeling, analysis of metals at the parts-per-million level will still continue to provide integral routine monitoring information.

Flame atomic absorption (FLAA) is a fast economical technique useful for the determination of a variety of elements in a wastewater matrix at the parts-per-million or lower levels. Graphite furnace atomic absorption (GFAA) can be used to determine elements required at lower levels and is available as an accessory to a flame instrument or in a dedicated format. In this paper we will demonstrate the performance of flame atomic absorption for a variety of elements in a standard wastewater reference material and sample from a wastewater treatment facility.

EXPERIMENTAL

Wastewater reference materials (Trace Metals WasteWatR™) from Environmental Resource Associates (Arvada, CO) were prepared using U.S. EPA Method 200.2 (1). Trace metals-grade nitric and hydrochloric acid was used in the digestion. Blanks and predigestion spikes of the blank and reference material were also carried through the digestion procedure. Summarizing the procedure, a measured 100-mL aliquot of the sample was heated to 95°C with nitric and hydrochloric acid and allowed to evaporate to approximately 20 mL. It was then brought up to 50 mL with Type I water. A sample and standard were received from the City of San Diego Wastewater Laboratory and prepared for ICP-OES analysis.

The Perkin-Elmer® AAnalyst™ 100 atomic absorption spectrometer was used for all instrumental analyses. The conditions used for each element are listed in Table I.

Background correction (AA-BG) was used for lower wavelength elements that might be more susceptible to interferences from molecular absorbance. Linear calibration was used when the linear range was sufficient to cover the expected range of concentrations. Nonlinear was used for elements that have a short linear dynamic range to extend the useful range for the analysis. If the quality control (QC) values are

TABLE I
AAnalyst 100 AAS Instrumental Operating Conditions

Element	Ba	Cd	Cr	Cu	Mn	Ni	Zn
Wavelength (nm)	553.6	228.8	357.9	324.8	279.5	232.0	213.9
Slit (nm)	0.2	0.7	0.7	0.7	0.2	0.2	0.7
Mode	AA	AA-BG	AA	AA	AA	AA-BG	AA-BG
Flame	Nitrous-	Air-	Air-	Air-	Air-	Air-	Air-
	----------Acetylene----------						
Burner	5 cm	10 cm	10 cm	10 cm	10 cm	10 cm	10 cm
Nebulizer	Universal	Universal	Universal	Universal	Universal	Universal	Universal
Calibration	Linear	Non-linear	Linear	Linear	Linear	Linear	Non-linear
Standards (mg/L)	5.0, 10.0, 15.0	0.25, 0.50, 1.0	0.5, 1.0, 2.5, 4.0	0.5, 1.0, 2.5, 4.0	0.25,0.50, 1.0	0.25,0.50, 1.0, 2.5	0.25, 0.50,1.0

acceptable, then the nonlinear algorithm is an acceptable alternative to diluting the sample, which will introduce some dilution error into the analysis. The range can be safely extended to approximately four times the concentration at the top of the linear range.

RESULTS AND DISCUSSION

In order to demonstrate the capability of the system for performing the analysis of wastewater, we first evaluated a reference material. The results are shown in Table II.

The recoveries for the elements determined were excellent. Elements expected to be below the detection limit in the reference sample were not determined. Flame analysis would also be useful for elements such as lead, silver, cobalt, and others not requiring trace determination.

Table III lists the recovery for reference wastewater spiked with the elements of interest. Each element was spiked at 0.5 mg/L, except for barium, which was spiked at 5.0 mg/L. Table IV shows the recovery of laboratory blanks carried through the digestion procedure and blanks fortified with each of the elements to be determined prior to digestion. The blanks did not pick up any contamination during the preparation procedures and the method detection limits (MDLs) are estimated as the lower limit for reporting and are listed in column one.

The recovery for spikes ranged from 95.8% to 103% of the concentration added to the matrix. These recoveries are well within the U.S. EPA-specified ranges of 85–115%. This demonstrates the capability of the method to yield accurate results over a range of concentrations. In addition, the digestion integrity is demonstrated, since the blanks are not contaminated and the spikes are not lost due to volatilization.

TABLE II
Results for Reference Wastewater

Element	Certified value (mg/L)	Target range (mg/)L)	Results Replicate 1 (mg/L)	Results Replicate 2 (mg/L)	Mean result (mg/L)	%Recovery
Ba	0.469	0.384–0.553	0.464	–	–	98.9
Cd	0.148	0.121–0.174	0.146	0.148	0.147	99.3
Cr	0.801	0.681–0.980	0.790	0.790	0.790	98.6
Cu	0.221	0.181–0.261	0.218	0.217	0.218	98.4
Mn	0.188	0.154–0.222	0.184	0.185	0.185	98.1
Ni	0.346	0.284–0.409	0.349	0.352	0.351	101
Zn	0.0995	0.082–0.117	0.108	0.107	0.108	108

TABLE III
Reference Wastewater Spikes

Element	Spike added (mg/L)	Mean result unspiked (mg/L)	Spike result (mg/L)	% Recovery
Ba	5.0	0.464	5.409	98.9
Cd	0.5	0.147	0.648	100
Cr	0.5	0.790	1.279	97.8
Cu	0.5	0.218	0.712	98.8
Mn	0.5	0.185	0.688	101
Ni	0.5	0.351	0.854	101
Zn	0.5	0.108	0.587	95.8

TABLE IV
Laboratory Blank and Fortified Blank Results

Element	Spike added (mg/L)*	Mean result unspiked (mg/L)	Spike result (mg/L)	% Recovery
Ba	<0.03	5.0	4.948	99.0
Cd	<0.003	0.5	0.504	101
Cr	<0.02	0.5	0.502	100
Cu	<0.003	0.5	0.508	102
Mn	<0.003	0.5	0.504	101
Ni	<0.06	0.5	0.516	103
Zn	<0.003	0.5	0.500	100

* Estimated method detection limits.

Results of a QC standard and digested sludge sample were evaluated to demonstrate the method performance on a more complex sample matrix. Table V shows the FLAA results for the standard and sample compared to ICP-OES results.

The agreement between the FLAA values and the ICP-OES values are generally within 10% of the expected value and demonstrate the ability of flame atomic absorption to accurately determine these metals in a more complicated matrix. ICP-OES provides a useful confirmation of the methodology, because it is a complimentary technique and is affected by different interference mechanisms.

TABLE V
Results for Wastewater District Samples

	Standard 062496 0038				Sludge Mix (062496 0037)		
Element	Dilution	Result (mg/L)	Label value	%Recovery	Dilution	Result (mg/L)	ICP-OES result (mg/L)
Ba		8.94	10.2	87.6		2.48	2.47
Cd	10	4.14	4.08	101		0.05	0.04
Cr	10	22.3	23.8	93.7	10	0.51	0.4
Cu	10	23.8	23.8	100	10	3.74	4.04
Mn		–	–	–	10	2.89	2.73
Ni	10	24.0	23.8	101	10	0.34	0.32
Zn	25	23.4	23.8	98.3	25	5.30	5.0

CONCLUSION

Wastewater analysis is an important environmental analysis where flame atomic absorption techniques can make a major contribution to on-going monitoring efforts. Modern flame instruments provide a level of automation that can increase productivity through unattended operation and quality control monitoring. Quality control standards can be monitored on a scheduled basis and actions specified that minimize the generation of data that might not meet the data quality objectives of the analysis.

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REFERENCES

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