



Determination of metals in TCLP extracts using RCRA ICP-OES METHOD 6010

Thomas J. Gluodenis, Dennis A. Yates, Zoe A. Grosser
PerkinElmer Instruments, 761 Main Avenue, Norwalk, CT 06859 USA

Introduction

The Resource Conservation and Recovery Act (RCRA) of 1976, updated by the Hazardous and Solid Waste Amendments of 1984, gives the U.S. Environmental Protection Agency (EPA) "cradle-to-grave" responsibility for the management of hazardous materials. Among many important tasks is the characterization of waste materials to determine if they are hazardous.

The EPA Office of Solid Waste has specified that the following four tests be performed to determine if an unknown waste material may be hazardous:

- Ignitability - causes or exacerbates a fire
- Corrosivity - pH limits exceeded or corrodes steel
- Reactivity - unstable
- Toxicity - may leach from a landfill and contaminate groundwater

The toxicity characteristic is the most quantitative of the four tests and is performed using the toxicity characteristic leaching procedure (TCLP). The TCLP mimics the type of process a waste might be exposed to under natural conditions in a landfill. If hazardous components migrate from the disposal site into a water source, drinking water supplies may be contaminated.

The TCLP test consists of two parts: extraction of contaminants using an acetic acid buffer solution

followed by analysis of the resultant extract to determine the concentration of representative contaminants. The inorganic contaminants and maximum contaminant levels (MCLs) are listed in Table 1. If a TCLP determination indicates that these elements are present at concentrations that exceed the MCLs, then the original waste is considered to be toxic and is subject to stringent disposal regulations.

In 1990, regulations extended the use of the TCLP to additional waste generators and expanded the target analyte list to include a number of additional organic contaminants (1). These and other factors contribute to the pressure on environmental laboratories to perform ever more efficiently.

Table 1. TCLP Regulatory Limits

Element	MCL (mg/L)
Ag	5.0
As	5.0
Ba	100
Cd	1.0
Hg	0.2
Cr	5.0
Pb	5.0
Se	1.0

Experimental

The PerkinElmer simultaneous Optima™ ICP-OES was used for analysis of the TCLP extract. The instrument is a simultaneous ICP with an echelle polychromator and Segmented Array Charge-coupled Device (SCD) detector. Simultaneous measurement of background analyte emission allows for accurate correction of transient background fluctuations. The instrument conditions used for determination of the method detection limits and analytical results are shown in Table 2.

Calibration standards were prepared from PerkinElmer Pure TCLP Multielement Standard (PerkinElmer Part No. N930-0241).

Table 2. ICP-OES Operating Conditions

Instrument	Optima 3000
RF Power	1100 W
Plasma Gas Flow	15 L/min
Auxiliary Gas Flow	1 L/min
Nebulizer Gas Flow	0.95 L/min
Sample Pump Flow	2 mL/min
Plasma Viewing	Radial
Viewing Height	15 mm
Processing Mode	Area
Integration Time	10 sec
Replicates	5
Background Correction	Manual, 1 or 2 points
Nebulizer	Cone Spray
Spray Chamber	Scott

Three standards and a blank were used for calibration. The standards were prepared in HNO₃/HCl matrix, as specified in Method 6010, to approximate the digested matrix of the samples.

Method 6010A, Revision 1 (1990), was followed for the analytical determination of the TCLP elements required in the extract. Method 6010A is a RCRA program method published in Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, publication SW-846, with revisions (2). The use of SW-846 methods for measurement of the analytes is not mandatory and the methods are provided as guidance.

Samples from a RCRA cleanup site were extracted using EPA Method 1311, by GTEL Environmental Laboratories, Inc. of Milford, NH USA. The extracts were received digested, in plastic bottles. The wavelengths chosen for analysis and their background correction points are listed in Table 3. The first wavelength given for each element is recommended in Method 6010. The second wavelength is an alternate emission line that was monitored in order to identify potential interferences. Mercury was not included in the analyte list, although it could be included if an axial- or dual-view plasma was used.

Table 3. Emission Wavelengths and Background Correction Intervals

Element	Wavelength (nm)	Lower Correction Interval (nm)	Upper Correction Interval (nm)
Ag	328.068	0	0.20
	338.289	0	0.21
As	193.696	0.018	0.012
	197.197	0	0.018
Ba	455.403	0.042	0.042
	233.527	0.022	0.022
Cd	266.502	0.021	0.021
	214.438	0	0.020
Cr	267.716	0.025	0.025
	357.869	0.025	0.025
Pb	220.353	0.020	0.020
	216.999	0.020	0
Se	196.026	0.012	0
	203.991	0	0.019

Results and Discussion

The performance of the instrument was evaluated by determining the method detection limits and by monitoring of several quality control (QC) parameters during the analysis. The method detection limits were determined using the procedure described in Chapter One of SW-846, which specifies that a solution containing the analytes of interest at levels between 3-5 times the estimated MDL should be analyzed three or more times. The standard deviation of the mean concentration is multiplied by the *t*-statistic and the resulting MDL is listed in Table 4. All of measured method detection limits are more than 10 times below the MCL, which ensures confidence in measurements taken near the decision point.

During the analysis, several QC checks were performed to ensure that the ICP was operating properly. The calibration was initially checked using a standard at the midpoint of the calibration range. This standard was recovered within the $\pm 5\%$ guidelines specified in the method. When analyzed later in the sample worklist the recovery was within the acceptable $\pm 10\%$.

An interference check sample was run to ensure that the wavelengths chosen for the method did not have any undetected spectral interferences. The check sample contained high concentrations of Al, Na, Ca, and Mg, with low levels of the analytes of interest. The analytes were recovered within the required limits indicating that no further method development was required. A dilution (1:5) was made

of sample 1 and the analytes recovered within 10% of the undiluted sample, further indicating freedom from interferences for this specific matrix.

A laboratory control sample (LCS) was run to verify the performance of the instrument and method. The control sample of known composition was prepared by an independent laboratory and verified by instrumental analysis at that laboratory. The values of the LCS were recovered within the $\pm 10\%$ limits required.

A duplicate sample was analyzed and the analytes recovered within 20% of the original sample, again indicating the entire process is in control.

The performance of the instrument and method was tested on TCLP extracts derived from RCRA

Table 4. TCLP Analytical Results

Element MDLs (mg/L)	Sample 1		Sample 2		Sample 3			
	Sample (mg/L)	Dilution (mg/L)	Spike (%Rec)	Sample (mg/L)	Spike (%Rec)	Sample (mg/L)	Spike (%Rec)	
Ag	0.001	ND	ND	95.4	ND	93.4	ND	87.0
As	0.048*	ND	ND	99.9	ND	102	ND	99.1
Ba	0.003	0.68	0.68	98.0	10.9	96.0	13.2	94.1
Cd	0.007	ND	ND	93.3	ND	93.9	0.016	90.3
Cr	0.004	ND	ND	95.1	ND	93.4	0.013	90.5
Pb	0.060	ND	ND	96.8	0.97	91.1	121	--
Se	0.110	ND	ND	96.9	ND	94.4	ND	93.9
Mean				96.4		94.8		93.5

soil samples. The samples were spiked before digestion (0.2 mg/L for Ag, Cr; 0.5 mg/L for Cd; 2 mg/L for As, Pb, Se; and 10 mg/L for Ba). The recoveries for the three samples, listed in Table 4, are excellent with an average recovery of 94.9%. The precision of the instrument was generally better than 1% at 0.1-ppm concentration levels.

The EPA RCRA limits for predigestion spike recoveries are 75-125% for this method. Because of a high lead content in Sample 3, the predigestion spiking level was inappropriate. The sample was diluted by a factor of 500 and a post-digestion spike of 2 mg/L was added for measurement, yielding 101% recovery.

The simultaneous Optima™ uses an SCD detection system for measurement of the emitted light. This feature of the instrument was used to make the TCLP determination more rugged by monitoring two wavelengths for each element. Analysis time is not sacrificed by monitoring additional lines because all measurements are made simultaneously. All the elements examined have a suitable secondary wavelength with sufficient sensitivity, especially for TCLP analysis, where the MCLs are in the ppm range.

Additional contaminants listed in Method 6010 were monitored during the analysis to characterize the samples more completely. Potential interferences might be identified or an unusual sample matrix defined. Low concentration of Al, Mn, Sr, and Zn were found. Higher concentrations of Ca and K were found in all three samples. In most cases, two wavelengths were chosen for each element to provide a rapid confirma-

tion of the concentrations identified.

The Optima ICP-OES performs the TCLP analytical determinations within all the limits set by Method 6010. Excellent spike recoveries and close agreement with established values for the LCS are demonstrated. The results were obtained quickly, with rapid confirmation by the use of a second wavelength for each element. It is possible to look at potential interfering elements and less significant elements without sacrificing analysis time because of simultaneous operation.

References

1. US Federal Register, 55 (126) Friday, June 29, 1990.
2. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Publication SW-846, 955-001-00000-1, 3rd Edition, Government Printing Office, Washington, D.C.

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Visit our website at www.perkinelmer.com

PerkinElmer Instruments
761 Main Avenue
Norwalk, CT 06859-0010 USA
Tel: 800-762-4000 or
(+1) 203-762-4000
Fax: (+1) 203-762-4228

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