Designation: C 1111 – 04

Standard Test Method for Determining Elements in Waste Streams by Inductively Coupled Plasma-Atomic Emission Spectroscopy[1]

This standard is issued under the fixed designation C 1111; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of trace, minor, and major elements in waste streams by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) following an acid digestion of the sample. Waste streams from manufacturing processes of nuclear and non-nuclear materials can be analyzed. This test method is applicable to the determination of total metals. Results from this test method can be used to characterize waste received by treatment facilities and to formulate appropriate treatment recipes. The results are also usable in process control within waste treatment facilities.

1.2 This test method is applicable only to waste streams that contain radioactivity levels that do not require special personnel or environmental protection.

1.3 A list of the elements determined in waste streams and the corresponding lower reporting limit is found in Table 1.

1.4 This test method has been used successfully for treatment of a large variety of waste solutions and industrial process liquids. The composition of such samples is highly variable, both between waste stream types and within a single waste stream. As a result of this variability, a single acid digestion scheme may not be expected to succeed with all sample matrices. Certain elements may be recovered on a semi-quantitative basis, while most results will be highly quantitative.

1.5 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:* [2]

C 1109 Test Method for Analysis of Aqueous Leachates from Nuclear Waste Materials Using Inductively Coupled Plasma-Atomic Emission Spectrometry

C 1234 Practice for Preparation of Oils and Oily Waste Samples by High-Pressure, High-Temperature Digestion for Trace Element Determinations

D 1129 Terminology Relating to Water

D 1193 Specification for Reagent Water

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

2.2 *US EPA Standard:*

Method 6010, Inductively Coupled Plasma Method, SW-846, Test Methods for Evaluating Solid Waste[3]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129, Terminology E 135, and Test Method C 1109.

4. Summary of Test Method

4.1 Elements are determined, either sequentially or simultaneously, by inductively coupled plasma-atomic emission spectroscopy (Method 6010, SW-846). If the sample is a clear acidified solution, the elements are determined with no further pretreatment. If the sample contains undissolved solids, the elements are determined using an aliquot of the thoroughly mixed sample after a nitric acid digestion.

5. Significance and Use

5.1 This test method is useful for the determination of concentrations of metals in many waste streams from various nuclear and non-nuclear manufacturing processes. The test method is useful for characterizing liquid wastes and liquid wastes containing undissolved solids prior to treatment, storage, or stabilization. It has the capability for the simultaneous determination of up to 26 elements.

5.2 The applicable concentration ranges of the elements analyzed by this procedure are listed in Table 1.

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[1] This test method is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards*volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from the U.S. Government Printing Office, Washington, DC 20402.

TABLE 1 Analytical Wavelengths and Applicable Concentration Ranges[A]

Element	Lower Limit,[B] mg/L	Upper Limit, mg/L	Wavelength, nm
Aluminum	0.02	5000	308.22, 237.01
Barium	0.001	100	493.41
Beryllium	0.0003	100	313.04
Boron	0.004	200	249.68
Cadmium	0.003	200	226.50
Calcium	0.004	1000	317.93, 393.37
Chromium	0.01	5000	267.72, 298.92
Cobalt	0.005	150	228.62
Copper	0.004	150	324.75
Iron	0.004	5000	271.44, 259.94
Lead	0.05	200	220.35
Lithium	0.004	150	670.78
Magnesium	0.0005	5000	293.65, 279.55
Manganese	0.001	150	257.61
Nickel	0.01	5000	231.60, 341.48
Phosphorus	0.2	250	178.29
Potassium	0.6	1000	766.49
Silver	0.006	150	328.07
Sodium	0.02	200	330.29, 588.99
Strontium	0.0004	100	421.55
Thorium	0.2	250	283.73
Titanium	0.003	150	334.94
Uranium	0.03	1000	409.01
Vanadium	0.005	250	292.40
Zinc	0.001	250	213.86
Zirconium	0.005	250	339.20

[A] The estimated upper and lower concentration limits are to be used only as a general guide. These values are instrument and sample dependent, and as the sample matrix varies, these concentrations may be expected to vary also.

[B] These limits obtained using a Jarrell-Ash ICAP-9000 ICP Spectrometer.

6. Interferences

6.1 Interferences in ICP-AES are primarily spectral and can be compensated for in the following ways:

6.1.1 *Interelement Interferences*—Interelement interferences are characterized by spectral overlap of one element line over another. This interference can be compensated for by correction of the raw data, which requires measurement of the interfering element at the wavelength of interest. Table 2 lists some interference effects for the recommended wavelengths given in Table 1. The data in Table 2 are intended for use only as a rudimentary guide for indicating potential spectral interferences. Various analytical systems may exhibit somewhat different levels of interferences. Therefore, the interference effects must be evaluated for each individual system.

6.1.2 *Molecular Band Interference*—Molecular band interference arising from overlap of molecular band spectra at the wavelength of interest can be eliminated by careful selection of wavelength.

6.1.3 *High Background*—High background effects from scattered light, etc., can be compensated for by background correction adjacent to the analyte line.

6.2 *Physical Interferences*—Physical interferences are effects associated with nebulization and transport processes in samples with either high solids or acid concentrations. These effects are reduced by a tenfold dilution of the sample and the use of a peristaltic pump in conjunction with a high-solids nebulizer.

7. Apparatus

7.1 *Spectrometer*—An inductively coupled plasma emission spectrometer with a spectral bandpass of 0.05 nm or less is required. The spectrometer may be of the simultaneous multi-element or sequential scanning type. The spectrometer may be of the air path, inert gas path, or vacuum type, with spectral lines selected appropriately for use with the specific instrument. Either an analog or digital readout system may be used.

8. Reagents

8.1 *Purity of Reagents*—Chemicals used in the preparation of the standards must be of ultrahigh purity grade. Chemicals used in the preparation of the samples shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,[4] where such specifications are available.

8.2 *Purity of Water*—References to water shall be understood to mean reagent water conforming to Specification D 1193, Type I.

8.3 *Stock Solutions*—Standard stock solutions may be purchased or prepared from ultrahigh purity grade metals or metal salts (Method 6010, SW-846). All salts must be dried for 1 h at 105°C unless otherwise specified. Stock solutions should

[4] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

TABLE 2 Analyte Concentration Equivalents Arising from Interferents at the 1000 mg/L Level

Analyte	Wave-lengths, nm	Interferent, mg/L									
		Aluminum	Chromium	Copper	Iron	Nickel	Antimony	Silicon	Tin	Uranium	Vanadium
Aluminum	308.22							0.0020		0.0044	0.0199
Aluminum	237.21		−0.0022		−0.0084					0.0350	
Barium	493.41										
Beryllium	313.04										0.0013
Boron	249.68				0.0015						
Cadmium	226.50				0.0002	−0.0004					
Calcium	317.93									−0.0018	
Calcium	393.37						0.0002				
Chromium	267.72									0.0025	0.0018
Chromium	298.92									0.0560	
Cobalt	228.62		0.0001							0.0001	
Copper	324.75										
Iron	259.94	0.0001				−0.0001				−0.0002	
Iron	271.44		0.0039			−0.0015				0.0220	
Lead	220.35	−0.0012	−0.0028		0.0002	0.0006				0.0016	
Lithium	670.78						0.0003				
Magnesium	279.55										
Magnesium	293.65		−0.0270		−0.1390					0.0350	
Manganese	257.61									0.0002	
Nickel	231.60				−0.0002		0.0003		0.0001	0.0003	
Nickel	341.48									0.0027	
Phosphorus	178.29	0.0002			−0.0079	0.0120	0.0004			0.0044	
Potassium	766.49		0.0010							−0.0005	0.0014
Silver	328.07									0.0003	
Sodium	330.29	0.0035	−0.0220		−0.0145					−0.1580	
Sodium	588.99						0.0006		0.0017	0.0002	
Strontium	421.55										
Thorium	283.73		0.0007		0.0005	0.0049				0.0500	
Titanium	334.94		0.0003								
Vanadium	292.40		−0.0029							−0.0014	
Zinc	213.85			0.0034	0.0001	0.0038					
Zirconium	339.20				−0.0003	−0.0002				−0.0005	

contain approximately 1 000 to 10 000 mg/L of the element of interest to ensure long term stability in dilute nitric acid..

8.4 *Multielement Working Calibration Standards*—Multielement working calibration standards are prepared from the single element stock solutions at appropriate concentration levels for each element. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing each multielement calibration standard solution that the elements be compatible and stable. An appropriate amount of concentrated nitric acid is added to stock standard aliquots and final volume brought to 100 mL with distilled-deionized water to ensure that the final nitric acid concentration is 10 volume %. Transfer each multielement calibration standard solution to a FEP fluorocarbon or new polyethylene bottle for storage. Fresh calibration standards should be prepared as needed with the realization that concentration can change with age. Calibration standards must be initially verified using a quality control sample monitored weekly for stability. The actual number of calibration standards needed will be a function of both chemical compatibility and the restrictions of the computer system used to control the spectrometer. Additional calibration standards may be needed if a second, less sensitive emission line is used to extend the linear range of one or more elements. Although not specifically required, some typical standard combinations are given below when using the specific analytical wavelengths listed in Table 1.

8.4.1 *Mixed Standard Solution I*—Aluminum, barium, chromium, copper, iron, potassium, magnesium, manganese, nickel, and sodium.

8.4.2 *Mixed Standard Solution II*—Beryllium, calcium, lithium, silver, strontium, thorium, titanium, vanadium, and zirconium.

8.4.3 *Mixed Standard Solution III*—Boron, cadmium, cobalt, lead, phosphorus, and zinc.

8.4.4 *Single Element Standard*—A single element standard solution is suggested for uranium due to the high probability of spectral interference with other elements.

8.5 *Interference Check Sample*—The interference check sample is prepared from single element stock standard solutions to contain elements and concentrations appropriate to the sample type.

8.6 *Calibration Blank*—The calibration blank is prepared by adding one volume of nitric acid (specific gravity 1.42) to nine volumes of distilled-deionized water. Prepare a sufficient quantity to be used for flushing the system between standards and samples.

8.7 *Reagent Blank*—The reagent blank must contain all of the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

8.8 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3).

8.9 *Nitric Acid*, 10 volume %—One volume of concentrated nitric acid (specific gravity 1.42) brought to ten volumes with distilled-deionized water.

9. Calibration and Standardization

9.1 After a warm-up time of at least 30 min, operate the spectrometer according to the operation manual for the instrument.

9.2 Calibrate the instrument by aspirating the blank and standards. A flush-out time of approximately 1½ to 2 min should be allowed between standards, during which a calibration blank [10 volume % HNO_3] is aspirated. The computer establishes the slope, intercept, and correlation statistics for each element. Suggested analytical wavelengths are listed in Table 1.

9.3 To minimize physical interferences caused by changes in sample transport processes (due to variations in sample viscosity and concentration), it may be necessary to use a peristaltic pump in conjunction with certain nebulizers.

10. Sample Preparation

10.1 Samples that are clear, without solids, and have a pH <5 require no sample pretreatment.

10.2 Samples that contain undissolved solids are treated as follows:

10.2.1 Pipette 10 mL of the well-mixed sample to 100 mL beaker and add 10 mL of HNO_3(sp gr 1.42).

NOTE 1—This test method is written for analysis of solutions containing 10 % (v/v) nitric acid. This test method can be modified to accomodate the use of another mineral acid at a different concentration. The user must determine the operating parameters and precision and bias under the modified conditions.

10.2.2 Heat the sample on a hotplate until the volume has been reduced to <2 mL.

10.2.3 Quantitatively transfer the contents of the beaker to a 100-mL volumetric flask while filtering undissolved solids using a 2.5 µm pore size, acid washed cellulose filter paper or equivalent, add 10 mL of HNO_3(sp gr 1.42), and dilute to volume with distilled-deionized water.

10.3 Oils and oily waste samples can be prepared using Standard Practice C 1234.

11. Procedure

11.1 Aspirate the samples, prepared in accordance with Section 10, into the calibrated ICP-AES using the same sample conditions as used for the calibration procedure.

11.2 Analyze instrument check standards (from one of the working standards), blanks, and a digested internal control sample at a 10 % frequency or better. The results on the instrument check standards are to be within ±10 %, and the internal control samples are to fall within established limits of deviation. If the results exceed these limits, investigate the cause and take corrective action.

11.3 Take a duplicate sample in the field. Analyze both the original sample and the duplicate. Process duplicates through the entire dissolution and analysis procedure at a 10 % frequency or better. The results are to fall within established limits of deviation. If the results exceed these limits, investigate the cause and take corrective action. Duplicate analysis data are a measure of an analytical and sampling reproducibility; these data are applicable only in situations in which sample homogeneity is ensured.

NOTE 2—Many waste stream samples will not be homogenous and duplicate field samples may not fall within established limits. Note this situation in the data report.

11.4 Analyze an interference check sample at the beginning and the end of each sample run or a minimum of twice per eight hour work shift, whichever is more frequent. This check sample should contain, in relatively high concentration, those elements which are expected to be present at significant levels in the waste stream samples and which are known interfering species (for example, aluminum, iron, chromium, uranium, vanadium, etc.). All other elements should be present at relatively low levels in order to assess the quality of interference corrections.

11.5 Use the background and interference corrected data to calculate the concentration of each element in the waste stream sample. The computer performs this calculation, including the dilution factor.

12. Precision and Bias

12.1 Table 3 gives typical data for the analysis of a simulated waste sample used to evaluate the precision and bias.

TABLE 3 Estimate of Precision and Bias

Element	n	Accepted Value, mg/L	Mean Concentration, mg/L	Standard Deviation	% Relative Standard Deviation	Bias Average, Accepted	% Bias Bias/Accepted × 100
Beryllium	39	10.0	9.72	0.682	7.02	−0.280	−2.80
Boron	35	30.0	29.2	1.85	6.33	−0.778	−2.59
Cadmium	34	10.0	9.93	0.608	6.12	−0.066	−0.660
Calcium	39	50.0	52.6	3.26	6.20	2.61	5.22
Cobalt	35	10.0	9.83	0.868	8.83	−0.173	−1.73
Lead	34	10.0	9.62	0.778	8.09	−0.376	−3.76
Phosphorus	34	30.0	30.6	2.94	9.61	0.592	1.97
Silver	39	10.0	9.53	0.653	6.85	−0.473	−4.73
Strontium	39	10.0	9.93	0.585	5.89	−0.066	−0.660
Thorium	39	20.0	19.4	1.34	6.91	−0.628	−3.14
Titanium	39	10.0	10.1	0.674	6.67	0.058	0.580
Vanadium	39	10.0	9.74	0.613	6.29	−0.260	−2.60
Zinc	34	10.0	9.91	0.583	5.88	−0.086	−0.860
Zirconium	39	10.0	10.2	0.684	6.71	0.146	1.46

The simulated sample was prepared by spiking 10 volume % HNO_3 with the concentration of the elements listed in Table 3. The simulated waste sample was prepared and analyzed as a routine sample at a frequency of one sample per week.

12.2 Results for the analysis of a blind control used to evaluate the precision in a typical sample matrix are given in Table 4. A batch of waste material was reserved for processing as the control, and the control sample was prepared and analyzed at a frequency of one sample per week.

13. Keywords

13.1 inductively coupled plasma; mixed waste; mixed waste analysis; spectroscopy; waste treatment

TABLE 4 Estimate of Precision (Blind Control)

Element	n	Mean Concentration, mg/L	% Relative Standard Deviation
Aluminum	19	498.0	2.30
Barium	18	1.52	3.81
Beryllium	19	0.159	7.04
Boron	18	<0.04	...
Cadmium	18	0.407	62.7
Calcium	18	1390.0	3.86
Chromium	19	4.47	7.62
Cobalt	17	0.224	9.86
Copper	19	25.8	6.49
Iron	19	7610.0	5.46
Lead	19	4.11	15.1
Lithium	18	1.81	4.25
Magnesium	18	89.5	3.09
Manganese	18	20.6	3.67
Nickel	18	25.7	4.43
Phosphorus	17	21.7	105.0
Potassium	19	369.0	5.32
Silver	17	0.117	19.2
Sodium	19	80.9	2.80
Strontium	18	0.821	6.98
Thorium	19	<2.0	...
Titanium	19	1.90	6.19
Vanadium	19	0.871	6.14
Zinc	19	49.8	3.63
Zirconium	17	6.79	5.55