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Standard Test Method for Analysis of Tin-Based Solder Alloys for Minor and Trace Elements Using Inductively Coupled Plasma Atomic Emission Spectrometry[1]

This standard is issued under the fixed designation F3139; 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 procedures for the analysis of tin-based solder alloys for minor and trace elements using inductively-coupled plasma atomic emission spectrometry (ICP-AES) instrumentation.

1.2 These test procedures were validated for the analytes and mass fractions listed below.

Element	Validated Mass Fraction Range, mg/kg
Lead	115 to 965
Cadmium	25 to 60
Mercury	5 to 530
Antimony	85 to 1330
Bismuth	80 to 210
Arsenic	95 to 360
Silver	4000 to 42100
Cobalt	0.5 to 60
Iron	15 to 115
Chromium	0.5 to 1.5
Copper	3000 to 30600
Indium	25 to 115
Nickel	5 to 150
Phosphorus	10 to 110
Selenium	1 to 30
Zinc	2 to 160
Aluminum	1 to 3

1.3 The procedures appear in the following order:

Procedure	Section
Internal Standardization	8
Calibration Solution Preparations	9
Preparation of Sample and Validation Solutions	10
Calibration	11
Analysis Procedure	12

1.4 The values stated in SI units are to be regarded as the standard. Any other values are for information only.

1.5 *This standard does not purport to address all of the safety concerns, 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]

D1129 Terminology Relating to Water

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E416 Practice for Planning and Safe Operation of a Spectrochemical Laboratory (Withdrawn 2005)[3]

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E1479 Practice for Describing and Specifying Inductively-Coupled Plasma Atomic Emission Spectrometers

3. Terminology

3.1 *Definitions*—For definitions of other terms used in this test method, refer to Terminology D1129.

3.2 *Acronyms:*

3.2.1 *ACS, n*—American Chemical Society

3.2.2 *ICP-AES, n*—inductively-coupled plasma atomic emission spectrometry

3.2.3 *PE, n*—polyethylene

3.2.4 *SI, n*—Le Système International d'Unités, International System of Units

3.3 *Definitions of Terms Specific to This Standard:*

3.3.1 *calibration blank, n*—a volume of water containing the same acid matrix as found in the calibration standards.

3.3.2 *calibration standards, n*—a series of known standard solutions used to calibrate an instrument.

3.3.3 *check standard, n*—standard used to verify proper instrument calibration.

[1] This test method is under the jurisdiction of ASTM Committee F40 on Declarable Substances in Materials and is the direct responsibility of Subcommittee F40.01 on Test Methods.

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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] The last approved version of this historical standard is referenced on www.astm.org.

3.3.4 *instrument linear range, n*—range where instrument response and accuracy remain within typically 5 to 10 % of known values.

3.3.5 *internal standard, n*—pure element(s) added in known amount(s) to a solution to be used to improve instrument accuracy.

3.3.6 *reference material solution, n*—solution standard with known certified mass fraction(s), typically commercially available.

3.3.7 *sample introduction system, n*—plasma torch, mixing chamber and nebulizer used to deliver solutions to the plasma for analysis.

3.3.8 *validation sample, n*—a solder alloy sample that has been certified or well characterized for mass fractions of analytes present, and can be used to validate the method.

4. Significance and Use

4.1 Tin-based solder alloys are commonly used to manufacture electrical and electronic goods. The elements lead, cadmium, mercury, antimony and bismuth are often declarable substances in solder materials. This test method provides a means of determining the listed declarable substances, as well as other minor and trace constituents, in tin-based solder alloys.

4.2 Two methods of dissolving tin-based solder alloys are given in this standard. The first method uses open-vessel hydrofluoric and nitric acid room temperature digestions; the second method employs closed-vessel nitric and hydrofluoric acid microwave digestions, both for use only with ICP-AES instruments equipped with a hydrofluoric acid resistant sample introduction system.

4.3 The method of preparing calibration solutions uses 1000 mg/kg single element reference material solutions, and uses matching concentrated acids for both the calibration solutions and the sample solutions.

4.4 This test method is intended for use by laboratories experienced with the set-up, calibration and analysis of samples using ICP-AES.

5. Reagents

5.1 *Purity of Reagents*—Reagent grade chemicals, at a minimum, shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[4] Other grades equivalent or better than the ACS grade reagents may also be used.

5.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean high purity water, that when produced, measures at minimum 18 Megohm cm^{-1} resistivity.

5.3 *Concentrated Acids*—When acids are specified by name or chemical formula only, it should be understood that concentrated reagents of the following mass fractions are intended:

Concentrated Acid	Nominal Mass Fraction
Hydrofluoric acid, HF	48 %
Nitric acid, HNO_3	69 %

5.4 *Single Element Reference Material Solutions*—All single element solutions used in this method must have assigned mass fraction values in mg/kg units as opposed to mg/L units. It is possible to derive mg/kg values from mg/L assigned values through determination of standard solution density and subsequent calculation of mg/kg unit values.

5.4.1 The method of preparing calibration solutions uses 1000 mg/kg single element reference material solutions of Pb, Cd, Hg, Sb, Bi, As, Ag, Co, Fe, Cr, Cu, In, Ni, P, Se, Zn, Al, Ge, and Tl. A single element reference material solution of Sc at 1000 mg/kg is required for use as an internal standard.

5.4.2 It is not important that the assigned value of the reference material solutions be exactly 1000 mg/kg; for example, the assigned value may be 1001 mg/kg or 997 mg/kg.

6. Equipment

6.1 *Inductively Coupled Plasma-Atomic Emission Spectrometry System (ICP-AES)*—Many makes and models of ICP-AES instruments are available on the market. See Practice E1479 for a general description of ICP-AES instrumentation. The specific instrumentation used is not as important as its performance with regard to precision and sensitivity. However, a few important considerations for successful method performance are given below:

6.1.1 *Sample Introduction System*—Measurement of samples prepared using hydrofluoric acid (HF) requires that the sample introduction system must be designed specifically to come in contact with HF. Glass sample introduction systems are not compatible with HF, as glass is dissolved (etched) by the acid. HF contact causes excessive wear of glass parts and contamination of samples, thus having a negative impact on the equipment as well as results. Consult with the instrument manufacturer before using solutions containing HF.

6.1.2 *Nebulizer*—Analysis of samples prepared using HF requires that the nebulizer, as part of the sample introduction system, must be compatible with HF. In addition, this method requires analysis of solutions with relatively high solids content on the order of 0.5 % by mass (5000 mg/kg). The nebulizer should be chosen to accommodate free flow of high-solids solutions such that the nebulizer does not clog during the procedure, thus allowing consistent sample introduction.

6.1.3 *Facility Design*—A general description of design considerations for a spectrochemical laboratory can be found in Practice E416. Temperature control within the laboratory housing the ICP-AES system, and consistent power supply to the instrument are two of the most important considerations. ICP-AES equipment tends to produce a significant amount of heat while in operation and variation in room temperature can

[4] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

have a significant impact on the stability of instrument measurements. Sufficient equipment warm-up period and subsequent stabilization of room temperature may be necessary to produce consistent measurements. Variations in power supplied to the instrument can likewise have an impact on the stability of instrument measurements, so stabilization of the power input may also be necessary to produce consistent measurements.

6.2 *Analytical Balance*—A balance with minimum readability of 0.0001 g for loads up to 150 g is required for successful performance of this method.

6.3 *Microwave Digestion Equipment*—Modern laboratory microwave equipment, including pressure vessels, provide heat and pressure to digest difficult samples without potential loss of analytes common to open hotplate digestions. Closed-vessel microwave digestion can help prevent possible loss of volatile elements, such as mercury, during sample preparation. Use only microwave equipment designed specifically for laboratory use.

7. Hazards

7.1 Hydrofluoric acid and hydrofluoric acid fumes can pose significant risk to the operator. Proper handling should be observed at all times, including the use of laboratory fume hoods, and laboratory coats, polymer gloves and protective eyewear. Carefully handle all solutions. Be sure to let microwave vessels cool for a sufficient amount of time before opening. Be sure to use only HF resistant sample introduction components so as not to cause damage to glass parts. Always maintain the capability to flush skin with water for at least 5 min in case of skin contact with HF; keep calcium gluconate or equivalent in the laboratory to neutralize contact with HF. Seek appropriate emergency medical help after contact with HF or HF fumes for unknown or extended periods of time.

8. Internal Standardization

8.1 The internal standard procedure requires that every test solution have the same mass fraction of an internal standard element that is not present in the original specimen. Specimen to specimen changes in the emission intensity of the internal standard element can be used to correct for variations in the test specimen introduction efficiency, which is dependent on the physical properties of the test specimen (such as dissolved solids content, acid mass fraction, etc).

8.2 *Internal Standard Solution*—Weigh approximately 5 g (to the nearest 10 mg) of 1000 mg/kg Sc reference material solution into a 100 mL polyethylene bottle and dilute to 100 g with 5 % v/v HNO_3. Prepare fresh at least monthly. The same batch of internal standard solution should be used for all blanks, calibrations standards, validation samples, and unknown samples within an analysis.

9. Calibration Solution Preparations

9.1 *Preparation of Calibration Solutions—Sample Preparation Method 1, Section 10.1:*

9.1.1 *Calibration Blank*—Prepare a calibration blank by making a 10 % v/v HNO_3/10 % v/v HF solution, and adding 2.0 g ± 20 mg (weighed to the nearest 10 mg) of 50 mg/kg Sc internal standard solution per 100 g final weight of blank solution. The Sc internal standard will be at the same mass fraction as in the calibration standards and samples (1.0 mg/kg Sc).

9.1.2 *Calibration Standards*—2 mg/kg and 10 mg/kg—Weigh 0.2 g ± 2 mg and 1 g ± 10 mg (to the nearest 1 mg), respectively, of each of the single element 1000 mg/kg reference material solutions into 100 mL polyethylene bottles. Dilute each with approximately 50 g of 10 % v/v HNO_3/10 % v/v HF, and add 2.0 ± 0.2 g (weighed to the nearest 10 mg) of 50 mg/kg Sc internal standard solution. Dilute to final weight of 100 g ± 1.0 g (weighed to the nearest 100 mg) with 10 % v/vHNO_3/10 % v/v HF.

9.1.3 *Check Standards*—Prepare at least one instrument check standard in the same manner as the calibration standards, such that the element mass fractions in the check standards are similar to the element mass fractions in the test samples.

9.1.4 Verify that the internal standard element is stable in solution by visually examining for cloudiness or precipitate.

9.2 *Preparation of Calibration Solutions—Sample Preparation Method 2, Section 10.2:*

9.2.1 Prepare calibration standards as directed in 9.1, using a 7 % v/v HNO_3/7 % v/v HF acid mixture, instead of the 10 % v/v HNO_3/10 % v/v HF solution.

10. Preparation of Sample and Validation Solutions

10.1 *Method 1–Open Vessel Digestion*—For each sample and validation sample, weigh out 0.5 g ± 10 mg (to the nearest 1 mg) and place into 60 mL polyethylene bottles. This sample weight is defined as SW_1. To digest, add 5 mL H_2O, followed by the slow addition of 5 mL concentrated HF. Add 5 mL concentrated HNO_3 in 0.2 mL increments to reduce volatility of the reaction. Most samples will dissolve immediately or within 5 to 10 min. Add approximately 20 g H_2O to sample and mix. Add 1.0 g ± 10 mg (weighed to the nearest 10 mg) of 50 mg/kg Sc internal standard solution (prepared from 1000 mg/kg Sc reference material solution), and dilute sample to final weight of 50 ± 0.5 g (weighed to the nearest 10 mg) with H_2O. The final weight of the diluted sample is defined as FW_1. Prepare a blank solution in the same manner. Verify the stability of the internal standard as described in 9.1.4.

NOTE 1—**Warning:** Take precautions to protect lab personnel from the harmful effects of contact with HF. Treat HF exposure immediately; see 7.1 for additional information.

10.2 *Method 2—Closed-Vessel Microwave Digestion*—For each sample and validation sample, weigh out 0.5 g ± 10 mg (to the nearest 1 mg) and place into a high-pressure microwave vessel. This sample weight is defined as SW_1. Add dropwise 10 mL of 1:1:1 H_2O/conc. HNO_3/conc. HF. Caution must be used as the reaction is quite vigorous and exothermic. Close vessel and digest in laboratory microwave oven according to the following program:

Heating Program: Ramp to Temperature
Max Power = 800 W
Power = 100 %
Power Ramp = 10 min
Maximum Pressure = 800 psi (5500 kPa)
Temperature = 180° C
Hold = 10 min

10.2.1 Allow vessels to cool completely following completion of the program. Carefully vent and remove the vessel caps. Transfer sample quantitatively to 60 mL polyethylene bottle and add approximately 20 g of H_2O to complete dissolution and mix. Add 1.0 g ± 10 mg (weighed to the nearest 10 mg) of 50 mg/kg Sc internal standard solution (prepared from 1000 mg/kg Sc reference material solution), and dilute sample to final weight of 50 ± 0.5 g (weighed to the nearest 10 mg) with H_2O. The final weight of the diluted sample is defined as FW_1. Prepare a blank solution in the same manner. Verify the stability of the internal standard as described in 9.1.4. If these specific microwave oven parameters cannot be reproduced, then the analyst must ensure that proper validation samples are prepared and analyzed in order to validate alternate microwave digestion conditions (see 10.4).

NOTE 2—Sample Preparation Method 2 is not recommended for the determination of Bi due to low observed recoveries.

10.3 *Second Dilutions*—Second dilutions are required for all samples containing element mass fractions that exceed the linear range of the calibration (see 11.1). In general, element mass fractions greater than 1000 mg/kg in the solid material should be diluted further. Prepare the second dilutions by weighing 0.5 g ± 10 mg (to the nearest 1 mg) aliquots of the sample solutions, prepared in 10.1 or 10.2, into 60 mL polyethylene bottles. The weight of this aliquot is defined as SW_2. Add 1.0 g ± 10 mg (weighed to the nearest 10 mg) of 50 mg/kg Sc internal standard solution (prepared from 1000 mg/kg Sc reference material solution), and dilute sample to final weight of 50 ± 0.5 g (weighed to the nearest 10 mg) with the same acid mixture used in Section 9 (if Method 1 is used, dilute with the acid mixture described in 9.1.2, and if Method 2 is used, dilute with the acid mixture described in 9.2.1). The final weight of this second dilution is defined as FW_2.

NOTE 3—**Warning:** Take precautions to protect laboratory personnel from the harmful effects of contact with HF. Treat HF exposure immediately; see 7.1 for additional information.

10.4 *Validation Samples*—Validation samples should be selected to match the type of tin-based solder alloy being analyzed, in terms of major and minor element mass fraction ranges. For example, a 97 % Sn 3 % Cu alloy should ideally have a validation sample that is close to those Sn and Cu mass fractions, while a 95 % Sn 5 % Ag alloy should have a validation sample more closely matching the mass fractions for Sn and Ag. In both cases, the minor and trace elements should be certified or well-characterized and include as many of the analytes of interest as possible.

11. Calibration

11.1 *Instrument Linear Range*—The linear range must be established once for the particular instrument being used. This is accomplished by measuring intermediate standards between the blank and the high calibration standard, and by measuring standards containing higher mass fractions than the high calibration standard. If standards are added having higher mass fractions above the 10 mg/kg calibration standard, they must be included in the calibration as well. As mass fractions increase, the response of the instrument will become non-linear. Analyses of test solutions must be performed within the linear range of response. Test solutions that exceed the linear range of the instrument must be diluted further according to 10.3.

11.2 *Calibration Standards*—At the beginning of the analysis, perform a three-point calibration (or more points, as indicated in 11.1) consisting of the calibration blank and the two calibration standards. Use the Check Standard to determine if each element is in calibration. When the results obtained with the Check Standard are within the laboratory's acceptable quality control range, proceed with test sample analysis. In the absence of established control limits, ±5 % is recommended for an acceptable range.

12. Analysis Procedure

12.1 Analyze the blank, sample and validation solutions in the same manner as the calibration standards, that is, the same integration time, background correction points, plasma conditions, etc. Calculate elemental mass fractions (X) by multiplying the measured mass fraction (Y) in the diluted test samples by the final dilution factor (DF), according to the equations below:

$$DF = (FW_1 / SW_1) \times (FW_2 / SW_2) \quad (1)$$

$$X(\text{mg}/\text{kg}) = Y(\text{mg}/\text{kg}) \times DF \quad (2)$$

NOTE 4—If no second dilution is performed, $FW_2/SW_2 = 1$

Example:

DF = 50.5 g FW_1/ 0.502 SW_1 = 100.6

X(mg/kg) = 8.54 mg/kg Y × 100.6 = 859 mg/kg

12.1.1 If the response for any given test solution does not fall within the linear range of calibration, then perform a second dilution according to 10.3.

12.2 *Quality Control with Check Standard*—Analyze the Check Standard after every 10th sample, and if any result is not within the laboratory's acceptable quality control range, recalibrate the instrument and reanalyze the test samples back to the previous acceptable check standard analysis. In the absence of established control limits, ±5 % is recommended for an acceptable range.

13. Report

13.1 Report mass fractions in mg/kg for all elements.

14. Precision and Bias

14.1 The precision and bias of this test method is based on an Interlaboratory study of WK9866, Standard Test Method for Analysis of Tin-Based Solder Alloys for Minor and Trace Elements Using Inductively-Coupled Plasma Atomic Emission Spectrometry, conducted in 2010. A total of five laboratories participated in this study in an effort to determine the intralaboratory and interlaboratory precision and bias of the test method for both room temperature and microwave analysis. Laboratories reported one to three test results per analyte, based upon individual preparations of each test analyte. Practice E691 was followed for the design and analysis of the data,