Designation: E 37 – 00

Standard Test Methods for Chemical Analysis of Pig Lead[1]

This standard is issued under the fixed designation E 37; 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 These test methods cover the chemical analysis of pig lead having chemical compositions within the following limits:

Element	Concentration Range, %
Antimony	0.001 to 0.02
Arsenic	0.0005 to 0.02
Bismuth	0.002 to 0.2
Copper	0.001 to 0.1
Iron	0.0005 to 0.005
Lead	99.5 to 99.99
Silver	0.001 to 0.03
Tin	0.001 to 0.02
Zinc	0.001 to 0.005

1.2 The test methods appear in the following order:

	Sections
Antimony by the Rhodamine-B Photometric Method	19-28
Copper, Bismuth, Silver, and Zinc by the Atomic Absorption Method	8-18

1.3 *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 consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For precautions to be observed in the use of certain reagents, refer to Practices E 50. Specific hazard statements are given in the individual test methods.

2. Referenced Documents

2.1 *ASTM Standards:*

B 29 Specification for Pig Lead[2]

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance With Specifications[3]

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals[4]

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals[4]

E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals[4]

3. Significance and Use

3.1 These test methods for the chemical analysis of metals and alloys are primarily intended to test such materials for compliance with compositional specifications. It is assumed that all who use these methods will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that work will be performed in a properly equipped laboratory.

4. Apparatus, Reagents, and Photometric Practice

4.1 Apparatus and reagents required for each determination are listed in separate sections of each test method. The apparatus, standard solutions, and certain other reagents used in more than one procedure are referred to by number and shall conform to the requirements prescribed in Practices E 50, except that photometers shall conform to the requirements prescribed in Practice E 60.

5. Sampling

5.1 For procedures for sampling the material, refer to Specification B 29.

6. Rounding Calculated Values

6.1 Calculated values shall be rounded to the desired number of places as directed in 3.4 to 3.6 of Practice E 29.

7. Interlaboratory Studies

7.1 These test methods have been evaluated in accordance with Practice E 173, unless otherwise noted in the precision section.

COPPER, BISMUTH, SILVER, AND ZINC BY THE ATOMIC ABSORPTION METHOD

8. Scope

8.1 This test method covers the determination of bismuth in concentrations from 0.002 to 0.2 %, copper from 0.001 to 0.1 %, silver from 0.001 to 0.03 %, and zinc from 0.001 to 0.005 %.

9. Summary of Test Method

9.1 The sample is dissolved in a nitric-perchloric acid mixture, the solution is fumed, and hydrochloric acid is added to precipitate lead chloride. The hydrochloric-perchloric acid solution is aspirated into the air-acetylene flame of an atomic

[1] These test methods are under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and are the direct responsibility of Subcommittee E01.05 on Zinc, Tin, Lead, Cadmium, Beryllium and Other Metals.

Current edition approved Nov. **10**, 2000. Published February 2001. Originally published as E 37 – 42 T. Last previous edition E 37 – 95.

[2] *Annual Book of ASTM Standards*, Vol 02.04.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] *Annual Book of ASTM Standards*, Vol 03.05.

absorption spectrophotometer. The absorption of the resonance line energy from the spectrum of each element is measured and compared with that of calibration solutions of the same element. The lines used were Cu 3247, Bi 2230, Ag 3280, and Zn 2138 Å.

10. Concentration Range

10.1 The concentration range for each element must be determined experimentally because the optimum range will depend upon the individual instrument. Determine the appropriate concentration range of each element as follows:

10.1.1 Prepare a dilute standard solution as directed in Section 14. Refer to 14.1 for suggested initial concentrations.

10.1.2 Prepare the instrument for use as directed in 16.1. Measure the instrument response while aspirating water, the calibration solution with the lowest concentration, and the two with the highest concentrations. Determine the minimum response and the curve linearity as directed in 12.1.1 and 12.1.2, respectively.

10.1.3 If the instrument meets or surpasses the minimum response and curve linearity criteria, the initial concentration range may be considered suitable for use. In this case proceed as directed in 10.1.5.

10.1.4 If the minimum response is not achieved, prepare another dilute standard solution to provide a higher concentration range, and repeat 10.1.2 and 10.1.3. If the calibration curve does not meet the linearity criterion, prepare another dilute standard solution to provide a lower concentration range, and repeat 10.1.2 and 10.1.3. If a concentration range cannot be found for which both criteria can be met, do not use this method until the performance of the apparatus has been improved.

10.1.5 Perform the stability test as directed in 12.1.3. If either of the minimum stability requirements is not met, do not use this method until the repeatability of the readings has been suitably improved.

11. Interferences

11.1 Elements ordinarily present do not interfere if their concentrations are under the maximum limits shown in 1.1.

12. Apparatus

12.1 *Atomic Absorption Spectrophotometer*—Use hollow-cathode lamps, operated in accordance with manufacturers' recommendations as sources for the following lines: Cu 324.7, Bi 223.0, Ag 328.0, and Zn 213.8 nm. Aspirate the solutions into an air-acetylene flame of a premix burner. Determine that the atomic absorption spectrophotometer is satisfactory for use in this method by proceeding as directed in 12.1.1-12.1.3.

NOTE 1—Optimum settings for the operating parameters of the atomic absorption spectrophotometer vary from instrument to instrument.

12.1.1 *Minimum Response*— Calculate the difference between the readings of the two highest of five equally spaced (14.2) calibration solutions. This difference must be at least 40 scale units.

NOTE 2—The scale unit is defined as the smallest numerical interval that is estimated in taking each reading on the instrument. If the scale is non-linear, the largest unit defined in this manner is used.

12.1.2 *Curve Linearity*— Calculate the difference between the scale readings obtained with water and the lowest of the five equally spaced calibration solutions. If necessary, convert this difference and the difference calculated in 12.1.1 to absorbance. Divide the difference for the highest interval by that for the lowest interval. If this ratio is not 0.70 or greater, proceed as directed in 10.1.4.

12.1.3 *Minimum Stability*—If the variability of the readings of the highest calibration solution and of water is not less than 1.8 % and 1.4 %, respectively, as calculated below, proceed as directed in 10.1.5.

$$V_C = \frac{100}{\bar{C}} \sqrt{\frac{\Sigma(C - \bar{C})^2}{n-1}} \qquad (1)$$

$$V_o = \frac{100}{\bar{C}} \sqrt{\frac{\Sigma(O - \bar{O})^2}{n-1}}$$

where:

V_C = percent variability of the highest calibration readings,

$\bar{C}$ = average absorbance value for the highest calibration solution,

$\Sigma (C - \bar{X})^2$ = sum of the squares of the n differences between the absorbance readings of the highest calibration solution and their average,

V_O = percent variability of the readings on water relative to $\bar{C}$,

$\bar{O}$ = average absorbance value of water,

$\Sigma (O - \bar{O})^2$ = sum of the squares of the n difference between the absorbance readings of water and their average, and

n = number of determinations, three or more.

13. Reagents

13.1 *Bismuth, Standard Solution* (1 mL = 1.00 mg Bi)—Transfer 1.00 g of bismuth (purity: 99.9 % min) to a 400-mL beaker and dissolve in 50 mL of HNO_3 (1 + 1), heating gently if necessary. When dissolution is complete, cool, transfer to a 1-L volumetric flask, add 100 mL of HNO_3 (1 + 1), dilute to volume, and mix. Store in a polyethylene bottle.

13.2 *Copper, Standard Solution* (1 mL = 1.00 mg Cu)—Proceed as directed in 13.1, but substitute 1.00 g of copper (purity: 99.9 % min) for the bismuth.

13.3 *Silver, Standard Solution* (1 mL = 1.00 mg Ag)—Proceed as directed in 13.1 but substitute 1.00 g of silver (purity: 99.9 % min) for the bismuth.

13.4 *Zinc, Standard Solution* (1 mL = 0.100 mg Zn)—Proceed as directed in 13.1 but substitute 0.100 g of zinc (purity: 99.9 % min) for the bismuth.

14. Calibration

14.1 *Dilute Standard Solution*—Using pipets, transfer to 500-mL volumetric flasks the following volumes of each standard solution: bismuth, 20 mL; copper, 10 mL; silver, 5 mL; and zinc, 10 mL. Dilute to volume and mix. Adjust the concentration of a dilute standard solution if the proper range is not obtained when the 5, 10, 15, 20, and 25-mL portions are diluted to 100 mL and tested.

14.2 *Calibration Solutions*—Prepare five calibration solutions for each element to be determined. Using pipets, transfer

5, 10, 15, 20, and 25-mL portions of the appropriate dilute standard solution to 100-mL volumetric flasks. Add sufficient volumes of HCl and $HClO_4$ to each flask to yield final acid concentrations equal to that of the corresponding test solution, dilute to volume, and mix. Do not use solutions that have stood more than 24 h.

15. Procedure

15.1 *Test Solution*:

15.1.1 Transfer a 10.0-g sample, weighed to the nearest 10 mg, to a 300-mL Erlenmeyer flask (Note 3). Add 3 mL of HNO_3 and 15 mL of $HClO_4$, and heat until dissolution is complete. Evaporate to strong fumes of perchloric acid and cool.

NOTE 3—Due to the limited solubility of silver chloride, the silver concentration in the sample solution should be less than 1 mg/100 mL. If the expected silver concentration is higher than 0.01 %, choose a sample weight that limits the silver concentration to less than 1 mg/100 mL.

15.1.2 Add 50 mL of water and, while swirling, heat to boiling. Add 25 mL of HCl. If less than a 10-g sample is used, add 20 mL HCl plus 0.5 mL for each gram of sample used. Heat again to boiling and cool to room temperature.

15.1.3 Transfer the solution and precipitate to a 100-mL volumetric flask, dilute to volume with water, and mix thoroughly. Allow the precipitated lead chloride to settle. Use the supernatant solution, or dilute an appropriate aliquot of the supernatant solution to provide a concentration of the element being measured which lies within the concentration range determined in Section 10.

15.2 *Reagent Blank Solution*—Prepare a reagent blank by adding 3 mL of HNO_3 and 15 mL of $HClO_4$ to a 300-mL Erlenmeyer flask and proceed as directed in 15.1.

16. Photometry

16.1 *Instrument Adjustment*—Optimize the response of the instrument as directed in 16.1.1-16.1.4.

16.1.1 Set the instrument parameters approximately at the values obtained in 12.1, and light the burner.

16.1.2 Adjust the instrument to the approximate wavelength for the element to be determined, permit the instrument to reach thermal equilibrium, and complete the wavelength adjustment to obtain maximum absorption while aspirating the highest calibration solution.

16.1.3 Optimize fuel, air, and burner adjustments while aspirating the highest calibration solution.

16.1.4 Aspirate water long enough to establish that the absorbance reading is stable and then set the initial reading (approximately zero absorbance or 100 % transmittance).

16.2 *Photometry*:

16.2.1 Aspirate the test solution and note, but do not record the reading.

NOTE 4—Avoid transferring particles of precipitated lead chloride that may clog the aspirator during the measurements of the test solution.

16.2.2 Aspirate water until the initial reading is again obtained. Aspirate the calibration solutions and test solution in order of increasing instrument response, starting with the reagent blank. When a stable response is obtained for each solution, record the reading.

16.2.3 Proceed as directed in 16.2.2 at least twice more.

17. Calculations

17.1 Calculate the variability of the readings for water and the highest calibration solution as directed in 12.1.3 to determine whether they are less than 1.4 % and 1.8 %, respectively. If they are not, disregard the data, readjust the instrument, and proceed again as directed in 16.2.

17.2 If necessary, convert the average of the readings for each calibration solution to absorbance. Calculate the net absorbance of the test solution by subtracting the absorbance of the reagent blank solution.

17.3 Prepare a calibration curve by plotting the absorbance values for the calibration solutions against milligrams of the elements per millilitre.

17.4 Convert the net absorbance value of the test solution to milligrams of the element per millilitre by means of the appropriate calibration curve.

17.5 Calculate the percentage of the element as follows (Note 5):

$$\text{Element, \%} = [(A \times B \times 0.977)/C] \times 100 \quad (2)$$

where:

A = milligrams of element per millilitre,
B = final volume of test solution in millilitres, and
C = milligrams of sample represented in final volume of test solution.

NOTE 5—The factor 0.977 is used to compensate for the volume error in the 100 mL of final test solution caused by the 13.1 g of lead chloride precipitate. If less than 10 g of sample is used, calculate and apply an appropriate factor.

18. Precision and Bias

18.1 Seven laboratories cooperated in testing this method, with one laboratory reporting a second pair of values; the data are summarized in Table 1.

18.2 The accuracy of this method could not be evaluated because adequate certified standard reference materials were unavailable at the time of testing. The user is cautioned to verify by the use of certified reference materials, if available, that the accuracy of this method is adequate for the contemplated use.

ANTIMONY BY THE RHODAMINE-B PHOTOMETRIC METHOD

19. Scope

19.1 This test method covers the determination of antimony in pig lead in concentrations from 0.0008 to 0.005 %.

20. Summary of Test Method

20.1 After nitric acid dissolution of the sample, lead is

TABLE 1 Statistical Information

Test Specimen		Element Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
Bi	B-2	0.0024	0.0010	0.0010
	A-2	0.223	0.016	0.021
Cu	B-2	0.0014	0.0002	0.0002
	A-2	0.112	0.010	0.012
Ag	B-2	0.0010	0.0002	0.0002
	A-2	0.0308	0.0052	0.0052
Zn	C-1	0.0001	0.0004	0.0004
	D-1	0.0021	0.0003	0.0009

separated as the sulfate. Antimony is oxidized with sulfatoceric acid and extracted into isopropyl ether; rhodamine-B is added and photometric measurement is made at approximately 550 nm.

21. Concentration Range

21.1 The recommended concentration range is from 0.002 to 0.020 mg of antimony per 20 mL of solution, using a 1-cm cell.

NOTE 6—This method has been written for cells having a 1-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

22. Stability of Color

22.1 Because of the volatility of ether, it is advisable to make readings promptly.

23. Interferences

23.1 Elements ordinarily present do not interfere if their concentrations are under the maximum limits shown in 1.1.

24. Reagents

24.1 *Antimony, Standard Solution A* (1 mL = 0.1 mg Sb)—Dissolve 0.100 g of antimony (purity: 99.8 % min) in 1 mL of HNO_3 and 20 mL of H_2SO_4. Heat until dissolution is complete and then fume for 5 min. Cool, dilute carefully to about 200 mL, and transfer to a 1-L volumetric flask. Cool, dilute to volume, and mix.

24.2 *Antimony, Standard Solution B* (1 mL = 0.005 mg Sb)— Using a pipet, transfer 10 mL of Solution A (1 mL = 0.1 mg Sb) to a 200-mL volumetric flask. Add 5 mL of H_2SO_4. Cool, dilute to volume, and mix.

24.3 *Isopropyl Ether, Washed*—Transfer 500 mL of isopropyl ether to a 1-L separatory funnel. Add 200 mL of HCl and shake for 1 min. (Take care to avoid pressure build-up.) Add 200 mL of water and shake for 30 s. Allow the phases to separate and discard the aqueous phase. Wash the organic phase with 200 mL of water, and shake for 30 s. Allow the phases to separate and discard the aqueous phase. Repeat one more time. Do not use the reagent if it has stood more than 24 h.

24.4 *Rhodamine-B Solution* (0.1 g/L in 0.5 *M* HCl)—Dissolve 50 mg of rhodamine-B in water. Add 22 mL of HCl and dilute to 500 mL.

24.5 *Sulfatoceric Acid Solution* (2.0 g/L)—Dissolve 200 mg of sulfatoceric acid ($H_4Ce(SO_4)_4$) in water. Add 3 mL of H_2SO_4 (1 + 1) and dilute to 100 mL.

25. Preparation of Calibration Curve

25.1 *Calibration Solutions*—Using pipets, transfer 1, 2, 3, 4, and 5 mL of Solution B (1 mL = 0.005 mg Sb) to 250-mL beakers. Add 1 mL of H_2SO_4 and evaporate to dryness, but do not bake. Proceed as directed in 33.4.

25.2 *Reference Solution*—Isopropyl ether, washed.

25.3 *Reagent Blank*— Transfer 1 mL of H_2SO_4 to a 250-mL beaker and evaporate to dryness, but do not bake. Proceed as directed in 33.4.

25.4 *Color Development*:

25.4.1 Add 10 mL of HCl and swirl to dissolve the residue. Transfer to a 125-mL separatory funnel. Rinse the beaker with 7 mL of HCl and add the rinsings to the separatory funnel. Using a pipet, add 1 mL of sulfatoceric acid solution and mix. Using a pipet, add 20 mL of the washed isopropyl ether. Shake for approximately 30 s, releasing the pressure periodically.

25.4.2 To the original beaker, add 6 mL of water, swirl, and transfer to the separatory funnel. Repeat one more time. Shake for approximately 30 s and allow to cool to room temperature.

25.4.3 Shake for another 30 s. Allow the phases to separate and discard the lower (aqueous) phase. Add 20 mL of rhodamine-B solution and shake for approximately 30 s. Allow the phases to separate and discard the lower phase.

25.4.4 Draw off the ether phase into a dry, stoppered test tube and allow to settle for approximately 30 s before transferring to the absorption cell.

25.5 *Photometry*:

25.5.1 *Multiple-Cell Photometer*—Measure the cell correction using absorption cells with a 1-cm light path and a light band centered at approximately 550 nm. Using the test cell, take the photometric readings of the calibration and reagent blank solutions.

25.5.2 *Single-Cell Photometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the photometer to the initial setting, using a light band centered at approximately 550 nm. While maintaining this adjustment, take photometric readings of the calibration and reagent blank solutions.

25.6 *Calibration Curve*—Plot the net photometric readings of the calibration solutions against milligrams of antimony per 20 mL of solution.

26. Procedure

26.1 *Test Solution*:

26.1.1 Transfer a 1.00-g sample, weighed to the nearest 1 mg, to a 250-mL beaker. Add 10 mL of HNO_3 (1 + 2) and heat gently until dissolution is complete. Add 5 mL of H_2SO_4 (1 + 1), dilute to 30 mL, mix thoroughly, and cool to room temperature. Filter through an 11-cm coarse paper into a 250-mL beaker. Wash the precipitate with three 5-mL portions of cold water. Discard the precipitate.

26.1.2 For antimony concentrations from 0.0008 to 0.002 %, use the entire filtrate for color development. For antimony concentrations from 0.002 to 0.005 %, transfer the filtrate to a 100-mL volumetric flask, dilute to volume, and mix (Note 7). Using a pipet, transfer 40 mL to a 250-mL beaker.

NOTE 7—If concentrations greater than 0.005% are encountered, a correspondingly larger volumetric flask or a smaller aliquot portion should be used.

26.1.3 Evaporate the filtrate or the aliquot to dryness, but do not bake. Remove from the heat and cool to room temperature. Proceed as directed in 34.4.

26.2 *Reagent Blank*— Carry a reagent blank through the entire procedure using the same amount of all reagents with the sample omitted.

26.3 *Reference Solution*—Isopropyl ether, washed.

26.4 *Color Development*—Proceed as directed in 33.4.

26.5 *Photometry*—Take the photometric readings of the reagent blank and test solutions as directed in 33.5.

27. Calculation

27.1 Convert the net photometric readings of the test and reagent blank solutions to milligrams of antimony by means of the calibration curve. Calculate the percent of antimony as follows:

$$\text{Antimony, \%} = (A - B)/(C \times 10) \quad (3)$$

where:

A = milligrams of antimony found in 20 mL of the final test solution,
B = milligrams of antimony found in 20 mL of final reagent blank solution, and
C = grams of sample represented in 20 mL of the final test solution.

28. Precision and Bias

28.1 Data on this test method were obtained by six laboratories, with two laboratories providing a second pair of values. The data are summarized in Table 2.

TABLE 2 Statistical Information

Test Specimen	Element Found, %	Repeatability (R_1, E 173)	Reproducibility (R_2, E 173)
1	0.0008	0.0002	0.0002
2	0.0045	0.0003	0.0007

28.2 The accuracy of this test method could not be evaluated because adequate certified standard reference materials were unavailable at the time of testing. The user is cautioned to verify by the use of certified reference materials, if available, that the accuracy of this method is adequate for the contemplated use.

29. Keywords

29.1 antimony; atomic absorption; bismuth; colorimetry; copper; lead; silver; zinc