Designation: E 1615 – 0~~0~~4

Standard Test Method for Iron in Trace Quantities Using the FerroZine Method[1]

This standard is issued under the fixed designation E 1615; 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] This test method is under the jurisdiction of ASTM Committee E15 on Industrial and Specialty Chemicals and is the direct responsibility of Subcommittee E15.01 on General Standards.

Current edition approved ~~April 10, 2000.~~ March 1, 2004. Published ~~July 2000.~~ April 2004. Originally ~~published as E 1615 – 94.~~ approved in 1994. Last previous edition approved in 2000 as E 1615 – ~~94~~00.

1. Scope

1.1 This test method covers the determination of iron in the range from 0.05 to 10 µg/L using FerroZine[2] reagent solution. The range may be extended through the use of a 1- or 10-cm cell or by suitable dilution of the sample solution.

1.2 This test method is intended to be general for the final steps in the determination of iron and does not include procedures for sample preparation.

1.3 Review the current material safety data sheets (MSDS) for detailed information concerning toxicity, first-aid procedures, and safety precautions.

1.4 *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.* For specific hazards statements, see 7.4.

2. Referenced Documents

2.1 *ASTM Standards:* [3]

D 1193 Specification for Reagent Water

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

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

3. Summary of Test Method

3.1 This test method is based upon a photometric determination of the FerroZine complex with the iron (II) ion.[4, 5] The sample is dissolved in a suitable solvent and the iron is reacted with FerroZine reagent solution which will convert the dissolved iron compounds to form a magenta color iron (II) complex. The iron content of the sample solution is determined by measurement of the magenta color at 560 nm using a suitable photometer.

4. Significance and Use

4.1 This test method is suitable for determining trace concentrations of iron in a wide variety of products, provided that appropriate sample preparation has rendered the iron and sample matrix soluble in water or other suitable solvent. Each sample matrix must be investigated for suitability using this test method.

4.2 This test method assumes that the amount of color developed is proportional to the amount of iron in the test solution. The calibration curve is linear over the specified range.

5. Interferences

5.1 Any ion that absorbs light at 560 nm will interfere with the determination. Anionic interferences include oxalate in concentrations over 500 ~~ppm,~~ mg/kg, cyanide, and nitrate.[4]

5.2 Of copper, cobalt, calcium, magnesium, lead, silver, molybdenum, aluminum, nickel, zinc, arsenic, manganese, hexavalent chromium, trivalent chromium, divalent cobalt, and monovalent copper are the only metals other than iron that form colored species with FerroZine under test conditions. At least 1000 mg/L of the alkalai metals and the alkaline earths had no effect on the determination. Many heavy metals will react with FerroZine in competition with iron, but with the excess reagent used in the test there is no effect on the results.[4]

5.3 The pH range of the final solution should be from 4 to 9 to give the best test results.[4,5]

5.4 All glassware used in this test method must be iron-free and scrupulously clean by precleaning with dilute hydrochloric acid and FerroZine reagent solution followed by a water rinse.

6. Apparatus

6.1 *Photometer*, capable of measuring light absorption at 560 nm and holding a 5-cm or larger cell.

6.2 *Absorption Cells*, 5-cm light path.

NOTE 1—A discussion of photometers and photometric practice is given in Practice E 60.

7. Reagents

7.1 Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical

---

[2] FerroZine is a trademark of Hach Chemical Company.

[3] 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*, ~~Vol 11.01.~~ volume information, refer to the standard's Document Summary page on the ASTM website.

~~*Annual Book of ASTM Standards*~~

[4] Stookey, L. L., "FerroZine—A New Spectrophotometric Reagent for Iron," *Analytical Chemistry*, Vol ~~03.05.~~ 42, No. 7, June 1970, pp. 779 – 781.

~~*Annual Book*~~

[5] Gibbs, C. R., "Characterization and Application of ~~ASTM Standards~~ FerroZine Iron Reagent as a Ferrous Iron Indicator," *Analytical Chemistry* , Vol ~~15.05.~~ 48, No. 8, July 1976, pp. 1197–1201.

Reagents of the American Chemical Society, where such specifications are available.[6] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*— Unless otherwise indicated, references to water shall be understood to mean Type II or Type III reagent water conforming to Specification D 1193.

7.3 *Iron, Standard Solution*, 1 mL = 1 µg Fe (see Note 2 and Note 3)—Dissolve 0.1000 g of iron wire in 10 mL of hydrochloric acid (HCl, 1 + 1) and 1 mL of saturated bromine water (400 mL water + 20 mL bromine). Boil until the excess bromine is removed. Add 200 mL of HCl, cool, and dilute to 1 L in a volumetric flask. Dilute 10 mL of this solution to 1 L.

NOTE 2—The preparation of this reagent is also described in Practice E 200.

NOTE 3—As an alternative, the standard iron solution may be prepared by diluting 1.00 mL of commercially available iron standard stock solution (1000 mg iron/L) to 1 L with water.

7.4 *FerroZine Reagent Solution* —Contains FerroZine color reagent [3-(2-pyridyl)-5,6-bis(4-phenylsulfonic acid)-1,2,4-triazine, monosodium salt, monohydrate], buffer, and a reducing agent.[7] (**Warning**—This solution contains thiols as reducing agents. Wear butyl rubber or neoprene gloves when handling the solution and avoid inhalation of the vapors.)

8. Sampling

8.1 Because this is a general test method for the final steps in determining iron, specific procedures for sample preparation are not included (see 4.1 and 4.2).

9. Calibration

9.1 By means of suitable pipets or a buret, transfer 0 (reagent blank), 2.0, 4.0, 6.0, 8.0, and 10.0 mL, respectively, of the standard iron solution and approximately 20 mL of water to each of six clean, dry, 50-mL, glass-stoppered volumetric flasks. These flasks represent 0, 2.0, 4.0, 6.0, 8.0, and 10.0 µg of iron. Add 2.0 mL of FerroZine reagent solution to each flask, dilute the contents of each flask to volume with water, stopper, and mix well by inverting the flasks several times. Let the solutions stand for a minimum of 5 min but not more than 10 min to develop the magenta color. Measure the absorbance of each calibration standard in accordance with 10.4.

9.2 Plot, on linear graph paper, the micrograms of iron as a function of absorbance.

NOTE 4—If the photometer readings are percent transmittance, they may be plotted on semilog paper or converted to absorbance as follows:

$$A = \log (100/T) \quad (1)$$

where:
A = absorbance, and
T = transmittance, %.

NOTE 5—If desired, the slope of the calibration line may be calculated as follows:

$$S = L \times W \quad (2)$$

where:
S = slope of calibration line, µg Fe·cm/absorbance unit,
L = cell path length, cm, and
W = iron, µg, corresponding to an absorbance of 1.000 on the calibration line.

NOTE 6—Many spectrophotometers have the ability to calculate a calibration graph automatically after measuring the calibration solutions and subsequently to show the concentration of the component being measured directly on a display. In such cases no manual calibration graphs need to be constructed. It is, however, recommended to verify the calculation procedure of the instrument and to establish the characteristics of the calibration graph according to suitable regression analysis software.

NOTE 7—The entire calibration graph is based on only one starting solution (standard iron solution). In such a case a weighing error, for example, could introduce significant errors when reading concentrations of test solutions. It is, therefore, recommended to prepare a separately weighed control solution containing an accurately known amount of approximately 5 µg of iron. Measure the absorbance of this solution according to 10.4. Obtain the iron concentration of the control solution from the calibration graph/function. If this value and the calculated value of the control solution differ by more than 5 % of their mean, repeat the calibration.

10. Procedure

10.1 Weigh to three significant figures a sample containing 0.05 to 10 µg of iron into a clean, dry 50-mL, glass-stoppered, volumetric flask (see Note ~~6).~~ 8). Add sufficient water to dissolve the sample but do not exceed 40 mL total volume.

NOTE 6~~8~~—Preliminary tests must be made to determine if the sample or any impurities in the sample interfere in any way with the analysis.

~~[6] Stookey, L. L., "FerroZine—A New Spectrophotometric Reagent~~

[6] *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 ~~Iron,"~~ Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *~~Analytical Chemistry~~United States Pharmacopeia and National Formulary, ~~Vol 42, No. 7, June 1970, pp. 779—781.~~ U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.*

~~[7] Gibbs, C. R., "Characterization and Application of FerroZine Iron Reagent as a Ferrous Iron Indicator," *Analytical Chemistry*, Vol 48, No. 8, July 1976, pp. 1197–1201.~~

[7] This reagent system, available from Hach Chemical Co. (Catalog Number 2301-53), has been found satisfactory for this purpose.

10.2 To prepare a reagent blank, add about 20 mL of water to a second clean, dry, 50-mL, glass-stoppered, volumetric flask.

NOTE ~~7~~9—When running a number of samples, only one reagent blank is needed.

10.3 Add 2.0 mL of the FerroZine reagent solution to each volumetric flask, stopper, and swirl to mix the contents. Dilute each volumetric flask to volume with water, stopper, and mix well by inverting the flask several times. The pH range of the final solution should be 4 to 9 to give the best test results.[4,5] Allow the sample solution and reagent blank to sit at room temperature for a minimum of 5 min for color development.

10.4 Measure the absorbance of each sample solution at 560 nm in a 5-cm cell using a suitable photometer. Use a matched 5-cm cell filled with the reagent blank to set the instrument at zero absorbance or 100 % transmittance.

10.5 Refer to a previously prepared calibration curve to determine the micrograms of iron found.

10.6 *Qualtiy Control*—Set up and maintain a control chart with an aqueous quality control sample of well-established iron concentration. Measure the control sample each time a (series of) test sample(s) is (are) tested or at least once a week. If the measured value exceeds the action limit of the control chart, take appropriate action before proceeding with sample tests.

11. Calculation

11.1 Calculate the iron content of the sample, ~~ppm,~~ mg/kg, as follows (see Note ~~8):~~ 10):

$$\text{iron} = B/W \tag{3}$$

where:

B = iron ~~r~~ found, µg, and
W = sample, g.

NOTE ~~8~~10—If the slope of the calibration line has been calculated, the micrograms of iron, B, may be calculated as follows:

$$B = A \times (S/L) \tag{4}$$

where:

A = absorbance of the sample,
B = iron, µg,
S = slope of calibration line, and
L = cell path length, cm.

12. Report

12.1 Report the iron content to the nearest 0.001 ~~ppm.~~ mg/kg.

13. Precision and Bias

13.1 *Precision*—The following criteria should be used to judge the acceptability of results (see Note ~~9):~~ 11):

13.1.1 *Repeatability (Single Analyst)* —The standard deviation for a single determination has been estimated to be 0.001 ~~ppm~~ mg/kg at 10 DF. The 95 % limit for the difference between two such runs is 0.003 ~~ppm.~~ mg/kg.

13.1.1.1 For results less than 0.050 ~~ppm,~~ mg/kg, duplicates that agree within 0.004 ~~ppm~~ mg/kg absolute are acceptable for averaging (95 % confidence level).

13.1.1.2 For results greater than 0.050 ~~ppm,~~ mg/kg, duplicates that agree within 7 % relative are acceptable for averaging (95 % confidence level).

13.1.2 *Within-Laboratory, Between-Days Variability ~~(formerly called Repeatability)~~* —The precision of the procedure for measuring iron ~~is being~~ will be determined.

13.1.3 *Reproducibility (Multilaboratory)* —The precision of the procedure for measuring iron ~~is being~~ will be determined.

NOTE ~~9~~11—The precision statements are preliminary based on 10 duplicate analyses by one analyst on one day of one sample of dimethylformamide containing approximately 0.08 ~~ppm~~ mg/kg iron. An interlaboratory study will be run once the necessary number of ~~p~~participants are identified.

13.2 *Bias*—The bias of this test method was determined by spiking six samples with 0.04 ~~ppm~~ mg/kg iron reagent standard and reanalyzing to parallel spiking. Recovery ranged from 99 to 102 %. The bias depends upon the accuracy of the calibration, weighing, and the extent of any interferences. These must be determined for each specific application.

14. Keywords

14.1 FerroZine; iron; photometric