Designation: E1615 – 22

# Standard Test Method for Determination of Trace Quantities of Iron by Visible Spectrophotometry[1]

This standard is issued under the fixed designation E1615; 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 iron in aromatic hydrocarbons, their derivatives, and related chemicals in the range from 0.01 to 0.2 µg/g using [3-(2-pyridyl)-5,6-bis(4-phenylsulfonic acid)-1,2,4-triazine, monosodium salt, monohydrate] (PDTS)[2] reagent solution. The range may be extended through the use of a 5- or 10-cm cell or by suitable dilution of the sample solution.

1.2 The limit of detection (LOD) is 0.01 µg/kg for iron and the limit of quantitation (LOQ) is 0.04 µg/kg.

NOTE 1—The LOD and LOQ were calculated using data from the ILS.

1.3 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.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 Review the current Safety Data Sheets (SDS) for detailed information concerning toxicity, first-aid procedures, and safety precautions.

1.6 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific warning statements, see Section 8.

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1193 Specification for Reagent Water

D6143 Test Method for Iron Content of Bisphenol A (4,4′-Isopropylidenediphenol)

D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[4]

E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

## 3. Summary of Test Method

3.1 Certain molecules like PDTS which contains the ferroin group -N=C-C=N- react as a bidentate ligands with ferrous metal ions forming a colored complex species.

3.2 This test method is based upon a photometric determination of the ferroin PDTS complex with the iron (II) ion.[2,5] The sample is dissolved in a suitable solvent, any ferric iron is reduced to ferrous iron when the iron is reacted with PDTS reagent solution which will also 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.

3.3 Quantitation of the iron content in the sample is accomplished by measuring the intensity of the color produced by the magenta complex described above. The Beer-Lambert law is

[1] This test method is under the jurisdiction of ASTM Committee D16 on Aromatic, Industrial, Specialty and Related Chemicals and is the direct responsibility of Subcommittee D16.04 on Instrumental Analysis.

Current edition approved May 1, 2022. Published June 2022. Originally approved in 1994. Last previous edition approved in 2016 as E1615 – 16. DOI: 10.1520/E1615-22.

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

[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* volume information, refer to the standard's Document Summary page on the ASTM website.

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

[5] 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.

***A Summary of Changes section appears at the end of this standard**

obeyed in this system at low concentrations of the colored complex. The Beer-Lambert law establishes a relationship among the absorbance, sample thickness, and the concentration of the absorbing specie as follows:

$$A = abc \quad (1)$$

where:

$A$ = absorbance = log ($I_0$/I = –log (T) T = I/$I_0$; transmittance = light exit cell/light to cell;
$a$ = microgram Fe absorptivity, (slope), liter/(mole cm) or mL/(mg cm);
$b$ = pathlength through sample, cm; and
$c$ = concentration of solute in µg Fe in sol'n, moles/liter or mg/mL.

NOTE 2—This method plots Abs vs. Conc; b = 1 cm; Slope (a) is rise/run or a = A/c; therefore c = A/a.

## 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 µg/g, cyanide, and nitrate.[2]

5.2 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 PDTS reagent solution under test conditions. At least 1000 mg/L of the alkali metals and the alkaline earths had no effect on the determination. Many heavy metals will react with PDTS reagent solution in competition with iron, but with the excess reagent used in the test there is no effect on the results.[2]

5.3 The pH range of the final solution should be from 4 to 9 to give the best test results.[2,5]

5.4 All glassware used in this test method must be iron-free and scrupulously clean by precleaning with dilute hydrochloric acid and PDTS 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 10-cm cell. Check the performance of the photometer at regular intervals according to the guidelines given in Practice E275 and the manufacturer's manual.

6.2 *Absorption Cells,* 5-cm or 10-cm light path.

NOTE 3—A discussion of photometers and photometric practice is given in Practices E60 and E275.

## 7. Reagents

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

7.2.1 *Water*—Unless otherwise indicated, references to water shall be understood to mean Type I reagent water conforming to Specification D1193.

7.2.2 *Methanol*—Use iron-free methanol such as HPLC grade methanol.

7.3 *Iron, Standard Solution,* 1 mL = 1 µg Fe (see Notes 4 and 5)—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 4—The preparation of this reagent is also described in Practice E200.

NOTE 5—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.

NOTE 6—When the solvent is methanol, use the reagent grade iron-free methanol.

7.4 *PDTS Reagent Solution*—Contains color reagent [3-(2-pyridyl)-5,6-bis(4-phenylsulfonic acid)-1,2,4-triazine, monosodium salt, monohydrate] or PDTS, buffer, and a reducing agent like thioglycolic acid or hydroxylamine hydrochloric acid.

7.4.1 Alternatively, the PDTS and PDTZ (2,4,6-tris(2-pyridyl)-1,3,5-triazine) reagent solution is available commercially, or the reagents may be prepared as described below.[2]

7.4.1.1 *Reducing Agent*—Hydroxylamine hydrochloride, 10 % by weight solution in hydrochloric acid: Dissolve 10 g of reagent grade hydroxylamine hydrochloride ($NH_2OH.HCL$) in 30 g of Type I water in a plastic bottle; add 50 mL of reagent grade concentrated hydrochloric acid and mix well. Prepare this solution fresh daily.

7.4.1.2 *Color Reagent,* 0.514 weight percent solution: Dissolve 0.514 g of PDTS reagent solution in 100 g of Type I water in a plastic bottle, and mix well. Discard the reagent after seven days.

7.4.1.3 *Buffer Reagent-pH 10.0 Buffer*—Dissolve 200 g of reagent grade ammonium acetate in a minimum of Type I water, add 175 mL of concentrated ammonium hydroxide and

[6] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.

dilute to 500 mL in a volumetric flask. Mix well. Check the pH of the buffer to verify that it is pH 10 ± 0.5. If it is not in the required pH range, remake the buffer. Store the buffer in a plastic bottle. Discard after four weeks.

## 8. Hazards

8.1 Consult current OSHA regulations, suppliers' Safety Data Sheets, and local regulations for all materials used in this test method.

8.2 *PDTS Reagent Solution*—This solution may contain thiols as the reducing agent. Wear butyl rubber or neoprene gloves when handling the solution and avoid inhalation of the vapors.

## 9. Sample Preparation

9.1 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). Most Committee D16 chemicals are finished liquid products which do not need sample preparation before running this analysis.

9.2 Appropriate sample preparation has rendered the iron and sample matrix soluble in water or an other suitable solvent such as methanol. Some sample preparation may include microwave sample digestion or heating samples in acid.

9.3 Iron III in the sample has been reduced to Iron II.

9.4 A sample containing 0.5 to 10 µg of iron is used. Dilutions are made for dark samples (11.2.5).

9.5 The pH range of the final solution should be 4 to 9 to give the best results.

## 10. Calibration

10.1 *PDTS Reagent Solution Method (7.4):*

10.1.1 By means of suitable pipets or a burette, 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 PDTS 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 11.3 and 11.4.

10.2 *Individual Solution Method (7.4.1):*

10.2.1 By means of suitable pipets or a burette, transfer 0 (reagent blank), 2.0, 4.0, 6.0, 8.0, and 10.0 mL, respectively, of the standard iron solution and approximately 40 mL of water to each of six clean, dry, 100-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 mL each of the individual reagents (reducing reagent, color reagent and buffer reagent) as described in 7.4 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 20 min to develop the magenta color. Measure the absorbance of each calibration standard in accordance with 10.3.

10.3 Construct a calibration graph by plotting the absorbances against the corresponding micrograms of iron present in the calibration solutions, including the blank. Obtain the best straight line through the points (calibration function) by applying simple linear regression. Determine the slope (S) of the linear calibration function.

10.3.1 Evaluate and verify the obtained calibration graph and function by checking for a random scatter of the y-residuals around an average of zero, and by preparing and analyzing a control solution.

NOTE 7—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 8—As the calibration function has been derived from a single prepared calibration standard, verify the accuracy of the calibration function by preparing and analyzing a control solution containing an accurately known amount of approximately 5 µg of iron. If reasonably possible this control solution should be completely independent, that is, prepared by a different operator, different batches of chemicals etc. The difference between the known value and the measured value should be within the confidence limits for the control solution, as derived from the confidence limits of intercept and slope of the calibration function.

## 11. Procedure

11.1 *PDTS Reagent Solution Method (7.4):*

11.1.1 Weigh to three significant figures a sample containing 0.5 to 10 µg of iron into a clean, dry 50-mL, glass-stoppered, volumetric flask (see Note 6). Add sufficient water to dissolve the sample but do not exceed 40 mL total volume.

NOTE 9—Preliminary tests must be made to determine if the sample or any impurities in the sample interfere in any way with the analysis.

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

NOTE 10—When running a number of samples, only one reagent blank is needed.

11.1.3 Add 2.0 mL of the PDTS 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.[2,5] Allow the sample solution and reagent blank to equilibrate at room temperature for a minimum of 5 min for color development.

11.2 *Individual Solution Method (7.4.1):*

11.2.1 Weigh 80.0 g of sample to the nearest 0.01 g into a 100 mL glass-stoppered volumetric flask. Add 80 mL of Type I water to a second volumetric flask and reserve as a reagent blank.

11.2.2 Pipet 2 mL of the hydroxylamine hydrochloride solution and 2 mL of the PDTS reagent solution into each of the flasks, stopper, and mix well by inverting several times. Do not shake.

11.2.3 After 5 min, pipet 2 mL of the buffer into each flask, stopper, and mix well by inverting several times. Do not shake.

**TABLE 1 ASTM E1615 Iron Photometric Determination[A]**

| Test Result, µg/g | Sample | Average over all Laboratories | Repeatability, Standard Deviation Sr | Intermediate Standard Deviation | Reproducibility, Standard Deviation SR | Repeatability Limit r | Intermediate Limit | Reproducibility Limit R | Limits of Detection (LOD) | Limits of Quantitation (LOQ) |
|---|---|---|---|---|---|---|---|---|---|---|
| Iron | MEG | 0.0987 | 0.0037 | 0.0075 | 0.0382 | 0.0104 | 0.0211 | 0.1070 | 0.0111 | 0.0371 |
| Iron | DEG | 0.2655 | 0.0093 | 0.0230 | 0.0897 | 0.0261 | 0.0644 | 0.2512 | | |
| Iron | TEG | 0.3535 | 0.0101 | 0.0101 | 0.1075 | 0.0282 | 0.0282 | 0.3009 | | |

[A] The ILS repeatability standard deviation Sr = 0.0037 was used to calculate the scope's LOD and LOQ.

Make up to 100 mL with Type I water. Mix well by inverting several times; do not shake. The pH of the solution should be in the range of 4 to 9. Color development will not be complete outside of this pH range.

11.2.4 Allow color development for at least 5 min. Measure the absorbance of the sample relative to the reagent blank at the maximum absorbance (560 nm) as in 11.3 and 11.4. Absorbance measurement should be completed within 20 min of adding the buffer.

11.2.5 If the absorbance of the sample is greater than the highest standard (10 µg of iron (10.2.1)) in the calibration curve, reduce the sample size so that the absorbance of the sample is within the calibration curve. Repeat the procedures in 11.2 using the reduced sample size.

11.2.5.1 When sample size in not known, option 2 is:

*(1)* Add PDTS, buffer, and reducing agent into the iron-free flask.

*(2)* Dilute approximately half the flask with iron-free solvent.

*(3)* Place the flask on the balance and tare the balance.

*(4)* Add the sample to the solution until a purple tint appears.

*(5)* Read and record weight of sample.

*(6)* Dilute with iron-free solvent up to the 100 mL mark.

NOTE 11—When using a 10-cm cell, the sample size for samples containing from 0.1 to 1 µg/g iron should be 8 g and for samples containing from 1 to 10 µg/g iron the sample size should be 1 g.

NOTE 12—The 80 g of sample in 100 mL is proportionally the same as the maximum of 40 g of sample in 50 mL in 10.1.

11.3 Measure the absorbance of each sample solution at 560 nm in a 5-cm or 10-cm cell using a suitable photometer. Use a matched cell filled with the reagent blank to set the instrument at zero absorbance or 100 % transmittance.

11.4 Refer to the previously prepared calibration curve (10.3) to determine the micrograms of iron found.

## 12. Calculation

12.1 Calculate the micrograms of iron, *B*, in the sample solution as follows:

$$B = A/(S \times L) \tag{2}$$

where:

*A* = absorbance of the sample solution, at 560 nm,
*B* = iron, µg, in sample solution,
*S* = slope of calibration line (10.3), and
*L* = cell path length, cm.

12.2 Calculate the iron content of the sample, µg/g, as follows (see 12.1):

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

where:

*B* = iron, µg, found in sample solution, and
*W* = sample, g.

## 13. Report

13.1 Report the iron content that is below the LOD as less than LOD.

## 14. Precision and Bias[7]

14.1 In 2007, Committee E15 on Industrial and Specialty Chemicals conducted and completed Interlaboratory Study #52 to determine precision data for six test methods used in the analysis of glycols. The precision of this test method is based on the interlaboratory study of E1615, Standard Test Method for Iron in Trace Quantities Using PDTS Photometric Determination. Each of fifteen laboratories were asked to test three different materials. Thirteen laboratories tested monoethylene glycol (MEG), eleven laboratories tested Diethylene glycol (DEG), and ten laboratories tested Triethylene glycol (TEG). Every test result represents an individual determination. Two test results were conducted on each of two days for a total of four test results per assay. Note that in the combined study, 8 labs used a single analyst, 7 labs used two analysts (on different days), and 2 labs did not record this information. In the event that there were missing values for one or more labs, this information was noted in the results. The details of this study are given in ASTM Research Report RR:E15-1064.

14.1.1 *Repeatability*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the "r" value for that material; "r" is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

14.1.2 *Reproducibility*—Two test results shall be judged not equivalent if they differ by more than the "R" value for that material; "R" is the interval representing the difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E15-1064. Contact ASTM Customer Service at service@astm.org.