Designation: ~~E394 – 09~~ E394 – 15

Standard Test Method for Iron in Trace Quantities Using the 1,10-Phenanthroline Method[1]

This standard is issued under the fixed designation E394; 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 the range from 1 to 100 µg.

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 This test method is applicable to samples whose solutions have a pH less than 2. It is assumed that the pH is adjusted to within this range in the sample preparation.

1.4 Review the current ~~material safety data sheets (MSDS)~~ Safety Data Sheets (SDS) for detailed information concerning toxicity, first-aid procedures, handling, and safety precautions.

1.5 The values given in SI units are the standard. Values in parentheses are for information only.

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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

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 This test method is based upon a photometric determination of the 1,10-phenanthroline complex with the iron(II) ion. The sample is dissolved in a suitable solvent and the iron is reduced to the divalent state by the addition of hydroxylamine hydrochloride. The color is then developed, by the addition of 1,10-phenanthroline. After a short reaction period, the absorbance of the solution is measured at approximately 510 nm using a suitable photometer. The absorbance of the solution, once the color is developed, is stable for at least several months.

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 (see 10.1 and Note ~~6~~5).

[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.

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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.

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

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. Possible interferences are described in Section 5.

5. Interferences

5.1 Fortune and Mellon[4] have made a comprehensive study of the interferences of various inorganic ions in this determination. Table 1 and Table 2, taken from their report, show the effects of various cations and anions on the determination of 2.0 µg/g (ppm) iron. If the maximum level of 500 µg/g (ppm) does not interfere, it is very likely that the ion will not interfere in any quantity. The data were obtained under slightly different conditions than those specified in the present test method, but the interferences should be similar. For a more detailed description of interferences, the original literature should be consulted.

5.2 Aldehydes, ketones, and oxidizing agents interfere by consuming the hydroxylamine hydrochloride added as a reducing agent.

6. Apparatus

6.1 *Photometer,* capable of measuring light absorption at 510 nm and holding a 5-cm or 1-cm cell. Check the performance of the photometer at regular intervals according to the guidelines given in Practice E275 and the manufacturer's manual.

NOTE 1—If a filter photometer is used, a narrow band filter having its maximum transmission at 480 to 520 nm should be used. A discussion of photometers and photometric practice is given in Practice E60.

6.2 *Absorption Cells,* 5-cm or 1-cm light path.

7. Reagents and Materials

7.1 *Purity of Reagents*—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.[5] 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 reagent water as defined in Specification D1193.

7.3 *Hydroxylamine Hydrochloride Solution* (100 g/L)—Dissolve 10 g of hydroxylamine hydrochloride ($HONH_2 \cdot HCl$) in approximately 60 mL of water, filter, and dilute to 100 mL.[6]

7.4 *Iron, Standard Solution* (1 mL = 0.01 mg Fe)[7] (Note 2)—Dissolve 0.1000 g of iron wire in 10 mL of hydrochloric acid (HCl, 1 + 1) and 1 mL of bromine water. Boil until the excess bromine is removed. Add 200 mL of HCl, cool, and dilute to 1 L in a volumetric flask. Dilute 100 mL of this solution to 1 L.

NOTE 2—As an alternative, the standard iron solution may be prepared by weighing exactly 0.7022 g of iron (II) ammonium sulfate hexahydrate ($FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, minimum purity, 99.5 %) in 500 mL of water containing 20 mL of sulfuric acid (H_2So_4, sp gr 1.84) and diluting to 1 L with water. Dilute 100 mL of this solution to 1 L.

7.5 *1,10-Phenanthroline Solution* (3 g/L)—Dissolve 0.9 g of 1,10-phenanthroline monohydrate in 30 mL of methanol and dilute to 300 mL with water.[6,8]

7.6 *Ammonium Acetate—Acetic Acid Solution*—Dissolve 100 g of ammonium acetate (CH_3COONH_4) in about 600 mL of water, filter, add 200 mL of glacial acetic acid to the filtrate, and dilute to 1 L with water.[6]

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 1.3, 4.1 and 4.2).

9. Calibration

9.1 By means of suitable pipets or a buret, transfer 0 (reagent blank), 2, 4, 6, 8, and 10 mL, respectively, of the standard iron solution to each of six 100-mL, glass-stoppered ~~graduated cylinders.~~volumetric flasks. These ~~cylinders~~flasks contain 0, 20, 40, 60, 80, and 100 µg of iron, respectively. Dilute the contents of each ~~cylinder~~flask to 80 mL with water. Develop the color and measure the absorbance of each calibration standard as described in 10.3 and 10.4.

[4] Fortune, W. B., and Mellon, M. G., *Industrial and Engineering Chemistry, Analytical Edition*, IENAA Vol 10, 1938, pp. 60–64.

[5] *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),~~(USP), Rockville, MD.

[6] This solution is also described in Practice E200.

[7] This solution is used for calibration only.

[8] Frederick, G., and Richter, F. P., *Phenanthrolines and Substituted Phenanthroline Indicators*, GFS Publication No. 205, 1944 (no charge).

TABLE 1 Effect of Cations on the Determination of 2 µg/g (ppm) Iron

Ion	Added As	Maximum Added Without Interference, µg/g (ppm)	Applicable pH Range
Aluminum	$AlCl_3$	500	2.0–3.0
Ammonium	NH_4Cl	500	2.0–9.0
Antimony	$SbCl_3$	30	3.0–9.0
Arsenic	As_2O_5	500	3.0–9.0
Arsenic	As_2O_3	500	3.0–9.0
Barium	$BaCl_2$	500	3.0–9.0
Beryllium	$Be(NO_3)_2$	500	3.0–5.5
Bismuth	$Bi(NO_3)_3$	...[A]	...[A]
Cadmium	$Cd(NO_3)_2$	50	3.0–9.0
Calcium	$Ca(NO_3)_2$	500	2.0–9.0
Chromium	$Cr_2(SO_4)_3$	20	2.0–9.0
Cobalt	$Co(NO_3)_2$	10	3.0–5.0
Copper	$Cu(NO_3)_2$	10	2.5–4.0
Lead	$Pb(C_2H_3O_2)_2$	500	2.0–9.0
Lithium	$LiCl$	500	2.0–9.0
Magnesium	$Mg(NO_3)_2$	500	2.0–9.0
Manganese	$MnSO_4$	500	2.0–9.0
Mercury	$HgCl_2$	1	2.0–9.0
Mercury	$Hg_2(NO_3)_2$	10	3.2–9.0
Molybdenum	$(NH_4)_6Mo_7O_{24}$	100	5.5–9.0
Nickel	$Ni(NO_3)_2$	2	2.5–9.0
Potassium	KCl	1000	2.0–9.0
Silver	$AgNO_3$	...[A]	...[A]
Sodium	$NaCl$	1000	2.0–9.0
Strontium	$Sr(NO_3)_2$	500	2.0–9.0
Thorium	$Th(NO_3)_4$	250	2.0–9.0
Tin	H_2SnCl_6	20	3.0–6.0
Tin	H_2SnCl_4	10	2.0–6.0
Tungsten	Na_2WO_4	10	2.5–9.0
Uranium	$UO_2(C_2H_3O_2)_2$	100	2.0–6.0
Zinc	$Zn(NO_3)_2$	10	2.0–9.0
Zirconium	$Zr(NO_3)_4$	50	2.0–9.0

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Arsenic	As_2O_5	500	3.0–9.0
Arsenic	As_2O_3	500	3.0–9.0
Barium	$BaCl_2$	500	3.0–9.0
Beryllium	$Be(NO_3)_2$	500	3.0–5.5
Bismuth	$Bi(NO_3)_3$	...[A]	...[A]
Cadmium	$Cd(NO_3)_2$	50	3.0–9.0
Calcium	$Ca(NO_3)_2$	500	2.0–9.0
Chromium	$Cr_2(SO_4)_3$	20	2.0–9.0
Cobalt	$Co(NO_3)_2$	10	3.0–5.0
Copper	$Cu(NO_3)_2$	10	2.5–4.0
Lead	$Pb(C_2H_3O_2)_2$	500	2.0–9.0
Lithium	$LiCl$	500	2.0–9.0
Magnesium	$Mg(NO_3)_2$	500	2.0–9.0
Manganese	$MnSO_4$	500	2.0–9.0
Mercury	$HgCl_2$	1	2.0–9.0
Mercury	$Hg_2(NO_3)_2$	10	3.2–9.0
Molybdenum	$(NH_4)_6Mo_7O_{24}$	100	5.5–9.0
Nickel	$Ni(NO_3)_2$	2	2.5–9.0
Potassium	KCl	1000	2.0–9.0
Silver	$AgNO_3$	...[A]	...[A]
Sodium	$NaCl$	1000	2.0–9.0
Strontium	$Sr(NO_3)_2$	500	2.0–9.0
Thorium	$Th(NO_3)_4$	250	2.0–9.0
Tin	H_2SnCl_6	20	3.0–6.0
Tin	H_2SnCl_4	10	2.0–6.0
Tungsten	Na_2WO_4	10	2.5–9.0
Uranium	$UO_2(C_2H_3O_2)_2$	100	2.0–6.0
Zinc	$Zn(NO_3)_2$	10	2.0–9.0
Zirconium	$Zr(NO_3)_4$	50	2.0–9.0

[A] Must be completely absent because of precipitation.

TABLE 2 Effect of Anions on the Determination of 2 µg/g (ppm) Iron

Ion	Added As	Maximum Added Without Interference, µg/g (ppm)	Applicable pH Range
Acetate	$NaC_2H_3O_2$	500	2.0–9.0
Tetraborate	$Na_2B_4O_7$	500	3.0–9.0
Bromide	NaBr	500	2.0–9.0
Carbonate	Na_2CO_3	500	3.0–9.0
Chlorate	$KClO_3$	500	2.5–9.0
Chloride	NaCl	1000	2.0–9.0
Citrate	$H_3C_6H_5O_7$	500	2.0–9.0
Cyanide	KCN	10	2.0–9.0
Dichromate	$K_2Cr_2O_7$	20	2.5–9.0
Fluoride	NaF	500	4.0–9.0
Iodide	KI	500	2.0–9.0
Nitrate	KNO_3	500	2.0–9.0
Nitrite	KNO_2	500	2.5–9.0
Oxalate	$(NH_4)_2C_2O_4$	500	6.0–9.0
Perchlorate	$KClO_4$	100	2.0–9.0
Phosphate	$(NH_4)_2HPO_4$	20	2.0–9.0
Pyrophosphate	$Na_4P_2O_7$	50	6.0–9.0
Silicate	Na_2SiO_3	100	2.0–4.5
Sulfate	$(NH_4)_2SO_4$	500	2.0–9.0
Sulfite	Na_2SO_3	500	2.0–9.0
Tartrate	$(NH_4)_2C_4H_9O_6$	500	3.0–9.0
Thiocyanate	KCNS	500	2.0–9.0
Thiosulfate	$Na_2S_2O_3$	500	3.0–9.0

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Tetraborate	$Na_2B_4O_7$	500	3.0–9.0
Bromide	NaBr	500	2.0–9.0
Carbonate	Na_2CO_3	500	3.0–9.0
Chlorate	$KClO_3$	500	2.5–9.0
Chloride	NaCl	1000	2.0–9.0
Citrate	$H_3C_6H_5O_7$	500	2.0–9.0
Cyanide	KCN	10	2.0–9.0
Dichromate	$K_2Cr_2O_7$	20	2.5–9.0
Fluoride	NaF	500	4.0–9.0
Iodide	KI	500	2.0–9.0
Nitrate	KNO_3	500	2.0–9.0
Nitrite	KNO_2	500	2.5–9.0
Oxalate	$(NH_4)_2C_2O_4$	500	6.0–9.0
Perchlorate	$KClO_4$	100	2.0–9.0
Phosphate	$(NH_4)_2HPO_4$	20	2.0–9.0
Pyrophosphate	$Na_4P_2O_7$	50	6.0–9.0
Silicate	Na_2SiO_3	100	2.0–4.5
Sulfate	$(NH_4)_2SO_4$	500	2.0–9.0
Sulfite	Na_2SO_3	500	2.0–9.0
Tartrate	$(NH_4)_2C_4H_9O_6$	500	3.0–9.0
Thiocyanate	KCNS	500	2.0–9.0
Thiosulfate	$Na_2S_2O_3$	500	3.0–9.0

9.2 Plot, on linear graph paper, the Plot the results in an X-Y graph, with the micrograms of iron as a function of absorbance.on the x-axis and the respective absorbances on the y-axis. Visually evaluate the calibration graph obtained for linearity and for the absence of obvious outlying values. If so, proceed to the next step. If not, investigate for an assignable cause.

NOTE 3—If the photometer readings are percent transmittance, they may be plotted on semi-log paper or converted to absorbance as follows:

9.2.1 Establish a linear regression function from the calibration data using the statistical method of least squares, for example, with the aid of a spreadsheet. The formula for a linear calibration function is:

$$y = a + bx \quad (1)$$

where:

b = slope of calibration line, and
a = intercept.

$$A = \log\left(\frac{100}{T}\right) \quad (1)$$