



Standard Test Methods for Sodium Salts of EDTA in Water¹

This standard is issued under the fixed designation D 3113; 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 approval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover the determination of either total or unchelated sodium salts of ethylenediaminetetraacetic acid (Na_4EDTA) in water, particularly water intended for use in steam boilers. Two test methods are given as follows:

	Sections
Test Method A—Total (Chelated and Unchelated) Sodium Salt of EDTA	7 to 15
Test Method B—Unchelated Sodium Salt of EDTA	16 to 23

1.2 Test Method A is capable of determining total (chelated and unchelated) chelating agent even though it may be in the form of heavy metal or alkaline earth chelates.

1.3 It is the user's responsibility to ensure the validity of these test methods for waters of untested matrices.

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.* A specific hazard statement is given in Note 4.

2. Referenced Documents

2.1 ASTM Standards:

- D 888 Test Methods for Dissolved Oxygen in Water²
- D 1066 Practice for Sampling Steam²
- D 1129 Terminology Relating to Water²
- D 1193 Specification for Reagent Water²
- D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water²
- D 3370 Practices for Sampling Water²
- D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water²
- D 4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data²
- E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals³
- E 275 Practice for Describing and Measuring Performance

¹ These test methods are under the jurisdiction of ASTM Committee D-19 on Water and are the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

Current edition approved Nov. 15, 1992. Published January 1993. Originally published as D3113 – 72 T. Last previous edition D3113 – 91.

² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 03.05.

of Ultraviolet, Visible, and Near Infrared Spectrophotometers⁴

3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, refer to Terminology D 1129.

4. Significance and Use

4.1 EDTA is used in steam boilers to prevent precipitation of calcium, magnesium, and other metal salts, and under some conditions, to remove deposits caused by these elements.

4.2 These test methods are used to monitor the presence of EDTA so that optimum concentration can be maintained.

5. Purity of Reagents

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. 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.

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

6. Sampling

6.1 Collect the samples in accordance with Practice D 1066 or Practices D 3370 as applicable.

TEST METHOD A—TOTAL SODIUM SALT OF EDTA

7. Scope

7.1 This test method as described may be applied to waters containing free Na_4EDTA or heavy metal or alkaline earth chelates of Na_4EDTA either individually or in combination, in concentrations from 0.5 to 20 mg/L. Higher concentrations may be determined by dilution.

⁴ *Annual Book of ASTM Standards*, Vol 03.06.

⁵ "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., 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."

7.2 It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

8. Summary of Test Method

8.1 The intensity of the red-colored zirconium-xylenol orange complex formed in a strong acid medium is reduced in the presence of free EDTA or its metallic complexes through formation of a more stable zirconium-EDTA complex. The reduction in color intensity is a measure of total EDTA in the sample reported as milligrams per litre of Na₄EDTA.

9. Interferences

9.1 Nitritotriacetate (NTA) produces erratic values in the test for waters treated with NTA or mixtures of NTA and EDTA.

9.2 Polyphosphates interfere in this analysis and produce high values for the EDTA concentration. Interference from concentrations up to 12 mg/L can be eliminated by adding 1 mL of a thorium nitrate solution (2.38 g/L of Th (NO₃)₄·4H₂O) to the sample. The addition should be made prior to the admixture of all other reagents. When used, the thorium solution should be added to all solutions, samples and blanks, during both the calibration and the actual determination of an unknown.

9.3 Other chelating agents may react the same as EDTA.

10. Apparatus

10.1 *Photometer*—Any photoelectric filter photometer or spectrophotometer suitable for measurements at 535 nm. Filter photometers and photometric practices prescribed in this test method shall conform to Practice E 60, and to Practice E 275.

10.2 *Cells*, 20-mm, for use with the photometer, or other appropriate cells for the method of color measurement used.

11. Reagents

11.1 *EDTA Solution, A-1, Standard* (1 mL = 2 mg Na₄EDTA)—Dissolve 1.958 g of disodium ethylenediaminetetraacetate dihydrate (Na₂C₁₀H₁₄O₈N₂·2H₂O) in water and dilute to 1000 mL in a volumetric flask.

11.2 *EDTA Solution, A-2, Standard* (1 mL = 0.04 mg Na₄EDTA)—Dilute 10.0 mL of solution A-1 to 500 mL with water in a volumetric flask. *Prepare fresh daily.*

11.3 *Xylenol Orange Indicator Solution*—Dissolve 0.80 g of xylenol orange in 335 mL of hydrochloric acid (HCl, sp gr 1.19), add this solution to one containing 100 g of hydroxylamine hydrochloride (NH₂OH·HCl) in 500 mL of water and dilute the mixture to 1000 mL with water in a volumetric flask. Allow this solution to stand overnight; then filter through a 10-μm membrane filter.

11.4 *Zirconium, Reagent Solution B-1*—Dissolve 4.237 g of zirconium oxychloride (ZrOCl₂·8H₂O) and 65 mL of HCl (sp gr 1.19) in 500 mL of water and dilute to 1000 mL with water in a volumetric flask.

11.5 *Zirconium, Reagent Solution B-2*—Dilute 10.0 mL of solution B-1 and 5 mL of HCl (sp gr 1.19) to 250 mL with water in a volumetric flask.

12. Calibration

12.1 Prepare a series of standards to cover the zero to 1.0-mg range of Na₄EDTA by pipetting 0, 5, 10, 15, 20, and 25-mL aliquots of standard solution A-2 into 50-mL volumetric flasks. Add 5 mL of xylenol orange indicator solution and 5 mL of zirconium reagent solution B-2 and dilute to the mark with water.

12.2 Prepare the calibration curve by plotting on semilog graph paper the photometer readings as percent transmittance against milligrams of Na₄EDTA contained in the aliquots.

NOTE 1—A separate calibration curve must be made for each photometer and a recalibration must be made if any alterations of the instrument are made or if new reagents are prepared. Check the curve with each series of tests by measuring two or more solutions of known Na₄EDTA concentration.

13. Procedure

13.1 Determine the size of the sample aliquot according to the expected range of Na₄EDTA concentration (Note 2). Pipet the sample aliquot into a 50-mL volumetric flask, add 5 mL of xylenol orange indicator solution and 5 mL of zirconium solution B-2 into the flask, and dilute to the mark with water.

NOTE 2—The sample aliquot must be sized so that it contains between 0.1 and 1.0 mg of Na₄EDTA or the equivalent in other metal chelates.

13.2 Prepare a color blank for each series of tests. To prepare the blank, pipet 5 mL of xylenol orange indicator solution into a 50-mL volumetric flask and dilute to the mark with water. Where turbidity or coloration are present in a sample, prepare the blank by diluting a sample aliquot and 5 mL of indicator solution to 50 mL with water.

13.3 After a 1-h color development period, set the photometer with the color blank (Note 3) and measure the transmittance of the sample solutions at a 535-nm wavelength, using a 20-mm cell depth.

NOTE 3—The color blank will establish the reference point at 100 % transmittance. An equivalent reading should be obtained when measuring the calibration solution which contains 1.0 mg of Na₄EDTA.

13.4 Determine the milligrams of chelate in the sample aliquot from the instrument calibration curve prepared as directed in Section 12.

14. Calculation

14.1 Calculate the total Na₄EDTA or equivalent other metal chelates, in milligrams per litre, using Eq 1:

$$\text{Total Na}_4\text{EDTA, mg/L} = (C/S) \times 1000 \quad (1)$$

where:

C = Na₄EDTA found in the sample aliquot, mg, and

S = sample used, mL.

15. Precision and Bias ⁶

15.1 Based on the results of ten analysts (five laboratories) at five concentration levels and four replicates, the precision of

⁶ Supporting data are available from ASTM Headquarters. Request RR: D-19-1002.