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An American National Standard

Standard Test Methods for Sodium Salts of EDTA in Water[1]

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 reapproval. 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 Water[2]

D 1066 Practice for Sampling Steam[2]

D 1129 Terminology Relating to Water[2]

D 1193 Specification for Reagent Water[2]

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water[2]

D 3370 Practices for Sampling Water[2]

D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water[2]

D 4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data[2]

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals[3]

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers[4]

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.

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[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.

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

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

[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 Na_4EDTA.

9. Interferences

9.1 Nitrilotriacetate (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 $(NO_3)_4 \cdot 4H_2O$) 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 Na_4EDTA)—Dissolve 1.958 g of disodium ethylenediaminetetraacetate dihydrate ($Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O$) in water and dilute to 1000 mL in a volumetric flask.

11.2 *EDTA Solution, A-2, Standard* (1 mL = 0.04 mg Na_4EDTA)—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 ($NH_2OH \cdot HCl$) 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 ($ZrOCl_2 \cdot 8H_2O$) 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 Na_4EDTA 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 Na_4EDTA 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 Na_4EDTA concentration.

13. Procedure

13.1 Determine the size of the sample aliquot according to the expected range of Na_4EDTA 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 Na_4EDTA 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 Na_4EDTA.

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 Na_4EDTA or equivalent other metal chelates, in milligrams per litre, using Eq 1:

$$\text{Total } Na_4EDTA, \text{ mg/L} = (C/S) \times 1000 \quad (1)$$

where:

C = Na_4EDTA 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.

this test method varies; the overall precision and the single operator precision are given in Table 1.

15.2 Information on the types of water used in generating the precision and bias data is not available.

15.3 Since this is an existing test method that has results from a minimum of five laboratories for a total of ten operators, it does not require further collaborative testing in accordance with Practice D 2777.

TEST METHOD B—UNCHELATED SODIUM SALT OF EDTA

16. Scope

16.1 This test method may be applied to waters containing unchelated EDTA in concentrations of 1 to 50 mg/L. Higher concentrations may be determined by diluting the sample.

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

17. Summary of Test Method

17.1 The unchelated EDTA is titrated with a standard magnesium solution to a purple or reddish color with chrome black T indicator.

18. Interferences

18.1 Iron, copper, and manganese cause decolorization or may otherwise interfere with the color change of the indicator.

18.2 Heavy metal EDTA complexes may undergo oxidation by the atmosphere, resulting in the release of EDTA which will be titrated in the procedure.

18.3 Other chelating agents may react the same as EDTA.

18.4 Aluminates in the sample may be converted to aluminum ion ($A1^{+3}$) during the titration that would complex with any unchelated EDTA resulting in erroneously low values.

19. Reagents

19.1 *Buffer Solution* (pH 10.0)—Dissolve 32.5 g of ammonium chloride (NH_4Cl) in 800 mL water. Add 200 mL of concentrated ammonium hydroxide (NH_4OH, sp gr 0.900). If necessary, adjust the pH of this solution to 10.0 by dropwise addition of concentrated hydrochloric acid (HCl, sp gr 1.19).

NOTE 4—**Precaution:** The addition of HCl should be carried out in a well-ventilated hood.

19.2 *Chrome Black T Indicator Solution* (6 g/L)—Dissolve 1.20 g of chrome black T in 200 mL of 98 % triethanolamine ($(HOCH_2CH_2)_3N$). Add 80 mL of anhydrous ethyl alcohol (C_2H_5OH), mix, and transfer to a brown bottle.

NOTE 5—This solution should be stable for 2 to 3 months.

19.3 *Standard Solution, Magnesium, A* (1 mL = 1 mg Na_4EDTA)—Dissolve 0.3166 g of anhydrous magnesium sulfate ($MgSO_4$) in water and dilute to 1 L.

19.4 *Standard Solution, Magnesium, B* (1 mL = 0.1 mg Na_4EDTA)—Dilute 100 mL of solution A to 1 L with water.

TABLE 1 Recoveries of Known Amounts of Na_2EDTA

Amount Added, mg/L	Amount Found, mg/L	*n*	s_t	s_o	Bias	% Bias	Statistical Significance, 95 % Confidence Level
7.5	7.52	39	0.72	0.38	0.018	0.2	no
87.5	86.64	40	2.04	1.36	−0.86	−1	yes
220	212.45	40	12.8	5.75	−7.55	−3	yes
366	360.12	40	11.8	5.85	−5.89	−2	yes
500	487.8	40	20.0	5.70	−12.2	−2	yes

20. Sample Storage

20.1 Because of possible oxidation or decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum (no longer than 15 min).

20.2 When samples cannot be analyzed within 15 min of collection, procedures that exclude air from the sample such as described in the apparatus section of Test Method A in Test Methods D 888 should be used.

21. Procedure

21.1 Pipet 100 mL of sample into a white porcelain casserole or evaporating dish (Note 6). Add 5 mL of buffer solution and mix thoroughly. Add 5 drops of chrome black T indicator solution and observe the color development. If the solution is blue, without a reddish coloration, titrate the sample with a standard magnesium solution. Add standard magnesium solution slowly from a buret with continuous stirring (magnetic stirrer preferred) until the color changes from blue to purple-red. Magnesium solution A is intended for use with sample aliquots containing 1 to 10 mg of unchelated Na_4EDTA and magnesium solution B for sample aliquots containing 0.1 to 1 mg of unchelated Na_4EDTA. A purple or red color indicates the absence of unchelated Na_4EDTA.

NOTE 6—When sufficient turbidity is present to obscure the end point the sample must be filtered. A1.0-μm pore size membrane filter, or equivalent, shall be used.

22. Calculation

22.1 Calculate the concentration of unchelated Na_4EDTA in milligrams per litre using Eq 2 or Eq 3:

$$\text{Unchelated } Na_4EDTA, \text{ mg/L} = T_A \times 1000/S \quad (2)$$

or

$$\text{Unchelated } Na_4EDTA, \text{ mg/L} = T_B \times 100/S \quad (3)$$

where:

T_A = standard magnesium solution A, mL,
T_B = standard magnesiumsolution B, mL, and
S = sample, mL.

23. Precision and Bias [6]

23.1 Based on the results of six analysts (three laboratories) at four concentration levels and three replicates, the precision of this test method varies. The overall precision and the single operator precision are given in Table 2.

23.2 Information on the types of water used in generating the precision data is not available.

23.3 Since this is an existing test method that has results from a minimum of three laboratories for a total of six

TABLE 2 Recoveries of Known Amounts of Unchelated Na_2EDTA

Amount Added, mg/L	Amount Found, mg/L	*n*	s_t	s_o	Bias	% Bias	Statistical Significance, 95 % Confidence Level
5.1	5.49	18	0.65	0.11	0.394	8	yes
9.0	9.19	18	0.53	0.08	0.190	2	no
44.5	44.84	18	1.47	0.44	0.339	1	no
76.0	76.04	18	2.60	0.68	0.039	0	no

operators, it does not require further collaborative testing in accordance with Practice D 2777.

24. Quality Assurance/Quality Control (QA/QC)

24.1 Before this test method is applied to the analysis of samples of unknown Na_2EDTA concentrations, the analyst must establish quality control by the procedures recommended in Practice D 4210 and Guide D 3856.

24.2 A duplicate sample and known standard must be analyzed each day that an analysis is performed. The duplicate and standard shall meet the limits as established by the control chart before a determination is considered satisfactory.

24.3 A blank and a spiked sample shall be analyzed each day that an analysis is performed. Spiking shall be in accordance with that outlined in 11.11 of Guide D 3856. The blank shall be low enough that it will not unduly influence the data.

24.4 One sample must be analyzed in duplicate with each group of 10 or less samples. The results must meet the criteria established in Table 1 and Table 2 of this test method before the data for that batch or set of 10 samples is acceptable.

24.5 Other QA/QC portions of this test method have not been completely established at this time. Analysts performing this test method will be required to measure their performance against the performance level achieved by the interlaboratory studies of this test method.

24.6 It is the intention of Subcommittee D19.06 to incorporate formal QA/QC procedures into this test method at such time as they have passed the consensus process and have been officially accepted by the Society.