



Designation: E538 – 17a

Standard Test Methods for Mercury in Caustic Soda (Sodium Hydroxide) and Caustic Potash (Potassium Hydroxide)¹

This standard is issued under the fixed designation E538; 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 routine determination of mercury in caustic soda and caustic potash liquors and anhydrous caustic soda in the solid, flake, ground, and bead form by the flameless atomic absorption method.

1.2 Two test methods are described as follows: Test Method A employs a direct analysis of the sample using an alkaline reducing agent with a lower limit of detection of 0.1 ppb (ng/g). Test Method A was developed using caustic soda and caustic potash. Test Method B requires a preliminary neutralization of the sample followed by a permanganate oxidation before it can be analyzed by an acidic reducing agent with a lower limit of detection of this test method of 0.01 ppm ($\mu\text{g/g}$). Test Method B was developed using caustic soda.

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

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 *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.* Specific hazards statements are given in Sections 7 and 18.

1.6 *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.*

¹ These test methods are under the jurisdiction of ASTM Committee D16 on Aromatic, Industrial, Specialty and Related Chemicals and are the direct responsibility of Subcommittee D16.15 on Industrial and Specialty General Standards.

Current edition approved July 1, 2017. Published July 2017. Originally approved in 1975. Last previous edition approved in 2017 as E538 – 17. DOI: 10.1520/E0538-17a.

2. Referenced Documents

2.1 *ASTM Standards*:²

D1193 Specification for Reagent Water

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

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)³

TEST METHOD A—ALKALINE REDUCING AGENT

3. Summary of Test Method

3.1 All forms of mercury are reduced to metallic mercury which is aerated from the solution and determined by cold vapor atomic absorption analysis.

4. Significance and Use

4.1 Mercury is a toxic material and is also deleterious if present in caustic soda and caustic potash used in certain manufacturing processes. It must therefore be controlled as a possible pollutant. These test methods provide a procedure for measuring mercury in liquid and solid caustic soda and caustic potash.

5. Apparatus

5.1 *Atomic Absorption Spectrophotometer*, equipped with mounting to hold an absorption cell and a fast response (0.5-s) recorder.

5.2 *Mercury Hollow Cathode Lamp*, primary line 253.7 nm.

5.3 *Absorption Cell*, 10-cm path length with quartz windows.

5.4 *Gas Washing Bottle*, 125-mL, with extra-coarse fritted bubbler. The bottle has a calibration line drawn at the 60-mL mark.

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

- 5.5 Gas Washing Bottle, 125-mL, without frit.
- 5.6 Stopcock, three-way, with TFE-fluorocarbon plug.
- 5.7 Needle Valve.
- 5.8 Drying Tube.
- 5.9 Vacuum Trap.

5.10 Flowmeter, capable of measuring and maintaining a flow rate of 1.5 standard ft³/h.

NOTE 1—The procedure as described in this test method employs a Perkin-Elmer Model 303 atomic absorption spectrophotometer. Any other equivalent atomic absorption spectrophotometer may be used as well as the many commercial instruments specifically designed for measurement of mercury by flameless atomic absorption now available. However, variation in instrument geometry, cell length, sensitivity, and mode of response measurement may require appropriate modifications of the operating parameters.

6. Reagents

6.1 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.⁴ 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.

6.2 Purity of Water—Unless otherwise indicated, references to water shall be understood to mean Type II or III reagent water conforming to Specification D1193.

6.3 Anhydrous Magnesium Perchlorate.

6.4 Sodium Hydroxide 50 %—Membrane grade caustic soda 50 %.

6.5 Aqua Regia—Carefully add 10-mL of concentrated HNO₃ (sp gr 1.42) to 30 mL of concentrated HCl (sp gr 1.19) in a 100-mL beaker. Let the mixture stand for 5 min before use. This mixture is unstable and should not be stored. (Warning—Use goggles when preparing this solution.)

6.6 Cadmium Chloride Solution (10 g/100 mL)—Dissolve 10 g of cadmium chloride in 50 mL of water and then add 50 mL of 50 % membrane grade caustic soda. Cadmium hydroxide will precipitate upon the addition of the caustic soda. This solution must be well shaken before use. (Warning—Use goggles when preparing this solution.)

6.7 Stannous Chloride Solution (10 g/100 mL)—Dissolve 10 g of stannous chloride (SnCl₂·2H₂O) in 100 mL of water. Prepare fresh once a week.

6.8 Mercuric Nitrate Stock Solution (0.05 M) (1 mL = 10 mg Hg)—Dissolve 17.1 g of mercuric nitrate (Hg(NO₃)₂·H₂O) in 100 mL of water containing 2 mL of concentrated HNO₃ in a 1-L volumetric flask. Dilute to volume with water and mix well.

⁴ 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), Rockville, MD.

6.9 Mercury Standard Solution (1 mL = 50 µg Hg)—Pipet 5.0 mL of 0.05 M mercuric nitrate stock solution into a 1-L volumetric flask, acidify with 5 mL of H₂SO₄ (1+4), and dilute to volume with water. Mix well.

6.10 Mercury Standard Solution (1 mL = 50 ng Hg)—Pipet 1.0 mL of the standard mercury solution containing 50 µg Hg/mL into a 1-L volumetric flask, acidify with 5 mL of H₂SO₄ (1+4), and dilute to volume with water. Mix well.

6.11 Mercury Standard Solution (1 mL = 5 ng Hg)—Pipet 10.0 mL of the standard mercury solution containing 50 ng Hg/mL into a 100-mL volumetric flask, acidify with 5 mL of H₂SO₄ (1+4), and dilute to volume with water. Mix well. Prepare fresh daily.

6.12 Sulfuric Acid (1+4)—Add slowly while stirring 200 mL of concentrated H₂SO₄ (sp gr 1.84) to 800 mL of water. This solution is dispensed from a 10-mL buret. (Warning—Use goggles when preparing this solution.)

7. Hazards

7.1 Sodium hydroxide, potassium hydroxide, and their solutions are extremely corrosive. Any splashes on the skin or eyes must be flushed with cold water. It is important that the eyelids be held open during the flushing period. Get medical attention immediately for any eye exposures.

8. Calibration

8.1 Take care to avoid contamination of the apparatus with mercury. Soak all glass apparatus (pipets, beakers, and gas-washing bottle) in aqua regia before use. Rinse thoroughly with water.

8.2 Connect the apparatus shown in Fig. 1 to the atomic absorption spectrophotometer and adjust the air flow rate to 1.5 standard ft³/h (see Notes 2 and 3).

NOTE 2—The magnesium perchlorate in the drying tube should be replaced frequently. A cork stopper should be used with the drying tube. All connections between glass should be made with minimum lengths of vinyl tubing.

NOTE 3—The optimum flow rate will vary with the geometric design of each apparatus. The flow rate should be adjusted to give the maximum absorbance and the best reproducibility without excessive foaming.

8.3 Adjust the operating conditions in accordance with the following parameters and allow the spectrophotometer to warm up for at least 15 min. Select the proper scale expansion for the

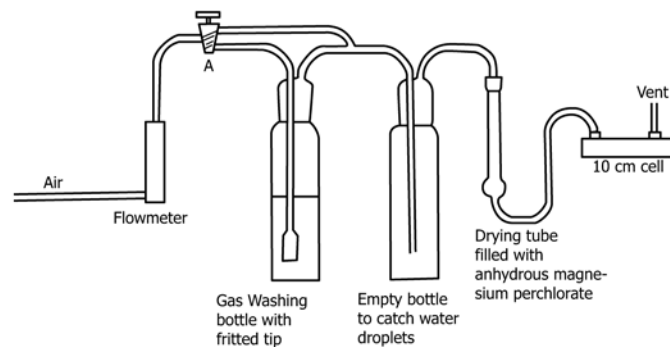


FIG. 1 Mercury Aeration Apparatus

standards used from **Table 1**. The conditions shown are for the Perkin-Elmer Model 303 (**Note 1**).

Wavelength	253.7 nm
Slit width	4 (6.5 Å)
Lamp current	approximately 10 mA
Recorder noise suppression	2, giving approximately 90 % of response in 1 s
Scale expansion	3×

8.4 Allow the base line to stabilize with Stopcock A in the bypass position and an empty gas-washing bottle connected to the apparatus.

8.5 Prepare a reagent blank by adding 20 mL of 50 % membrane grade caustic soda into the gas-washing bottle.

8.6 Add 2 mL of the cadmium chloride solution into the gas-washing bottle.

8.7 Add 20 mL of water to the gas-washing bottle by slowly delivering the water down the side of the bottle. This will layer the water on top of the cadmium chloride solution and minimize premature mixing of the reagents.

8.8 Add 2 mL of SnCl₂ solution to the gas-washing bottle delivering the solution down the side of the bottle and connect the gas-washing bottle to the aeration apparatus. Turn Stopcock A from the bypass to the aeration position and aerate the solution.

8.9 Determine the percent absorption from the peak height on the recorder chart when a constant reading is obtained.

NOTE 4—Steps 8.5 – 8.9 should be carried out in sequence with as little delay as possible between operations.

8.10 An absorption peak of less than 10 % should be obtained at 3× scale expansion. Continue running blanks until this is achieved. Consistently higher blanks indicate a contamination problem from dirty glassware or reagents. Clean the apparatus with aqua regia and prepare fresh reagents until a satisfactory blank is obtained.

8.11 The concentration of mercury in the standards should cover the expected concentration in the sample to be analyzed. **Table 1** suggests the standards to be prepared for various concentration levels. Prepare a series of at least three standards in 150-mL borosilicate extraction flasks in accordance with **Table 2**. Analyze each standard by adding it with the water in 8.7 and completing the analysis as described in 8.8 to 8.9.

TABLE 1 Expected Range and Sample Size

Test Method A			
Expected Range, ng/g	Sample Size, g	Standards, ng	Scale Expansion
>60	1	10, 50, 100	3×
30-60	2.5	10, 50, 100	3×
15-30	5	10, 50, 100	3×
7-30	10	10, 50, 100	3×
3-7	20	10, 50, 100	3×
<3	40	0.5, 10, 50	3×
Test Method B			
Expected Range, µg/g	Sample Size, g	Standards, µg	Scale Expansion
0.2 to 10	2	2.5, 10, 20	1×
0.01 to 0.5	5	0.2, 0.5, 1, 2	3×

TABLE 2 Standard Stock Solutions

Test Method A			
ng Hg in Standard	mL of water in gas bottle	mL of 50 ng/mL Hg Standard	mL of 5 ng/mL Hg Standard
0.0	20	...	0.0
0.5	20	...	0.1
2.5	20	...	0.5
5.0	19	...	1.0
10	20	0.2	...
50	19	1.0	...
100	18	2.0	...
500	10	10	...
1000	0	20	...
Test Method B			
µg Hg in Standard	mL of NaCl Brine	mL of 10 µg/mL Hg Standard Solution	mL of 1 µg/mL Hg Standard Solution
0.1	5	...	0.1
0.2	5	...	0.2
0.3	5	...	0.3
0.5	5	...	0.5
1.0	5	...	1.0
2.0	5	...	2.0
5	5	...	5.0
10	5	1.0	...
20	5	2.0	...

8.12 Repeat Steps 8.5 – 8.11 for each reagent blank and standard in order of increasing concentration.

8.13 Convert the values for percent absorption to absorbance using the tables in the instrument instruction manual or an optical density scale ruler. Subtract the absorbance of the reagent blank from the absorbance of each standard. Draw a calibration curve by plotting absorbance versus nanograms of mercury. At 3× scale expansion, the readings in recorder chart divisions are approximately equal to absorbance and may be used directly as the ordinate of the calibration curve.

8.14 Alternatively, in instruments where the signal is recorded in percent absorption, semilog paper can be used to plot percent absorption versus concentration. A good deal of time is saved using this method of plotting a calibration curve.⁵

9. Analysis of Sample

9.1 Select a sample size in accordance with the anticipated mercury concentration from **Table 1**.

9.2 The sample, in the form of 50 % caustic soda or caustic potash, is added to the gas-washing bottle before the 50 % membrane caustic soda in 8.5. Weigh the amount of sample added to the gas-washing bottle to the nearest 0.01 g. When large samples of caustic soda are analyzed, the volume of 50 % membrane caustic soda added to the gas-washing bottle should be reduced to keep the total concentration of caustic soda in the final solution in the gas-washing bottle at or below 25 %.

9.3 Proceed with 8.5 – 8.11 for each sample to be analyzed.

9.4 Convert the values for percent absorption to absorbance as described in 8.13 and 8.14. Subtract the absorbance of the reagent blank carried through the entire procedure from the absorbance of the sample. Obtain the nanograms of mercury in the sample from the calibration curve.

⁵ Harre, Gustav N., *Atomic Absorption News Letter*, Vol 8, No.2, 1969.