



# Standard Test Methods for Mercury in Caustic Soda (Sodium Hydroxide) and Caustic Potash (Potassium Hydroxide)<sup>1</sup>

This standard is issued under the fixed designation E 538; 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 ( $\epsilon$ ) 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 The values stated in SI units are to be regarded as the standard.

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.* Specific hazards statements are given in Section 7 and 17.

1.5 Review the current material safety data sheets (MSDS) for detailed information concerning toxicity, first-aid procedures, and safety precautions.

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 1193 Specification for Reagent Water<sup>2</sup>

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals<sup>3</sup>

## 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.

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 ft<sup>3</sup>/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.

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee E-15 on Industrial Chemicals and is the direct responsibility of Subcommittee E15.52 on Alkalies.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 15.05.

## 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.<sup>4</sup> 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 D 1193.

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  $\text{HNO}_3$  (sp gr 1.42) to 30 mL of concentrated  $\text{HCl}$  (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. **Caution**—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. **Caution**—Use goggles when preparing this solution.

6.7 *Stannous Chloride Solution (10 g/100 mL)*—Dissolve 10 g of stannous chloride ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) 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 ( $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ) in 100 mL of water containing 2 mL of concentrated  $\text{HNO}_3$  in a 1-L volumetric flask. Dilute to volume with water and mix well.

6.9 *Mercury Standard Solution (1 mL = 50  $\mu\text{g}$  Hg)*—Pipet 5.0 mL of 0.05 M mercuric nitrate stock solution into a 1-L volumetric flask, acidify with 5 mL of  $\text{H}_2\text{SO}_4$  (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  $\mu\text{g}$  Hg/mL into a 1-L volumetric flask, acidify with 5 mL of  $\text{H}_2\text{SO}_4$  (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  $\text{H}_2\text{SO}_4$  (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  $\text{H}_2\text{SO}_4$  (sp gr 1.84) to 800 mL of water. This solution is dispensed from a 10-mL buret. **Caution**—Use goggles when preparing this solution.

## 7. Hazards

7.1 Sodium hydroxide, potassium hydroxide, and their so-

lutions 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  $\text{ft}^3/\text{h}$  (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 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 $\times$

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  $\text{SnCl}_2$  solution to the gas-washing 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.

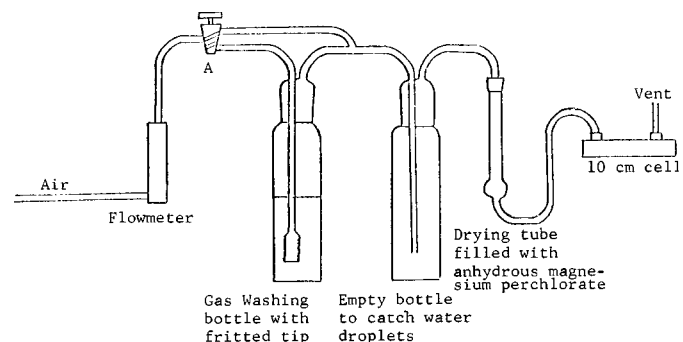


FIG. 1 Mercury Aeration Apparatus

<sup>4</sup> *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.

**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×

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.

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

**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	...

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.<sup>5</sup>

**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.

**10. Calculation**

10.1 Calculate the mercury content of the sample as follows:

$$\text{Hg, ppb} = \frac{A}{B} \tag{1}$$

where:

A = mercury in sample, ng, and

B = sample weight, g.

**11. Report**

11.1 Report the parts per billion mercury to the nearest 0.01 ppb.

**12. Precision and Bias**

12.1 The following criteria should be used in judging the acceptability of results (Note 5):

12.1.1 *Repeatability (Single Analyst)*—The standard deviation and coefficient of variation for a single determination has been estimated to be the values listed in Table 3 at the indicated degrees of freedom. The 95 % limits for the difference between two such runs are also listed in Table 3.

12.1.2 *Laboratory Precision (Within-Laboratory, Between Days Variability, Formerly Called Repeatability)*—The laboratory precision for this test method has not been determined.

12.1.3 *Reproducibility (Multilaboratory)*—The reproducibility for this test method has not been determined.

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

**TABLE 3 Precision Estimates for Mercury, Method A**

Sample Type	Sodium Hydroxide	Potassium Hydroxide	Sodium Hydroxide	Potassium Hydroxide
Mercury level, ppb	0	2	6	14
Average, ppb Hg	0.074	1.82	5.99	14.2
Standard deviation, ppb	0.0117	0.1813	0.4595	0.9042
Degrees of freedom	9	9	9	9
95 % range, ppb	0.033	0.51	1.29	2.53
Coefficient of variation, % relative	15.86	9.97	7.67	6.36
95 % range, % relative	44.4	27.9	21.5	17.8

12.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

NOTE 5—The preceding precision statements are based on a study performed in one laboratory in 1997 on 2 samples of sodium hydroxide containing approximately 0.07 and 0.5 ppb Hg, and 2 samples of potassium hydroxide containing approximately 2 and 14 ppb Hg. One analyst performed 10 replicate determinations on each sample on one day for a total of 40 determinations.<sup>6</sup>

### TEST METHOD B—PERMANGANATE OXIDATION FOLLOWED BY ACIDIC REDUCING AGENT

#### 13. Summary of Test Method

13.1 Mercury is converted to mercuric ion by oxidation with potassium permanganate then reduced to metallic mercury which is aerated from the solution and determined by cold vapor atomic absorption analysis.

#### 14. Significance and Use

14.1 Mercury is a toxic material and is also deleterious if present in caustic soda used in certain manufacturing processes. It must therefore be controlled as a possible pollutant. This test method provides a procedure for measuring mercury in liquid and solid caustic soda.

#### 15. Apparatus

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

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

15.3 *Absorption Cell*, 1-cm path length with quartz windows.

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

15.5 *Gas-Washing Bottle*, 125-mL, without frit.

15.6 *Stopcock*, three-way, with TFE-fluorocarbon plug.

15.7 *Needle Valve*.

15.8 *Drying Tube*.

15.9 *Vacuum Trap*.

15.10 *Flowmeter*, capable of measuring and maintaining a flow rate of 1.5 standard ft<sup>3</sup>/h.

NOTE 6—The procedure as described in this test method employs a Perkin-Elmer Model 303 atomic absorption spectrophotometer. Any other

<sup>6</sup> Details of the interlaboratory study are available as Research Report E15:1051 from ASTM Headquarters.

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.

#### 16. Reagents

16.1 *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.<sup>4</sup> 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.

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

16.3 *Anhydrous Magnesium Perchlorate*.

16.4 *Aqua Regia*—Carefully add 10-mL of concentrated HNO<sub>3</sub> (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. **Caution**—Use goggles when preparing this solution.

16.5 *Hydrochloric Acid (1+1)*—Carefully add 250 mL of concentrated HCl (sp gr 1.19) to 250 mL of distilled water. Wear goggles.

16.6 *Hydroxylamine Hydrochloride Solution (100 g/L)*—Dissolve 10 g of hydroxylamine hydrochloride (NH<sub>2</sub>OH·HCl) in 100 mL of water. This reagent is dispensed with a dropping bottle.

16.7 *Mercuric Nitrate Stock Solution (0.05 M) (1 mL = 10 mg Hg)*—Dissolve 17.1 g of mercuric nitrate (Hg(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O) in 100 mL of water containing 2 mL of concentrated HNO<sub>3</sub> in a 1-L volumetric flask. Dilute to volume with water and mix well.

16.8 *Mercury Standard Solution (1 mL = 200 µg Hg)*—Pipet 5.0 mL of 0.05 M mercuric nitrate solution into a 250-mL volumetric flask, acidify with 5 mL of H<sub>2</sub>SO<sub>4</sub> (1+4), and dilute to volume with water. Mix well.

16.9 *Mercury Standard Solution (1 mL = 10 µg Hg)*—Pipet 5.0 mL of the standard mercury solution containing 200 µg Hg/mL into a 100-mL volumetric flask, acidify with 5 mL of H<sub>2</sub>SO<sub>4</sub> (1+4), and dilute to volume with water. Mix well.

16.10 *Mercury Standard Solution (1 mL = 1 µg Hg)*—Pipet 10.0 mL of the standard mercury solution containing 10 µg Hg/mL into a 100-mL volumetric flask, acidify with 5 mL of H<sub>2</sub>SO<sub>4</sub> (1+4), and dilute to volume with water. Mix well. Prepare fresh daily.

16.11 *Potassium Permanganate Solution (40 g/L)*—Weigh 40 g of KMnO<sub>4</sub> into a 1000-mL beaker. Add about 800 mL of water and stir with a mechanical stirrer until completely dissolved. Transfer to a 1-L volumetric flask, dilute to volume, and store in a brown bottle.

16.12 *Sodium Chloride Brine (300 g/L)*—Weigh 300 g of NaCl into a 1-L volumetric flask. Make up to volume with water and mix until all the NaCl has dissolved.

16.13 *Stannous Chloride Solution (100 g/L)*—Dissolve 20 g of stannous chloride (SnCl<sub>2</sub>·2H<sub>2</sub>O) in 40 mL of warm concentrated HCl. Add 160 mL of water when all the stannous

chloride has dissolved. Mix and store in a 250-mL reagent bottle. Prepare fresh once a week.

16.14 *Sulfuric Acid* (1+4)—Add slowly while stirring 200 mL of concentrated H<sub>2</sub>SO<sub>4</sub> (sp gr 1.84) to 800 mL of water. This solution is dispensed from a 10-mL buret. **Caution**—Use goggles when preparing this solution.

## 17. Hazards

17.1 Sodium hydroxide and its 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.

17.2 Sulfuric acid will cause severe burns if allowed to come in contact with skin or eyes. All exposures must be immediately flushed from the skin or eyes with cold water. Get medical attention immediately for any eye exposure. This acid must always be added slowly to water with adequate stirring since heat is developed and spattering occurs if the acid is added too quickly.

## 18. Calibration

18.1 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.

18.2 Connect the apparatus shown in Fig. 1 to the atomic absorption spectrophotometer and adjust the air flow rate to 1.5 standard ft<sup>3</sup>/h (see Notes 7 and 8).

NOTE 7—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 8—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.

18.3 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 standards used from Table 1. The conditions shown are for the Perkin-Elmer Model 303 (Note 6).

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	1× and 3×

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

18.5 Add 2 mL of SnCl<sub>2</sub> solution and 60 mL of water to the wash bottle and aerate. 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.

18.6 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.

18.7 Dilute each standard to the same volume as the samples with water.

18.8 Prepare a series of at least three reagent blanks by pipeting 5 mL of the NaCl brine into an extraction flask. Dilute to the same volume as the sample with water.

18.9 To the flask, add 1 mL of H<sub>2</sub>SO<sub>4</sub> (1+4) and 1 mL of the KMnO<sub>4</sub> solution from automatic burets. Add sufficient water to bring the volume to 30 mL. Cover the flask with a watchglass.

18.10 Boil the solution for a few seconds and allow to cool.

18.11 If the standard solution contains KMnO<sub>4</sub>, destroy the excess by adding a few drops of hydroxylamine hydrochloride solution until the solution is colorless.

18.12 Wash the solution into the gas-washing bottle and dilute to the 60-mL mark with water.

18.13 Add 2 mL of SnCl<sub>2</sub> solution and connect the gas-washing bottle to the aeration apparatus. Turn Stopcock A from the bypass to the aeration position.

NOTE 9—Steps 18.10-18.13 should be carried out in sequence with as little delay as possible between operations.

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

18.15 Repeat Steps 18.9-18.14 for the reagent blanks and each standard in order of increasing concentration.

18.16 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 micrograms 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.

18.17 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.<sup>5</sup>

## 19. Analysis of Sample

19.1 Select the sample size in accordance with the anticipated mercury concentration from Table 1.

19.2 Mix the sample thoroughly, and accurately weigh the thoroughly mixed sample into a 150-mL extraction flask. Add approximately 10 mL of water and 2 drops of phenolphthalein indicator solution and, with constant stirring and cooling, slowly and carefully neutralize with HCl (1+1).

19.3 Proceed with Steps 18.9-18.14.

19.4 Convert the values for percent absorption to absorbance as described in 18.16 and 18.17. Subtract the absorbance of the reagent blank carried through the entire procedure from the absorbance of the sample. Obtain the micrograms of mercury in the sample from the calibration curve.

## 20. Calculation

20.1 Calculate the mercury content of the sample as follows:

$$\text{Hg, ppm} = \frac{A}{B} \quad (2)$$

where:

*A* = Mercury in sample, µg, and

*B* = sample weight, g.

## 21. Report

21.1 Report the parts per million mercury to the nearest 0.001 ppm.

## 22. Precision and Bias

22.1 The following criteria should be used in judging the acceptability of results (Note 10):

22.1.1 *Repeatability (Single Analyst)*—The coefficient of variation for a single determination has been estimated to be 6.5 % relative to 32 df. The 95 % limit for the difference between two such runs is 18.2 % relative.

22.1.2 *Laboratory Precision (Within-Laboratory, Between Days Variability)*—The coefficient of variation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 6.1 % relative at 16 df.

The 95 % limit between two such averages is 17.1 % relative.

22.1.3 *Reproducibility (Multilaboratory)*—The coefficient of variation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 38.6 % relative at 7 df. The 95 % limit for the difference between two such averages is 108 % relative.

22.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference material.

NOTE 10—The preceding precision estimates are based on an interlaboratory study<sup>7</sup> with two samples of sodium hydroxide covering the range from 0.023 to 0.030 ppm Hg. One analyst in each of nine laboratories performed duplicate determinations and repeated one day later for a total of 36 determinations. Practice E 180 was used in developing these precision estimates.

## 23. Keywords

23.1 caustic potash; caustic soda; flameless atomic absorption; mercury; potassium hydroxide; sodium hydroxide

<sup>7</sup> Supporting data are available at ASTM Headquarters. Request RR: 15-1022 (1975).

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