



Standard Test Method for Mercury in Liquid Chlorine¹

This standard is issued under the fixed designation E 506; 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 method² covers the determination of mercury in liquid chlorine with a lower limit of detection of 0.1 ppb.

1.2 *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 precautionary statements are given in Sections 7, 6.3, 6.4, 6.5, and Note 2.

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

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water³

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals⁴

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis⁴

3. Summary of Test Method

3.1 Liquid chlorine samples are taken in chilled glass flasks, then allowed to evaporate slowly to dryness. The mercury is left in the residue. The residue is dissolved in dilute nitric acid and diluted to volume. The addition of nitric acid prevents any loss of mercury from the aqueous solution on standing. For analysis, an aliquot of the acidic aqueous solution is boiled with excess permanganate to remove interfering materials. The

mercuric ions are then reduced to metallic mercury with stannous chloride. The solution is aerated and the mercury, now in the air stream, is determined using an atomic absorption spectrophotometer.

4. Significance and Use

4.1 This test method was developed primarily for the determination of traces of mercury in chlorine produced by the mercury-cell process.

5. Apparatus

5.1 *Atomic Absorption Spectrophotometer*, equipped with mounting to hold absorption cell and a fast response (0.5 s) recorder.⁵

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

5.3 *Absorption Cell*, 10-cm path length with quartz windows.⁶

5.4 *Gas Washing Bottle*, 125 mL, with extra-coarse fritted bubbler.⁷ The bottle has a calibration line drawn at the 60-mL mark.

5.5 *Stopcock*, 3-way, with plug of TFE-fluorocarbon.⁸

5.6 *Gas Washing Bottle*, 125-mL without frit.⁹

5.7 *Drying Tube*.¹⁰

5.8 *Flow Meter*, capable of measuring and maintaining a flow of 1.5 standard ft³/h (42.5 L/h).¹¹

5.9 *Large Dewar Flasks*, two, with sufficient capacity to hold a 500-mL flask and a large volume of dry ice cooling mixture.

5.10 *Flexible Connections*.¹²

5.11 *Stainless Steel Compression Nut*.

5.12 *Two-Hole Rubber Stopper*.

¹ This test method is under the jurisdiction of ASTM Committee E-15 on Industrial Chemicals and is the direct responsibility of Subcommittee E15.57 on Compressed Gases.

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² *Analytical Methods for Atomic Absorption Spectrophotometry*, Perkin-Elmer Ltd., September 1968.

³ "Determination of Mercury in Effluents and Process Streams from a Mercury-Cell Chlorine Plant (Atomic Absorption Flameless Method)" CAS-AM-70.13, June 23, 1970, Analytical Laboratory, Dow Chemical of Canada, Ltd., Sarnia, Ontario, Canada.

⁴ "Determination of Mercury in Liquid Chlorine," CSAL-M72.4, Feb. 25, 1972, Analytical Laboratory, Dow Chemical of Canada, Ltd., Sarnia, Ontario, Canada.

Chlorine Institute Reference No. MIR-104.

⁵ *Annual Book of ASTM Standards*, Vol 11.01.

⁶ *Annual Book of ASTM Standards*, Vol 15.05.

⁵ A Beckman 10-in. recorder Model No. 100502, available from Beckman Instruments Inc., 2500 Harbor Blvd., Fullerton, CA 92634, is suitable.

⁶ Beckman 75144, available from Beckman Instruments Inc., 2500 Harbor Blvd., Fullerton, CA 92634, has been found suitable.

⁷ Corning 31770 (125 EC), available from Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785, has been found suitable.

⁸ Corning 7382, available from Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785, has been found suitable.

⁹ Corning 1760, available from Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785, or equivalent has been found suitable.

¹⁰ Corning 7775, available from Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785, has been found suitable.

¹¹ Brooks Tube P-2-15A with sapphire float, available from Brooks Instrument Div., Emerson Electric Co., 407 West Vine St., Hatfield, PA 19440, or equivalent has been found suitable.

¹² Tygon, available from Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785, has been found suitable.

5.13 Fluorocarbon Tubing.

NOTE 1—The procedure, as described in this test method, was developed using a Perkin-Elmer Model 303 atomic absorption spectrophotometer equipped with a 10-cm absorption cell. Any other equivalent atomic absorption spectrophotometer may be used as well as one of the many commercial instruments specifically designed for measurement of mercury by flameless atomic absorption. 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 should conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.¹³ Blanks should be run on all reagents to assure a negligible mercury content.

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

6.3 *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. **Precaution:** Use goggles when preparing or using this solution.

6.4 *Nitric Acid (1 + 9)*—Pipet 25 mL of concentrated HNO₃ (sp gr 1.42) into a 250-mL volumetric flask containing about 150 mL of water. Dilute to volume with water and mix well. **Precaution:** Use goggles when preparing this solution.

6.5 *Sulfuric Acid (1 + 4)*—Add slowly with stirring 200 mL of concentrated H₂SO₄ (sp gr 1.84) to 800 mL of water. **Caution:** Use goggles when preparing this solution.

6.6 *Cooling Mixture for Dewar Flasks*—Fill two thirds of the Dewar flask with dichloromethane. Add dry ice slowly, allowing time for the solution to cool, until there is no sublimation of dry ice on further addition. Replenish the dry ice when necessary. See the MSDS sheet for dichloromethane before using this material.

6.7 *Hydroxylamine Hydrochloride Solution (100 g/L)*—See Practice E 200. This reagent is dispensed with a dropping bottle.

6.8 *Mercury Standard Solution (50 µg Hg/mL)*—As prepared in Practice E 200.

6.9 *Mercury Standard Solution (10 µg Hg/mL)*—Pipet 10 mL of the standard mercury solution containing 50 µg Hg/mL into a 50-mL volumetric flask, acidify with 5 mL of 1 + 4 H₂SO₄ and dilute to volume with water. Mix well. Prepare fresh daily.

6.10 *Mercury Standard Solution (1 µg Hg/mL)*—Pipet 10 mL of the standard mercury solution containing 10 µg Hg/mL into a 100-mL volumetric flask, acidify with 5 mL 1 + 4 H₂SO₄ and dilute to volume with water. Mix well. Prepare fresh daily.

6.11 *Potassium Permanganate Solution (40 g/L) (4 %)*—

Weigh 40 g of KMnO₄ into a 1000-mL beaker. Add about 800 mL of water and stir with a mechanical stirrer until completely dissolved. Allow the solution to stand overnight and filter. Transfer to a 1000-mL volumetric flask, dilute to volume, and store in a brown bottle.

6.12 *Stannous Chloride (10 %)*—Dissolve 20 g of stannous chloride (SnCl₂·2H₂O) in 40 mL of warm concentrated HCl (sp gr 1.19). Add 160 mL of water when all the stannous chloride has dissolved. Allow the solution to stand overnight and filter. Mix and store in a 250-mL reagent bottle. Prepare fresh once a week. A piece of metallic tin in the bottle allows longer term storage if the bottle is well sealed.

7. Safety Precautions

7.1 Sulfuric acid will cause severe burns if allowed to come in contact with any part of the skin or eyes. All spillages must be immediately flushed from the skin or eyes with cold water. 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.

7.2 Aqua regia contains both HNO₃ and HCl, which will cause severe burns if allowed to come in contact with any part of the skin or eyes. All spillages must be immediately flushed from the skin or eyes with cold water. Vapors produced by aqua regia can cause burns if inhaled. It should be used only in a hood or with similar ventilation. This solution is unstable and must *not* be placed in a *stoppered* flask or bottle.

7.3 Nitric acid will cause severe burns if allowed to come in contact with any part of the skin or eyes. All spillages must be immediately flushed from the skin or eyes with cold water.

7.4 Chlorine is a corrosive and toxic material. A well-ventilated fume hood should be used to house all test equipment when this product is analyzed in the laboratory.

7.5 Liquid chlorine sampling should be performed only by those persons thoroughly familiar with the handling of this material and the operation of the sampling system. Personnel should be equipped with monogoggles, gloves (if desired), and a respirator. Sampling should be done in a well-ventilated area or in a hood.

7.6 The analysis should be attempted only by persons who are thoroughly familiar with the handling of chlorine, and even an experienced person should not work alone. The operator must be provided with adequate eye protection and a respirator. Splashes of liquid chlorine destroy clothing and, if such clothing is next to the skin, will produce irritations and burns.

7.7 When sampling and working with chlorine out of doors, people downwind from such operation should be warned of the possible release of chlorine vapors.

7.8 It is recommended that means be available for disposal of excess chlorine in an environmentally safe and acceptable manner. If chlorine cannot be disposed of in a chlorine consuming process, the chlorine should be discharged into a caustic scrubber containing an appropriate amount of 20 % caustic solution to neutralize all the chlorine. This reaction is exothermic, and care should be taken to avoid excess heating by choosing a sufficiently large volume of caustic solution to serve as a heat sink. When the analysis and sampling regimen requires an initial purging of chlorine from a container, the purged chlorine should be similarly handled. Purging to the

¹³ *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 Pharmacopoeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

atmosphere should be avoided.

7.9 In the event chlorine is inhaled, first aid should be summoned immediately and oxygen administered without delay.

7.10 Handle all other reagents as recommended by the supplier.

8. Sampling

8.1 Soak all 500-mL receiver flasks carefully in 50°C aqua regia and rinse with water before use.

8.2 Cool two receiver flasks in the dichloromethane-dry ice mixture.

8.3 Assemble the sampling apparatus as shown in Fig. 1.

8.4 With a respirator ready for immediate use, locate yourself upwind of the receiver flask.

8.5 Keeping the receiver flask in the dry ice solution, purge the sampling system allowing 100 to 200 mL of liquid chlorine to flow through the sampling system into the flask. This purges any residual mercury deposits from the lines and sample point.

8.6 Stop the flow of liquid chlorine.

8.7 Cap the waste liquid chlorine flask with an open, one-hole stopper and store in a dry ice bath for disposal in an environmentally safe and acceptable manner.

8.8 Attach the delivery system to a cooled 500-mL receiver flask and fill with liquid chlorine to the 200-mL mark. Other volumes may be used if desired.

8.9 Stop the flow of liquid chlorine.

8.10 Cap the flask with an open, one-hole stopper and store in a dichloromethane-dry ice mixture.

NOTE 2—**Caution:** Except for properly designed cylinders, never completely stopper a vessel containing liquid chlorine. A vent must always be present to relieve the pressure from evaporating liquid chlorine.

8.11 Remove the sample of liquid chlorine and waste liquid chlorine from the dichloromethane-dry ice mixture and allow them to evaporate to dryness into a chlorine absorption system or some other type of environmentally safe and acceptable manner of chloride disposal. Discard the residue from the waste chlorine.

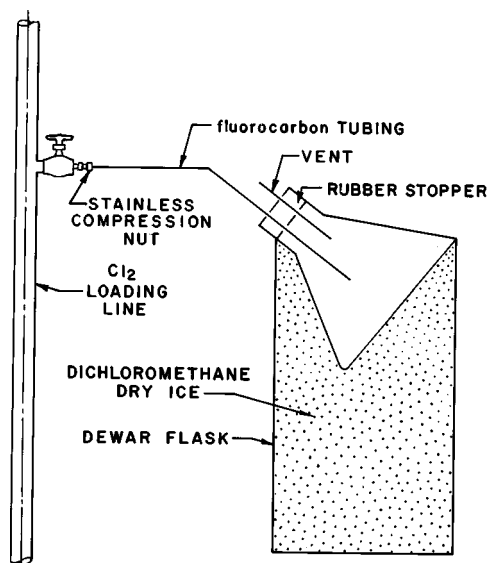


FIG. 1 Sampling System for Liquid Chlorine

8.12 Add 10 mL of HNO₃ (1 + 9) to the flask containing the residue from the liquid chlorine sample. Swirl to assure complete solution of the residue. Add 25 mL of water and transfer to a 50-mL volumetric flask. Dilute to volume with the water used to rinse the flask and mix well.

8.13 Prepare a blank consisting of 10 mL of HNO₃(1 + 9) in a 50-mL volumetric flask, dilute to volume with water, and mix well.

9. Calibration

9.1 Care must be taken to avoid contamination of the apparatus with mercury. Soak all glass apparatus (pipets, beakers, and gas washing bottle) in aqua regia prior to use and rinse thoroughly with water before use.

9.2 Connect the apparatus shown in Fig. 2 to the atomic absorption spectrophotometer and adjust the air flow rate to 1.5 standard ft³/h or 42.5 L/h.

9.3 Adjust the operating conditions in accordance with the manufacturer's recommendations for doing mercury analysis and allow the spectrophotometer to warm up for at least 15 min (see Note 1). Listed below are typical conditions for one instrument.

Wavelength	253.7 nm
Slit width	(0.65 nm)
Lamp current	approximately by 10 mA
Recorder noise suppression	2, giving approximately 90 % of response in 1 s
Scale expansion	1× for 0.05 to 2 µg Hg 3× for 0.01 to 0.5 µg Hg
Cell	10 cm pathlength with quartz windows
Operating mode	absorbance

9.4 Allow the base line to stabilize with stopcock A in the by-pass position and an empty gas washing bottle connected to the apparatus.

9.5 Add 2 mL of 10 % SnCl₂ solution and 60 mL of water to the wash bottle and aerate. An absorbance peak of less than 0.03 % 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.

9.6 Prepare at least three standards by pipeting the following volumes of the 1 µg Hg/mL standard into 50-mL beakers.

mL of 1 µg/mL Standard	µg Hg in Standard
0.1	0.1
0.2	0.2
0.5	0.5
1.0	1.0
2.0	2.0

9.7 Dilute each standard and a reagent blank with water to the same volume as the sample aliquot.

9.8 Add 1 mL of H₂SO₄ (1 + 4) and 1 mL of KMnO₄ solution. Add sufficient water to bring the volume to 30 mL. Cover the beaker with a watch glass.

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

9.10 If the standard solution contains excess KMnO₄, destroy the excess by adding a few drops of hydroxylamine hydrochloride solution until the solution is colorless.

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

9.12 Add 2 mL of 10 % SnCl₂ solution and connect the gas washing bottle to the aeration apparatus. Turn stopcock A from the bypass to the aeration position.

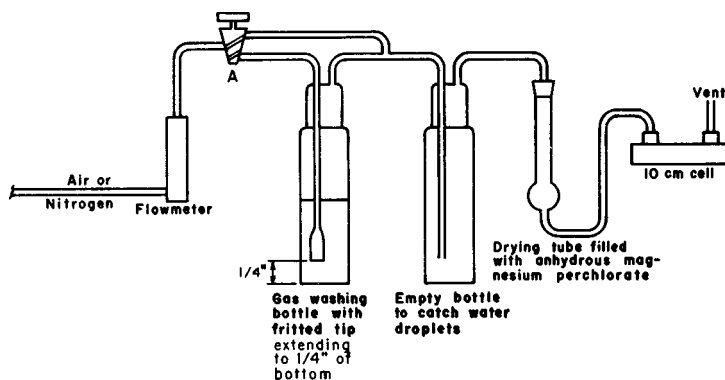


FIG. 2 Apparatus for Sample Aeration

NOTE 3—Steps 9.10-9.12 should be carried out in sequence with as little delay as possible between operations.

9.13 Determine the absorbance from the peak height on the recorder chart, adjusting for the scale expansion setting.

9.14 Repeat steps 9.8-9.13 for the reagent blank and each standard adjusting for the scale expansion setting.

9.15 Subtract the absorbance of the reagent blank from the absorbance of each standard. Construct a calibration curve by plotting absorbance versus micrograms of mercury.

10. Analysis of Sample

10.1 Pipet 10 mL or any suitable aliquot of the sample and reagent blank into 50-mL beakers.

10.2 Proceed with 9.8-9.13.

10.3 Convert the values for percent absorption to absorbance. 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.

11. Calculation

11.1 ppm Hg in sample =

$$\frac{A}{B \times C} \times \frac{50}{D} \quad (1)$$

where:

A = micrograms of Hg in sample aliquot,

B = millilitres of liquid chlorine taken,

C = density of liquid chlorine = 1.557 g/mL, and

D = sample aliquot, mL.

12. Report

12.1 Report the mercury content to the nearest 0.0001 ppm.

13. Precision and Bias

13.1 The following criteria should be used for judging the acceptability of results (Note 4):

13.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.00042 ppm absolute at 26 df. The 95 % limit for the difference between such runs is 0.0012 ppm absolute.

13.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability, Formerly Called Repeatability)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.0040 ppm absolute at 13 df. The 95 % limit for the difference between two such averages is 0.0011 ppm absolute.

13.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.00043 ppm absolute at 6 df. The 95 % limit for the difference between two such averages is 0.0012 ppm absolute.

NOTE 4—The preceding precision statements are based on an interlaboratory study performed in 1972 with two samples of liquid chlorine containing approximately 0.00091 and 0.00083 ppm mercury. A Perkin-Elmer Model 303 instrument, which is no longer available, was used in the study, but the precision obtained with more modern instruments is expected to be at least as good. For the sample containing 0.00091, one analyst in each of seven laboratories performed duplicate determinations and repeated them on a second day, for a total of 28 determinations. For the other sample, one analyst in each of six laboratories followed the same design for a total of 24 determinations.¹⁴ Practice E 180 was used in developing these precision estimates.

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

14. Keywords

14.1 atomic absorption; chlorine; cold vapor; flameless; mercury

¹⁴ Details of the interlaboratory study are available as Research Report E15-1018 from ASTM Headquarters.

 **E 506**

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