~~Designation:E506–98 (Reapproved 2003)~~ Designation: E 506 – 08

Standard Test Method for Mercury in Liquid Chlorine[1]

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 method[2] ~~covers the determination of mercury in liquid chlorine with a lower limit of detection of 0.1 ppb.~~

~~1.2~~*covers the determination of mercury in liquid chlorine with a lower limit of detection of 0.1 µg/L.*

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *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~~4~~ 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:*[3]

D 1193 Specification for Reagent Water

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

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

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.[4]

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

[1] This test method is under the jurisdiction of ASTM Committee E15 on Industrial and Specialty Chemicals and is the direct responsibility of Subcommittee E15.02 on Product Standards.

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

"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.

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

Chlorine Institute Reference No. MIR-104.

[3] 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* ~~, Vol 11.01.~~volume information, refer to the standard's Document Summary page on the ASTM website.

~~[4] Annual Book of ASTM Standards, Vol 15.05.~~

[4] The sole source of supply of the Beckman 10–in. recorder Model No. 100502 known to the committee at this time is Beckman Instruments Inc., 2500 Harbor Blvd., Fullerton, CA 92634. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee , which you may attend.

***A Summary of Changes section appears at the end of this standard.**

5.3 *Absorption Cell*, 10-cm path length with quartz windows.[4,5]

5.4 *Gas Washing Bottle*, 125 mL, with extra-coarse fritted bubbler.[4,6] The bottle has a calibration line drawn at the 60-mL mark.

5.5 *Stopcock*, 3-way, with plug of TFE-fluorocarbon.[4,7]

5.6 *Gas Washing Bottle*, 125-mL without frit.[8]

5.7 *Drying Tube*. [9]

5.8 *Flow Meter*~~, capable of measuring and maintaining a flow of 1.5 standard ft^3/h (42.5 L/h).~~ , capable of measuring and maintaining a flow of 42.5 L/h. [10]

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 Connection*. [4,11]

5.11 *Stainless Steel Compression Nut*.

5.12 *Two-Hole Rubber Stopper*.

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.[12] 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 HNO_3 (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 or using this solution.)

6.4 *Nitric Acid (1 + 9)*—Pipet 25 mL of concentrated HNO_3 (sp gr 1.42) into a 250-mL volumetric flask containing about 150 mL of water. Dilute to volume with water and mix well. (**Warning—**Use goggles when preparing this solution.)

6.5 *Sulfuric Acid (1 + 4)*—Add slowly with stirring 200 mL of concentrated H_2SO_4 (sp gr 1.84) to 800 mL of water. (**Warning—**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 H_2SO_4 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 H_2SO_4 and dilute to volume with water. Mix well. Prepare fresh daily.

6.11 *Potassium Permanganate Solution* (40 g/L) (4 %)—Weigh 40 g of $KMnO_4$ into a 1000-mL beaker. Add about 800 mL

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[5] The sole source of supply of the Beckman 75144 known to the committee at this time is Beckman Instruments Inc., 2500 Harbor Blvd., Fullerton, CA 92634. I

[6] The sole source of supply of the Beckman 75144 known to the committee at this time is Beckman Instruments Inc., 2500 Harbor Blvd., Fullerton, CA 92634. I

[6] The sole source of supply of the Corning 31770 (125 EC) known to the committee at this time is Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785. I

[7] The sole source of supply of the Corning ~~31770 (125 EC)~~ 7382 known to the committee at this time is Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785. ~~I~~

[8] The sole source of supply of the Corning 7382 known to the committee at this time is Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785.

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

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

[9] The sole source of supply of the Corning 7775 known to the committee at this time is Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785.

[10] The sole source of supply of the Corning 7775 known to the committee at this time is Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785.

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

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

[11] The sole source of supply of Tygon known to the committee at this time is Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785.

[12] The sole source of supply of Tygon known to the committee at this time is Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785.

[12] *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.

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 ($SnCl_2 \cdot 2H_2O$) 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 HNO_3 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 familar 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 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—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 enviornmentally safe and acceptable manner of chloride disposal. Discard the residue from the waste chlorine.

8.12 Add 10 mL of HNO_3 (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.