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Designation: D 2361 – 95 (Reapproved 2001)


Designation: D 2361 – 02

Standard Test Method for Chlorine in Coal¹

This standard is issued under the fixed designation D 2361; 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 This test method is under the jurisdiction of ASTM Committee D05 on Coal Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis. Current edition approved Sept. 10, ~~1995~~, 2002. Published ~~November 1995~~, December 2002. Originally published as D 2361 – 65T. Last previous edition D 2361 – 95 (Reapproved 2001).

1. Scope

- 1.1 This test method pertains to the determination of total chlorine content in a coal sample.
- 1.2 The values stated in SI units are regarded as the standard. The values shown in parentheses are for information only.
- 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.* For specific hazard statements, see Note 2 and Section 8.

2. Referenced Documents

- 2.1 *ASTM Standards:*
- D 121 Terminology of Coal and Coke²
 - D 1193 Specification for Reagent Water³
 - D 2013 Test Method of Preparing Coal Samples for Analysis²
 - D 3180 Practice for Calculating Coal and Coke Analyses from As- Determined to Different Bases²
 - E 144 Practice for Safe Use of Oxygen Combustion Bombs⁴
 - E 832 Specification for Laboratory Filter Paper⁴

3. Terminology

- 3.1 For definitions of terms used in this test method, refer to Terminology D 121.

4. Summary of Test Method

- 4.1 The specimen is oxidized by combustion and the contained chlorine is absorbed in alkaline reagents using one of the following two procedures:
 - 4.1.1 A weighed specimen is burned in a combustion bomb containing oxygen under pressure and a small amount of ammonium carbonate solution.
 - 4.1.2 A weighed specimen is mixed with Eschka mixture and heated at a specified temperature in an oxidizing atmosphere.
- 4.2 The chlorides contained in the ammonium carbonate solution noted in 4.1.1 or extracted from the incinerated Eschka mixture noted in 4.1.2 are determined by potentiometric titration.

5. Significance and Use

- 5.1 The purpose of this test method is to measure the total chlorine content of coal. The chlorine content of coals may be useful in the evaluation of slagging problems, corrosion in engineering processes, and in the total analysis of coal and coke. When coal specimens are combusted in accordance with this test method, the chlorine is quantitatively retained and is representative of the total chlorine content of the whole coal.

6. Apparatus

- 6.1 *Balance*, analytical, with a sensitivity of 0.1 mg.
- 6.2 *Apparatus for Bomb Combustion of the Specimen:*

² *Annual Book of ASTM Standards*, Vol 05.05.

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ *Annual Book of ASTM Standards*, Vol 14.02.

6.2.1 *Combustion Bomb*, constructed of materials that are not affected by the combustion process or products. The bomb shall be designed so that all liquid combustion products can be completely recovered by washing the inner surfaces. There shall be no gas leakage during a test. The bomb shall be capable of withstanding a hydrostatic pressure test of 20 MPa (300 psig) at room temperature without stressing any part beyond its elastic limit.

6.2.2 *Combustion Crucible*—An open crucible of platinum, quartz, or acceptable base-metal alloy. Base-metal alloy crucibles are acceptable, if after a few preliminary firings, the weight does not change significantly between tests.

NOTE 1—Stable crucible weight may be obtained by heat treating base-metal crucibles in a muffle furnace for 4 h at a temperature of 500°C.

6.2.3 *Ignition Wire*, nickel-chromium (Chromel C) alloy or iron, 100 mm length, 0.16-mm diameter (No. 34 B&S gage). Platinum or palladium wire, 0.10-mm diameter (No. 38 B&S gage), may be used.

6.2.4 *Ignition Circuit*, for ignition purposes, capable of providing 6 to 16-V ac or dc to the ignition wire. The ignition circuit shall be controlled with a momentary switch to avoid electrical shock to the operator. An ammeter or pilot light is required in the circuit to indicate when current is flowing. A step-down transformer, connected to an ac lighting circuit or batteries, may be used.

6.2.5 *Water Bath*—A container large enough to hold the combustion bomb with enough cooling water to cover the bomb and dissipate the heat generated during the combustion process. The container shall be designed to allow a constant flow of water around the combustion bomb.

6.3 *Apparatus for Eschka Combustion of Specimen:*

6.3.1 *Crucibles*, porcelain, 30-mL capacity, high or low-form, or platinum or silica crucibles of similar size, for igniting the specimen with the Eschka mixture.

6.3.2 *Muffle Furnace*, electrically heated, capable of maintaining a uniform hot zone at $675 \pm 25^\circ\text{C}$, and with good circulation of air.

6.4 *Apparatus for Potentiometric Titration:*

6.4.1 *Potentiometric Titration Assembly*, using silver and silver-silver chloride electrodes.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals conforming to the specifications of the Committee on Analytical Reagents of the American Chemical Society shall be used in all tests.⁵

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

NOTE 2—**Warning:** Some reagents used in this test method are hazardous. Follow the precautions listed in the Material Safety Data Sheet of the manufacturer for each reagent.

7.3 *Ammonium Carbonate Solution*—Dissolve 10 g of ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$) in 100 mL of water. Use only a freshly prepared solution.

7.4 *Eschka Mixture*—Thoroughly mix two parts by weight of light calcined magnesium oxide (MgO) with one part of anhydrous sodium carbonate (Na_2CO_3).⁶ The Eschka mixture shall be as free as possible from chlorides.

7.5 *Nitric Acid (1 + 1)*—Mix equal volumes of concentrated nitric acid (HNO_3 , sp gr 1.42) and water.

7.6 *Oxygen*—The oxygen used for combustion shall be free of combustible matter. Oxygen manufactured from liquid air, guaranteed to be greater than 99.5 % pure, will meet this requirement.

7.7 *Silver Nitrate, Standard Solution*, (0.025 N)—Heat crushed crystalline silver nitrate (AgNO_3) at 125°C for 2 to 3 h. Dissolve 4.247 g of the dried AgNO_3 in water and dilute to 1 L. Store in an amber glass bottle.

8. Hazards

8.1 **Precaution**—The following precautions are recommended for safe operations in the use of the oxygen combustion bomb. Additional precautions are given in Recommended Practice E 144, for use of oxygen combustion bombs.

8.1.1 The weight of the coal specimen and the pressure of the oxygen admitted to the bomb must not exceed the bomb manufacturer's recommendation.

8.1.2 Inspect the bomb parts carefully after each use. Frequently check the threads on the main closure for wear. Replace the cracked or significantly worn parts. Return the bomb to the manufacturer occasionally for inspection and proof testing.

8.1.3 The oxygen supply cylinder should be equipped with an approved type of safety device, such as reducing valve, in addition to the needle valve and pressure gage used in regulating the oxygen feed to the bomb. Valves, gages, and gaskets shall meet industry safety code.⁷ Check the pressure gage periodically for accuracy.

8.1.4 During ignition of a specimen, the operator shall not permit any portion of his body to extend over the combustion bomb or its container.

⁵ *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

⁶ Eschka mixture is also available commercially.

⁷ Suitable reducing valves and adaptors for 3 to 5-MPa (300 to 500-psi) discharge pressure are available from commercial sources for compressed gas equipment.

8.1.5 Exercise extreme caution when combustion aids are employed so as not to exceed the bomb manufacturer's recommendations and to avoid damage to the bomb.

8.1.6 Admit oxygen slowly into the bomb to avoid blowing powdered material from the crucible.

8.1.7 Do not fire the bomb if it has been filled to greater than 3-MPa (30 atm) pressure with oxygen, if the bomb has been dropped or turned over after loading, or if there is evidence of a gas leak when the bomb is submerged in the water bath.

9. Sample

9.1 The sample shall be the material pulverized to pass a 250- μm (No. 60) sieve in accordance with Method D 2013.

10. Procedure

10.1 *Procedure for Bomb Combustion Method:*

10.1.1 Thoroughly mix the analysis sample of coal. Carefully weigh approximately $1 \text{ g} \pm 0.1 \text{ mg}$ into a previously ignited crucible in which it is to be combusted.

10.1.2 Transfer 5 mL of ammonium carbonate solution into the combustion bomb. Attach the fuse wire to the bomb electrodes. Place the crucible with the specimen into the electrode support of the bomb, and insert the fuse wire so that it just touches the surface of the specimen.

10.1.3 Assemble the bomb in the normal manner and charge it with oxygen to a pressure between 2.5 to 3 MPa (25 to 30 atm). Admit oxygen slowly to avoid blowing coal from the crucible. If the oxygen should exceed the specified pressure, do not proceed with the combustion. In this case, detach the filling connection, exhaust the bomb in the usual manner, and discard the specimen.

NOTE 3—**Precaution:** See Section 8.

10.1.4 Place the bomb in a cooling water bath with water flowing around the bomb. Attach the ignition wires from the firing circuit, and ignite the specimen by pushing the momentary switch on the firing circuit. Allow the bomb to remain in the cooling water for 15 min to allow cooling and absorption of soluble vapors within the bomb.

10.1.5 Remove the bomb and release the pressure at a uniform rate, such that the operation will require not less than 2 min. Examine the bomb interior and discard the test if unburned or sooty deposits are found.

10.1.6 Thoroughly rinse the bomb, electrodes, and crucible into a beaker with a fine jet of hot water. Take special care not to lose any washing water.

10.1.7 Acidify the bomb washings in the beaker with 3 mL of concentrated HNO_3 (sp gr 1.42). The clear solution usually obtained can be used directly for titration. If the ash or ferric oxide content is high enough to mask the end point of the titration, filtering is required. Then proceed as directed in 10.4.

10.2 *Eschka Method:*

10.2.1 *Preparation of Specimen*—Thoroughly mix the analysis sample in the sample bottle, weigh approximately $1 \text{ g} \pm 0.1 \text{ mg}$ of the air-dried coal sample, and mix intimately with 3 g of Eschka mixture in the 30-mL crucible. Cover the coal mixture in the crucible with a uniform layer of 2 g of Eschka mixture.

10.2.2 *Combustion*—Place the crucible in a cold muffle furnace and gradually raise the temperature to $675 \pm 25^\circ\text{C}$ within about 1 h. Maintain this maximum temperature for $1\frac{1}{2}$ h, then withdraw the crucible. Stir with a platinum or steel wire and examine to see whether any unburned coal remains. If any is found, return the crucible to the furnace for an additional $\frac{1}{2}$ h, or until no unburned coal remains.

10.2.3 *Preparation of the Chloride Solution*—Transfer the incinerated mixture quantitatively to a beaker. Add a small quantity of hot water, then cautiously add 40 mL of $\text{HNO}_3(1 + 1)$. Cover the beaker with a watchglass, swirling and stirring the contents occasionally to expedite solution. Filter the solution through a rapid-filtering, hardened, and acid-washed filter paper conforming to the requirements Class D of Specification E 832. If a low-ash coal is being tested, it may not be necessary to filter. To determine the chlorine, proceed as directed in 10.4.

10.3 *Blank Determination*—Prepare a solution for blank determination containing all the reagents used in the determination, and in the same quantities. If the Eschka method were used, carry out the blank determination under the same conditions, but omitting the coal. Use the same method of chlorine determination as used in the analysis.

10.4 *Potentiometric Titration of the Chloride*—Titrate with 0.025 N AgNO_3 solution, using silver and silver-silver chloride electrodes and determine the end point with the potentiometer.

11. Calculation

11.1 If potentiometric titration (10.4) is used, calculate the percent chlorine present, D , as follows:

$$D = 0.0886(A - B)/C \quad (1)$$

where:

A = AgNO_3 required for titration of the specimen, mL,

B = AgNO_3 required for titration of the blank, mL, and

C = specimen weight, g.

12. Precision and Bias

12.1 *Precision:* The precision of this test method for the determination of Chlorine in coal, are shown in Table 1.

TABLE 1 Concentrations Range and Limits for Repeatability and Reproducibility for Chlorine in Coal

Repeatability Limit <i>r</i>	Reproducibility Limit <i>R</i>
0.03%	0.06%

12.1.1 *Repeatability Limit (r)*—~~The value below which the absolute difference between two test results calculated to a dry basis (Practice D3180) of separate and consecutive test determinations, carried out at different times on the same sample, in the same laboratory, by the same operator, with using the same apparatus; on representative portions samples taken at random from the same 250- μ m (No. 60) sample shall not differ by more than 0.03 % chlorine. a single quantity of homogeneous material, may be expected to occur with a probability of approximately 95%.~~

12.1.2 *Reproducibility Limit (R)*—~~The m value below which the absolute difference between two test results of duplicate determinations calculated to a dry basis (Practice D 3180) carried out in each of two different laboratories on representative portions using samples taken from the same sample after the last stage at random from, a single quantity of the reduction process shall not differ by more than 0.06 % chlorine. material that is as homogeneous as possible, may be expected to occur with a proability of approximately 95%.~~

12.2 *Bias*—No statement regarding the bias of this test method is made due to the unavailability of a standard coal sample of known chlorine concentration.

13. Keywords

13.1 chlorine content; coal; coal products; combustion bomb method

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