Designation: D4208 – 13

Standard Test Method for Total Chlorine in Coal by the Oxygen Bomb Combustion/Ion Selective Electrode Method[1]

This standard is issued under the fixed designation D4208; 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 covers the analysis of total chlorine in coal.

1.2 *Units*—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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D121 Terminology of Coal and Coke
D1193 Specification for Reagent Water
D3173 Test Method for Moisture in the Analysis Sample of Coal and Coke
D3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases
E144 Practice for Safe Use of Oxygen Combustion Bombs
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology D121.

4. Summary of Test Method

4.1 Total chlorine is determined in this method by combusting a weighed sample in an oxygen bomb with dilute base adsorbing the chlorine vapors. The bomb is rinsed into a beaker with water and following the addition of an ionic strength adjuster, the chloride is determined by ion-selective electrode.

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 samples are combusted in accordance with this method, the chlorine is quantitatively retained and is representative of the total chlorine content of the whole coal.

6. Apparatus

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

6.2 *Water Bath*—A container large enough to hold the combustion bomb and enough cooling water to 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 *Combustion Crucibles*—Samples shall be burned in an open crucible of platinum, quartz, or acceptable base-metal alloy.

6.4 *Firing Wire,* 100-mm, nickel-chromium alloy, No. 34B & S gage, or platinum, No. 34 or No. 38B & S gage.

6.5 *Firing Circuit*—A 6 to 16-V alternating or direct current is required for ignition purposes with an ammeter or pilot light in the circuit to indicate when current is flowing. A step-down transformer connected to an alternating-current lighting circuit or batteries can be used. (**Warning—**The ignition circuit switch shall be of the momentary double-contact type, normally open, except when held closed by the operator. The switch should be depressed only long enough to fire the charge.)

6.6 *Balance,* analytical, with a sensitivity of 0.1 mg.

[1] This test method is under the jurisdiction of ASTM Committee D05 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

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[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.

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

6.7 *Specific-Ion Meter*—A pH meter with an expandable millivolt scale, specific-ion meter, sensitive to 0.1 mV, suitable for method of standard addition determinations.[3]

6.8 *Electrodes,* chloride-sensing, with the appropriate reference-type electrode as recommended by the manufacturer.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. 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.

7.2 *Purity of Water,* deionized, high-purity, low-specific conductivity, Type II reagent water as defined in Specification D1193.

7.3 *Ionic Strength Adjuster Solution* (5*M* $NaNO_3$)—Dissolve 42.5 g of sodium nitrate in 100 mL water.

7.4 *Sodium Carbonate Solution*(Na_2CO_3) (2 %)—Dissolve 2.0 g of sodium carbonate in 100 mL water.

7.5 *Chloride, Standard Stock Solution* (1000 µg/mL)—Dissolve 1.6486 g of sodium chloride (NaCl) in water and dilute to 1 L. The NaCl should be dried for 1 h at 105°C and cooled to room temperature in a desiccator before weighing.

7.6 *Chloride, Standard Stock Solution* (100 µg/mL)—Dilute 10.0 mL of chloride stock solution to 100 mL in a volumetric flask with water.

7.7 *Oxygen,* free of combustible matter and guaranteed to be 99.99 % pure.

8. Sample

8.1 A convenient sample is the air-dried coal that must be pulverized to pass a No. 60 (250-µm) sieve.

8.2 A separate portion of the analysis sample shall be analyzed simultaneously for moisture content in accordance with Test Method D3173 if calculation to other than the as-determined basis is desired.

9. Procedure for Bomb Combustion

9.1 Thoroughly mix the analysis sample of coal. Carefully weigh approximately 1g ± 0.1 mg into a previously ignited crucible in which it is to be combusted.

9.1.1 For samples in excess of 5 % sulfur, the mass of coal must be reduced to 0.5 ± 0.1 g to ensure that all the acidic vapors produced in the combustion process are quantitatively retained in solution.

9.2 Transfer 5 mL of 2 % Na_2CO_3 solution into the combustion bomb. Attach the fuse wire to the bomb electrodes. Place the crucible with the sample into the electrode support of the bomb, and insert the fuse wire so that it just touches the surface of the sample.

9.3 Assemble the bomb in the normal manner and charge it with oxygen to a pressure between 2.0 to 3.0 MPa. 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 sample. (**Warning—**The following precautions are recommended for safe operations in the use of the oxygen combustion bomb. Additional precautions are given in Recommended Practice E144, for use of oxygen combustion bombs.)

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

9.3.2 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 possibly proof testing.

9.3.3 The oxygen supply cylinder should be equipped with an approved type of safety device, such as a reducing valve, in addition to the needle valve and pressure gage used in regulating the oxygen feed to the bomb. Valves, gages, and gaskets must meet industry safety code. Suitable reducing valves and adaptors for approximately 3.0 to 5.0-MPa discharge pressure are obtainable from commercial sources of compressed-gas equipment. Check the pressure gage periodically for accuracy.

9.3.4 During ignition of a sample, the operator must not permit any portion of his body to extend over the combustion bomb or its container.

9.3.5 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.

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

9.3.7 Do not fire the bomb if it has been filled to greater 3.0 MPa 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.

9.4 Place the bomb in a cooling water bath, with water moving. Attach the ignition wires from the firing circuits, and ignite the sample. Allow the bomb to remain in the cooling water for 15 min to allow cooling and absorption of soluble vapors within the bomb.

9.5 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.

9.6 Thoroughly rinse the bomb, electrodes, and crucible into a 100-mL graduated cylinder with several small washings of water, keeping the volume below 90 mL.

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[3] Midgley, D., and Torrance, K., *Potentiometric Water Analysis,* John Wiley and Sons, 1978.

[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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

10. Procedure for Ion-Selective Electrode Analysis

10.1 Add 2 mL of the ionic-strength adjustor and adjust the volume to 100 mL with water and transfer to a 250-mL beaker.

10.2 Determine the potential of the solution with a chlorine ion-selective electrode. Add 10.0 mL of the chloride standard solution to the beaker with constant stirring and again determine the potential.

10.2.1 For maximum electrode response, all solutions should be measured at ambient temperatures. Electrode response may also be affected if the membrane is dirty or etched. It is recommended that the electrode membrane be repolished before each use.

11. Calculation

11.1 Determine the chlorine content of the solution from the change in potential (ΔE) resulting from the addition of the (chloride) standard solution. Calculate the concentration of chlorine in ppm (µg/g) in the analysis sample as follows:
Chlorine, ppm in solution

$$= \frac{V_a C_a}{V_s\left[\left(\text{antilog}\left[\frac{\Delta E}{S}\right]\right)\left(\frac{V_a}{V_s}+1\right)-1\right]} - C_B \quad (1)$$

$$\text{Chlorine, ppm in sample} = \frac{(\text{chlorine in solution})\ V_s}{W_s} \quad (2)$$

where:

V_a = volume of added standard, mL,
C_a = standard concentration, µg/g,
C_B = blank concentration, µg/g,
W_s = mass of sample, g,
V_s = volume of sample, mL,
ΔE = potential change, mV, and
S = electrode slope constant.

NOTE 1—Microprocessor pH/mV meters (ion meters) perform the necessary calculations and display the ion concentration directly.

11.1.1 Determine a reagent blank concurrently with the test determination using the same amounts of all reagents and following all steps of the procedure.

11.1.2 The electrode slope constant (S) may be determined as follows:

11.1.2.1 Add by pipet, 100 mL of standard solution of concentration C_1 to a 250-mL beaker.

11.1.2.2 Add 2 mL of the ionic strength adjustor.

11.1.2.3 Stir the solution and when the electrodes give a steady reading, note the reading, E_1.

11.1.2.4 Repeat step 11.1.2.1 with a second solution of concentration, C_2. Preferably $C_2 = 10\ C_1$ and should not be less than $2\ C_1$.

11.1.2.5 Repeat steps 11.1.2.2 and 11.1.2.3, noting the steady reading, E_2.

11.1.2.6 Calculate the slope constant S, which should be about −58 mV per tenfold increase in concentration at 20°C.

$$S = \frac{E_1 - E_2}{\log C_1 - \log C_2} \quad (3)$$

12. Report

12.1 The results of the chlorine analysis may be reported on any of a number of basis, differing from each other in the manner by which moisture is treated.

12.2 Use the percent moisture, in accordance with Test Method D3173, in the analysis sample passing a No. 60 (250-µm) sieve (see 8.2), to calculate the results of the analysis to a dry basis.

12.3 Procedures for converting the value obtained on the analysis sample to other bases are described in Practice D3180.

13. Precision and Bias[5]

13.1 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

Concentration Range, µg/g	Repeatability Limit, r	Reproducibility Limit, R
220 to 2100	$48.4+0.13\bar{X}$	$200+0.23\bar{X}$

13.1.1 *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 on the same sample, in the same laboratory, by the same operator, using the same apparatus on samples taken at random from a single quantity of homogeneous material, may be expected to occur with a probability of approximately 95 %.

13.1.2 *Reproducibility Limit (R)*—The value below which the absolute difference between two test results calculated to a dry basis (Practice D3180), carried out in different laboratories, using samples taken at random from a single quantity of material that is as homogeneous as possible, may be expected to occur with a probability of approximately 95 %.

13.2 *Bias*—Bias for this method has not been determined.

[5] An interlaboratory study, designed consistent with Practice E691, was conducted in 1989. Six laboratories participated in this study. Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D05-1005.

ANNEX

A1. PRECISION STATISTICS

A1.1 The precision of this test method, characterized by repeatability (S_r, r) and reproducibility (S_R, R), has been determined from results compiled from six laboratories for seven samples spanning the analyte concentration range listed in Table A1.1. Each laboratory provided four individual test results for each sample.

A1.2 *Repeatability Standard Deviation (S_r)* – The standard deviation of test results obtained under repeatability conditions. $r = 2.8 * S_r$

A1.3 *Reproducibility Standard Deviation (S_R)* – The standard deviation of test results obtained under reproducibility conditions. $R = 2.8 * S_R$

TABLE A1.1 Repeatability (S_r, r) and Reproducibility (S_R, R) Parameters Used for Calculation of the Precision Statement

Sample	Average	S_r	S_R	r	R
1	226.7	42.5	88.2	119.0	247.0
2	291.3	24.3	90.4	68.0	253.1
6	488.4	44.1	88.6	123.5	248.1
5	709.6	42.7	99.4	119.6	278.3
7	1021.5	37.2	180.5	104.2	505.4
3	1588.0	106.8	268.0	299.0	750.4
4	2154.0	111.8	182.1	313.0	509.9

SUMMARY OF CHANGES

Committee D05 has identified the location of selected changes to this standard since the last issue (D4208 – 02(2007)) that may impact the use of this standard.

(1) 1.2 *Units*, was added.
(2) Section 3*Terminology*, was added.
(3) Previous Notes 1, 2, 4, and 5 were incorporated into the main text of the test method. All other notes were renumbered.
(4) Footnote [5] was revised.
(5) Annex A1 was added.