Designation: D 6721 – 01

Standard Test Method for Determination of Chlorine in Coal by Oxidative Hydrolysis Microcoulometry[1]

This standard is issued under the fixed designation D 6721; 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 determination of total chlorine in coal.

2. Referenced Documents

2.1 *ASTM Standards:*

D 2013 Method of Preparing Coal Samples for Analysis[2]

D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke[2]

D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases[2]

D 4621 Guide for Accountability and Quality Control in the Coal Analysis Laboratory[2]

D 5142 Test Methods for Proximate Analysis of the Analysis Samples of Coal and Coke by Instrumental Procedures[2]

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[3]

2.2 *Other Standards*

ISO 5725-6:1994 Accuracy of measurement methods and results-Part 6: Use in practice of accuracy values[4]

3. Summary of Test Method

3.1 A 5.00 to 40.00 mg sample of coal is combusted with tungsten accelerator in a humidified oxygen gas flow, at 900°C. Halogens are oxidized and converted to hydrogenated halides, which are flushed into a titration cell where they accumulate. Chlorine is converted to hydrochloric acid. Once the chloride is captured in the electrolyte of the titration cell, it can be quantitatively determined by microcoulometery, where chloride ions react with silver ions present in the electrolyte. The silver ion thus consumed is coulometrically replaced and the total electrical work needed to replace it is proportional to the chloride in the test sample.

4. Significance and Use

4.1 This test method permits measurements of the chlorine content of coals.

5. Interferences

5.1 Bromides and iodides, if present are calculated as chloride. However, fluorides are not detected by this test method.

6. Apparatus

6.1 *Hydrolysis Furnace*, which can maintain a minimum temperature of 900°C.

6.2 *Hydrolysis Tube*, made of quartz and constructed such that when the sample is combusted in the presence of tungsten accelerator and humidified oxygen, the byproducts of combustion are swept into a humidified hydrolysis zone. The inlet end shall allow for the introduction and advancement of the sample boat into the heated zone. The inlet shall have a side arm for the introduction of the humidified oxygen gas. The hydrolysis tube must be of ample volume, and have a heated zone with quartz wool so that complete hydrolysis of the halogens is ensured.

6.3 *Titration Cell*, containing a reference electrode, a working electrode, and a silver sensor electrode, a magnetic stirrer as well as an inlet from the hydrolysis tube.

6.4 *Microcoulometer*, capable of measuring the potential of the sensing-reference electrode pair, comparing this potential with a bias potential, and amplifying the difference to the working electrode pair to generate current. The microcoulometer output voltage should be proportional to the generating current.

6.5 *Controller*, with connections for the reference, working, and sensor electrodes, for setting operating parameters and for data integration.

6.6 *Hydration Tube*, containing water, positioned before the gas inlet on the side arm of the combustion tube, through which oxygen gas bubbles to provide a hydrated gas flow.

6.7 *Dehydration Tube*, positioned at the end of the hydrolysis tube so that effluent gases are bubbled through a 95 % sulfuric acid solution. Water vapor is subsequently trapped while other gases flow into the titration cell.

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[1] This test method is under the jurisdiction of ASTM Committee D05 on Coal and Coke and is the direct responsibility of Subcommittee D05.29 on Major Elements in Ash and Trace Elements of Coal.

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[2] *Annual Book of ASTM Standards*, Vol 05.06.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] Available from International Organization for Standardization 1 Rue de Varembé, Case Postale 56, CH-1211, Geneva 20, Switzerland

6.8 *Gas-Tight Sampling Syringe*, having a 50 µL capacity, capable of accurately delivering 10 to 40 µL of standard solution.

6.9 *Sample Boats*, made of quartz, ceramic or platinum.

6.10 *Balance*, analytical, with a sensitivity to 0.00001 g.

7. Reagents and Materials

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 specification of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

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

7.3 *Acetic Acid (sp gr. 1.05)*, glacial acetic acid (CH_3COOH).

7.4 *Argon or Helium*, carrier gas, minimum 99.9 % purity.

7.5 *Sodium Acetate*, anhydrous, ($NaCH_3CO_2$), fine granular.

7.6 *Cell Electrolyte Solution*—Dissolve 1.35 g sodium acetate ($NaCH_3CO_2$) in 100 mL water. Add to 850 mL of acetic acid (CH_3COOH) and dilute to 1000 mL with water.

7.7 *Tungsten Powder*, combustion accelerator, (-100 mesh) minimum 99.9 % purity.

7.8 *Oxygen*, combustion gas minimum 99.6 % purity.

7.9 *Gas Regulators*—Use two-stage gas regulators for the carrier and combustion gases.

7.10 *Potassium Nitrate (KNO_3)*, fine granular.

7.11 *Potassium Chloride (KCl)*, fine granular.

7.12 *Working Electrode Solution (10 % KNO_3)*, Dissolve 50 g potassium nitrate (KNO_3) in 500 mL of water.

7.13 *Inner Chamber Reference Electrode Solution (1 M KCl)*—Dissolve 7.46 g potassium chloride (KCl) in 100 mL of water.

7.14 *Outer Chamber Reference Electrode Solution (1 M KNO_3)*—Dissolve 10.1 g potassium nitrate (KNO_3) in 100 mL of water.

7.15 *Sodium Chloride (NaCl)*, fine granular.

7.16 *Sulfuric Acid (sp gr. 1.84), (H_2SO_4)*, concentrated.

7.17 *2,4,6-Trichlorophenol (TCP) ($C_6H_3OCl_3$)*, fine granular.

7.18 *Methanol (MeOH) (CH_3OH)*, 99.9 % minimum purity.

7.19 *Working Chlorine Standard (1µg/µL)*—Weigh accurately 0.1856 g of 2,4,6-Trichlorophenol to the nearest 0.1 mg. Transfer to a 100 mL volumetric flask. Dilute to the mark with methanol.

$$WS_{CI} = (\text{g of } TCP \times 0.5386 \times 1000/100) \qquad (1)$$

where:

TCP = 2,4,6-Trichlorophenol, and

WS_{CI} = the working chlorine standard concentration.

8. Hazards

8.1 Consult the current version of OSHA regulations, supplier's Material Safety Data Sheets, and local regulations for all materials used in this test method.

9. Sampling

9.1 Prepare the analysis sample in accordance with Method D 2013 to pass a 250-µm (60 mesh) sieve.

9.2 Analyze a separate portion of the analysis sample for moisture content in accordance with Test Method D 3173 or Test Methods D 5142.

10. Preparation of Apparatus

10.1 Fill the hydration tower with water and connect it to the quartz furnace tube inlet.

10.2 Set the furnace temperature to 900°C.

10.3 Adjust the gas flows according to manufacturers specification, typically 200 mL/min for oxygen and 100 mL/min for the carrier gas.

10.4 Prepare the sulfuric acid dehydration scrubber, and connect it to the outlet of the quartz furnace combustion tube.

10.5 Clean and prepare the electrode system for the titration cell per instrument specifications.

10.6 Fill the titration cell with fresh electrolyte solution to just above the top fill mark.

10.7 Place the titration cell on the magnetic stirring device and connect the electrode system to the controller. Do not connect the gas flow from the dehydration scrubber to the titration cell.

10.8 Initiate a conditioning run of the titration cell to establish titration gain and endpoint values.

10.9 Once the titration cell is properly conditioned, connect the gas flow from the dehydration scrubber to the titration cell.

10.10 Let the titration cell stabilize to a background potential of less then 1.0 mv.

10.11 To ensure quality data, care must be taken to avoid contaminating the sample boats during the course of the analytical procedure. Do not touch the boats with fingers. Handle and transfer the boats using tongs and store said boats in a sealed container such as a glass desiccator, containing no desiccant. Prepare the combustion boats by heating them in the combustion tube with oxygen flow for a minimum of five min.

11. Recovery Factor

11.1 Confirm the instrument carrier gas and time delay settings. Typical delays for solvent injections are 2.0 min for carrier gas and 2.5 min to titration start.

11.2 Inject 10 µL of chlorine standard solution through the injection port into a prepared combustion boat. Advance the combustion boat slowly into the heated zone of the furnace. Record the recovered µg Chlorine as RC.

11.3 Repeat this recovery measurement a minimum of three times.

11.4 Calculate the Recover Factor (RF) for each measurement according to Eq 2.

$$RF = \frac{(WS_{Cl} \times 10)}{RC} \qquad (2)$$

where:

RF = the recover factor,

WS_{Cl} = the working chlorine standard concentration, and

RC = the recovered chlorine value.

11.5 Calculate the average recovery factor.

11.6 If the average recovery factor is from 0.95 to 1.05, the recovery factor shall be assumed to be 1.0 and the instrument can be used for sample analysis.

11.7 If the average recovery factor is less than 0.95 or greater than 1.05, then the instrument shall be re-calibrated by running 5 µL, 10 µL, 20 µL, 30 µL and 50 µL volumes of the Chlorine working standard, after confirming that the apparatus is in proper working condition and after setting up the apparatus in accordance with Section 10 Preparation of Apparatus (Note 1).

NOTE 1—A low recovery factor is usually indicative of leaks in the combustion system or improper packing of the combustion tube. High recovery factors are generally indicative of contamination.

12. Blank Determination

12.1 Carry out a conditioning run with 100 mg ± 10 mg of tungsten powder. Note the value of chlorine recovered but do not use this value in any blank calculations.

12.2 Weigh 100 mg ± 10 mg of tungsten into the prepared combustion boat and record the µg of chlorine in 100 mg tungsten.

12.3 Repeat the blank measurement until three successive measurements of less than 0.1 µg of chlorine are obtained.

12.4 Calculate the average blank value from the three measurements less than 0.1 µg chlorine and record as B.

13. Procedure

13.1 Follow the manufacturers instructions to program the carrier gas to switch to oxygen immediately after the sample boat is completely inside the combustion furnace. Delay the start of the titration for a time sufficient to collect the byproducts of the sample combustion in the titration cell, typically 2.0 min.

13.2 Weigh approximately 10 mg of sample into a prepared combustion boat. Record the weight to the nearest 0.01 mg as W. The recommended sample sizes for coals with higher and lower chlorine respectively are outlined in the following table.

Chlorine Range, mg/kg	Sample Size, mg
20.0 to 100	40
100 to 300	20
>300	10

13.3 Cover the specimen with approximately 100 mg of tungsten powder accelerator.

13.4 Proceed with the combustion titration analysis by first starting the controller count down and then advancing the sample boat directly into the combustion furnace hot zone. Record the measured Chlorine value as M.

14. Calculation

14.1 The as determined chlorine concentration is calculated as follows:

$$\text{Chlorine, mg/kg} = (1000 \times (M - B)/W) \qquad (3)$$

where:

M = measured chloride value, µg,
B = blank chloride value, µg, and
W = weight of sample, mg.

15. Report

15.1 The results of the chlorine analysis can be reported to other bases, differing from each other in the manner by which moisture is treated.

15.2 Use the percent moisture, as determined by Test Method D 3173 or Test Method D 5142, in the analysis sample passing a N 60 (250 µm) sieve, to calculate the results of the analysis to a dry basis.

15.3 Procedures for converting the values obtained on the analysis sample to other bases are described in Practice D 3180.

16. Precision and Bias

16.1 The precision of this test method for the determination of Chlorine in coal, is shown in Table 1. The precision characterized by the repeatability (Sr, r) and reproducibility (SR, R) is described in Table A1.1 in Annex A1.

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

Concentration Range, ppm	Repeatability Limit r	Reproducibility Limit R
22 – 1136	$1.92 + 0.06\,\bar{x}$	$6.13 + 0.07\,\bar{x}$

16.1.1 *Repeatability Limit (r)*—The value below which the absolute difference between two test results 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 %.

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

16.2 *Bias*—NIST Standard Reference Material NIST 1630a was included in the interlaboratory study to ascertain possible bias between reference material values and those determined by this method. A comparison of the NIST values and those obtained in the interlaboratory study are given in Table 2.

NOTE 2—When possible , the analysis of several reference materials , spanning the concentration range of interest, is the most meaningful way to investigate measurement bias. When a matrix match is possible the uncertainty in sample measurements can be equatable to that observed in measurement of the Certified Reference Material (CRM). When such a match is not possible, but a CRM with a related matrix is available, the test sample uncertainty may be related to those observed when measuring the CRM. Different methods of measurement of a property may not be

TABLE 2 Comparison of Certified Values for Standard Reference Material NIST 1630a with Interlaboratory Study Values for Chlorine in Coal

Reference CRM	Method Value	CRM Value	Bias	Significant (95% Confidence Level)
NIST 1630a	1107	1139	–32	no

capable of equal repeatability. Accordingly, instances could arise where the method of measurement has greater variability than that or those used in certification of the CRM.[5]

16.3 An interlaboratory study, designed consistent with ASTM Practice E 691, was conducted in the year 2000. Six labs participated.[6]

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[5] ISO 5725-6:1994 Accuracy of measurement methods and results-Part 6: Use in practice of accuracy values, Section 4.2.3 Comparison with a reference value for one laboratory.

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: **D05 1027**.

ANNEX

(Mandatory Information)

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 for the following materials as listed in Table A1.1.

A1.2 *Repeatability Standard Deviation (S_r)*—The standard deviation of test results obtained under repeatability conditions.

A1.3 *Reproducibility Standard Deviation (S_R)*—The standard deviation of test results obtained under reproducibility conditions.

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

Material	Average	S_r	S_R	r	R
hvAb Pennsylvania	1136.38	27.22	33.11	76.23	92.71
hvBb Ohio	468.42	10.25	14.60	28.71	40.87
hvBb Colorado	25.58	2.82	2.82	7.89	7.89
subA Wyoming	93.04	2.74	4.27	7.68	11.95
ligA Texas	211.29	6.60	6.64	18.47	18.60
NIST 1630a	1107.46	25.78	29.60	72.19	82.87
NIST 2685b	530.38	12.68	16.71	35.5	46.78
CAN 44	380.54	7.16	19.79	20.04	55.41
CAN 48	356.63	5.17	10.49	14.46	29.36
CAN 50	21.92	1.79	2.99	5.00	8.36
CAN 62	131.58	3.42	7.57	9.59	21.18
hvCb Arizona	91.00	3.99	3.99	11.16	11.16