



Test Method for Sampling and Testing for Ash and Total Iron in Steel Mill Dispersions of Rolling Oils¹

This standard is issued under the fixed designation D 4042; 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.

^{ε1} NOTE—Warning notes were editorially moved into the standard text in June 2003.

1. Scope

1.1 This test method describes a procedure for sampling and testing dispersions of rolling oils in water from operating steel rolling mills for determination of ash and total iron content. Its purpose is to provide a test method such that a representative sample may be taken and phenomenon such as iron separation, fat-emulsion separation, and so forth, do not contribute to analytical error in determination of ash and total iron.

1.2 The values stated in SI units are to be regarded as the standard. The values given 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 warning statements, see Sections 6 and 7.

2. Referenced Documents

2.1 ASTM Standards:

D 482 Test Method for Ash from Petroleum Products²

D 1068 Test Methods for Iron in Water³

D 1193 Specification for Reagent Water³

D 2795 Test Method for Analysis of Coal and Coke Ash⁴

E 50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials⁵

E 832 Specification for Laboratory Filter Papers⁶

3. Summary of Test Method

3.1 Polyethylene disposable sample bags in a suitable holding device are used to collect representative samples of

nonhomogeneous dispersions of rolling mill oils in water from an operating mill coolant system.

3.2 The collected sample and disposable bag are analyzed as one for ash and total iron.

3.2.1 Ash content is determined gravimetrically by evaporating all water from the sample bag before heating the residue and bag in a muffle furnace to a constant weight (Test Method D 482).

3.2.2 Total iron content is determined by digesting the iron in the ashed sample and bag in an acidified solution. The iron in the solution is reduced with stannous chloride and titrated with standardized potassium dichromate.

3.2.3 The ash and total iron contributed by a sample bag alone are determined separately and are subtracted from the values of bag and sample to obtain the values for the sample alone.

NOTE 1—There are a number of alternative methods available for determining total iron in an ashed solution such as Test Methods D 2795 and D 1068.

4. Significance and Use

4.1 The life cycle and cleanliness of a recirculating steel mill rolling oil dispersion is affected by the amount of iron present. This iron consists mainly of iron from acid pickling residues and iron from attrition of the steel sheet or rolls during cold rolling. In sampling rolling oils for total iron it is difficult to prevent adherence of iron containing sludge to the sample container. Thus, the accuracy of a total iron determination from an aliquot sample is suspect. This practice provides a means for ensuring that all iron contained in a sample is included in the analysis.

4.2 Although less significant, the ash content is still an essential part of the procedure for obtaining a total iron analysis. Generally, the ash will be mostly iron, and in many cases, could be used as a substitute for total iron in determining when to change the dispersion.

5. Sampling

5.1 Apparatus:

¹ This practice is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.L0 on Industrial Lubricants (Joint ASTM-ASLE).

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² *Annual Book of ASTM Standards*, Vol 05.01.

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

⁴ Discontinued. See 2000 *Annual Book of ASTM Standards*, Vol 05.05.

⁵ *Annual Book of ASTM Standards*, Vol 03.05.

⁶ *Annual Book of ASTM Standards*, Vol 14.04.

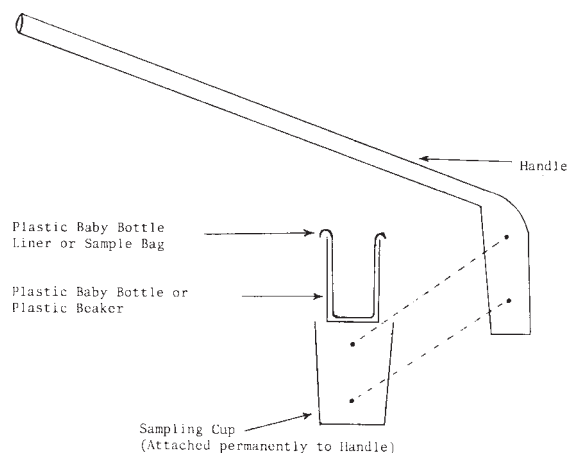


FIG. 1 Possible Holding Fixture and Assembly System

5.1.1 *Disposable Plastic (Polyethylene) Sampling Bags*⁷ 177 and 473 cm³ (6 and 16 oz) complete with closure wire.

5.1.2 *Holding Fixture.*

NOTE 2—A plastic baby bottle holder with an open 177-cm³ (6-oz) sampling bag inserted makes a suitable holder.

5.1.3 *Sampling Cup and Handle.*

NOTE 3—A hockey stick or similar formed apparatus of steel, plastic, or wood with or without a separate cup can be used to hold the holding fixture or the fixture itself can be attached to the handle (see Fig. 1).

5.2 *Sampling Procedure:*

5.2.1 Weigh a number of identified sample bags on an analytical balance to the nearest 0.1 mg. Record the weight of each as W_{B1} .

5.2.2 Using a different, preweighed, identified plastic disposable sampling bag for each sample, remove samples from the mill only while the coolant is circulating and the mill running. Take samples from the same location between the second and third stand whenever possible. Fill the bag approximately two thirds full to allow for tying of the bag.

NOTE 4—Occasionally, due to mill configuration or other reasons, it may be advisable to obtain the sample from other points in the mill system. If so, record complete details on location and time of sampling.

5.2.3 Tie and seal each sample with the wire provided in another disposable plastic sampling bag 473 cm³ (16 oz) to prevent loss of material in transit. Individual rigid plastic bottles of suitable size are also satisfactory containers for shipment and can be substituted for the outer 473-cm³ (16-oz) plastic bag.

5.2.4 Take extreme care not to soil the exterior of the sampling bag with the dispersion or any foreign material.

6. Ash Content

6.1 *Apparatus:*

6.1.1 *Borosilicate-Glass Beaker*, 400-mL, or *Evaporating Dish*, 350-mL, designed for ashing in an electric furnace. Do not use platinum crucibles because of the tendency to alloy with metallic iron.

6.1.2 *Electric Muffle Furnace*, capable of maintaining a temperature of $775 \pm 25^\circ\text{C}$ ($1427 \pm 45^\circ\text{F}$), preferably having suitable apertures at the front and rear that allow a slow natural draft of air to pass through.

6.1.3 *Oven*, capable of maintaining a temperature of $105 \pm 2^\circ\text{C}$ ($221 \pm 4^\circ\text{F}$).

6.1.4 *Analytical Balance*, 200-g capacity, accurate to 0.1 mg.

6.1.5 *Top-Loading Balance*, 600-g minimum capacity, accurate to 0.01 g.

6.2 *Procedure:*

6.2.1 Heat the empty beaker or evaporating dish at 700 to 800°C (1240 to 1470°F) for 10 min or more. Cool at room temperature in a suitable container (Note 5) and weigh on an analytical balance to the nearest 0.1 mg.

NOTE 5—The container in which the beaker or evaporating dish is cooled should not contain a desiccating agent.

6.2.2 Remove the bagged sample from its carrier container and place it, still tied, in the dish. Remove the wire and weigh the bag with sample on a top loading balance to the nearest 0.01 g. Subtract the weight of the beaker or evaporating dish and record the weight in grams as W_{S1} .

6.2.3 Place the beaker or dish, sample, and bag in an oven at 105°C (221°F) overnight or until the moisture has been evaporated from the sample.

6.2.4 Cover the beaker or evaporating dish with ashless filter paper (Note 6) to prevent loss due to spatter. Add this filter paper to the sample prior to ashing.

NOTE 6—Filter paper should conform to Specification E 832, Type II.

6.2.5 Place the beaker or evaporating dish containing the dried sample, bag, and filter paper in the muffle furnace. Carefully heat the beaker or evaporating dish and sample by progressively advancing it into the muffle furnace where it will eventually ignite.

6.2.5.1 Maintain at such a temperature that the sample continues to burn at a uniform and moderate rate, leaving only ash and carbon when burning ceases. (**Warning**—Fumes from burning polyethylene are hazardous.)

6.2.6 Heat the residue in the muffle furnace at $775 \pm 25^\circ\text{C}$ ($1427 \pm 45^\circ\text{F}$) until all carbonaceous material has disappeared.

6.2.7 Remove the dish and ashed sample from the furnace and cool in a suitable container to room temperature. Weigh on a 200-g analytical balance to the nearest 0.1 mg.

6.2.8 Reheat the dish to $775 \pm 25^\circ\text{C}$ ($1427 \pm 45^\circ\text{F}$) in the muffle furnace for 30 min, and cool to room temperature in a suitable container and reweigh, as in 6.2.6. Repeat the heating, cooling, and weighing until consecutive weighings differ by not more than 0.5 mg.

6.2.9 Subtract the weight of the evaporating dish (6.2.1) and record the final ash weight as W_{S2} .

6.2.10 Place a new, empty polyethylene bag trimmed to the weight of the original sample bag ± 0.01 g (5.2.2) in a preweighed evaporating dish (6.2.1) and reduce to ash following the procedure described by 6.2.4, 6.2.5, 6.2.6, 6.2.7, and 6.2.8.

6.2.11 Record the final ash weight in grams to the nearest 0.1 mg as W_{B2} .

⁷ Sampling bags (with wires) can be found in most common laboratory supply catalogues.

NOTE 7—In repeat tests for duplicate samples or separate samples, if all sample bags used are from the same source and are of the same size, an average weight from three or more bags can be used for W_{B1} . This avoids having to preweigh all bags as in 5.2.2. Also, the weight of the ashed empty bag W_{B2} can be used in subsequent calculations for ash determination. This avoids having to ash one sample bag for each duplicate or separate sample.

6.3 *Calculation of Percent Ash*—Calculate the weight of ash for the dispersion sample as a percentage of the original sample, as follows:

$$\text{Ash, \%} = (W_{S2} - W_{B2}) / (W_{S1} - W_{B1}) \times 100 \quad (1)$$

where:

- W_{S2} = ash from sample and bag, g,
- W_{B2} = ash from empty bag, g,
- W_{S1} = sample and bag, g, and
- W_{B1} = bag, g.

NOTE 8—Both the ash from the sample bag and the ash from the empty bag are to be used for subsequent total iron determination.

7. Iron Content

7.1 Apparatus:

7.1.1 *Analytical Balance*, 200-g capacity, accurate to 0.1 mg.

7.1.2 *Beakers*, 400-mL, borosilicate glass, Griffin form.

7.1.3 *Buret*, 50-mL with 0.1-mL graduations.

7.2 Reagents:

7.2.1 *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.⁸ 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.

7.2.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined in Specification D 1193, Type II.

7.2.3 *Hydrochloric Acid (HCL)* (36 %). (**Warning—Poison.** Causes severe burns. Harmful or fatal if swallowed or inhaled.)

7.2.4 *Iron Standard Solution* (1 mL = 0.10 mg Fe)—Make in accordance with Practices E 50, iron, standard solution, or as follows: Transfer 1.000 g of NBS Standard 55e (ingot iron) or equivalent to a 100-mL beaker (Note 9). Dilute 10 mL of HCl with 10 mL of distilled water. Add this solution to the 100-mL beaker. Cover and heat below the boiling temperature to dissolve the iron. Cool the solution and transfer quantitatively to a 1-L volumetric flask. Cool to room temperature and dilute to 1-L volume with distilled water. Mix thoroughly. One millilitre of standard iron solution = 1 mg of iron.

NOTE 9—Prior to use, all beakers and glassware must be cleaned as

follows: Add approximately $\frac{1}{4}$ the total volume of HCl to beaker or other glassware. Cover loosely and heat to boiling under a fume hood. Maintain boiling for approximately 10 min. Cool and rinse thoroughly with distilled water.

7.2.5 *Mercuric Chloride Solution (saturated)*—Add 100 g of mercuric chloride (HgCl_2) to 1000 mL of hot distilled water and mix thoroughly. Allow to stand 12 to 24 h to obtain a saturated solution at room temperature. (**Warning—Poison.** May cause skin irritation. Harmful or fatal if swallowed.)

7.2.6 *Potassium Dichromate* (0.020 N)—Transfer 1.0 g of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) to a 1-L volumetric flask. Dissolve in distilled water and dilute volume to 1 L. Allow to stand 12 to 24 h prior to standardization and use. Standardize in accordance with Annex A1. (**Warning—Causes skin irritation.**)

7.2.7 *Sodium Diphenylamine Sulfonate Indicator Solution* (2 g/L)—Dissolve 1 g of sodium diphenylamine sulfonate in 500 mL of distilled water.

7.2.8 *Stannous Chloride* (15 g/L)—Dissolve 7.5 g of stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in 150 mL of HCl (36%). When solution is complete, dilute to 500 mL with distilled water and add 5 g of tin metal. Some undissolved tin metal should be present at all times to maintain the stannous chloride in the reduced state. (**Warning—Causes skin irritation.**)

7.2.9 *Sulfuric-Phosphoric Acid Mixture* (150 mL H_2SO_4 + 150 mL H_3PO_4 + 700 mL H_2O)—Transfer 700 mL of distilled water to a 1-L borosilicate-glass beaker. Slowly add 150 mL of concentrated sulfuric acid (95%) (**Warning—Poison.** May cause skin irritation. Harmful or fatal if swallowed), stirring the solution during addition of the acid. Cool the solution to room temperature. Carefully add 150 mL of phosphoric acid (86 %) (**Warning—Causes skin irritation.** Do not get in eyes, on skin, or on clothing) and mix thoroughly.

7.3 Procedure:

7.3.1 Obtain ashed samples of (1) oil sample and polyethylene bag (6.2.7) and (2) new empty polyethylene-sample bag (6.2.9) in original evaporating dishes or beakers.

NOTE 10—If total iron analysis only is desired, (no percent ash determination) Steps 6.2.6, 6.2.7, 6.2.8, 6.2.10, and 6.3.1 may be eliminated in the ash content procedure.

7.3.2 Add 10 mL of HCl to the ashed samples (1) and (2). Cover and heat slowly below the boiling point to digest to effect the solution of all iron present.

7.3.3 Cool the samples (1) and (2) to room temperature and transfer each to individual 400-mL beakers. Rinse the original evaporating dish or beaker with HCl and add the rinse to the respective beaker.

7.3.4 Cover the beakers loosely and digest by heating near boiling for 5 min.

7.3.5 Rinse the cover and sides of the beakers with distilled water, heat to near boiling and add stannous chloride solution dropwise until the solution changes from yellow to colorless. Add one drop in excess. Cover and just bring to a boil.

7.3.6 Cool to room temperature. Rinse the cover and sides of the beakers with freshly boiled distilled water. Add 10 mL of HgCl_2 solution to each and allow to stand for 3 to 5 min.

7.3.7 To each beaker add 20 mL of sulfuric-phosphoric acid mixture. Dilute each solution to approximately 300 mL with

⁸ *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.

freshly boiled and cooled distilled water. To each solution add 10 to 15 drops of indicator solution and titrate to a violet end point, with potassium dichromate ($K_2Cr_2O_7$, 0.02 *N*).

7.3.8 Record the millilitres of potassium dichromate ($K_2Cr_2O_7$) used for titration of the ashed sample plus bag and new empty bag as K_1 and K_2 respectively.

7.4 Calculation:

7.4.1 Calculate the iron content of the dispersion sample as follows:

$$\text{Fe, ppm} = ((K_1 - K_2) \times (\text{mg Fe/mL } K_2Cr_2O_7) \times 1000) / (W_{S1} - W_{B1}) \quad (2)$$

where:

K_1 = millilitres of $K_2Cr_2O_7$ used for ashed sample and bag (7.3.8),

K_2 = millilitres of $K_2Cr_2O_7$ used for ashed empty bag (7.3.8),

$$(\text{mg Fe/mL } K_2Cr_2O_7) = \text{Iron equivalent of } K_2Cr_2O_7 \text{ (Annex A1).} \quad (3)$$

where:

W_{S1} = grams of sample and bag (6.2.2), and

W_{B1} = grams of empty bag (5.2.2 or 6.2.10, Note 7).

8. Precision and Bias

8.1 The purpose of this test method is to provide a means of sampling dispersions from operating mill systems and to test that sample for ash and iron content. The nature of operating dispersion systems precludes obtaining identical or standard samples for determination of precision and bias data.

9. Keywords

9.1 ash; iron; rolling oil; steel mill

ANNEX

(Mandatory Information)

A1. DETERMINATION OF IRON EQUIVALENT OF POTASSIUM DICHROMATE SOLUTION

A1.1 Pipet 20 mL of standard iron solution (7.2.8) into a 400-mL beaker. Add 10 mL of HCl, cover and heat below boiling for 1 to 2 min.

A1.2 Complete the standardization by following the procedures described in 7.3.5, 7.3.6, 7.3.7, and 7.3.8, using the solution described in A1.1 for one of the sample solutions.

A1.3 Calculate the iron equivalent of the potassium dichro-

mate solution ($K_2Cr_2O_7$) as follows:

$$\text{mg Fe/mL } K_2Cr_2O_7 = (A \times B) / (C) \quad (A1.1)$$

where:

A = millilitres of standard iron solution,

B = milligrams of iron per millilitre of standard iron solution, and

C = millilitres of $K_2Cr_2O_7$ solution used for titration.

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