

METHOD 5050

BOMB PREPARATION METHOD FOR SOLID WASTE

1.0 SCOPE AND APPLICATION

1.1 This method describes the sample preparation steps necessary to determine total chlorine in solid waste and virgin and used oils, fuels and related materials, including: crankcase, hydraulic, diesel, lubricating and fuel oils, and kerosene by bomb oxidation and titration or ion chromatography. Depending on the analytical finish chosen, other halogens (bromine and fluorine) and other elements (sulfur and nitrogen) may also be determined.

1.2 The applicable range of this method varies depending on the analytical finish chosen. In general, levels as low as 500 µg/g chlorine in the original oil sample can be determined. The upper range can be extended to percentage levels by dilution of the combustate.

1.3 This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems 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 safety statements are given in Section 3.0.

2.0 SUMMARY OF METHOD

2.1 The sample is oxidized by combustion in a bomb containing oxygen under pressure. The liberated halogen compounds are absorbed in a sodium carbonate/sodium bicarbonate solution. Approximately 30 to 40 minutes are required to prepare a sample by this method. Samples with a high water content (> 25%) may not combust efficiently and may require the addition of a mineral oil to facilitate combustion. Complete combustion is still not guaranteed for such samples.

2.2 The bomb combustate solution can then be analyzed for the following elements as their anion species by one or more of the following methods:

Method	Title
9252	Chloride (Titrimetric, Mercuric Nitrate)
9253	Chloride (Titrimetric, Silver Nitrate)
9056	Inorganic Anions by Ion Chromatography (Chloride, Sulfate, Nitrate, Phosphate, Fluoride, Bromide)

NOTE: Strict adherence to all of the provisions prescribed hereinafter ensures against explosive rupture of the bomb, or a blowout, provided the bomb is of proper design and construction and in good mechanical condition. It is desirable, however, that the bomb be enclosed in a shield of steel plate at least 1/2 in. (12.7 mm) thick, or equivalent protection be provided against unforeseeable contingencies.

3.0 INTERFERENCES

3.1 Samples with very high water content (> 25%) may not combust efficiently and may require the addition of a mineral oil to facilitate combustion.

3.2 To determine total nitrogen in samples, the bombs must first be purged of ambient air. Otherwise, nitrogen results will be biased high.

4.0 APPARATUS AND MATERIALS

4.1 Bomb, having a capacity of not less than 300 mL, so constructed that it will not leak during the test, and that quantitative recovery of the liquids from the bomb may be readily achieved. The inner surface of the bomb may be made of stainless steel or any other material that will not be affected by the combustion process or products. Materials used in the bomb assembly, such as the head gasket and lead-wire insulation, shall be resistant to heat and chemical action and shall not undergo any reaction that will affect the chlorine content of the sample in the bomb.

4.2 Sample cup, platinum or stainless steel, 24 mm in outside diameter at the bottom, 27 mm in outside diameter at the top, 12 mm in height outside, and weighing 10 to 11 g.

4.3 Firing wire, platinum or stainless steel, approximately No. 26 B & S gage.

4.4 Ignition circuit, capable of supplying sufficient current to ignite the nylon thread or cotton wicking without melting the wire.

NOTE: The switch in the ignition circuit shall be of the type that remains open, except when held in closed position by the operator.

4.5 Nylon sewing thread, or Cotton Wicking, white.

4.6 Funnel, to fit a 100-mL volumetric flask.

4.7 Class A volumetric flasks, 100-mL, one per sample.

4.8 Syringe, 5- or 10-mL disposable plastic or glass.

4.9 Apparatus for specific analysis methods are given in the methods.

4.10 Analytical balance: capable of weighing to 0.0001 g.

5.0 REAGENTS

5.1 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. 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.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Oxygen. Free of combustible material and halogen compounds, available at a pressure of 40 atm.

WARNING: Oxygen vigorously accelerates combustion (see Appendix A1.1)

5.4 Sodium bicarbonate/sodium carbonate solution. Dissolve 2.5200 g NaHCO_3 and 2.5440 g Na_2CO_3 in reagent water and dilute to 1 L.

5.5 White oil. Refined.

5.6 Reagents and materials for specific analysis methods are given in the methods.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2 Ensure that the portion of the sample used for the test is representative of the sample.

6.3 To minimize losses of volatile halogenated solvents that may be present in the sample, keep the field and laboratory samples as free of headspace as possible.

6.4 Because used oils may contain toxic and/or carcinogenic substances appropriate field and laboratory safety procedures should be followed.

7.0 PROCEDURE

7.1 Sample Preparation

7.1.1 Preparation of bomb and sample. Cut a piece of firing wire approximately 100 mm in length and attach the free ends to the terminals. Arrange the wire so that it will be just above and not touching the sample cup. Loop a cotton thread around the wire so that the ends will extend into the sampling cup. Pipet 10 mL of the $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ solution into the bomb, wetting the sides. Take an aliquot of the oil sample of approximately 0.5 g using a 5- or 10-mL disposable plastic syringe, and place in

the sample cup. The actual sample weight is determined by the difference between the weight of the empty and filled syringe. Do not use more than 1 g of sample.

NOTE: After repeated use of the bomb for chlorine determination, a film may be noticed on the inner surface. This dullness should be removed by periodic polishing of the bomb. A satisfactory method for doing this is to rotate the bomb in a lathe at about 300 rpm and polish the inside surface with Grit No. 2/0 or equivalent paper¹ coated with a light machine oil to prevent cutting, and then with a paste of grit-free chromic oxide² and water. This procedure will remove all but very deep pits and put a high polish on the surface. Before using the bomb, it should be washed with soap and water to remove oil or paste left from the polishing operation. Bombs with porous or pitted surfaces should never be used because of the tendency to retain chlorine from sample to sample.

NOTE: If the sample is not readily combustible, other nonvolatile, chlorine-free combustible diluents such as white oil may be employed. However, the combined weight of sample and nonvolatile diluent shall not exceed 1 g. Some solid additives are relatively insoluble but may be satisfactorily burned when covered with a layer of white oil.

NOTE: The practice of alternately running samples high and low in chlorine content should be avoided whenever possible. It is difficult to rinse the last traces of chlorine from the walls of the bomb, and the tendency for residual chlorine to carry over from sample to sample has been observed in a number of laboratories. When a sample high in chlorine has preceded one low in chlorine content, the test on the low-chlorine sample should be repeated, and one or both of the low values thus obtained should be considered suspect if they do not agree within the limits of repeatability of this method.

NOTE: Do not use more than 1 g total of sample and white oil or other chlorine-free combustible material. Use of excess amounts of these materials could cause a buildup of dangerously high pressure and possible rupture of the bomb.

7.1.2 Addition of oxygen. Place the sample cup in position and arrange the thread so that the end dips into the sample. Assemble the bomb and tighten the cover securely. Admit oxygen slowly (to avoid blowing the oil from the cup) until a pressure is reached as indicated in Table 1.

¹Emery Polishing Paper grit No. 2/0 may be purchased from the Behr-Manning Co., Troy, NY.

²Chromic oxide may be purchased from J.T. Baker & Co., Phillipsburg, NJ.

NOTE: Do not add oxygen or ignite the sample if the bomb has been jarred, dropped, or tiled.

7.1.3 Combustion. Immerse the bomb in a cold water bath. Connect the terminals to the open electrical circuit. Close the circuit to ignite the sample. Remove the bomb from the bath after immersion for at least 10 minutes. Release the pressure at a slow, uniform rate such that the operation requires at least 1 min. Open the bomb and examine the contents. If traces of unburned oil or sooty deposits are found, discard the determination, and thoroughly clean the bomb before using it again.

7.1.4 Collection of halogen solution. Using reagent water and a funnel, thoroughly rinse the interior of the bomb, the sample cup, the terminals, and the inner surface of the bomb cover into a 100-mL volumetric flask. Dilute to the mark with reagent water.

7.1.5 Cleaning procedure for bomb and sample cup. Remove any residual fuse wire from the terminals and the cup. Using hot water, rinse the interior of the bomb, the sample cup, the terminals, and the inner surface of the bomb cover. (If any residue remains, first scrub the bomb with Alconox solution). Copiously rinse the bomb, cover, and cup with reagent water.

7.2 Sample Analysis. Analyze the combustate for chlorine or other halogens using the methods listed in Step 2.2. It may be necessary to dilute the samples so that the concentration will fall within the range of standards.

7.3 Calculations. Calculate the concentrations of each element detected in the sample according to the following equation:

$$C_o = \frac{C_{com} \times V_{com} \times DF}{W_o} \quad (1)$$

where:

C_o = concentration of element in the sample, $\mu\text{g/g}$
 C_{com} = concentration of element in the combustate, $\mu\text{g/mL}$
 V_{com} = total volume of combustate, mL
DF = dilution factor
 W_o = weight of sample combusted, g.

Report the concentration of each element detected in the sample in micrograms per gram.

Example: A 0.5-g oil sample was combusted, yielding 10 mL of combustate. The combustate was diluted to 100 mL total volume and analyzed for chloride, which was measured to be 5 µg/mL. The concentration of chlorine in the original sample is then calculated as shown below:

$$C_o = \frac{5 \frac{\mu\text{g}}{\text{mL}} \times (10 \text{ mL}) \times (10)}{0.5 \text{ g}} \quad (2)$$

$$C_o = 1,000 \frac{\mu\text{g}}{\text{g}} \quad (3)$$

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 One sample in ten should be bombed twice. The results should agree to within 10%, expressed as the relative percent difference of the results.

8.3 Analyze matrix spike and matrix spike duplicates - spike samples with the elements of interest at a level commensurate with the levels being determined. The spiked compounds should be similar to those expected in the sample. Any sample suspected of containing > 25% water should also be spiked with organic chlorine.

8.4 For higher levels (e.g., percent levels), spiking may be inappropriate. For these cases, samples of known composition should be combusted. The results should agree to within 10% of the expected result.

8.5 Quality control for the analytical method(s) of choice should be followed.

9.0 PERFORMANCE

See analytical methods referenced in Step 2.2.

10.0 REFERENCES

1. ASTM Method D 808-81, Standard Test Method for Chlorine in New and Used Petroleum Products (Bomb Method). 1988 Annual Book of ASTM Standards. Volume 05.01 Petroleum Products and Lubricants.

2. Gaskill, A.; Estes, E. D.; Hardison, D. L.; and Myers, L. E. Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels. Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, WA 80. July 1988.

TABLE 1.
GAGE PRESSURES

Capacity of bomb, mL	Minimum gage pressure ^a , atm	Maximum gage pressure ^a , atm
300 to 350	38	40
350 to 400	35	37
400 to 450	30	32
450 to 500	27	29

^aThe minimum pressures are specified to provide sufficient oxygen for complete combustion, and the maximum pressures represent a safety requirement. Refer to manufacturers' specifications for appropriate gage pressure, which may be lower than those listed here.

APPENDIX

A1. PRECAUTIONARY STATEMENTS

A1.1 Oxygen

Warning--Oxygen vigorously accelerates combustion.

Keep oil and grease away. Do not use oil or grease on regulators, gages, or control equipment.

Use only with equipment conditioned for oxygen service by careful cleaning to remove oil, grease, and other combustibles.

Keep combustibles away from oxygen and eliminate ignition sources.

Keep surfaces clean to prevent ignition or explosion, or both, on contact with oxygen.

Always use a pressure regulator. Release regulator tension before opening cylinder valve.

All equipment and containers used must be suitable and recommended for oxygen service.

Never attempt to transfer oxygen from cylinder in which it is received to any other cylinder. Do not mix gases in cylinders.

Do not drop cylinder. Make sure cylinder is secured at all times.

Keep cylinder valve closed when not in use.

Stand away from outlet when opening cylinder valve.

For technical use only. Do not use for inhalation purposes.

Keep cylinder out of sun and away from heat.

Keep cylinders from corrosive environment.

Do not use cylinder without label.

Do not use dented or damaged cylinders.

See Compressed Gas Association booklets G-4 and G4.1 for details of safe practice in the use of oxygen.

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