

TEST METHOD FOR TOTAL CHLORINE IN NEW AND USED PETROLEUM
PRODUCTS BY OXIDATIVE COMBUSTION AND MICROCOULOMETRY

1.0 SCOPE AND APPLICATION

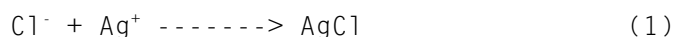
1.1 This test method covers the determination of total chlorine in new and used oils, fuels and related materials, including crankcase, hydraulic, diesel, lubricating and fuel oils, and kerosene by oxidative combustion and microcoulometry. The chlorine content of petroleum products is often required prior to their use as a fuel.

1.2 The applicable range of this method is from 10 to 10,000 µg/g chlorine.

2.0 SUMMARY OF METHOD

2.1 The sample is placed in a quartz boat at the inlet of a high-temperature quartz combustion tube. An inert carrier gas such as argon, carbon dioxide, or nitrogen sweeps across the inlet while oxygen flows into the center of the combustion tube. The boat and sample are advanced into a vaporization zone of approximately 300°C to volatilize the light ends. Then the boat is advanced to the center of the combustion tube, which is at 1,000°C. The oxygen is diverted to pass directly over the sample to oxidize any remaining refractory material. All during this complete combustion cycle, the chlorine is converted to chloride and oxychlorides, which then flow into an attached titration cell where they quantitatively react with silver ions. The silver ions thus consumed are coulometrically replaced. The total current required to replace the silver ions is a measure of the chlorine present in the injected samples.

2.2 The reaction occurring in the titration cell as chloride enters is:



The silver ion consumed in the above reaction is generated coulometrically thus:



2.3 These microequivalents of silver are equal to the number of micro-equivalents of titratable sample ion entering the titration cell.

3.0 INTERFERENCES

3.1 Other titratable halides will also give a positive response. These titratable halides include HBr and HI (HOBr + HOI do not precipitate silver). Because these oxyhalides do not react in the titration cell, approximately 50% microequivalent response is detected from bromine and iodine.

3.2 Fluorine as fluoride does not precipitate silver, so it is not an interferant nor is it detected.

3.3 This test method is applicable in the presence of total sulfur concentrations of up to 10,000 times the chlorine level.

4.0 APPARATUS AND MATERIALS¹

4.1 Combustion furnace. The sample should be oxidized in an electric furnace capable of maintaining a temperature of 1,000°C to oxidize the organic matrix.

4.2 Combustion tube, fabricated from quartz and constructed so that a sample, which is vaporized completely in the inlet section, is swept into the oxidation zone by an inert gas where it mixes with oxygen and is burned. The inlet end of the tube connects to a boat insertion device where the sample can be placed on a quartz boat by syringe, micropipet, or by being weighed externally. Two gas ports are provided, one for an inert gas to flow across the boat and one for oxygen to enter the combustion tube.

4.3 Microcoulometer, Stroehlein Coulomat 702 CL or equivalent, having variable gain and bias control, and capable of measuring the potential of the sensing-reference electrode pair, and comparing this potential with a bias potential, and applying the amplified difference to the working-auxiliary electrode pair so as to generate a titrant. The microcoulometer output signal shall be proportional to the generating current. The microcoulometer may have a digital meter and circuitry to convert this output signal directly to a mass of chlorine (e.g., nanograms) or to a concentration of chlorine (e.g., micrograms of chlorine or micrograms per gram).

4.4 Titration cell. Two different configurations have been applied to coulometrically titrate chlorine for this method.

4.4.1 Type I uses a sensor-reference pair of electrodes to detect changes in silver ion concentration and a generator anode-cathode pair of electrodes to maintain constant silver ion concentration and an inlet for a gaseous sample from the pyrolysis tube. The sensor, reference, and anode electrodes are silver electrodes. The cathode electrode is a platinum wire. The reference electrode resides in a saturated silver acetate half-cell. The electrolyte contains 70% acetic acid in water.

4.4.2 Type II uses a sensor-reference pair of electrodes to detect changes in silver ion concentration and a generator anode-cathode pair of electrodes to maintain constant silver ion concentration, an inlet for a gaseous sample that passes through a 95% sulfuric acid dehydrating tube from the pyrolysis tube, and a sealed two-piece titration cell with an exhaust tube to vent fumes to an external exhaust. All electrodes can be removed and replaced independently without reconstructing the cell assembly. The anode electrode is constructed of silver. The cathode

¹Any apparatus that meets the performance criteria of this section may be used to conduct analyses by this methodology. Three commercial analyzers that fulfill the requirements for apparatus Steps 4.1 through 4.4 are: Dohrmann Models DX-20B and MCTS-20 and Mitsubishi Model TSX-10 available from Cosa Instrument.

electrode is constructed of platinum. The anode is separated from the cathode by a 10% KNO_3 agar bridge, and continuity is maintained through an aqueous 10% KNO_3 salt bridge. The sensor electrode is constructed of silver. The reference electrode is a silver/silver chloride ground glass sleeve, double-junction electrode with aqueous 1M KNO_3 in the outer chamber and aqueous 1M KCl in the inner chamber.

4.5 Sampling syringe, a microliter syringe of 10 μL capacity capable of accurately delivering 2 to 5 μL of a viscous sample into the sample boat.

4.6 Micropipet, a positive displacement micropipet capable of accurately delivering 2 to 5 μL of a viscous sample into the sample boat.

4.7 Analytical balance. When used to weigh a sample of 2 to 5 mg onto the boat, the balance shall be accurate to ± 0.01 mg. When used to determine the density of the sample, typically 8 g per 10 mL, the balance shall be accurate to ± 0.1 g.

4.8 Class A volumetric flasks: 100 mL.

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 Acetic acid, $\text{CH}_3\text{CO}_2\text{H}$. Glacial.

5.4 Isooctane, $(\text{CH}_3)_2\text{CHCH}_2\text{C}(\text{CH}_3)_3$ (2,2,4-Trimethylpentane).

5.5 Chlorobenzene, $\text{C}_6\text{H}_5\text{Cl}$.

5.6 Chlorine, standard stock solution - 10,000 ng $\text{Cl}/\mu\text{L}$, weigh accurately 3.174 g of chlorobenzene into 100-mL Class A volumetric flask. Dilute to the mark with isooctane.

5.7 Chlorine, standard solution. 1,000 ng $\text{Cl}/\mu\text{L}$, pipet 10.0 mL of chlorine stock solution (Sec. 5.6) into a 100-mL volumetric flask and dilute to volume with isooctane.

5.8 Argon, helium, nitrogen, or carbon dioxide, high-purity grade (HP) used as the carrier gas. High-purity grade gas has a minimum purity of 99.995%.

5.9 Oxygen, high-purity grade (HP), used as the reactant gas.

5.10 Gas regulators. Two-stage regulator must be used on the reactant and carrier gas.

5.11 Cell Type 1.

5.11.1 Cell electrolyte solution. 70% acetic acid: combine 300 mL reagent water with 700 mL acetic acid (Sec. 5.3) and mix well.

5.11.2 Silver acetate, $\text{CH}_3\text{CO}_2\text{Ag}$. Powder purified for saturated reference electrode.

5.12 Cell Type 2.

5.12.1 Sodium acetate, $\text{CH}_3\text{CO}_2\text{Na}$.

5.12.2 Potassium nitrate, KNO_3 .

5.12.3 Potassium chloride, KCl .

5.12.4 Sulfuric acid (concentrated), H_2SO_4 .

5.12.5 Agar, (jelly strength 450 to 600 g/cm²).

5.12.6 Cell electrolyte solution - 85% acetic acid: combine 150 mL reagent water with 1.35 g sodium acetate (Sec. 5.12.1) and mix well; add 850 mL acetic acid (Sec. 5.3) and mix well.

5.12.7 Dehydrating solution - Combine 95 mL sulfuric acid (Sec. 5.12.4) with 5 mL reagent water and mix well.

CAUTION: This is an exothermic reaction and may proceed with bumping unless controlled by the addition of sulfuric acid. Slowly add sulfuric acid to reagent water. Do not add water to sulfuric acid.

5.12.8 Potassium nitrate (10%), KNO_3 . Add 10 g potassium nitrate (Sec. 5.12.2) to 100 mL reagent water and mix well.

5.12.9 Potassium nitrate (1M), KNO_3 . Add 10.11 g potassium nitrate (Sec. 5.12.2) to 100 mL reagent water and mix well.

5.12.10 Potassium chloride (1M), KCl . Add 7.46 g potassium chloride (Sec. 5.12.3) to 100 mL reagent water and mix well.

5.12.11 Agar bridge solution - Mix 0.7 g agar (Sec. 5.12.5), 2.5g potassium nitrate (Sec. 5.12.2), and 25 mL reagent water and heat to boiling.

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 Because the collected sample will be analyzed for total halogens, it should be kept headspace free and refrigerated prior to preparation and analysis

to minimize volatilization losses of organic halogens. Because waste oils may contain toxic and/or carcinogenic substances, appropriate field and laboratory safety procedures should be followed.

6.3 Laboratory subsampling of the sample should be performed on a well-mixed sample of oil.

7.0 PROCEDURES

7.1 Preparation of apparatus.

7.1.1 Set up the analyzer as per the equipment manufacturer's instructions.

7.1.2 Typical operating conditions: Type 1.

Furnace temperature.....	1,000°C
Carrier gas flow.....	43 cm ³ /min
Oxygen gas flow.....	160 cm ³ /min
Coulometer	
Bias.....	250 mV
Gain.....	25%

7.1.3 Typical operating conditions: Type 2.

Furnace temperature.....	H-1 850°C
	H-2 1,000°C
Carrier gas flow.....	250 cm ³ /min
Oxygen gas flow.....	250 cm ³ /min
Coulometer	
End point potential (bias).....	300 mV
Gain G-1.....	1.5 coulombs/) mV
G-2.....	3.0 coulombs/) mV
G-3.....	3.0 coulombs/) mV
ES-1 (range 1).....	25 mV
ES-2 (range 2).....	30 mV

NOTE: Other conditions may be appropriate. Refer to the instrumentation manual.

7.2 Sample introduction.

7.2.1 Carefully fill a 10- μ L syringe with 2 to 5 μ L of sample depending on the expected concentration of total chlorine. Inject the sample through the septum onto the cool boat, being certain to touch the boat with the needle tip to displace the last droplet.

7.2.2 For viscous samples that cannot be drawn into the syringe barrel, a positive displacement micropipet may be used. Here, the 2-5 μ L of sample is placed on the boat from the micropipet through the opened hatch port. The same technique as with the syringe is used to displace the last droplet into the boat. A tuft of quartz wool in the boat can aid in completely transferring the sample from the micropipet into the boat.

NOTE: Dilution of samples to reduce viscosity is not recommended due to uncertainty about the solubility of the sample and its chlorinated constituents. If a positive displacement micropipet is not available, dilution may be attempted to enable injection of viscous samples.

7.2.3 Alternatively, the sample boat may be removed from the instrument and tared on an analytical balance. A sample of 2-5 mg is accurately weighed directly into the boat and the boat and sample returned to the inlet of the instrument.

$$2-5 \mu\text{L} = 2-5 \text{ mg}$$

NOTE: Sample dilution may be required to ensure that the titration system is not overloaded with chlorine. This will be somewhat system dependent and should be determined before analysis is attempted. For example, the MCTS-20 can titrate up to 10,000 ng chlorine in a single injection or weighed sample, while the DX-20B has an upper limit of 50,000 ng chlorine. For 2 to 5 μL sample sizes, these correspond to nominal concentrations in the sample of 800 to 2,000 $\mu\text{g/g}$ and 4,000 to 10,000 $\mu\text{g/g}$, respectively. If the system is overloaded, especially with inorganic chloride, residual chloride may persist in the system and affect results of subsequent samples. In general, the analyst should ensure that the baseline returns to normal before running the next sample. To speed baseline recovery, the electrolyte can be drained from the cell and replaced with fresh electrolyte.

NOTE: To determine total chlorine, do not extract the sample either with reagent water or with an organic solvent such as toluene or isooctane. This may lower the inorganic chlorine content as well as result in losses of volatile solvents.

7.2.4 Follow the manufacturer's recommended procedure for moving the sample and boat into the combustion tube.

7.3 Calibration and standardization.

7.3.1 System recovery - The fraction of chlorine in a standard that is titrated should be verified every 4 hours by analyzing the standard solution (Sec. 5.7). System recovery is typically 85% or better. The pyrolysis tube should be replaced whenever system recovery drops below 75%.

NOTE: The 1,000 $\mu\text{g/g}$ system recovery sample is suitable for all systems except the MCTS-20 for which a 100 $\mu\text{g/g}$ sample should be used.

7.3.2 Repeat the measurement of this standard at least three times.

7.3.3 System blank - The blank should be checked daily with isooctane. It is typically less than 1 µg/g chlorine. The system blank should be subtracted from both samples and standards.

7.4 Calculations.

7.4.1 For systems that read directly in mass units of chloride, the following equations apply:

$$\text{Chlorine, } \mu\text{g/g (wt/wt)} = \frac{\text{Display}_s}{(V_s) (D_s) (RF)} - B \quad (3)$$

or

$$\text{Chlorine, } \mu\text{g/g (wt/wt)} = \frac{\text{Display}_s}{(M) (RF)} - B \quad (4)$$

where:

Display = Integrated value in nanograms (when the integrated values are displayed in micrograms, they must be multiplied by 10³)
 Display_B = blank measurement Display_S = sample measurement

V = Volume of sample injected in microliters
 V_B = blank volume V_S = sample volume

D = Density of sample, grams per cubic centimeters
 D_B = blank density D_S = sample density

RF = Recovery factor = ratio of chlorine determined in standard minus the system blank, divided by known standard content = $\frac{\text{Found} - \text{Blank}}{\text{Known}}$

B = System blank, µg/g chlorine = $\frac{\text{Display}_B}{(V_B) (D_B)}$

M = Mass of sample, mg

7.4.2 Other systems internally compensate for recovery factor, volume, density, or mass and blank, and thus read out directly in parts per million chlorine units. Refer to instrumentation manual.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 Each sample should be analyzed twice. If the results do not agree to within 10%, expressed as the relative percent difference of the results, repeat the analysis.

8.3 Analyze matrix spike and matrix spike duplicates - spike samples with a chlorinated organic at a level of total chlorine commensurate with the levels being determined. The spike recovery should be reported and should be between 80 and 120% of the expected value. Any sample suspected of containing >25% water should also be spiked with organic chlorine.

9.0 METHOD PERFORMANCE

9.1 These data are based on 66 data points obtained by 10 laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate. A data point represents one duplicate analysis of a sample. One laboratory and four additional data points were determined to be outliers and are not included in these results.

9.2 Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method the following values only in 1 case in 20 (see Table 1):

$$\text{Repeatability} = 0.137 x^*$$

*where x is the average of two results in $\mu\text{g/g}$.

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$\text{Reproducibility} = 0.455 x^*$$

*where x is the average value of two results in $\mu\text{g/g}$.

9.3 Bias. The bias of this test method varies with concentration, as shown in Table 2:

$$\text{Bias} = \text{Amount found} - \text{Amount expected}$$

10.0 REFERENCE

1. 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, WA80. July 1988.
2. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
3. Standard Instrumentation, 3322 Pennsylvania Avenue, Charleston, WV 25302.

TABLE 1.
 REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN
 USED OILS BY MICROCOULOMETRIC TITRATION

Average value μg/g	Repeatability, μg/g	Reproducibility, μg/g
500	69	228
1,000	137	455
1,500	206	683
2,000	274	910
2,500	343	1,138
3,000	411	1,365

TABLE 2.
 RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS
 BY MICROCOULOMETRIC TITRATION

Amount expected, μg/g	Amount found μg/g	Bias, μg/g	Percent bias
320	312	-8	-3
480	443	-37	-8
920	841	-79	-9
1,498	1,483	-15	-1
1,527	1,446	-81	-5
3,029	3,016	-13	0
3,045	2,916	-129	-4

METHOD 9076
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