



A Honeywell Company

Chloride in Petroleum Distillates by Microcoulometry

UOP Method 779-08

Scope

This method is for determining chloride in liquid hydrocarbons at concentrations ranging from approximately 0.3 to 1000 ppm. Higher concentrations can be determined with appropriate sample dilution. The method determines the total organic chloride. Some inorganic chloride present as salts is not included (see *Note 1*). Except for fluoride, other halogens that may be present in the sample are determined as chloride. Both nitrogen and sulfur compounds interfere at concentrations greater than approximately 0.1%.

Reference

ASTM Method D 4052, Density and Relative Density of Liquids by Digital Density Meter,
www.astm.org

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Outline of Method

A commercial microcoulometer is set up and calibrated with liquid standards. Two modes of sample introduction are permitted, direct injection into the combustion tube or boat inlet. Using the direct injection technique, the sample is injected at a controlled rate into the combustion tube. Using the boat inlet technique, a measured volume of sample is injected, either manually or with an autosampler, into an argon purged quartz boat. After the volatile components of the sample have evolved, the boat is moved into a heated zone of the pyrolysis tube, which contains oxygen blended with argon. The combustion products are sparged through a sulfuric acid dryer and into a cell where the halogens are automatically titrated to a coulometric endpoint. The number of halide equivalents are calculated automatically (as chloride ions) and then reported in the concentration units selected.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Balance, readability 0.1-mg

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

© COPYRIGHT 1977, 1992, 2008 UOP LLC. All rights reserved.

Nonconfidential UOP Methods are available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959, USA. The UOP Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Beakers, borosilicate glass, 50-, 100-, and 250-mL, Fisher Scientific, Cat. Nos. 02-539-G, -H, and -K, respectively

Bottles, washing, low density polyethylene, 125-, 250- and 500-mL, Fisher Scientific, Cat. Nos. 03-409-10AA, -10BB and -10CC, respectively

Flasks, volumetric, Class A, borosilicate glass, 25-, 50-, 100-, 250- and 1000-mL, Fisher Scientific, Cat. Nos. 10-210-8A, -8B, -8C, -8E and -8G, respectively

Flowmeter, digital, gas, operating range 0.5 to 500 mL/min, Fisher Scientific, Cat. No. 11-164-45

Microcoulometer, with attached furnace, cell, autosampler, controls and computer, Model TCL-100, Dia Instruments Co., Ltd., available from COSA Instrument. Microcoulometers from other manufacturers such as Thermo ECS-3000, Analytik Jena Multi EA 3100, or Dohrmann MCTS-120 (no longer manufactured), are also available, but have not been tested. Follow the manufacturer's recommendations for maintaining a supply of spare parts and consumables.

Pipet filler, Fisher Scientific, Cat. No. 13-681-102A

Pipet, transfer, disposable plastic, 152-mm length, Fisher Scientific, Cat. No. 13-711-5A

Pipet, volumetric, Class A, 2-, 5- and 10-mL, Fisher Scientific, Cat. No. 13-650-2C, -2F and -2L, respectively

Refrigerator, flammable storage or explosion proof, Fisher Scientific, Cat. Nos. 97-938-1 or 97-950-1

Regulator, argon, single-stage, with stainless steel diaphragm, Matheson Gas Products, Cat. No. 3231. This regulator is installed downstream of the two-stage regulator to provide better flow control.

Regulator, argon, two-stage, with stainless steel diaphragm, Matheson Gas Products, Cat. No. 3104-580

Regulator, oxygen, single-stage, with stainless steel diaphragm, Matheson Gas Products, Cat. No. 3231. This regulator is installed downstream of the two-stage regulator to provide better flow control.

Regulator, oxygen, two-stage, with stainless steel diaphragm, Matheson Gas Products, Cat. No. 3104-540

Syringes, liquid, 10-, 25-, 50- and 100- μ L, Hamilton 1700 Series, Alltech, Cat. Nos. 80000, 80200, 80900 and 81000, respectively (if an autosampler is not used)

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. References to water mean deionized or distilled water.

The following items are required to perform the analysis. Additional reagents and materials may be required depending on the specific microcoulometer utilized. Where different reagents are specified in the instrument manual, follow the manufacturer recommendations.

Acetic acid, glacial, Fisher Scientific, Cat. No. A38

Ammonium hydroxide, concentrated, Fisher Scientific, Cat. No. A669

Argon, compressed gas, 99.99% minimum purity.

Chlorobenzene, CHROMASOLV 99.9% minimum purity, Aldrich Chemical, Cat. No. 270644-100ML

1-Chlorobutane, CHROMASOLV $\geq 99.8\%$ purity, Aldrich Chemical, Cat. No. 34958-100ML

Inorganic chloride standard (NaCl or HCl Solution), as recommended by the microcoulometer manufacturer

Oxygen, compressed gas, 99.98% minimum purity

Quartz wool, high purity, Alltech Associates, Cat. No. 4033

Sodium bicarbonate, Aldrich Chemical, Cat. No. 34,094-4

Sulfuric acid, concentrated, Aldrich Chemical, Cat. No. 32,050-1

Isooctane (2,2,4-Trimethylpentane), chloride free, Mallinckrodt Baker, Cat. No. 9335. Verify that the isooctane is chloride free by analysis on the microcoulometer.

Procedure

The analyst is expected to be familiar with general laboratory practices, with the technique of microcoulometry, and with the equipment being used. This procedure is written for the Dia Instruments microcoulometer listed in *Apparatus*. If a different microcoulometer is used, modify the procedure as needed.

Preparation of Standards

1-Chlorobutane or chlorobenzene, diluted in isooctane is used in this procedure as an example of how a standard solution is made. Other standards, such as 2,4,5-trichlorophenol in HPLC grade methanol, may be used provided that the solvent is chloride free and that equivalent results can be obtained as from the chlorobenzene.

For a 1-chlorobutane standard, prepare a nominally 10,000- $\mu\text{g Cl/mL}$ stock solution as follows:

1. Weigh approximately 2.611 g of 1-chlorobutane to the nearest 0.1 mg into a tared, 100-mL volumetric flask that is chloride free.
2. Dilute to the mark with isooctane
 - Store the stock solution in the volumetric flask in a refrigerator.
 - When stored in a refrigerator, the stock solution is stable for one month. Prepare fresh solution monthly, or as needed, and store in a refrigerator. If the stock solution is not stored in a refrigerator, prepare fresh solutions daily when the analysis is performed.
3. Calculate the concentration of chloride in the 1-chlorobutane stock solution using Equation 1:

$$\text{Chloride, } \mu\text{g/mL} = 10000 \text{ M} \left(\frac{35.45}{92.57} \right) \quad (1)$$

where:

M = mass of 1-chlorobutane weighed into flask, g

35.45 = atomic weight of chlorine

92.57 = molecular weight of 1-chlorobutane

10000 = factor to convert to $\mu\text{g/mL}$

4. Prepare working solutions containing nominally 1000-, 100-, 10- and 1- $\mu\text{g Cl/mL}$ by dilution of the stock solution with isooctane in chloride-free volumetric flasks.

- Remove the stock solution from the refrigerator and allow it to come to room temperature before performing the dilutions. Return the stock solution to the refrigerator immediately thereafter.
- Other working solutions may be prepared if needed.
- Use volumetric pipets and volumetric flasks to keep concentration as $\mu\text{g Cl/mL}$.
- When stored in a refrigerator, the working solutions are stable for one week. Prepare fresh working solutions weekly, or as needed, and store in a refrigerator. If the working solutions are not stored in a refrigerator, prepare fresh working solutions daily when the analysis is performed.

For a chlorobenzene standard, prepare a nominally 10,000- $\mu\text{g Cl/mL}$ stock solution as follows:

1. Weigh approximately 3.174 g of chlorobenzene to the nearest 0.1 mg into a tared, 100-mL volumetric flask that is chloride free.
2. Dilute to the mark with isooctane and reweigh.
 - Store the stock solution in the volumetric flask in a refrigerator.
 - When stored in a refrigerator, the stock solution is stable for one month. Prepare fresh stock solution monthly, or as needed, and store in a refrigerator. If the stock solution is not stored in a refrigerator, prepare fresh stock solutions daily when the analysis is performed.
3. Calculate the concentration of chloride in the chlorobenzene stock solution using Equation 2:

$$\text{Chloride, } \mu\text{g/mL} = 10000 \text{ N} \left(\frac{35.45}{112.56} \right) \quad (2)$$

where:

N = mass of chlorobenzene weighed into flask, g

35.45 = atomic weight of chlorine

112.56 = molecular weight of chlorobenzene

10000 = factor to convert to $\mu\text{g/mL}$

4. Prepare working solutions containing nominally 1000-, 100-, 10- and 1- $\mu\text{g Cl/mL}$ by dilution of the stock solution with isooctane in chloride-free volumetric flasks.
 - Remove the stock solution from the refrigerator and allow it to come to room temperature before performing the dilutions. Return the stock solution to the refrigerator immediately thereafter.
 - Other working solutions may be prepared if needed.
 - Use volumetric pipets and volumetric flasks to keep concentration as $\mu\text{g Cl/mL}$.
 - When stored in a refrigerator, the working solutions are stable for one week. Prepare fresh working solutions weekly, or as needed, and store in a refrigerator. If the stock solution is not stored in a refrigerator, prepare fresh working solutions daily when the analysis is performed.

Preparation of Apparatus

1. Set up the microcoulometer in accordance with the instructions of the manufacturer. If desired, a chart recorder can be connected to the instrument.
2. Polish the electrodes as directed by the manufacturer. Clean the coulometric cell and fill the cell with the appropriate electrolyte solution. Fill the sulfuric acid scrubber and assemble the instrument according to manufacturer directions. Pack the boat with quartz wool, if a boat inlet autosampler is used.
 - The quartz wool is packed into the quartz boat so that it remains in the boat throughout the analysis.
3. Set the furnace temperature(s) and establish gas flows at the manufacturer's suggested rates. Verify that the gas flow rates are correct using the digital flowmeter. Adjust the flow rates if necessary.

4. Enter the appropriate operation parameters into the instrument computer.
 - These instrument parameters are selected by either using the manufacturer's suggestions or based on the operator's prior experience. One or more of these parameters may need to be modified as more experience is gained and as different sample matrices are analyzed.
5. Condition the electrodes according to the manufacturer's specifications by direct injection of the inorganic chloride solution into the cell followed by titration to a stable baseline.
 - The baseline stability is determined by inspection of the onscreen or chart recorder trace.

Calibration of Apparatus

1. Select appropriate chloride standards for a linear calibration. It is recommended to include at least 3 standards (and a solvent blank for samples <10 ppm). Follow instrument manufacturer's guidelines to determine maximum injectable volume.
 - The linear calibration can be made from injections of the same volume of standards of different concentrations or of different volumes of a single standard concentration.
 - It is recommended that an autosampler is used with the instrument.
 - Instruments with direct autosampler introduction into the combustion tube can analyze larger sample volumes than boat inlet instruments.
 - Boat inlet instruments will require separate introduction programs depending on the volatility of the sample.
2. Create a calibration program sequence in the instrument control software. The solvent blank and the lowest standard on the calibration should be analyzed in duplicate.
3. Initialize the coulometer according to the manufacturer's instructions.
 - The coulometer must be started prior to any injection so that a true baseline can be used and to make certain that any volatile halides are not lost. This is done automatically when a computer controlled autosampler is used
4. For a direct injection instrument, the standard is slowly injected directly into the combustion tube. The use of an autosampler is recommended for control of the injection rate.
 - If the combustion tube, sulfuric acid scrubber, or coulometric cell become coked during the injection, they must be removed and cleaned appropriately. Coking can be minimized by slowing the rate at which the sample is introduced into the furnace.
5. For a boat inlet instrument, the standard is injected into the quartz wool contained in the boat making certain that the entire sample is contained by the boat and none of the sample spatters. The boat position is programmed for proper volatilization and combustion of the sample matrix.
 - The rate at which the boat is moved into the furnace will depend on the volume of the injection and the boiling range of the standard's components. The boat should be moved into the furnace in such a manner so as to prevent the sample from flash combusting and forming coke in the pyrolysis tube.
 - If the combustion tube, sulfuric acid scrubber, or coulometric cell become coked during the injection, they must be removed and cleaned appropriately. Coking can be minimized by slowing the rate at which the sample is introduced into the furnace.
6. Retract the combustion boat from the furnace upon completion of the coulometric titration and allow the boat to cool to ambient temperature before starting the next analysis.
7. Record the amount of chloride titrated and verify that the titration was performed properly by examining the titration profile onscreen or on the chart recorder.
 - The profile should be examined for, but not limited to, excessive tailing, overshoot; insufficient integration time, excessive integration time, and unstable baseline. If any of these problems occur, the appropriate corrective action must be taken before proceeding.

- Most instruments will record the titration data and calculate the results automatically.
8. Repeat the analysis of the remaining standards and create a linear calibration.
 - If the calibration is non-linear (a plateau or obvious non-linearity), clean the combustion tube (see *Note 2*) and recalibrate the equipment by repeating the above steps with a new standard stock solution and working standards unless recalibration has already failed once.
 - If recalibration fails, repeat the set up of the coulometer as specified in *Preparation of Apparatus* and see *Note 3*.

Sample Analysis

If the approximate concentration of chloride in the sample is known, proceed with the analysis or dilution as required. If the concentration of chloride is not known, dilute the sample with chloride-free solvent before analysis to avoid overloading the microcoulometer. If the chloride concentration is then found to be low, reanalyze the sample without dilution. Typically, samples will contain low concentrations of chloride, where dilution is not required or very high (%-range) concentrations of chloride where the two-step dilution described below is required. If a sample contains an intermediate concentration of chloride, a single-step dilution may be performed.

Dilution Not Required — Less Than 1000-ppm Chloride

1. Select the same injection volume that was used to calibrate the coulometer.
2. Follow the procedure outlined in *Calibration of Apparatus*, Steps 3 through 7, for the analysis of the sample.
 - Sample analysis is generally performed in duplicate.

Dilution Required — Greater Than 1000-ppm Chloride

1. Add approximately 45 mL of isooctane to a 50-mL volumetric flask and tare to the nearest 0.1 mg.
2. Using a disposable pipet, add approximately one gram of sample and weigh the flask to the nearest 0.1 mg.
3. Dilute the sample to the mark with isooctane and shake the flask well to mix.
4. Pipet 2 mL from the first dilution into a second 50-mL volumetric flask.
5. Dilute to the mark with isooctane and shake the flask well to mix.
6. Select the same syringe that was used to calibrate the coulometer.
7. Follow the procedure outlined in *Calibration of Apparatus*, Steps 3 through 7, for the analysis of the diluted sample.
 - Sample analysis is generally performed in duplicate.

Calculations

1. Calculate the chloride concentration of the undiluted hydrocarbon sample in $\mu\text{g/g}$ (mass-ppm) to the nearest integer above 10 ppm and one decimal place below 10 ppm. The calculations can often be done automatically in the instrument software. If the density of the sample is entered, the results will be calculated as mass-ppm. If the density is unknown, it can be determined by ASTM D 4052.

If the software does not calculate the results, calculate the concentration of chloride in the sample using Equation 3.

$$\text{Chloride, mass-ppm} = \frac{1000 B}{CD} \quad (3)$$

where:

B = chloride detected by coulometer in sample, μg

C = volume of sample injected, μL

D = density of sample, g/mL

1000 = factor to convert μL to mL

For samples that did require dilution, calculate the chloride concentration of the original sample in mass-% to one decimal place above 1% and two decimal places below 1% using Equation 4:

$$\text{Chloride, mass-\%} = \frac{B}{10 C} \left(\frac{FH}{EG} \right) \quad (4)$$

where:

B, C = previously defined, Equation 1

E = mass of sample diluted, g

F = volume of first dilution, mL

G = volume of aliquot taken from the first dilution, mL

H = volume of second dilution, mL

10 = factor to convert to mass-%

If the instrument calculates the results as $\mu\text{g Cl/mL}$, the mass-% result can be calculated using Equation 5:

$$\text{Chloride, mass-\%} = \frac{J}{10000} \left(\frac{FH}{EG} \right) \quad (5)$$

where:

J = Chloride, $\mu\text{g/mL}$

E, F, G, H = previously defined, Equation 2

10000 = factor to convert to mass-%

Notes

1. Instruments with direct injection of the sample into the combustion tube have better recovery for inorganic chloride compared to boat inlet instruments. The boat does not get hot enough to decompose or vaporize most inorganic chlorides.
2. If the standards or blanks give an unstable response during analysis, deionized water can be injected in place of hydrocarbons to clean the combustion tube. Repeat until the response is stable.
3. If frits between the electrodes and the coulometric cell become fouled with AgCl , soak in aqueous ammonia solution, and then rinse well with deionized water before reassembling the cell.

Precision

It is expected that the various microcoulometers listed would provide similar precision, at least above a few mass-ppm. The precision data listed below, near and below 1 mass-ppm, was obtained

using the listed Dia Instruments microcoulometer. If another microcoulometer is to be used, confirm its precision and accuracy at the chloride concentrations to be measured.

The testing protocols of UOP Method 999, concerning the number of analysts and days were not used for all concentrations, but the calculation protocols for UOP Method 999 were used in all cases.

Repeatability and Intermediate Precision

Analysts performed replicate analyses as shown in the Table. The within-day estimated standard deviation (esd) was calculated for each concentration and is listed in the Table. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference shown in the Table with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the intermediate precision allowable difference shown in the Table with 95% confidence.

The data in the Table is a short-term estimate of repeatability. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term repeatability.

Table
Repeatability and Intermediate Precision, Chloride, mass-ppm and mass-%

<u>Sample</u>	<u>Number of Analysts</u>	<u>Number of Days</u>	<u>Number of Replicates per Day</u>	<u>Mean Chloride Concentration</u>	<u>Repeatability</u>		<u>Intermediate Precision</u>	
					<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
A	1	2	9	0.3 ppm	0.08	0.3		
B	1	2	9	1.1 ppm	0.10	0.3		
C	2	2	2	168 ppm	3.16	9.5	3.34	13.1
D	2	2	2	62.4 %	0.37	1.1	0.43	1.7

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

Time for Analysis

The elapsed time and labor requirement for one analysis, including calibration are identical, 1.5 hours. Each succeeding analysis requires 0.5 hour.

Suggested Suppliers

Aldrich, 1000 W. Saint Paul Ave., Milwaukee, WI 53233 (414-273-3850) www.sigma-aldrich.com

Alltech Associates Inc., 2051 Waukegan Rd., Deerfield, IL 60015 (847-948-8600)
www.alltechweb.com

Analytik-Jena USA, Inc., 26009 Budde Rd., Suite D-100, The Woodlands, TX 77380 (281-367-6130) www.analytik-jena.com

Cosa Instrument Corporation, 7125 North Loop East, Houston, TX 77028 (713-947-9591)
www.cosa-instrument.com, U.S.A. distributor for Dia Instruments Co., Ltd. 370 Enzo, Chigasaki, Kanagawa Pref., 253-0084, Japan (+81-467-86-3864)

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785 (412-490-8300) www.fishersci.com

Mallinckrodt Baker, Inc. 222 Red School Lane, Phillipsburg NJ 08865 (908-859-2151)

www.mallbaker.com

Matheson Tri-Gas, 166 Keystone Drive, Montgomeryville, PA 18936 (215-641-2700)

www.mathesontrigas.com

Thermo Electron North America LLC, 5225 Verona Road, Madison, WI 53711-4495 (608-276-6100) www.thermo.com