



A Honeywell Company

Total, Inorganic, and Organic Chloride in Hydrocarbons

UOP Method 588-12

Scope

This potentiometric method is for determining total and inorganic chloride, and calculating organic chloride, in hydrocarbons. The method is applicable to samples with chloride concentrations of 1 mass-ppm or higher. For lower levels of chloride use UOP Method 991 "Chloride, Fluoride, and Bromide in Liquid Organics by Combustion Ion Chromatography (CIC)." Iodide and/or bromide, if present, are calculated as chloride. Samples that are polymerized by sodium biphenyl (such as styrene) cannot be analyzed by this method. Results for samples containing ammonia and/or amines may be biased high (see *Note 1*).

Reference

UOP Method 991, "Chloride, Fluoride, and Bromide in Liquid Organics by Combustion Ion Chromatography (CIC)," www.astm.org

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

Outline of Method

To determine total chloride, the hydrocarbon sample is weighed and transferred to a separatory funnel containing toluene. Sodium biphenyl reagent is added to promote rapid conversion of the organic chloride into inorganic chloride. Excess reagent is decomposed with alcohol and water, and the phases are separated. The chloride containing aqueous phase is acidified, concentrated, acetone is added, and the solution titrated potentiometrically.

Inorganic chloride determination is identical to total chloride except that the addition of sodium biphenyl reagent is omitted. Organic chloride is then calculated as the difference between the total chloride and inorganic chloride determinations.

Apparatus

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

Balance, readable to 0.0001 g

Balance, readable to 0.01 g

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).

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Beaker, 250-mL, tall, without spout, borosilicate glass, Wilmad-LabGlass, Cat. No. G-9906-002

Boiling chips, Fisher Scientific, Cat. No. 09-191-12

Bottles, glass, 60-mL, Fisher Scientific, Cat. No. 02-911-787

Cylinders, graduated, Class B, 10-, 25-, 50-, and 100-mL, Fisher Scientific, Cat. Nos. 08-550B, C, D, and E, respectively

Desiccator, with plate, Fisher Scientific, Cat. No. 08-615B

Electrode, combination silver/glass Titrode Model 6.0430.100, Metrohm USA, Cat. No. 020948507

Flask, volumetric, Class A, 500-mL, Fisher Scientific, Cat. No. 10-208K

Funnel, separatory, 250-mL, Fisher Scientific, Cat. No. 10-437-5C

Hot plate, electric, capable of maintaining 150°C, Fisher Scientific, Cat. No. 11-100-49H

Oven, drying, capable of operation at 110°C, Fisher Scientific, Cat. No. 13-247-725G

Pipet, volumetric, Class A, 50-mL, Fisher Scientific, Cat. No. 13-650-2S

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

Stirring bars, Teflon-coated, Fisher Scientific, Cat. No. 14-512-148

Titration, potentiometric, recording, ± 2000 -mV range, 1-mV resolution, with dispenser having a volume readout of 0.00 to 99.9 mL and 0.01% resolution, Titration Model 904, Metrohm USA

Tongs, beaker, Fisher Scientific, Cat. No. 02-622

Tray, for ice bath, polypropylene, Fisher Scientific, Cat. No. 13-361-10

Reagents and Materials

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

Acetone, 99.9% minimum purity, Fisher Scientific, Cat. No. A18-4

Cleaning pad, synthetic, mildly abrasive, Scotch-Brite™, Runco Office Supply, Cat. No. MMM-96

Congo red paper, VWR, Cat. No. 60791-006

Detergent, cleaning compound, Liqui-Nox, Fisher Scientific, Cat. No. 04-322-15B

Desiccant, Drierite, indicating, 10- to 20-mesh, Fisher Scientific, Cat. No. 07-578-4A

Gloves, nitrile, Fisher Scientific, Cat. No. 11-395-19C

Ice, water

Isooctane, 99.9% minimum purity, Fisher Scientific, Cat. No. O301-4

Isopropyl alcohol, 99.9% minimum purity, Fisher Scientific, Cat. No. A416-4

Nitric acid, concentrated, Certified ACS Plus, Fisher Scientific, Cat. No. A200-212

Nitric acid, approximately 5N. Add 160 mL of concentrated nitric acid slowly to approximately 200 mL of water in a 500-mL volumetric flask. Dilute to the mark with water, cap and invert several times to mix thoroughly.

Pipet, disposable, LDPE, Fisher Scientific, Cat. No. 13-711-9AM

Potassium chloride, 99.995% minimum purity, Alfa Aesar, Cat. No. 87626, VWR. Oven dry an aliquot before each use at 105°C for 2.5 hours, and cool in a desiccator.

Silver nitrate, 0.1N solution, Fisher Scientific, Cat. No. SS72-4, see *Silver Nitrate Standardization*

Silver nitrate, 0.01N standard aqueous solution. Prepare by diluting the 0.1N solution, see *Silver Nitrate Standardization*.

Sodium biphenyl reagent, commercially obtainable under the name of “Organic Halogen Reagent” from GFS Chemicals. The reagent is packed in 18-mL bottles (hereafter referred to as “vials”). One vial contains 13 to 15 milli-equivalents of active sodium. The reagent cannot be used after the expiration date stated on the package (see *Note 2*).

Toluene, 99.9% minimum purity, Fisher Scientific, Cat. No. T324-4

Water, deionized or distilled

Wipers, Kimwipes, lint free, Fisher Scientific, Cat. No. 06-666A

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of titration, and the equipment being used. Dispose of used reagents, materials, and samples in an environmentally safe manner according to local regulations.

Silver–Silver Chloride Electrode Preparation and Reconditioning

Proper electrode preparation is essential to obtain reproducible and noise-free titration curves having good endpoints. An electrode should be dedicated to chloride analysis. Prepare and recondition the silver-silver chloride electrode as follows:

1. Clean the silver surface with a Scotch-Brite pad. Rinse with water and dry.
2. Weigh approximately 0.1 g of potassium chloride and place in a beaker. Using a graduated cylinder, add 20 mL of 5N nitric acid and 80 mL of water to the beaker. Immerse the electrode; and titrate to the endpoint with 0.1N silver nitrate.
3. Remove the electrode from the solution and rinse with water.
4. Wipe the excess silver chloride from the electrode with a wiper.
 - The electrode should be cleaned after each titration by rinsing with water.

The freshly coated silver-silver chloride electrode may be stored in water or carefully dried using wipers and stored for future use. It is necessary to repeat the electrode preparation when the AgCl begins to peel from the surface.

Silver Nitrate Standardization

The 0.1N silver nitrate solution may be purchased at a certified concentration. Alternatively, the solution may be standardized as follows.

1. Weigh 0.10 ± 0.01 g of dried potassium chloride to the nearest 0.0001 g into a clean, dry 250-mL electrolytic beaker.
2. Using a graduated cylinder, add 100 mL of water and a stirring bar to the beaker. Add a few drops of 5N nitric acid to acidify.

3. Titrate the potassium chloride solution, while stirring, with the nominally 0.1N silver nitrate solution.
4. Calculate the normality of the silver nitrate solution to 3 significant figures using Equation 1.

$$\text{AgNO}_3, N = \frac{A}{0.07455 B} \quad (1)$$

where:

A = mass of potassium chloride weighed into beaker, g

B = volume of silver nitrate solution used in titration, mL

N = calculated normality of AgNO₃, moles/liter

0.07455 = molecular mass of the potassium chloride, g/mole, multiplied by 0.001, the factor to convert mL to liter

5. Repeat Steps 1 through 4 two more times, average the three values and record the average normality thus obtained.
6. Prepare a 0.01N silver nitrate solution by pipeting 50 mL of the standardized 0.1N solution into a 500-mL volumetric flask. Dilute to the mark with water, cap and invert several times to mix thoroughly. Calculate and record the normality of this solution to three decimal places; the average of the three replicates of N from Equation 1 divided by 10.

Sample Preparation

Caution: This method cannot be used on samples that polymerize with sodium biphenyl, such as styrene, since a violent reaction may occur.

Extreme care must be used to prevent contamination. All glassware should be exclusively reserved for this analysis. Clean glassware using detergent, rinse with water followed by acetone.

Determine a blank for each group of samples using all the reagents, including as many vials of the sodium biphenyl reagent as used in the samples. Follow all the steps of the analysis, except omit the sample itself.

1. Proceed to Step 1 under *Total Chloride Determination* for chloride estimates below 10 mass-%, or Step 1 under *Sample Dilution* for chloride estimates at or above 10 mass-%, if no heavy oils or solids are to be analyzed.
2. Heat viscous heavy oils or solids in the 110°C oven until fluid. Loosen caps or lids to allow expansion of the samples during heating.
3. Remove the sample from the oven using gloves or tongs and shake well to homogenize the sample.
4. Proceed immediately to the next step: either Step 1 under *Sample Dilution* for samples with chloride estimates at 10 mass-% or higher, or Step 1 under *Total Chloride Determination* for samples with chloride estimates below 10 mass-%.

Sample Dilution

1. Tare a 60-mL capped bottle on the four-place balance.
2. Add 30 mL of toluene to the bottle using a graduated cylinder.
3. Cap the bottle and reweigh. Record the mass of toluene to four decimal places.

4. Tare the bottle again and add, dropwise, 5 g of sample to the bottle containing the toluene. Record the sample mass added to four decimal places.
5. Cap the bottle and shake well to thoroughly mix the contents.
6. Repeat Steps 1 through 3 with a second 60-mL bottle.
7. Tare the second bottle containing toluene and add dropwise 5 g of the diluted sample from the first bottle. Record the diluted sample mass added to four decimal places.
8. Cap the second bottle and shake well to thoroughly mix the contents.
9. Use 18 to 20 g of this second dilution (see Table 1) for the sample size in Step 1 under *Total Chloride Determination*.

Table 1

<u>Expected Halide Concentration</u>	<u>Sample Size, g</u>	<u>Normality of Silver Nitrate</u>
1-5 mass-ppm	50-100	0.01
5-10 mass-ppm	25-35	0.01
0.5-10 mass-%	3-5	0.1
10-50 mass-%	18-20*	0.1

* See *Sample Dilution*, Step 9.

10. Calculate the dilution factor using Equation 2:

$$Z = \frac{(U + V)(X + Y)}{VY} \quad (2)$$

where:

- U** = toluene mass used in first dilution, g
- V** = sample mass used in first dilution, g
- X** = toluene mass used in second dilution, g
- Y** = first dilution sample mass used in second dilution, g
- Z** = dilution factor

Total Chloride Determination

1. Place 50 mL of toluene in a 250-mL separatory funnel. Weigh the container plus sample (or dilution) to four significant figures, and add the appropriate amount of sample to the separatory funnel using Table 1 as a reference.
2. Reweigh the sample container and remaining contents to determine the exact mass of sample transferred to at least four significant figures.
3. Add the contents of two vials of sodium biphenyl reagent to the separatory funnel.
4. Stopper the separatory funnel and swirl to mix the contents thoroughly, invert and vent frequently through the stopcock.
5. Add one additional vial of sodium biphenyl reagent if the solution or suspension resulting from Steps 3 and 4 is not blue-green in color; otherwise proceed to Step 6 (see *Note 3*).
 - If, after addition of the third vial of sodium biphenyl reagent, the solution or suspension is still not blue-green in color, discontinue the procedure and begin again using less sample.
6. Allow 10 minutes after repeated mixing for the reaction to reach completion.

7. Add 5 mL of isopropyl alcohol to the separatory funnel, stopper and shake. Invert and vent frequently. This destroys excess reagent (the blue-green color changes to clear, water-white).
 - The solution temperature will rise during the reaction.
8. Add 20 mL of water, stopper the funnel again and rock it gently for approximately one minute. Invert and vent pressure frequently through the stopcock. Allow the contents to return to room temperature before proceeding to Step 9 (about 15 minutes).
9. Add 10 mL of 5N nitric acid, stopper and shake gently for one minute, releasing pressure frequently through the stopcock.
10. Drain the aqueous phase into a second separatory funnel containing 50 mL of isooctane, stopper and shake well, venting frequently.
11. Drain the aqueous phase from Step 10 into a 250-mL electrolytic beaker.
12. Extract the sample in the first separatory funnel a second time with 20 mL of water acidified with 6 drops of 5N nitric acid.
13. Stopper and shake the first separatory funnel well, venting frequently, and then drain the aqueous phase into the second separatory funnel containing the isooctane.
14. Stopper and shake the second separatory funnel well, venting frequently, and then drain the aqueous phase into the electrolytic beaker containing the first aqueous extract.
15. Test the aqueous extract in the beaker with Congo red paper. If the paper does not turn blue, add dropwise 5N nitric acid until the blue color is obtained.
16. Add a few boiling chips to the beaker and evaporate the solution on a hot plate, kept just below the boiling point of the liquid, until 25 to 30 mL remains. Do not allow the solution to boil.
 - Loss of chloride can occur if the sample is boiled or evaporated to a volume of less than 25 mL.
17. Cool the solution to ambient temperature in an ice bath, and then add 100 mL of acetone.
18. Titrate the solution potentiometrically with standardized 0.1N or 0.01N silver nitrate, see Table 1, using the conditioned combination silver/glass electrode. The blank is titrated with the 0.01N silver nitrate.
19. Determine and record the volume of titrant used to reach the chloride endpoint.
 - The Figure shows a typical titration curve with the chloride endpoint noted. If more than one halide is present, the chloride endpoint is determined by the potential as shown in the Figure.
 - Blanks exhibiting more than one endpoint are an indication of contaminated solvents or sodium biphenyl reagent, and purer solvents and sodium biphenyl reagent must be obtained before analyzing samples, especially at low concentration levels. Titration blank values higher than 0.2 mL of the 0.01N titrant are unacceptable. Assignment of the blank value to chloride is dependent on the potential at endpoint (see Figure).
20. Clean the electrodes after each titration by rinsing with water.

Inorganic Chloride Determination

Follow the procedure under *Total Chloride Determination* above, omitting the steps involving addition of sodium biphenyl reagent to either the sample or blank.

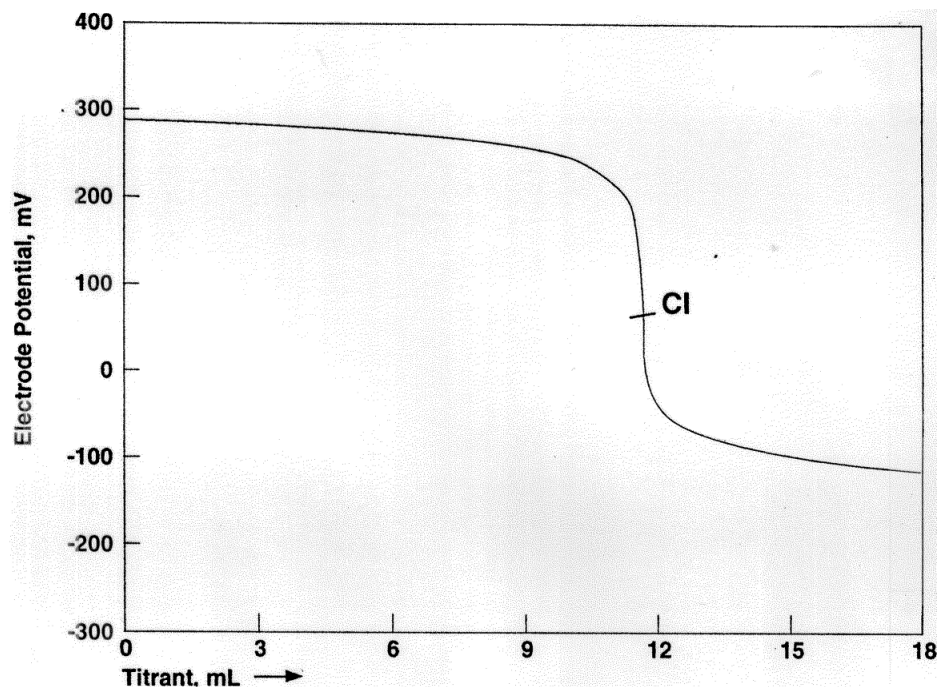


Figure
Typical Titration Curve

Organic Chloride Determination

Organic chloride is determined by subtracting inorganic chloride from total chloride. Follow both of the procedures under Total Chloride Determination and Inorganic Chloride Determination above.

Calculations

Calculate total chloride or inorganic chloride using Equation 3:

$$\text{Chloride, mass-ppm} = \frac{35,453 (CQ - DT) Z}{W} \quad (3)$$

where:

C = volume of titrant used to reach the sample chloride endpoint, mL

D = volume of titrant used to reach the blank chloride endpoint, mL. If there is no chloride endpoint (no chloride in blank), then D equals zero.

Q = molarity of the silver nitrate solution used (from *Silver Nitrate Standardization*, Step 5 or Step 6), moles/liter

T = molarity of the more dilute silver nitrate solution (from *Silver Nitrate Standardization*, Step 6), moles/liter

W = mass of sample (or dilution) used, g

Z = dilution factor (Equation 2), equals 1 if no dilution

35,453 = molecular mass of chloride, g/mole, divided by 1000 to convert mL to liters and multiplied by 10^6 to convert g/g to mass-ppm ($\mu\text{g/g}$)

Calculate organic chloride using Equation 4:

$$\text{Organic Chloride, mass-ppm} = E - F \quad (4)$$

where:

E = total chloride, mass-ppm

F = inorganic chloride, mass-ppm

Report results below 1000 mass-ppm to the nearest mass-ppm and results above 1000 mass-ppm to 3 significant figures. Report results above 1000 mass-ppm in mass-% by dividing the mass-ppm values by 10,000. If there is no chloride endpoint, report less than one mass-ppm chloride.

Notes

1. Ammonia and/or amines that are soluble in the aqueous extract will bias the results high by complexing with the silver in the titrant. From the literature, it is expected that the relative effect would be $\text{NH}_3 > \text{NH}_2\text{R} > \text{NHR}_2 > \text{NR}_3$. The effect would increase with increasing ammonia/amine concentration, and be more evident at lower chloride concentrations.

2. In general, the sodium biphenyl reagent cannot be used beyond the expiration date, typically 6 months after production. The active life can be extended if the reagent has been stored at temperatures below 20°C (do not refrigerate). It is recommended that the reagent be ordered shortly before use and in smaller quantities to avoid exceeding the expiration date.

3. If a third vial of sodium biphenyl reagent is required for any sample, and additional samples are being analyzed concurrently, it is suggested that an additional vial of reagent be added to each of the other samples and the blank. Otherwise, two blanks must be carried through the analysis.

Precision

Precision statements were determined using UOP Method 999, "Precision Statements in UOP Methods."

Repeatability and Site Precision

A nested design was carried out for determining components or groups of components on two samples by two analysts, with each analyst performing analyses on two separate days, performing two analyses each day for a total of 16 analyses. Using a stepwise analysis of variance procedure, the within-day and within-lab estimated standard deviations (esd) were calculated at the concentration means listed in Table 2. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 2 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 2 with 95% confidence.

Table 2
Repeatability and Site Precision, mass-ppm

<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
	<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
5	0.1	1	0.3	2
517	3.8	15	16.9	103

The data in Table 2 represent short-term estimates of the repeatability of the method. When the test is run routinely, use of a control standard and a control chart is recommended to generate an estimate of long-term repeatability.

Reproducibility

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

Time for Analysis

The elapsed time is 2 hours per sample without dilution, 2.5 hours with dilution. The labor requirement without dilution is one hour, and 1.5 hours with dilution, when running one sample with a blank. The labor requirement is increased by 0.5 hour for each additional sample not requiring dilution, or one hour with dilution, when samples are analyzed in batches.

Suggested Suppliers

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

GFS Chemicals, Inc., Powell, OH 43065, USA (740-881-5501) www.gfschemicals.com

Metrohm USA, 6555 Pelican Creek Circle, Riverview, FL 33578, USA (813-316-4700)
www.metrohmusa.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380, USA (610-431-1700)
www.vwr.com

Wilmad/Lab-Glass, 1002 Harding Hwy., Buena, NJ 08310, USA (856-697-3000) www.wilmad-labglass.com