

TOTAL CHLORIDE IN PETROLEUM DISTILLATES BY COLORIMETRY

UOP Method 395-95

SCOPE

This colorimetric method is for determining chloride in the range of 0.1 to 1 mass-ppm in liquid hydrocarbons that are free of hydrogen sulfide and low in total sulfur content. The method is not applicable to samples with sulfur levels that exceed 10 mass-ppm, or that are colored. UOP Method 588 can be used for chloride concentrations above 1 mass-ppm. Bromides and iodides, although rarely present, are calculated as chloride. Samples that are polymerized by sodium biphenyl (such as styrene) cannot be analyzed by this method. The method can be used to determine whether the chloride is organic or inorganic.

OUTLINE OF METHOD

To determine total chloride, a weighed hydrocarbon sample is transferred to a separatory funnel containing toluene. Sodium biphenyl reagent is added to promote rapid conversion of the organic halogen to inorganic halide. Excess reagent is decomposed, the mixture acidified and the phases separated. The aqueous phase is analyzed colorimetrically, using the mercuric thiocyanate ferric ion method. The intensity of the ferric thiocyanate color is measured at 460 nm and the chloride concentration is read directly from a calibration curve.

Inorganic chloride determination is identical to the total chloride except that the addition of the sodium biphenyl reagent is omitted.

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-g

Balance, readability 0.01-g

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 1966, 1979, 1990, 1995 UOP LLC
ALL RIGHTS RESERVED

UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The 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.

Bottle, amber, 473-mL, Fisher Scientific, Cat. No. 03-442-2B

Cell, spectrophotometer, 50-mm light path

Cylinders, graduated, 10-, 25-, 100- and 500-mL, Fisher Scientific, Cat. Nos. 08-548A, B, D and F, respectively

Dessicator, with plate, Fisher Scientific, Cat. Nos. 08-595-5A and 08-641B, respectively

Flasks, volumetric, Class A, 25-, 50-, 500- and 1000-mL, Fisher Scientific, Cat. Nos. 10-210-5A, -5B, -5F and -5G, respectively

Funnel, 35-mm diameter, Fisher Scientific, Cat. No. 10-322A

Funnel, fluted, 75-mm OD, Fisher Scientific, Cat. No. 10-326-2C

Funnels, separatory, 250- and 500-mL, with PTFE-plug stopcock and polyethylene stopper, Fisher Scientific, Cat. Nos. 10-437-5C and -5D, respectively

Oven, drying, capable of maintaining 105°C

Pipets, Mohr, 1- and 10-mL, Fisher Scientific, Cat. Nos. 13-665-G and -M, respectively

Pipets, volumetric, Class A, 2-, 10-, 20-, 50- and 100-mL, Fisher Scientific, Cat. Nos. 13-650-2C, -2L, -2N, -2S and -2U, respectively

Spectrophotometer, capable of measuring absorbance at 460 nm

Stopper, Size No. 8, one-hole, Fisher Scientific, Cat. No. 14-135M

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified. References to water mean deionized or distilled water.

Acetone, 99.5% minimum purity, low chloride, Fisher Scientific, Cat. No. A18

Alcohol, denatured, 95% ethanol-5% methanol, Formula 3A, J.T. Baker, Cat. No. 9229-01

Chloride solution, stock, 10 mg/L chloride (or 250 µg/25 mL). Dry the sodium chloride in a drying oven for two hours at 105°C immediately prior to use. Cool in a dessicator. Place 0.1648 ± 0.0002 g of dry sodium chloride in a 1000-mL volumetric flask. Dissolve the salt completely in water. Dilute to volume with water and mix thoroughly. Transfer, by pipet, a 100-mL aliquot of the solution to another 1000-mL flask. Dilute to volume with water and thoroughly mix. The final stock solution will contain 10 mg/L chloride (or 250 µg/25 mL).

Dessicant, indicating Drierite, Fisher Scientific, Cat. No. 07-578-3A

Detergent, cleaning compound, Alconox, Fisher Scientific, Cat. No. 04-322-4

Ferric ammonium sulfate, $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, 99% minimum purity, Fisher Scientific, Cat. No. I75

Ferric ammonium sulfate, solution, 0.25-M. Place 60.3 ± 0.1 g of ferric ammonium sulfate in a 500-mL volumetric flask. Add approximately 100 mL of water. Using a graduated cylinder, carefully add 280 mL of concentrated nitric acid and dilute to volume with water. If the salt does not dissolve completely after adding the acid, filter through Whatman 42 filter paper before diluting to volume.

Filter paper, Whatman 42, 125-mm, Fisher Scientific, Cat. No. 09-855D

Isooctane, 99.5% minimum purity, low chloride, Fisher Scientific, Cat. No. O299

Isopropyl alcohol (2-propanol), 99% minimum purity, low chloride, Fisher Scientific, Cat. No. A416

Mercuric thiocyanate, $\text{Hg}(\text{SCN})_2$, 99.9% minimum purity, less than 0.002% chloride, J.T. Baker, Cat. No. P651

Mercuric thiocyanate, saturated solution. Weigh approximately 50 g of mercuric thiocyanate in a 473-mL amber bottle, add approximately 250 mL of denatured alcohol, shake and store in a dark location. Over a period of time, mercuric thiocyanate releases thiocyanate ions that cause the absorbance of the calibration blank to increase. When the absorbance of the blank increases to higher than 0.35 absorbance unit, decant and discard the supernatant saturated solution, wash the remaining mercuric thiocyanate crystals several times with fresh alcohol and use them to prepare a new reagent solution.

Nitric acid, concentrated

Nitric acid, 1:1 by volume. Using a graduated cylinder, add 250 mL of concentrated nitric acid to 200 mL of water in a 500-mL volumetric flask, dilute to volume with water and thoroughly mix.

Sodium biphenyl reagent, commercially available under the name of “Organic Halogen Reagent” from SACHEM, Cat. No. 500. 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 1).

Sodium chloride, crystal, 99.95% minimum purity, Fisher Scientific, Cat. No. S671

Toluene, 99.8% minimum purity, low chloride, Fisher Scientific, Cat. No. T291

PROCEDURE

Preparation of Calibration Curve

1. Prepare calibration standards by pipeting 0.5, 1.0, 2.0, 4.0, 6.0, 8.0 and 10.0 mL of the 10 mg/L chloride stock solution into 6 separate 25-mL volumetric flasks using a Mohr pipet. Pipet no chloride stock solution into a seventh flask that is used as a reagent blank.
 - The calibration standards contain 5, 10, 20, 40, 60, 80 and 100 μg chloride per 25 mL, respectively. The reagent blank contains zero μg chloride per 25 mL.

2. Use a graduated cylinder to add water to all flasks to bring each volume to no more than 20 mL.
3. Pipet 2.0 mL of 0.25-*M* ferric ammonium sulfate solution into each flask and swirl to mix.
4. Pipet 2.0 mL of the supernatant from the saturated alcoholic mercuric thiocyanate solution into each flask, swirl to mix, dilute to volume with water and mix thoroughly.
5. Allow the colored complex to develop for 10 minutes.
6. Measure the absorbance at 460 nm in a 50-mm cell within 10 minutes after color development is complete, using distilled water as a reference solution.
7. Subtract the reagent blank absorbance from the chloride solutions absorbances.
8. Plot the net absorbances obtained vs. micrograms of chloride per 25 mL.

Total Chloride Analysis

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. Pipet 50 mL of toluene into a 500-mL separatory funnel.
2. Add the appropriate amount of sample, depending on the expected chloride concentration (see Table).
3. Pipet 50 mL of toluene into a second, 250-mL separatory funnel that is used as a blank.
4. Add the contents of two vials of sodium biphenyl reagent to each separatory funnel.

Table

Selection of Sample Size

<u>Expected Range, mass-ppm Chloride</u>	<u>Sample Size, g</u>
0.1-0.5	250
0.5-1.0	125

5. Stopper the separatory funnels and invert several times to mix, venting frequently through the stopcock.

- The resulting suspensions should be blue-green. If not, add another vial of sodium biphenyl reagent to each separatory funnel. Repeat Step 5, and if the suspension is still not blue-green, discontinue the procedure and begin again using less sample, or use UOP Method 588.
6. Allow the suspensions to stand an additional 10 minutes to complete the reaction.
 7. Use a graduated cylinder to add 5 mL of isopropyl alcohol to each separatory funnel and swirl gently with the funnels unstoppered until excess reagent is destroyed (blue-green color changes to white).
 8. Use a graduated cylinder to add 20 mL of water, stopper and rock the funnels gently back and forth for one minute, frequently venting through the stopcock.
 9. Pipet 10 mL of 1:1 nitric acid into each funnel, stopper and shake gently, again releasing pressure frequently through the stopcock.
 10. Allow the phases to separate. Drain the lower aqueous phases into separate 250-mL separatory funnels containing 50 mL of isooctane.
 11. Shake the isooctane and aqueous phases vigorously and then allow the phases to separate.
 12. Transfer the lower aqueous phases to separate 50-mL volumetric flasks using the 35-mm transfer funnels.
 13. Make a second extraction of the contents of the 500-mL separatory funnels with approximately 10 mL of water acidified with 6 drops of 1:1 nitric acid. Shake well and allow the phases to separate.
 14. Drain the lower aqueous layers from the second extraction into the previously used 250-mL separatory funnels containing the isooctane. Shake well and allow the phases to separate.
 15. Drain the lower aqueous phases from this second extraction into the 50-mL flasks containing the first aqueous extract.
 16. Rinse the tips of the separatory funnels and the inside of the transfer funnels with water, collecting the rinsing in the 50-mL flasks. Dilute to volume with water, stopper and shake to mix.
 17. Pipet 20-mL aliquots of the sample and blank solutions into separate 25-mL volumetric flasks.
 18. Pipet 2 mL of the ferric ammonium sulfate solution into each flask.
 19. Dilute to volume with water, stopper and mix thoroughly.
 - The blank and sample are "B" and "C", respectively, in *CALCULATIONS*.
 20. Pipet a second 20-mL aliquot from each of the 50-mL flasks into two additional 25-mL volumetric flasks.
 21. Pipet 2 mL of ferric ammonium sulfate solution and 2 mL of the supernatant from the saturated alcoholic mercuric thiocyanate solution into each 25-mL flask.
 22. Swirl the mixtures, dilute to volume with water and mix thoroughly.

- The blank and sample which contain both ferric ammonium sulfate and supernatant from the saturated alcoholic mercuric thiocyanate are "A" and "D", respectively, in *CALCULATIONS*.
23. Allow the colored complex to develop for 10 minutes.
 24. Measure the absorbance of each solution at 460 nm in a 50-mm cell within 10 minutes after color development is complete, using distilled water as a reference solution (see Note 2).

Inorganic Chloride Analysis

Follow the procedure for *Total Chloride Analysis* except do not add the sodium biphenyl reagent to either the sample or blank.

CALCULATIONS

Blank

$$\text{Total Blank Absorbance, } E = A + (C - B) \quad (1)$$

where:

- A** = absorbance of ferric ammonium sulfate, mercuric thiocyanate solution of the reagent blank
- B** = absorbance of the ferric ammonium sulfate solution of the blank
- C** = absorbance of the ferric ammonium sulfate solution of the sample
- E** = total blank absorbance of each sample

Sample

$$\text{Net Absorbance} = D - E \quad (2)$$

where:

- D** = absorbance of the color-developed sample
- E** = previously calculated (Eq. 1)

From the calibration curve obtain the micrograms of chloride in 25 mL of colored solution (M) corresponding to the net absorbance. Finally, calculate the total or inorganic chloride concentration in the sample to the nearest 0.1 mass-ppm as follows:

$$\text{Chloride, mass-ppm} = \frac{2.50 M}{W} \quad (3)$$

where:

- M** = mass of chloride in 25 mL of colored solution, μg
- W** = mass of sample, g
- 2.50** = volume ratio of total sample solution to sample solution aliquots

To obtain the organic chloride concentration in the sample, subtract the inorganic chloride value from the total chloride value.

NOTES AND PRECAUTIONS

1. 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. Orders can be expedited by contacting SACHEM using FAX No. 512-445-5066.

2. The sample absorbance correction scheme (blank) takes into account the following: (a) contributions to the absorbance of the trace chloride impurities in the reagents, as well as the inherent color reagents themselves (the value “A” in *CALCULATIONS*); and (b) corrects for inherent extractable color in the sample as this color may have been modified by interaction with the ferric reagent. The value “C” (see *CALCULATIONS*) combines the contribution of the inherent sample color (modified) with the ferric reagent color itself. Hence, to obtain the correction in (b), it is necessary to measure the inherent color contribution of the ferric reagent alone in the extraction procedure, and this is given by “B”. Thus, “C–B” is a measure of the inherent extractable color (modified) from the sample.

3. The sample containers should be new glass, screw capped bottles with plastic inserts in the caps rather than paraffin coated paper inserts. The bottles must be washed with detergent and rinsed with distilled water followed by a chloride-free acetone rinse, and air blown to dryness. Rinse the bottle 3 to 4 times with the sample prior to taking the sample. Soldered tin cans may be used as a second choice for sample containers. However, the chloride in the soldering flux must first be removed by a hot water wash followed by the same cleaning procedure used for the glass bottles.

4. Reserve exclusively all glassware for the chloride determination and clean prior to use as described above. Do not use chlorine-containing stopcock grease, such as chlorotrifluoro-ethylene polymer grease.

5. This method must not be used on samples that polymerize, such as styrene. This type of sample may react violently.

PRECISION

Repeatability

Based on two tests performed by each of two analysts, on each of two days (8 tests) in one laboratory, the within-laboratory estimated standard deviation (esd) was calculated to be 0.02 mass-ppm at a chloride concentration of 0.9 mass-ppm. Two tests performed in one laboratory by different analysts on different days should not differ by more than 0.1 mass-ppm at the stated level (95% probability).

Reproducibility

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

TIME FOR ANALYSIS

The elapsed time for one total chloride determination is 1.5 hours. The labor requirement is 1.25 hours when running one sample and a blank, and 0.5 hour for each additional sample run at the same time.

REFERENCE

UOP Method 588, "Total, Inorganic and Organic Chloride in Hydrocarbons by Potentiometric Titration"

SUGGESTED SUPPLIERS

J. T. Baker Inc., 222 Red School Lane, Phillipsburg, NJ 08865 (908-859-2151)
Fisher Scientific Co., 711 Forbes Ave., Pittsburgh, PA 15219 (412-562-8300)
SACHEM, Inc., P.O. Box 485, Austin, TX 78767 (512-444-3626)