



A Honeywell Company

Chloride in Liquid Hydrocarbons by Dry Colorimetry

UOP Method 799-08

Scope

This method is for determining the sum of organic chloride and hydrogen chloride (HCl) in liquid hydrocarbons at concentrations ranging from approximately 0.5 to 500 mass/volume-ppm (mg/L). Other halogens, if present, are determined as chloride.

References

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

ASTM Method D 4307, "Preparation of Liquid Blends for Use as Analytical Standards,"
www.astm.org

Instrument instruction manual, C.I.Analytics PN 2010-Cl-man

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

Outline of Method

A commercial chloride analyzer utilizing dry colorimetric detection is set up according to the manufacturer's specifications. The sample is subjected to pyrolysis which converts the organic chlorides to HCl. The pyrolysis product is then passed to a detector where the HCl causes a color change on sensitized paper. The measured color change is proportional to the quantity of chloride in the sample. Calibration is performed using blends of known concentrations of chloride in a liquid hydrocarbon.

Apparatus

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

Chloride analyzer, with Dry Colorimetric Detector (DCD), C.I.Analytics, 2010L. Stock replacement parts as recommended by the manufacturer.

Regulator, air, two-stage, high purity, with stainless steel diaphragm, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Cat. No. 3122-590

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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Regulator, nitrogen, two-stage, high purity, with stainless steel diaphragm, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Cat. No. 3122-580

Regulator, oxygen, two-stage, high purity, with stainless steel diaphragm, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Cat. No. 3122-540

Reagents and Materials

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

Air, compressed gas, 99.99% minimum purity

Chlorobenzene, 99.9% minimum purity, Burdick & Jackson, VWR International, Cat. No. BJ043-4

Isooctane (2,2,4-Trimethylpentane), halogen free, Burdick & Jackson, VWR International, Cat. No. BJ362-4. Verify that the isooctane is chloride free by analysis on the instrument.

Nitrogen, compressed gas, 99.99% minimum purity

Oxygen, compressed gas, 99.99% minimum purity

Purifiers, compressed gas, removes hydrocarbons and moisture, Grace, Cat. No. 81350, three required

Water, deionized or distilled

Procedure

The analyst is expected to be familiar with general laboratory practices and with the equipment being used.

Preparation of Apparatus

Install the analyzer as recommended by the manufacturer and perform any required performance tests. Figure 1 shows a general diagram of the instrument. Establish operating parameters as recommended by the manufacturer for the sample types to be analyzed.

When not in use, keep the analyzer in Stand-By Mode (reactor at 600°C and vaporizer at 200°C with nitrogen gas flowing). Without the flow of nitrogen gas, the Teflon fittings at the end of the reactor tube may be damaged.

When analyzer is to be turned off, maintain flow of reactor gas until the reactor temperature is below 400°C. Otherwise damage to the Teflon fittings may occur.

Preparation of Standards

Prepare Calibration Blends of nominally 1.0 and 100 mg/kg chlorobenzene in halogen-free isooctane as described in ASTM Method D 4307, "Preparation of Liquid Blends for Use as Analytical Standards." Other concentrations may be prepared to suit samples of different chloride levels. Confirm that the isooctane is halogen-free by analyzing an aliquot on the instrument; if the isooctane is not halogen-free, find another source for the isooctane. Calculate the chloride concentration to three significant figures in each of the Calibration Blends using Equation 1.

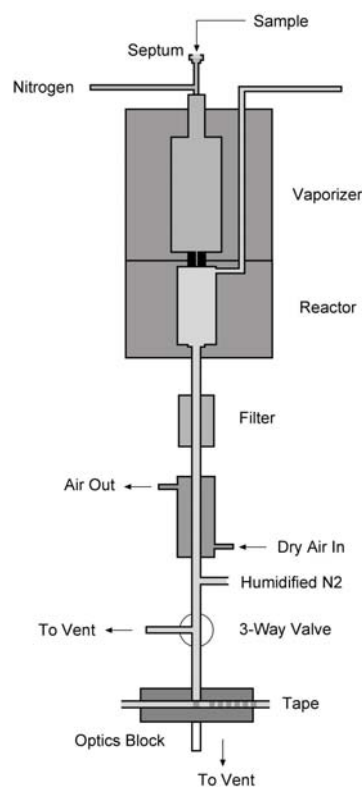


Figure 1
Diagram of Chloride Analyzer

$$C = \frac{35.5A}{112.6} \quad (1)$$

where:

A = concentration of chlorobenzene in Calibration Blend, mg/kg

C = concentration of chlorine in blend, mg/kg

35.5 = atomic weight of chlorine

112.6 = molecular weight of chlorobenzene

Determine the density of the calibration blend, either by using ASTM Method D 4052, "Density and Relative Density of Liquids by Digital Density Meter," or by using a literature value for the density of isooctane.

Calibration

Calibrate the instrument as described in the instrument manual. After all required parameters are entered into the instrument, the calibration factors are calculated by the instrument software.

Sample Analysis

Analyze the samples according to the instrument manufacturer's instructions.

Calculations

All calculations are performed by the instrument software and printed out automatically. Results will be shown in mass/volume-ppm (mg/L).

If results in mass-ppm (mg/kg) are desired, determine the density of the sample using ASTM Method D 4052. Convert mg/L to mg/kg using Equation 2.

$$D = \frac{B}{S} \quad (2)$$

where:

B = chloride, mg/L

D = chloride, mg/kg

S = density of the sample, g/mL

Report the results to one significant figure below one mg/L (or mg/kg), and to two significant figures at or above one mg/L (or mg/kg).

Note

In refinery applications, it may be advantageous to analyze for chloride using an online analyzer. Similar online analyzers using dry colorimetric detection are available from the suggested supplier and may be substituted.

Precision

Analyses of the samples used for the precision statement were performed by the suggested vendor.

Repeatability and Site Precision

A nested design was carried out by two analysts, with each analyst performing analyses on two separate days, performing two analyses each day for a total of eight analyses. Using a stepwise

analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in the Table. 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 the Table 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 the Table with 95% confidence.

Table
Repeatability and Site Precision, Chloride, mg/kg

<u>Mean Concentration</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>
0.5	0.004	0.01	0.049	0.30
50	0.28	1.1	1.25	7.6

The data in the Table 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 and labor requirement for one analysis is one hour, including calibration. Each succeeding analysis requires 0.3 hour.

Suggested Suppliers

C.I.Analytics, 2085 Industrial Blvd., Chambly, Quebec, Canada J3L 4C5 (450-658-4965)
www.cianalytics.com

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

Matheson Tri-Gas, 166 Keystone Drive, Montgomeryville, PA 18936 (215-648-4000)
www.mathesontrigas.com

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