



A Honeywell Company

Chloride in LPG and Gaseous Hydrocarbons by Dry Colorimetry

UOP Method 930-07

Scope

This method is for determining the sum of organic chloride and hydrogen chloride (HCl) in liquefied petroleum gas (LPG) and refinery gas streams at concentrations ranging from approximately 0.02 to 1000 mass-ppm (mg/kg) for LPG samples or 0.02 to 1000 ng/mL for gas samples. Other halogens present are determined as chloride.

References

ASTM Practice D 1265, "Sampling Liquefied Petroleum (LP) Gases (Manual Method)," www.astm.org

ASTM Method D 1657, "Density or Relative Density of Light Hydrocarbons by Pressure Hydrometer," www.astm.org

ASTM Method D 2421, "Interconversion of Analysis of C₅ and Lighter Hydrocarbons to Gas-Volume, Liquid-Volume, or Mass Basis," www.astm.org

ASTM Method D 2598, "Calculation of Certain Physical Properties of Liquefied Petroleum (LP) Gases from Compositional Analysis," www.astm.org

ASTM Practice D 3700, "Obtaining LPG Samples Using a Floating Piston Cylinder," www.astm.org

ASTM Practice D 5287, "Automatic Sampling of Gaseous Fuels," www.astm.org

ASTM Method D 6849, "Storage and Use of Liquefied Petroleum Gases (LPG) in Sample Cylinders for LPG Test Methods," www.astm.org

Instrument instruction manual, CI Analytics, PN 2010-CI-man

UOP Method 516, "Sampling of Gasolines, Distillate Fuels and C₃ - C₄ Fractions," www.astm.org

UOP Method 539, "Refinery Gas Analysis by Gas Chromatography," www.astm.org

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

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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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 during which the organic chlorides are converted to HCl. The pyrolysis product is then passed to a detector where the HCl produces a color change on sensitized paper. The measured color change is proportional to the quantity of chloride in the sample. Calibration is by blends for LPG samples and permeation tubes for gas samples.

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), Gas/LPG Introduction Module, and AccuGas Blend Generator (PN 096), C.I. Analytics, Model 2010L

Cylinder, gas sampling, stainless steel, internally coated with Teflon, Siltek, Sulfinert, or other similar inert coating, 500- or 1000-mL, Restek, Cat. No. 24133 or 24144, with valve Cat. No. 24100 and valve with rupture disk Cat. No. 21403, several required

Cylinder, LPG sampling, stainless steel, internally coated with Teflon, Siltek, Sulfinert, or other similar inert coating, 500- or 1000-mL, with outage tube, Restek, Cat. No. 24133 or 24144, with valve with outage tube Cat. No. 21402 (specify %-outage, e.g., 30%) and valve with rupture disk Cat. No. 21403, several required

Fittings, tube, as needed for connecting gases and sample cylinders to instrument, local supply or Swagelok

Gauge, test, pressure, 0 to 2760 kPa gauge (0 to 400 psig), Matheson Tri-Gas, Cat. No. 63-5642

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

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, nitrogen, two-stage, high purity, with stainless steel diaphragm, delivery pressure range 70-1700 kPa (10-250 psi), Matheson Tri-Gas Cat. No. 3126-580, if needed to pressurize an LPG sample

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

Tubing, 316 stainless steel, 3.18-mm OD (1/8-inch) x 2.16-mm ID (0.085-inch), Alltech Associates, Cat. No. 30105

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

Nitrogen, compressed gas, 99.99% minimum purity

Oxygen, compressed gas, 99.99% minimum purity

Calibration blends, certified, LPG, 0.5- and 50-mass-ppm (as chloride) 2-chlorobutane in isobutane, Matheson Tri-Gas. Adjust concentrations and components to fit typical samples.

Reference blank, gas or LPG, less than 10 ppb chloride

Permeation devices, for gas-phase calibration; select one or more from:

1,2-Dichloropropane, C.I. Analytics, Cat. No. PN-per-cl2-003a

1,1,1-Trichloroethane, C.I. Analytics, Cat. No. PN-per-cl2-002a

1,1,2-Trichloroethane, C.I. Analytics, Cat. No. PN-per-cl2-002b

1,1,2-Trichloroethylene, C.I. Analytics, Cat. No. PN-per-cl2-002aa

1,2,3-Trichloropropane, C.I. Analytics, Cat. No. PN-per-cl2-003c

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

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 and Figure 2 shows a diagram of the LPG and gas sampling module. 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 heater 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 the 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.

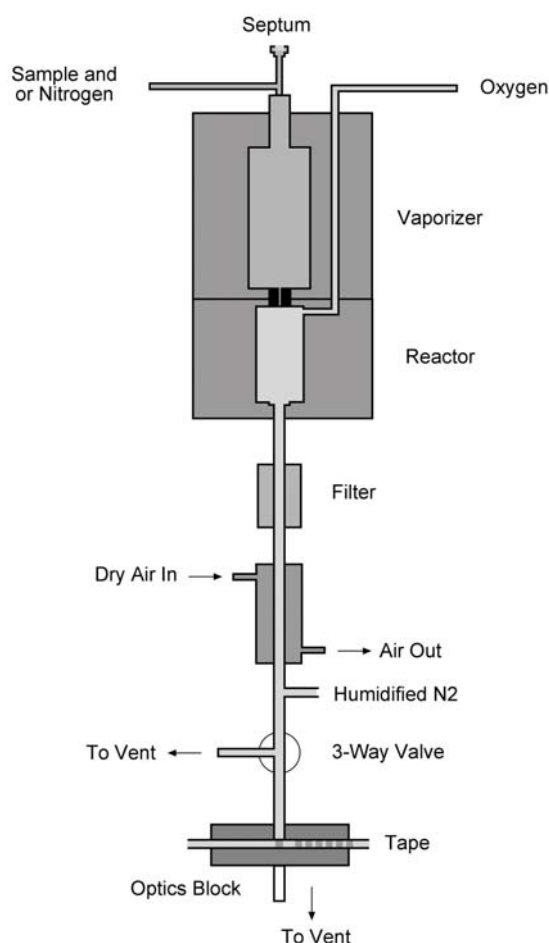


Figure 1
Diagram of Chloride Analyzer

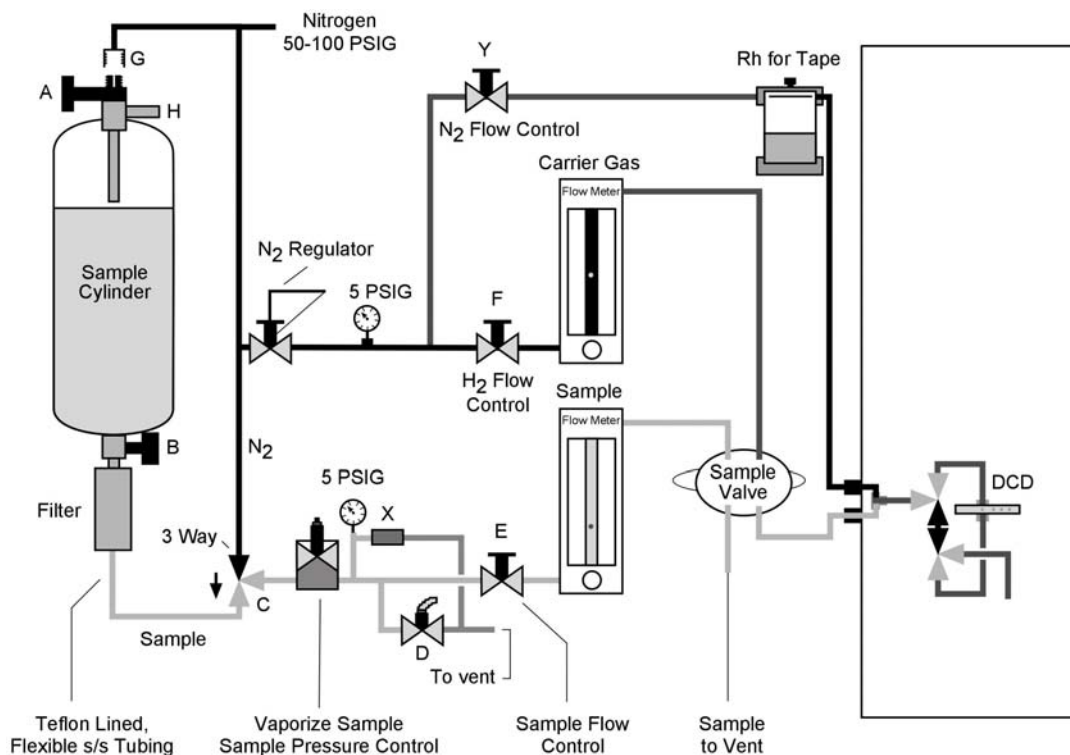


Figure 2
Diagram of LPG Module

Calibration

For gas-phase samples, calibrate using the AccuGas Blend Generator and the permeation devices as described in the instrument manual. For LPG samples, calibrate using the LPG calibration blends 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

Collect the LPG or gas samples in the stainless steel cylinders. For LPG samples follow the procedures as described in ASTM Practice D 1265, "Sampling Liquefied Petroleum (LP) Gases (Manual Method)," ASTM Practice D 3700, "Obtaining LPG Samples Using a Floating Piston Cylinder," or UOP Method 516, "Sampling of Gasolines, Distillate Fuels and C₃ - C₄ Fractions." See also ASTM Method D 6849, "Storage and Use of Liquefied Petroleum Gases (LPG) in Sample Cylinders for LPG Test Methods." For gas samples follow the procedures as described in ASTM Practice D 5287, "Automatic Sampling of Gaseous Fuels," or other reliable technique.

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

Calculations

For gas samples, the instrument is calibrated in mol-ppm using permeation tubes. All calculations are performed by the instrument software and printed out automatically. Report the results to one significant figure below one ng/mL, and to two significant figures at or above one ng/mL.

For LPG samples, the instrument is calibrated in mass-ppm using calibration blends. If the calibration blend is prepared in the same matrix as the sample matrix, all calculations are performed by the instrument software and printed out automatically. If the blend matrix differs from the sample matrix, calculate the density of the Calibration Blend using ASTM Method D 2421, "Inter-conversion of Analysis of C₅ and Lighter Hydrocarbons to Gas-Volume, Liquid-Volume, or Mass Basis," and ASTM Method D 2598, "Calculation of Certain Physical Properties of Liquefied Petroleum (LP) Gases from Compositional Analysis." If the matrix of the sample is known, calculate the density of the sample in the same manner. If the matrix of the sample is unknown, analyze the sample by UOP Method 539, "Refinery Gas Analysis by Gas Chromatography," and then calculate the density of the sample as above. Alternatively, the density of the sample may be determined directly using ASTM Method D 1657, "Density or Relative Density of Light Hydrocarbons by Pressure Hydrometer." Using the densities of the Calibration Blend and the sample, calculate the density correction factor using Equation 1 and enter it into the instrument's computer. Results will print automatically. Report the results to one significant figure below one mass-ppm, and to two significant figures at or above one mass-ppm.

$$\text{Density correction factor} = \frac{D}{S} \quad (1)$$

where:

D = liquid density of the Calibration Blend, g/mL

S = liquid density of the sample, g/mL

Notes

1. 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.
2. Some loss of HCl can occur in the equipment particularly in the presence of water. When the most accurate determination of the HCl is required, a known quantity of the sample is sparged through a known quantity of water to dissolve the HCl quantitatively. The water is injected directly into the instrument for chloride determination.

Precision

Analyses of the samples used for the precision statement were performed by the suggested vendor and another company. The testing protocols of UOP Method 999, concerning the number of analysts and days were not used, but the calculation protocols for UOP Method 999 were used.

Repeatability

Analysts performed replicate analyses as shown in the Table. The precision data are summarized in the Table. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference 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.

Reproducibility

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

Table
Repeatability, Chloride, ng/mL (gas)

<u>Sample</u>	<u>Instrument Number</u>	<u>Number of Days</u>	<u>Number of Replicates per Day</u>	<u>Mean Chloride Concentration</u>	<u>Repeatability</u>	
					<u>Within-Day esd</u>	<u>Allowable Difference</u>
A	4	1	30	0.13	0.006	0.01
B	1	1	10	0.78	0.037	0.08
C	4	1	51	0.88	0.025	0.05
D	1	1	10	0.90	0.050	0.11
E	2	1	20	3.24	0.454	0.95
F	4	1	66	3.73	0.099	0.20
G	1	1	10	4.02	0.125	0.28
H	3	3	5	4.13	0.105	0.29
I	1	2	10	7.44	0.139	0.31
J	2	1	10	14.71	0.183	0.41
K	1	1	10	17.16	0.254	0.58
L	2	1	10	22.56	0.231	0.52
M	2	1	10	45.07	0.555	1.26

Time for Analysis

The elapsed time and labor requirement for one analysis of an LPG or gaseous sample, including calibration, are identical, 1 hour. Each succeeding analysis requires 0.3 hour. An additional 0.5 hour is required for sampling.

Suggested Suppliers

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

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

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

Restek, 110 Benner Circle, Bellefonte, PA 16823 (814-353-1300) www.restek.com

Swagelok Company, 29500 Solon Rd., Solon, OH 44139 (440-248-4600) www.swagelok.com