



A Honeywell Company

Total Chloride in LPG and Gaseous Hydrocarbons by Microcoulometry

UOP Method 910-07

Scope

This method is for determining total chloride in gaseous hydrocarbons or liquefied petroleum gas (LPG) at concentrations ranging from approximately 1 to 1000 ng/mL for gas or mass-ppm ($\mu\text{g/g}$) for LPG. Except for fluoride, other halogens present are calculated as chloride. Chloride cannot be determined quantitatively if sulfur is present at concentrations greater than approximately 1 mass-%, see *Note 1*.

References

Perry's Chemical Engineering Handbook

UOP Method 516, "Sampling of Gasolines, Distillate Fuels and C_3 - C_4 Fractions", www.astm.org

Outline of Method

A commercial microcoulometer is set up according to the manufacturer's specifications. Gaseous and LPG samples are collected in stainless steel cylinders. Measured volumes of the LPG or gaseous samples are analyzed by injecting them into a heated combustion tube containing oxygen blended with argon. The organic halides are converted quantitatively to hydrogen halide, hydrogen oxyhalide, carbon dioxide and water. The gaseous combustion products are passed through a dryer and then pass into a coulometric cell containing a buffer, in which the halide ions are dissolved. The instrument automatically titrates the halide ions to a coulometric endpoint and calculates the number of equivalents of halide in the sample. The halide is reported as the equivalent number of chloride ions, given in nanograms. The concentration of chloride in the sample is then calculated in $\mu\text{g/g}$ for LPG or in ng/mL for gases. Any HCl content is non-quantitative because of losses to the vessel walls, especially in the presence of water, and special care must be exercised to determine the HCl content quantitatively (see *Note 2*).

The other halogens that respond are bromine and iodine. Fluorine does not react with silver so it is not detected. In the case of bromine and iodine, only the HX form titrates with silver, while for chlorine, both HCl and HOCl react with silver. All chlorine is determined, but only approximately 50% of the bromine and iodine is detected. In the chlorine mode, the apparent response to bromine and iodine is

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further reduced to 25 and 15% of the chloride response, respectively, due to the differences in their atomic weights.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. Additional items may be required depending on the specific instrument used.

Bottle, Teflon, 1000-mL, Fisher Scientific, Cat. No. 02-923-30D

Cylinder, graduated, 500-mL, borosilicate glass, Fisher Scientific, Cat. No. 08-552-4E

Flask, Erlenmeyer, 1000-mL, borosilicate glass, Fisher Scientific, Cat. No. 10-041C

Flowmeter, digital, soap film, range 0.50- to 500-mL/min, Alltech Associates, Cat. No. 4068

Gauge, pressure, 0 to 2760 kPa gauge (0 to 400 psig), Matheson Tri-Gas, Cat. No. 63-2242

Microcoulometer, with attached furnace, cell, gas/LPG module, controls and computer; a printer is optional, but recommended, Mitsubishi TCL-100 (Cosa Instruments), Thermo ECS-3000, or Analytik Jena Multi EA 3100. A Dohrmann MCTS-120, no longer manufactured, may also be used. Follow the manufacturer's recommendations for maintaining a supply of spare parts and consumables.

Regulator, argon, 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 35-2400 kPa (5-350 psi), Matheson Tri-Gas, Cat. No. 3128-580, only needed for analysis of LPG

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. 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.

Argon, compressed gas, 99.99% minimum purity

2-Chlorobutane in isobutane, (LPG and Gas Reference Standard, see *Note 3*). Liquefied Petroleum Gas and Gas Reference Standards are available by special order from most gas suppliers. Request preparation on a mass/mass basis at a concentration similar to that expected for the sample of LPG or on a nominal volume/volume basis at a concentration similar to that expected for the sample of gas. In addition, request that the LPG cylinder be supplied with a full length dip tube to deliver the liquefied gas from the bottom of the cylinder and under ~250 psig (1750 kPa) of nitrogen pressure. This will keep the LPG liquefied for instrumental loop-sampling, free of bubbles. The material is certified by the supplier to be stable for at least six months. Matheson Tri-Gas or local supply.

Inorganic chloride standard (NaCl or HCl Solution), prepared to meet manufacturer's recommendations, if needed

Isobutane, (LPG and Gas Blank). Liquefied Petroleum Gas and Gas Reference Blanks are available on special order from a gas supplier and should be ordered when the Reference Standards are

ordered. Request that the LPG cylinder be supplied with a full length dip tube to deliver the liquefied gas from the bottom of the cylinder and under ~250 psig (1750 kPa) of nitrogen pressure. This will keep the LPG liquefied for instrumental loop-sampling, free of bubbles. Matheson Tri-Gas or local supply.

Leak detector, liquid solution, Matheson Tri-Gas, Cat. No. BUBL-01

Nitrogen, compressed gas, 99.98% minimum purity, only needed for analysis of LPG

Oxygen, compressed gas, 99.98% minimum purity

Quartz combustion tube, replacement, as supplied for the instrument used

Sulfuric acid, concentrated, Fisher Scientific, Cat. No. A300-212

Sulfuric acid, 90%, for drying combustion exit gases. Pour 50 mL of water into a 1000-mL Erlenmeyer flask cooled in an ice bath. Slowly and carefully add, from a 500-mL graduated cylinder, 450 mL of concentrated sulfuric acid, mix, allow to cool to ambient temperature, and store in a stoppered or capped, air-tight, glass or Teflon bottle.

Calibration of Apparatus

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

Set up the instrument according to the instrument manufacturer's instructions and perform any required tests prior to calibrating and analyzing samples (see the instrument manual for any instructions). See the *Figure* for an example of a setup. Alternative configurations, as recommended by the manufacturer of the microcoulometer, may be used.

The instrument should be calibrated using standards made from an appropriate matrix (LPG calibration should use LPG standards; gas calibration should use gas phase standards). The best calibration is obtained when multiple standard injections are used to build a calibration line. This can be obtained by using standards of varying concentrations or by using multiple injections of a single standard, for example calibrating with 1, 2 and 4 injections of a standard. If the sample is analyzed with 2 injections, then the calibrated range is half the standard concentration to twice the standard concentration. This process can be extended to more than 4 injections if needed, but the injection volume of a single portion of LPG into the combustion tube should be 25 μ L or less.

Some instrument software may use only single or two point calibrations. The blank is assumed to be zero for the single point calibration. This calibration mode can be used for LPG samples above 10 mass-ppm and gas samples above 10 ng/mL where the blank is insignificant. The two point calibration uses both a solvent blank and a standard to generate a linear calibration curve. This curve is useful for LPG samples at or below 10 mass-ppm and gas samples at or below 10 ng/mL where the blank is significant. The level where the blank becomes significant depends on such factors as the system condition, inlet mode, gas purity used and accuracy desired.

Calibration for LPG Samples

1. Select calibration standard that covers the range expected in the sample(s). A stainless steel loop of 10 to 25 μ L is used for LPG samples.
 - Multiple injections of a single standard can be used to extend the range of calibration (for single point calibration) or to build a linear calibration with a single LPG standard.
 - The LPG reference standard concentration can be converted from μ g Cl/g (mass-ppm) to μ g Cl/mL by multiplying by the density (g/mL) (Table 1 and *Note 3*) of the liquefied LPG.

2. Assemble the instrument and LPG sampling system according to manufacturer instructions. Replace the coulometric cell solution and sulfuric acid scrubber solution each day the instrument is used. Start the flow of oxygen and argon through the instrument.
3. Allow the instrument sufficient time to stabilize before beginning the calibration.
4. Connect the LPG reference standard cylinder to the Gas/LPG module.
 - It is important to sample the LPG in a liquid state. To keep it as a liquid, the LPG cylinder must be sampled from the bottom and at an elevated pressure. This pressure may be applied by an internal or external high pressure gas source ~[1750 kPa gauge (~250 psig) of nitrogen].
5. Close the needle valve used to control sample flow through the LPG sampling module.
6. Open the LPG cylinder valve slowly to allow the sample into the inlet module. Use a leak checking solution to check the system for leaks.
7. Watch the viewer located behind the window on the front of the Gas/LPG module. Slowly open the needle valve just enough so that the LPG sample flows continuously through the sample loop, up the viewer tube and out to vent.
 - Be sure that the sample moves at such a speed that no bubbles are visible in the viewer.
8. Let the LPG sample flow through the system for one minute.
9. Start the analysis in the instrument software. Turn the valve to inject LPG into the combustion tube. Wait until the analysis has completed before proceeding to Step 10.
 - If multiple injections of the standard will be done, wait until the flame stops, then refill the loop and repeat the injection.
 - For a system blank measurement, do not inject during data collection. If an LPG blank has been obtained, inject the volume (number of injections) which will be used for the sample.
10. Repeat the analysis of the standard until the average from the last three injections is within 5% of the certified value and the relative standard deviation is within 5% (for single point calibration) or until enough different sample concentrations/volumes have been run to create the calibration line.
 - Experience has shown that, especially on low Cl concentrations, it takes 3 repeat injections before the analysis is reliable, so that only injection Nos. 3, 4 and 5 can be used to average the results with acceptable precision.
11. Depending on the instrument model and software, either the instrument will calculate the calibration or provide the ng of Cl measured for use externally.
12. Proceed as described for the *Analysis of LPG*, under *Procedure*.

Calibration for Gas Samples

The use of a gas standard is the most accurate means of analysis of gas samples. The gas standard is passed through the gas port of the Gas/LPG module. A glass or stainless steel loop ranging from 5 to 20 mL is used for gas samples.

1. Select a calibration standard that covers the range expected in the sample(s).
 - The gas calibration standard concentration can be converted from vol-ppm to ng/mL, see *Note 4*.
2. Assemble the instrument and gas sampling system according to manufacturer instructions. Replace the coulometric cell solution and sulfuric acid scrubber solution each day the instrument is used. Start the flow of oxygen and argon through the instrument.
3. Allow the instrument sufficient time to stabilize before beginning the calibration.

4. Connect the gas reference standard cylinder to the Gas/LPG-module.
5. Close the valve used to control sample flow through the gas sampling module.
6. Open the gas cylinder valve slowly to allow the sample into the inlet module. Use a leak checking solution to check the system for leaks.
7. Open fully the gas flow valve. If the gas sampling module has a ball flowmeter, the ball in the flowmeter should be halfway up the scale. Allow the gas to purge through the port for about 1 minute.
8. Close the valve on the sample cylinder or gas line and allow the ball in the flowmeter to drop to zero. Wait 20 seconds.
 - This is done in order to allow the gas sample to equilibrate to atmospheric pressure.
9. Start the analysis using the instrument software. Inject the sample into the combustion tube. Wait until the analysis has completed before proceeding to Step 10.
 - For a system blank measurement, do not inject during data collection. If an LPG blank has been obtained, inject the volume (number of injections) which will be used for the sample.
10. Repeat the analysis of the standard until the average from the last three injections is within 5% of the certified value and the relative standard deviation is within 5% (for single point calibration) or until enough different sample concentrations/volumes have been run to create the calibration line.
 - Experience has shown that, especially on low CI concentrations, it takes 3 repeat injections before the analysis is reliable, so that only injection Nos. 3, 4 and 5 can be used to average the results with acceptable precision.
11. Depending on the instrument model and software, either the instrument will calculate the calibration or provide the ng of CI measured for use externally.
12. Proceed as described for the *Analysis of Gas Sample*, under *Procedure*.

Procedure

Analysis of LPG Samples

1. Collect the LPG sample in an appropriate stainless steel cylinder as described in UOP Method 516.
2. Calibrate the instrument as described above with *Calibration for LPG Samples*.
3. Proceed, following Steps 4 - 10 only of *Calibration for LPG Samples*, for the analysis of an LPG sample.

Analysis of Gas Sample

1. Collect the gas sample in an appropriate stainless steel cylinder as described in UOP Method 516.
2. Calibrate the instrument as described above with *Calibration for Gas Samples*.
3. Proceed, following Steps 4 - 10 only of *Calibration for Gas Samples*, for the analysis of an LPG sample.

Calculations

LPG Samples

Calculate the concentration of chloride in the LPG sample in $\mu\text{g/g}$, equivalent to ng/mg (mass-ppm), to two significant figures at or above $10 \mu\text{g/g}$, or one significant figure below $10 \mu\text{g/g}$, using Equation 1.

$$L = \frac{M}{DNV} \quad (1)$$

where:

D = density of the LPG (see Table 1 and *Note 3*), $\text{mg}/\mu\text{L}$

L = concentration of chloride in the LPG, $\mu\text{g/g}$

M = chloride detected by the coulometer, ng

V = volume of the sample loop, μL

N = number of injections of the sample (if multiple injections are not done, then **N** = 1)

Table 1

Pure Component LPG Densities at Selected Temperatures, see Note 3

<u>Temperature</u>	<u>Propane Density,</u> <u>mg/μL</u>	<u>Butane Density,</u> <u>mg/μL</u>	<u>Isobutane Density,</u> <u>mg/μL</u>
15°C	0.5065	0.5847	--
20°C	0.4989	0.5788	0.557
25°C	0.4911	0.5730	0.5510

Gas Samples

Calculate the concentration of chloride in the gas sample at 0°C in ng/mL (mass-volume) to two significant figures at or above 10 ng/mL , or one significant figure below 10 ng/mL , using Equation 2.

$$G = \frac{M(T + 273)}{273NS} \quad (2)$$

where:

G = concentration of chloride in the sample at 0°C , at atmospheric pressure, ng/mL (see *Note 5*)

M, N = previously defined, Equation 1

S = volume of the gas sample injected (sample loop size) at atmospheric pressure

T = temperature of the gas sample at atmospheric pressure, $^\circ\text{C}$

273 = factor to convert **T** to the absolute scale

Notes

1. Sulfur at concentrations greater than approximately 1% is converted to oxides and then dissolves in the coulometer cell. Partial coulometric titration of the resulting oxy-acids interferes with the quantitative measurement of chloride.
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 coulometer cell for chloride determination.

3. The densities cited in Table 1 are for pure propane-LPG, pure butane-LPG, and pure isobutane-LPG. An average density can be calculated for known mixtures of the two gases if necessary. Densities of other gases at other temperatures can be calculated as shown in Perry's Chemical Engineering Handbook.
4. An estimate of the gas calibration standard concentration in ng/mL can be obtained from volume-ppm gas calibration standard concentration using Equation 3:

$$E = \frac{273(35.453)F}{22.414(H + 273)} \quad (3)$$

where:

E = chloride concentration of gas calibration standard at room temperature, µg/mL

F = chloride concentration of gas calibration standard, volume-ppm

H = temperature of gas calibration standard, °C

273 = factor to convert temperature to absolute scale

35.453 = atomic mass of chlorine, g/mole

22.414 = molar volume of ideal gas at 0°C and 1 Atm., L/mole

5. For gas samples, the concentration of chloride in g/g can be calculated from the gas density at 0°C and 1 atmosphere, if desired. The varied composition of the gas analyzed by the method makes it impractical to provide such density data for a specific gas in the method.
6. Commercial LPG sampling apparatus incorporating a stainless steel multiport valve may cause potential chloride losses.
7. If the combustion tube, sulfuric acid scrubber or coulometric cell become coked during the injection and combustion of a sample, they must be removed and cleaned.

Precision

The precision statements were determined using UOP Method 999.

Repeatability and Intermediate Precision

For LPG samples, a nested design was carried out for determining µg/g (mass-ppm) chloride with one analyst in one laboratory. The analyst carried out four tests on each of two samples on two separate days. The total number of tests for each sample was eight.

For gas phase samples, a nested design was carried out for determining µg/mL chloride with two analysts in one laboratory. Each analyst carried out two tests on each of two samples on two separate days. The total number of tests for each sample was eight.

Using a stepwise analysis of variance procedure, the within-day estimated standard deviation (esd) was calculated for each concentration and is listed in Tables 2 and 3. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference shown in Tables 2 and 3 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 Table 3 with 95% confidence.

The data in Tables 2 and 3 are 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 2
Repeatability, LPG, $\mu\text{g/g}$ chloride

<u>Sample</u>	<u>Mean</u>	<u>Repeatability</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>
Organic chloride in hydrocarbon	4	0.1	0.3
Organic chloride in hydrocarbon	347	1.5	5

Table 3
Repeatability and Intermediate Precision, gas, $\mu\text{g/mL}$ chloride

<u>Sample</u>	<u>Mean</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>
Organic chloride in hydrocarbon	8	0.2	0.7	0.4	3
HCl in nitrogen	11	0.6	2	0.7	3

Time for Analysis

The elapsed time and labor requirement for one analysis of an LPG or gaseous sample, including calibration, are identical, 2 hours. Each succeeding analysis requires 0.75 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

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

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

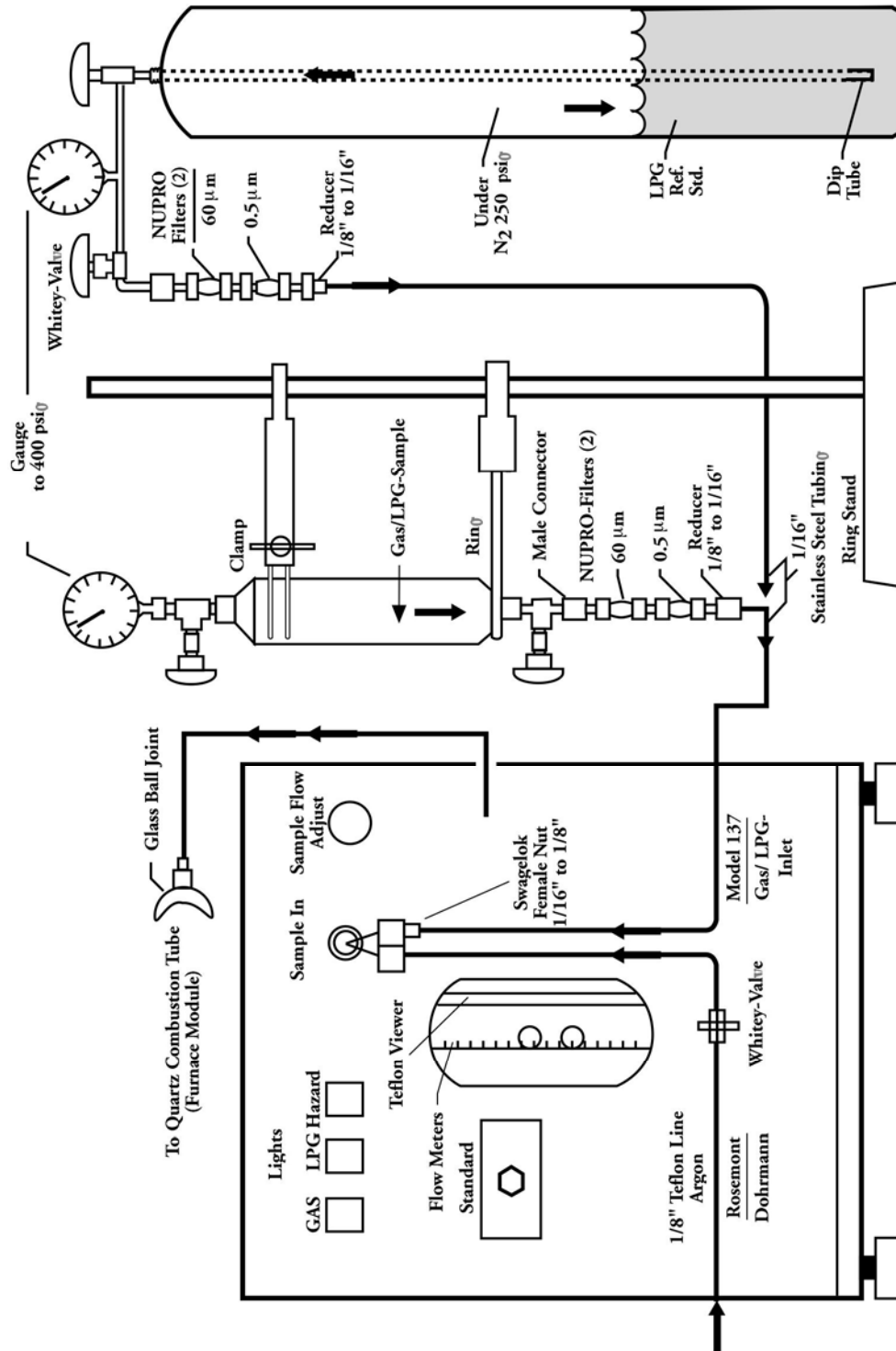


Figure
Example of a Gas/LPG-Sampling Assembly

UOP Method 910