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 (µg/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 µg/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

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 µL 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 µL 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 µg Cl/g (mass-ppm) to µg Cl/mL by multiplying by the density (g/mL) (Table 1 and *Note 3*) of the liquefied LPG.