



A Honeywell Company

Chloride and Fluoride in Liquefied Petroleum Gases (LPG) by Combustion Ion Chromatography (CIC)

UOP Method 1001-14

Scope

This method is for determining trace concentrations of chloride and fluoride in liquefied petroleum gases (LPGs) by Combustion Ion Chromatography (CIC). This method has a range of quantitation from 1 to 1500 mg/kg (mass-ppm) for fluoride and chloride.

References

Instruction Manual for Automatic Quick Furnace, Model AQF-2100H, www.cosa-instrument.com

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

Outline of Method

A reproducible volume of a liquefied petroleum gas sample is introduced into a multi-position horizontal furnace under controlled temperature and moisture. The sample is then combusted in a pyrohydrolytic, oxygen enriched environment. The halogens in the sample are converted to hydrogen halides and halogen gas. These gases are then absorbed into a solution of constant volume. An aliquot of the solution is injected into an ion chromatograph (IC) where chloride and fluoride are separated by anion exchange and measured by a conductivity detector with ion suppression. External standards are used for quantitation.

Apparatus

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

Chromatographic column, IonPac AS11-HC Analytical, 250-mm length by 4-mm ID, Dionex, Thermo Fisher, Cat. No. 052960

Combustion system, AQF-2100H, equipped with HF-210 horizontal furnace, GA-210 gas adsorption unit, ABC-210 Automatic Boat Controller, ASC-250L Liquid Autosampler, GI-240 Gas Injection Box, and AQF Software, COSA Instrument Corp. Newer models from the same manufacturer are also expected to be suitable.

Deionized water system, Nanopure Water Purification System with Total Organic Carbon Analyzer, Thermo Scientific, VWR, Cat. No. 47729-610

<p>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. SAFETY DATA SHEETS (SDS) OR EXPERIMENTAL SAFETY DATA SHEETS (ESDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).</p>

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Ion chromatograph, equipped with a pump, injection valve/autosampler, eluent generator, continuously regenerated trap column, suppressor, conductivity detector, computer, and Chromeleon software, Dionex, Thermo Fisher, Model ICS-2100

Muffle furnace, compact benchtop, capable of operation at 800 °C, Barnstead/ThermoLyne, VWR, Cat. No. 30631-230

Refrigerator, laboratory, explosion proof or flammable storage, Fisher Scientific, Cat. No. 97-950

Regulator, argon, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-580

Regulator, oxygen, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), cleaned for oxygen service, Matheson Tri-Gas, Model 3810-540

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 and distilled water that is subsequently treated to produce ionically pure, 18.2 megaohm-cm, organic-free, water.

Adsorption tube, 10-mL, COSA Instrument Corp., Cat. No. MC25000 (replacement)

Argon, 99.999% pure, local supply

Ball joint with U-shaped tube, COSA Instrument Corp., Cat. No. MC28017 (replacement)

Calibration standard blends, LPG, dichlorodifluoromethane (5, 50, 500, and 5000 mg/kg) in isobutene, 10 lbs each, Airgas Specialty Gases, Cat. Nos. X02BI99CLP2C000, X02BI99CLP2C001, X02BI99CLP2C002, X02BI99CLP2C003, respectively

Nitrogen, 99.99% pure, local supply

Oxygen, 99.999% pure, local supply

Pipet, Pasteur, disposable, borosilicate glass, 146-mm length, Fisher Scientific, Cat. No. 13-678-20A

Potassium hydroxide cartridge, RFIC EluGen, EGC II KOH, Dionex, Thermo Fisher, Cat. No. 058900

Pyrohydrolysis tube, inner and outer, COSA Instrument Corp., Cat. Nos. AQ3QP (inner w/ flange joint), FN2QPG (outer), replacement set MC28002

Quartz wool, fine grade, 10 g, COSA Instrument Corp., Cat. No. MC06175

Septum, sample injection, for use with Automatic Boat Controller, COSA Instrument Corp., Cat. No. MC15652

Toluene, B&J Brand, >99.8%, VWR, Cat. No. BJ347

Water, deionized, subsequently treated with a Thermo Scientific Nanopure Water Purification Systems with Total Organic Carbon Analyzer to produce ionically pure, 18.2 megaohm-cm, organic-free, VWR, Cat. No. 47729-610

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of CIC, and the equipment being used, especially LPG cylinders. Dispose of all supplies and samples in an environmentally safe manner according to applicable regulations.

Preparation of Instrument

The specifics of this procedure are written for the COSA AQF-2100H combustion system with GI-240 Gas Injection Box. The procedure using a later model from COSA Instrument or alternative instrumentation would be similar. Follow the instructions provided with the instrumentation being used.

Combustion Preparation

1. Assemble and test all combustion system components as per the manufacturer's specifications.
2. Insert quartz wool in the end of the pyrolysis tube before inserting into the furnace. Do not connect ball joint from GA-210 to AQF-2100H.
 - The quartz wool should fill 3-4 mm from the ball joint end of the pyrolysis tube
 - The wool is used as a filter to prevent coke from entering the adsorption unit
 - The wool in the pyrolysis tube will become powdery and/or brittle over time. Replace wool if this occurs
 - Inspect pyrolysis tube for devitrification. White discoloration would be signs of devitrification on the pyrolysis tube. These areas will become brittle, crack and cause mechanical failure. If devitrification has occurred, look for cracks in the devitrified area. Replace tube if there are any signs of cracks in the inspected area.
 - Refer to section 6-1-2 of the HF-210 manual for a list of periodic maintenance checks.
3. Turn on all modules and gases. Turn on the furnace heater. Use the operating conditions listed in Table 1.

Table 1
HF-210 Parameters

Inlet temperature	730 °C
Outlet temperature	1050 °C
Argon GI-240 flow rate	100 mL/min
Argon flow rate	100 mL/min
Oxygen flow rate	400 mL/min
Argon replace time	30 seconds
Valve sel. ON time	1 second
Ar→O₂ valve sel. time	10 seconds
O₂→Ar valve sel. time	10 seconds

4. Log into AQF software and connect to the modules needed for operation.
 - a. ABC-210, GA-210, PC

These modules are used for analysis of samples and standards using the *LPG Injection* procedure.
5. When the set temperature is reached, a pop-up window on the AQF software will notify the analyst to turn on the water pump. Set the water flow rate to 4 for analysis.
6. Select the LPG burn program (see *Appendix*).
7. Connect ball joint from GA-210 to AQF-2100H.

Chromatography Preparation

1. Assemble and test all ion chromatographic system (IC) components per the manufacturer's specifications.
2. Install the analytical column and suppressor (configured in recycle mode).