



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

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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. AQ3QPN (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).

3. Turn on IC and set it to the recommended chromatographic conditions in Table 2.

Table 2 Recommended Chromatographic Conditions	
Analytical column	Dionex IonPac AS11-HC
Suppressor	Dionex ASRS 300(4-mm)
Suppressor current	81 mA
Mobile phase	27 mM KOH
Mobile phase flow rate	1.2 mL/min
Column temperature	30 °C
Background	<1 µS
Analysis time	12 minutes
Injection loop	25 µL

4. Allow the IC to equilibrate. Typical background conductivity should be at or below 1 µS.
 - Change the source of deionized water or check the functionality of the suppressor if the background conductivity is above 1 µS.

Communication Between IC and AQF Software

The AQF and Chromeleon software do not directly communicate with each other. The AQF software initiates the injection into the IC by timed events. Set the time equal to or greater than the IC analysis time in the analysis parameters tab in the AQF software. This will ensure that there will not be an injection into the IC while the instrument is running a sample. A contact closure is set up to relay the signal to the IC to start each sample run once the combustion apparatus fills the sample loop. These connections are made during installation.

Operating Conditions

Table 1 summarizes the AQF parameters for analysis. These conditions should not be changed. See the *Appendix* for method editing for combustion programs.

Table 2 summarizes the recommended chromatographic operating conditions for the convenience of the method user. Other conditions may be used, provided they produce the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatogram (see Figure).

Calibration

Calibration factors are required that relate to the instrument response for each analyte. Detector response is measured in microsiemens (µS) units of conductivity. It is proportional to the ionic concentration and the inherent mobility of each analyte type present when measured by the conductivity detector. External standard calibration with a linear curve fit is performed using purchased pre-made blends. Calibrate the instrument with calibration standards each day samples are to be analyzed. Do not use standards that are older than the certified date listed on the cylinders.

Constant Volume Function

The GA-210 uses a liquid level sensor in order to provide an adsorption solution of constant volume. For 1 to 1500 mg/kg samples in a 10-mL capacity adsorption tube, set the liquid volume sensor to low and the adsorption solution volume to 5 mL.

- For higher concentration samples, it may be necessary to change to the 20 mL adsorption tube, raise the liquid level sensor and increase the adsorption solution volume.

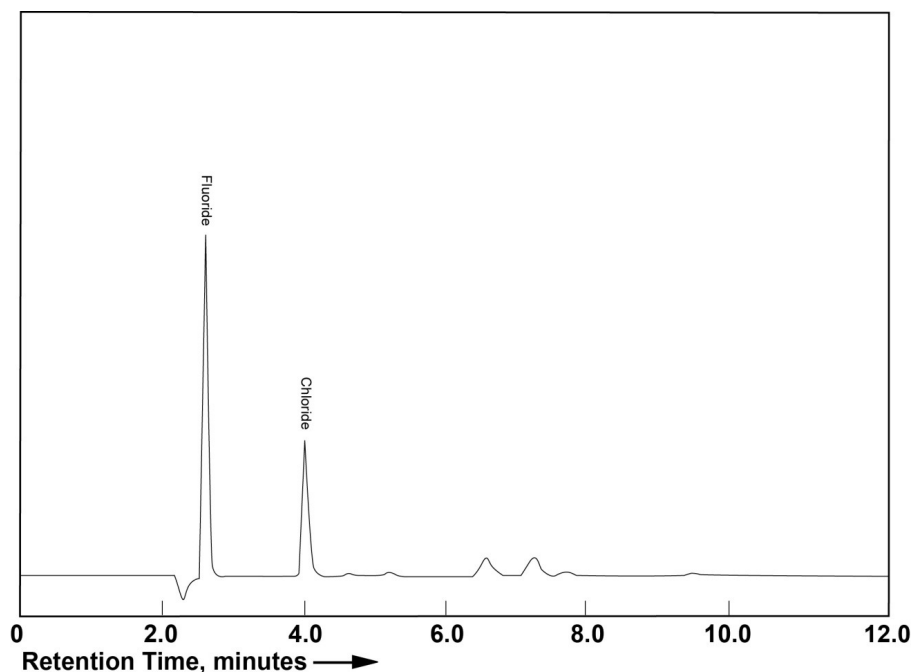


Figure
Typical Chromatogram

Preparation of Standards

Pre-made individual blended cylinders may be purchased from Airgas Speciality Gases or other appropriate suppliers. Standards must bracket the sample concentration range. These standards have concentrations listed as the component, not by chloride or fluoride level. The actual analyte concentrations are determined in *Calculations*.

Analysis of Calibration Standard

1. Secure the calibration standard.
2. Connect the standard to the GI-240 Gas Box.
3. Set the Carrier switch to LPG and ensure the carrier flow is 100 mL/min.
4. Set the Sampling Valve to Load Position.
5. Set the Purge Valve on the Gas Box to the Open Position and open the calibration standard cylinder to allow the sample to fill the lines.
6. Check all lines and connections from the calibration standard to the GI-240 for leaks.
7. Purge the LPG liquid through the sight glass and sample valve at a slow rate until air bubbles are no longer seen in the sight glass.
8. Set the Purge Valve to the Closed Position and block in the sample.
9. Set the Sampling Valve to the Inject Position. A bright white light will appear in the pyrohydrolysis tube when the sample begins to volatilize.
 - Cumulative multiple injections in the absorption solution increase the effective concentration of the analytes of interest. For low concentrations, it may be required to run three cumulative injections to increase the response of fluoride and chloride. For high concentrations, a single injection is sufficient.

10. Press the Start button in the AQF software once the combustion is complete.. The combustion program will cycle through the injection process in the GA-210 which is around 90 seconds. Once the program is complete, the GA-210 will inject and start the IC.
 - Combustion is complete once the bright white light from volatilization dims in the pyrohydrolysis tube.
11. Reset the Sampling Valve to the Load Position.
12. Close the calibration standard cylinder.
13. Set the Purge Valve to the Open Position to clear the lines of sample and pressure.
14. Once the sight glass is clear, Set the Purge Valve to the Closed Position and disconnect the calibration standard.
15. Identify and integrate each peak for the calibration standards. Identification can be aided by comparing to the typical standard chromatogram (see Figure).
16. Calculate the response factor for each analyte using the chromatography software or Equation 3 in *Calculations*.
17. Repeat Steps 1 through 15 with the other calibration standard cylinders.

Sample Analysis

1. Prepare the LPG sample you wish to analyze.
2. Pressurize the cylinder to 1700 kPa (250 psig) with high purity nitrogen.
 - Confirm that the sample container can handle the desired pressure, prior to pressurizing
 - Confirm that the cylinder is not liquid full by venting a small amount of the contents into a laboratory fume hood
3. Secure the LPG cylinder.
4. Connect the sample to the GI-240 Gas Box.
5. Set the Carrier Valve to LPG and set the carrier flow to 100 mL/min.
6. Set the Sampling Valve to the Load Position.
7. Set the Purge Valve to the Open Position and open the LPG cylinder allowing the sample to fill the lines.
8. Check all lines and connections from the cylinder to the GI-240 for leaks.
9. Purge the LPG liquid through the sight glass and sample valve at a slow rate until air bubbles are no longer seen in the sight glass.
10. Set the Sampling Valve to the Inject Position. A bright white light will appear in the pyrohydrolysis tube when the sample begins to volatilize.
 - If accumulated injections were run on the standards, the exact same number of accumulated injections must be run on the samples, for example if injections were made for the calibration standards, then three injections are required for the samples.
11. Press the Start button in the AQF software once the combustion is complete.. The combustion program will cycle through the injection process in the GA-210 which is around 90 seconds. Once the program is complete, the GA-210 will inject and start the IC.
 - Combustion is complete once the bright white light from volatilization dims in the pyrohydrolysis tube.

12. Reset the Sampling Valve to the Load Position.
13. Close the LPG cylinder.
14. Set the Purge Valve to the Open Position to clear the lines of sample and pressure.
15. Once the sight glass is clear, set the Purge Valve to the Closed Position and disconnect the LPG cylinder.
16. Identify each analyte by retention time (see Figure). Integrate the analyte peaks of interest to calculate area response.
17. If the areas obtained for any of the analytes are above the highest standard, obtain a higher calibration standard. Repeat Steps 1 through 16 of *Analysis of Calibration Standards* for the calibration standard.

Calculations

All calculations are performed by the instrument software using a linear curve fit. Results are displayed and printed in mass-ppm (mg/kg). The calculations below are included for information and for single point manual calculation, if desired.

Convert the component concentrations in the calibration standards to chloride and fluoride analyte concentrations using Equation 1:

$$C = BF \quad (1)$$

where:

B = concentration of dichlorodifluoromethane in each calibration blend, mg/kg

C = concentration of each analyte in each calibration blend, mg/kg

F = mass fraction of analyte in compound, from Table 3

Table 3
Concentration of Analyte in Dichlorodifluoromethane

<u>Analyte</u>	<u>Mass Fraction of Analyte in compound</u>
Fluoride	0.3143
Chloride	0.5864

Calculate the response factor for each analyte in each gas calibration blend to three significant figures using Equation 2.

$$M = \frac{C}{K} \quad (2)$$

where:

C = concentration of each analyte in each calibration blend, mg/kg, from Equation 1

K = analyte response area

M = response factor for each analyte

Calculate each analyte concentration in the sample to the nearest 0.1 mg/kg, not to exceed two significant figures, using Equation 3:

$$\text{Concentration of analyte in the sample, mg/kg} = MN \quad (3)$$

where:

M = response factor for each analyte, from Equation 2

N = area response of analyte in sample

Precision

Precision statements were determined using UOP Method 999, "Precision Statements in UOP Methods."

Repeatability and Site Precision

A nested design was carried out for determining halogens in liquid organics by two analysts, with each analyst performing analyses on three samples on two separate days, performing two analyses each day for a total of 24 analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in Table 4. 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 Table 4 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 Table 4 with 95% confidence.

Table 4
Repeatability and Site Precision, mg/kg

<u>Component</u>	<u>Mean</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>
Chloride	2.3	0.07	0.3	0.18	0.8
Chloride	9.6	0.15	0.6	0.19	0.8
Chloride	27.2	0.12	0.5	0.17	0.7
Fluoride	1.3	0.19	0.7	0.23	0.9
Fluoride	14.7	0.58	2.3	0.59	2.3

The data in Table 4 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 for the preparation and analysis of one sample is 2 hours. The labor requirement is 1 hour.

Suggested Suppliers

COSA Instrument Corp., 55 Oak St., Norwood, NJ 07648, USA, 1-201-767-6600, distributor for Mitsubishi Chemical Analytech 370 Enzo, Chigasaki, Kanagawa Pref., 253-0084, Japan, +81-467-86-3864, www.cosa-instrument.com

Dionex, Thermo Fisher Scientific Inc. 81 Wyman Street, Waltham, MA 02454, USA, 1-781-622-1000, www.thermoscientific.com

Fisher Scientific, 300 Industry Dr., Pittsburgh, PA 15275, USA, 1-412-490-8300, www.fishersci.com

Matheson Tri-Gas, 166 Keystone Drive, Montgomeryville, PA 18936, USA, 1-215-641-2700, www.mathesontrigas.com

Sigma-Aldrich, 3050 Spruce St., St. Louis, MO 63103, USA, 1-314-771-5765, www.sigma-aldrich.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380, USA, 1-610-431-1700, www.vwr.com

Appendix Combustion Methods

The correct combustion program is needed to prevent coking in the combustion furnace and adsorption unit. Use Table A1 as a reference to start the process of identifying the appropriate combustion program for analysis. Do not carry over combustion programs from older instruments as small differences in pyrolysis tube length and quick furnace insulation have a great effect on combustion programs. Refer to the ABC-210 Manual, Section 4-1, for further assistance.

Table A1
Combustion Programs, Showing Time in Seconds

<u>Program</u>	<u>End Time</u>	<u>Cool Time</u>	<u>Boat Speed</u>	<u>Home Time</u>	<u>Ar Time</u>	<u>O₂ Time</u>
LPG	30	30	30	30	999	0

A flash of light coming from the combustion of the sample should begin within 30 seconds of rotating the valve to the inject position. After a gradual brightening and dimming, begin the burn program. A very intense and fast flash of light could lead to coking. If coking does occur during analysis, abort the run per manufacturer's instructions. Turn off all gases and modules. Once the furnace is at ambient temperature, disconnect the contaminated glassware and clean with toluene. Bake glassware in a furnace for approximately 1-2 hours. All quartz glassware can be baked at 800 °C. All other standard glassware should be baked at a maximum of 400 °C.