

FLUORINE IN LIQUID HYDROCARBONS AND LPG BY OXIDATIVE COMBUSTION WITH ION-SELECTIVE ELECTRODE DETECTION

UOP Method 975-02

SCOPE

This method is for determining total fluorine in liquid hydrocarbons or liquefied petroleum gas (LPG) using the Antek 9000F analyzer. It is applicable to liquid hydrocarbons with fluorine levels of 1 to 500 ng/ μ L (m/v-ppm) with appropriate calibration standards. Higher concentrations can be analyzed by dilution in a solvent such as isooctane or toluene. The fluorine concentration in LPG can be measured down to 0.5 ng/ μ L. This method is an alternative to UOP Method 619, which uses the potentially troublesome Wickbold combustion apparatus.

OUTLINE OF METHOD

Liquid samples are injected by syringe using an automated syringe drive. LPG is pressurized with nitrogen, or other inert gas, and then sampled with a rotary injection valve. The LPG is pre-vaporized into an argon carrier stream before introduction into the combustion tube. The sample is introduced into a quartz combustion tube that is maintained at 1050°C where it combusts in an argon/oxygen/steam atmosphere. The fluorine is converted to hydrofluoric acid (HF). The carrier gas blend transports the HF to a buffer which traps the fluorine as sodium fluoride for detection. The liquid is cooled and pulled through a flow cell for potentiometric detection by an ion-selective electrode (ISE). Note that the calibrations for liquids and LPG are not interchangeable.

LPG samples should be collected as described in UOP Method 516.

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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APPARATUS

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

In addition to the equipment listed below, the apparatus specified in UOP Method 516 is also required for LPG samples.

Balance, readability 0.1-mg

Fittings and tubing, as needed to connect gas cylinders and LPG sample cylinders

Fluoride analyzer, Antek Instruments, Model 9000F with optional equipment:

Controlled rate syringe drive, Antek Instruments, Model 735

Syringes, 25- μ L gas-tight, Antek Instruments, Hamilton Model 1702

LPG sampling box, Antek Instruments, Model 734

Computer and printer

Regulator, argon, stainless steel, two-stage, high purity, Matheson Gas Products, Model 3810-580

Regulator, nitrogen, stainless steel, two-stage, high purity, Matheson Gas Products, Model 3810-580

Regulator, oxygen, stainless steel, two-stage, high purity, Matheson Gas Products, 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, unless stated otherwise.

In addition to the reagents and materials listed below, the reagents and materials specified in UOP Method 516 are also required for LPG samples.

Argon, UHP, 99.999%, Matheson Gas Products

Fluorine standards, liquid, fluorohexane in isooctane, blank, 1-, 5-, 25-, 50-, 100-, 250-, and 500- μ g/mL, Antek Instruments, Cat. No. 37048. (See Note 1.)

Fluorine standards, LPG, such as fluorohexane or a fluorocarbon refrigerant in *n*-butane. The fluorine content should be appropriate to the range of interest, e.g., 2- and 5- μ g F/g. Matheson Gas Products

Nitrogen, HP, 99.99%, Matheson Gas Products

Oxygen, UHP, 99.98%, Matheson Gas Products

Receiving Solution A, Antek Instruments, Cat. No. 37037

Receiving Solution B, Antek Instruments, Cat. No. 37038

Reference electrode filling solution, Antek Instruments, Cat. No. 37200

Vials, screw cap, Fisher Scientific, Cat. No. 03-343-6B

Water, deionized or distilled

SAMPLING

LPG samples should be collected as described in UOP Method 516. LPG cylinders should be pressurized to 250 psig with an inert gas such as nitrogen or argon before analysis.

PROCEDURE

Instrument Set Up

1. Set up the instrument according to the manufacturer's instructions. Set the combustion furnace temperature to 1050°C. Set the gas and solution flow rates as recommended by the manufacturer. Refill the reference electrode salt bridge with the fill solution provided by the instrument manufacturer.
 - Instrument configurations vary, follow directions specific to your instrument.
2. Allow instrument to stabilize before calibration. Test baseline drift by running blank analysis (no injection) and monitoring the signal.
 - Blank value should be an area of approximately -10 to 50 counts. If the value differs greatly from this range, there is most likely a drifting baseline.

Liquid Calibration

1. Select the appropriate standards for calibration based on range of interest. Set the 9000F software to "Run Calibration" and open or create a calibration file.
 - A four point calibration, including the isooctane blank and 1-, 5- and 25-ng/ μ L fluorine standards, is recommended for low concentration samples. Higher ranges can be covered by using the higher concentration standards.
2. Fill the syringe with the isooctane blank, making sure there are no bubbles in the syringe. Adjust volume in syringe to the 20- μ L mark, and pull back syringe plunger until air can be seen in the syringe body.

3. Place syringe on the controlled rate syringe drive, inserting the syringe needle fully through the septum. Move the push block of the controlled rate syringe drive to just make contact with the syringe plunger without displacing the air bubble in front of the sample.
4. Run the analysis according to the program. Enter a concentration of zero for the blank and set injection volume to 20 μL .
5. Repeat the blank measurement at least two more times.
 - Blank value should be an area of approximately -10 to 50 counts. If the value differs greatly from this range, there is most likely a drifting baseline.
6. Analyze the standards according to the same procedure.
 - The relative standard deviation (RSD) should be < 10% for each standard.
 - Calibrate weekly or as needed when the instrument is in use.
7. Save the calibration file.
 - The calibration line and correlation coefficient are calculated automatically.

Liquid Sample Analysis

1. Set the 9000F software to “Run Samples” and open or create a sample data file.
2. Fill the syringe with the first sample, making sure there are no bubbles in the syringe. Adjust volume in syringe to the 20- μL mark, and pull back syringe plunger until air can be seen in the syringe body.
3. Place syringe on the controlled rate syringe drive, inserting the syringe needle fully through the septum. Move the push block of the controlled rate syringe drive to just make contact with the syringe plunger without displacing the air bubble in front of the sample.
4. Run the analysis according to the program. Enter a sample identification in the worksheet and set injection volume to 20 μL .
 - It is recommended that samples containing less than 10-ppm fluorine be run in duplicate.
5. Repeat Steps 2 through 4 for each additional sample.
6. Save the sample file.
 - Concentration results and average values are calculated automatically by the software.

7. If the result obtained exceeds the calibrated range, weigh an aliquot of the sample, recording the mass to the nearest 0.1 mg. Dilute with an appropriate solvent, such as isooctane or toluene, and record the total mass to the nearest 0.1 mg. Mix thoroughly, and repeat steps 2 through 4 for the diluted sample.
 - The dilution solvent blank value should be determined. Solvent should contain less than 1 ng/μL fluorine.

LPG Calibration

LPG fluorine standards are typically prepared gravimetrically, whereas the analyzer is calibrated in mass/volume units. Convert mass/mass units of the standards to mass/volume units using Eq. 1.

$$V = DS \quad (1)$$

where:

D = density of blend, for *n*-butane, 0.579 g/mL

S = concentration of fluorine in blend, μg /g

V = concentration of fluorine in blend, ng/μL

1. Connect the LPG sampling box (Antek Model 734) to the instrument. Insert the outlet tubing through the septum and approximately 6 cm into the combustion tube. Connect the sample line to the LPG inlet on the front of the box. The liquid vent line must be connected to a suitable exhaust such as a fume hood.
2. Turn on the power to the LPG sampling box and allow the temperature to stabilize at 85°C.
3. Set the 9000F software to “Run Calibration” and open or create a calibration file.
 - An instrument blank and two LPG standards are used to create the calibration curve.
4. Run the analysis according to the program. Without connecting an LPG sample, turn the valve to inject an argon carrier blank.
 - The concentration should be entered as zero and sample volume as 15 μL.
3. Repeat the blank at least two more times.
 - Blank value should be an area of approximately -10 to 50 counts. If the value differs greatly from this range, there is most likely a drifting baseline.
6. Connect the lower value LPG standard. Flush the sample line for at least two minutes before filling loop and injecting.
7. Analyze the standard according to the program directions. Enter the sample concentration as ng/μL for the calibration. The sample volume remains at 15 μL.

8. Repeat the low standard at least twice.
 - The RSD should be < 10%.
9. Repeat Steps 6 through 8 for the high value standard.
10. Save the calibration file. The calibration line and correlation coefficient are calculated automatically.

LPG Sample Analysis

1. Set the 9000F software to “Run Samples” and open or create a sample file.
 - The LPG sampling box should remain connected the entire time the calibration and sample analyses are done.
2. Connect the first sample to the LPG inlet. Allow the sample to flush the sample lines for 5 minutes to remove any residual fluorine compound from the high calibration standard.
 - If the lines are not thoroughly flushed, the first injection of the sample could be much higher than later replicates.
3. Run the analysis according to the program. Enter a sample identification in the worksheet and set injection volume to 15 µL.
 - It is recommended that samples containing less than 5-ppm fluorine be run in duplicate.
4. Repeat Steps 2 and 3 for each additional sample.
5. Save the sample worksheet.
 - Concentration results and average values are calculated automatically by the software.

CALCULATIONS

All calculations, except for any necessary dilutions, are performed by the computer. The fluorine content is reported as ng/µL (m/v-ppm). If the liquid sample was diluted, correct for the dilution using Eq. 2.

$$C = R \left(\frac{T_1}{A_1} \right) \left(\frac{T_2}{A_2} \right) \dots \quad (2)$$

where:

C = concentration of fluorine in the sample, ng/ μ L

R = instrument result for concentration of fluorine in diluted sample, ng/ μ L

A_n = mass of sample aliquot taken, g; n = dilution number

T_n = total mass of aliquot plus diluent, g; n = dilution number

To convert to mass-ppm, divide the instrument result by the sample density as determined by an appropriate method.

For values below 10 ng/ μ L, report to the nearest 0.1 ng/ μ L. For values at or above 10 ng/ μ L, report to the nearest 1 ng/ μ L.

NOTES

1. The liquid standards from Antek are supplied in ampules. The standards should be transferred into screw-cap vials when the ampules are opened. They can be stored for 1 week after opening if stored capped.
2. For long-term storage of the ISE, more than two weeks, follow the supplier's recommendations.

PRECISION

For LPG, calibration standards of 1.99- and 3.29-ng F/ μ L have relative standard deviations of 1-3% and 1-5% respectively. RSD of 5% or less can be achieved as long as there is a stable baseline.

For liquid calibration, the premade Antek isooctane based standards have RSDs of 1-4% at 1 ppm and ~5% at 5 ppm, although less data has been collected for liquids than LPG.

TIME FOR ANALYSIS

The elapsed time for one analysis including calibration is 6 hours. The labor requirement is 2 hours. Additional samples run at the same time add 0.5 hours elapsed time and 0.2 hours of labor.

REFERENCES

UOP Method 516 "Sampling of Gasolines, Distillate Fuels and C₃-C₄ Fractions"

UOP Method 619 "Fluorine in Hydrocarbons by Oxy-hydrogen Combustion"

SUGGESTED SUPPLIERS

Antek Instruments, Inc., 300 Bammel Westfield Rd., Houston, TX 77090-3508 (281-580-0339)
www.antekhou.com

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 (412-562-8300) www.fishersci.com

Matheson Gas Products, 932 Paterson Plank Road, P.O. Box 85, East Rutherford, NJ (201-933-2400) www.mathesontrigas.com