



Standard Test Method for the Approximate Determination of Low Molecular Weight Hydrocarbons in Anhydrous Hydrogen Fluoride¹

This standard is issued under the fixed designation E 1230; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method is applicable for the approximate determination of C1–C6 hydrocarbons in anhydrous hydrogen fluoride (HF) in the range of 0.0001 to 0.1 %.

1.2 The values as stated in SI units are to be regarded as the standard, except in cases where measures for fittings are given and where standard gases are certified in terms of part per million. The values given in parentheses are given for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 8.

2. Referenced Documents

2.1 ASTM Standards:

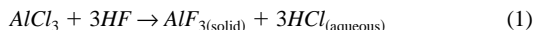
D 1193 Specification for Reagent Water²

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals³

E 260 Practice for Packed Column Gas Chromatography⁴

3. Summary of Test Method

3.1 This test method is designed to measure contaminant hydrocarbons in liquid anhydrous hydrogen fluoride (HF). An anhydrous HF sample is collected in a 10 mL sample cylinder. The cylinder is then attached to a larger cylinder (500 mL) that has been fitted with a septum at one end and contains a solution of aluminum chloride (AlCl_3). The HF sample is allowed to flow into the 500-mL cylinder and mix with the AlCl_3 producing the following reaction.



The hydrocarbons are expelled into the vapor space, and a vapor sample is obtained from the cylinder via the septum by

using a gas tight syringe. The vapor sample is analyzed by gas chromatography using a flame ionization detector (FID). The resulting chromatogram permits qualitative and semi-quantitative determination of the hydrocarbons. A discussion of gas chromatography is presented in Practice E 260.

4. Significance and Use

4.1 Anhydrous HF may be contaminated with low levels of hydrocarbons. This is due in part to the high affinity of hydrocarbons to HF. This test method provides a means for the approximate determination of hydrocarbons in commercial anhydrous HF.

5. Interferences

5.1 The impurities in the aluminum chloride hexahydrate solution, from which the HF precipitates solid AlF_3 , can be a source of interference. Whenever interfering compounds are traced to the neutralizing solution, a new source of aluminum chloride solution should be obtained. This procedure is quantitative as long as the solution interference contributes less than 10 % to the component concentration in the sample.

5.2 Compounds that have little or no response in the flame ionization detector and hence do not interfere are hydrogen sulfide gas (H_2S), sulfur dioxide gas (SO_2), carbon dioxide gas (CO_2), carbon monoxide gas (CO), silicon tetrachloride (SiCl_4), trichlorosilane (SiHCl_3), and silicon tetrafluoride (SiF_4).

6. Apparatus

NOTE 1—All apparatus or equipment used in direct contact with HF must be constructed from stainless steel or materials resistant to HF.

6.1 *Sample Cylinder*, consisting of a 10-mL stainless steel cylinder with 1/8-in. (3.1-mm) female NPT end fittings⁵ to which are attached stainless steel shut-off valves.⁶ The outlet of each valve is a 1/4-in. (6.2-mm) stainless steel Swagelok fitting. (See Fig. 1.)

6.2 *Reaction Cylinder* (Fig. 2), consisting of a 500-mL

¹ This test method is under the jurisdiction of ASTM Committee E-15 on Industrial Chemicals and is the direct responsibility of Subcommittee E 15.51 on Mineral Acids.

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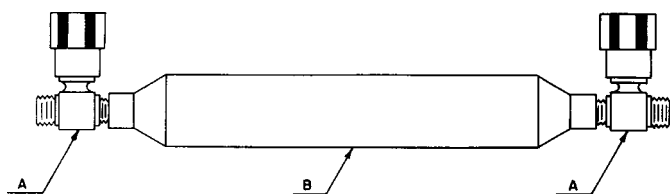
² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 15.05.

⁴ *Annual Book of ASTM Standards*, Vol 14.01.

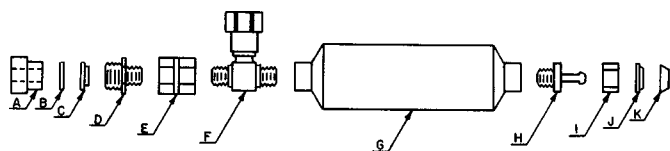
⁵ A sampling cylinder available from Hoke Inc., 1 Tenakill Park, Cresskill, NJ 07626, has been found satisfactory for this purpose. Request Catalogue No. 2HDY10.

⁶ A shut-off valve available from the Whitey Co., 318 Bishop Rd., Highland Heights, OH 44143, has been found satisfactory for this purpose. Request Catalogue No. SS-ODKM2-S4.



CODE	DESCRIPTION
A	1/4" Swagelok X 1/8" NPT Needle Valve
B	10mL Cylinder

FIG. 1 HF Sample Cylinder



CODE	DESCRIPTION
A	Cap
B	12.5mm Septum
C	Back Ferrule
D	1/4" NPT Male Adapter
E	Female Hex Coupling
F	1/4" MNPT Needle Valve
G	500mL TFE Lined Cylinder
H	1/4" NPT Male Tube Connector
I	1/4" Swagelok Nut
J	Back Ferrule
K	Front Ferrule

FIG. 2 Reaction Cylinder

stainless steel (polytetrafluoroethylene) PTFE lined cylinder⁷ with 1/4-in. (6.2-mm) female NPT end fittings at both ends.

6.2.1 The septum assembly attaches to the 500-mL reaction cylinder (Fig. 2) in the following manner: A knurled cap (A) encloses a 12.5-mm septum (B),⁸ backed by a ferrule (C) and a 1/4-in. (6.2-mm) NPT male adapter (D).⁹ The septum assembly is joined to the 500-mL cylinder by a stainless steel hex coupling (E)¹⁰ and a stainless steel shutoff valve¹¹ with 1/4-in. (6.2-mm) NPT end fittings (F).

6.2.2 The 500-mL cylinder attaches to the HF sample cylinder (Fig. 1) in the following manner: The 1/4-in. (6.2-mm)

NPT male tube adapter (H)¹² is fitted with a 1/4-in. (6.2-mm) Swagelok nut (I)¹³ with back (J) and front ferrules (K).

6.3 *Gas Chromatograph*, having accessories and capabilities as follows:

6.3.1 *Sample Injection Port*, lined with stainless steel and maintained at 125°C.

6.3.2 *Column Oven*, capable of isothermal operation at 55°C.

6.3.3 *Detector*, flame ionization type, capable of operation at 150°C.

6.3.4 *Column Packed with Chromosil 310*,¹⁴ 8-ft by 1/8-in. (2.4-m by 3.1-mm) outside diameter polytetrafluoroethylene (PTFE).

NOTE 2—The column described in 6.3.4 has been found suitable for this analysis. If other columns are used, the precision and bias of this test method should be ascertained.

6.3.5 *Attenuator Switch*, to permit accurate, variable attenuation of the detector signal.

6.4 *Recorder*, range to match chromatograph output signal, 1-s full scale deflection with a chart speed of approximately 3 cm/min or other convenient speed that will produce a satisfactory chromatogram. Alternatively, an integrating recorder can be used to facilitate measurement of the peak areas.

6.5 *Timer*, 60-min, adjustable to 1-min intervals.

6.6 *Cylinder Rotator*, adjustable to approximately 6 rpm.

6.7 *Vacuum Pump*, capable of reducing pressure to less than 10 torr.

6.8 *Syringe*, gas tight, 1-mL capacity.

6.9 *Syringe*, gas tight, 10-mL capacity.

6.10 *Syringe*, gas tight, 50-mL capacity.

7. Reagents

7.1 *Purity of Reagents*—Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.¹⁵ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II or Type III reagent water conforming to Specification D 1193.

7.3 *Aluminum Chloride Hexahydrate Solution (120 g/L)*—Dissolve 120 g of aluminum chloride hexahydrate

⁷ A cylinder available from the Whitey Co., 318 Bishop Rd., Highland Heights, OH 44143, has been found satisfactory for this purpose. Request Catalogue No. 304-L-HDF4-500T.

⁸ A septum available from Supelco, Inc., Supelco Park, Bellefonte, PA 16823, has been found satisfactory for this purpose. Request Catalogue No. 2-0413.

⁹ The Ultra-Torr male adapter, available from the Cajon Co., 9760 Shepard Road, Macedonia, OH 44056, has been found satisfactory for this purpose. Request Catalogue No. SS-6-UT-1-4.

¹⁰ A hex-coupling, available from the Cajon Co., 9760 Shepard Road, Macedonia, OH 44056, has been found satisfactory for this purpose. Request Catalogue No. SS-4-HCG.

¹¹ A shut-off valve, available from the Whitey Co., 318 Bishop Road, Highland Hts., OH 44143, has been found satisfactory for this purpose. Request Catalogue No. SS-14DKM4.

¹² A fractional tube adapter to male pipe, available from the Cajon Co., 9760 Shepard Road, Macedonia, OH 44056, has been found satisfactory for this purpose. Request Catalogue No. SS-4-TA-1-4.

¹³ The fractional tube size nut, available from Swagelok Co., 31400 Aurora Road, Solon, OH 44139, has been found satisfactory for this purpose. Request Catalogue No. SS-402-1.

¹⁴ A Chromosil 310 column, available from Supelco, Inc., Supelco Park, Bellefonte, PA 16823, has been found satisfactory for this purpose. Request Catalogue No. 1-1501.

¹⁵ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopoeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

(AlCl₃·6H₂O) in water and dilute to 1 L.

7.4 *Hydrocarbon Standard Gas Mixture*—Methane through hexane (*n*-paraffins) prepared in 100 ppm by volume quantities for each component in helium.¹⁶

7.5 *Hydrocarbon Standard Gas Mixture*—Branched paraffins isobutane through branched hexane prepared in 100 ppm by volume quantities for each component in helium.¹⁷

7.6 Helium, 99.995 % minimum purity.

7.7 Hydrogen, 99.8 % minimum purity.

7.8 Air, high purity breathing air, 99.9 % minimum.

7.9 Air, zero grade, <0.1 ppm as methane gas (CH₄).

8. Hazards

8.1 Anhydrous HF is an extremely hazardous chemical capable of inflicting serious and painful burns. Written precautions and first aid details are available and should be required reading for anyone working with anhydrous HF.

NOTE 3—Producers and distributors of anhydrous HF can provide Material Safety Data Sheets (MSDSs) recommending appropriate safety procedures.

8.2 Take every precaution in the handling of anhydrous HF to avoid contact with any part of the body. If contact does occur, immediately wash the affected area thoroughly and continuously until medical attention can be obtained.

8.3 Avoid inhalation of acid fumes, as they are extremely irritating to all parts of the respiratory system. Exposure cases should receive prompt medical care.

8.4 Clean up all spills immediately by washing the spill area with water, followed by sodium carbonate solution or lime slurry to neutralize the acid.

8.5 It is imperative in the following analytical procedures that all weighings of the concentrated acid are performed in a well-ventilated hood.

9. Sampling

9.1 Sampling of anhydrous HF is not within the scope of this test method. The sample to be analyzed shall be considered to be the sample in a single container submitted to the analytical laboratory. The size of the sample shall be sufficient to perform all analyses without reuse of any portion of the sample.

10. Procedure

10.1 *Chromatographic Conditions:*

10.1.1 Prior to performing the GC headspace analysis on the prepared sample (10.2) and calibration standard (10.3), adjust the operating conditions in accordance with the parameters listed below. Allow the instrument to equilibrate as indicated by a stable base line on the chart at the maximum sensitivity setting to be used. Conditions should be as follows:¹⁸

Recorder	0–1 mV range
Attenuation	variable
Chart speed	3 cm/min
Column	Chromosil 310, 8 ft by 1/8-in. (2.4-m by 3.1-mm) PTFE
Column temperature	55°C, isothermal
Detector	Flame ionization
Carrier gas	Helium at 30 mL/min
Air flow rate	255 mL/min
Hydrogen flow rate	30 mL/min
Injection port temperature	125°C
Detector block temperature	150°C

10.2 *Sample Analysis:*

10.2.1 Evacuate the clean, dry 10-mL sample cylinder (Fig. 1) to less than 10 torr and tare to the nearest 0.01 g.

10.2.2 Connect the evacuated sample cylinder to the anhydrous HF sample source and carefully introduce an 8 to 10 g liquid sample. Close the valves to the sample source and sample cylinder, evacuate the sample fill line and then carefully disconnect the sample cylinder.

NOTE 4—**Warning:** Anhydrous HF is present at the joint to be disconnected. **Precaution:** Take extreme precautions to remove the HF without danger to the operator. Also, wash and dry the joint before weighing.

10.2.2.1 Weigh to the nearest 0.01 g to determine the exact sample weight.

10.2.3 Remove the 1/4-in. (6.2-mm) tube adapter from the 500-mL reaction cylinder and close the valve on the opposite end (Fig. 2). Add 450 ± 1 mL of aluminum chloride solution (7.3), then screw the 1/4-in. tube adapter securely into place.

10.2.4 Connect the sample cylinder to the reaction cylinder by the tube adapter and position on the sample rotator located in a fume hood. Orient the two tandem cylinders vertically with the 500-mL reaction cylinder in the upper position.

10.2.5 Open the valve on the reaction cylinder to the maximum open position and inject 10 mL of zero grade air through the septum to prepressurize the headspace, then close the valve.

10.2.6 Orient the two cylinders on the sample rotator to a vertical position with the 10 mL sample cylinder containing the HF in the upper position.

10.2.7 Carefully open the valve on the 10 mL sample cylinder allowing the anhydrous HF to gently flow into the aluminum chloride solution. Turn on the rotator and rotate at 6 rpm for 30 min.

10.2.8 After 30 min, stop the rotator and orient the two cylinders in a vertical position with the 500-mL reaction cylinder in the upper position.

10.2.9 Open the valve on the 500-mL reaction cylinder and allow the cylinders to stand in this position for 30 min. This permits the hydrocarbon gases to collect in the headspace above the aluminum chloride solution.

10.2.10 Insert a 10-mL gas syringe through the septum and activate the plunger several times to assure thorough mixing of the head space gas, then depress the plunger and remove the syringe.

¹⁶ Scott Specialty Gases, available from Scott Specialty Gases, Route 611, Plumsteadville, PA 18949, have been found satisfactory for this purpose. Request Catalogue No. 3-30-200.

¹⁷ Scott Specialty Gases, available from Scott Specialty Gases, Route 611, Plumsteadville, PA 18949, have been found satisfactory for this purpose. Request Catalogue No. 2-2501.

¹⁸ The parameters apply to a Hewlett Packard Model 5830 gas chromatograph equipped with a flame ionization detector, available from Hewlett-Packard Co., 3000 Hanover St., Palo Alto, CA 94304. Any similar instrument can be used for this method with appropriate modification of the parameters.

10.2.11 Obtain a 0.5-mL sample of the headspace gas through the septum using a 1-mL gas syringe and inject it into the chromatograph.

10.2.12 Record the chromatogram for approximately 20 min or until all C-6 components have eluted. A typical chromatogram of an anhydrous HF sample is shown in Fig. 3.

10.2.13 Measure the areas of the component hydrocarbon peaks and identify each by comparison with the retention times of the components of the hydrocarbon calibration standards (10.3).

10.2.14 Repeat steps 10.2.11 to 10.2.12 and calculate the average area for each component peak. Duplicate injections should agree within 10 % relative for each component.

10.3 Standardization:

10.3.1 As soon as the sample analysis is completed, inject 25 mL of each gas standard (7.4 and 7.5) into the headspace of the prepared HF sample (10.2.9 and 10.2.10) using a 50-mL gas syringe. Close the uppermost valve on the reaction cylinder.

10.3.2 Turn on the rotator and rotate the cylinder for 30 min at 6 rpm.

10.3.3 After 30 min, stop the rotator and orient the two cylinders in a vertical position with the 500-mL reaction cylinder in the upper position.

10.3.4 Allow the headspace gas to equilibrate, then mix and inject a 0.5-mL sample of the headspace gas into the chromatograph as described in steps 10.2.9-10.2.11.

10.3.5 Record the chromatogram for approximately 20 min or until all C-6 components have eluted. A typical chromatogram of a sample, via standard addition, is shown in Fig. 4.

10.3.6 Inject a second 0.5-mL sample of the headspace gas into the chromatograph, obtain the chromatogram, and calculate the average area for each component peak. Duplicate injections should agree within 10 % relative for each component.

10.3.7 Subtract the average area of each component peak obtained in the sample analysis (10.2.13 and 10.2.14) from the average area of the respective component peaks obtained in the calibration run (10.3.5) and calculate a response factor for each component.

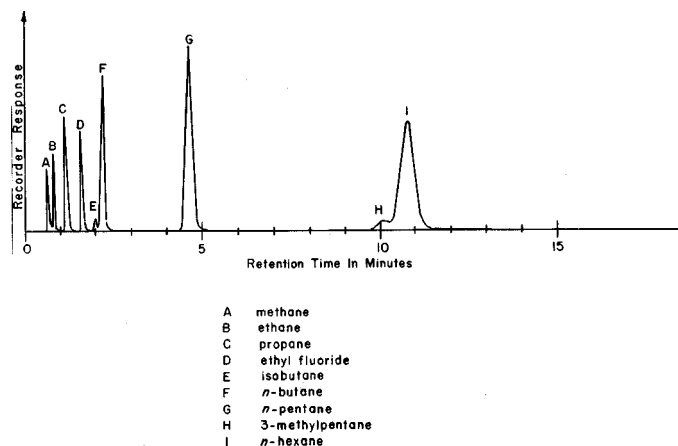


FIG. 3 Chromatogram of Commercial Anhydrous HF

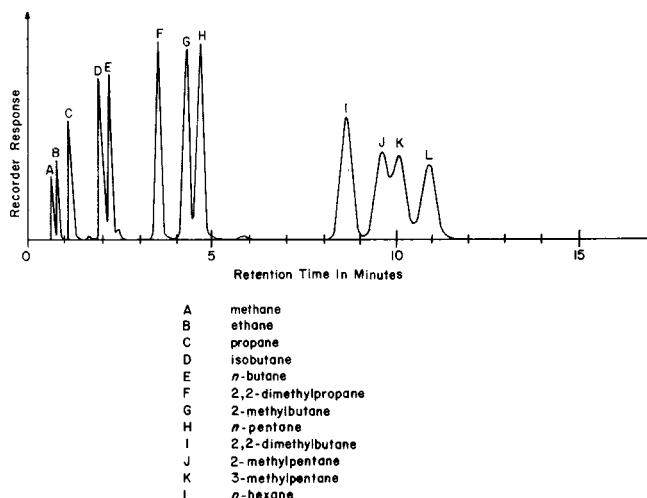


FIG. 4 Chromatogram of Hydrocarbon Standard

11. Calculation

11.1 Calculate the response factor R_N for each component utilized in the standard addition method, as follows:

$$R_N = \frac{V \times P_N \times 10^{-6}}{22,400} \times (MW)_N \times 10^6 \div \frac{A_N - B_N}{A_N} \quad (2)$$

where:

- R_N = response factor for component N , μg per unit area,
- P_N = exact concentration of a component N in standard, ppm by volume,
- V = volume of standard injected, mL = 25,
- $(MW)_N$ = molecular weight of component, N ,
- B_N = area component N in sample chromatogram (10.2.13 and 10.2.14), and
- A_N = area component N in chromatogram of standard addition method (10.3.5).

11.2 Calculate the ppm of each hydrocarbon component in the original anhydrous HF sample, as follows:

$$C_N = \frac{B_N \times R_N}{S} \quad (3)$$

where:

- C_N = concentration hydrocarbon component N in original anhydrous HF sample, ppm,
- B_N = area component N in sample chromatogram,
- R_N = response factor for component N , μg per unit area, and
- S = weight of anhydrous HF sample, g.

11.3 The total hydrocarbon content of the anhydrous HF sample in parts per million (ppm) is equal to the sum of the concentrations of the individual hydrocarbon components in 11.2.

12. Report

12.1 Report the total ppm hydrocarbons to two significant figures.

13. Precision and Bias

13.1 The following criteria should be used for judging the acceptability of results (Note 5):

13.1.1 *Repeatability (Single Analyst)*—The coefficient of variation for a single determination has been estimated to be 12.8 % relative at 28 dF. The 95 % limit for difference between two such runs is 36 % relative.

13.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability), formerly called repeatability*— The coefficient of variation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 17 % relative at 14 dF. The 95 % limit for the difference between two such averages is 49 % relative.

13.1.3 *Reproducibility (Multilaboratory)*—The coefficient of variation of results (each the average of duplicates), obtained by analysts in different laboratories has been estimated to be 38.4 % relative at 4 dF. The 95 % limit for the difference between two such averages is 10.8 % relative.

NOTE 5—The above precision estimates are based on an interlaboratory study of analyses performed in 1985 on three samples of anhydrous HF (as received, 10 to 25 ppm spike and greater than 25 ppm spike). One analyst in each of five laboratories performed duplicate determinations and repeated one day later for a total of 60 determinations.¹⁹ The average concentrations obtained for these samples were 1.74, 17, and 47 ppm total hydrocarbons. Practice E 180 was used in developing these precision estimates.

13.2 *Bias*—The bias for this test method has not been determined because of the lack of acceptance reference material.

¹⁹ Supporting data are available from ASTM Headquarters. Request RR: E15-1037.

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