



A Honeywell Company

Analysis of Hydrogen Fluoride Alkylation Catalysts and Regenerator Bottoms

UOP Method 629-08

Scope

This 4-part procedure is for the sampling of liquid hydrogen fluoride (HF) streams and the analysis of these streams for acidity, water content and acid-soluble oil. The method is applicable to fresh acid and alkylation process system acid. The acid-soluble oil determination is also applicable to regenerator bottoms samples. However, acidity and water determinations on regenerator bottoms samples must be conducted according to UOP Methods 379 and 382, respectively. The Appendix provides information about an online instrumental option that could significantly reduce the number of samples that are brought into the lab for analysis.

Caution!

HF is toxic and may be fatal if inhaled, absorbed through skin or swallowed. It is extremely corrosive and destructive to tissue, and specialized medical treatment is required for all exposures. All appropriate safety procedures, including those listed in the HF MSDS, must be read, understood, and followed. Appropriate protective equipment must be worn throughout the procedure and all laboratory work must be performed in an appropriate fume hood.

References

MSDS, Hydrofluoric Acid, available from the supplier of the chemical.

UOP Method 379, "Hydrogen Fluoride in HF Alkylation Regenerator Bottoms," www.astm.org

UOP Method 382, "Water in Regenerator Bottoms from Hydrogen Fluoride Alkylation," www.astm.org

Outline of Method

A cleaned and dried sample cylinder is used to take a plant sample of liquid HF. The cylinder containing the sample is taken to the laboratory, where 3 portions of the sample are transferred to respective polypropylene bottles and analyses for acidity, water, and acid-soluble oil are made.

To determine acidity, the sample is diluted with neutralized 2-propanol. An aliquot is titrated with standard 1-M sodium hydroxide.

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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To determine water, the HF is allowed to volatilize from the sample and any remaining acid is neutralized with dried pyridine. The neutralized sample is transferred to a moisture analyzer and titrated coulometrically.

To determine oil in liquid HF, pentane is added to the oil residue after all the excess HF has been volatilized. The pentane-oil mixture is warmed until a constant mass is achieved. The mass of the oil residue is calculated. Oil in regenerator bottoms is determined in a similar fashion to the liquid HF.

Part I — Plant and Laboratory Sampling

Apparatus

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

Balance, readability 0.01-g, 1800 g capacity

Beaker, 150-mL, Griffin, borosilicate glass, VWR, Cat. No. 89000-202

Beaker, polypropylene, 4-L, VWR, Cat. No. 13890-181 (3 required)

Bottles, polypropylene, narrow mouth, with screw caps, 125-mL (2 required) and 500-mL, VWR, Cat. Nos. 16067-066 and 16067-102, respectively

Bottle, polyethylene, 1000-mL, VWR, Cat. No. 16129-704 (used for waste)

Bottles, polyethylene, wash, 500-mL, VWR, Cat. No. 16651-493

Box, wood, with hinged cover and 2 hasp-type locks, large enough to accommodate several sampling cylinders

Bucket, polypropylene, 7.6-L, VWR, Cat. No. 73470-016

Clamp, 3-prong, utility, VWR, Cat. No. 21573-265

Cylinder sampling tube, U-tube, 316 stainless steel, form as shown in Figure 1, EG & G Chandler Engineering Drawing No. 60-167, AMETEK Chandler Instruments

Flask, filtering, with side arm, 1000-mL, VWR, Cat. No. 89000-386

Gloves, heat resistant, VWR, Cat. No. 32888-340

Manifold, acid sampling, EG & G Chandler Engineering Drawing No. 60-170, AMETEK Chandler Instruments

Oven, drying, capable of operation at 50°C and 65°C

Pipet, glass, volumetric, Class A, 100-mL, VWR, Cat. No. 89003-368

Pipet filler, VWR, Cat. No. 53497-115

Regulator, air, two-stage, high purity, delivery pressure range 15-200 kPa (2-30 psi), Matheson Tri-Gas, Model 3121-590, if needed to control air pressure

Sample cylinder, Monel, 150-mL, see Figure 2 for details and construction. A sample cylinder assembly equipped with valve caps is available from AMETEK Chandler Instruments by specifying the sample cylinder described by their Drawing No. 60-120; includes Valve Stem, "K" Monel; Valve Gland, "R" Monel; Valve Body, "R" Monel; pressure test to 1.72×10^4 kPa (2500 psi) hydrostatic.

Stirring rod, fluoropolymer, 20-cm long, Fisher Scientific, Cat. No. 14-518-10C

Support stand, 61-cm rod length, 15- x 23-cm base, VWR, Cat. No. 60110-244

Tubing, FEP fluoropolymer, 5.0-mm ID, VWR Scientific, Cat. No. 63014-714

Tubing, rubber or flexible plastic

Vacuum system, house vacuum or vacuum pump

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. Unless otherwise specified, references to water mean deionized or distilled water.

Acetone (2-propanone), 99.5% minimum purity, VWR, Cat. No. BJ010-1

Air, compressed

Ice, crushed

Phenolphthalein, 1% solution, VWR, Cat. No. VW3341-2

Sodium hydroxide, 50% solution, VWR, Cat. No. VW3246-1

Tags, with string, white and red

Water, deionized or distilled

Water, tap, cold and hot

Procedure

CAUTION: HF is a highly hazardous material. All appropriate safety procedures, as well as those listed in the HF MSDS, must be read, understood, and followed. Appropriate protective equipment must be worn throughout the analysis and all laboratory work must be performed in an appropriate fume hood.

Cylinder Preparation

1. Remove any previous sample by emptying the cylinder into a polypropylene bucket containing crushed ice. Open the valve slowly at first to prevent splashing.
 - If the cylinder is new, begin the cleaning procedure with Step 7.
2. Add several mL of phenolphthalein indicator solution to the crushed ice-HF mixture.
3. Neutralize the HF by slowly adding 50% sodium hydroxide solution, while stirring with a Teflon rod, until a persistent pink color is obtained.
4. Squirt approximately 25 to 30 mL of acetone from a wash bottle into the cylinder.
5. Close the valve on the cylinder and place the cylinder in hot (approximately 50°C) tap water.
6. Shake the cylinder, invert it and release the acetone into the bucket containing the previously neutralized sample.
 - This bucket is used to temporarily contain neutralized samples and acetone washes. Dispose of the waste material following local safety practices and in an environmentally safe manner.
7. Attach the cylinder sampling tube to the cylinder and evacuate the cylinder with a vacuum pump protected by a filtering flask.
8. Close the valve on the cylinder and disconnect it from the vacuum system.

9. Cool the cylinder in cold (approximately 15°C) tap water.
 - If local tap water is warm, fill a container with tap water; add sufficient ice to cool to approximately 15°C; and place the cylinder in the container.
10. Place the tip of the cylinder sampling tube into a 150-mL beaker containing approximately 125 mL of acetone.
11. Open the valve on the cylinder and draw acetone into the cylinder.
12. Close the valve and heat the cylinder under hot (approximately 50°C) running tap water.
13. Remove the cylinder from the hot water and shake.
14. Invert the cylinder and open the valve to discharge the acetone into the bucket containing the previously neutralized sample.
 - If cleaning a new cylinder, dispose of the acetone according to locally appropriate procedures.
15. Repeat Steps 7 through 14 two more times.
16. Evacuate the cylinder one final time (Step 7).
17. Disconnect the HF cylinder sampling tube and place the cylinder in an oven at 65°C for 20 minutes with the valve open.
18. Remove the cylinder from the oven and, with the valve still open, allow it to cool to room temperature.
19. Close the valve on the cylinder and cap it.
20. Weigh the cylinder to the nearest 0.5 g with the valve cap on the cylinder and record the weight.

Obtaining the Sample at the Plant

1. Remove the valve cap from the cylinder.
2. Open and close the valve to make certain that the cylinder is filled with air.
3. Connect the cylinder vertically to the sample connection, using an acid sampling manifold, with the valve-end down.
 - This creates an air pocket in the cylinder that prevents overfilling.
4. Collect the sample from the plant.
 - Follow all safety procedures.
5. Close the valve and carefully disconnect the cylinder from the plant.
6. Replace the valve cap.
 - Document the sample location and time of sampling.
7. Place the cylinder in a wood box and transport the box to the analytical laboratory.
8. Weigh the cylinder to the nearest 0.5 g immediately; subtract the previously recorded tare weight to obtain the mass of the sample in the cylinder.
 - The sample mass should be at least 40 g in order to have enough sample for all the analyses, but should not exceed 100 g.

Preparation of Laboratory Apparatus

1. Fill the three 4-L polypropylene beakers approximately 1/2 full with crushed ice and place the 1000-mL polyethylene waste bottle in one of them. Add sufficient cold tap water to the other two beakers to just cover the ice.
2. Clean two 125-mL and one 500-mL polypropylene screw cap bottles with deionized or distilled water, rinse with acetone, and dry with air.
 - As an aid in estimating sample volumes, the 125-mL bottles may be marked at 5 and 15 mL, and the 500-mL bottle at 100 and 115 mL.
3. Identify one of the 125-mL bottles, cap included, to be used for the sample for the determination of acid-soluble oil in HF.
 - This is to prevent the possibility of switching the cap of the bottle used for the determination of water in liquid HF.
4. Weigh each of the the sample bottles with caps to the nearest 0.01 g.
5. Pipet 100 mL of deionized or distilled water into the tared 500-mL polypropylene bottle and cap it.
 - Take care to exclude any water from the upper portion of the neck of the bottle.
6. Reweigh the capped 500-mL polypropylene bottle containing the water to the nearest 0.01 g.
7. Arrange the apparatus, as illustrated in Figure 1, in a fume hood.
 - Confirm that the fume hood is operating according to specifications.
8. Remove the cylinder from the wood box.
 - Perform all cylinder handling in a fume hood while wearing appropriate protective clothing.
9. Invert the cylinder several times to ensure complete mixing of the sample.
10. Remove the valve cap and attach the cylinder sampling tube.
11. Immerse the U-shaped portion of the cylinder sampling tube to at least 1/2 its depth in a 4-L beaker containing crushed ice.
12. Clamp the cylinder to the stand with the valve end down.
13. Place the end of the Teflon tubing from the cylinder sampling tube into the 1000-mL polyethylene waste bottle, which is in a 4-L beaker containing crushed ice.
14. Place all three of the tared bottles in another of the 4-L beakers containing crushed ice.
 - Take the samples before the ice has melted significantly and it can no longer stabilize the bottles.

Laboratory Sampling for Analysis

1. Open the cylinder valve slowly and allow approximately 5 g of sample to flow into the waste bottle.
 - Steps 1 through 7 must be performed as rapidly as possible to minimize losses of HF through volatilization.
2. Close the valve and remove the tubing from the waste bottle.
3. Remove the screw caps from the sample bottles.

4. Insert the Teflon tubing into the 125-mL polypropylene bottle designated for the acid-soluble oil determination.
 - The end of the tubing should be approximately 5 cm above the bottom of the bottle.
5. Slowly open the valve of the sample cylinder. Transfer approximately 5 g of sample into the bottle, close the cylinder valve and cap the bottle.
 - Markings previously placed on the bottles may be used as an aid in estimating the correct amount of sample to be transferred.
6. Insert the FEP tubing into the second 125-mL bottle. Transfer approximately 15 g of sample for the water determination and cap the bottle.
 - The end of the tube should be approximately 5 cm above the bottom of the bottle.
7. Insert the tubing into the 500-mL bottle. Transfer 10 to 15 g of sample for the acidity measurement and cap the bottle.
 - Do not allow the sampling tube to contact the water.
8. Place the end of the Teflon tubing in the waste bottle.
 - Make certain the cylinder valve is fully closed.
9. Allow the bottles to remain in the ice until the analyses are performed.

Disposal of Sampling Waste

1. Loosen, but do not remove, the lock nut on the cylinder sampling tube.
 - **CAUTION:** Since some of the condensed HF still remains in the iced part of the stainless steel tubing, care must be used in its removal.
2. Position the tip of the Teflon tubing so that the flow is down and away from the analyst.
3. Direct the expelled HF into the 1000-mL waste bottle.
4. Hold an air line (rubber or flexible plastic tubing) tightly against the hole in the lock nut (Detail “A”, Figure 1), and allow a moderate flow of air to blow through the tubing until no more HF can be observed coming from the tubing.
5. Remove the lock nut from the cylinder, immediately rinse it and the cylinder threads with acetone and blow them dry using air.
 - The rinsings are collected in the waste bottle.
6. Remove the “U” portion of the cylinder sampling tube from the 4-L beaker containing the crushed ice.
7. Clean the cylinder sampling tubing using a stream of acetone from a wash bottle to flush the residue into the waste bottle.
8. Dry the tube using a stream of air.
9. Replace the valve cap on the cylinder.
10. Remove the cylinder from the stand and place it in a wood storage box.
11. Add crushed ice and neutralize the waste material contained in the 1000-mL waste bottle as described under *Cylinder Preparation*, Steps 2 and 3.
12. Dispose of the neutralized mixture according to local safety practices and in an environmentally safe manner.

Part II — Analysis for Total Acidity of HF

Apparatus

The apparatus listed are in addition to those listed in Part I. References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Beaker, Teflon, 250-mL, VWR, Cat. No. 13917-540

Buret, 50-mL, PTFE stopcock, 0.1-mL subdivisions, VWR, Cat. No. 89001-624

Stirrer, magnetic, with fluoropolymer-covered stirring bar, VWR, Cat. No. 12365-380

Reagents and Materials

The reagents and materials listed are in addition to those listed in Part I. References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

2-Propanol (isopropyl alcohol), 99.9% minimum purity, VWR, Cat. No. BJAH323-4. Neutralize to a faint pink phenolphthalein endpoint by adding, dropwise, 0.1-*M* sodium hydroxide, to a quantity of the 2-propanol.

Sodium hydroxide solution, aqueous, 0.1-*M*, standardized, VWR, Cat. No. VW3219-2

Towels, paper

Procedure

CAUTION: HF is a highly hazardous material. All appropriate safety procedures, as well as those listed in the HF MSDS, must be read, understood, and followed. Appropriate protective equipment must be worn throughout the analysis and all laboratory work must be performed in an appropriate fume hood. In addition, the analyst is expected to be familiar with general laboratory practices and the technique of titration.

1. Remove the 500-mL sampling bottle from the ice.
2. Dry the outside of the bottle thoroughly and reweigh it to the nearest 0.01 g.
 - The mass obtained minus the mass of the capped bottle and water is the sample mass, **W** in Equation 1.
3. Adjust the contents of the sample bottle to a final mass of approximately 400 g with neutral 2-propanol, recap and weigh to the nearest 0.01 g.
 - The mass obtained minus the mass of the capped bottle is the final mass to which the sample was diluted, **A** in Equation 1.
4. Shake the bottle with the cap directed away from the analyst for approximately 30 seconds.
5. Allow it to stand for 15 minutes.
6. Weigh, to the nearest 0.01 g, a clean, dry 250-mL Teflon beaker containing a Teflon-covered magnetic stirring bar.

7. Pour approximately 30 mL of the diluted acid sample into the Teflon beaker and reweigh the beaker to the nearest 0.01 g.
 - The mass obtained minus the mass of the beaker is the mass of the aliquot used for titration, **B** in Equation 1..
8. Add 3 drops of phenolphthalein indicator solution to the aliquot and turn on the magnetic stirrer.
9. Titrate the aliquot with standard 0.1-*M* sodium hydroxide to a persistent pink color.
 - Stir continuously and wash down the sides of the beaker frequently with water.

Calculations

Calculate the mass-% HF (acidity) in the sample to one decimal place using Equation 1:

$$\text{HF, mass-\%} = \frac{2VMA}{BW} \quad (1)$$

where:

A = final mass to which sample was diluted, g

B = mass of aliquot taken for titration, g

M = molarity of the sodium hydroxide

V = volume of sodium hydroxide used for titration, mL

W = mass of sample taken for analysis, g

$$2 = \frac{(20.01)(100)}{(1000)}$$

where:

20.01 = molecular weight of HF

100 = conversion of g/g to mass-%

1000 = conversion of mL to L, mL/L

Precision

Repeatability

There is insufficient data to calculate the repeatability of total acidity at this time, however, the accepted value for repeatability for this test is ± 2.7 mass-%.

Reproducibility

There is insufficient data to calculate the reproducibility of total acidity at this time.

Time for Analysis

The elapsed time and labor requirement for Part II are identical, one hour.

Part III — Analysis for Water in Liquid HF

Apparatus

The apparatus listed are in addition to those listed in Parts I and II. References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Desiccator, VWR, Cat. No. 89001-722, with plate, Cat. No. 25060-046

Dish, evaporating, 385-mL, VWR, Cat. No. 25310-198

Drying column, 28-mm diameter, 625-mm high (Figure 3) with a 500-mL reservoir at the top and a PTFE plug stopcock at the bottom, Kimble Chase, Custom Glass Shop. Connect a 500-mL flask at the bottom, Kimble Chase, Cat. No. 605020-0624, and provide calcium chloride filled drying tubes on the flask and reservoir (Figure 3), Kimble Chase, Custom Glass Shop.

Furnace, muffle

Moisture analyzer, Mitsubishi Moisturemeter, Model CA-200, Cosa Instrument

Pipet, glass, volumetric, Class A, 50-mL, VWR, Cat. No. 89003-366

Regulator, nitrogen, two-stage, Matheson, Model 3122-580

Reagents and Materials

The reagents and materials listed are in addition to those listed in Parts I and II. References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Aquamicron, solution for coulometric moisture analyzer, Cosa Instrument

Calcium chloride, desiccant, Drierite, indicating, 8 mesh, VWR, Cat. No. 22891-040, for desiccator and drying tube

Glass wool, VWR, Cat. No. EM-GX0090-2

Grease, high-vacuum, VWR, Cat. No. 59344-055

Molecular sieves, type 5A, 4-8 mesh beads, Fisher Scientific, Cat. No. M521-500

Nitrogen, 99.9% minimum purity, extra dry

Pyridine, 99.8% minimum purity, VWR, Cat. No. BJAS332-1

Syringe, 5-mL, disposable plastic, with attached needle, Fisher Scientific, Cat. No. 14-823-70

Procedure

CAUTION: HF is a highly hazardous material. All appropriate safety procedures, as well as those listed in the HF MSDS, must be read, understood, and followed. Appropriate protective equipment must be worn throughout the analysis and all laboratory work must be performed in an appropriate fume hood. In addition, the analyst is expected to be familiar with general laboratory practices and the technique of titration.

Instrument Preparation

1. Dry approximately 250 mL of the molecular sieves in an evaporating dish at 500°C for 16 hours in a muffle furnace and cool to ambient temperature in a desiccator.
2. Fill the drying column (Fig. 3) with the dried molecular sieves.
3. Dry the pyridine by passing it through the molecular sieves at a rate not to exceed 1 mL/minute.
4. Set up the moisture analyzer as described in the manufacturer's instruction manual.
5. Add the Aquamicron solution to the moisture analyzer as directed by the manufacturer.
6. Turn on the instrument.
 - When an audible signal is heard, the instrument is ready for the analysis of samples.

Sample Preparation

1. Remove the 125-mL sample bottle designated for water determination from the ice.
2. Dry the outside of the bottle thoroughly and reweigh it to the nearest 0.01 g.
 - The mass increase over the mass of the empty bottle is the sample mass taken for analysis, **G** in Equation 2.
3. Uncap the sample bottle cautiously and place it in the hood.
4. Blanket the mouth of the sample bottle with a slow dry nitrogen flow to prevent condensation of moisture from ambient air.
5. Allow the HF to volatilize at room temperature until approximately 60% has been volatilized.
 - It is not necessary to remove all traces of HF. The hydrogen fluoride that remains will be neutralized.
6. Add 50 mL of dry pyridine by pipet (dropwise at first).
7. Replace the cap, swirl the bottle and place it in an ice bath. Allow it to remain in the ice bath until the contents are cool.

Analysis of Blank

1. Place a syringe and needle in the drying oven at 50°C for approximately one minute.
2. Remove them from the oven and allow the syringe and needle to cool to the touch.
3. Draw 2 to 3 mL of dried pyridine into the syringe, weigh the syringe with the pyridine to the nearest 0.1 mg and record the mass.
 - It is necessary to run a reagent blank on the dried pyridine first.
4. Inject the pyridine through the septum into the solution contained in the large cell of the instrument.
5. Press the “start” switch to begin the titration.
6. Reweigh the empty syringe, to the nearest 0.1 mg, immediately.
 - The mass of the pyridine injected is equal to the difference in mass between the filled and emptied syringe, **C** in Equation 2.
7. Read the μg of water from the meter when the audible signal from the instrument is heard, and record this value, **K** in Equation 2.

Analysis of Sample

1. Remove the sample bottle from the ice bath, dry the outside thoroughly and weigh it to the nearest 0.01 g.
 - The mass obtained minus the mass of the capped bottle is the mass of the pyridine-sample solution, **F** in Equation 2.
2. Repeat the steps under *Analysis of Blank*, this time with the HF/pyridine sample using a new dry syringe and needle.
 - Take care to uncap the sample bottle in a fume hood.
 - The mass of the pyridine-sample solution injected is equal to the difference in mass between the filled and emptied syringe, **H** in Equation 2.
 - The μg of water read from the meter corresponds to the water in the pyridine-sample solution injected, **E** in Equation 2.

- If the titration is slow and the endpoint is not distinct, replace the cell solutions and rerun the blank and the sample.
3. Discard the syringes and needles safely.
 4. Dispose of the HF/pyridine mixture following local safety practices and in an environmentally safe manner.

Calculations

Calculate the mass-% water in the sample to one decimal place using Equation 2:

$$\text{Water, mass-\%} = \frac{\left(E - \frac{KD}{C}\right) F}{10^4 GH} \quad (2)$$

where:

- C** = mass of dry pyridine injected, g
- D** = mass of pyridine in the pyridine-sample solution injected, g
 - Because the pyridine-sample solution is primarily pyridine, the value for **D** is assumed (as an approximation) to be the same as **H**.
- E** = water in pyridine-sample solution injected, μg
- F** = mass of pyridine-sample solution, g
- G** = mass of HF sample taken from cylinder, g
- H** = mass of pyridine-sample solution injected, g
- K** = water in dry pyridine injected, μg
- 10⁴** = factor to convert $\mu\text{g/g}$ to mass-%

Precision

Site Precision

Based on five determinations of the water in liquid HF performed by two analysts on two days, the estimated standard deviation (esd) was calculated to be 0.20 mass-% at a concentration of 2.7 mass-%. Two tests performed in one laboratory by different analysts on different days should not differ by more than 0.8 mass-% (95% probability) at this level.

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

Time for Analysis

The elapsed time for one analysis, in Part III, is 3 hours. The labor requirement is 1.5 hours.

Part IV — Analysis for Acid-Soluble Oil in HF and Regenerator Bottoms

Apparatus

The apparatus listed are in addition to those listed in Parts I, II, and III. References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Bath, hot water, capable of operation at 60 C, 6-L capacity, VWR, Cat. No. 14002-364

Beaker, polypropylene, 400-mL, VWR, Cat. No. 13890-104

Bottle, polypropylene, with screw cap, 125-mL, VWR, Cat. No. 16067-066

Pipet, glass, volumetric transfer, Class B, 25-mL, VWR, Cat. No. 37000-25

Pipet, polyethylene, disposable transfer, 10-mL, Cole Parmer, Cat. No. C-06226-50

Reagents and Materials

The reagents and materials listed are in addition to those listed in Parts I, II, and III. References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Air, compressed

n-Pentane, 98% minimum purity, VWR, Cat. No. BJ312-1

Procedure

CAUTION: HF is a highly hazardous material. All appropriate safety procedures, as well as those listed in the HF MSDS, must be read, understood, and followed. Appropriate protective equipment must be worn throughout the analysis and all laboratory work must be performed in an appropriate fume hood.

Acid-Soluble Oil in Liquid HF

The analyst is expected to be familiar with general laboratory practices and the safe handling of HF.

1. Remove the 125-mL sample bottle designated for this analysis from the ice and cap it.
2. Dry the outside of the bottle thoroughly, allow it to cool to ambient temperature, and reweigh it to the nearest 0.01 g.
 - The increase in mass is the sample mass taken for analysis, **T** in Equation 3.
3. Uncap the polypropylene bottle cautiously and place it in a 400-mL beaker half-filled with warm tap water.
4. Allow the excess HF to vaporize in a hood.
 - Keep the tap water in the beaker warm (approximately 40°C) by periodically changing the water until no more HF vapors can be seen coming off.
5. Add approximately 25 mL of pentane to the oil residue and swirl to mix.
6. Place the bottle in a hot water bath at approximately 60°C until there is no further evidence of boiling pentane.
7. Remove the polypropylene bottle from the hot water and add another 25 mL of pentane to the oil residue.
8. Swirl the bottle to mix the pentane and oil residue.
9. Replace the bottle in the 60°C water bath until there is no further evidence of boiling pentane.
10. Remove the sample bottle from the hot water bath.
11. Dry the outside thoroughly and reweigh the capped bottle to the nearest 0.01 g.
12. Return the uncapped bottle to the 60°C water bath and heat for 15 minutes.
13. Reweigh the dried recapped bottle and compare the mass to that previously obtained.
 - Steps 12 and 13 are repeated until a constant mass to 0.01 g is achieved.

- When no decrease in mass is observed, all volatiles have been removed.
14. Record the mass of the bottle, with cap, containing the oil residue after pentane removal, **R** in Equation 3.

Acid-Soluble Oil in Regenerator Bottoms

1. Clean a 125-mL screw cap polypropylene bottle with water, wash it with acetone and dry it with air.
2. Weigh the capped polypropylene bottle to the nearest 0.01 g.
3. Using a disposable pipet, pipet an approximate 10-mL sample of regenerator bottoms into the tared bottle.
4. Cap the bottle and weigh it to the nearest 0.01 g.
 - The mass increase is the sample mass taken for analysis, **T** in Equation 3.
5. Follow Steps 3 through 14 as described under the section *Acid-Soluble Oil in Liquid HF*.

Calculations

Calculate the mass-% acid-soluble oil in either the liquid HF or in regenerator bottoms to one decimal place using Equation 3:

$$\text{Acid soluble oil, mass-\%} = \frac{100(R - S)}{T} \quad (3)$$

where:

- R** = mass of residue, bottle and cap after pentane removal, g
- S** = mass of bottle and cap, g
- T** = mass of sample taken for analysis, g
- 100** = factor to convert g/g to mass-%

Precision

Repeatability

There is insufficient data to calculate the repeatability of acid-soluble oil at this time, however, the accepted value for repeatability for this test is ± 5.5 mass-%.

Reproducibility

There is insufficient data to calculate the reproducibility of acid-soluble oil at this time.

Time for Analysis

The elapsed time for one analysis, in Part IV, is 2 hours. The labor requirement is 1.0 hour.

Suggested Suppliers

Cole-Parmer, 625 East Bunker Court, Vernon Hills, IL 60061 (847-549-7600)
www.coleparmer.com

Cosa Instrument Corporation, 7125 North Loop East, Houston, TX 77028 (713-947-9591)
www.cosa-instrument.com

AMETEK Chandler Instruments, 2001 North Indianwood Avenue, Broken Arrow, OK 74012-1163 (918-250-7200) www.chandlereng.com

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785 (412-490-8300) www.fishersci.com

Kimble Chase LLC, 1022 Spruce Street, Vineland, NJ 08360 (856-692-8500) www.kimble-chase.com

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

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

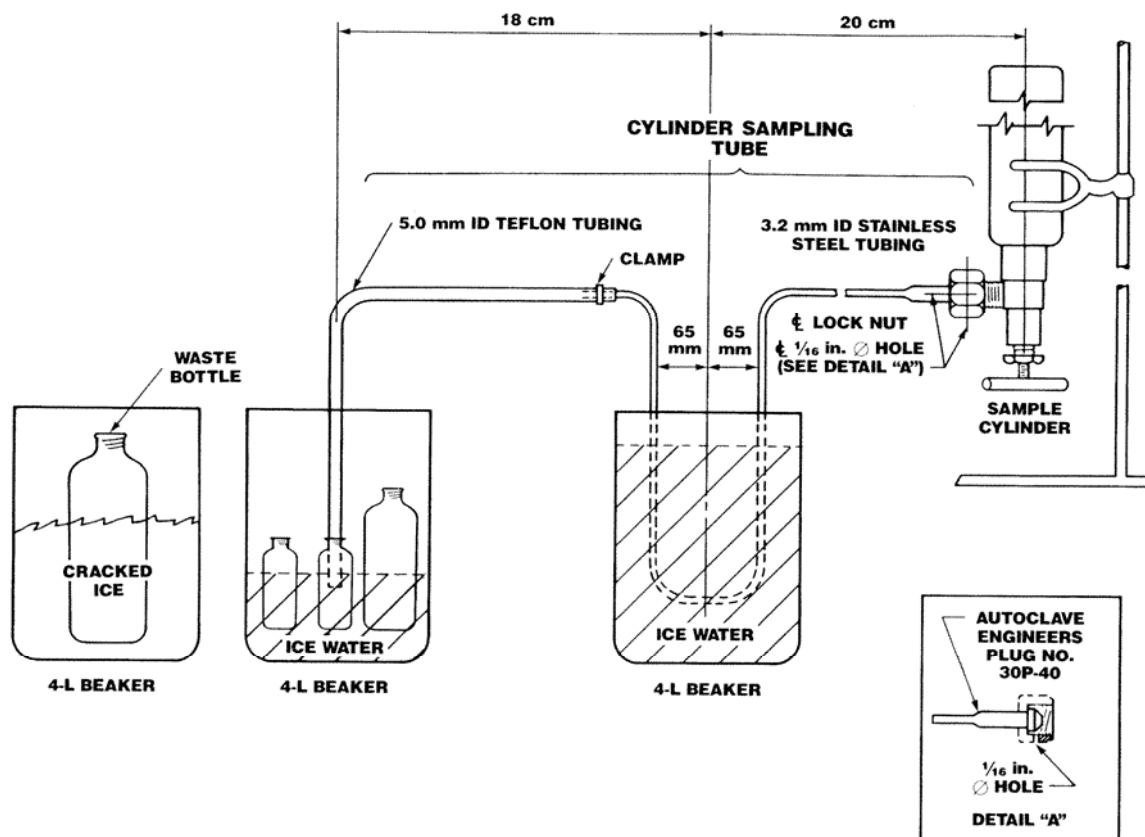


Figure 1
 Laboratory Sampling Arrangement

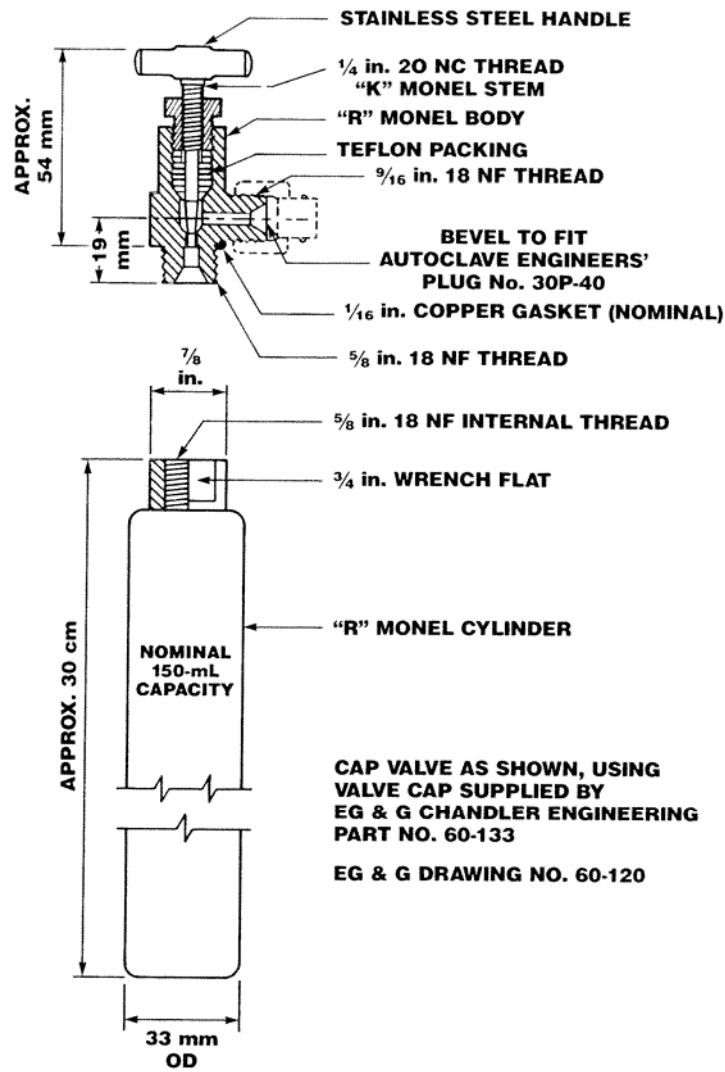


Figure 2
Monel Sampling Cylinder Assembly

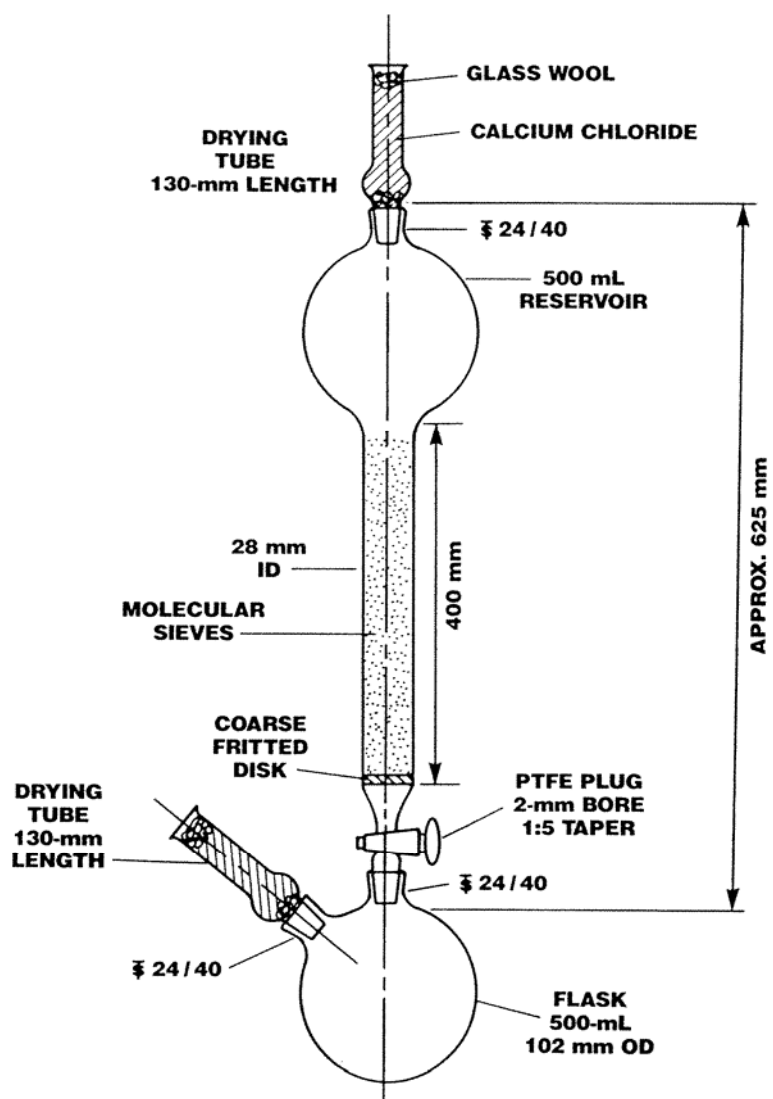


Figure 3
Drying Column

Appendix

Introduction

An online process analyzer used to measure total acidity, water, and acid-soluble oil has the potential of reducing the number of samples that are brought to the lab for analysis as well as providing faster analysis than that obtainable by the lab. The FT-NIR based HF Alkylation Process Acid Analyzer from ABB is such a unit. Occasional laboratory tests must continue to be performed to confirm the online analyzer's results.

Apparatus

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

HF Alkylation Process Acid Analyzer, ABB. This is the only instrument known to be available for this application at this time.

Procedure

CAUTION: HF is a highly hazardous material. All appropriate safety procedures, as well as those listed in the HF MSDS, must be read, understood, and followed, and the analyzer must be operated according to the manufacturer's instructions. Appropriate protective equipment must be worn and all laboratory work must be performed in an appropriate fume hood.

Reagents and Materials

Information on reagents and materials needed to support the instrument is supplied by the instrument manufacturer.

Precision

The precision of the online analyzer, as published by the instrument manufacturer, is listed in Table A below.

Table A	
<u>Precision of the Online Analyzer</u>	
<u>Analysis</u>	<u>Repeatability</u>
Total acidity	±0.10%
Water	±0.03%
Acid-soluble oil	±0.10%

Suggested Supplier

ABB, 585 boul. Charest est, suite 300, Quebec, QC G1K 9H4 Canada (+1 418 877 2294)
www.abb.com/analytical