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## **FLUORIDE IN CATALYSTS AND ORGANIC COMPOUNDS BY SPECTROPHOTOMETRY**

### **UOP Method 667-86**

#### **SCOPE**

This method is for determining fluoride in catalyst and organic compounds. The range of fluoride typically determined is 0.01 to 0.3%. Higher levels can, however, be determined by appropriate reduction in sample size and/or aliquoting volumes.

#### **OUTLINE OF METHOD**

Organic samples are fused with sodium peroxide in a peroxide bomb. The fusion product is dissolved and an aliquot is subjected to the Willard-Winter steam distillation to isolate fluoride. Catalyst samples are added directly to the distillation flask. After distillation is complete, an appropriate sized aliquot of the distillate is treated with a buffered lanthanum-alizarin complexone reagent which forms a violet-colored complex with fluoride. The absorbance is measured by a spectrophotometer against a reagent blank and the corresponding micrograms of fluoride are read from a previously prepared calibration curve.

#### **APPARATUS**

*Balance*, readability 0.1-mg

*Beakers*, 50- and 400-mL, Griffin, low form, double graduated, borosilicate, Sargent-Welch Scientific, Cat. Nos. S-4675-G and S-4675-L, respectively, or equivalent

*Cells*, rectangular, type UV silica, path length 10-mm, matched with covers, Beckman Instruments Inc., Cat. No. 580012, or equivalent

*Cylinders*, graduated, 10- and 100-mL, double graduated, borosilicate, Sargent-Welch Scientific, Cat. Nos. S-24663-B and S-24663-E, respectively, or equivalent

*Distillation apparatus*, as shown in Figs. 1, 2, 3 and 4, UOP Inc., or equivalent

*Flasks*, volumetric, 25- and 200-mL, polyethylene stopper, borosilicate, Sargent-Welch Scientific, Cat. Nos. S-34841-E and -J, respectively, or equivalent

*Flasks*, volumetric, 100-, 250-, 500- and 1000-mL, polypropylene, Nalgene, Sargent-Welch Scientific, Cat. Nos. S-34814-70G, J, K and L, respectively, or equivalent

*Funnel*, analytical, 60°, fluted, short stem, borosilicate, Sargent-Welch Scientific, Cat. No. S-34350-E, or equivalent

*Heating mantle*, for 500-mL round bottom flask, 270W-115V, Glas-Col Apparatus Co., Cat. No. TM106, or equivalent

EFFECTIVE HEALTH AND SAFETY PRACTICES SHOULD BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN MAY BE HAZARDOUS. IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE.

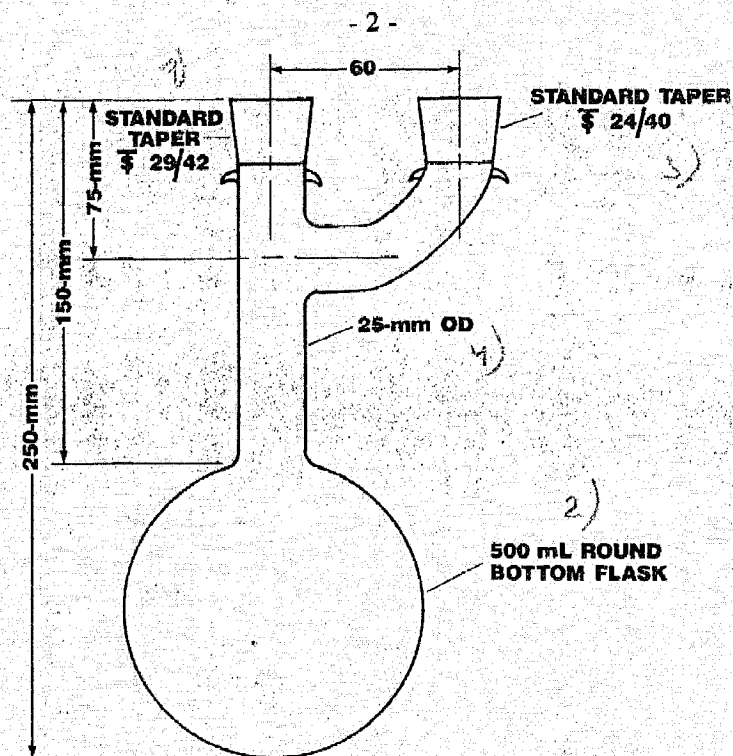


Figure 1

### Distillation Flask

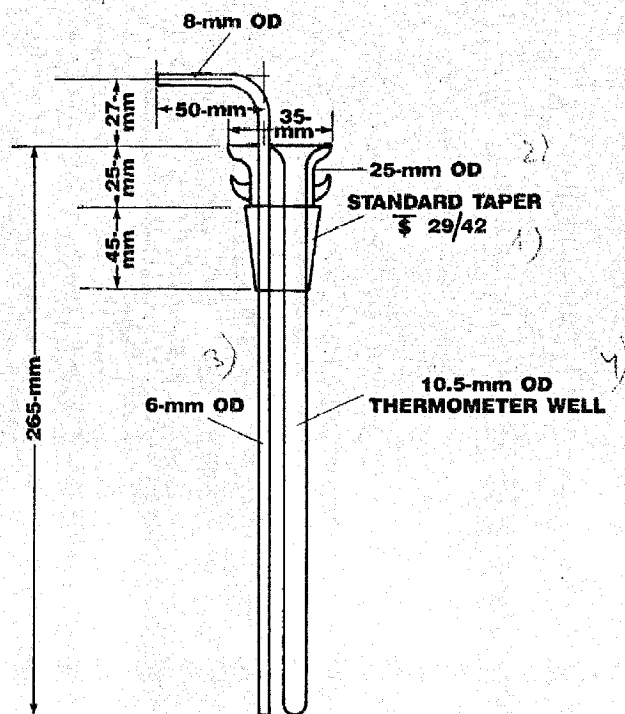
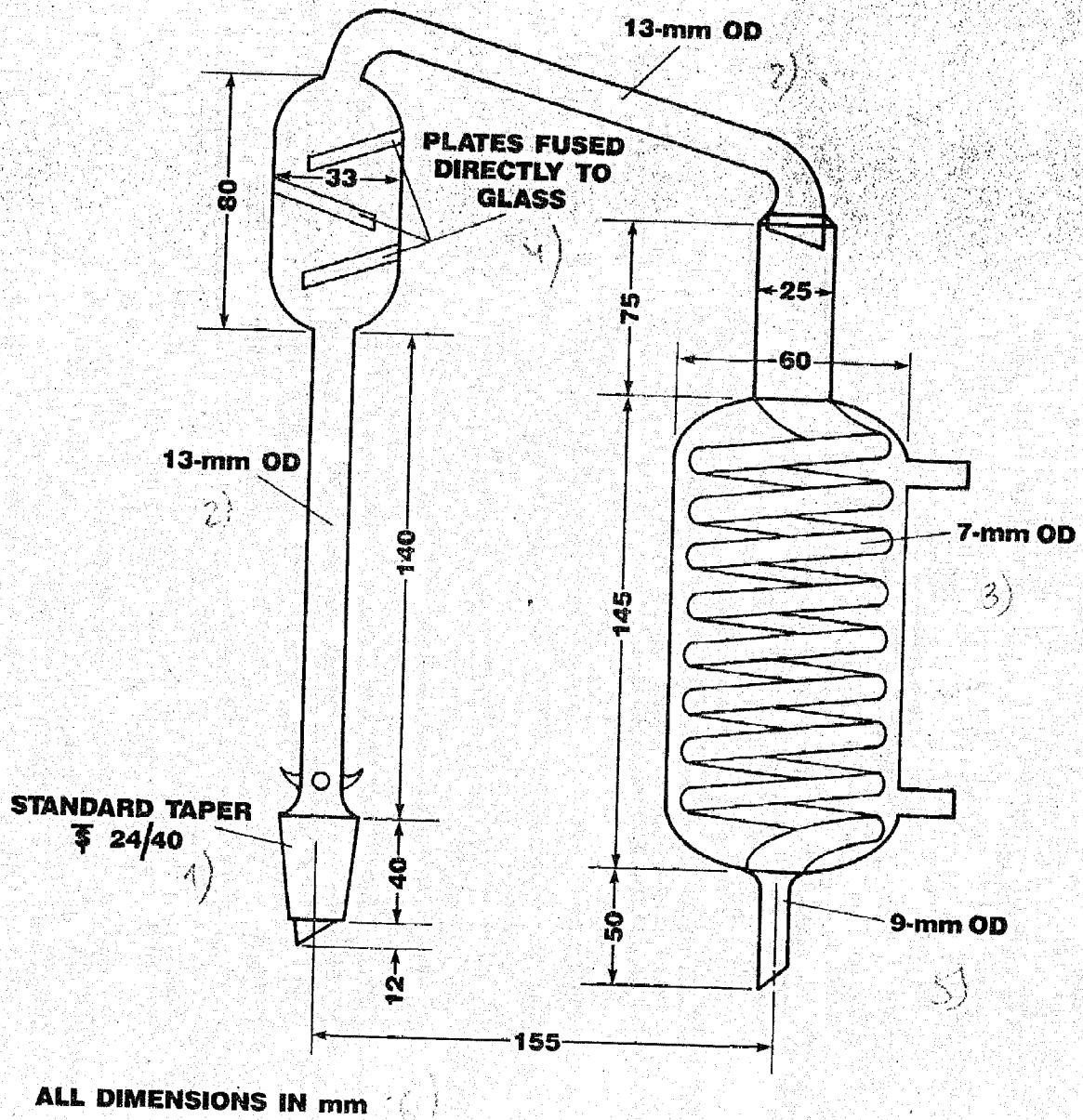


Figure 2

### Steam Delivery System



**Figure 3**  
**Condenser**

*Mortar*, porcelain, 300-mL capacity, Sargent-Welch Scientific, Cat. No. S-62270-E, or equivalent

*Peroxide bomb*, Type AC2E and accessories including measuring scoop, Parr Instrument Co., or equivalent

*Pestle*, porcelain, Sargent-Welch Scientific, Cat. No. S-62272-E, or equivalent

*pH Meter*, equipped with a combination standard size epoxy body flat bulk electrode and an ATC probe, Beckman Instruments Inc., Model pH70, or equivalent

*Pipets*, Mohr, 1- and 10-mL, Sargent-Welch Scientific, Cat. Nos. S-69555-C and S-69555-G, or equivalent

*Pipets*, transfer, 1-, 2-, 3-, 5-, 10-, 15-, 25- and 50-mL, Class B, Sargent-Welch Scientific, Cat. Nos. S-69505-A, -B, -C, -E, -F, -G, -J and -K, respectively, or equivalent

*Pipets*, transfer, special 25- and 50-mL. Carefully break or grind approximately 3-mm (1/8-inch) off the lower end of the pipet so that the tip of the pipet is changed sufficiently to allow very small pieces of carbon to pass through without plugging the pipet. Recalibrate the pipet.

*Power controller*, to fit above heating mantle, 600W-120V-5A, Glas-Col Apparatus Co., Cat. No. PL-112, or equivalent

*Spatula*, double blade, spoon end, Sargent-Welch Scientific, Cat. No. S-75288, or equivalent

*Spectrometer*, minimum of  $\pm 0.5\%$  spectrophotometric accuracy, Beckman, Model 35, or equivalent

*Steam generator*, see Fig. 4. The following components, available from Sargent-Welch Scientific, or equivalent, are required:

*Cork ring*, supporting, 170-mm OD, 120-mm ID, Cat. No. S-23125D

*Flask*, round bottom, short ring neck, borosilicate glass, 2-L, Cat. No. S-33865K

*Heater*, immersion, 1000W, Cat. No. S-40835-10E

*Rubber stopper*, black, size No. 10, Cat. No. S-73305P

*Tubing*, borosilicate glass, standard wall, 6-mm OD, Cat. No. S-40125-E (1.2 m required)

*Tubing*, plastic, Tygon, medium wall, 9.5-mm OD  $\times$  6.4-mm ID and 12.7-mm OD  $\times$  9.5-mm ID, Cat. Nos. S-73650-D and F, respectively

*Transformer*, variable, 120V, 10 A, Cat. No. S-30940

*Steam trap*, to remove condensed water from steam, see Fig. 4, comprised of the following:

*Funnel*, separatory, Squibb, stopper with Teflon plug, 250-mL, Sargent-Welch Scientific, Cat. No. S-35815-80D, or equivalent

*Rubber stopper*, black, size No. 4, Sargent-Welch Scientific, Cat. No. S-73305F, or equivalent

*Tube*, connecting, glass "T", 6.4-mm OD, Sargent-Welch Scientific, Cat. No. S-82725A, or equivalent

*Thermometer*, digital, Omega Engineering, Inc., Digicator Model 402B, or equivalent

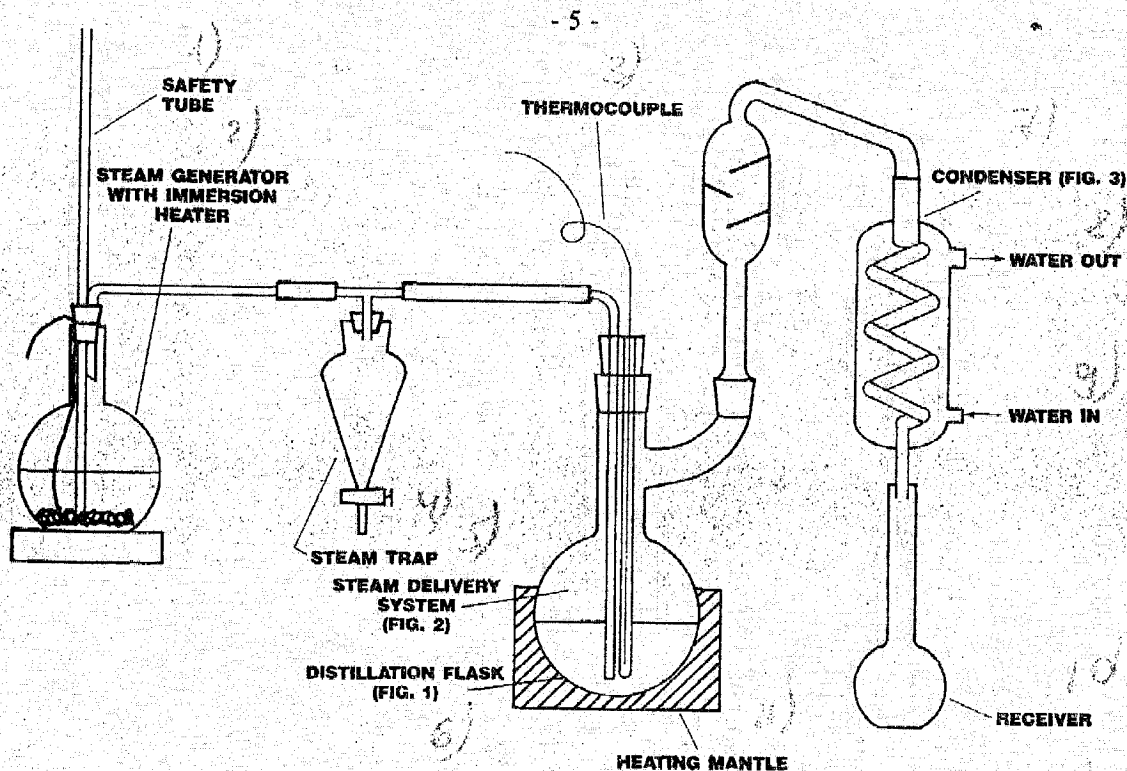


Figure 4

## Distillation Apparatus Assembly

*Thermocouples*, iron constantan, with 304 SS sheath, ungrounded, Omega Engineering, Inc., Digicator Model TJ 36-ICSS-184-12, or equivalent

## REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified. References to water mean deionized or distilled water.

*Acetic acid*, glacial, 99.7% minimum purity, Sargent-Welch Scientific, Cat. No. SC10256, or equivalent

*Acetic acid*, 6-M. Prepare by diluting 35 mL of glacial acetic acid to 100 mL in a polypropylene volumetric flask.

*Acetone*, 99.7% minimum purity, Sargent-Welch Scientific, Cat. No. SC10280, or equivalent

*Alizarin complexone*, 1,2-dihydroxy-3-anthraquinonyl-methylamine-N,N-diacetic acid, Sargent-Welch Scientific, Cat. No. EK8426, or equivalent

*Ammonium acetate*, 99.9% minimum purity, crystal, Sargent-Welch Scientific, Cat. No. SC-10570, or equivalent. Prepare a 20 mass-% solution by weighing  $20 \pm 0.01$  g of ammonium acetate into a 100-mL volumetric flask. Dilute to volume with water.

*Ammonium hydroxide*, concentrated, Sargent-Welch Scientific, Cat. No. SC-10592, or equivalent

*Buffer solution*, pH 7, Sargent-Welch Scientific, Cat. No. S30141-15B, or equivalent

*Capsule*, gelatin, Parke Davis and Co., Size O, or equivalent

*Filter paper*, 12.5-cm, Whatman No. 41, Sargent-Welch Scientific, Cat. No. S-33155-F, or equivalent

*Hydrochloric acid 2-M*, Sargent-Welch Scientific, Cat. No. SC12701, or equivalent

*Lanthanum oxide*, 99.99% minimum purity, Sargent-Welch Scientific, Cat. No. SC13017, or equivalent

*Lanthanum-alizarin complexone combined reagent*. Dissolve  $0.0480 \pm 0.001$  g of alizarin complexone in 0.1 mL of concentrated ammonium hydroxide and 1.0 mL of 20% ammonium acetate, together with 10 to 15 mL of water in a 50-mL beaker. Filter through Whatman No. 41 paper into a 200-mL volumetric flask containing 8.2 g of anhydrous sodium acetate, 6.0 mL of glacial acetic acid and sufficient water to dissolve the solids. Wash the paper with a small amount of water. Slowly add 100 mL of acetone while swirling.

In a 50-mL beaker dissolve  $0.0410 \pm 0.001$  g of lanthanum oxide in 2.5 mL of 2-M hydrochloric acid, warming gently to aid dissolution. Transfer this quantitatively to the 200-mL flask containing the aqueous acetone solution. Dilute to almost 200 mL with water. Mix, cool to ambient temperature and adjust the volume to the mark with water. Store in a refrigerator. Prepare fresh reagent every two weeks.

*Lens paper*, optical, Sargent-Welch Scientific, Cat. No. S-44315, or equivalent

*Silver sulfate*, powder, 99.9% minimum purity, Sargent-Welch Scientific, Cat. No. SC14678, or equivalent

*Sodium acetate*, anhydrous, powder, 99.9% minimum purity, Sargent-Welch Scientific, Cat. No. SC14711, or equivalent

*Sodium fluoride*, powder, 99.9% minimum purity, Sargent-Welch Scientific, Cat. No. SC14815, or equivalent

*Sodium fluoride*. Standard stock solution containing 1 mg F/mL. Dissolve  $1.015 \pm 0.001$  g of oven-dried (175 C for 16 hours) sodium fluoride in 100 mL of water containing 2 mL of 0.05-M sodium hydroxide, and dilute to 500 mL in a polypropylene volumetric flask, and store in this container.

*Sodium fluoride*. Working standard containing 10  $\mu$ g F/mL. With a pipet transfer 5.0 mL of the standard stock solution into a 500-mL polypropylene volumetric flask. Add 2 mL of 0.05-M sodium hydroxide and dilute to the mark with water and store in the flask.

*Sodium hydroxide*, 0.05-M, Sargent-Welch Scientific, Cat. No. SC14867, or equivalent

*Sodium peroxide*, 93% minimum purity, Sargent-Welch Scientific, Cat. No. SC14915, or equivalent

*Sucrose*, crystal, 99.9% minimum purity, Sargent-Welch Scientific, Cat. No. SC15095, or equivalent

*Sulfuric acid*, 95 to 98%, in safety bottle, Sargent-Welch Scientific, Cat. No. SC15130, or equivalent

*Sulfuric acid-silver sulfate solution*. Add 600 mL of concentrated sulfuric acid to 400 mL of water and add  $5.0 \pm 0.01$  g of silver sulfate; mix until dissolved. Store in a one-liter volumetric flask.

## PROCEDURE

### Organic Samples

Organic samples must be fused before distillation. Thoroughly clean the peroxide bomb by boiling it in water for 1-1/2 hours and then air dry. When the organic material is a solid, grind the sample in a mortar and weigh a ground portion not greater than 0.7 g to the nearest 0.1 mg into the fusion cup. Alternatively, when the sample is a liquid, weigh not more than 0.7 g into a gelatin capsule and introduce the capsule and contents into the fusion cup. In both cases add one scoop, approximately 15 g, of sodium peroxide and 0.5 to 0.6 g of sucrose. Mix the cup contents with a spatula. Wipe the spatula with a piece of filter paper and add the filter paper to the contents of the cup, taking care to cover the paper as much as possible with the mixture.

Place the fusion cup in the bomb assembly, install the bomb closure and fire electrically, following all the precautions specified by the manufacturer. Disassemble the bomb when cool. Add the fusion cup and bomb head to a 400-mL beaker and add sufficient water to just cover both the cup and the bomb head. Dissolve the melt in water, warming slightly to hasten solution. Transfer the solution to a 200-mL polypropylene volumetric flask. Do not filter even though it may be turbid.

### Catalyst Samples

The sample size to be taken is governed by several factors but should never be greater than 1.5 g since aluminum ions, if present, have a retarding effect on the volatilization of fluoride in the Willard-Winter steam distillation. Under *Color Development* it is stated that the maximum aliquot of distillate that can be used for color development is 15 mL. The optimum amount of fluoride in the aliquot for the color development is 5 to 20  $\mu\text{g}$ . Therefore, the sample weight, total volume of distillate, and the distillate aliquot volume all must be adjusted to secure the optimum amount of fluoride desired for color development.

Weigh the appropriate amount of the ground sample to the nearest 0.1 mg into a gelatin capsule. If the analytical result is to be calculated on a volatile free basis, determine the volatile matter on a separate ground sample in accordance with the UOP method prescribed for the type of catalyst involved.

### Distillation of Organic and Catalyst Samples

Assemble the distillation apparatus as shown in Fig. 4. Place 100 mL of sulfuric acid-silver sulfate solution into the distillation flask. Then add either the capsule containing the catalyst sample or an aliquot, not to exceed 50 mL, from the fusion volumetric flask, with the special pipet. Place a 500-mL polypropylene volumetric flask containing 5 mL of 0.05-M sodium hydroxide under the delivery tube of the condenser as a receiver.

Start the distillation without heating the distillation flask, using only a slow flow of steam at the beginning. Apply heat only after the initial temperature rise has halted. Then increase the heat and the steam rate to maintain a temperature of 140 to 145 C, and a distillation rate of 4 to 5 mL per minute throughout the distillation. Keep the distillation rate below 5 mL per minute to avoid possible carry-over of interfering ions.

Discontinue the distillation after about 475 mL of distillate has been collected. Dilute the distillate in the 500-mL volumetric flask to the mark with water and mix well.

### Color Development

Pipet a 15 mL or less aliquot containing from 5 to 20  $\mu\text{g}$  of fluoride from the 500 mL of distillate. Place this in a 25-mL volumetric flask. Add 0.40 mL of 6 M acetic acid and 8.00 mL of the lanthanum-alizarin complexone reagent. Dilute to the mark with water, mix well and allow the color to develop for 10 minutes. Fill the cells with the sample and blank solutions. Read the absorbance within 6 hours, using a reagent blank as a reference, with covers on the cells to avoid evaporation of the acetone, at a wavelength of 625 nm. Convert the absorbance to micrograms of fluoride from the calibration curve.

### Preparation of the Calibration Curve

Pipet exactly 0.25-, 0.50-, 0.75-, 1.00-, 1.50-, 2.00- and 2.50-mL portions, respectively, of the working standard sodium fluoride solution into each of seven 25-mL volumetric flasks. Add 0.40 mL of 6 M acetic acid to each flask and also to an eighth 25-mL volumetric flask for a reagent blank. Then, using a 10-mL Mohr pipet, add 8.00 mL of lanthanum-alizarin complexone reagent to all 8 flasks. Dilute each to the mark with water, mix well and allow the color to develop for 10 minutes. The color is stable for up to 6 hours. Fill the cells and cover. Read the absorbance of the samples, using the reagent blank as the reference, with covers on the cells, at a wavelength of 625 nm. Construct a *calibration* curve to show micrograms of fluoride in the 25-mL volumetric flasks versus the respective absorbances. The curve will be a straight line, ideally passing through the origin.

### CALCULATIONS

Calculate the mass-% fluoride in the as received sample using the following equation:

$$\text{Fluoride, as received, mass-\%} = \frac{AB}{10^4 WC}$$

where:

- A = mass of fluoride from calibration curve,  $\mu\text{g}$
- B = volume of the distillate, mL
- C = aliquot taken for color development, mL
- W = mass of sample, g
- $10^4$  = converts  $\mu\text{g}$  to percent

Calculate the mass-% fluoride in the catalyst sample on a volatile free (VF) basis as follows:

$$\text{Fluoride, VF, mass-\%} = \frac{AB}{10^4 WC \frac{(100 - D)}{100}}$$

where:

- D = volatile matter in sample, mass-%
- A, B, C, W and  $10^4$  are as previously defined

### PRECISION

Based on 6 replicate determinations, the estimated standard derivation (esd) was calculated for fluoride in two samples as shown in the following table. Duplicate results by the same operator should not differ by more than the allowable difference shown (95% probability).

| <u>Sample</u>  | <u>Level,<br/>mass-%</u> | <u>esd,<br/>mass-%</u> | <u>Allowable<br/>Difference,<br/>mass-%</u> |
|----------------|--------------------------|------------------------|---------------------------------------------|
| Catalyst       | 0.013                    | 0.002                  | 0.008                                       |
| Vacuum gas oil | 0.11                     | 0.012                  | 0.044                                       |

### TIME FOR ANALYSIS

The elapsed time for one analysis of an organic sample requiring fusion is 4 hours. The labor requirement is 0.4 hour.

The elapsed time for one analysis of a catalyst sample is 2 hours. The labor requirement is 0.3 hour.

### SUPPLIERS

Beckman Instruments Inc., 2500 Harbor Blvd., Fullerton, CA 92634-3100  
Glas-Col Apparatus Co., 711 Hulman St., Terre Haute, IN 47802  
Omega Engineering Inc., P.O. Box 4047, Stamford, CT 06907-0047  
Parr Instrument Co., 211 Fifty-third St., Moline, IL 61265  
Sargent-Welch Scientific, 7300 N. Linder Ave., P.O. Box 1026, Skokie, IL 60077  
Parke Davis and Co., 1350 Estes, Elk Grove, IL 60007  
UOP Inc., Box 5017, Des Plaines, IL 60017