

FLUORIDE IN CATALYSTS, MOLECULAR SIEVES AND AQUEOUS SOLUTIONS BY ION SELECTIVE ELECTRODE

UOP Method 912-94

SCOPE

This method is for determining total fluoride in aluminosilicate catalysts and molecular sieves, and inorganic fluoride in aqueous samples. The method is particularly useful for catalysts containing zirconia or other metals that interfere with other procedures. The range of fluoride typically determined is from 0.005 to approximately 20 mass-% for catalysts or molecular sieves, and 0.005 to approximately 50 mass-% for aqueous samples.

OUTLINE OF METHOD

Fluoride is quantitatively separated from a solid sample by fusion with vanadium pentoxide at 1000°C in a steam atmosphere. The fluoride is converted to hydrofluoric acid (HF) and is collected with the steam condensate. Sodium hydroxide is added to the condensate solution to prevent volatilization of the HF by converting it to sodium fluoride. The condensate solution is then diluted to a specific volume and mixed with an ionic strength activity buffer. The fluoride concentration is measured potentiometrically by comparison to standard fluoride solutions using a high sensitivity pH meter and a fluoride ion-selective electrode.

Inorganic fluoride is determined in aqueous samples by dilution to a specific volume with water. The solution is mixed with an ionic strength activity buffer and the fluoride concentration is determined potentiometrically as described above.

APPARATUS

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

Aluminum press and die, for forming nickel boats and boat covers, UOP

Balance, readability 0.1-mg

Beaker, graduated, 150-mL, polypropylene, Fisher Scientific, Cat. No. 02-591-10C

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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Boat puller, fabricate by bending a hook at one end of a 500-mm length of a 4-mm diameter nickel welding rod, UOP

Connector, glass, T-shaped, 7.9-mm OD, Fisher Scientific, Cat. No. 15-328B

Crucible, porcelain, high form, 10-mL, Fisher Scientific, Cat. No. 07-965C

Desiccator, with plate, Fisher Scientific, Cat. No. 08-615A

Electrode, combination fluoride, Orion, Model 96-09, Fisher Scientific, Cat. No. 13-641-904

Flasks, volumetric, polypropylene, Class B, 100-, 250-, 500- and 1000-mL, Fisher Scientific, Cat. Nos. 10-198-50B, D, E and F, respectively

Flask, round bottom, borosilicate glass with three vertical necks and 24/40 joints, 3-liter, Fisher Scientific, Cat. No. 10-164-2D

Furnace, split-tube, capable of maintaining $1100 \pm 1^\circ\text{C}$, Fisher Scientific, Cat. No. 10-472-50

Heater, immersion, Fisher Scientific, Cat. No. 11-463-14

Jack, 150- x 180-mm, Fisher Scientific, Cat. No. 14-673-10, 2 required

Magnetic stir bar, Fisher Scientific, Cat. No. 14-511-94

Magnetic stirrer, Fisher Scientific, Cat. No. 14-493-120MR

Meter, pH, Orion, Model EA 940, Fisher Scientific, Cat. No. 13-641-741

Nickel boats, heavy wall, Fisher Scientific, Cat. No. 07-645

Oven, drying, Fisher Scientific, Cat. No. 13-246-506G

Pinchcock, Day, Fisher Scientific, Cat. No. 05-867

Pipets, volumetric, Class A, 1-, 5-, 10-, 25- and 50-mL, Fisher Scientific, Cat. Nos. 13-660A, E, F, J and K, respectively

Reaction chamber-condenser assembly, nickel pyrohydrolysis tube (see Fig. 1), UOP

Rubber stopper, black, solid, size No. 4, Fisher Scientific, Cat. No. 13-130F

Rubber stopper, black, two-hole, size No. 4, Fisher Scientific, Cat. No. 14-140F

Spatula, micro-, Fisher Scientific, Cat. No. 21-401-15

Support ring, cork, 140-mm OD, Fisher Scientific, Cat. No. 07-835B

Transformer, variable 120V, 10A, Fisher Scientific, Cat. No. 09-521-110

Tubing, borosilicate glass, standard wall, 6-mm OD, Fisher Scientific, Cat. No. 11-362D

Tubing, clear, silicone rubber, 9.5-mm OD, Fisher Scientific, Cat. No. 14-169-3C

Tubing clamp, vacuum, Fisher Scientific, Cat. No. 14-199

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.

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

Desiccant, 8-mesh, indicating, Fisher Scientific, Cat. No. 07-578-3A

Electrode filling solution, fluoride combination electrode, Fisher Scientific, Cat. No. 13-641-899

Gloves, Playtex, Fisher Scientific, Cat. No. 11-394-10B

Methyl purple indicator, Aldrich Chemical, Cat. No. 27, 733-9

Nickel ribbon, nickel No. 200 ASTM-B162-74, 0.002- x 1.00-inch, Teledyne Rodney Metals of Penn. Fabricate disposable boats and lids from nickel ribbon using the aluminum press and die.

Phosphate rock, verification standard, approximately 3.82% fluorine, NIST, Cat. No. SRM 120C

Sodium fluoride, 99.99% minimum purity, Aldrich Chemical, Cat. No. 21,530-9

Sodium hydroxide, pellets, Aldrich Chemical, Cat. No. 30,657-6

Sodium hydroxide, 0.1-M. Dissolve 2 g of sodium hydroxide pellets in approximately 500 mL of water.

TISAB II (total ionic strength activity buffer), fluoride electrode activity standard, Fisher Scientific, Cat. No. 13-641-873

Toothpaste, non-gel type containing fluoride

Vanadium pentoxide, 99.99% purity, Aldrich Chemical, Cat. No. 20,485-4

PROCEDURE

Preparation of Fluoride Standards

Fluoride Standard, Approximately 10,000- $\mu\text{g/mL}$ F

1. Place approximately 4 g of sodium fluoride in a clean crucible and dry at 110°C for 2 hours in a drying oven.
2. Remove the crucible from the oven and place it in a desiccator to cool.
3. Weigh approximately 2.2 g, weighed to the nearest 0.1 mg, of the dried sodium fluoride into a 150-mL polypropylene beaker and dissolve in approximately 10 mL of water.
4. Transfer the sodium fluoride solution quantitatively into a 100-mL volumetric flask with water.
5. Dilute to the mark with water, and invert several times to mix.

6. Calculate the concentration of the fluoride in the standard to four significant figures as follows:

$$\text{Fluoride, } \mu\text{g/mL} = \frac{(10^6)(0.4525)M}{V} \quad (1)$$

where:

M = mass of sodium fluoride weighed into the flask, g

V = dilution volume, mL

0.4525 = molecular weight of fluoride (19.00) divided by the molecular weight of sodium fluoride (41.99)

10^6 = factor to convert g to μg

Fluoride Standard, Approximately 100- $\mu\text{g/mL}$ F

Pipet 10 mL of the 10,000- $\mu\text{g/mL}$ F standard into a 1000-mL volumetric flask and dilute to the mark with water. Invert several times to mix.

- The actual concentration of this standard will be one-hundredth of the standard (calculated from Eq. 1) being diluted.

Fluoride Standard, Approximately 10- $\mu\text{g/mL}$ F

Pipet 10 mL of the 100- $\mu\text{g/mL}$ F standard into a 100-mL volumetric flask and fill to the mark with water. Invert several times to mix.

- The actual concentration of this standard will be one-tenth of the standard being diluted.

Fluoride Standard, Approximately 1- $\mu\text{g/mL}$ F

Pipet one milliliter of the 100- $\mu\text{g/mL}$ F standard into a 100-mL volumetric flask and fill to the mark with water. Invert several times to mix.

- The actual concentration of this standard will be one-hundredth of the standard being diluted.

Instrument Set Up

Refer to Figure 3 for assembly of the apparatus described in the following steps.

- Place the reaction chamber-condenser assembly (Fig. 1) into the furnace with the handle (Fig. 2) attached to the end as shown in Fig. 3 and close the furnace. Insert the sample port closure (Fig. 4) into the inlet of the reaction chamber.
- Connect one leg of the sample port closure to the tap water supply using plastic tubing.
 - Water is used to keep the rubber port closure at low temperature to prevent thermal decomposition.
- Connect the other leg of the sample port closure to the inlet tube of the condenser using plastic tubing.
- Connect the plastic tubing to the outlet tube of the condenser and direct the exit to drain.
- Attach a short length of plastic tubing to the condenser exit for the collection of condensate.
- Place the round bottom flask on the cork support ring.

7. Place the immersion heater into the round bottom flask so that it rests on the bottom.
8. Pass the wires from the immersion heater through the two holes of a two-hole rubber stopper and insert the stopper in one of the side openings of the flask as shown in Fig. 3. Connect the wires to the transformer.
9. Insert a 60-cm length of glass tubing through a second two-hole rubber stopper so that the end almost touches the bottom of the flask.
 - This tubing is to relieve pressure build-up in the flask.
10. Insert a short length of glass tubing through the second hole of the rubber stopper and insert this stopper into the center opening of the flask.
 - This is the steam generator outlet.
11. Place a solid rubber stopper into the third opening of the flask.
 - This opening is used to add water to the flask.
12. Connect the steam generator outlet to a T-shaped glass connector with plastic tubing.
13. Connect one of the exits of the T-shaped connector to the copper tube on the inlet of the reaction chamber using a section of plastic tubing. Connect a length of plastic tubing to the third exit that leads to a drain.
 - The steam flow to either position is controlled by a pinchcock.

Sample Preparation

Catalyst Samples (non-hygroscopic)

1. Fill the round-bottom flask approximately 3/4 full with water. Turn on the tap cooling water to the sample port closure/condenser. Turn on the transformer connected to the immersion heater and adjust it to produce a slow constant boiling of the water (approximately 4 to 5 mL/min). Turn on the tube furnace and raise the temperature to the setpoint of 1000°C. Open the pinchcock on the tubing to the drain and close the pinchcock to the reaction chamber. Follow the manufacturer's instructions for operation of the furnace.
 - When not in use, the furnace and transformer should be turned off.
 - The cooling water should be turned off after the furnace has cooled to ambient temperature.
2. Run blanks in duplicate as described in Steps 3 through 18 but omit the sample.
 - The first blank is used to condition the reactor and is to be discarded. The second blank is used to determine the F, mass-% as shown under *CALCULATIONS*.
3. Place the disposable nickel boat inside the heavy wall nickel boat.
4. Weigh approximately 0.5 g of vanadium pentoxide into the bottom of the disposable nickel boat.
 - To prevent the escape of fluoride from the reactor tube before reacting with the steam, a layer of vanadium pentoxide is placed on the bottom of the boat to act as a thermal insulator and thus inhibit volatilization of the sample until steam has reached the reactor area.
 - Care must be taken when handling the vanadium pentoxide including the wearing of gloves because it is toxic and an irritant.

5. Determine the mass of the combined boat and contents to the nearest 0.1 mg.
6. Obtain approximately 5 g of the ground catalyst sample according to UOP Method 918.
7. Weigh, in duplicate, approximately 2-g samples at the same time that the analytical sample is weighed and determine the LOI by UOP Method 275.
8. Weigh the sample to be used for the fluoride analysis, to the nearest 0.1 mg, into the disposable boat.
 - The sample amount depends on the concentration of fluoride present. Use Table 1 as a guide to choose the appropriate sample mass.

Table 1

<u>Estimated Fluoride, mass-%</u>	<u>Approximate Sample Mass, g</u>
0.1 to 1	0.2
1 to 10	0.1
10 to 20	0.05

9. Weigh approximately 0.8 g of vanadium pentoxide, on top of the sample and mix with a spatula.
10. Weigh an additional 0.8 g of vanadium pentoxide and place it over the top of the sample and vanadium pentoxide mixture. Carefully cover the disposable nickel boat with the lid.
 - The top layer of vanadium pentoxide is placed on the sample to provide a reaction zone through which vapors will pass in intimate contact with the vanadium pentoxide before leaving the boat.
11. Place a 150-mL polypropylene beaker containing approximately 5 mL of 0.1-*M* NaOH and 4 drops methyl purple indicator under the condenser so that the tubing on the outlet of the condenser tube is immersed into the solution.
12. Verify the generation of steam by observing the production of condensate at the outlet to drain. Drain the condensate and close the pinchcock in the tubing connected to the reaction chamber before starting Step 13.
13. Remove the inlet port closure and push the covered nickel boat into the reactor using the boat puller. Position the boat so that the rear (flat end) of the boat is at the mid-point of the hottest zone in the reactor.
 - For this procedure, the hottest zone is identified as the mid-point of the furnace.
14. Close the reactor as soon as possible after positioning the boat and immediately begin the introduction of steam by opening the pinchcock on the tubing connected to the reaction chamber. Ensure that the pinchcock on the tubing connected to the drain is closed.
15. Collect approximately 60 mL of condensate (nominally about 15 minutes) in the 150-mL polypropylene beaker periodically adding 0.1-*M* NaOH dropwise to maintain the solution basic as indicated by a green color.
 - The solution is maintained basic to prevent hydrofluoric acid from volatilizing.

16. Remove the beaker so that the condenser tip is no longer submerged and set the beaker aside. The passage of steam is continued for 5 more minutes to flush out the reactor. Collect the condensate from the flushing in a separate beaker. The condensate from the flushing is discarded.
 - Additional flushing time is required after a sample of high fluoride content is analyzed.
17. Open the pinchcock to the drain and close the pinchcock to the reaction chamber. Remove the nickel boats from the reaction chamber with the boat puller and discard the inner disposable boat, lid and contents in a safe manner.
18. Transfer the condensate solution in the 150-mL beaker quantitatively to a 250-mL volumetric flask and dilute to volume with water. Cap and mix well by inverting several times.
 - The analysis of the solution must be performed on the same day as the pyrohydrolysis.

Molecular Sieve Samples (hygroscopic)

1. Obtain approximately 5 g of the sample according to UOP Method 918.
2. Spread the ground sample in a thin layer on a non-porous, non-contaminating surface.
 - The sample is covered with an acceptable media such as a paper towel to prevent foreign matter from falling on it and to provide ventilation access from all sides.
3. Expose the spread sample for at least four hours in the laboratory where weighing is to be performed.
4. Weigh, in duplicate, approximately 2-g samples at the same time that the analytical sample is weighed and determine the LOI using the same procedure as UOP Method 275, except set the muffle furnace temperature at 1000°C. Analyze the sample as described in Steps 1 through 18 under *Catalyst Samples*, excluding Steps 6 and 7.

Aqueous Samples

1. Weigh the sample into a tared 100-mL polypropylene volumetric flask, weighed to the nearest 0.1 mg.
 - Table 2 shows the sample mass to be used.

Table 2

Estimated Fluoride Content of Liquid Sample, mass-%	Sample Mass for Analysis, g	Aliquot, mL
0.5	1	0
5	2	2
10	1	2
15	1	2
50	0.5	1

2. Dilute the sample with water to the mark, stopper and thoroughly mix by inverting several times.
3. Transfer by pipet, an aliquot of the sample solution into a 100-mL polypropylene volumetric flask.
 - Table 2 shows the appropriate aliquot volume to be used. The zero aliquot volume for the 0.5 mass-% solution indicates that no further dilution is necessary.

4. Dilute the aliquot solution with water to the mark, stopper and thoroughly mix by inverting several times.

Analysis of Solutions

After addition of the TISAB as directed in the sections below, the standards and samples must be analyzed within approximately 15 min. All solutions must be analyzed at the same temperature. Magnetic stirrers may generate sufficient heat to change solution temperature. Therefore, a piece of insulating material such as cork or cardboard should be placed between the stirrer and beaker for standards, blank and samples.

Standards

1. Drain the electrode filling solution from the electrode each day, rinse twice with water and refill with fresh solution.
 - The filling solution level should be at least 25 mm above the expected level of the sample in the beaker to ensure a proper flow rate. If the filling solution is less than 25 mm above the sample level, the electrode potential may be erratic.
2. Choose two standards, see *Preparation of Standards*, that bracket the F concentration expected in the sample condensate solution or liquid sample.
 - For example, if the sample reading is expected to be 30 $\mu\text{g/mL}$ choose the 10- and 100- $\mu\text{g/mL}$ standards.
3. Pipet 50 mL of the more dilute standard and 50 mL of TISAB into a 150-mL beaker and add a stirring bar.
4. Place the beaker on a magnetic stirrer and stir at a moderate rate.
5. Rinse the electrode with water, blot dry, and place it in the standard solution.
 - Do not wipe or rub the sensing element.
6. Wait for a stable reading, then adjust the meter to display the fluoride value of the standard.
 - Instructions for this measurement accompany the electrode when purchased.
7. Repeat Steps 3 through 5 using the more concentrated standard.
8. Wait for a stable reading and then adjust the meter to display the fluoride value of the second standard.
 - The slope of the calibration as calculated by the meter should be in the range of -54 to -60 mV per decade when the solution temperature is 25°C. If the value is not within this range remove the electrode from the solution, polish it lightly with toothpaste and reanalyze fresh aliquots of the standards.
9. Verify the calibration every two hours that samples are being run by reanalyzing fresh aliquots of the standards.

Blank

1. Add, by pipet, 50 mL of the blank solution and 50 mL of TISAB to a 150-mL beaker and add a stirring bar.
2. Place the beaker on a magnetic stirrer and stir at a moderate rate.

3. Rinse the electrode with water, blot dry, and place it in the blank solution. The fluoride concentration is displayed on the meter. Record the reading displayed for the blank.

Verification Standard

1. Perform the pyrohydrolysis of the phosphate rock verification standard before and after each series of analyses as described under *Sample Preparation, Catalyst Samples*, Steps 3 through 5 and 8 through 18.
2. Add, by pipet, 50 mL of the verification standard condensate solution and 50 mL of TISAB to a 150-mL beaker and add a stirring bar.
3. Place the beaker on a magnetic stirrer and stir at a moderate rate.
4. Rinse the electrode with water, blot dry, and place it in the verification standard solution. The fluoride concentration is displayed on the meter. Record the reading as “verification standard”.
 - If the value obtained for the verification standard deviates by more than $\pm 0.13\%$ F from the established value, isolate the components of the system (meter, electrode and standard) and check each in turn to determine the cause of the discrepancy.
 - Low Verification Standard recoveries and high blanks are characteristic of nickel pyrohydrolysis tubes in unsatisfactory condition. If such conditions exist, replace the tube.

Samples

1. Add, by pipet, 50 mL of the sample condensate solution or diluted liquid sample and 50 mL of TISAB to a 150-mL beaker and add a stirring bar.
2. Place the beaker on a magnetic stirrer and stir at a moderate rate.
3. Rinse the electrode with water, blot dry, and place it in the sample. Record the fluoride concentration displayed on the meter.
4. Store the electrode when not in use in 100- $\mu\text{g/mL}$ fluoride standard.

CALCULATIONS

When using Equations 2, 3 or 4, report total fluoride to one significant figure below 0.1 mass-%, to two significant figures between 0.1 and 1.0 mass-%, to three significant figures between 1.0 and 10 mass-%, and to two significant figures above 10 mass-%.

Catalyst or Molecular Sieve Samples

Calculate the total fluoride in the catalyst or molecular sieve sample on an as-received basis as follows:

$$\text{Fluoride, mass - \%} = \frac{K(L - N)}{10^4 W} \quad (2)$$

where:

K = dilution volume, 250-mL

L = fluoride concentration of 250-mL volumetric flask containing sample, $\mu\text{g/mL}$

N = fluoride concentration of 250-mL volumetric flask containing blank, $\mu\text{g/mL}$

W = sample mass, g
10⁴ = factor to convert to mass-%

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

$$\text{Fluoride, VF, mass} - \% = \frac{K(L - N)}{10^4 \left[\frac{100_A - D}{100} \right] W} \quad (3)$$

where:

D = volatile matter in sample, mass-%
100 = factor to convert mass-% residue after ignition to a decimal fraction
100_A = factor to convert mass-% residue after ignition
K, L, N,
W and 10⁴ = as previously defined (Eq. 2)

Aqueous Samples

Calculate the inorganic fluoride in the solution as follows:

$$\text{Fluoride, mass} - \% = \frac{EFG}{10^4 H} \quad (4)$$

where:

E = volume of original sample dilution, mL
F = fluoride concentration in final sample dilution, $\mu\text{g/mL}$
G = dilution factor (if successive dilutions are required) $\frac{V_1}{V_2}$

where:

V₁ = volume to which **V₂** was diluted, mL
V₂ = aliquot taken for final sample dilution, mL
H = mass of original sample, g
10⁴ = factor to convert to mass-%

PRECISION

Repeatability

Based on two tests performed by each of two analysts on each of two different days (8 tests), the within-laboratory estimated standard deviations (esd) were calculated for fluoride at the concentrations listed in Table 3. Two tests performed in one laboratory by different analysts on different days should not differ by more than the allowable differences shown in Table 3 at the concentrations shown (95% probability).

Table 3

Sample Type	Fluoride Concentration, mass-%	Within-Lab esd, mass-%	Allowable Difference, mass-%
Catalyst	0.02	0.001	0.01
Catalyst	0.85	0.017	0.07
Aqueous	44	1.0	4

Reproducibility

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

TIME FOR ANALYSIS

The elapsed time for one analysis including calibration is 3.5 hours. The labor requirement is 2.0 hours. Each additional sample analyzed at the same time increases the labor requirement by 0.75 hour.

REFERENCES

UOP Method 275, "Loss on Ignition of Catalyst at 900°C"

UOP Method 918, "Collection and Grinding of Adsorbents and Catalysts for Analysis"

SUGGESTED SUPPLIERS

Aldrich Chemical Co., Inc., P.O. Box 355, Milwaukee, WI 53201 (414-273-3850)

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

National Institute of Standards and Technology (NIST), Office of Standard Reference Materials,
Gaithersburg, MD 20899 (301-975-6776)

Teledyne Rodney Metals of Penn., 1045 Pulinski, Ivyland, PA 18974 (215-441-0205)

UOP, Process Performance Systems and Equipment, 25 E. Algonquin Rd., Des Plaines, IL 60017-5017
(708-391-2529)

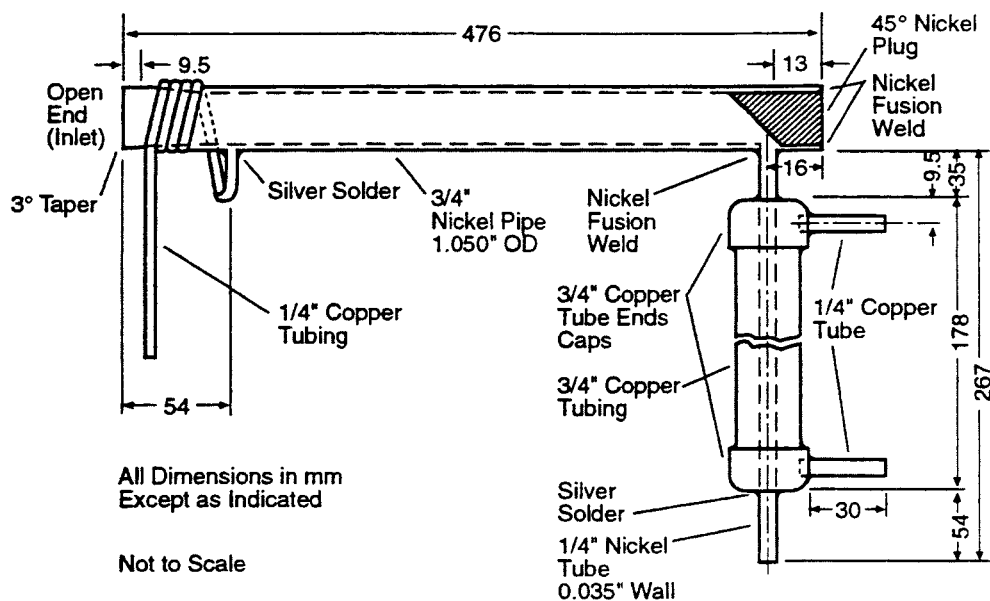


Figure 1

Reaction Chamber - Condenser Assembly

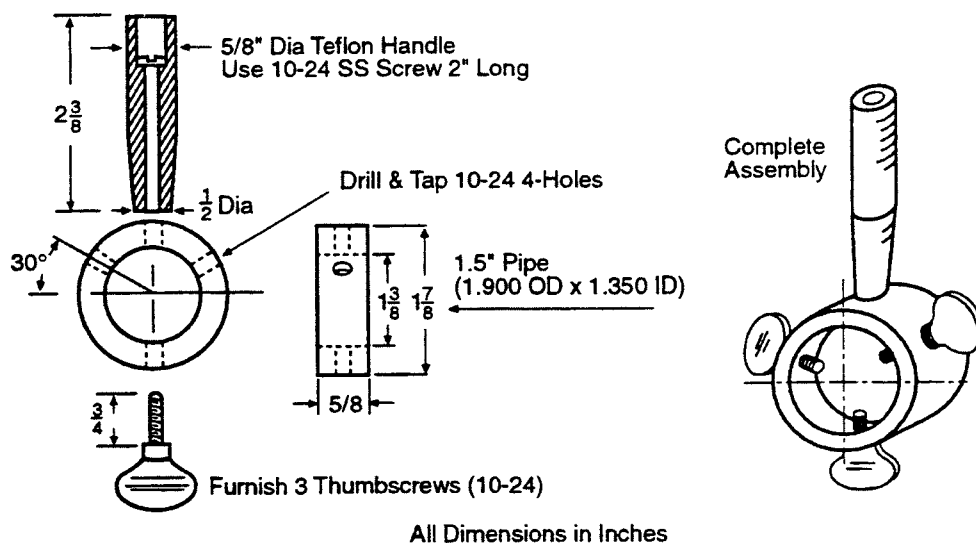


Figure 2

Handle Assembly

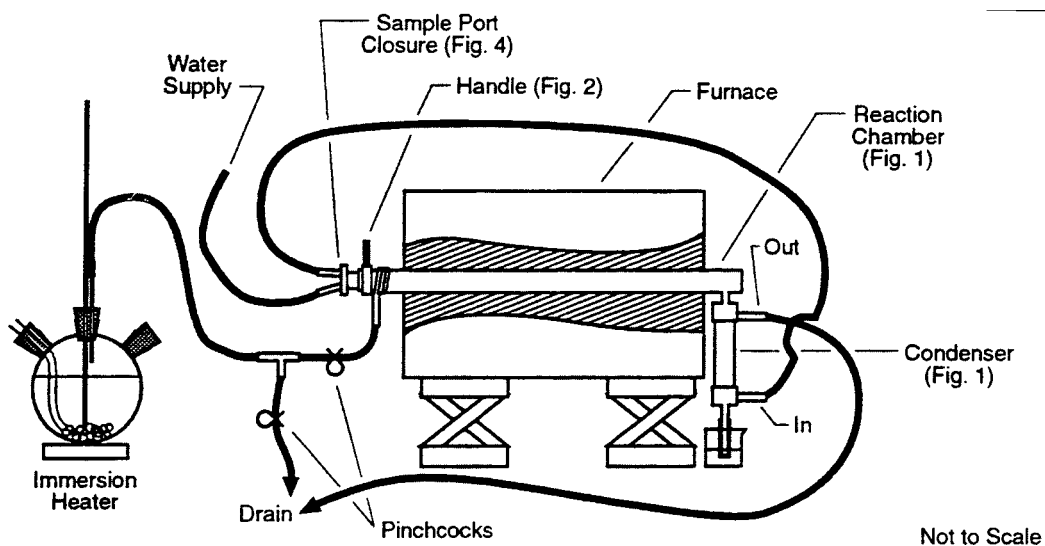


Figure 3

Apparatus Assembly

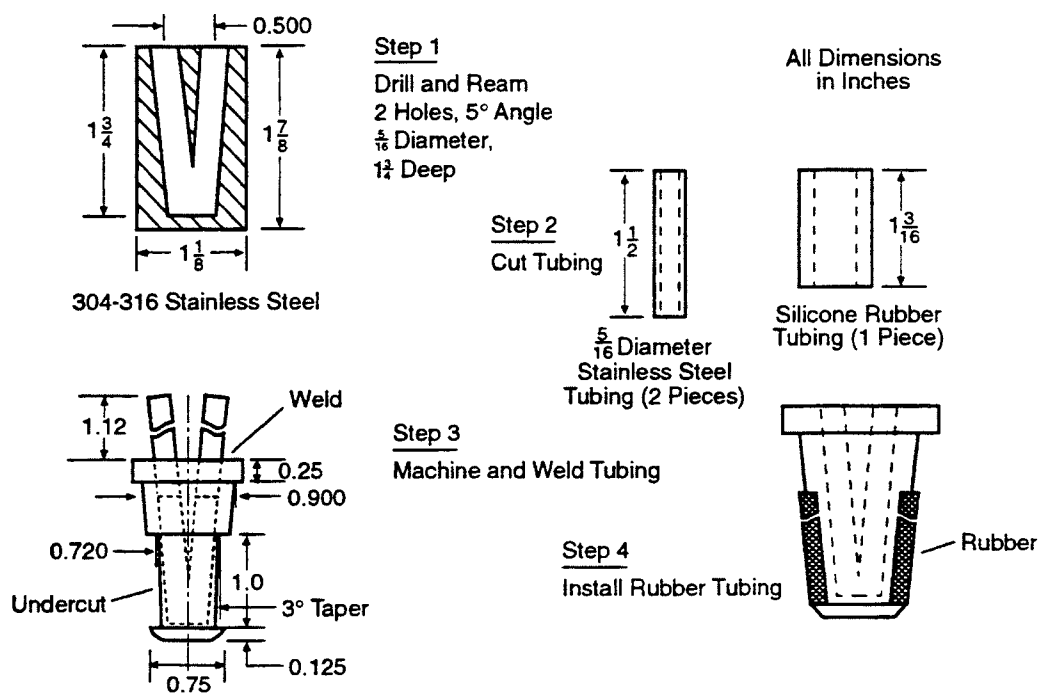


Figure 4

Sample Port Closure