

FREE WATER AND VOLATILE HYDROCARBON CONTENT OF MOLECULAR SIEVES

UOP Method 434-83

SCOPE

This method is for determining the free water content of either fresh or used molecular sieves down to a lower limit of 0.1 mass-%. Free water content of fresh sieves is defined as the loss in mass as the result of a prescribed period of heating at 350 C. The free water content, calculated on a hydrocarbon free basis, and the volatile hydrocarbon content of used sieves can also be determined.

OUTLINE OF METHOD

A weighed quantity of fresh sieves is heated in a tube for 2 hours at 350 C to volatilize the water present, while being purged with dry nitrogen. The cooled sieves are weighed and the loss in mass is calculated as mass-% water. Used sieves are treated in the same fashion except that the volatile materials are collected, and the amount of water in the condensate is determined by Karl Fischer titration. From these data the free water and hydrocarbon content of the sieves are calculated.

APPARATUS

Balance, readable to 0.1 mg

Balance, triple beam, readable to 0.01 g

Bottle, dropping, with ground pipet stopper, 30-mL capacity, Sargent-Welch Scientific, Cat. No. S-8755-C, or equivalent

Clamp, glass grinding, Thomas, size No. 12, Sargent-Welch Scientific, Cat. No. S-40222-D, or equivalent

Cylinder, graduated, 100-mL

Flask, Dewar, wide mouth, 665-mL, Sargent-Welch Scientific, Cat. No. S-34707-A, or equivalent (2 required)

Flask, volumetric, 250-mL

Flowmeter, Matheson, Model 7631H, Size 602 tube, and Model 7966 stand, or equivalent

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).

Furnace, upright, tubular, electric, with mounting, Marshall Furnace Co., Model 1034, or equivalent. The furnace should have a temperature profile so that, with the sample tube in place and the gas flow as specified, the set temperature of 350 C does not drop more than 15 C over a 20 cm section of the furnace.

Gas purifier, filled with indicating Drierite and 5A molecular sieves, Alltech Associates, Cat. No. 8153, or equivalent

Glass wool, borosilicate

Karl Fischer Apparatus, electrometric endpoint (see *NOTE*), Beckman Instruments, Inc., Aquameter, Cat. No. KF-4B, or equivalent

Lab jacks, 15 × 18.5 cm platform, Sargent-Welch Scientific, Cat. No. S-79151, or equivalent (2 required)

Pipet, Mohr, 25-mL, Sargent-Welch Scientific, Cat. No. S-69570-H, or equivalent

Regulator, nitrogen, Matheson, 8-BF, CGA No. 580, or equivalent

Sample tube, with top section, Pyrex, see Fig. 1, Reliance Glass Works, special order, or equivalent

Springs, glass grinding, Sargent-Welch Scientific, Cat. No. S-40220-C, or equivalent (2 required)

Stoppers, rubber, micro, solid, red rubber, Sargent-Welch Scientific, Cat. No. S-73460, or equivalent (5 required)

Stoppers, rubber, solid, Size 0 and 5-1/2, to close ends of sample tube, Sargent-Welch Scientific, Cat. No. S-73305 B and H, or equivalent

Temperature controller, 0 to 600 C, West Instrument Co., West 800, or equivalent

Temperature indicator, Doric Trendicator, -200 to 933 C. Doric Scientific Div., Cat. No. 410A-J-C, with lab or bench mounting, accessory W5, or equivalent

Thermocouple, Iron-Constantan, 4.5 m, Sargent-Welch Scientific, Cat. No. S-71860-10, or equivalent

Thermocouple well, stainless steel, 5-mm OD thin-wall, 700-mm long, closed on one end, UOP Inc., or equivalent

Trap, condensate, type No. 1, see Fig. 2, fabricated from a 15-mL centrifuge tube, Reliance Glass Works, special order, or equivalent

Trap, condensate, type No. 2, see Fig. 2, fabricated from a 15-mL centrifuge tube, Reliance Glass Works, special order, or equivalent

Tubing, Tygon, 7.9-mm ID (3-m required)

Tubing, Tygon, 9.5-mm ID (3-m required)

Valve, Adjustable Safety Relief, 69-207 kPa, brass, Air Products, Cat. No. E33-41121, 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.

Acetone

CO₂, solid, (dry ice)

Ice

Karl Fischer reagent, Sargent-Welch Scientific, Cat. No. SC12960-500ML, or equivalent

Methanol, 99.5% minimum purity, not more than 0.01% water

Nitrogen, dry, 99.99% minimum purity

PROCEDURE

Fresh Sieves

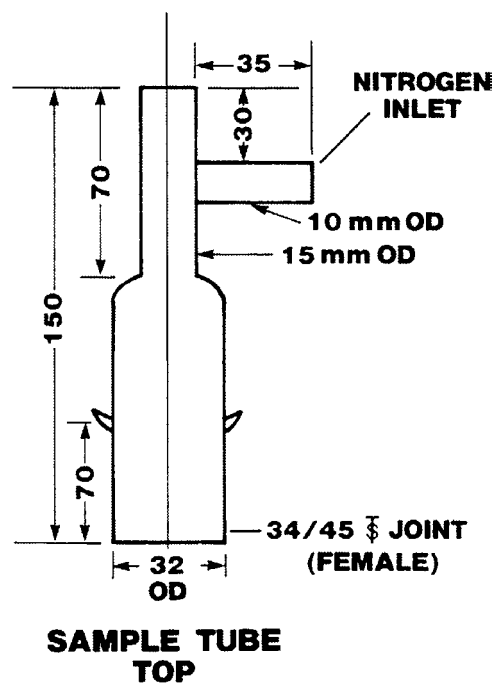
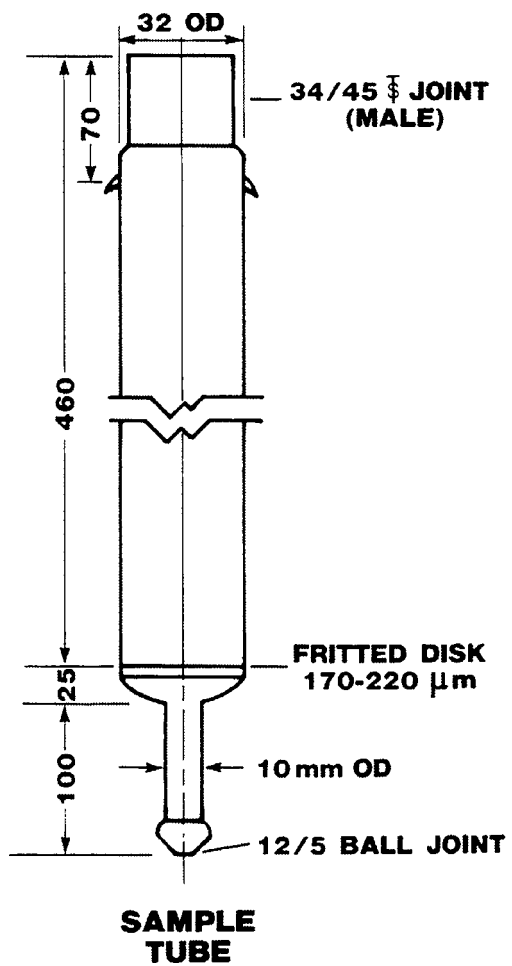
Weigh the clean empty sample tube to the nearest 0.01 g, without the top but including the rubber stoppers for each end. Remove the upper stopper and pour approximately 75 g of the molecular sieve sample into the tube, usually to a depth of about 20 cm. Restopper the tube and weigh the tube and contents to the nearest 0.01 g. Remove the stoppers and place the top on the sample tube. Secure the top to the tube with glass grinding springs. Position the tube in the furnace so that the section containing the sample coincides with the 20-cm section of only 15 C or less temperature variation. Insert the thermocouple well to the midway point of the hottest section of the sample bed. Support it with a stopper in the sample tube top. Place the thermocouple in the well and connect the nitrogen tube to the nitrogen inlet. Fig. 3 illustrates how the completed set-up should look, however, the traps are not required for the fresh sieves analysis. Adjust the nitrogen pressure to 140 kPa (20 psig) on the outlet pressure gauge of the regulator. Install and adjust the safety relief valve to vent at 170 kPa. Set the flow rate of the nitrogen, which has been passed through a gas purifier, at 25 L per hour by means of the valve on the outlet of the regulator. Measure the flow rate at the outlet from the sample tube with the flowmeter. Plug the opening at the end of the furnace, not taken up by the sample tube or covered with the furnace sliding plates, with glass wool. Adjust the temperature controller so that a bed temperature of 350 C is obtained in about one hour. Regulate the rate of heating as the temperature approaches 350 C so that the maximum temperature does not exceed 350 C by more than 5 C. (A temporary overshoot can be tolerated.) Continue heating at 350 C for two hours. Then remove the tube from the furnace and allow it to cool to room temperature while maintaining the nitrogen flow. When cool, remove the top along with the thermocouple well from the tube. Stopper both ends of the tube with the stoppers used for the initial weighing and weigh to 0.01 g.

Used Sieves

The water content of used sieves is determined as described under *Fresh Sieves* except that the volatilized material is condensed and collected. Before heating is begun, connect the traps in series to the outlet of the sample tube (see Fig. 3). The first trap with the socket joint is placed in a water/ice bath in a Dewar flask and connected to the ball joint of the sample tube. The second trap is placed in a dry ice/acetone bath in another Dewar flask and connected to the first trap with a piece of Tygon tubing attached to the center tube of the second trap. Use the lab jacks to adjust the level of the traps. **CAUTION:** The dry ice trap occasionally plugs and must be thawed with a jet of air directed toward the outside of the trap.

After heating the sample for two hours, remove and stopper the traps. Remove the sample tube and allow it to cool to room temperature while maintaining the nitrogen flow. Stopper the sample tube, using the original stoppers, and then weigh the tube and contents to 0.01 g.

Perform a Karl Fischer water determination on the contents of the traps as described below.



STANDARD PYREX TUBING
ALL DIMENSIONS IN mm
NOT DRAWN TO SCALE

Figure 1
Sample Tube Components

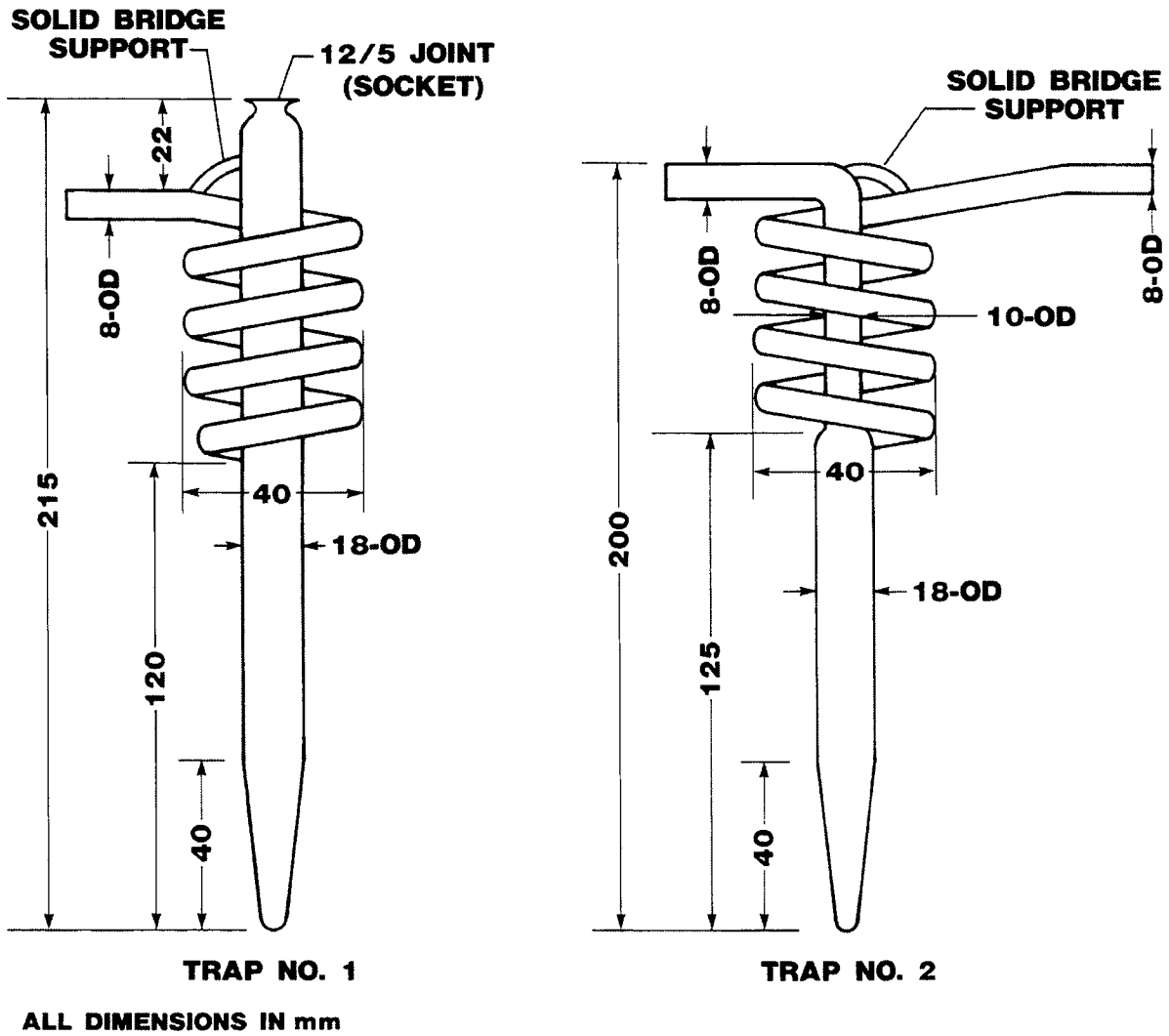


Figure 2
Condensate Traps

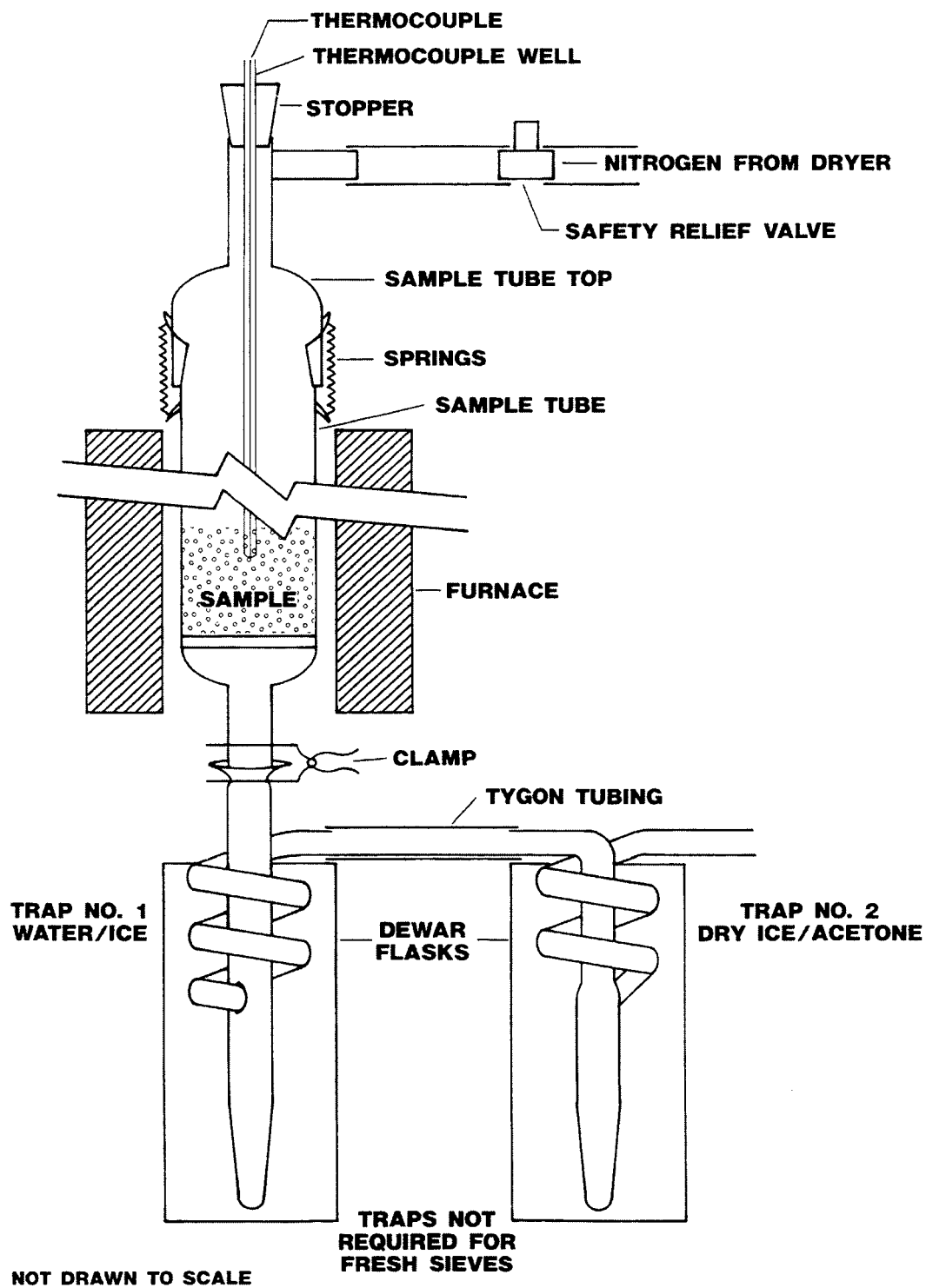


Figure 3

Assembled Sample Tube Plus Traps

Water Determination

Sample Transfer

Add 10 mL of methanol to each of the traps and quantitatively transfer the contents to a 250-mL volumetric flask. Follow by two 10-mL methanol rinses of each trap, adding the rinses to the volumetric flask. Dilute to the mark with methanol. Mix by inverting the stoppered flask several times. Carefully measure and record the volume of all methanol used.

Reagent Calibration

Assemble the Karl Fischer apparatus in accordance with the manufacturer's recommendations. From a previously-weighed dropping bottle, add 2 drops of water to the titration vessel. Reweigh the dropping bottle to the nearest 0.1 mg to obtain the mass added. Titrate the solution with the Karl Fischer (KF) reagent and record the volume of reagent used. Calculate the titer for the KF reagent from the following equation:

$$\text{Reagent titer, } T, \text{ mg H}_2\text{O/mL KF reagent} = \frac{W}{Y}$$

where:

W = mass of distilled water, mg

Y = volume of KF reagent, mL

Sample and Blank Titration

Pipet a sample aliquot from the 250-mL volumetric flask, usually between 1 and 25 mL, depending on the quantity of water present. Titrate the sample according to the manufacturer's instructions for the specific Karl Fischer equipment used. Determine a methanol blank by titrating an aliquot of the methanol that was used for the sample transfer. To determine the volume of methanol to be titrated see *CALCULATIONS, Used Sieves*.

CALCULATIONS

Fresh Sieves

$$\text{Free Water, mass - \%} = 100 \frac{A - B}{A - C}$$

where:

A = mass of tube, stoppers and sample before heating, g

B = mass of tube, stoppers and sample after heating, g

C = mass of tube and stoppers, g

Used Sieves

Calculate the volume of methanol to be titrated as a methanol blank as follows:

$$G = \frac{V_m M}{V_a}$$

where:

- G** = volume of methanol to be titrated for a blank, mL
M = total volume of methanol used for sample transfer, mL
V_a = volume of volumetric flask containing sample and methanol, mL
V_m = volume of sample aliquot used for analysis, mL

Calculate the mass of water in the hydrocarbon-water trap sample as follows:

$$D = \frac{TV_a(V_s - V_B)}{V_m 10^3}$$

where:

- D** = mass of water from Karl Fischer analysis, g
T = reagent titer, previously defined
V_B = volume of KF reagent used for titration of the methanol blank, mL
V_S = volume of KF reagent used for titration of the methanol diluted sample, mL
10₃ = milligrams to grams conversion factor, mg/g
V_a and **V_m** are as previously defined

Calculate the mass-% water and hydrocarbons in the used sieve sample as follows:

$$\text{Free Water (hydrocarbon free basis), mass - \%} = 100 \frac{D}{B + D - C}$$

$$\text{Hydrocarbon in total sample, mass - \%} = 100 \frac{A - B - D}{A - C}$$

where:

- A** = mass of tube, stoppers and sample before heating, g
B = mass of tube, stoppers and sample after heating, g
C = mass of tube and stoppers, g
D = mass of water from Karl Fischer analysis, g

NOTE

There are a number of Karl Fischer titration assemblies that are commercially available, some of which automatically stop the titration at the endpoint. However, coulometric type titrators are not acceptable.

PRECISION

Based on 6 replicate determinations of each type of sample, the estimated standard deviations (esd) were calculated and are shown in the following table. Results by the same operator should not differ by more than the allowable difference shown (95% probability).

Sample	Water Content, mass-%	Hydrocarbon Content, mass-%	esd, mass-%	Allowable Difference, mass-%
Fresh Sieves	3.2	—	0.10	0.36
Fresh Sieves	15.3	—	0.055	0.20
Used Sieves	2.6		0.15	0.55
Used Sieves		4.5	0.27	0.99

TIME FOR ANALYSIS

The elapsed time for one analysis of a fresh sieve is 3 hours. The labor requirement is 0.75 hour.

The elapsed time for one analysis of a used sieve is 5 hours. The labor requirement is 2.42 hours.

SUGGESTED SUPPLIERS

Alltech Associates, Inc., 2051 Waukegan Rd., Deerfield, IL 60015

Air Products and Chemicals, Inc., Specialty Gas Dept., Box 538, Allentown, PA 18105

Beckman Instruments, Inc., Scientific Instruments Div., 2500 Harbor Blvd., Fullerton, CA 92634

Doric Scientific Division, Emerson Electric Co., 3883 Ruffin Rd., San Diego, CA 92123

Matheson, P. O. Box 96, Joliet, IL 60434

Marshall Furnace Co., 30 Janis Way, Scotts Valley, CA 95066

Reliance Glass Works, Inc., 2220 Gateway Rd., Bensenville, IL 60106

Sargent-Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60077

West Instrument Co., Div. of Gulton Ind., 3860 River Rd., Schiller Park, IL 60176