

CARBON DIOXIDE IN AMINE SOLUTION

UOP Method 826-81

SCOPE

This method is for determining carbon dioxide in amine solution. Carbon dioxide is reported as volumes of carbon dioxide per volume of solution corrected to 0 C at 101.3 kPa, or it can be converted to cubic feet of carbon dioxide per gallon of amine solution.

OUTLINE OF METHOD

A measured volume of amine sample is acidified with phosphoric acid which liberates carbon dioxide from the amine solution. The evolved carbon dioxide is measured in a gas measuring buret and the volume obtained is corrected to normal conditions (0 C and 101.3 kPa).

APPARATUS

Balance, torsion or top loading, 500 g capacity, capable of weighing to 0.01 g

Beaker, 250- and 1000-mL

Carbonimeter, Van Slyke, see Fig. 1 for details and construction. The complete apparatus is available from SGA Scientific, Inc., Cat. No. JC-4150, or equivalent. The connecting sleeves and tubing are rubber. The apparatus consists of two gas burets, a reaction buret and a measuring buret. The reaction buret contains mercury and the measuring buret contains a gas confining solution. The reaction buret is fitted with three two-way stopcocks, C, E and G, and two small tubes, A and B. Tube B is graduated in mL. Between Stopcocks E and G is a calibrated tube with a mark indicating one-milliliter at F. This volume is measured down to the top of the mercury meniscus from E, when Stopcock E is closed. Stopcock C has a discharge Tube D used for cleaning the reaction buret. The measuring buret is calibrated in 0.5-mL divisions and is equipped with one two-way Stopcock H.

Cylinder, graduated, 100-mL

Flask, volumetric, 1000-mL

Pipets, volumetric, 5- and 10-mL

Thermometer, -20 to 110 C range, 1 degree subdivisions

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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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.

Confining solution. Dissolve 200 g of sodium sulfate in a solution composed of 800 mL of water and 40 mL of concentrated sulfuric acid (see Note 1).

Mercury, triple distilled

Phosphoric acid solution, aqueous, 50%. To prepare, add 118 g of 85% phosphoric acid to 82 g of water.

Potassium dichromate solution, aqueous, 10%

Sodium sulfate, 99.9% minimum purity

Sulfuric acid, concentrated

PROCEDURE

If the amine sample contains other substances which are evolved as gases when the sample is acidified, they will be measured with the carbon dioxide. Such interfering substances are hydrogen sulfide, sulfur dioxide and nitrogen oxides (see Note 2).

Calibration of the Measuring Tube

Arrange the apparatus in an efficient hood, making sure that all stopcocks are well ground and greased to prevent leaks. Before a new reaction buret is used the volume of the calibrated tube between Stopcock E and mark F must be accurately calibrated by determining the weight of mercury it contains. This may be done as follows: Before adding mercury to the leveling bulb, disconnect the rubber tubing at M and the connection between Stopcocks G and H. Invert the reaction buret and place B in a beaker of mercury. Apply vacuum at M and using Stopcocks E and G draw the mercury into the calibrated tube exactly up to mark F. Shut Stopcocks E and G and remove the vacuum from M. Return the reaction tube to its normal position. Using Stopcock G, draw off the mercury contained between Stopcock E and mark F, allowing the mercury to flow through M where it is collected in a weighed beaker, taking care that no drops adhere to the glass. Reweigh the beaker containing the mercury, calculate the weight of mercury and using the density of mercury, determine the volume of the calibrated tube. If the volume varies from the one-milliliter specification, a volume correction factor must be applied to the results obtained.

Sampling and Determination of CO₂ in Amine Solution

Fill the measuring buret and the tube between Stopcocks H and G with confining solution by opening Stopcocks H to G and G to H and the reaction buret. Raise the confining solution leveling bulb until the confining liquid just fills the connecting tube joining H and G. Close Stopcocks H and G.

Pipet a sufficient amount of the amine sample to fill sample Tube A. Pipet 4 mL of 50% phosphoric acid into Tube B (see Note 2). Open Stopcocks G, E and C to vent the reaction buret through D. Raise the mercury leveling bulb to force any air or water present in the reaction buret out through D. Open Stopcock C to sample Tube A and allow a small amount of mercury to be forced up into A to ensure the absence of air in the system. Close Stopcock C and slowly open Stopcock E to Tube B and allow a small amount of

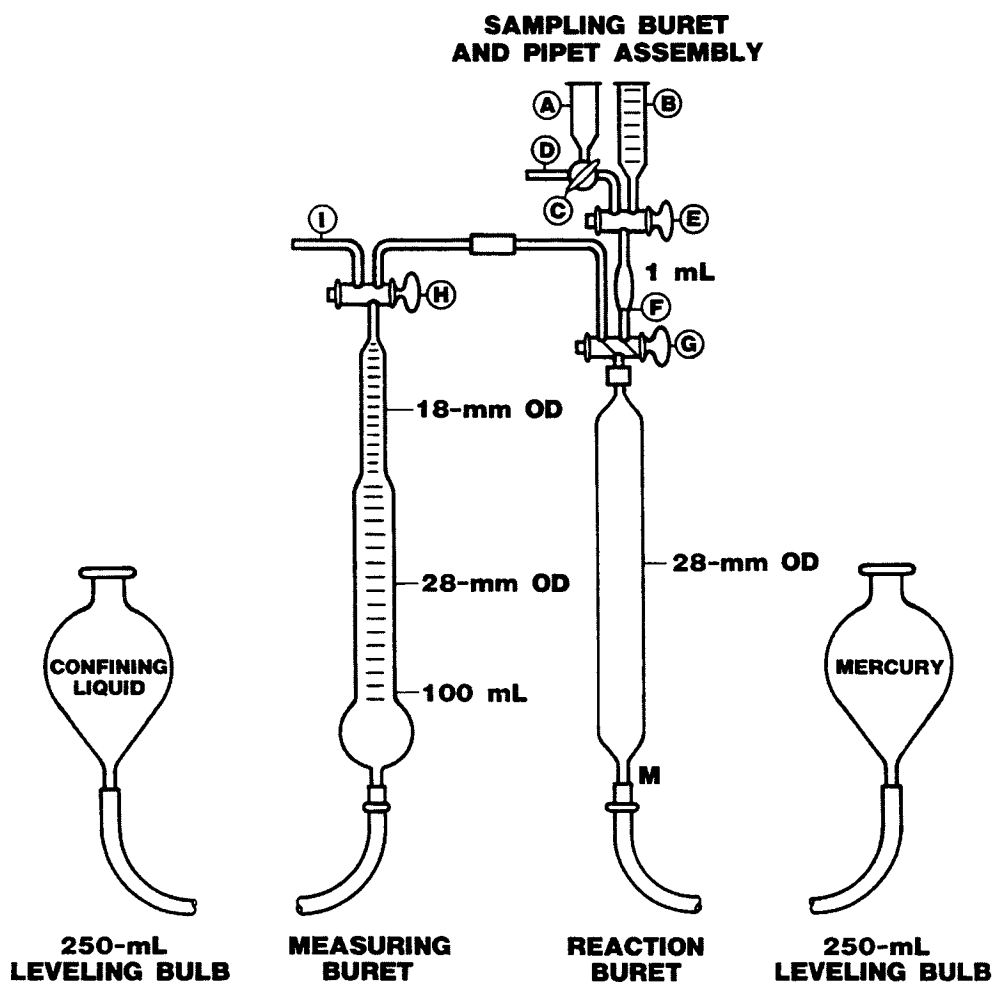


Figure 1
Carbonimeter

mercury to be forced into B. Open Stopcock E to C and open Stopcock C to Tube A. Draw sample into the measuring tube by lowering the mercury leveling bulb carefully until the level of the mercury is at F. Open Stopcock C to D and raise the mercury leveling bulb to flush the first sample taken through discharge Tube D. Open Stopcock C to sample Tube A and take a second sample of the amine solution by again lowering the mercury leveling bulb until the mercury level is at F. Close Stopcocks C, E and G. There is now a one-milliliter sample of the amine solution in the calibrated tube of the reaction buret. Open Stopcock G and lower the mercury leveling bulb until the mercury level in the bulb is 6-7 cm below Stopcock G. Open Stopcock E slowly to Tube B and allow 2 to 3 mL of the 50% phosphoric acid to drain from B into the reaction buret. Close Stopcocks E and G (see Note 3).

Raise and lower the mercury leveling bulb several times to mix the phosphoric acid and amine solution thoroughly. Open Stopcock H to G. Open Stopcock G to H. Raise the mercury leveling bulb forcing the gas in the reaction buret through G and H into the measuring buret. Do not allow the acid and amine solution to enter Stopcock G. Close Stopcock H. Turn Stopcock G so that it is open to E and the reaction buret. Evacuate the area from E and the reaction buret by lowering the mercury leveling bulb. Open Stopcocks G to H and H to G and pump the gas from the reaction buret into the measuring buret by raising the mercury leveling bulb. Repeat the evacuation and pumping process until no further carbon dioxide gas remains dissolved in the acidified sample.

After the acidified sample is degassed, open Stopcocks G to H and H to G. Raise the mercury leveling bulb forcing enough of the acidified sample over to fill the tube from G to H with liquid. Close Stopcock H and raise or lower the gas confining solution leveling bulb until the liquid level is the same in both the measuring buret and the leveling bulb. Record the volume of gas to the nearest 0.25 mL.

Run the determination in duplicate and report the average. Duplicate determinations should check within 0.50 mL, gas volume. Record the barometric pressure and room temperature.

Cleaning of the Carbonimeter

Remove the gas in the measuring buret by opening Stopcock H to Tube I and raising the confining liquid leveling bulb so that the gas is forced out through Tube I. Open Stopcock H to G. Open Stopcock G to H, lower the mercury leveling bulb and draw acidified sample out of the tube between Stopcocks G to H into the reaction buret. Open Stopcock G to the Reaction buret and Stopcock E. Open Stopcocks E to C and C to Tube D. Raise the mercury leveling bulb to force the acidified sample out of the reaction buret and out through Tube D. Fill sample Tube A with water, open Stopcock C to A and allow water to drain into the reaction buret. Open Stopcock C to Tube D and the reaction buret. Pump the water in the reaction buret out through Tube D by raising and lowering the mercury leveling bulb. Two water washes are sufficient.

CALCULATIONS

Calculate the volume of dry CO₂ at normal conditions (0 C and 101.3 kPa) per mL of amine solution as follows:

$$\text{Volume of dry CO}_2 \text{ at normal conditions per mL of amine solution, mL} = \frac{AB}{C}$$

or,

$$\text{Cubic feet of CO}_2 \text{ at 0 c and 101.3 kPa per gal of amine solution} = \frac{0.134 AB}{C}$$

where:

A = reading of gas buret, mL

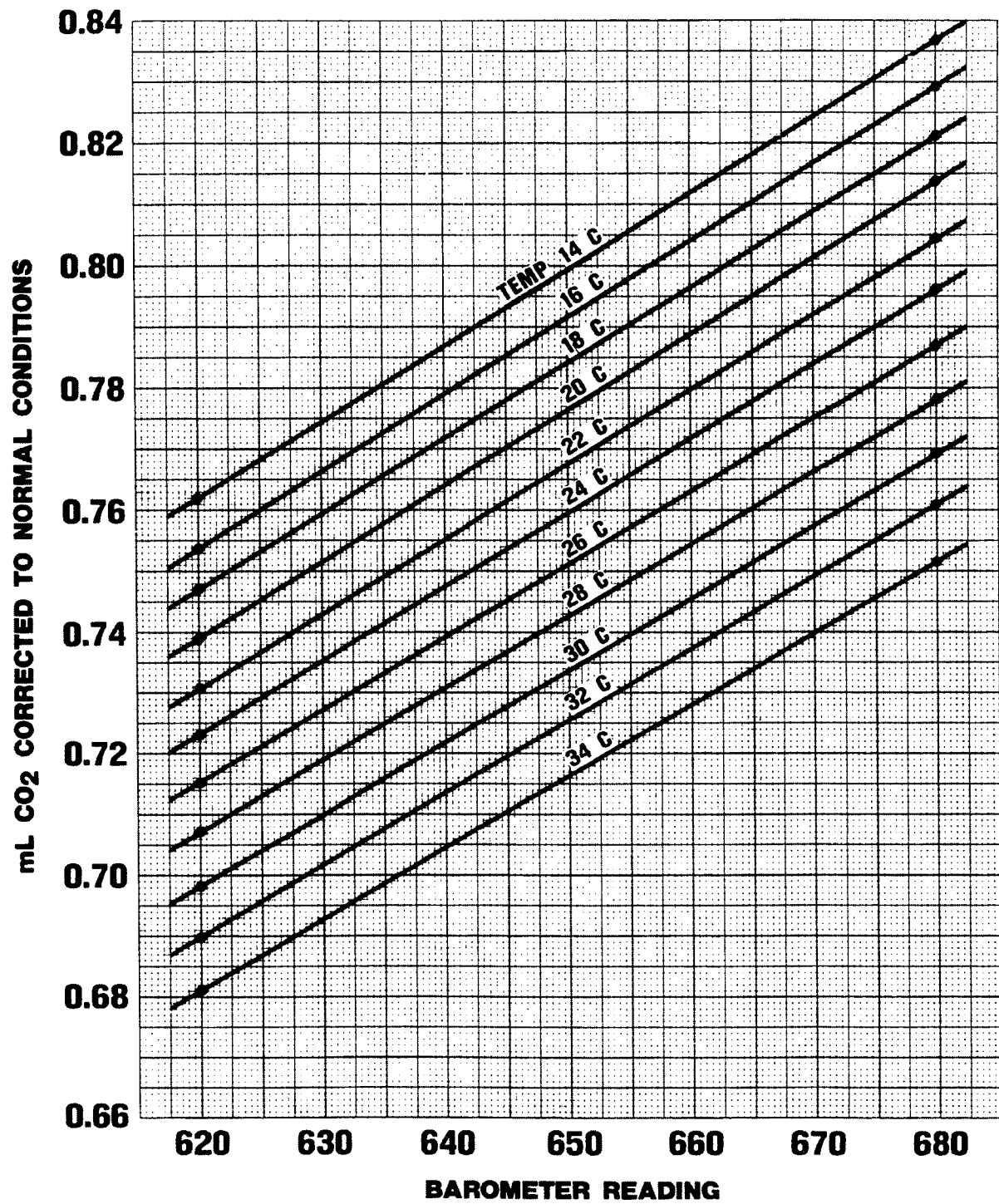


Figure 2
Correction Factors

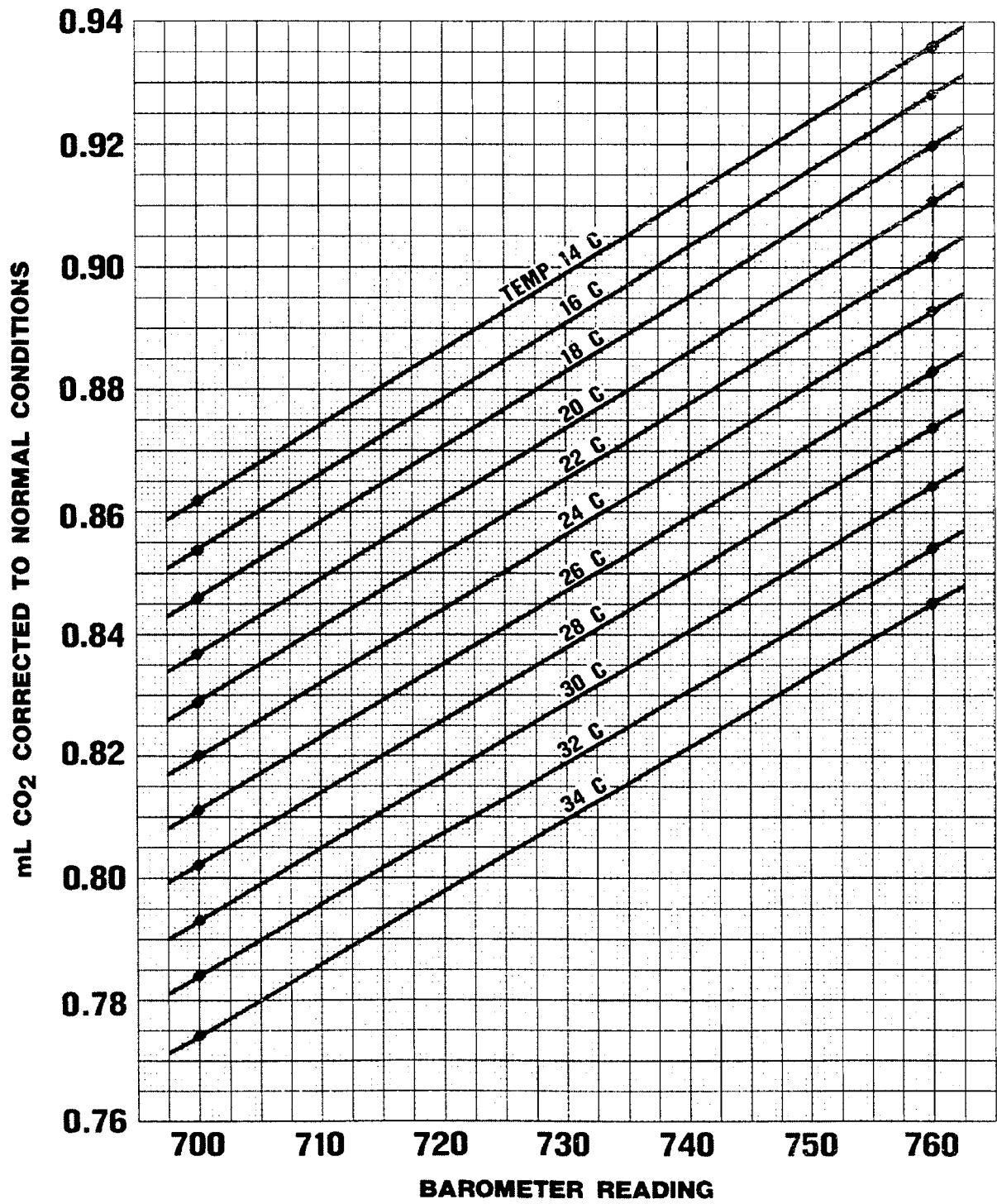


Figure 3

Correction Factors

B = correction factor to convert gas volume to normal conditions, from Fig. 2 or 3

C = volume of amine sample, mL

Carbon Dioxide Recovery

When determinations are made on both rich and lean amine solutions the CO₂ recovery in pounds per hour may be calculated as follows:

$$\text{CO}_2, \text{ lb/hr} = 0.984 (E - F) G$$

where:

E = mL of dry CO₂ at 0 C and 101.3 kPa per mL of rich amine

F = mL of dry CO₂ at 0 C and 101.3 kPa per mL of lean amine

G = amine circulation rate, U.S. gal per min

NOTES

1. This confining solution was proposed by Koble and Kenton (*Ind. Eng. Chem., An. Ed.* **10**, 76, 1938). CO₂ is much less soluble in this solution than in water.

2. When hydrogen sulfide is present in the amine solution along with carbon dioxide, it is necessary to remove it by adding 3 mL of 10% potassium dichromate to the amine sample in the reaction buret to oxidize the hydrogen sulfide to sulfur before the sample is acidified. The potassium dichromate may be added through Tube B prior to filling it with the 50% phosphoric acid.

Sulfur dioxide is not normally present in amine solutions containing carbon dioxide, however, it can also be removed by the dichromate treatment.

Nitrogen oxides may be present in cases where the gases being scrubbed contain nitrogen oxides in addition to carbon dioxide. If this occurs, the apparent carbon dioxide determined by this method will be in error.

3. It is also permissible to add the sample directly through Tube B using a pipet. The sample is then washed into the reaction buret with 2 to 3 mL of water. The addition of the sample by this alternative technique is useful when the amount of carbon dioxide is low and a larger sample is required.

PRECISION

An estimated standard deviation is not reported since insufficient data are available at present to permit this calculation with at least 4 degrees of freedom.

TIME FOR ANALYSIS

The elapsed time for one analysis is 1.0 hour. The labor requirement is 0.5 hour.

REFERENCE

Method SM-5, The Girdler Corp., Louisville, KY

SUGGESTED SUPPLIER

SGA Scientific, Inc., 735 Broad St., Bloomfield, NJ 07003