

FLUE GAS ANALYSIS

UOP Method 172-89

SCOPE

This method is for determining carbon dioxide, oxygen and carbon monoxide in flue gases. The lower limit of detection is 0.2 mol-%. If hydrogen sulfide or other acidic compounds are present, the carbon dioxide determination will require correction. This method is designed as a rapid control room test. UOP Method 539, a gas chromatographic technique, is the recommended laboratory test, provided the separation of oxygen and argon is not required.

OUTLINE OF METHOD

A measured volume of gas is admitted into a series of pipets for the successive removal of the individual components by absorption with selective liquid reagents. Volume measurements are taken with a buret before and after each absorption. The decrease in volume as the gases are absorbed represents the amount of the particular component present in the sample. The results are expressed in mole-percent.

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

Beaker, 1000-mL

Bottle, glass-stoppered, one-liter, Fisher Scientific, Cat. No. 02-940E

Cylinders, graduated, 25-, 250- and 1000-mL

Flue gas analyzer (see Figure), Master Model 211, Burrell Corporation, Cat. No. 39-106, including the following replacement parts:

Absorption pipets, Nos. 1, 2, 3 and 4 (regular bubbler type), Cat. No. 40-105-10

Aspirator bags, rubber, Cat. No. 40-470

Buret, B, 100-mL, graduated in 0.2-mL divisions, Cat. No. 39-980

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).

Flushing pipet, No. 5 (contact type), Cat. No. 40-130

Leveling bottle, 175-mL, Cat. No. 40-460

Regulator, nitrogen, Matheson, Model 8-850

Tube, gas sampling, A (see Figure), 250-mL, Fisher Scientific, Cat. No. 10-921B (optional, not necessary if analyses are run at the source)

Tubing, chemical-resistant, black rubber, 4.8-mm (3/16-inch) ID, 2.4-mm (3/32-inch) wall, Fisher Scientific, Cat. No. 14-158C

Tubing, transparent, amber latex, 4.8-mm (3/16-inch) ID, 1.6-mm (1/16-inch) wall, Fisher Scientific, Cat. No. 14-178B

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 shall mean distilled water.

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

Acetone, 99.5% minimum purity, Fisher Scientific, Cat. No. A18

Ammonium chloride, 99.9% minimum purity, Fisher Scientific, Cat. No. A661

Ammonium hydroxide, 28.0-30.0% as NH_3 , Fisher Scientific, Cat. No. A669

Copper, wire or turnings, 99% minimum purity, Fisher Scientific, Cat. No. C575

Cuprous chloride, 90.0% minimum purity, Fisher Scientific, Cat. No. C457

Methyl orange, Fisher Scientific, Cat. No. M216

Nitrogen, extra dry, 99.9% minimum purity

Potassium hydroxide, pellets, 85.0% minimum purity, Fisher Scientific, Cat. No. P250

Pyrogallol, 99.9% minimum purity, Fisher Scientific, Cat. No. A263

Sodium sulfate, anhydrous, 99.5% minimum purity, Fisher Scientific, Cat. No. S421

Sulfuric acid, concentrated, 95.0-98.0% purity, Fisher Scientific, Cat. No. A300

Stopcock grease, Fisher Scientific, Cat. No. 14-635M

PREPARATION OF REAGENTS

The following directions are for the preparation of the reagents in quantities of one liter each. Mix the reagents in one-liter beakers and store the surplus in one-liter glass-stoppered bottles. The pipets in which they are used are referred to in numerical order, 1 being closest to the buret (see Figure).

Pipet 1: Potassium hydroxide, 33 mass-%

Weigh 513 ± 0.01 g potassium hydroxide into 805 ± 5 mL of water. Mix thoroughly. Add 170 ± 5 mL of this reagent to pipet 1 to absorb carbon dioxide, hydrogen sulfide and acidic gases.

Pipet 2: Potassium pyrogallate solution

Weigh 891 ± 0.01 g potassium hydroxide into 625 ± 5 mL of water. Mix thoroughly. Add 140 ± 5 mL of this solution to pipet 2. Weigh 15 ± 0.01 g of pyrogallol into 25 ± 1 mL of water. Mix thoroughly. Add the entire quantity of the pyrogallol solution to pipet 2 and stopper immediately. This solution is used to absorb oxygen.

Pipets 3 and 4: Ammoniated cuprous chloride solution

Weigh 250 ± 0.01 g ammonium chloride, 200 ± 0.01 g cuprous chloride and 50 ± 0.01 g copper wire, or turnings, into a one-liter glass-stoppered bottle. Add 750 ± 5 mL of water. Let stand for at least 24 hours. Decant 125 ± 5 mL into each of pipets 3 and 4. Add 45 ± 1 mL of ammonium hydroxide and 10 ± 0.01 g of copper turnings to each pipet. Pipets 3 and 4 are used for the determination of carbon monoxide.

Pipet 5, leveling bottle, buret and manifold: Sodium sulfate retaining solution

Add 30 ± 0.01 g of sulfuric acid to 965 ± 5 mL water in a one-liter glass bottle. Mix thoroughly. Add 142 ± 0.01 g of sodium sulfate and a sufficient amount of methyl orange to color the solution.

PROCEDURE

Carefully lubricate all stopcocks with a minimum of stopcock grease. Connect the pipets to the manifold with 30-mm (1-1/4 inch) lengths of transparent amber latex tubing. At all points where there is glass-to-glass contact, butt the glass terminals firmly against one another to avoid excessive dead space. Refer to the manufacturer's instruction manual for additional information on set-up and operation of this apparatus.

Prepare the various reagents according to directions given under *PREPARATION OF REAGENTS*. Fill pipets 1 through 4 using the following procedure: Open the pipet to the atmosphere through the manifold. Remove the rubber stopper and aspirator bag. Pour the appropriate solution into the rear compartment. Close the manifold stopcock, inflate the aspirator bag slightly with nitrogen gas and replace the stopper.

A clean buret is essential for accurately reading volumes. Clean by draining the buret and rinsing with acetone followed by water.

Connect the leveling bottle to the buret with chemical resistant black rubber tubing. Fill the leveling bottle, buret, pipet 5, and manifold with the sodium sulfate retaining solution. Examine the apparatus to ensure that it is completely filled and no air bubbles are present. Care must be exercised to avoid bubbles in the pipets and the manifold throughout the measurement.

Before starting an analysis and when removing the residual gas after absorption, the solution in each pipet must be brought to a reference mark located on the capillary stem approximately 3 mm below the stopcock. Open each pipet in sequence to the buret and by carefully adjusting the leveling bottle, bring the solution to the proper point. The aspirator bags are inflated slightly when the pipets are filled to permit drawing the solution up into the capillary. Approximately 50 mL of nitrogen gas should be maintained in each pipet when the apparatus is not in use. This will eliminate the freezing or sticking of the stopcocks due to contact with strong alkaline solutions.

Connect the sample source to the buret. Flush the lines thoroughly and measure exactly 100 mL of the gas into the buret. To accomplish this, draw approximately 101-102 mL of sample into the buret, and turn the buret stopcock to connect the buret to the manifold and flushing pipet. Raise the leveling bottle to

compress the gas to about the 99-mL mark and pinch the rubber tubing between the thumb and forefinger. Set the leveling bottle down and permit the gas to expand to exactly 100 mL by releasing the pressure on the rubber tubing. Turn the buret stopcock for an instant to allow the slight excess of gas to vent to the air. The gas sample is now ready for analysis.

Raise the buret leveling bottle slightly, thus putting the gas in the buret under slight pressure to avoid any possibility of pulling solution from the pipet into the manifold. Turn the manifold stopcock to connect to pipet 1, which contains the 33% potassium hydroxide solution. Continue raising the leveling bottle until the retaining liquid reaches the top of the buret and all the gas has been passed into the pipet. Lower the leveling bottle bringing the gas back into the buret. Repeat this procedure 3 or 4 times, or until a constant volume reading is obtained in the buret. Final residual volumes are read after flushing the gas from the manifold to the buret with sodium sulfate solution from pipet 5. Record the final gas volume. Subtract this value from 100 to determine the amount of carbon dioxide absorbed.

This applies only in the absence of hydrogen sulfide. If hydrogen sulfide is expected to be present, determine its content by UOP Method 9. To obtain percent carbon dioxide, subtract the percent hydrogen sulfide from the percent of the total gas absorbed in the 33% potassium hydroxide solution.

Pass the residual gas from the carbon dioxide determination through the alkaline pyrogallol solution, pipet 2, in the same manner as described above. Passes in groups of 4 are to be made until a constant reading is obtained. If more than 12 passes are necessary to obtain a constant reading, change the solution. Record the final residual volume and indicate the difference as oxygen.

Transfer the gas to pipet 3, which contains the first cuprous chloride solution. After 10 passes, remove the gas to the buret, read the volume and pass it to pipet 4, containing fresh cuprous chloride reagent. Make sufficient passes in groups of 3 until a constant reading is obtained. Record the final gas residue volume and indicate the total contraction of the gas volume in pipets 3 and 4 as carbon monoxide. It is essential to have fresh cuprous chloride in the second cuprous chloride pipet to remove traces of carbon monoxide. After 10 mL of carbon monoxide has been absorbed in pipet 4, move this pipet to the 3 position. Replace the solution in pipet 3 and put it in the 4 position. Make certain that sufficient clean copper wire or turnings are present in the cuprous chloride solutions at all times.

CALCULATIONS

Calculate the individual mol-% of carbon dioxide, oxygen and carbon monoxide by the following equation:

$$\text{Component, mol-\%} = \frac{100(A - B)}{C}$$

where:

A = volume of gas taken before absorption

B = volume of gas after absorption

C = volume of the total sample taken for analysis

PRECAUTIONS

Sufficient passes to obtain constant readings, as described in *PROCEDURE*, are required when contacting the sample with the reagents. If an excessive number of passes is required, change the reagent involved.

Do not permit the retaining solution to enter the absorption pipets and allow no reagent to enter the manifold. Keep the retaining solution slightly acidic as indicated by its red color.

PRECISION

An estimated standard deviation is not reported since insufficient data are available to permit this calculation.

TIME FOR ANALYSIS

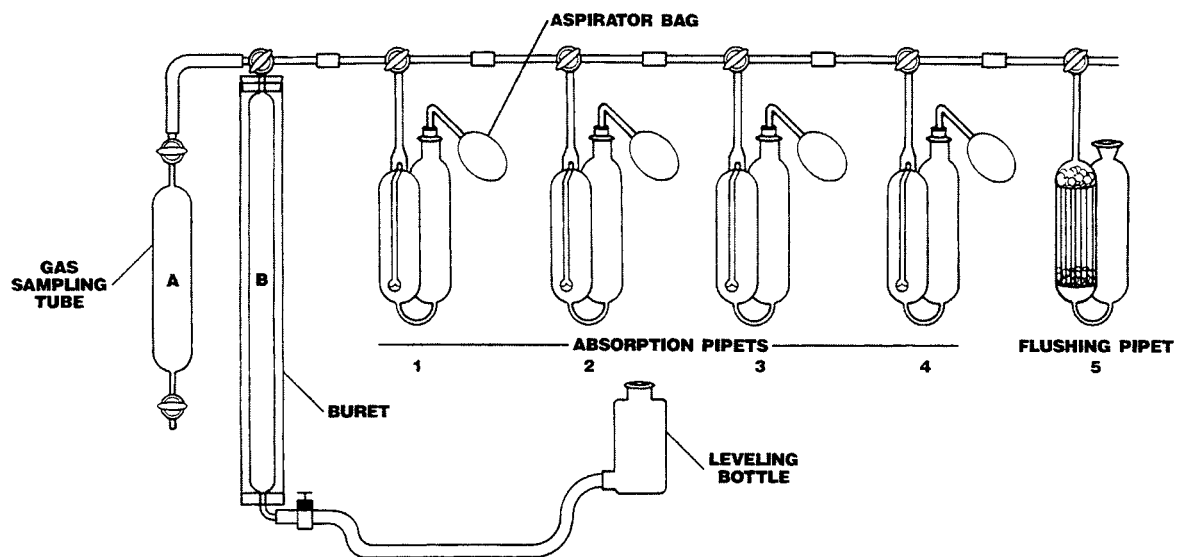
The elapsed time and labor requirement, without preparation of solutions, are identical, 0.5 hour.

REFERENCES

UOP Method 9, "Hydrogen Sulfide in Gases by the Tutweiler Method"
UOP Method 539, "Gas Analysis by Gas Chromatography"

SUGGESTED SUPPLIERS

Burrell Corporation, 2223 Fifth Avenue, Pittsburgh, PA 15219
Fisher Scientific, 1600 W. Glenlake Ave., Itasca, IL 60143
Matheson, P.O. Box 96, Joliet, IL 60434



Apparatus for Flue Gas Analysis