

PEROXIDE IN GASOLINE

UOP Method 33-82

SCOPE

This method is for determining the degree of oxidation that a gasoline has undergone. It may be used with all gasolines except those whose color tends to interfere with the endpoint of the titration. The degree of oxidation is expressed as the Peroxide Number.

OUTLINE OF METHOD

The sample is reacted with ferrous thiocyanate solution. The resulting ferric ion is titrated with a titanous chloride solution using thiocyanate as an indicator. The endpoint is indicated by a change from red to colorless and the peroxide number is calculated.

DEFINITION

Peroxide Number is equal to the number of moles of oxygen in 1000 liters of gasoline (see Note).

APPARATUS

Balance, capable of weighing to 0.1-mg

Buret, automatic, 50-mL, available from SGA Scientific Inc., Cat. No. JB-7670, or equivalent, and referred to as “A” in the attached figure, for ferrous thiocyanate solution. The buret is supplied with a 2000-mL bottle having a 29/42 ground glass joint. This bottle is replaced with a 9000-mL reagent bottle, SGA Scientific Inc., Cat. No. JB-1610, having a 40/50 ground glass joint. A ground glass joint adapter, 40/50 to 29/42, SGA Scientific Inc., Cat. No. JA-2250, is required. The lower stem of the buret is extended to the bottom of the bottle by using a piece of Tygon tubing (see Fig.).

Buret, automatic, 25-mL, available from SGA Scientific Inc., Cat. No. JB-7670, or equivalent, and referred to as “B” in the attached figure, for titanous chloride solution. The buret is supplied with a 2000-mL clear glass bottle. Replace this bottle with an amber 2000-mL Pyrex bottle having a 29/42 joint, SGA Scientific Inc., Cat. No. JB-1690, to prolong the stability of the light sensitive TiCl_3 solution.

Flask, Erlenmeyer, 125-mL, ground glass stoppered

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).

Flasks, volumetric, 100-, 250- and 1000-mL

Hot plate

Manifold, nitrogen gas supply for filling the burets and supplying an oxygen-free atmosphere to both the ferrous thiocyanate and the titanous chloride solution. The burets, interconnected by the manifold, as shown in the attached drawing, are operated according to the buret operating procedures (see *PREPARATION OF APPARATUS*).

Pipets, volumetric, 10-, 20-, 25- and 50-mL

Shaker, wrist action, Burrell, Model DD, SGA Scientific Inc., Cat. No. S-1700, or equivalent

Stirring apparatus, magnetic, variable speed, with 25-mm (one-inch) Teflon coated stirring bar, Sargent-Welch Scientific, Cat. No. S-76490, 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 shall mean distilled or deionized water.

Dry ice

Ferric chloride solution, 0.01-*M*, containing 5.596 g of iron wire (99.8% pure), 85 mL of 6-*M* hydrochloric acid, and 2.1 g of potassium chlorate. Add the iron wire to the 6-*M* hydrochloric acid, prepared by diluting concentrated hydrochloric acid with an equal volume of water. Heat gently until all the iron wire is dissolved, but do not boil. Add the potassium chlorate slowly, oxidizing the iron from the ferrous to the ferric state. Boil for 20 minutes in a well vented hood to expel the excess chlorine. Cool to room temperature. Dilute to one-liter with water. The resulting solution is 0.1-*M*. Dilute 25 mL of the 0.1-*M* ferric chloride solution to 250 mL with water, to make a 0.01-*M* solution of ferric chloride. Prepare the latter solution fresh just before standardization.

Ferrous thiocyanate solution, containing 37.5 g of ferrous sulfate, 37.5 g of ammonium thiocyanate, 3750 mL of water, 3750 mL of CP acetone, 37.5 mL of 98% sulfuric acid and 7.5 g of pure iron wire. In a 9000-mL buret-reservoir bottle dissolve the ferrous sulfate and ammonium thiocyanate in the water, add the acetone and mix. Distribute the iron wire throughout the bottle and carefully add the sulfuric acid. Shake vigorously for several minutes to ensure complete mixing. Slowly bubble a continuous flow of inert nitrogen gas through the solution at all times in order to remove any traces of oxygen, and to assist, by slow bubble agitation, the maintenance of an Fe^{+++} free solution. After a few days any ferric salts present as impurities will have been reduced by the iron wire to ferrous salts and the red color will disappear. Only when the solution is colorless, it is ready for use.

Nitrogen, cylinder, 99.995% minimum purity, with a pressure reducer to supply gas at a low gauge pressure of 21-35 kPa (3-5 psig) to the buret manifold

Potassium thiocyanate, (KSCN), indicator solution, approximately 2-*M*. To prepare, dissolve 20-g KSCN in water and dilute to 100 mL.

Titanous chloride solution, 0.01-M. To a 2-liter amber buret reservoir bottle containing 1480 mL of water, add 10 mL of concentrated hydrochloric acid followed by 10 mL of 20% titanium trichloride solution (Sargent-Welch Scientific, Cat. No. SC-15419, or equivalent). Shake well until the solution is thoroughly mixed and purge the solution with nitrogen. As with the ferrous thiocyanate, the solution must be kept under a slow continuous nitrogen gas purge. Storage in an amber buret bottle will prevent photochemical action. Due to instability, the molarity must be determined daily by titration against the 0.01-M ferric chloride.

PREPARATION OF APPARATUS

Filling the Buret

Operate one buret at a time by closing stopcock 2 (see attached figure), and opening screw clamps A and B of the buret which is to be filled with reagent, while closing screw clamps A and B of the opposite buret. Open stopcock 4 to fill position and connect the Tygon tubing with a gentle, slow flow of nitrogen to the "Fill-TEE" (F). When the reagent solution is overflowing at the zero mark of the buret, release the pressure by simultaneously closing stopcock 4 and opening stopcock 2. The buret is now ready for dispensing and the nitrogen is in the flow-through mode.

This procedure is repeated identically for the opposite buret.

Stand-By/Purge Mode

Drain both burets by opening stopcocks 4 to the drain position, close both stopcocks 2 and open all screw clamps. Connect the Tygon tubing with a gentle, slow flow of N₂ to the "Purge-TEE" (P) and connect another Tygon tubing to the "Fill-TEE" (F) leading to an exhaust for the purpose of venting any acetone vapors from the FeSCN solution (Buret A). Leave both burets in this stand-by mode until the next analysis, continuously purging with nitrogen at the rate of about one bubble per second.

STANDARDIZATION OF REAGENT

Standardize the titanous chloride solution by titrating 20 mL of the 0.01-M ferric chloride solution (containing 4 drops of 2-M potassium thiocyanate solution as indicator) with the titanous chloride. Keep the solution under an atmosphere of CO₂ by adding a small lump, about one cubic centimeter, of dry ice to the flask. Stir the solution briskly and continuously on a magnetic stirrer until the color changes from red to colorless. Standardize the solution daily.

Calculate the molarity of the titanous chloride solution as follows:

$$\text{Molarity of titanous chloride} = \frac{20 F}{V}$$

where:

F = molarity of ferric chloride solution

V = volume of titanous chloride solution, mL

20 = volume of ferric chloride solution, mL

PROCEDURE

The volume of sample taken for analysis depends on the expected peroxide number. For samples that are expected to be greater than 2, pipet 10 mL of the gasoline to be tested into glass-stoppered Erlenmeyer flask. For gasolines that are expected to produce a peroxide number of 2 or less, use a 50-mL sample. Add 50 mL of ferrous thiocyanate solution. Shake vigorously either manually or on an automatic shaker, for exactly 5 minutes. Keep the solution under an atmosphere of CO₂ by adding a small lump, about one cubic centimeter, of dry ice to the flask and titrate immediately on a magnetic stirrer with freshly standardized titanous chloride solution. A change of color from red to milky white or colorless indicates the endpoint.

CALCULATIONS

Calculate the peroxide number using the following equation:

$$\text{Peroxide Number} = \frac{1000 \text{ CM}}{\text{T}}$$

where:

C = volume of titanous chloride solution used to titrate the sample, mL

M = molarity of titanous chloride solution, calculated previously

T = volume of sample taken for analysis, mL

NOTE

The unit mole conforms to the new SI nomenclature and IUPAC rules and is defined *for this method* to be equal to the old gram equivalent unit. The numerical value determined by this method is also the same as that determined by previous methods.

PRECAUTIONS

High-purity nitrogen is specified for blanketing the reagents. Do not substitute ordinary nitrogen as it contains too much oxygen.

The molarity of the titanous chloride must be checked daily. Keep the titanous chloride buret empty when it is not in use. A white flocculent or gelatinous precipitate of TiO₂ indicates the need to prepare a fresh solution.

Titration must be made carefully, yet as rapidly as possible. Slow titrations tend to raise peroxide number values.

Flush the dispensing pipets before beginning the analysis in order to ensure fresh solutions for the test.

PRECISION

The estimated standard deviation (esd) based on the indicated replicates is shown below. Duplicate results by the same operator should not be considered suspect unless they differ by more than the amounts shown in the "Allowable Difference" column (95% probability).

Type of Sample	Replicates	Peroxide Number		
		Level	esd	Allowable Difference
FCC Gasoline	6	0.8	0.05	0.18

TIME FOR ANALYSIS

The elapsed time and labor requirement are identical. The time for a single analysis including standardization is 1.0 hour. In multiples of 10, the time for a single analysis is 0.3 hour.

REFERENCE

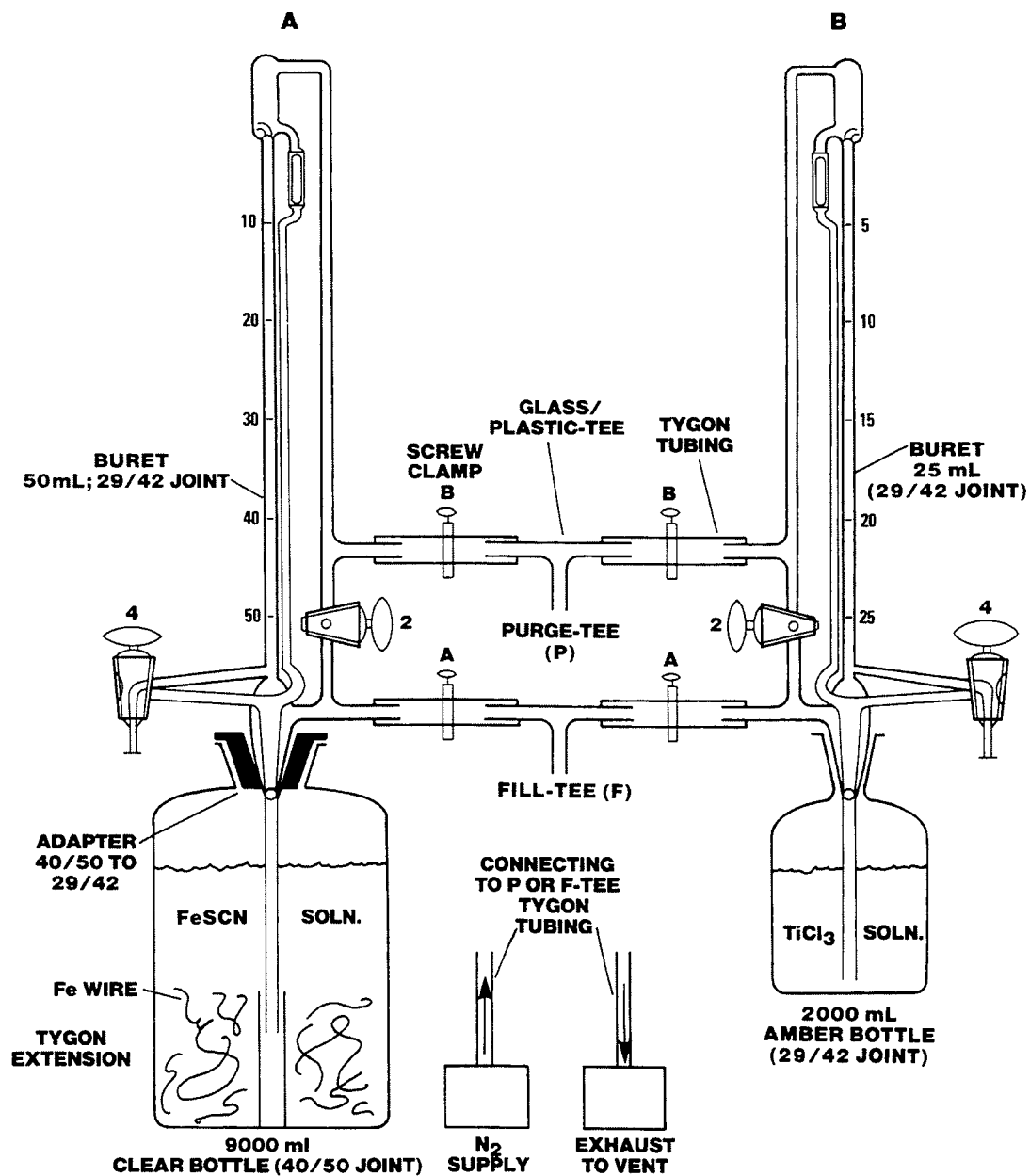
Yule, F. A. C., and Wilson, C. P., Jr., *Ind. Eng. Chem.* **23**, 1254 (1931)

Morrel, J. C., Dryer, C. G., Lowry, C. D., Jr., and Egloff, G., *Ind. Eng. Chem.* **26**, 655 (1934)

SUGGESTED SUPPLIERS

SGA Scientific Inc., 770 N. Church Road, Elmhurst, IL 60126

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



PEROXIDE IN GASOLINE AUTOMATIC BURET MANIFOLD

Figure

Peroxide in Gasoline
Automatic Buret Manifold