

INDUCTION PERIOD OF GASOLINES USING THE UOP OXYGEN PRESSURE VESSEL

UOP Method 6-82

SCOPE

This method is for determining the induction period of gasolines. It is useful as a control test and will show responses of gasolines to inhibitors. The method does not give the same numerical induction periods as ASTM Method D 525 because of differences in construction of the pressure vessel, the amount of oxygen in the pressure vessel, heat transfer, surface area of gasoline to be oxidized, the sample volume, and the type of bath used to heat the vessel. The results, however, are parallel but may be somewhat higher and this method is faster and more convenient to perform.

OUTLINE OF METHOD

The sample is placed in a pressure vessel at 15-25 C (59-77 F) and subjected to oxygen at 690 kPa (100 psi). The pressure vessel is heated as rapidly as possible to 100 C (212 F). The pressure is recorded continuously until the break point has been passed. The induction period is then determined from the chart record.

DEFINITIONS

Break Point is that point in the pressure-time curve that is preceded by a pressure drop of exactly 13.8 kPa (2 psi) in 15 minutes and succeeded by a drop of not less than 13.8 kPa (2 psi) in 15 minutes.

Induction Period is the elapsed time, in minutes, from the instant at which the sample is initially heated, as evidenced by the recording of the pressure increase, to the break point. The temperature is maintained at 100 C throughout the heating period.

APPARATUS

Induction period apparatus, as shown in the drawing, consists of an enclosed water bath (1) or a multiple thereof, each containing 4 stainless steel oxygen pressure vessels (2) having inside dimensions of 54 mm (preferred) to 57 mm diameter by 210 mm height, sufficient to hold a 250 mL Pyrex sample bottle

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).

(3). The head (4) of each pressure vessel has a square-groove joint and fits closely (with a gasket) onto the pressure vessel. The head is held in place by 6 bolts with hexagonal nuts. The flange at the top of the pressure vessel is tapped and a stainless steel tube connects the pressure vessel with a pressure recorder (5).

The recorder may be operated with 1 to 4 points, allowing a different color pen for each pressure vessel in the bath. A manifold (6) connects each pressure vessel to the pressure-regulated oxygen tank (7) via individual needle valves (17) and is provided with a 690 kPa (100 psi) relief valve (14), a block valve (15), and a vent valve (16). Heating or cooling is achieved by introducing either steam (18) or cold water (19) into the water bath (1). (This apparatus is not commercially available at this time.)

Bottles, 250-mL, Pyrex, 51 mm OD, standard wall tubing, 190-mm high including a 22-mm ID neck opening, UOP Inc., or equivalent

Cylinder, graduated, 200-mL

Gaskets, 0.79 mm thick, asbestos composition, for pressure vessels. John Crane Packing Co., gasket No. 888, or equivalent, has been found suitable when used in conjunction with the Teflon gasket lubricant.

Gasket lubricant, Teflon, aqueous suspension, used to coat gasket and to prevent sticking. Available from DuPont, as Teflon No. 30 TFE, or equivalent, resin aqueous dispersion, in 4-L quantities only. Gaskets are soaked for 5 minutes in a 1:1 aqueous dilution, then allowed to air dry hanging from a horizontal rod, for at least 3 hours.

Pipet, automatic, 150-mL capacity, SGA Scientific Inc., Cat. No., JP-6875 (special order), or equivalent

Pipet, Mohr, long tip Pyrex, 2-mL graduated, 0.01 mL divisions, Sargent-Welch Scientific Co., Cat. No. S-69585-EE, or equivalent

Recorder, Foxboro, Model 47986, 4 pen spiral type, range 0-1380 kPa (0-200 psi), or equivalent

Shaker, Junior Orbit Shaker, Lab Line Instruments Inc., Model 3520 with Model 3520-6 platform, or equivalent

Thermometer, ASTM Saybolt viscosity thermometer No. 22 F, having a range of 95 to 103 C (204 to 218 F) as prescribed in ASTM Specifications E 1.

REAGENTS AND MATERIALS

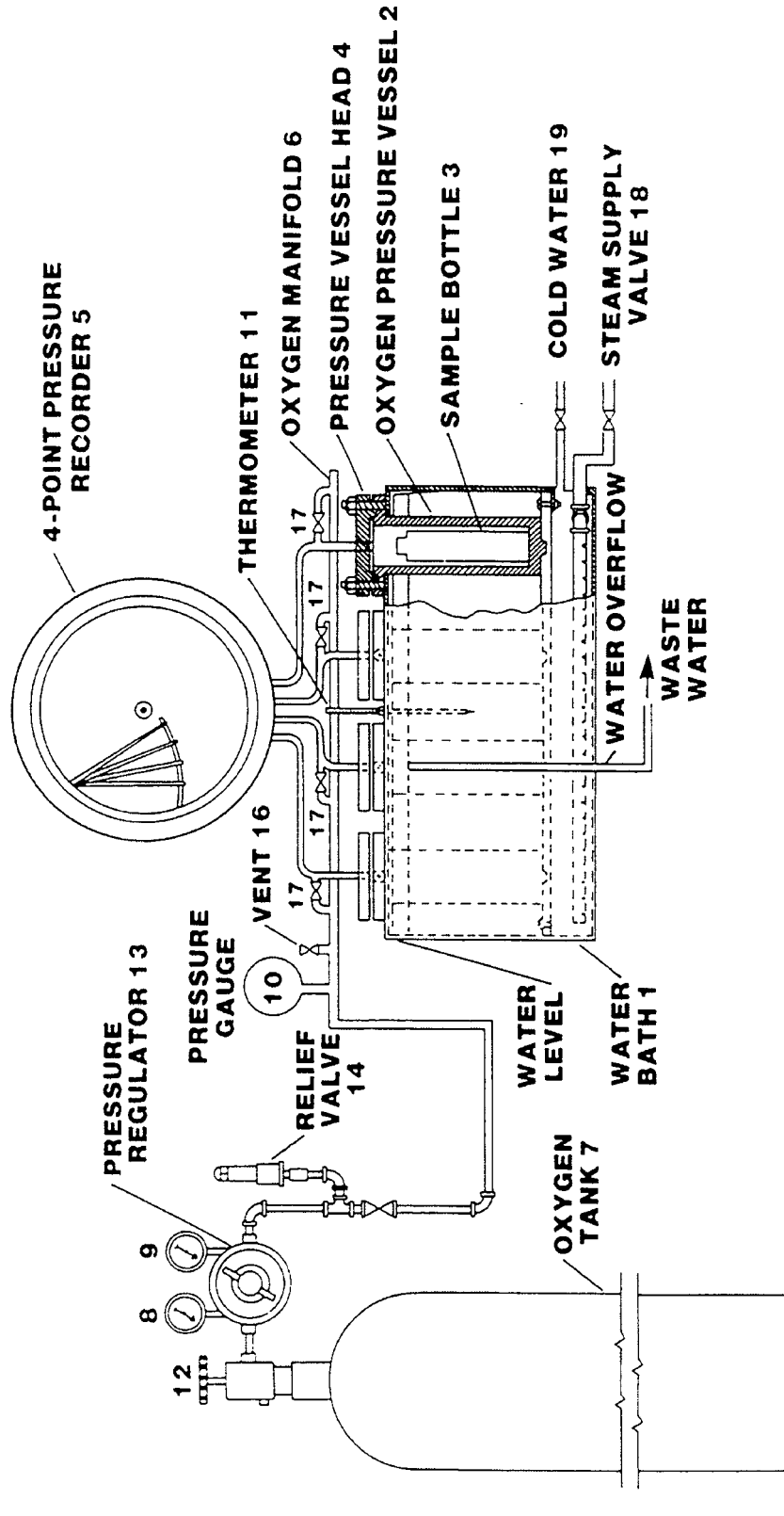
All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified. References to water mean deionized or distilled water. Unqualified references to solutions mean aqueous solutions.

Acetone, dry

Gum solvent, Toluene-Acetone-Methanol (TAM) mixture, 1:1:1 by volume

Hydrochloric acid, 1:1 by volume

Oxygen, extra dry, 99.6% minimum purity. *CAUTION*, use extreme care in the handling of compressed oxygen.



Figure

UOP Induction Period Pressure Vessel Bath

PREPARATION OF APPARATUS

(Refer to drawing)

Thoroughly clean all pressure vessels (2), heads and gasket seats (4) so that they are free from any traces of gasoline, oil or gum deposits with acetone soaked paper towels. Be certain that all traces of acetone are removed from the pressure vessels, etc. Using brief bursts of oxygen from the oxygen tank (7), set at 690 kPa (100 psi) according to gauges 9 and 10, make sure that the oxygen inlet to the pressure vessel via the oxygen manifold (6) is dry and free of any traces of acetone. Clean several Pyrex sample bottles to remove any trace of lead deposits, which may remain from leaded fuels, using 1:1 HCl. Next remove detergents, oils and gums by using gum solvent (TAM) followed by first an acetone and then a distilled water rinse with subsequent drying at 105 C.

PREPARATION OF SAMPLES

If the induction period of a given gasoline is to be tested, no special sample preparation is needed. The sample bottle is charged from an automatic pipet, or a 200-mL graduated cylinder, with 150 mL of the gasoline to be tested and is placed into the center of the pressure vessel well (2).

If the induction period of a given gasoline is to be tested with an inhibitor-additive, which is normally added in the range of 2 to 100 wt-ppm, accurately prepare 100 mL of a 1-2 wt/vol-% toluene solution of the additive. Follow this by a second toluene dilution in such a way that an aliquot of 1 to 2 mL from a graduated 2-mL pipet, when added to the 150-mL gasoline, produces the desired wt-ppm additive concentration. Simultaneously agitate up to 9 sample bottles using the Junior Orbit Shaker on a safe rotational speed setting for about 10 minutes. Place the sample bottles into the pressure vessel wells (2).

PROCEDURE

Oxygen Purge

Bring all oxygen pressure vessels containing the test samples to a uniform temperature of 15-25 C (59 to 77 F) by turning on the cold water supply valve (19) at the water bath (1) of the induction period apparatus and allowing the water to exit freely at the stand pipe overflow for approximately 60 minutes. Properly label the circular charts of the pressure recorder (5), as well as each oxygen pressure vessel (2), by recording the sample description, sample number, name, concentration of additive, if any, the analyst's initials and the date.

Position a new Teflon-coated gasket on the pressure vessel head (4), cover the pressure vessel (2) with the lid and hand tighten all nuts. Using a manually operated torque wrench or a pneumatic wrench with an air supply at 620 kPa (90 psi), first tighten opposite nuts lightly, then firmly to 275 kPa (40 psi).

Flush out the air in the pressure vessel with oxygen by closing the exhaust vent (16), opening the oxygen tank valve (12), block valve (15), needle valves (17), and slowly adjusting the cylinder regulator valve (13) until the gauges (9 and 10) read 690-705 kPa (~ 100 psi). Next, close block valve (15), slowly release all pressure by opening the exhaust vent (16) leading outdoors, to vent any gasoline fumes. Close the exhaust vent (16), slowly reopen the block valve (15) to repressurize the system with oxygen, and repeat two more purges as described. Finally, leaving the pressure vessels pressurized under exactly 690 kPa (100 psi) of oxygen by closing all needle valves (17) as well as block valves (15), slowly open exhaust valve (16) until

pressure gauge (10) indicates zero kPa, and check for pressure vessel leaks by observing the pens of the pressure-recorder (5).

Ignore an initial rapid drop (<40 kPa or 6 psi) which may be observed because of oxygen dissolving in the sample and/or cooling of the sample. Readjust the pressure to 690 kPa (100 psi). If the rate of pressure drop does not exceed 7 kPa (1 psi) in 10 minutes, assume the absence of leaks and proceed as follows: With all pressure vessels pressurized with oxygen at 690 kPa (100 psi) and all needle valves (17) closed, turn off the oxygen by closing tank valve (12), opening block valve (15) to release all line pressure through the open exhaust valve (16) until pressure gauge (10) again reads zero kPa.

Start Up

Close the cold water supply valve (19) and move the chart of the pressure recorder (5) to the actual hour. Fully open the steam supply valve (18) to heat up the water bath as rapidly as possible. Record the start-up time (steam valve opened) on the chart of the pressure recorder (5) and make sure that all pens are recording properly. When the bath has reached a temperature of 100 C (212 F) in about 20 minutes time, adjust the steam supply valve so that a reduced steam supply will assure a temperature of 100 C for the duration of the test as indicated by the thermometer (11). (The maximum obtainable temperature may vary slightly depending on the barometric pressure.) Let the system run for up to 20 hours or less if samples have reached the induction period (see *CALCULATIONS*). If after a maximum of 20 hours the gasoline samples have not yet inducted, probably indicating a very stable fuel with an induction period result of greater than 1200 minutes, terminate the test.

Shut-down

Record the bath temperature from the thermometer (11) on the chart. Turn off the steam supply valve (18) and open fully the cold water valve (19). Only after the pressure vessel lids are cold to the touch, *slowly* release all pressure vessel pressures by opening the exhaust valve (16) and all needle valves (17), until the pens of the recorder (5) indicate zero pressure. Remove and discard the samples. Clean out the sample bottles and pressure vessels as described under *PREPARATION OF APPARATUS*.

CALCULATIONS

Examine the recording for each sample to determine the point at which the oxygen pressure had declined exactly 13.8 kPa (2 psi) in 15 minutes and is followed by a further decline of not less than 13.8 kPa (2 psi) in 15 minutes. This is the break point. Also find the point at which there was an abrupt increase in pressure, which occurs about 5 minutes after the steam is turned on in the bath. Determine the elapsed time from this point to the break point, and report this as the induction period in minutes.

PRECAUTIONS

The pressure vessels and bottles must be scrupulously clean to obtain reproducible results.

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	Number of Replicates	Induction Period, Minutes	esd, Minutes	Allowable Difference, Minutes
Gasoline (no additives added)	10	350	12	36

TIME FOR ANALYSIS

The elapsed time for one to twenty analyses is 20 hours. The labor requirement for one to seven analyses is 0.75 hour for one analysis. In groups of eight to twenty, the labor requirement is 0.5 hour for one analysis.

REFERENCES

Egloff, G., Morrell, J. C., Lowry, C. D., Jr., and Dryer, C. G., *Ind. Eng. Chem.* **24**, 1375 (1932)
ASTM Method D 525, www.astm.org

SUGGESTED SUPPLIERS

E. I. DuPont & Co., PPR Dept., Customer Service, Wilmington, DE 19898
Foxboro Co., 2050 Algonquin Rd., Schaumburg, IL 60195
John Crane Packing Co., 6400 Oakton St., Morton Grove, IL 60053
Lab Line Instruments Inc., Lab-Line Plaza, Melrose Park, IL 60160
SGA Scientific Inc., 770 N. Church Rd., Elmhurst, IL 60126
Sargent-Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60077
UOP Inc., Process Division, 20 UOP Plaza, Des Plaines, IL 60016