Designation: D7739 – 11 (Reapproved 2016)

An American National Standard

Standard Practice for Thermal Oxidative Stability Measurement via Quartz Crystal Microbalance[1]

This standard is issued under the fixed designation D7739; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This laboratory practice covers the quantitative determination of surface deposits produced during the thermal oxidation of gas turbine fuels by monitoring the oscillation frequency of a quartz crystal during thermal exposure. In this practice, "thermal oxidative stability" refers to the tendency of a fuel to resist surface deposit formation during heating.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Summary of Practice

2.1 A quartz crystal, fitted with gold electrodes, is fully immersed in test fuel contained within a reactor. An oscillator circuit, connected to the crystal, supplies energy to excite the quartz crystal and monitors its resonant frequency (nominally 5 MHz) over time via a computer interface. The reactor is equipped with a magnetic stir bar, pressure gauge/transducer, oxygen sensor (not recommended for certain test conditions, see 4.11), and thermocouple to monitor and control test conditions. Prior to testing, the fuel is bubbled with the test gas for 30 min to equilibrate. After equilibration, the reactor vessel is isolated and raised to test temperature and pressure. As deposits accumulate on the crystal surface during the run, the crystal frequency decreases. The shift in resonance frequency can be quantitatively related, in real time, to surface deposit accumulation via a variation of the Sauerbrey equation.[2]

3. Significance and Use

3.1 The tendency of a jet fuel to resist the formation of deposits at elevated temperature is indicative of its oxidative thermal stability. This practice provides a technique for the simultaneous determination of deposit formation and oxygen consumption during the thermal oxidation of jet fuels and other hydrocarbon liquids. The practice can be used to evaluate the thermal stability of fuels and to determine the efficacy of additives in inhibiting deposition or slowing oxidation, or both. A test temperature of 140 °C and run length up to 16 h has been found to be effective for the relative evaluation of fuels and fuel additives. This practice has also been employed for other hydrocarbon liquids, such as gasoline and diesel fuels, but additional safety issues may need to be addressed by the user.

4. Apparatus

4.1 All dimensions without tolerance limits are nominal values.

4.2 *Reactor*—A T316, 100 mL stainless steel reactor cylinder with an internal diameter of 5.23 cm (2.06 in.) and a depth of 4.93 cm (1.94 in.).[3,4] A T316 stainless steel reactor head with several openings (for example, gas inlet via dip tube, gas release fitted with a dial gauge or pressure transducer, thermocouple, safety rupture disk, frequency signal connection, sleeve for oxygen concentration probe). A 0.952 cm (⅜ in.) hole is drilled in the center of the reactor head to accommodate the frequency signal connectors. This hole shall have a 0.952 cm (⅜ in.) clearance from any adjacent opening.

4.3 *SMA Coaxial Connector Assembly*—This assembly provides the electronic connection through the reactor head to the quartz crystal and consists of several key parts (see Fig. 1). The cable from the oscillator (see 4.6) connects to a subminiature

[1] This practice is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.J0.03 on Combustion and Thermal Properties.

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[2] Klavetter, E. A., Martin, S. J., and Wessendorf, K. O., "Monitoring Jet Fuel Thermal Stability Using a Quartz Crystal Microbalance," *Energy & Fuels*, Vol 3, 1993, pp. 582-588.

[3] The sole source of supply of the apparatus (Parr Instrument cylinder model #452HC8 (100 mL)) known to the committee at this time is Parr Instrument Company, 211 Fifty-Third St., Moline, IL 61265-1770.

[4] If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

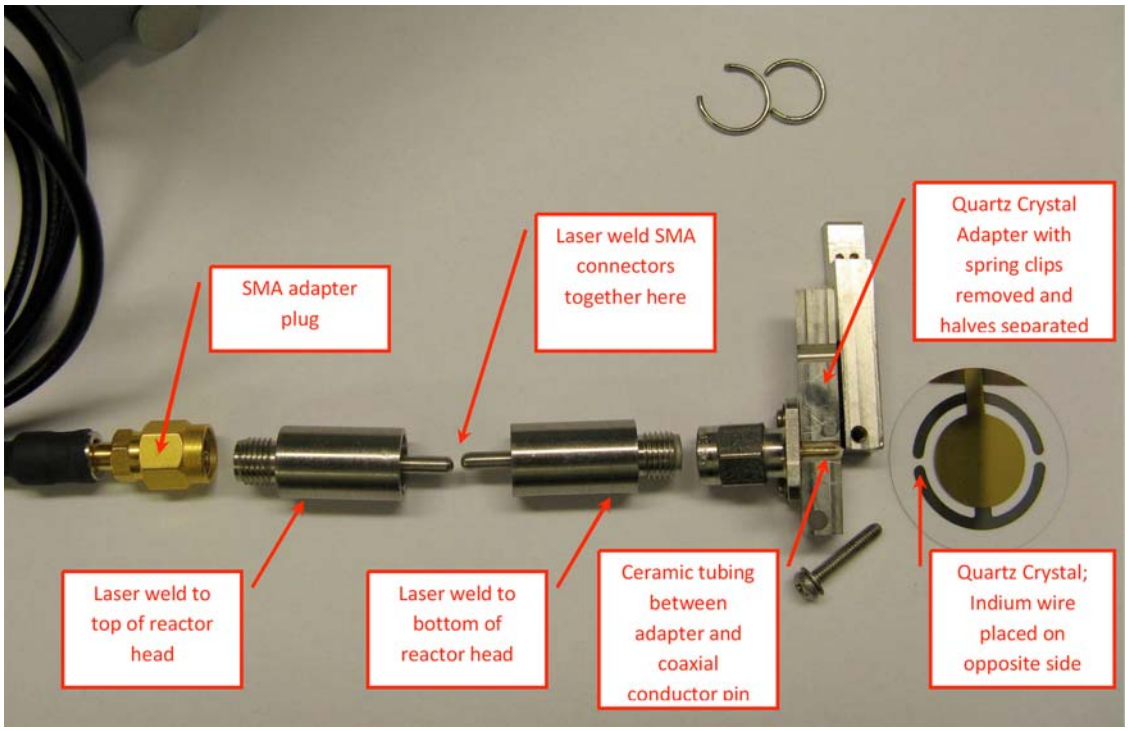

FIG. 1 SMA Coaxial Connector Assembly

version A (SMA) adapter plug.[5,4] The SMA adapter plug connects to two male SMA connectors.[6,4] The male SMA connectors are first welded together, and then laser welded in place on both sides of the reactor head.[7,4] A mating set of SMA connectors (male and female) was not used since these were not available in 0.952 cm (⅜ in.) diameter. The threaded end of the SMA connector on the bottom of the reactor head connects to the Quartz Crystal Adapter (see 4.5).

4.4 *Reactor Heater*—Open bottom band heater used to bring test fuel to temperature.[8,4]

4.5 *Heater Controller*—Proportional-integral-derivative (PID) controller for regulating the open bottom reactor band heater.[9,4] A second heater controller may be used as a high temperature safety cut-off should the outside skin temperature of the reactor exceed a preset limit.

4.6 *Quartz Crystal Adapter*—Required to both properly align the quartz crystal and suspend the quartz crystal in the test fuel. Proper installation of the quartz crystal in the adapter will complete an electrical circuit in which the quartz crystal is the frequency controlling element of the oscillator. The adapter is based on a design by the Sandia National Laboratories and may be purchased commercially.[10,4] The insulator between the adapter and the coaxial conductor pin may be fashioned by machining or carefully fracturing ceramic tubing.[11,4]

4.7 *Oscillator*—A phase lock oscillator that measures the frequency of the quartz crystal and provides a DC voltage signal proportional to the conductance of the crystal. Suitable for quartz crystals with a resonance frequency of 5 MHz.[12,4]

4.8 *Frequency Counter*—To measure the frequency from the oscillator. Frequency resolution shall be ±0.1 Hz.[13,4]

4.9 *Multimeter/Data Acquisition System (DAS)*—Measures the conductance voltage, pressure, temperature, and other monitored parameters and transmits data to a computer.[14,4]

4.10 *Thermocouples*—K-type used to measure test fuel temperature and outside reactor skin temperature (if so equipped).

[5] The sole source of supply of the apparatus (Part No. 3037M-1) known to the committee at this time is Coaxial Components Corp., 10 Davinci Dr., Bohemia, NY 11716-2601.

[6] The sole source of supply of the apparatus (Part No. 9251000) known to the committee at this time is Insulator Seal Inc., 6460 Parkland Dr., Sarasota, FL 34243-4036.

[7] The sole source of supply of the apparatus (laser welding) known to the committee at this time is Precision Joining Technologies, Miamisburg, OH.

[8] The sole source of supply of the apparatus (Parr Instruments Model A2235 HC2EB, 110 VAC and A865HC11EB) known to the committee at this time is Parr Instrument Company, 211 Fifty-Third St., Moline, IL 61265-1770.

[9] The sole source of supply of the apparatus (Eurotherm 2216E, Cal 9500P, and Parr 4842 controllers) known to the committee at this time is Parr Instrument Company, 211 Fifty-Third St., Moline, IL 61265-1770.

[10] The sole source of supply of the apparatus (part numbers 950132, 950133, 950135 through 950138) known to the committee at this time is Raytheon Ktech, 1300 Eubank Blvd. SE, Albuquerque, NM 87123.

[11] The sole source of supply of the apparatus (Part No. R1201) known to the committee at this time is Scientific Instrument Services, Inc., 1027 Old York Road. Ringoes, NJ 08551-1054.

[12] The sole source of supply of the apparatus (Inficon PLO-10i phase lock oscillator) known to the committee at this time is Inficon, Two Technology Place, East Syracuse, NY 13057.

[13] The sole source of supply of the apparatus (Agilent Models #53131A or 53181A) known to the committee at this time is Agilent Technologies, Inc., 5301 Stevens Creek Blvd., Santa Clara, CA 95051.

[14] The sole source of supply of the apparatus (Keithley Model #2700) known to the committee at this time is Keithley Instruments, Inc., 28775 Aurora Rd., Cleveland, OH 44139.

4.11 *Magnetic Stir Plate and Stir Bar*—To maintain test fuel temperature homogeneity. The stir bar is polytetrafluoroethylene (PTFE) coated with the following dimensions, 3 mm diameter by 12.7 mm long.[15,4]

4.12 *Oxygen Concentration Sensor and Transmitter*—To monitor and record the consumption of oxygen throughout the run.[16,4] The use of an oxygen concentration sensor and transmitter is not recommended when operating with a test gas containing more than 25 % by volume oxygen. Oxygen operation presents the possibility of detonation and this equipment may not withstand this sudden increase in pressure.

4.13 *Pressure Transducer*—A pressure transducer can be used in place of a dial gauge.[17, 4] When operating with oxygen or a test gas containing more than 25 % by volume oxygen extra caution is needed. Oxygen operation presents the possibility of detonation and the pressure transducer may not withstand this sudden increase in pressure.

5. Reagents and Materials

5.1 *Quartz Crystal*—A 2.54 cm (1 in.) diameter, AT-cut, polished silica wafer sandwiched between gold electrodes.[18,4] A new quartz crystal shall be used for each run. The front side of the crystal contains the smaller of the two circular electrodes. The crystal will be installed in the Quartz Crystal Adapter (see 4.5) in a specific orientation.

5.2 *TAM*—A solution comprised of equal parts by volume reagent grade toluene, acetone, and methanol.

5.3 *Acetone*—Reagent grade

5.4 *Wire*—The 0.5 mm diameter wire is used to ensure good electrical contact between the electrodes on the front side of the quartz crystal and the Quartz Crystal Adapter. Indium wire may be used for testing below 155 °C.[19,4] Gold wire may be used for higher temperature runs.[20,4]

5.5 *Test Gas*—Either ultra-zero air or any combination of oxygen, 99.8 % purity, and nitrogen, 99.8 % purity.

6. Hazards

6.1 Observe all normal precautions when using oxygen under pressure and at high temperatures in the presence of combustible liquids. Appropriate shielding should be used for any containers under pressure. Pressurize and depressurize the reactor vessel slowly using the appropriate personnel shielding. Never attempt to open the reactor vessel while it is pressurized. Where appropriate, fuel and solvent handling should be conducted in a fume hood.

FIG. 2 Quartz Crystal (Front) Showing Proper Location of Indium Wire

7. Preparation of Apparatus

7.1 *Quartz Crystal and Adapter:*

7.1.1 Attach the quartz crystal adapter to the reactor head.

7.1.2 After attaching the cable to the quartz crystal adapter, energize the frequency counter.

7.1.3 Energize the multimeter. Select DC volts display (that is, DCV) and set the range to 10 volts (that is, 10 V).

7.1.4 Prepare a new nominal 5 MHz quartz crystal by applying with light pressure two small, approximately 1.5 mm, pieces of wire on the quartz crystal electrodes. The wire promotes good electrical contact. The wire is only placed on the front side of the quartz crystal and shall be oriented as shown in the Fig. 2. Take care to avoid skin contact with the quartz crystal as transfer of trace amounts of oily residue could affect test results.

7.1.5 Attach the quartz crystal to the quartz crystal holder (see Fig. 3). The coaxial conductor pin on the adapter shall contact the leftmost piece of wire. The raised area of the adapter shall contact the rightmost piece of wire. Carefully tighten the securing screw; overtightening can cause the quartz crystal to fracture, while under-tightening will not create a suitable electrical connection.

7.1.6 Lock the quartz crystal per the oscillator manufacturers' instructions.[21] If locked properly, frequency will vary no

[15] The sole source of supply of the apparatus (combination of a Cole-Parmer part #04660-40 stir plate and a Fisher Scientific part#14-513-98 stir bar) known to the committee at this time is Cole-Parmer Instrument Company, 625 East Bunker Court, Vernon Hills, IL 60061-1844. and Thermo Fisher Scientific, 81 Wyman St., Waltham, MA 02454.

[16] The sole source of supply of the apparatus (Mettler Toledo InPro 6800 sensor and 4100e transmitter) known to the committee at this time is Mettler-Toledo Inc., 1900 Polaris Parkway, Columbus, OH 43240.

[17] The sole source of supply of the apparatus (Honeywell TJE pressure transducer with a GM display unit) known to the committee at this time is Honeywell International, 101 Columbia Rd., Mailstop - M6/LM, Morristown, NJ 07962.

[18] The sole source of supply of the apparatus (Inficon Model SC-501-1, Part #149211-1) known to the committee at this time is Inficon, Two Technology Place, East Syracuse, NY 13057.

[19] The sole source of supply of the apparatus (Aldrich Catalog #26,406-7) known to the committee at this time is Sigma-Aldrich, 3050 Spruce St., St. Louis, MO 63103.

[20] The sole source of supply of the apparatus (Alfa Aesar #14728) known to the committee at this time is Alfa Aesar, 26 Parkridge Rd., Ward Hill, MA 01835.

[21] See Section 4.1, PLO-10 Series Phase Lock Oscillator, Operation and Service Manual, Inficon IPN 605800, Rev. G.

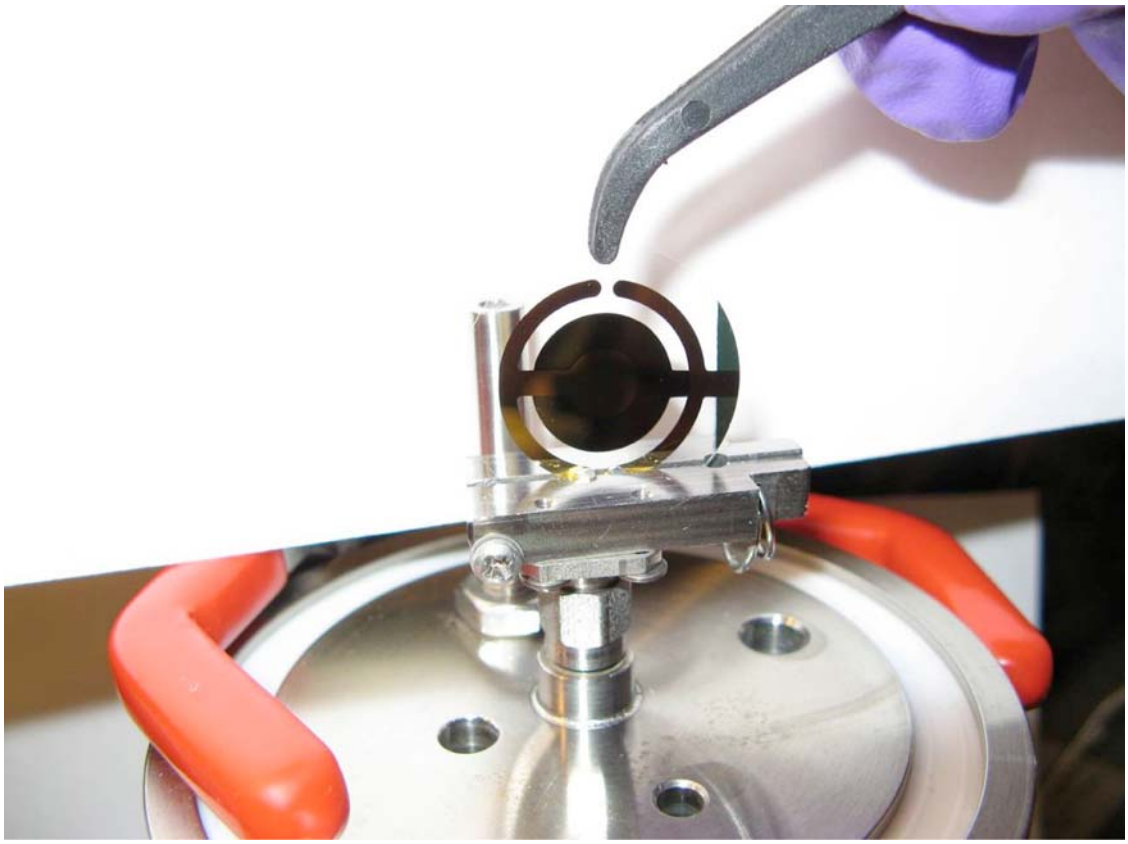

FIG. 3 Attachment of Quartz Crystal to Adapter

more than approximately 5 Hz and voltage will vary no more than approximately 5 mV. If the readings are not steady, the crystal may not be secure.

7.1.7 An optional best practice is to record the voltage (also known as conductance) of the quartz crystal in air, mV, prior to installing the reactor head (typically 3215 mV).

7.2 *Reactor:*

7.2.1 Insert the magnetic stir bar in the bottom of the reactor vessel.

7.2.2 Charge the vessel with 60 mL of test fuel, ensuring the quartz crystal is full immersed.

7.2.3 An optional best practice is to carefully remove any air bubbles from the upper surface of the test fuel. A disposable pipette has been found effective for this task. The proper setting for the magnetic stir bar should be established during the initial test setup with the reactor head off. The bar should create a slight vortex on the surface of the test fuel. Note this setting for future runs.

7.2.4 Mate the reactor head to the reactor vessel and loosely attach the split ring assembly.

7.2.5 Loosely attach the outer locking ring.

7.2.6 Orient the split ring assembly so the tightening bolts will not contact any part of the head assembly. Tighten the bolts on the split ring assembly to 33.9 N-m (25 lbf-ft) incrementally and in an alternating pattern to gradually and evenly secure the head to the vessel.

7.2.7 Tighten the outer locking ring.

7.2.8 Insert the reactor into the heater assembly.

7.2.9 Ensure the green “LOCK” indicator on the oscillator is lit. If not, adjust as necessary per the oscillator manufacturers’ instructions.

7.2.10 An optional best practice is to record the voltage (also known as conductance) of the quartz crystal immersed in the test fuel, mV (typically 150 mV).

7.2.11 Adjust the magnetic stirrer to the proper setting (see 7.2.3).

7.2.12 Attach the thermocouple, flexible pressure relief tubing, gas inlet and release tubing, to the reactor head. The thermocouple should be placed just off the bottom of the vessel. Complete connections to the pressure transducer and oxygen concentration transmitter, if so equipped.

7.2.13 Tighten the heating band securely to the outside of the reactor vessel and attach the skin thermocouple if so equipped (see Fig. 4 and Fig. 5).

7.2.14 Secure any safety shielding around the reactor if so equipped.

7.2.15 A best practice is to ensure the reactor is sealed properly via the following, optional steps.

7.2.15.1 Slowly pressurize the reactor vessel with nitrogen to 689 kPa gauge (100 psig).

7.2.15.2 Isolate the reactor and ensure there is no significant pressure drop for 30 min. Some minor pressure drop due to saturation of the test fuel may be observed and is acceptable.

7.2.15.3 After 30 min, slowly release the nitrogen pressure. Releasing too quickly could disturb or possibly expel the test fuel.

FIG. 4 Fully Assembled Reactor

7.2.16 Slowly introduce the test gas to saturate the test fuel. Saturation may be conducted at either atmospheric or elevated pressure. If saturation is to be conducted at atmospheric pressure, ensure the reactor exhaust valve is open and slowly increase test gas flow to 50 mL/min ± 10 mL/min. If saturation is to be conducted at elevated pressure, close the reactor exhaust valve, slowly introduce the test gas and allow pressure to build to the required pressure. Use the reactor exhaust valve to then regulate test gas flow to 50 mL/min ± 10 mL/min.

7.2.17 While saturating the test fuel, frequency stabilization should be verified.

7.2.18 After 30 min, achieve test pressure by adjusting the test gas inlet and exhaust valves. Once test pressure has been achieved, ensure both the test gas inlet and exhaust valves are securely closed, isolating the reactor.

8. Procedure

8.1 Energize the heater controller and activate data logging on the control software if so equipped. A data logging interval between 15 s and 60 s has been found informative for this test.

8.2 Initiate the test program via the control software.

8.3 After the test run, turn the heater off and slowly depressurize the reactor.

8.4 Ensure the vessel has cooled to near ambient conditions prior to opening.

8.5 Remove the reactor head and dispose of the test fuel properly.

8.6 Clean all hardware that came in contact with test fuel using wipes or swabs with the TAM solution applied (see 5.2). Perform a subsequent rinse with acetone and allow the hardware to air dry.

9. Calculation or Interpretation of Results

9.1 Calculate the surface mass per unit area, ρs, per Eq 1:

$$\rho_s = (-2.21 \times 10^5) * (f_o - f)/f_o^2 \quad (1)$$

where:

ρ_s = surface mass per unit area, μg/cm^2,
f_o = initial quartz crystal resonant frequency after high temperature stabilization, MHz, and
f = quartz crystal resonant frequency at some reaction time, t, after f_o, MHz.

10. Report

10.1 Report test temperature, °C.

10.2 Report test gas utilized (for example, ultra-zero air, or 60 % oxygen and 40 % nitrogen).

10.3 Report initial total gas pressure, kPa.

10.4 Report the calculated surface mass, ρs, versus test time.

10.5 If recorded, report oxygen concentration versus test time.

10.6 If recorded, report total pressure versus test time.

11. Precision and Bias

11.1 Due to the limited number of installations, precision and bias has not been established for this practice.

12. Keywords

12.1 gas turbine fuels; quartz crystal microbalance; thermal oxidative stability

FIG. 5 Close-Up of Reactor (Skin Thermocouple Shown Below Dial Pressure Gauge)