National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material 1817c

A Catalyst Package for Lubricant Oxidation (ASTM Sequence IIID Engine Test)

This Standard Reference Material (SRM) is intended primarily for use in evaluating the oxidation stability of lubricating oils, i.e., automotive crankcase lubricants. SRM 1817c contains: (1) an oxidized/nitrated fuel fraction; (2) a metal naphthenate mixture; and (3) distilled water. The metal naphthenate mixture has the following weight ratio of metal elements: 20:2:1:1:1 for lead, iron, copper, manganese, and tin, respectively.

SRM 1817c is used to simulate the chemical environment in an operating engine, specifically under the ASTM sequence IIID engine test conditions. Eleven IIID oils have been tested using SRM 1817c. Both the Thin-Film Oxygen Uptake Test (TFOUT) [1] and the Differential Scanning Calorimetry (DSC) test [2] were used to determine the oxidation induction times of these oils.

The certified values for oxidation induction times by TFOUT and DSC are given in Tables 1 and 2, respectively. The uncertainties of the certified values are expressed at ± two standard deviations of the certified value. Correlation between the two methods is shown in Figure 1.

Notice and Warning to Users:
Expiration of Certificate: This certification of SRM 1817c is valid, within the limits certified, for one year from the date of shipment.

Storage: Sealed ampoules, as received, should be stored in dark at a temperature between 10-25 °C.

Use: Each ampoule should be shaken thoroughly before opening. Samples should be taken immediately after opening an ampoule, and should be used without delay for the certified values to be valid. Certified values are not valid for ampoules that have been opened and resealed.

The technical planning, coordination and testing leading to the certification of this SRM were performed by P.T. Pei, C.S. Ku, R. Premachandran (guest scientist) and S.M. Hsu, of the NIST Ceramics Division, Materials Science and Engineering Laboratory.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Standard Reference Materials Program by T. E. Gills.

Gaithersburg, MD 20899
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William P. Reed, Chief
Standard Reference Materials Program

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PREPARATION

Fuel Fraction

The fuel fraction was produced by the oxidation/nitration of a high boiling point VD gasoline fraction (ASTM VD engine test fuel) [3]. The neutralized product was used as the fuel fraction. The total acid number (mg KOH/g) of the fuel fraction of SRM 1817c was determined to be 4.5 ± 0.3. The infrared spectrum of the fraction is shown in Figure 2.

Metal Naphthenates

The metal naphthenate mixture in SRM 1817c is made of commercially available metal naphthenates and is based on used oil analyses. The total metal concentration of all 5 metals was 10.6 wt. %. The remaining weight was composed of naphthenic liquids and mineral spirits as diluents. The mixture was used at NIST to generate Tables 1 and 2. In general, the metal content and the molecular weight distribution of any metal naphthenate may vary from batch-to-batch from the supplier. To avoid any potential effects on oxidation results caused by this variance, each metal naphthenate has been carefully characterized by comparing with a previous batch. Each metal naphthenate has been filtered through a 0.2 μm filter. During a one-year period, some precipitates may be observed in the metal mixture, but oxidation test repeatability has not been found to be affected by the presence of such precipitates.

Comparison Between SRM 1817b and SRM 1817c

The comparison of TFOUT data between SRM 1817c and SRM 1817b is shown in Figure 3. As shown, a correlation coefficient of 0.98 is obtained for TFOUT. In this figure, the solid line represents the ideal relation with a slope of 1.0.

Among the eleven IIID lubricant oils tested, "Oil D" showed shorter TFOUT and DSC induction times with SRM 1817c than with SRM 1817b. The TFOUT induction time (t_{ind}) was reduced from 143 minutes to 111 minutes and DSC induction time (t_{ind}) was reduced from 19.3 to 15.9 minutes. However, the t_{ind} for "Oil D" is now more in line with "Oil E" of equivalent IIID Break-Point Hours. The correlation between t_{ind} for SRM 1817c and 1817b is good at 0.98 for TFOUT and 0.98 for DSC, respectively.

REFERENCES

1. Ku, C.S. and Hsu, S.M., "A Thin-Film Oxygen Uptake Test for the Evaluation of Automotive Crankcase Lubricants," Lubrication Engineering, **40**, 2, pp. 75-83, (1984).

2. Hsu, S.M., Cummings, A.L., and Clark, D.B., "Evaluation of Automotive Crankcase Lubricants by Differential Scanning Calorimetry," SAE SP-526, pp. 127-138, Society of Automotive Engineers, Warrendale, PA, (1982).

3. Forbes, E.S. and Wood, J.M., "Development of a Bench Detergency Test for Automotive Oils and its Correlation with MS Sequence V Engine Test," I&EC Product R&D, **8**, 1, pp. 48-54, (1960).

Table 1. Induction Times of IIID Oils from Thin-Film Oxygen Uptake Test

Test Conditions:
1.5 g Oil
4 wt. % Fuel Catalyst
4 wt. % Metal Catalyst
2 wt. % Water
620 kPa (90 psig) Oxygen
160 °C

Oil	IIID HR*	No. of Tests	Oxidation Induction Time, min. Avg.	Std. Dev.
A	64	7	220	± 6
B	56	5	144	± 2
C**	48	7	86	± 3
D	40	5	111	± 3
E	40	7	100	± 2
F	24	8	75	± 1
G	16	7	38	± 1
H	16	7	42	± 3
I***	64	7	122	± 5
J***	56	7	157	± 2
K***	40	7	135	± 4

*Viscosity Break-Point Hour.
**Passed the IIID engine test oxidation criterion (less than 375% viscosity increase at 40 hr), but failed the wear criterion.
***Oils I, J and K are from a different series of IIID oils.

Table 2. Induction Times of IIID Oils from Differential Scanning Calorimetry

Test Conditions:
3 vol. % Fuel Catalyst
3 vol. % Metal Catalyst
175 °C
3.62 MPa Oxygen
120 cc/min Flow
Gold Pan

Oil	IIID HR*	No. of Tests	Oxidation Induction Time, min. Avg.	Std. Dev.
A	64	6	31.1	± 2
B	56	7	19.1	± 0.8
C**	48	7	17.1	± 0.9
D	40	7	15.9	± 0.5
E	40	7	13.1	± 0.4
F	24	7	10.6	± 0.6
G	16	7	5.7	± 0.3
H	16	7	6.6	± 0.3
I***	64	7	19.1	± 0.6
J***	56	7	16.0	± 0.8
K***	40	7	18.7	± 0.9

*Viscosity Break-Point Hour.
**Passed the IIID engine test oxidation criterion (less than 375% viscosity increase at 40 hr), but failed the wear criterion.
***Oils I, J and K are from a different series of IIID oils.

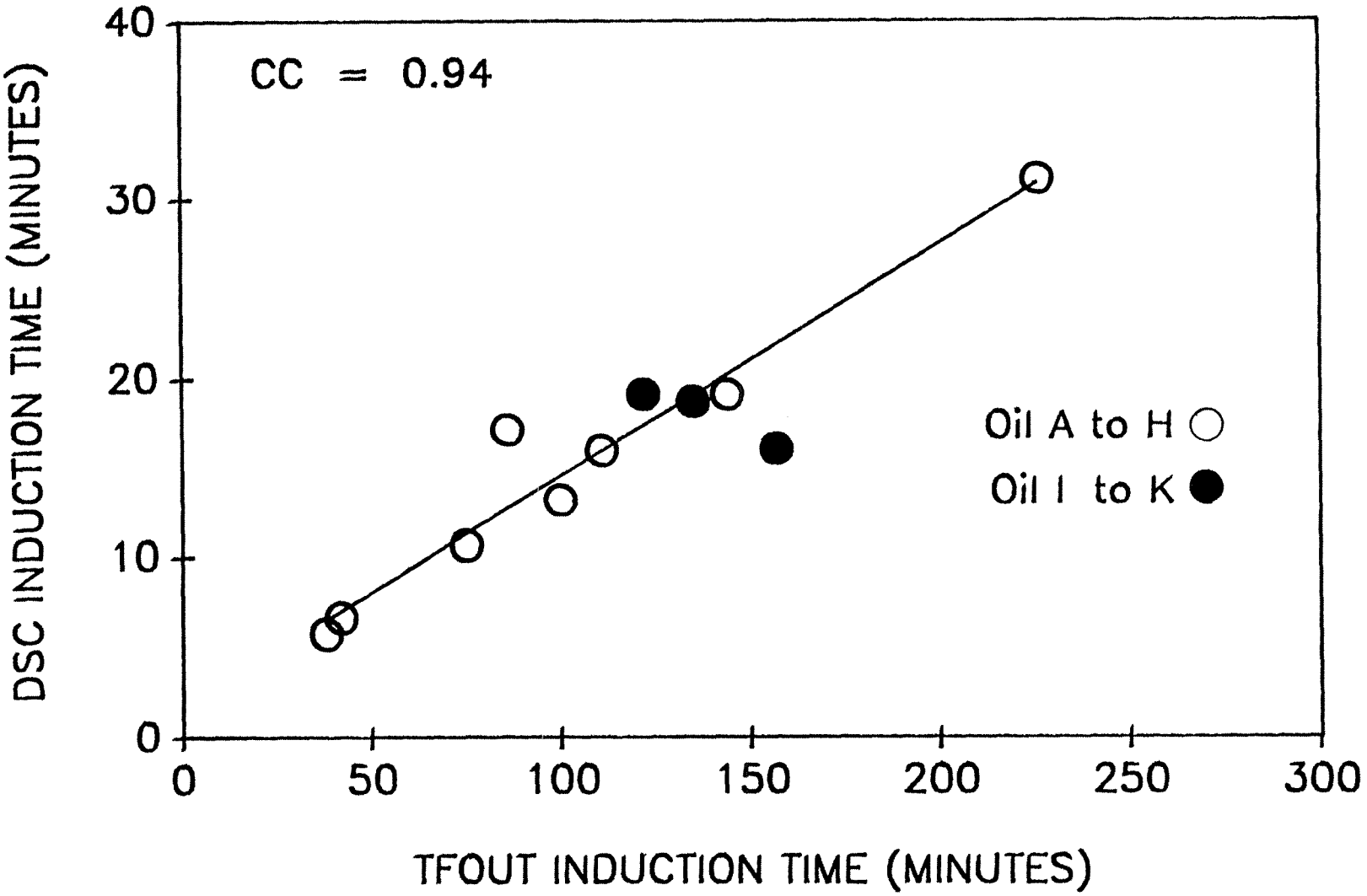

Figure 1: Correlation Between TFOUT and DSC Induction Time

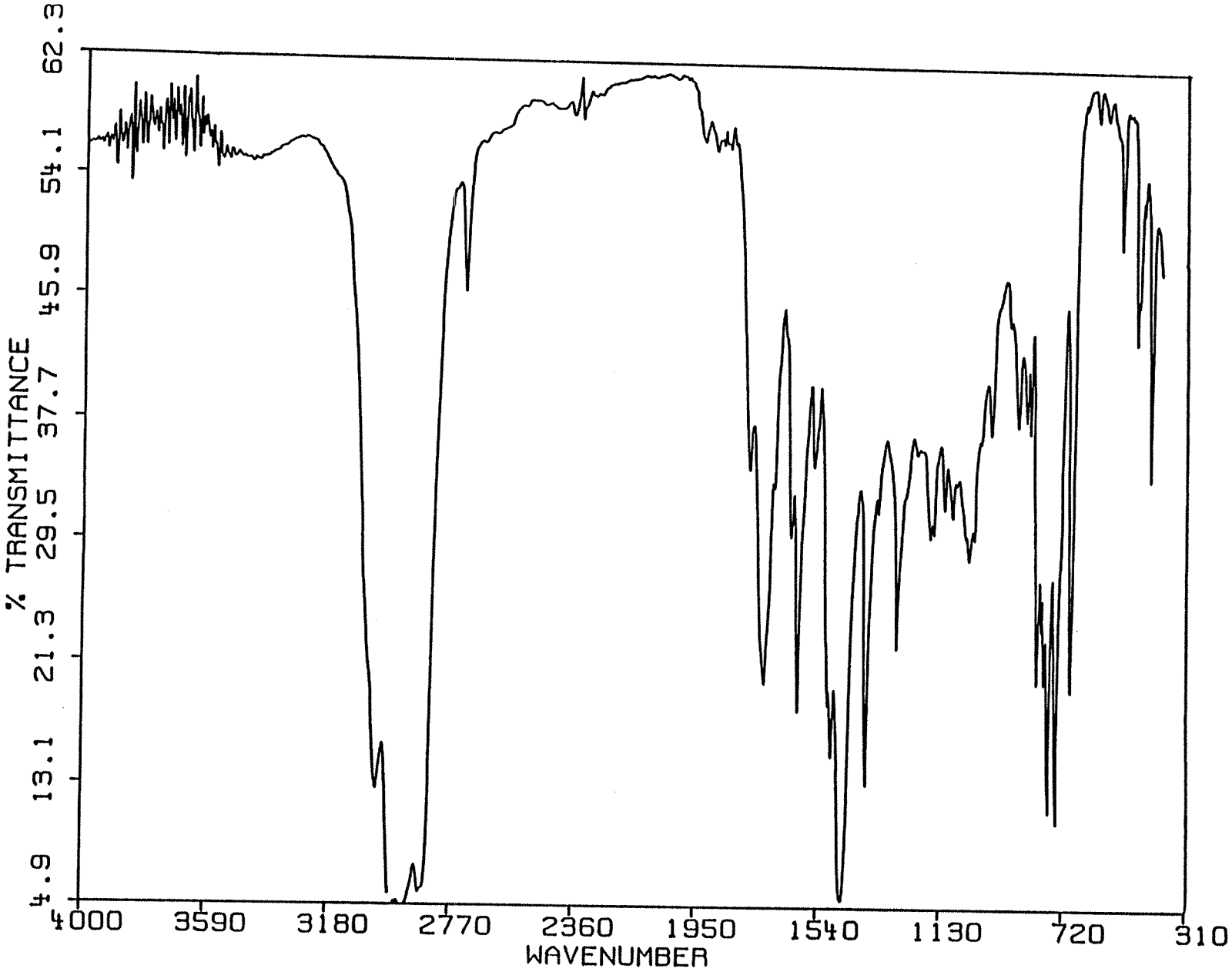

Figure 2: The Infrared Spectrum of the Fuel Catalyst

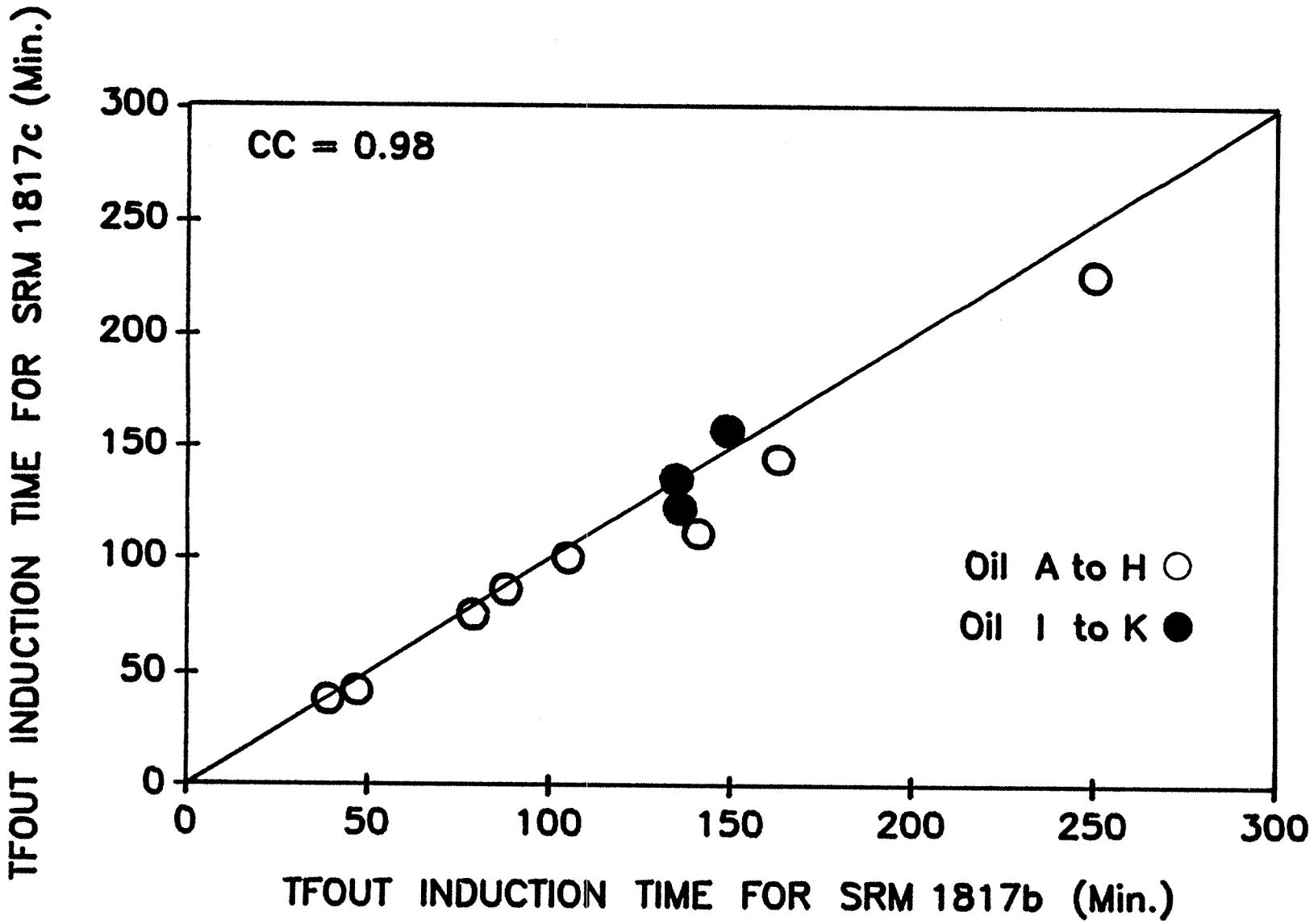

Figure 3: Correlation Between SRM 1817b and 1817c (TFOUT)