Thermochimica Acta, 154 (1989) 367–376
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

DETERMINATION OF ENGINE OIL VOLATILITY BY THERMOGRAVIMETRY

MIKIO ZINBO and L.M. SKEWES
Ford Motor Company, Research Staff, P.O. Box 2053, Dearborn, MI 48121 (U.S.A.)
(Received 28 March 1989)

ABSTRACT

A TG method for determination of the volatility of engine oils was developed as an alternative laboratory test to the Noack method (DIN 51581). The method involves standardizing a TG system with tetracosane ($C_{24}H_{50}$) and determining the relative evaporative loss of engine oils at the heating time of 30% tetracosane weight loss under the standardized TG conditions. The evaporative loss values for 48 engine oils of different viscosity grades were determined by this TG method and compared with corresponding values determined by the Noack method. The relative standard deviation obtained for an SAE 5W-30 multigrade oil was 4.1% ($n = 8$).

INTRODUCTION

The demand for fuel-efficient engine oil possessing good low temperature properties continues to increase. As a consequence, SAE 5W-30 oils are quickly becoming a major engine oil segment preferred by the gasoline-powered light duty vehicle manufacturers of North America. This shift in viscosity recommendations raises new concerns about the effects of engine oil volatility and viscosity on oil consumption. The importance of volatility, as well as viscosity, in controlling oil consumption has been recently confirmed, both in laboratory test engines and in vehicle fleet testing [1]. As engine oil volatility is not directly addressed by the new American Petroleum Institute (API) SG gasoline engine oil category [2], engine manufacturers are individually specifying their own volatility requirements.

Volatility characteristics of engine oil have been measured by various analysis techniques and procedures, including nonvolatile organo-silicon fluid internal standard IR analysis [3], 'simulated distillation' [4], TG analysis [5–7], '22-h cell evaporation' [8], and '1-h crucible evaporation' (the Noack method) [9]. This last method was originally approved by the German Standards Committee in 1958, and was tentatively adopted as the 'unified' method by the Co-ordinating European Council for the Development of Performance Tests for Lubricants and Engine Fuels (CEC) in 1987 [10].

Ford introduced the Noack method in its first worldwide engine oil specifications for initial fill in 1985 [11]. The minimum acceptable volatility specifications for SAE 5W-30, 10W-30 and 15W-30 allow maximum evaporative weight losses of 25, 20 and 15%, respectively, after 1 h at 250 ° C by the Noack method. Ford also included simulated distillation at 371° C by gas chromatography [4] as an alternative method in its second generation worldwide specifications for initial fill [12] and service fill [13].

The Noack test procedure is known to be poor in repeatability and reproducibility. Thus, in 1984 we initiated the development of a new TG method that would provide more reliable data than the Noack method. It was reported by a thermal analysis panel of the UK Institute of Petroleum (IP) in 1983 that temperature calibration of TG instruments appeared to be the main source of error in preliminary oil volatility measurements [14]. A number of different approaches to the temperature calibration of TG equipment have been adopted, including the use of magnetic transition [15] and dropping-weight techniques [16]. However, a standard method of temperature calibration for all commercial instruments is not likely to be attainable.

The present work describes a TG analysis method for determination of the relative evaporative weight loss of engine oils which does not require any direct temperature calibration of TG instruments, and discusses the correlation of results obtained by this method with results obtained by the Noack method.

EXPERIMENTAL

Materials

Eicosane (99%, m.p. 36–38 ° C), docosane (99%, m.p. 43–45 ° C), tetracosane (99%, m.p. 49–52 ° C), hexacosane (99%, m.p. 57–58 ° C) and octacosane (97%, m.p. 61–63 ° C) were purchased from the Aldrich Chemical Co. (Milwaukee, WI). Forty-eight engine oils of varying SAE viscosity grades (see Table 3) were obtained from six different suppliers. The Noack test results for these oils were provided by the suppliers.

Apparatus

A DuPont Model 951 TG analyser was used with a model 1090B thermal analyzer and TG data analysis program.

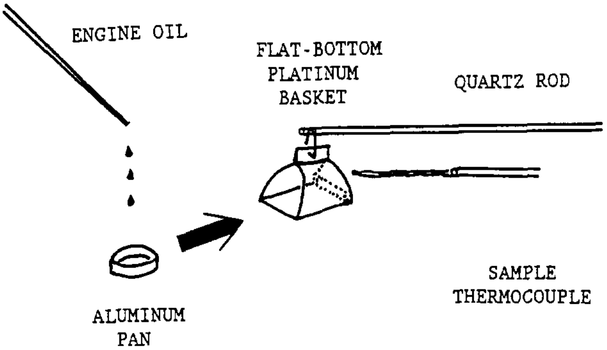

Fig. 1. Engine oil sample placement.

Procedure

An engine oil sample (ca. 15 μl, or 12–14 mg) was pipetted into an aluminum pan (6 mm diameter, 1.5 mm height). The aluminum sample pan was placed horizontally on a standard platinum sample basket which had been reshaped to have a flat base and open down-stream end. The placement of the oil sample aluminum pan, the shape of the platinum basket and the relative location of the sample thermocouple (chromel–alumel) are shown in Fig. 1. The sample was heated from a starting temperature of $25 \pm 2\,^\circ C$ to a final isothermal temperature, X, of 200–205 °C at a heating rate of $25\,^\circ C\ min^{-1}$, and kept isothermally at $X \pm 1.5\,^\circ C$ for 30–35 min under an air flow, Y, of 95–105 ml min^{-1} with an accuracy of $Y \pm 2$ ml min^{-1}. The stabilized air flow rate was checked at both the inlet and the outlet of the sample tube prior to standardization of the TG system.

Standardization

The TG system was standardized with tetracosane which had been melted at ca. 80 °C, solidified at room temperature, and then cut into small chunks for easier handling. The standardization was performed under the TG conditions described above to determine the heating time of 30% tetracosane weight loss.

RESULTS AND DISCUSSION

To select an external TG system calibration standard, a series of *n*-alkane thermograms were obtained. For example, Fig. 2 shows thermograms obtained for eicosane ($C_{20}H_{42}$), tetracosane ($C_{24}H_{50}$) and octacosane ($C_{28}H_{58}$) under a particular set of TG conditions. From knowledge of the TG behaviors of various engine oils and *n*-alkanes, tetracosane was chosen as

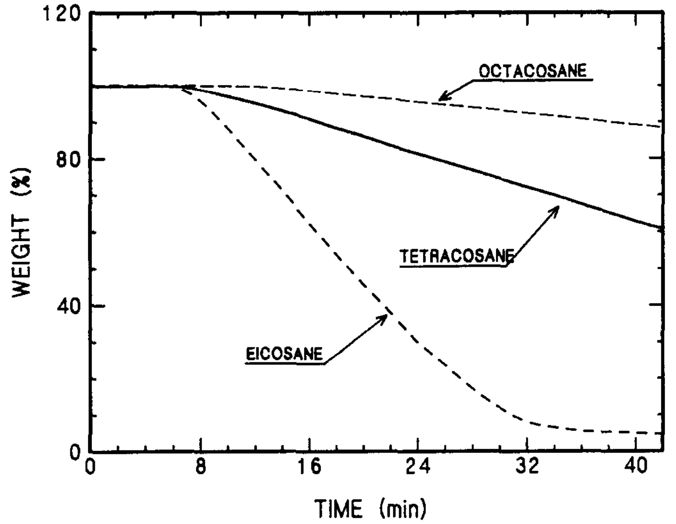

Fig. 2. A series of *n*-alkane thermograms for selection of a TG system calibration standard.

the external standard, on the basis of its wide linear weight loss range and moderate weight loss rate under the TG conditions.

Once a thermogram was obtained for the external standard sample under a selected set of TG conditions, those conditions became the standardized TG conditions for the subsequent engine oil evaporative loss measurements. To obtain a TG evaporative loss value comparable with that of the Noack method, TG engine oil volatility was defined as the evaporative weight loss at a 30% weight loss time of tetracosane. The procedure for the determina-

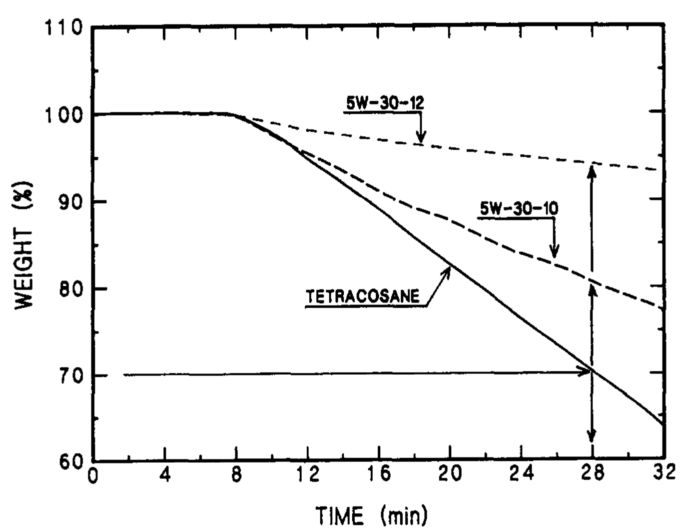

Fig. 3. Determination of relative engine oil volatility by TG.

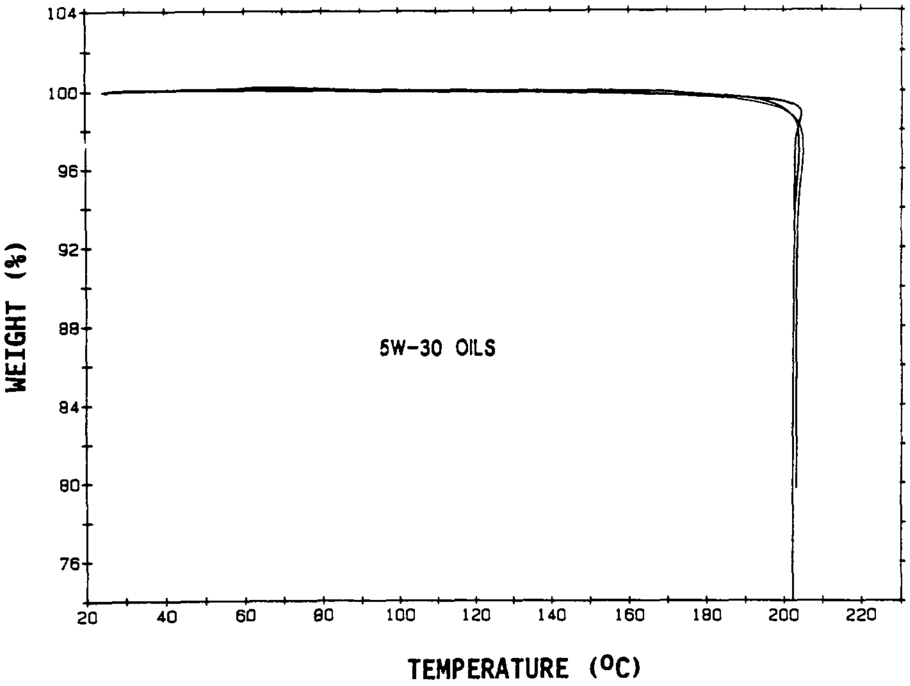

Fig. 4. TG heating profiles shown by sample temperature versus weight loss curves for three 5W-30 oils.

tion of relative volatility is illustrated in Fig. 3. In this case, 30% weight loss of tetracosane occurs at 28.0 min, and the relative volatilities of two 5W-30 oils tested were 6.4 and 19.4%, respectively. A calibrated 30% weight loss time could be in the range 25–35 min, depending on TG system conditions, but it should be within half a minute of the calibrated time during the same series of measurements.

Plots of sample weight (%) as a function of temperature (Fig. 4) demonstrate the TG heating profiles, which can be used as a measure of isothermal heating reproducibility. The isothermal temperature differential in the figure is within 1° C.

After standardization of a TG system, the TG conditions applied should be kept similar or controlled within the given ranges for the series of weight loss measurements. The TG conditions include the shape of the platinum basket, the position of the sample pan in the platinum basket, the location of the sample thermocouple, the starting and final isothermal temperatures and, most importantly, the rate of air flow.

To evaluate repeatability of the TG method, an SAE 5W-30 oil was analyzed on three consecutive days. The results are summarized in Table 1. The average weight loss at the 30% tetracosane weight loss time was 28.8%, with a relative standard deviation of 4.1% ($n = 8$). Deviation of the isother-

TABLE 1

Precision of TG method (A) [a]

Run	Sample ID	Heating time [b] (min)	Weight loss (%)	Isotherm temp. (°C)
1	n-$C_{24}H_{50}$	28.0	(30.0)	202.2
2	5W-30-5 (1)	(28.0)	28.4	202.4
3	n-$C_{24}H_{50}$	28.4	(30.0)	202.2
4	5W-30-5 (2)	(28.4)	28.5	201.8
5	5W-30-5 (3)	(28.4)	28.5	201.9
6	5W-30-5 (4)	(28.4)	29.7	202.7
7	5W-30-5 (5)	(28.4)	30.8	203.8
8	n-$C_{24}H_{50}$	28.4	(30.0)	202.4
9	5W-30-5 (6)	(28.4)	29.5	202.2
10	5W-30-5 (7)	(28.4)	27.3	202.5
11	5W-30-5 (8)	(28.4)	27.4	202.0

[a] Sample weight range: 13.5 ± 0.9 mg.
[b] 30% tetracosane weight loss time.

mal temperature during the measurements was within 1.5°C of the mean temperature (202.5°C). As a second test of repeatability, a set of four 5W-30 oils was analyzed by the same operator on two distant days (see Table 2). The weight loss differential between the two series of measurements for each 5W-30 oil was in the approximate range −(0 ± 6%).

The reproducibility of the TG method between two Ford Laboratories is shown in Fig. 5. TG evaporative loss values obtained at the 30% tetracosane

TABLE 2

Precision of TG method (B) [a]

Run	Sample ID	Heating time [b] (min)	Weight loss (%)	Isotherm temp. (°C)
1	n-$C_{24}H_{50}$ (1)	28.0	(30.0)	202.3
2	5W-30-10 (1)	(28.0)	19.2	202.3
3	5W-30-11 (1)	(28.0)	19.6	202.2
4	5W-30-12 (1)	(28.0)	5.9	202.8
5	5W-30-13 (1)	(28.0)	6.6	204.0
6	5W-30-14 (1)	(28.0)	24.0	201.7
7	n-$C_{24}H_{50}$ (2)	28.8	(30.0)	204.4
8	5W-30-10 (2)	(28.8)	19.5	203.4
9	5W-30-11 (2)	(28.8)	20.9	203.0
10	5W-30-12 (2)	(28.8)	5.9	203.6
11	5W-30-13 (2)	(28.8)	6.2	203.5
12	5W-30-14 (2)	(28.8)	24.5	202.8

[a] Sample weight range: 13.2 ± 1.0 mg.
[b] 30% tetracosane weight loss time.

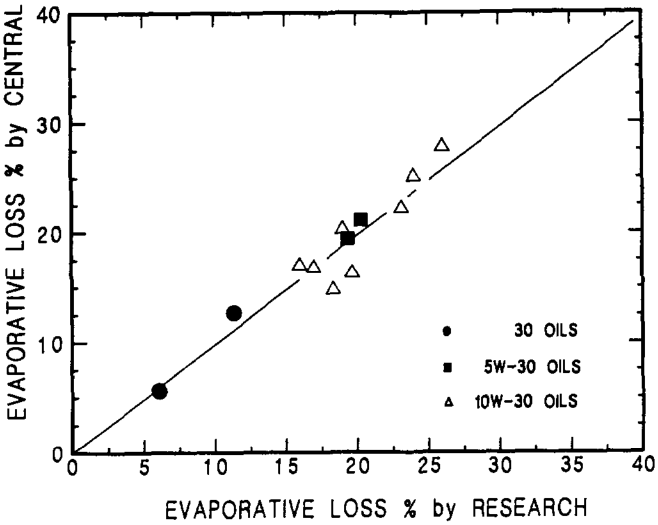

Fig. 5. Reproducibility of the TG method obtained in two Ford laboratories.

weight loss time were within 5% of the mean values for ca. 90% of the analysis. Regression analysis of this data gives a linear relationship with a correlation coefficient of 0.953 and a standard error of estimate of 0.02 for two SAE 30, two SAE 5W-30 and eight SAE 10W-30 oils.

The evaporative loss values determined by the present TG method for 48 engine oils of six different viscosity grades are compared with those obtained by the Noack method in Figs. 6 and 7. The correlation coefficients obtained by linear regression analyses of the six different viscosity grade oils are summarized in Table 3. The standard errors of estimate for SAE 30, 5W-30, 10W-30, 10W-40, 15W-40 and 20W-40 were 3.1, 2.4, 3.9, 6.1, 4.4 and 2.7%, respectively. As can be seen from Fig. 6, the smallest evaporative loss was shown by a group of nine SAE 30 oils. For the nine SAE 5W-30 oils, three oils met and another three oils failed to meet the 25% maximum evaporative loss requirement of Ford factory-fill engine oil specifications [11] by both methods. One of the remaining three 5W-30 oils barely met the requirement by the Noack method, but failed to meet it by the TG method. Finally, two 5W-30 oils were borderline. The results of the two methods are basically in agreement for eight out of the nine 5W-30 oils on the basis of the 25% maximum evaporative loss requirement. For the nine 10W-30 oils, three met and two failed to meet the 20% maximum evaporative loss requirement by both methods. Six out of the nine 10W-30 oils met the requirement by both methods. In Fig. 7, the evaporative loss values determined by the TG and the Noack methods for seven of each of the 10W-40, 15W-40 and 20W-40 oils are compared. The correlation between the two methods for 20W-40 oils is excellent, but the correlation for 10W-40 and 15W-40 oils is poor. A possible explanation for this discrepancy between the results of the two

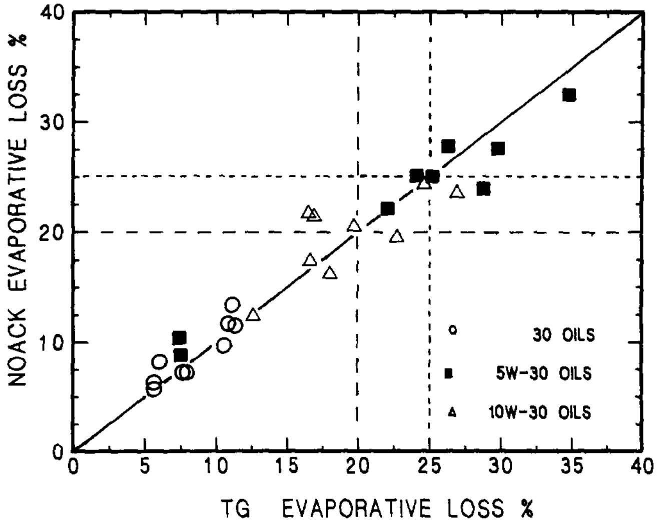

Fig. 6. Comparison of engine oil volatility determined by TG and Noack methods: SAE 30, 5W-30 and 10W-30.

methods is that poor reproducibility of the Noack method has contributed to the unsatisfactory correlations, as the Noack method values for the 48 engine oils tested were not determined at a single laboratory.

In conclusion, the proposed TG method is a simple and reproducible laboratory test method for determination of engine oil volatility characteris-

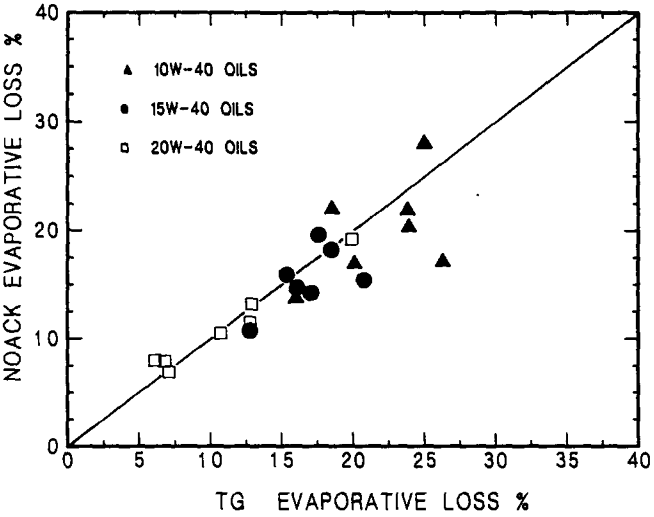

Fig. 7. Comparison of engine oil volatility determined by TG and Noack methods: SAE 10W-40, 15W-40 and 20W-40.

TABLE 3

Correlation between TG and Noack methods

SAE viscosity grade	n	Correlation coefficient [a]
30	9	0.9045
5W-30	9	0.9574
10W-30	9	0.5947
10W-40	7	0.4289
15W-40	7	0.5697
20W-40	7	0.9668

[a] Forced through zero.

tics from a weight loss/temperature profile, which could be used as an alternative to the Noack method.

ACKNOWLEDGEMENTS

We thank Kim D. Bruley of Central Laboratory Services, Car Product Development, for performing the comparative TG analyses of some of the engine oils; and Stefan Korcek of the Chemical Engineering Department, Research Staff, for coordinating this work.

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