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THERMOGRAVIMETRY OF FILTER-BORNE DIESEL PARTICULATES *

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ABSTRACT

A direct thermogravimetric (TG) method is described for determining the percentage of volatile components in filter-borne diesel particulates. The procedure gives a quick estimate of total solvent extractable hydrocarbon components. A silica gel fractionation/size exclusion chromatographic (SGF/SEC) procedure has also been developed to analyze further the solvent-extractable hydrocarbons of the particulates. The solvent extraction SGF/SEC procedure determines the contribution of lubricating oil and unburned fuel to particulates emitted from diesel engines. Results from this study indicate that the TG method yields a comparable measure of adsorbed hydrocarbons with those obtained by solvent extraction.

INTRODUCTION

As the extent of diesel engine particulate emissions is lowered to approach the 0.25 g/BHP-hr level required by the Federal 1991 heavy-duty diesel engine standards [1], the fraction of solvent-extractable hydrocarbon components tends to increase since many of the particle reduction techniques reduce the carbon or soot particles, which are basically formed due to pyrolysis of the unburned fuel in oxygen poor regions [2]. Therefore, it is important to know the degree of lubricating oil and fuel component contribution to the exhaust particulate emissions in determining engine modifications.

Analytical methods for determining the contribution of lubricating oil and unburned fuel to particulates emitted from diesel engines have been reported from several laboratories [3–6]. A silica gel fractionation/size

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exclusion chromatographic (SGF/SEC) procedure following ultrasonic solvent extraction has been developed recently in our laboratory [7] for the analysis of solvent-extractable diesel particulate fraction into unoxidized and oxidized components of oil and fuel to overcome the shortcomings with gas-chromatographic techniques [3,4,6] and the use of radioactive tracers [5].

The dual-gas thermogravimetric (TG) methods using inert and oxidative carrier gases have been applied to the compositional analysis of rubber formulations [8], diesel engine exhaust [9], used diesel engine oils [2], engine deposits [10] and various other substances containing carbonaceous materials [11].

The purpose of this work was to develop a direct TG analysis method for determining the amount of volatile components in filter-borne diesel particulates to evaluate the completeness of the ultrasonic solvent extraction in the diesel particulate analysis of solvent-extractable hydrocarbon fraction by the extraction/SGF/SEC procedure [7].

EXPERIMENTAL

Source of particulates

A 1.6 l, single-cylinder diesel engine running on an engine dynamometer was used to generate the particulate exhaust emissions. The steady-state conditions used were typical of engine speeds and loads encountered in the light-duty passenger vehicle (LDPV) and heavy-duty truck (HDT) cycles [7].

Fuel and engine oil

A No. 2-D diesel test fuel and commercial SAE 30 API SF oil (ash, 0.91 wt.%; zinc, 0.14 wt.%) were used for all particulate collection experiments.

Collection of filter-borne particulates

Fifteen diesel particulate samples were collected on polytetrafluoroethylene (PTFE) bonded glass-fiber filters (Pallflex TX40; diameter, 142 mm), using a simulated mini-dilution tunnel with a 10-to-1 dilution ratio and for a period of 10–20 min [7]. The engine was mechanically modified between runs to study the effect of piston-ring tightness on the exhaust particulate emissions. About 15% of each diesel particulate sample collected on a PTFE bonded glass-fiber filter, i.e. 1–10 mg of particulates on a 54° filter sector, was used for TG compositional analysis and the rest of a major filter sector (ca. 306°) was saved for the solvent-extractable hydrocarbon analysis described elsewhere [7].

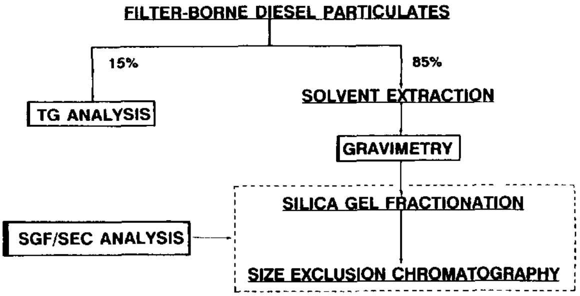

Fig. 1. An overall analytical scheme for filter-borne diesel particulates.

An overall analytical scheme for filter-borne diesel particulates is given in Fig. 1. The SGF/SEC analysis determines the amounts of solvent-extractable, oxidized and unoxidized hydrocarbon components originating from lubricating oil and unburned fuel, respectively [7].

Thermogravimetry

TG analysis was carried out using a Du Pont model 951 thermogravimetric analyzer in conjunction with a model 1090B thermal analyzer. TG measurements for preliminary characterization of reference samples were performed on sample sizes of 3–5 mg for standard reference “diesel particulate matter” (NBS/SRM-1650) and of 12–14 mg for oil and fuel with a heating rate of 10 °C min^{-1} to ca. 700 °C under a gas flow rate (argon or air) of 100 ml min^{-1}. For TG compositional analysis of the NBS standard, the analyses were performed under the TG conditions applied for the particulate sample filter analysis described below.

The particulate sample filters and corresponding unexposed circumferential filter edges (as reference blanks) were cut into ca. 4 × 10 mm rectangles for the analysis of filter-borne diesel particulates. A sample size of 15–25 mg (ca. ten rectangles) was heated from room temperature to 380 °C in argon at a rate of 20 °C min^{-1}, and then the purge gas was switched to air while heating to 700 °C at a rate of 20 °C min^{-1} under a gas flow rate of 100 ml min^{-1}.

Ultrasonic solvent extraction of NBS/SRM-1650

The standard reference particulate sample (ca. 50 mg) was ultrasonically extracted with methylene chloride in a plain-top test tube (Pyrex brand borosilicate glass, 13 × 100 mm). The detailed extraction procedure has been described elsewhere [7].

RESULTS AND DISCUSSION

TG analysis of reference materials

TG curves of the NBS/SRM-1650 diesel particulates, before and after ultrasonic solvent extraction, were obtained in both argon and air to see the effect of solvent extraction on thermal weight-loss behaviors. Since 20.9% of the reference diesel particulate sample fraction was extracted as the soluble organic fraction (SOF) with methylene chloride as determined by gravimetry [7], TG curves obtained for the post-extraction particulate residue under both air and argon were redrawn in Fig. 2 on the basis of 79.1% as their initial sample weights. A major portion of the solvent-extractable fraction appears to be volatile from 25 ° C to 380 ° C, i.e. ca 74.6% and 73.9% under air and argon atmospheres, respectively, based on the areas between two particulate TG curves of pre- and post-extraction. The percentage of solvent-extractable/volatile particulate components can be estimated by overlaying the original argon TG curve (100% as initial weight) of post-extraction residual particulates onto that of pre-extraction particulates at the temperature range of 400 ° C to 600 ° C as shown in Fig. 3, assuming that the particulate components heated at those temperatures in argon atmosphere are not affected by the solvent extraction. The solvent-extractable/TG volatile particulate components determined by this overlaying procedure is about 20%.

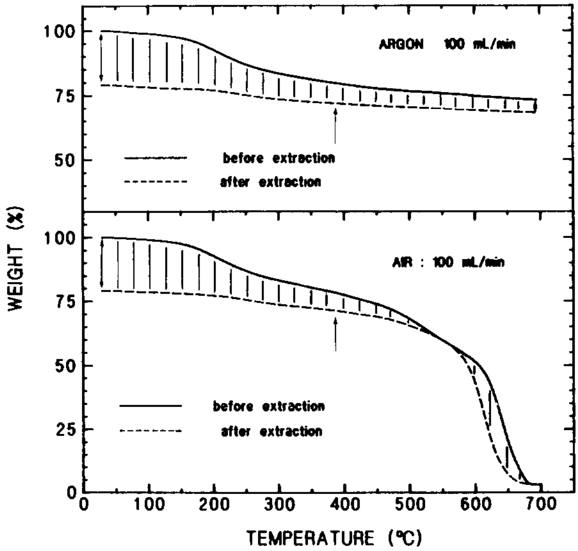

Fig. 2. Comparative TG curves of NBS/SRM-1650 diesel particulate matter before and after solvent extraction with methylene chloride.

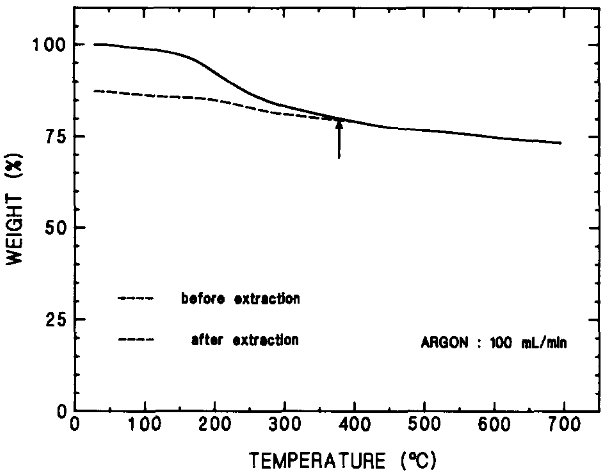

Fig. 3. TG estimation of solvent-extractable volatiles in the standard reference diesel particulates in argon.

The percentage of the solvent-extractable/volatile components is very similar to that of the solvent-extractable particulate components (20.9%), but these overlaid TG curves indicate that the TG volatile components differ somewhat from the solvent-extractable components in volatility and possibly in chemical composition; some volatile diesel particulate components (ca. 3%) are still left after the solvent extraction at around 200–300 °C.

A gradual weight loss of the reference diesel particulate sample beyond 380 °C under argon suggests the presence of hydrated and/or volatile inorganic compounds, and/or the thermolysis of oligomerized (i.e. semi-carbonized) particulate hydrocarbons [10]. This gradual-weight-loss phe-

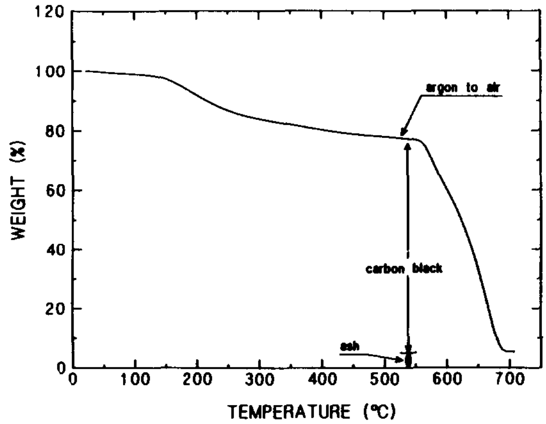

Fig. 4. Dual-gas TG compositional analysis of the standard reference diesel particulates for carbon black and ash.

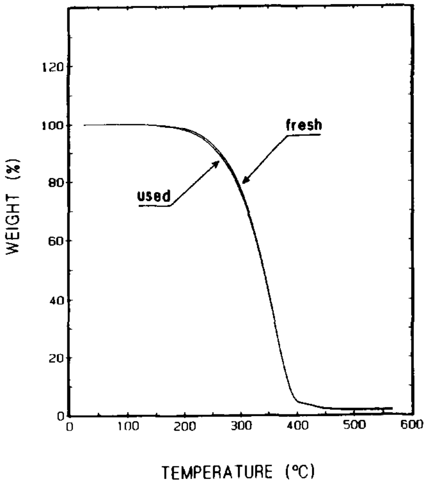

Fig. 5. TG of fresh and 400 h used SAE 30 oils under an argon atmosphere.

nomenon may lead to some error for TG determination of carbon black or soot and ash in diesel particulates.

The solvent-extractable fraction (20.9%) of the reference diesel particulate matter contains 73.4% of polar hydrocarbons (the sum of the acetone and methanol fractions by SGF/SEC analysis) [7]. The carbon black and ash contents of this reference particulate matter were 70.7% and 5.4%, respectively, determined by a dual-gas TG analysis method [10] and shown in Fig. 4.

TG examination of the fresh and used SAE 30 oils shown in Fig. 5 indicates a very minor change in thermal stability, as well as polydispersity determined by size exclusion chromatography [7]. The used diesel oil analyzed was drained at 400 h engine test operation, covering the 15 diesel particulate samplings.

TG analysis of filter-borne particulates

The 15 diesel particulate samples collected on PTFE bonded glass-fiber filter were less oxidized than the reference particulate matter. The polar fractions ranged from 3% to 50% of the total extractable hydrocarbons as determined by SGF/SEC analysis [7].

Under the present TG analysis conditions the blank PTFE bonded glass-fiber filter reaches a constant weight under argon at about 350 °C, maintains the constant weight under air to 380 °C, and reaches another constant weight at 600 °C. It has been reported that PTFE decomposes cleanly in a temperature range of 450–600 °C under a nitrogen atmosphere [12]. The glass-fiber content of the filters varies significantly from one batch to the next, i.e. ca. 83% to 89%, and even within a batch, i.e. 83.3% to 84.7%.

Since the weight losses of the probable solvent-extractable "volatiles" (room temperature to 380°C under argon) and carbon black (380–570°C under air) are calculated on the basis of the PTFE binder and glass-fiber contents of a set of reference and sample filters, it is mandatory to obtain both the reference and sample TG curves from the same filter. In this analysis a reference filter TG curve was obtained from the unexposed edge of each particulate sample filter. No TG detectable difference was observed in the glass-fiber content between the filter edge and middle portions of a PTFE bonded glass-fiber filter, subjecting relatively large filter sample sizes (ca. 4 cm^2) to TG analysis.

An assumption has been made for this TG method that the non-volatile inorganic ash content of diesel particulates studied here is very small, i.e. less than 1% of particulate masses on the basis of the engine oil ash content. Precision of the TG procedure is estimated to be $\pm 0.3\%$ ($n = 4$). This TG analysis procedure is presented graphically in Fig. 6.

Results of the percent "volatiles" obtained for the 15 particulate samples collected under both LDPV and HDT cycles are listed in Table 1 together

TABLE 1

Mass data for direct TG analysis of filter-borne diesel particulates collected on PTFE-bonded glass-fiber filter

Filter No.	Total particulates collected (mg) [a]	Particulates per unit filter surface (mg cm^{-2}) [b]	TG volatiles (%) [c]
1	23.3	0.18	82.7
2	13.1	0.10	36.9
3 [d]	64.0	0.50	68.1
4	17.0	0.13	81.4
5	15.0	0.12	35.0
6	19.8	0.15	75.2
7	8.4	0.07	63.5
8	12.4	0.10	42.7
9	11.5	0.09	49.4
10	8.3	0.06	37.8
11	7.6	0.06	35.2
12 [d]	29.1	0.23	24.2
13 [d]	27.4	0.21	18.1
14 [d]	6.6	0.05	33.5
15 [d]	7.8	0.06	23.0

[a] The effective surface area of each filter was ca. 128.7 cm^2.

[b] Approximately 4 cm^2 each of the particulate sample filters was used per TG analysis.

[c] The average of two measurements for both sample and reference filters.

[d] Collected under a heavy-duty truck cycle; the rest collected under a light-duty passenger vehicle cycle.

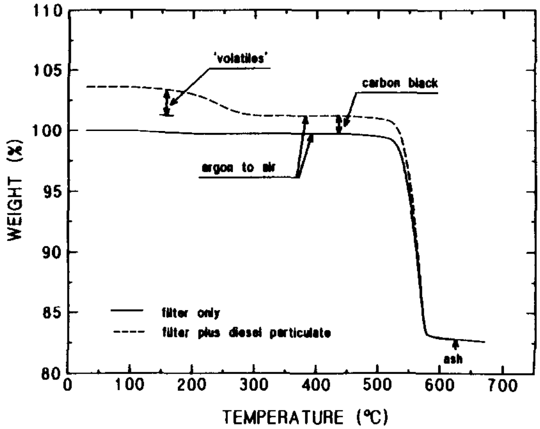

Fig. 6. Direct determination of volatile components in filter-borne diesel particulates by a dual-gas TG method.

with total particulate mass collected and particulate mass per unit filter area. In Fig. 7, the results of TG volatiles in the filter-borne diesel particulates are compared with the results of "solvent extractables" and solvent-extractable "hydrocarbons" as determined using gravimetry and SGF/SEC analysis, respectively [7]. Linear regression analyses yield correlation coefficients of 0.939 for TG volatiles versus gravimetric extractables and 0.808 for TG volatiles versus SGF/SEC hydrocarbons.

Results from this study indicate that the TG method yields a comparable measure of adsorbed hydrocarbons on filter-borne diesel particulates with those obtained by gravimetric and SGF/SEC analyses. The TG procedure in determining the fractions of volatile diesel particulate components corre-

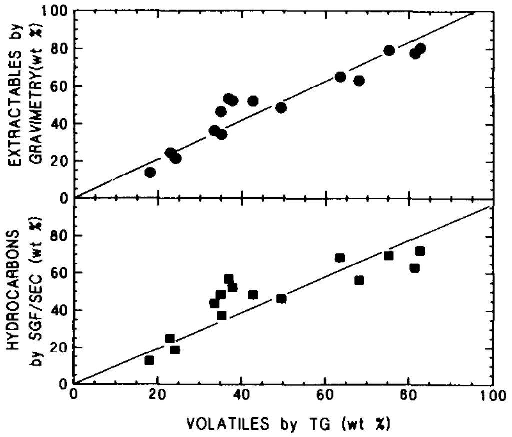

Fig. 7. Plots of TG volatiles vs. gravimetric extractables and SGF/SEC hydrocarbons in filter-borne diesel particulates.

lates strongly with both the gravimetry and SGF/SEC methods in determining those fractions of solvent extractables and solvent-extractable hydrocarbons, respectively.

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