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Thermogravimetry of filter-borne gasoline engine-out particulates [1]

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Abstract

A thermogravimetric (TGA) method has been developed to determine the percentage of unburned engine oil, carbon black, and inorganic residue for gasoline (petrol) engine-out particulates. In general, the range of recent gasoline engine-out particulate mass emissions is 5–20 mg per mile from the US EPA Urban Dynamometer Driving Schedule (UDDS) test procedure (11.1 miles per test). To make TGA measurements possible with such a low particulate mass emission level, each diluted exhaust particle sample (approx 1–3 mg) was collected on an ultra-thin polytetrafluoroethylene (PTFE) membrane filter (thickness, 25 μm; pore size, 2 μm) over the duration of four consecutive EPA UDDS test procedures, which was 0.3–0.5% of the total particulate mass emitted. This method can be very useful for providing a quick evaluation of unburned oil at the relatively low engine-out emission levels needed for improved catalyst durability.

INTRODUCTION

Interest in the adverse health effects of mobile source emissions of particulates has been focused on diesel particles. Thus, relatively few studies [1–4] have been reported for gasoline (petrol) particle emissions, which represents a gap in our knowledge of unregulated emissions.

Because of the US Clean Air Act Amendments of 1990 [5], which mandate the useful life requirements of passenger car emission control systems from 5 years or 50 000 miles to 10 years or 100 000 miles, knowledge of the unburned oil content of gasoline engine-out particulates is very important to the improvement of catalyst durability [6] and the reduction of overall hydrocarbon emission.

The development of a thermogravimetric (TGA) method for low levels of particle emissions requires the availability of a low tare-mass filter with a high aerosol retention [7]. This paper describes a rapid TGA analysis

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procedure that was developed to determine the percentage of unburned gasoline engine base-oil components, other evaporative substances, carbon black, and inorganic residue for each gasoline engine-out particle sample, taking advantage of ultra-thin polytetrafluoroethylene (PTFE) membrane filter characteristics.

MATERIALS AND METHODS

Test vehicle

The test vehicle was a 1990 Ford Taurus with a 3.0-l engine, 0.4 g per mile NO_x California calibration and a non-coated catalyst brick in place of the production catalyst. The odometer reading was 5856 miles at the start of the test. The fuel was a certification unleaded gasoline for exhaust and evaporative emission (EEE) testing [8].

Sample collection

All engine-out particle samples were collected from the test vehicle operated on a Ford Research dilution tube [9]. The particle emissions were collected at two probe sites on PTFE-bonded (approx. 27%) glass-fiber filters (Pallflex T60A20) and 25-μm ultra-thin PTFE-membrane filters (Gelman 2-μm Teflo). The filters were mounted in Swagelok modified 47-mm in-line SS holders (Gelman #2220), connected in series for primary and secondary collection. The inlet diameter of the sampling probes was 19 mm. The duration of the sample collection was four consecutive US EPA Urban Dynamometer Driving Schedule (UDDS) test procedures (total test miles driven, 44.61) [10], accumulated over four days. Total diluted exhaust-gas volumes of 6.99 m^3 and 5.15 m^3 at the sampling sites 1 and 2, respectively, were passed with the highest attainable sampling flow-rates through the filters out of a total dilution tube volume of 1485.54 m^3 at 20°C and 101.3 kPa. The air/exhaust dilution ratio was approximately 10:1 during sample collection.

Thermogravimetry

A particle sample (diluted particle mass, 1.53 mg) collected on the primary 2-μm Teflo PTFE-membrane filter with a diameter of 47 mm (including a 3-mm wide polymethylpentene support ring) and an effective PTFE-membrane weight of 4.29 mg was analyzed by a Du Pont 951 thermogravimetric analyzer. The blank or sample PTFE-membrane filter

without the support ring (approx. 5 mg) was heated from 25 to 400°C in argon at a rate of 20°C min^{-1}, and then the purge gas was switched to air while heating to 650°C at the same heating rate under a flow rate of 50 ml min^{-1}. In addition, SAE 5W-30 and 10W-30 engine oil samples were analyzed under the same TGA conditions applied for the particulate sample analysis [11].

The weight of the TGA inorganic residue was also monitored by an electronic microbalance (readability, 1 μg).

Solvent extraction

The particle sample (diluted particle mass, 2.28 mg) collected on the primary T60A20 PTFE-bonded glass-fiber filter with a diameter of 47 mm and a weight of 73.97 mg was ultrasonically extracted with dichloromethane (DCM) in a plain-top test tube (13 mm × 100 mm). The detailed extraction procedure has been described elsewhere [12]. The DCM extract (1.3 mg) was further separated into hexane-soluble (1.0 mg) and -insoluble (0.3 mg) fractions by hexane dissolution (4 × 2 ml) [13].

Capillary gas chromatography (GC)

The hexane-soluble fraction was quantitatively transferred into a 1.0-ml conical screw-top vial and redissolved into 500 μl of hexane for GC analysis of the engine oil components. GC/FID analysis was performed on an HP 5890 gas chromatograph with a J&W BD-5 fused silica capillary column (55 m × 0.32 mm i.d.; 0.25 μm film thickness). A 1.0-μl aliquot was introduced into the capillary column using a J&W Model I fixed-position on-column injector at ambient temperature [14]. The oven temperature was initially at 150°C for 2 min, heated to 270°C at the rate of 6°C min^{-1}, and then kept at 270°C for 38 min. The linear velocity of the hydrogen carrier gas was 30 cm s^{-1} at 150°C under a gauge pressure of 124 kPa.

RESULTS AND DISCUSSION

PTFE-bonded glass-fiber filters, e.g., Pallflex TX40 and T60A20, have been frequently utilized for the collection of engine particulate emissions [2, 3, 11]. The use of Gelman 2-μm Teflo PTFE-membrane filters has been reported recently for the collection of various urban aerosol emissions, including from automobiles, to determine aerosol mass, trace metals content, and ionic species [4].

To compare the filter performance of particle sample collection, both Pallflex T60A20 PTFE-bonded glass-fiber and Gelman 2-μm Teflo PTFE-membrane filters were used simultaneously for the collection of diluted particle emissions at two equivalent dilution sampling sites. Typical

TABLE 1

Typical filter characteristics

Filter ID	Diameter/ mm	Pore size/ μm	Air flow/ l min^{-1} cm^{-2} [a]	Total wt./ mg	PTFE wt./ mg
2-μm Teflo	47 [b]	2.0	53	≈140	≈5 [c]
1-μm Teflo	47 [b]	1.0	(39)	≈165	≈10 [d]
T60A20	47	0.2	(39)	≈75	≈20 [e]
TX40HI20	47	0.2	(34)	≈90	≈15 [e]

[a] At 520 mmHg (10 psi); the bracketed values are estimated by the maximum flow rate measurements of each filter type. [b] Including a 3-mm-wide polymethylpentene support ring. [c] Approximate weight of the ultra-thin 25-μm (1 mil) PTFE-membrane filter without the support ring. [d] Approximate weight of the thin 50-μm (2 mil) PTFE-membrane filter without the support ring. [e] Approximate weight of PTFE binders for glass fibers.

characteristics of the filters are summarized in Table 1. Also included in the table are an additional closely related filter of each type, i.e., membrane (Gelman 1-μm Teflo) and bonded glass-fibre (Pallflex TX40HI20), to show the differences in filter characteristics. The aerosol retention for the 2-μm Teflo PTFE-membrane filter is 99.99% by the monodisperse dioctyl phthalate smoke test (0.3 μm) tested at a flow rate of 32 l min^{-1} through 100 cm^2 media [7].

The flow rates through the primary and secondary filters of both Pallflex T60A20 (site 1) and Gelman 2-μm Teflo (site 2) were not adjusted with that of the dilution tube for isokinetic sampling. The sample pumping systems at the two sampling sites were operated at their maximum flow capacities to achieve maximum diluted particle-mass collection on both types of filters. The flow ratios of actual and isokinetic samplings were 1.21 and 0.89 at sites 1 and 2, respectively. The average particle-mass emission rate obtained from both sites was 11.06 mg per mile (or 6.87 mg per km). The changes in the sampling volumes over four consecutive UDDS test procedures at both collection sites for diluted vehicle emissions are given in Table 2, demonstrating the filtering characteristics of two tested filters. The estimated maximum particle mass collectable on the PTFE-membrane filter within a reasonable collection-time period would be approx. 3 mg per filter with an effective collection area of 10.2 cm^2 on the basis of decreases in the sampling volumes over the four test procedures. However, the primary filter of Gelman 2-μm Teflo collects more diluted particle mass (97%) than that of Pallflex T60A20 (91%).

TGA curves of the fresh factory-fill SAE 5W-30 and 10W-30 oils are shown in Fig. 1. The SAE 5W-30 oil was in use when the vehicle particulate emissions were collected. The weight-loss profiles of both oils are very similar and the weight losses of the major base-oil components occur in a

TABLE 2

Changes in sampling volumes over four consecutive US EPA UDDS test procedures at two sampling probe sites

No. of UDDS	Sampling volume/m^3 [a]	
	Pallflex T60A20 filter	Gelman 2-μm Teflo filter
1	1.77	1.68
2	1.80	1.42
3	1.75	1.11
4	1.67	0.94
Total	6.99	5.15

[a] Corrected at 20°C and 101.3 kPa.

temperature range of 200–350°C under the present TGA conditions. In general, fresh and normally used engine oils demonstrate a very minor change in thermal stability [11], and higher and cleaved molecules formed by high-temperature oxidation of base-oil hydrocarbons are unlikely to be a part of particulate constituents [12].

A TGA thermal curve of the diluted engine-out particulate mass collected on the primary 2-μm Teflo PTFE-membrane filter is shown in Fig. 2. Prior to the analysis, the 3-mm-wide polymeric support ring was carefully cut out with a stainless steel blade to increase the sample-to-media mass ratio, i.e., from 0.011 to 0.357. The percentage of the inorganic residue, i.e., ash, was determined directly from this thermal curve because the PTFE membrane does not contribute to the residue under the analysis conditions.

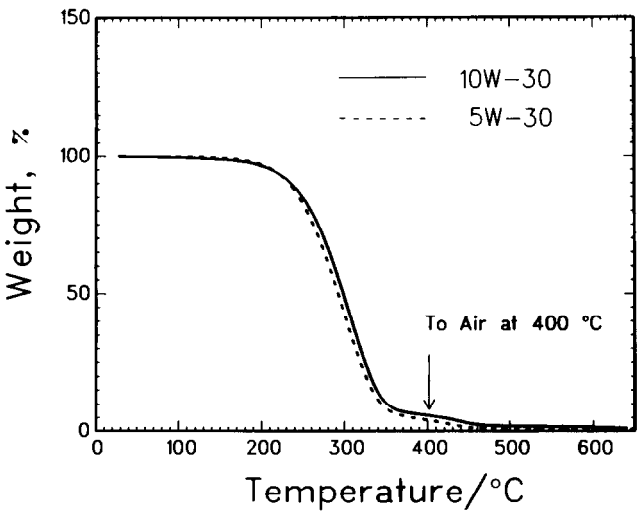

Fig. 1. TGA thermal curves of fresh factory-fill SAE 5W-30 and 10W-30 oils.

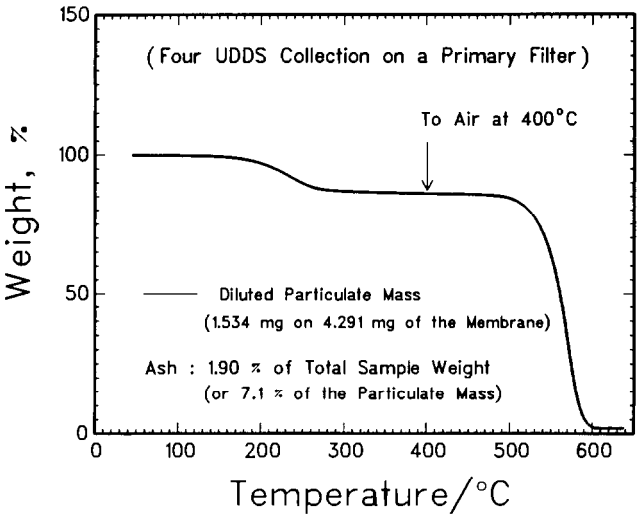

Fig. 2. TGA compositional analysis of engine-out particulates collected on an ultra-thin 25-μm PTFE-membrane filter with EEE-testing fuel.

Also, the percentage of the inorganic residue was determined by gravimetry using a microbalance, thus confirming the result of TGA residue analysis.

A residue-subtracted, membrane-mass-adjusted TGA curve of the sample PTFE membrane is redrawn in Fig. 3, together with a TGA curve of the blank PTFE membrane, to determine other compositional percentages of the gasoline engine-out particle components. As shown in Fig. 3, the blank PTFE membrane decomposes cleanly in a temperature range of

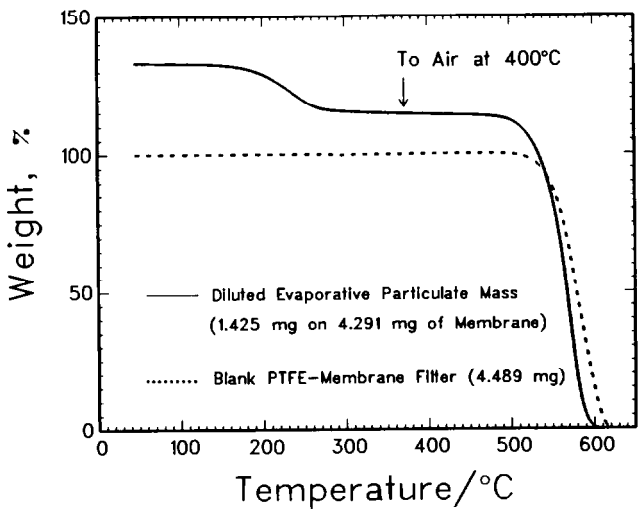

Fig. 3. A residue-subtracted, membrane-mass-adjusted TGA thermal curve of the sample PTFE-membrane filter together with that of the blank PTFE-membrane filter for compositional analysis.

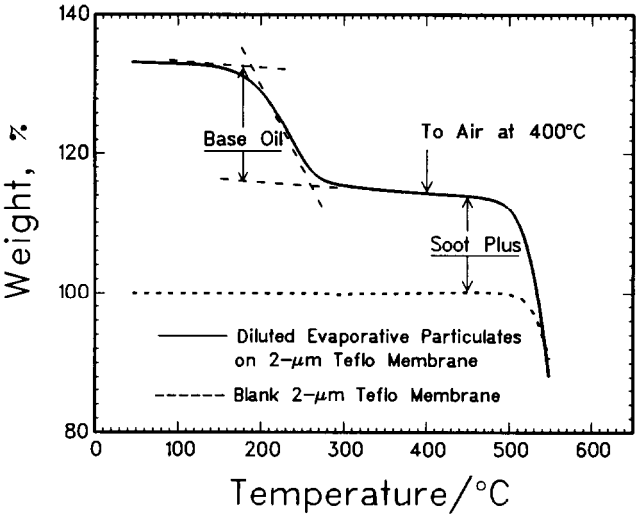

Fig. 4. Scale-expanded TGA thermal curves of particulate sample and blank PTFE-membrane filters for the compositional analysis of particulate evaporatives.

500–620°C under an air atmosphere. Figure 3 also shows that the presence of soot accelerates the rate of oxidative thermal degradation of PTFE membranes. In Fig. 4, the TGA thermal curves of the sample and blank PTFE membranes are expanded in a weight range of 80–140% for the compositional analysis of the particulate evaporatives, i.e., particulate mass minus ash. The weight loss (approx. 48%) occurring in the 200–270°C range under an argon atmosphere is attributed to the volatilization of largely unoxidized low and medium boiling base-oil hydrocarbons. The result of the TGA compositional analysis is summarized in Table 3.

About 56% of the engine-out particle mass collected on a primary

TABLE 3

TGA compositional analysis of the filter-borne gasoline engine-out particulates collected on a primary Gelman 2-μm Teflo PTFE-membrane filter

Component	Composition in wt.%
Non-evaporative	
Inorganic residue [a]	7.1
Evaporative	
Low-temp. evaporatives (40–190°C)	2.4
Base-oil components (190–270°C)	47.8
High-temp. evaporatives (270–450°C)	4.8
Soot plus [b]	38.3

[a] Also checked with gravimetry using an electronic microbalance. [b] Not likely, but it could contain additional materials, i.e., polymeric VI improvers, oxidizable and/or thermally degradable inorganic salts, etc.

PTFE-bonded glass-fiber filter was extracted with DCM. The amount of solvent extractables is in good agreement with the sum percentage of the particulate evaporatives minus soot (approx. 55%) obtained by TGA analysis of the particle mass collected on the primary PTFE-membrane filter. The GC separation of a hexane-soluble fraction (77% of the DCM extract) [13] showed the major presence of base-oil hydrocarbon components (C_{20}–C_{26}).

CONCLUSIONS

Methodologies have been developed for rapid determination of the unburned engine base-oil content of engine-out particulates emitted from gasoline internal combustion engines. This information is useful in development programs to reduce particle emissions and improve catalyst durability. The ultra-thin (25 μm) PTFE-membrane filter with a support ring effectively collects gasoline engine-out particulate emissions, even through there is a limitation in the amount of particle collection by membrane-pore clogging.

The proposed TGA method can be utilized in developing the low engine-oil consumption technology needed to meet future tailpipe emissions and durability regulations.

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