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## **Thermogravimetric analysis of carbon black and engine soot – towards a more robust oil analysis method**

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**Abstract**

This work examined the thermal behaviour of diesel engine produced soot and commercial carbon black using thermogravimetric analysis (TGA). It was found that during TGA analysis of the carbon matrices (at a temperature range commonly used for soot-in-oil content determination), a gradual mass loss occurred. This was attributed to pyrolysis effects and combustion processes occurring due to poor hydrodynamic design of some commercial thermobalances. This process resulted in a significant mass loss of the carbon during TGA. This finding may strongly effect soot-in-oil analysis conducted using current methods. Experiments were conducted using a range of soot-in-oil mixtures according to the widely used thermogravimetric standard method ASTM 5967-08 which showed a significant underestimation of the soot content in the oil as a result of carbon mass loss due to combustion and/or pyrolysis effects. An improved oil analysis method is proposed which provides a significantly increased accuracy of soot determination in lubricant oils.

**Key Words:** Oil Analysis, Lubricant, ASTM 5967, Soot in Oil

## 1. Introduction

Lubricant oils are highly sophisticated blends of hydrocarbons and additives and are used for a broad range of duties in diesel and petrol engines (see Table 1, [1]) as well as many other applications. These duties include lubrication of bearings, pistons, piston rings and the cylinder walls in order to prevent wear and corrosion as well as sealing gaps between pistons and cylinder walls to maintain combustion chamber pressure.

Lubricant oil is also the main means of cooling engine parts and therefore the oil is exposed to high thermal and mechanical stress. This stress can affect the oil properties due to combustion processes, evaporation of volatiles or thermal degradation and polymerization to form a heavier fraction [2]. These processes may lead to a higher viscosity of the oil and lead to pumping and lubrication problems, which can lead to excessive metal-to-metal contact and finally result in possible engine damage [3]. Incomplete combustion of diesel fuel results in the formation of soot, some of which will pass the pistons with blow-by gases or by adsorption into the thin oil film around the pistons whereby it can eventually enter into the sump and interact with the oil, influencing its properties unfavourably and inducing engine wear [4]. Although the soot induced wear mechanism is not fully understood, soot related lubricant thickening is believed to be a major cause of engine wear [3]. Therefore it is vital to perform regular oil analysis checks to ensure good oil quality and low soot content.

Several analytical techniques exist to observe the condition of engine oils [5], with Fourier Transform Infra Red (FTIR) analysis representing one of the most common

methods for determining soot in routine soot-in-oil analysis. However thermogravimetric analysis (TGA) is considered to be a more accurate technique for soot content determination [6]. TGA as a tool for compositional analysis was developed in the late 1980's [7] and since then has been used extensively for commercial diesel engine oil analysis. In 1996 the *American Society for Testing and Materials (ASTM)* developed a TGA procedure for soot-in-oil analysis, which has been standardized and is now part of the ASTM 5967-08 [8] diesel engine oil testing method and is recognized as a reference for oil testing worldwide.

Elemental analysis of typical diesel engine derived soot has shown that it is primarily composed of carbon with small traces of sulphur, oxygen, hydrogen and wear metals [1]. It is known that carbon can combust with even small amounts of oxygen [9] at temperatures well in the range of the ASTM 5967-08 method. Therefore it is vital to ensure that the gaseous atmosphere in the reaction chamber of the thermo balance is free of oxygen. Mullens [10] showed that commercially available thermo balances may retain or imbibe oxygen / air in the flow chamber due to poor hydrodynamic design. This means that after the chamber is opened to insert a sample, an extensive time period is required in order to completely evacuate all oxygen. Such remaining traces of oxygen can lead to partial combustion of the sample and therefore significantly influence the results of the TGA. A simple method to test the equipment for oxygen traces is the usage of Copper(II)-Oxalate [10].

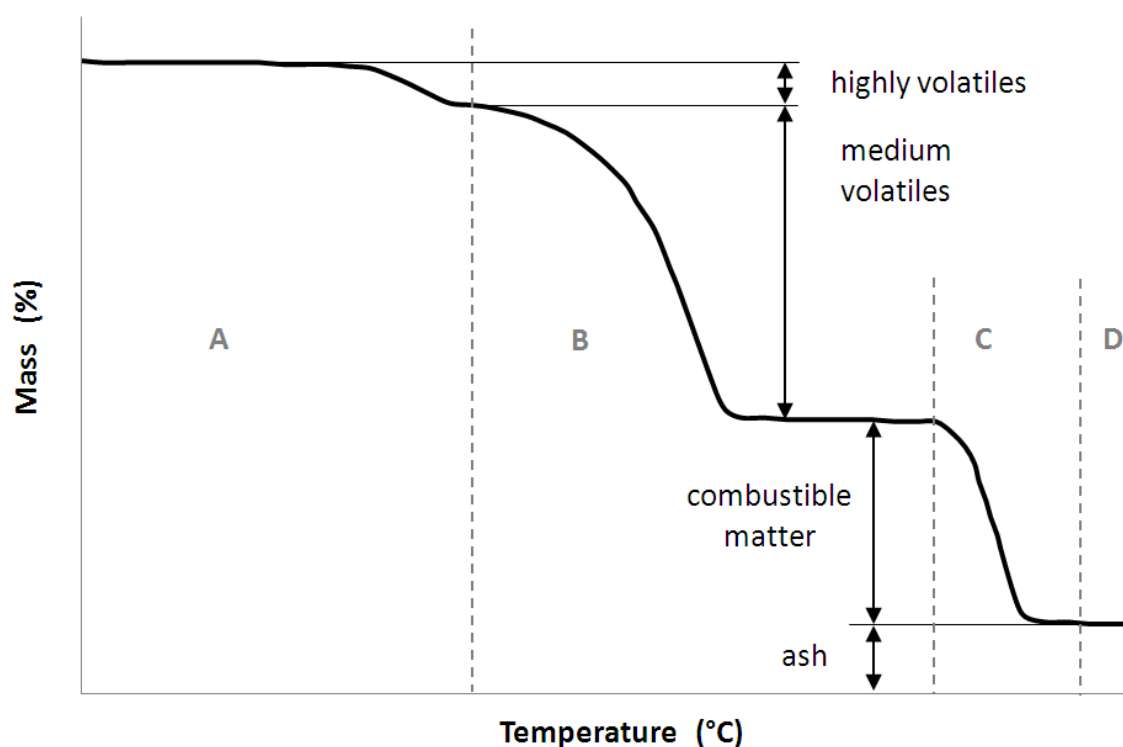
It is also known that coals with a similar composition as engine soot [11] show distinctive mass loss due to pyrolysis of the carbon within the temperature range of the ASTM 5967-08 oil analysis method. Pyrolysis of soots [12] from different origins -

including engine produced soot - showed a conversion of soot into several volatile poly aromatic hydrocarbons (PAH) under similar conditions to those at which oil analysis is conducted. In recently published findings [5, 13] reduction in sample mass could also be observed during TGA of engine oil under an inert atmosphere at temperatures far beyond the oil evaporation point, possibly leading to distorted results when determining soot content.

We therefore propose two possible mechanisms for mass loss of diesel soot during TGA: (a) pyrolysis and (b) poor TGA design / inadequate purging prior to the analysis. This work will study the TGA of soot, lubricant oils and mixtures of both matrices. Variations due to oil and soot composition will be examined and compared to the ASTM 5967-08 method for soot-in-oil analysis. This work will also examine the influence on the results if oxygen is not completely evacuated or the thermo balance is poorly designed.

### 1.1. Oil Analysis by TGA

Work completed by Larkin [7] showed that four mass loss stages occur during the TGA of used lubricating oils, due to the different thermal stability of the compounds present: loss of highly volatiles (A), loss of medium volatiles (B), loss due to combustible matter after switching to an oxidising atmosphere (C) and remaining mass due to ash (D).



**Fig. 1** Typical mass loss profile of a carbon containing sample during thermogravimetric analysis. The purge gas is switched from inert to oxidizing atmosphere to combust the soot content after the highly (A) and medium (B) volatiles have been evaporated so as to oxidize combustible matter (C). The remaining material is defined as ash (D) (after Larkin [7]).

Although there is no standardized definition of these components, it is generally agreed that they are defined as indicated in Fig. 1 and referred to as follows. The

highly volatile components are classified as those which result in a reduction of mass as measured by the TGA trace at less than 200°C (Section A), typically due to the presence of moisture or highly volatile compounds. Medium volatile components (Section B) are those responsible for the mass loss in the range from 200°C to 700°C. Oil and polymer degradation products are typical representatives of this group. Combustible matter (Section C) refers to non volatile but oxidisable material in its yet unoxidized form and is, according to the ASTM 5967-08 definition, termed as soot. Carbon is the main constituent of this material. Material which is neither volatile nor oxidisable under the given conditions is referred to as ash (Section D).

The evaporation of A and B usually occurs in an inert atmosphere, as it allows the highly and medium volatile fractions to evaporate without affecting the soot with which it is mixed. Once evaporation is complete, the reaction chamber atmosphere is switched to an oxidative gas (air or O<sub>2</sub>) to combust the soot. If the soot is combusted completely, the mass loss during this step is referred to as the soot content of the sample.

Usually, the quantity of highly volatile components is negligible in used diesel engine lubricant oil, since they have already been evaporated during engine operation. Therefore the first step (Section A in Fig. 1) was not visible for all lubricant oil samples used in this work. However, in cases where the oil was contaminated significantly with coolant or fuel, this stage would be present in the TGA.

TGA methods for diesel engine lubricant oil analysis can generally be divided into two steps. In the first step (Sections A and B, Fig. 1) oil is evaporated under inert gas



flow, commonly nitrogen or argon, with these steps being essentially completed by 525°C [5]. For the combustion step (Section C), an oxidizing purge gas (dry air or oxygen) is used to combust the carbon-containing components of the sample. The remaining ash is composed of traces of wear metals, non reactive oil additives or crusted matter which has contaminated the oil (for example dust).

## 1.2. The ASTM 5967-08 Standard Method

The ASTM 5967-08 method stipulates a heating program which reaches 750°C as shown in Fig. 2 and listed below:

### Purge gas: nitrogen

Step I: Isothermal at 50°C for 1 minute

Step II: Heat to 550°C at 100°C /min

Step III: Isothermal at 550°C for 1 min

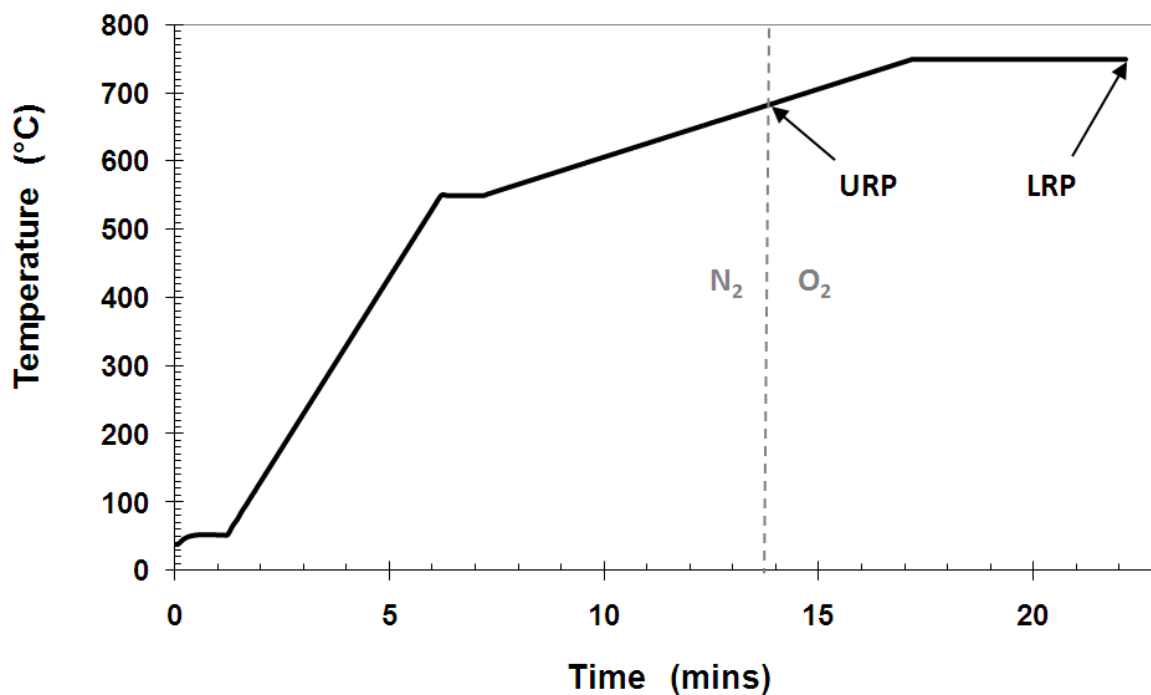
Step IV: Heat to 650°C at 20°C /min

### **(Upper Reference Point URP)**

### Purge gas: oxygen

Step V: Heat to 750°C at 20°C /min

### **(Lower Reference Point LRP)**



**Fig. 2** Temperature profile as proposed by the ASTM 5967-08 standard method showing the upper (URP) and lower (LRP) reference points. Reaction chamber purge gas changes from nitrogen to oxygen at around 13mins 40secs.

The program is considered to be complete once the weight of the residue remains unchanged for 5 minutes. The soot content is defined as the difference in mass between the purge gas switching point (Upper Reference Point, URP) and the Lower Reference Point (LRP), at which mass remains unchanged. The mass at the LRP is calculated as the ash content.

## 2. Experimental apparatus and methods

### 2.1. Soot and oil characterization

Two soot / carbon samples were used in this study. Soot A was collected from the exhaust pipe section immediately after the turbocharger of a medium duty direct injection turbo diesel engine (ISUZU 4BDIT, Japan). Soot B was a commercially produced carbon black (Printex U, Degussa Pty Ltd, Germany). Printex U has been used in several previous studies [14-16] and has been considered to be a suitable substitute for diesel soot since its thermal behaviour and particle size distribution are well characterised. The diesel soot was collected with a plastic spatula to reduce metal particle contamination and stored in a sealed plastic container without further treatment. The compositional analysis of the soot used is showed in Table 1 and was conducted using a Thermo Finnigan EA 1112 Series Flash Elemental Analyser (Finnigan, Switzerland).

**Table 1** Compositional analysis of the soots used in this work.

	<b>Soot A</b>	<b>Soot B</b>
	<b>Diesel Soot</b>	<b>Printex U</b>
<b>C (wt%)</b>	76.25	91.43
<b>N (wt%)</b>	0.44	0.09
<b>H (wt%)</b>	0.37	0.19
<b>S (wt%)</b>	<0.05	<0.05
<b>O (wt%)</b>	22.92	8.28

Two engine oils were used for this study, Castrol RX Super (Castrol Ltd., UK) and Penrite HPR50 (Penrite, Australia), as they were considered to represent a typical diesel engine oil and an oil at the upper limit of viscosity which could be used. The specifications of the oils are shown in Table 2.

**Table 2** Characterization of the engine lubrication oils used in this work (as given by the manufacturers).

	<b>Castrol RX Super</b>	<b>Penrite HPR50</b>
SAE Grade	15W-40	40W-70
API Grade	CI-4/SL	SL
Kinematic Viscosity @ 40°C	114 cSt	289 cSt
Kinematic Viscosity @ 100°C	15.2 cSt	30.1 cSt
Flash Point	230°C	230°C
Sulfated Ash	1.20%	0.88%
Density	0.875* kg/L	0.873* kg/L

\*Measured by the author as not available from manufacturer

Mixtures of unused (i.e. as provided by the manufacturer) engine oil and soot were produced using a balance accurate to  $\pm 0.05$ mg (OHAUS AS120, New Jersey, USA). Soot and oil were weighed and prepared as described in section 2.2.

## 2.2. ASTM 5967-08 Sample Preparation

Before conducting the analysis, the oil sample was prepared according to ASTM 5967-8. The sample was first stirred with a spatula to mix the particulate material

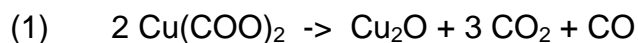
with the oil and then shaken upright and inverted until the oil was of homogenous appearance and drained uniformly from a spatula. The sample mass used for the experiments was 20mg, as suggested.

### **2.3. Thermogravimetric Analysis**

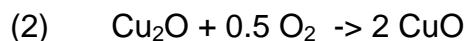
In order to exclude instrument specific variations from the results, four different TGA instruments were used. The majority of the experiments were conducted using a TA SDT Q600 instrument which also possessed DSC (Differential Scanning Calorimetry) capability (TA Instruments, Delaware, USA) using aluminium oxide crucibles. The reaction chamber was purged with nitrogen (BOC, Australia) or dry air (BOC, Australia) with a flow rate of 100ml/min. Purge gases were of a minimum of 99.99% purity. This TGA instrument's effluent gas was monitored using a Pfeiffer ThermoStar TM mass spectrometer (Pfeiffer Vacuum GmbH, Asslar, Germany) via a fused silica capillary column inserted into the effluent gas stream. For comparison, selected measurements were repeated on a TA TGA Q5000 (TA Instruments, Delaware, USA), a NETZSCH STG 209F3 (Netzsch GmbH, Germany) and a NETZSCH STA 409 PC/PG (Netzsch GmbH, Germany) device. All TGA instruments were maintained and calibrated regularly, either by the manufacturer or an experienced service company.

#### 2.4. Copper-(II)-Oxalate as an indicator for oxygen in the TGA

It has been shown [10] that copper oxalate is a highly sensitive indicator for oxygen presence in the TGA. Copper oxalate decomposes into copper-(I)-oxide at approximately 300°C according to (1) with a theoretical mass of 41.9% remaining.



If oxygen is present the copper-(I)-oxide can be further combusted into copper-(II)-oxide between 300°C and 600°C according to (2). This reaction results in a mass gain. Given that 100% copper-(I)-oxide was formed during the decomposition step, the mass gain is 11.4% of the initial mass.



In this work copper-(II)-oxalate hemihydrate (STREM Chemicals, Newburyport, USA) was used for the indication of oxygen presence in the TGA.

### **3. Results and discussion**

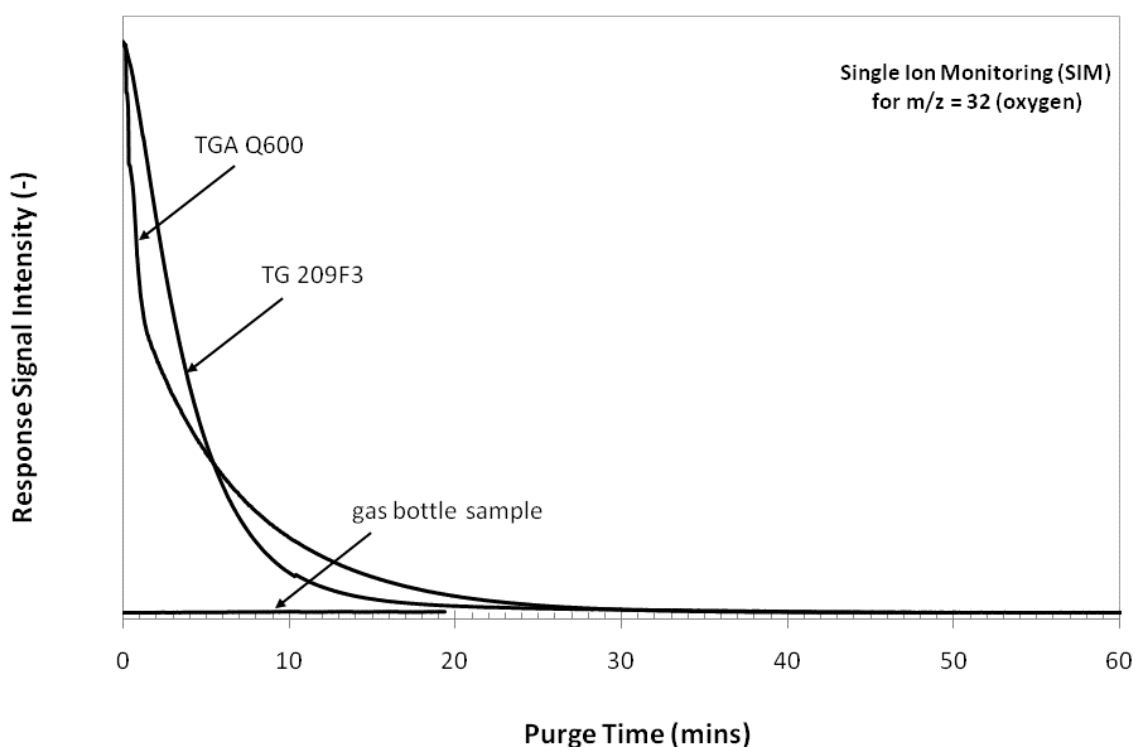
#### **3.1. Oxygen presence in the TGA instruments**

##### **3.1.1. Pre-Purging**

As shown in [10] the geometry of the furnace chamber and the position of the gas inlet is crucial for the expulsion of oxygen prior to a TGA. It is inevitable that oxygen is in the chamber due to the fact that the furnace has to be opened to put the sample in place. To determine the purging time required for the current experiments (sufficient to expel the oxygen in the furnace chamber), the chamber was purged with nitrogen at the same flow rate as used during the experiments (100ml/min for the TA SDT Q600 and 20ml/min for the TG 209F3) and the exhaust gas stream was monitored using mass spectrometry (MS) in the selected ion monitoring mode (SIM,  $m/z = 32$ ) (Fig. 3). A reference nitrogen sample was also taken directly from the cylinder at the same flow rate. As shown in Fig. 3, the oxygen concentration after the commencement of purging decreased rapidly for both instruments, reaching a constant value after approximately 40 minutes for the TA SDT Q600 and 30 minutes for the TG 209F3. Although both instruments have major differences in furnace chamber size and different flow rate this experiment shows that more than 30 minutes is required for the oxygen concentration in both instruments to reduce to a constant limit - which is believed to be the detection limit of the MS device. The final concentration was identical to the oxygen concentration obtained by a direct sample taken from the gas cylinder, and could be considered as less than 10 ppm as given by the manufacturer's gas specifications. All experiments in this work therefore

underwent 60 minutes purging at room temperature or instrument default temperature prior to the analysis if not otherwise stated.

The ASTM 5967-08 method suggests a short purging time of 1 minute which, according to Fig. 3, implies more than 50% of the initial amount of oxygen remaining in the chamber for the TA Q600 SDT instrument used in this study. For the TG S209F3 instrument, the percentage was even higher (88%).

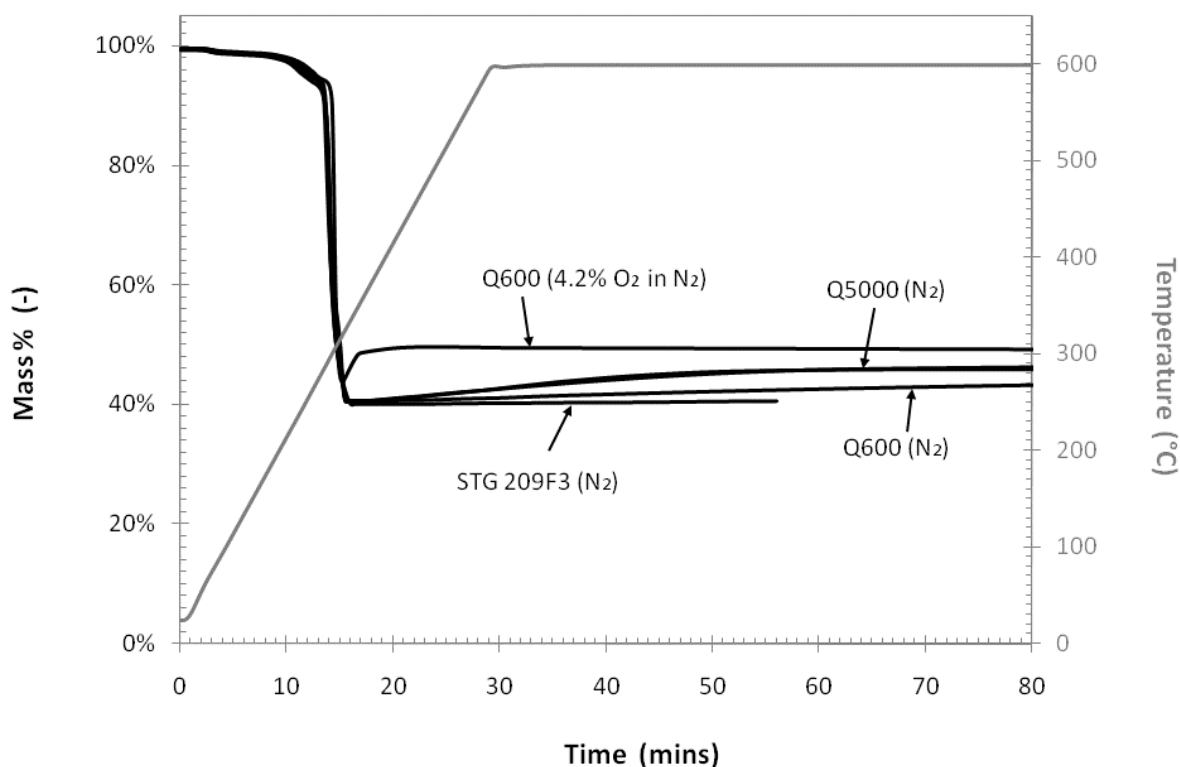


**Fig. 3** MS signal in SIM mode for  $m/z=32$  (oxygen) for the TGA Q600 and the TG 209F3 instrument exhaust during a preliminary experiment to determine the necessary pre-purge time of the furnace chamber with  $N_2$  at a flow rate of 100ml/min and 25ml/min respectively. The third curve shows a reference sample taken directly from the  $N_2$  cylinder.



### 3.1.2. Copper-(II)-Oxalate Hemihydrate Test

As small traces of oxygen can significantly influence the results obtained during TGA of carbon containing samples [10], it is vital to ensure that the atmosphere in the furnace chamber is inert. Therefore, a preliminary test was conducted using copper-(II)-oxalate hemihydrates in an inert N<sub>2</sub> atmosphere. Prior to the test the furnace chamber was purged with nitrogen for 60 minutes to expel oxygen remaining after sample insertion (not shown). During purging the signal was monitored by MS in SIM mode and did not show any signal above background indicating oxygen was not present after purging. After the sample was heated up to 600°C at a heating rate of 20°C/min it was held isothermal for 50 minutes (Fig. 4). The test was conducted with three instruments (TA SDT Q600, TA TGA Q5000, Netzsch STG 209F3) as shown in Fig. 4.



**Fig. 4** Decomposition and mass gain of copper-(II)-oxalate in three different TGA instruments (TA SDT Q600, TA TGA Q5000, Netzsch STG 209F3) during the heating process under inert nitrogen atmosphere as an indicator for oxygen presence in the furnace chamber. As comparison the mass loss of the same experiment in a mixture of 4.2% oxygen in nitrogen is added.

All TGA instruments showed a significant mass drop at approximately 300°C as expected due to decomposition of the copper oxalate into copper-(I)-oxide. The remaining mass of 41% is nearly identical with the value found in literature [10]. Beyond 300°C both TA instruments showed a steady mass gain which indicates the presence of oxygen in the chamber and the oxidation process from copper-(I)-oxide to copper-(II)-oxide. The Netzsch instrument however showed no significant mass gain after the copper oxalate decomposed which suggests that no/negligible oxygen was present in the chamber. Additionally a further leak test was conducted in which

Helium was sprayed around the instrument. Monitoring the exhaust gas allowed the detection of Helium which would be imbibed via leaks in the apparatus. Since no traces of Helium were observed in the exhaust gas the instrument was considered to be leak free.

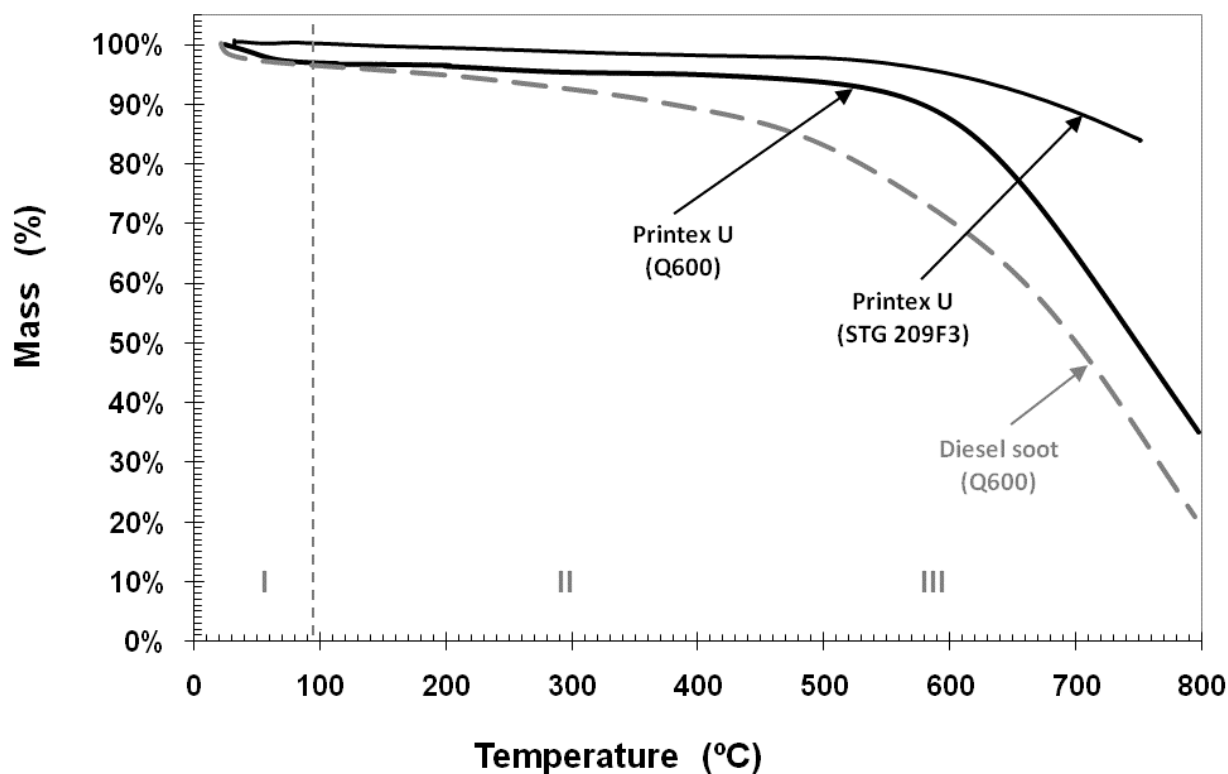
The results shown were gathered immediately after the instruments were serviced. Tests with different sample sizes (23mg and 9mg) showed nearly identical results, thus sample size effects could be excluded. As can be seen in Fig. 4 reproducibility was outstanding. One test was kept isothermal for 120 minutes (instead of 50 minutes as shown in Fig. 4) with no further mass gain being observed after approximately 90 minutes. The remaining mass was 44.5% of the initial sample mass. Conducting the same test in a nitrogen mixture containing 4.2% oxygen revealed a residual mass of 51% compared to 52.5% in literature [10].

This experiment shows that even after 60 minutes pre-purging of the furnace chamber trace levels of oxygen can still be found in the two TA instruments which can react with the sample. Since both instruments have recently been serviced and tested / calibrated, these findings suggest, that it is likely that traces of oxygen remain in the furnace chamber after the experiments commenced due to TGA geometry, which can significantly affect the results of soot-in-oil analysis.

### **3.2. Impact of traces of oxygen on the TGA of soot**

As Printex U has been proven previously [14, 15] to be a suitable surrogate for engine-derived diesel soot, it was used for all preliminary experiments. Diesel

engine-derived soot was used for later experiments to validate the results found using Printex U. To closely examine the thermal characteristics of both Printex U and the diesel soot sample used, a 7 mg sample of each was analysed using the TGA TA Q600 and the STG 209F3 with a low heating rate of 1°C/min from ambient temperature up to 750°C (800°C respectively) in a nitrogen atmosphere after 60 minutes of pre-purging with nitrogen. The TGA trace obtained is shown in Fig. 5. The Printex U sample used in the STG 209F3 instrument was dried prior to the experiment.



**Fig. 5** Mass loss during the TGA of Printex U and diesel soot in a nitrogen atmosphere. Three characteristic regions where mass loss occurs can be distinguished: I (highly volatiles evaporation), II (medium volatiles evaporation) and III (combustion and/or pyrolysis of the soot).

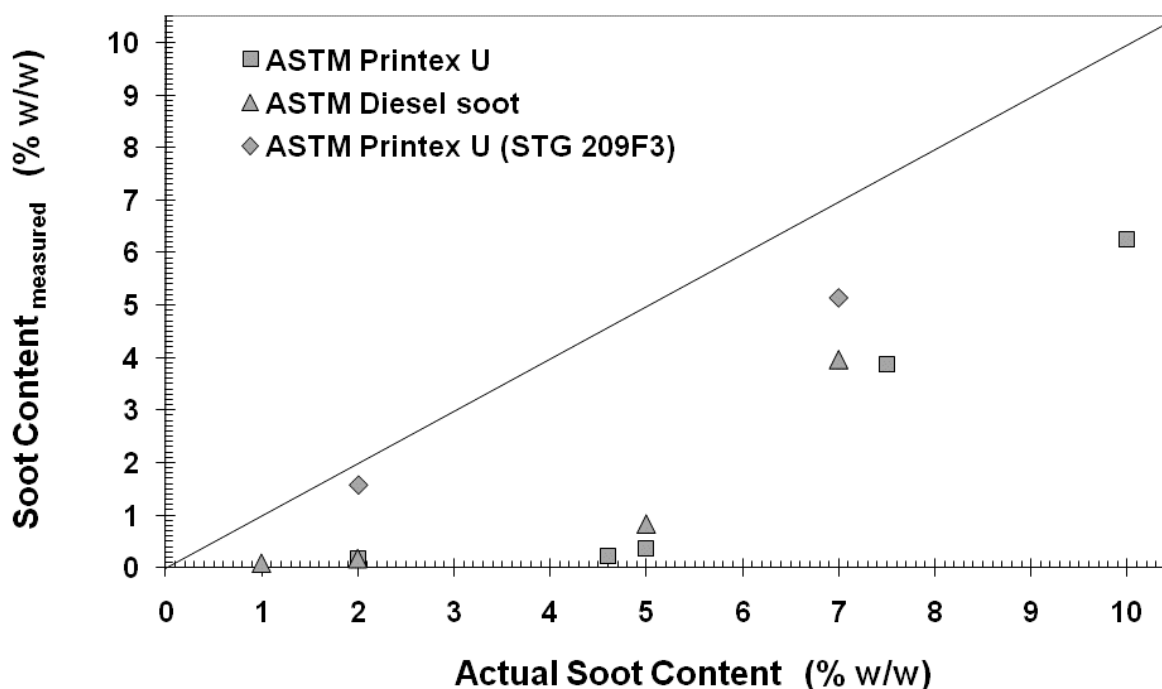
The initial isothermal step (Region I) after heating up to 110°C shows a mass loss of approximately 3.5% for the Q600 instrument. This loss is most likely due to evaporation of water present [17] for both Printex U and diesel soot. Beyond 110°C, Printex U shows a slow decay of the order of 1.5% until approximately 470°C (Region II) for both instruments. In contrast, the equivalent mass loss for soot is significantly higher, measured at 8% to 470°C. This mass loss for Printex U is most likely due to the volatilization of adsorbed hydrocarbon compounds [16]. The mass loss for diesel soot is greater due to the greater proportion of unburnt hydrocarbons. Beyond 450°C (Region III) an increasing rate of mass loss could be observed for all samples, leading to a near identical decay of approximately 25% (of the initial weight) per 100°C beyond 650°C for the Q600 instrument. The mass loss for the STG 209F3 was significantly lower (approximately 7% per 100°C). At 650°C, the mass loss for Printex U was 22% for the Q600, while for soot it was 38%. Further measurements showed that when a sample was maintained at 750°C for 240 min only a residue of approximately 1% of the initial mass remained. The residue was non combustible in oxygen at temperatures of up to 1300°C and was thus believed to be ash.

Hence, it appears that the mass loss observed in the Q600 instrument beyond 450°C was most likely attributable to combustion of carbon in the soot due to traces of oxygen. However, it is also known that the carbon matrix can decompose due to pyrolysis processes at this temperature [12] and Fig. 4 suggests that, in the case of the STG 209F3 instrument, where no significant oxygen content was left in the furnace chamber, it is believed that the mass loss for this instrument is mainly due to pyrolysis since impurities in the purge gas would not provide enough oxygen to

account for the magnitude of mass loss observed. Therefore the difference in residual mass between the STG 209/F3 and the other instruments is assumed to be due to a reason in combustion. Conclusively it can be said that both combustion and pyrolysis can occur at this temperature range, depending on the condition/geometry of the TGA instrument and thus the oxygen content in the reaction chamber either due to residual oxygen or due to leaks. It is however evident that mass loss through either mechanism could affect the determination of soot content in lubricant oils.

### **3.3. The TGA of engine oil**

To investigate the influence of the observed mass loss of soot during heating on the TGA oil analysis process, calibration mixtures of oil with differing soot content were prepared. Two different mixtures of Castrol RX Super oil containing 2%, 4.6%, 5%, 7.5% and 10% (w/w) Printex U or 1%, 2%, 5% and 7% Diesel soot respectively were analysed by TGA using the ASTM 5967-08 standard with 20mg samples. The instrument was not purged with nitrogen prior to the experiment to conform the suggested method. The Thermal Analyser used (TA Q600) was not designed to be operated with oxygen as stipulated in the ASTM method, therefore air was used as a replacement oxidizing gas. It is expected that this would have no influence on the quantity of soot oxidized but only the combustion rate. To ensure complete combustion of the soot present, a final weight reading for this step was only taken after the weight remained stable for 5 minutes. The results are shown in Fig. 6. Each data point was gathered from at least two tests with a standard deviation of less than 0.2% throughout.



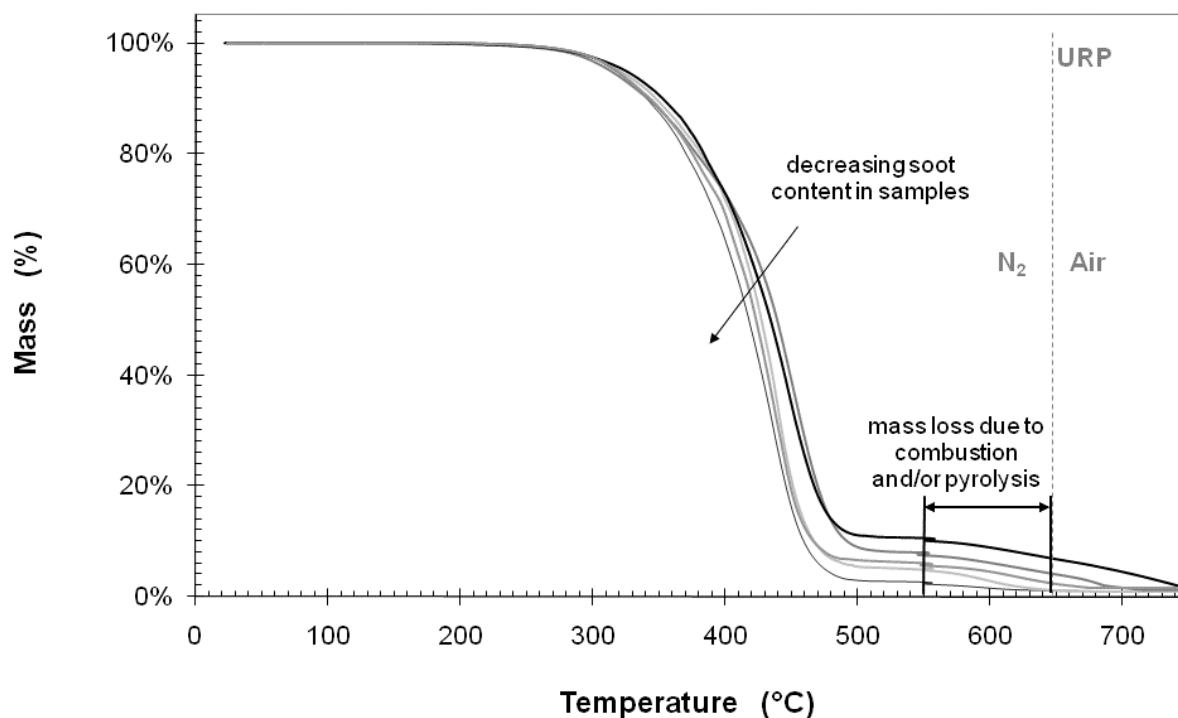
**Fig. 6** Soot content of prepared soot-oil mixtures (2%, 4.6%, 5%, 7%, 7.5% and 10% Printex U and 1%, 2%, 5% and 7% Diesel soot in Castrol RX Super 15W40) as determined by ASTM 5967-08.

All samples showed a significantly lower soot content as determined by ASTM 5967-08 compared to their actual values, with the determined soot contents for the 10% and 7.5% soot samples being 43% lower than their actual value in case of Printex U and 33% lower for Diesel soot. Additionally, the soot value determined for samples with a known value of 5% soot was underestimated by more than 92%. For the samples of Printex U or Diesel soot in Castrol RX Super 15W40 with a known soot content of <5%, no soot could be detected using this method. The results obtained using the STG 209F3 instrument showed slightly higher soot contents, however these values remained approximately 35% lower than the actual content.

The above results can be interpreted in terms of the soot combustion and mass loss observed in Fig. 5. For each ASTM 5967-08 analysis, our results suggest that a constant amount (in relative % weight terms) of soot is combusted. If the amount of soot in the sample is higher than the amount of soot combusted, the results will be merely shifted by the constant percentage of soot combusted towards lower values as can be seen in Fig. 6. This threshold value is the intersection of the regression line with the abscissa and could be calculated as approximately 4.6% for Printex U and the Diesel soot used. It should be noted that the threshold would be expected to vary from this value for differing soot/oil combinations. The results determined for the 1%, 2% and 4.6% mixtures lied away from this trend as the mass of soot remaining is below the detection limit of the technique.

According to Fig. 2, a significant portion of the ASTM 5967-08 method occurred in the temperature range between 550°C and 650°C. As has been demonstrated in this work, combustion of soot with minimal traces of oxygen has been found to occur even in well maintained TGA instruments and even after extensive pre-purging. As mentioned earlier, other effects like pyrolysis cannot be excluded at this temperature. Therefore it is very likely that most commercial TGA instruments using the ASTM 5967-08 method will underestimate the soot content of oil samples, since a portion of the soot has been already combusted or pyrolysed before the purge gas is switched to an oxidising atmosphere to combust the remaining soot. This is demonstrated in Fig. 7 which shows the mass loss during heating of different soot-oil samples using the ASTM 5976-08 method.





**Fig. 7** TGA of 2%, 4.6%, 5%, 7.5% and 10% soot-oil standard sample using the ASTM 5967-08 method. The mass at the Upper Reference Point (URP) is reduced due to prior loss by reactions of the soot. The anomaly at 550°C is caused by a temperature overshoot of the TGA device.

The mass loss due to combustion and/or pyrolysis of the soot in the temperature range between 550°C and 650°C is clearly visible. This mass loss results in a significantly lower mass remaining at 650°C, reducing the mass of soot present in the sample at the Upper Reference Point by approximately 4.6% for Printex U and 3.8% for soot. It is expected that the mass loss for other soot samples will be at a similar rate. For samples with a soot content less than 5% all soot was already decomposed before reaching the URP at 650°C.

The results obtained by the STG 209/F3 instrument show an average soot content of 5.2% for the 7% sample and 1.5% for the 2% sample and therefore lie above the

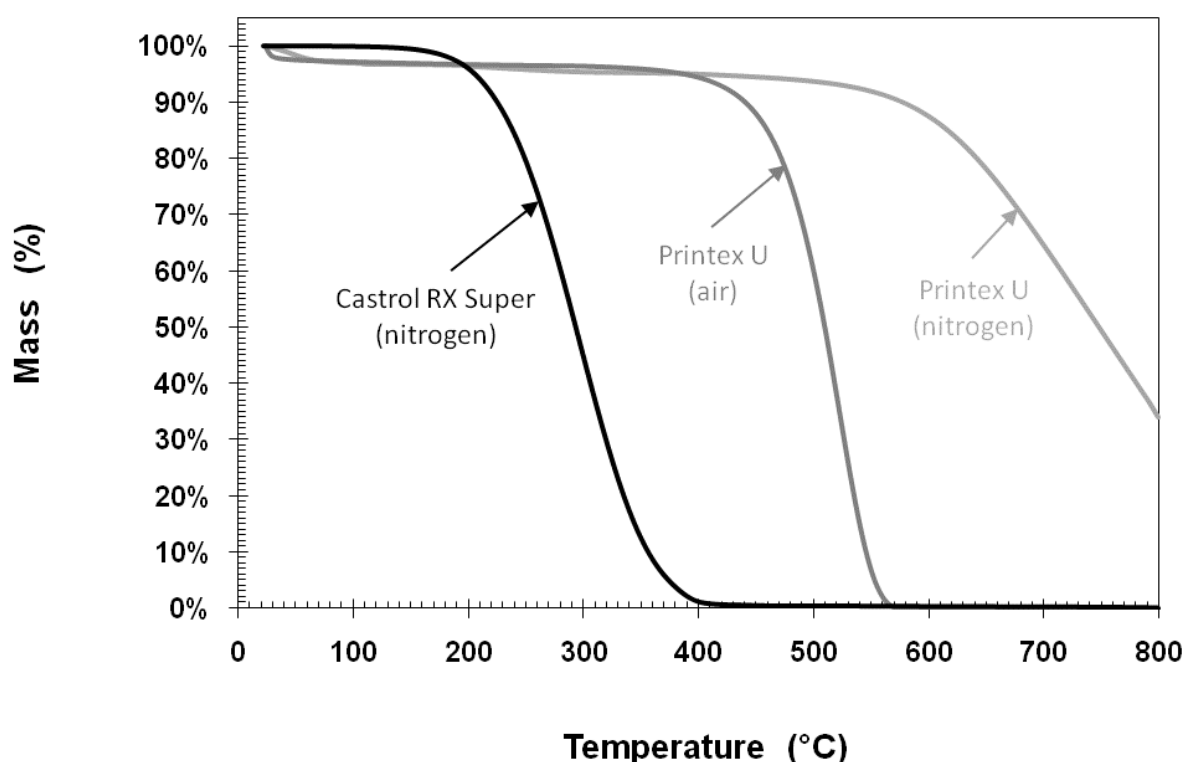
results obtained by the other two instruments. As was seen in Fig. 5, a significantly lower mass loss during the heating of the carbon sample was again observed for the STG 209/F3 (in comparison to the other two instruments) and is considered to be the loss due to pyrolysis only – hence it was expected that the soot mass loss was also lower during the analysis of a soot-in-oil mixture for the STG 209/F3 instrument and therefore the measured contents were closer to the actual content.

#### **3.4. Towards an improved TGA Oil Analysis method**

As has been shown, combustion and/or pyrolysis of soot is responsible for inaccuracy in soot determination when using the ASTM 5967-08 TGA method. Especially at temperatures beyond 500°C these effects become significant, leading to a much lower mass remaining at the Upper Reference Point. As an improvement to the method, it is therefore desirable to commence the determination of combustible matter as soon as possible after the removal of the medium volatiles. The selection of the URP at this point should reduce the amount of soot lost due to combustion and give a more accurate result.

However, care must be taken that the URP temperature is not selected too low, as it is essential for the accuracy of the analysis that all oil is evaporated by the time the Upper Reference Point is reached. Any remaining oil in the mixture at the URP would be included in the soot weight and shift the analytical result towards higher-than-actual values.

Another consideration which must be taken into account when choosing the minimum URP temperature is that that carbon combustion as completed in the second part of the oil analysis requires a certain temperature to overcome the activation energy for the process. Hence, to determine the combustion characteristics of Printex U, it was heated in a TGA from ambient to 650°C at 1° C/min in dry air. The results are shown in Fig. 8.



**Fig. 8** Mass loss of Printex U and clean engine oil (Castrol RX Super 15W40) in nitrogen and dry air in a TGA using a heating rate of 1°C/min.

After an initial mass loss in the region below 110°C due to evaporation of moisture and highly volatiles, a slight decrease of approximately 1.5% could be observed until 400°C. This decrease is due to evaporation of volatiles, as discussed previously and is independent from the purge gas (for comparison the mass loss of Printex U in

nitrogen is added to the graph). At approximately 400°C, combustion commences and proceeds with an increasing combustion rate towards higher temperatures, achieving a maximum at ≈500°C. The same peak temperature was also observed in other work [15]. At ≈580°C all soot had burnt off and combustion could be considered as being completed. According to these results a minimum combustion temperature between 430°C and 450°C would be ideal in order to provide a fast combustion rate and minimise analysis time.

Additionally, the evaporation curve of the Castrol RX Super diesel oil used in this work is also shown in Fig. 8. The experiment was conducted in a nitrogen atmosphere until all oil was evaporated at approximately 400°C as evident by its constant mass. In order to check for the presence of oxidisable material, which could affect soot analysis, the purge gas was switched to dry air. However, there was no further mass loss found beyond 410°C in air. Although the boiling point of lubricant oils differs depending on the operational conditions of the oil and its properties, other studies have observed evaporation temperatures of commonly used diesel engine oil in the same temperature range [5].

Combustion and/or pyrolysis of soot has been found to be moderate up to 500°C as can be seen in Fig. 8. Despite the initial mass loss due to evaporation of moisture, a mass loss of less than 2% was observed within this temperature range.

It is therefore evident that a temperature of 430°C for the URP would be ideal for this sample with an isothermal step included at this temperature to ensure that oil evaporation was complete. After switching the purge gas to dry air the sample is

heated up to 700°C to combust the soot contained in the sample. At this temperature, another isothermal step is provided to ensure that all soot has been combusted. Once no further mass loss can be observed, this step can be considered complete. The remaining sample mass is then classed as ash and therefore constitutes the Lower Reference Point for the calculation.

The analytical parameters for the improved oil analysis method are shown in Fig. 9 and detailed below:

Purge gas: nitrogen

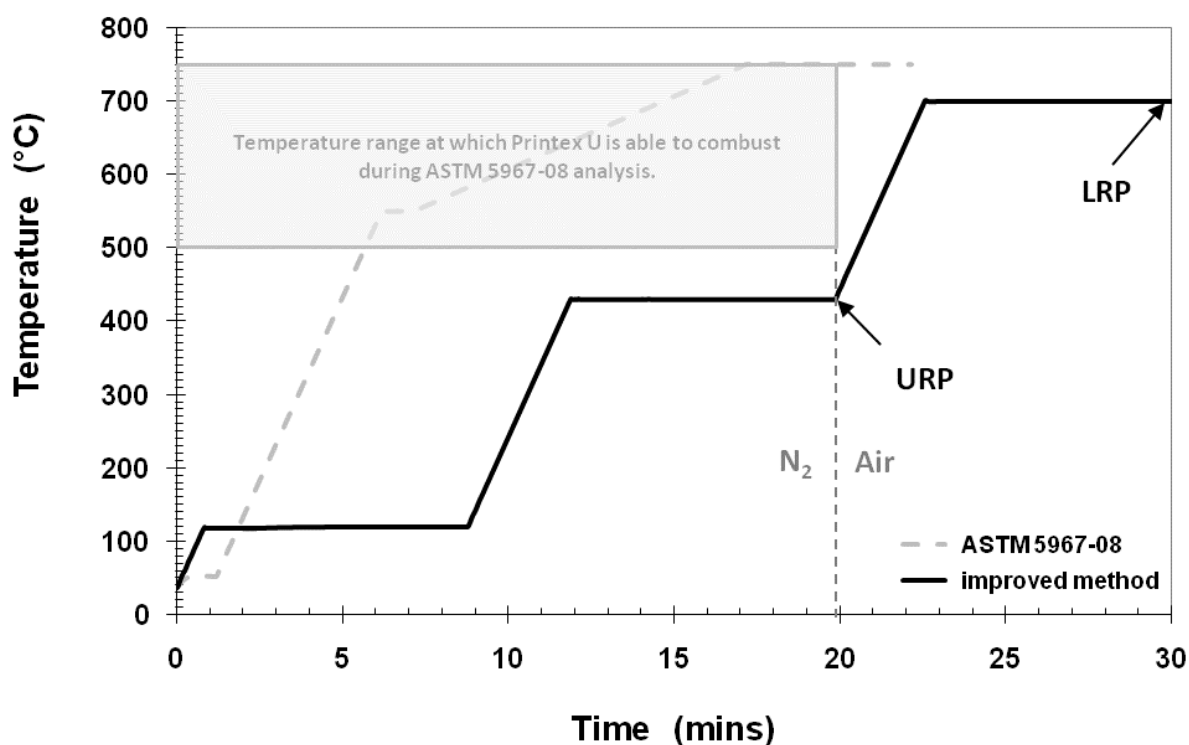
- Step I: Heat to 120°C at 100°C/min
- Step II: Isothermal for 8 min
- Step III : Heat to 430°C at 100°C/min
- Step IV: Isothermal for 8 min

**(Upper Reference Point URP)**

Purge gas: dry air

- Step V: Heat to 700°C at 100°C/min
- Step VI: Isothermal for 8 min (or until stable weight)

**(Lower Reference Point LRP)**



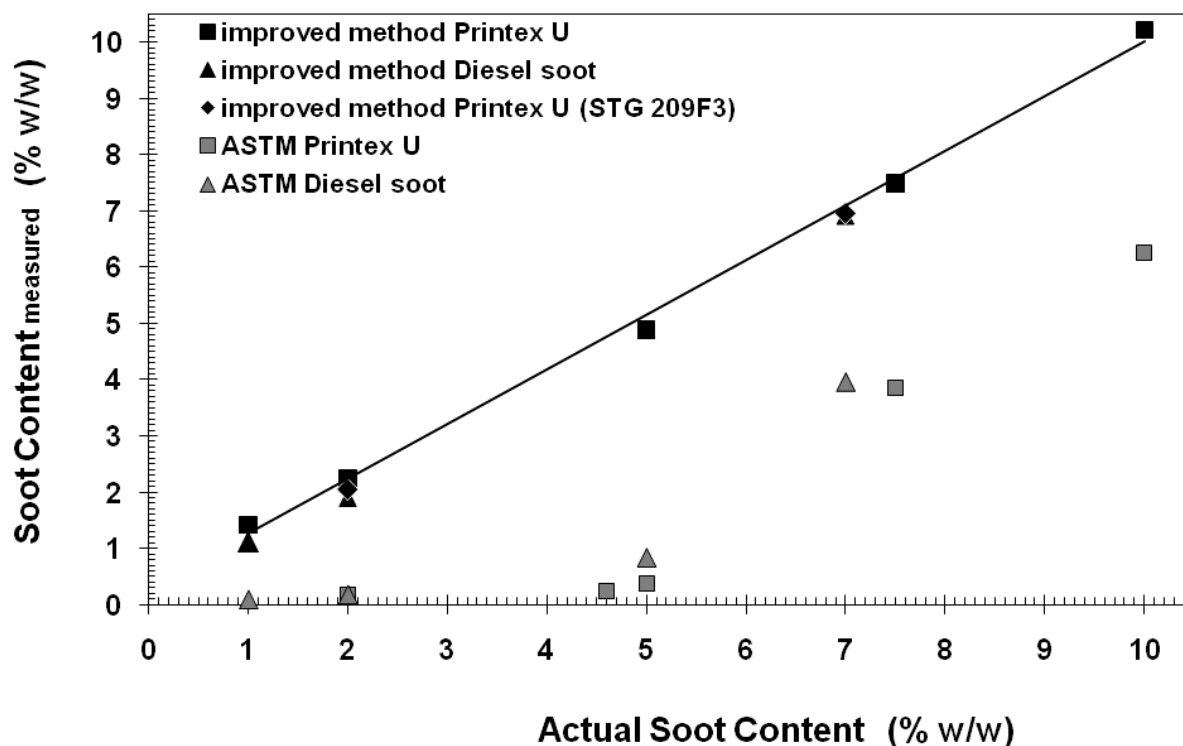
**Fig. 9** Improved temperature profile with the Upper (URP) and Lower (LRP) Reference Points shown. The soot oxidizing range (as previously discussed in this paper) with which the ASTM 5967-08 method conflicts is avoided with this improved method. Reaction chamber purge gas changes from nitrogen to air at around 19mins 55secs.

The initial isothermal step at 120°C is to purge the reaction chamber to reduce oxygen remains in the chamber and to evaporate moisture in the sample. It is, as pointed out earlier, advisable to purge the instrument with nitrogen to reduce the amount of oxygen left in the furnace chamber. The purging time depends significantly on the geometry of the chamber and the gas inlet position as shown before and is therefore instrument specific. In order to reduce the experiment time and keep conditions similar to ASTM 5967-08, an extended pre-purge step was relinquished for these experiment since this method was aimed to be less prone to

oxygen traces present during the analysis and therefore was suspected to be able to perform well even with significantly shorter purging times.

### **3.5. Comparison with the ASTM 5967-08 method**

The improved method was tested for accuracy by using a set of prepared soot-in-oil samples. Using Castrol RX Super 15W40 diesel engine oil and Printex U or Diesel soot, the following samples were made (w/w): 1%, 2%, 5%, 7.5% and 10% for Printex U mixtures and 1%, 2%, 5% and 7% for Diesel soot mixtures. Sample size, preparation, purge gases and instrument parameters were used as previously. The results are shown in Fig. 10. Each data point was gathered from at least two experiments. The standard deviation was less than 0.25% for all points.



**Fig. 10** Soot content of calibration soot-oil mixtures (1%, 2%, 5%, 7.5% and 10% Printex U and 1%, 2%, 5%, and 7% Diesel soot in Castrol RX Super 15W40) analysed using the improved method in comparison to the ASTM 5967-08 method.

The results gained with the improved method as shown in Fig 10 agree well with the actual values of the prepared standards, with determined values all being within 0.5% of the actual values. The linear fit (improved method) reveals a slope of near unity with a correlation coefficient ( $R^2$ ) of 0.998.

The duration of the isothermal steps was chosen at 8 minutes in order to provide a high resolution for the experimental work and the development of the method. However it would be possible to shorten the isothermal steps to 5 or less minutes for routine oil analysis use, which would ensure that this method requires an equivalent



analysis duration as the ASTM 5967-08 method. Measurements using a 2 minute isothermal step were conducted, with no loss in accuracy found. The high heating rate was chosen to further shorten analysis time, however to make this method applicable to a broad range of different TGA instruments which possibly experience problems with temperature control (overshooting) the heating rate can be reduced. Measurements with a heating rate of 50°C / min were conducted and were found not to influence the result. The results obtained by the STG 209/F3 instrument were very similar to those obtained by the other two TGA instruments. This strongly suggest that the impact of combustion, which is believed to account for the different results obtained by the STG 209/F3 and the other instruments using the ASTM 5967-08 method, is significantly reduced using the improved method.

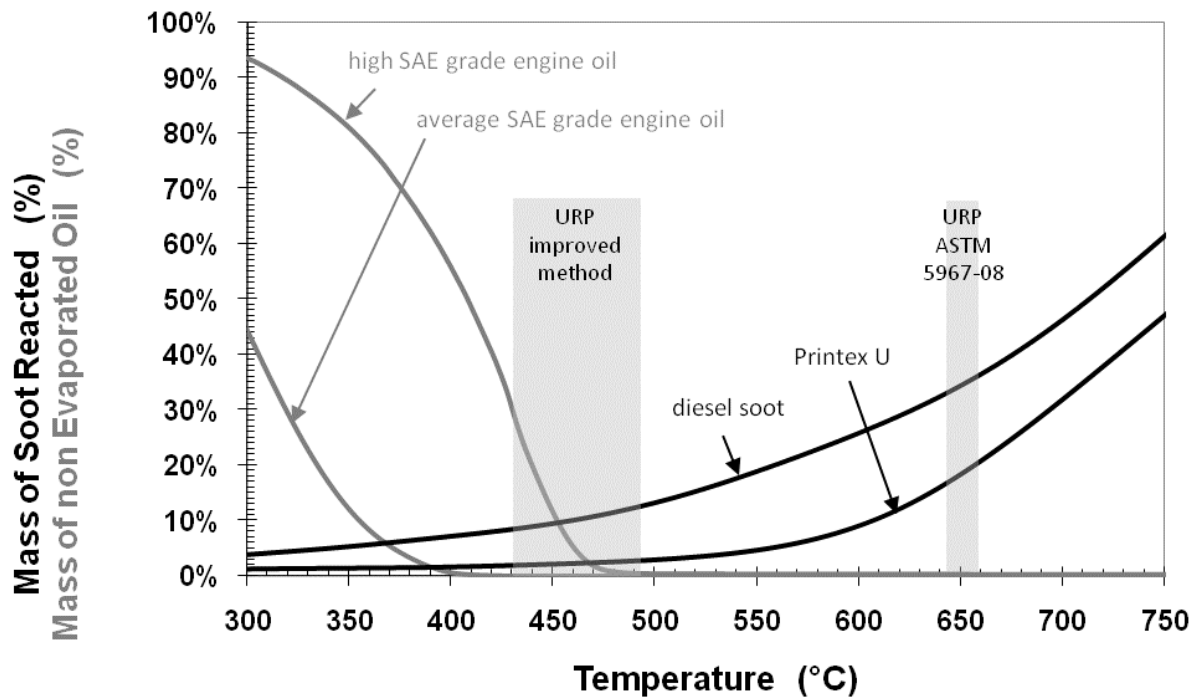
Furthermore, it was found that the duration of pre-purging the TGA instrument prior to the analysis did not affect the accuracy of the improved method. For the ASTM 5967-08 method however, the affect was found to be significant. This is due to a the fact, that once the critical reaction temperature is reached (approximately 500°C according to Fig. 8) the soot combustion rate is obviously higher if conducted in an atmosphere with a higher oxygen concentration as is the case when the furnace chamber is not pre-purged. As can be seen in Fig. 9 residence time above the critical temperature is higher for the ASTM 5967-08 method, which promotes mass loss due to soot combustion and/or pyrolysis and therefore faulty results.

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### 3.6. TGA of higher SAE graded oils

A commercial 15W40 oil, which is assumed to be representative of typical diesel lubricant oil for engines operation in tropical environments (and therefore of higher SAE grade and lower volatility than a typical engine oil for temperate or cold climate conditions), was used in this work. This oil, however, may not be as heavy as some fractions which can be found in-service in diesel vehicles due to polymerization, which could possibly occur at high temperatures. Since the final evaporation temperature is vital for soot content calculation (Upper Reference Point) in the improved oil analysis method, it is important to determine the effect of less volatile oils on the result. If the oil could not evaporate completely, the remaining oil will shift the Upper Reference Point to a higher value, leading to an overestimation of the soot content.

For this reason, the heaviest engine oil which is readily available commercially (Penrite HPR50, graded as SAE 40W70) was also tested. Although this is a petrol/gasoline engine oil and a higher SAE grade than commercial diesel oils, it should nevertheless be representative of the heaviest fractions found in used diesel oil. In-service diesel engine oil samples taken during a separate research project were also analysed by TGA as part of this work. The oils were obtained at various service intervals (5000 – 25000 km) from a range of direct injection and commonrail turbo diesel engines. It was found that even the oil with the highest mileage and therefore the highest grade of thermal degradation suspected evaporated completely below 450°C degrees. This suggests that for engine oils subjected to typical service conditions, the URP could be chosen below 450°C degrees and therefore still lies in the boundaries between the two oils used in the current experiment.



**Fig. 11** Proportion of non evaporated oil and reacted (combusted/pyrolysed) soot as a function of temperature. Different oils and soots have been used to span a representative range for each curve.

Fig. 11 shows the evaporation curve in nitrogen for higher SAE grade engine oil (Penrite HPR50) to mark the expected upper boundary of oil evaporation. Evaporation can be considered to be concluded at approximately 500°C for this oil. The area under the curve marks the range of possible evaporation curves of lighter engine oils with that of an average diesel engine oil (Castrol Super RX 15W40 as used in this work) also included. The shift towards higher temperatures for the higher SAE graded oil is clearly visible.

Furthermore, the soot loss due to combustion in nitrogen is also shown in this graph for the two soots. As already shown (Fig. 5) Printex U showed a lower mass loss

rate. The area between both curves symbolizes possible mass loss rate curves for common carbon blacks and soots.

Fig. 11 shows the difficulty of choosing the correct temperature for switching the purge gas. A compromise must be made, especially for higher SAE graded oils between complete oil evaporation and a reasonably low soot combustion/pyrolysis prior to gas change. The higher the temperature needed for complete oil evaporation, the more pronounced the issue of soot mass loss becomes, as can be seen in Fig. 11. It may be desirable to choose an individual temperature for the URP for each oil, which can be found by conducting a TG analysing of a sample of clean oil first to determine the temperature of complete oil evaporation. Such a method would however mean that some variability in accuracy of soot determination would exist when comparing results from different oils. Additionally, it is possible that some oil polymerization during engine operation may occur [2]. The occurrence of such would imply that the “used” oil would require a higher temperature than the new oil for complete evaporation. This would lead to an overestimation of soot in the oil as some oil will be combusted along with the soot. However, such an effect may not be completely un-advantageous in practice (“false positive”), since the oil’s ability to perform its lubrication and cooling duties is negatively influenced by polymerisation.

The suggestions above may not be suitable as a standard method if comparison between engine oils of different SAE grades is to be conducted. This is due to the fact that a variable quantity of soot would react prior to gas change during analysis for each oil type / SAE grade. If a universal standard for all oils were to be desired, the evaporation temperature of the higher graded oil can be used as URP

temperature for all oils. This leads to an underestimation of soot as shown before, however the mass percentage of combusted soot is the same for all samples.

Depending on the application one of both or a combination of both methods can be chosen. If only oils with a similar SAE grade are used, it is advantageous to choose one temperature for the URP which is, for accuracy reasons, close to the evaporation temperature of the clean oils to prevent unnecessary soot mass loss. This temperature is assumed to be similar for oils of a similar SAE grade. If oils with different SAE grades are to be compared, the evaporation temperature of the highest graded oil should be used as URP temperature. Some soot mass loss due to reactions will in this case occur for all samples, however since the temperature profile is the same for all samples, the mass percentage of reacted soot will be similar and therefore results comparable.

The difference in the quantity of combusted soot between the ASTM method and the improved method is clearly visible. The improved method shows at least 70% lower soot mass loss for the same soot-oil configuration than the ASTM 5967-08. The difference becomes more significant for low SAE graded oils as it is possible to evaporate them at relatively lower temperatures, in order to further reduce soot combustion/decomposition. During this work it was not able to find an engine oil which requires a temperature of 650°C for the Upper Reference Point as proposed by the ASTM 5967-08 method.

#### **4. Conclusion**

This work has investigated the influence of TGA hydrodynamic design, and trace oxygen on the combustion of Printex U and diesel engine derived soot during thermogravimetric analysis. It has been found that significant combustion and/or pyrolysis occur at temperatures above 450°C. The lower end of this temperature range conflicts with the temperature specified by the ASTM 5967-08 engine oil analysis standard. This carbon mass loss effect can significantly affect the results of soot-in-oil determination by TGA.

This work has shown, that a constant relative amount of soot is lost during analysis, which leads to an underestimation of the soot content by approximately 30-40% for samples with more than 5% (w/w) for the soot-in-oil combinations examined. For samples containing significantly less than 5% (initially) the remaining soot amount is close to the detection limit of this technique.

This work proposes an improved oil analysis method which is able to provide increased accuracy of soot determination compared to the ASTM 5967-08 method. The method has been proven to be significantly more robust and therefore far less sensitive to mass loss induced by combustion with oxygen traces in the instrument and pyrolysis effects.

**Acknowledgement**

The Authors would like to acknowledge financial support from the Australian Research Council (LP0883877) and MANN+HUMMEL GmbH.

The Authors would also like to acknowledge the support and assistance of the staff of the Curtin Centre for Advanced Energy Science and Engineering.

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