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Application of nanoparticle tracking analysis platform for the measurement of soot-in-oil agglomerates from automotive engines ☆

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ABSTRACT

Nanoparticle Tracking Analysis (NTA) has been applied to characterising soot agglomerates of particles and compared with Transmission Electron Microscoscopy (TEM). Soot nanoparticles were extracted from used oil drawn from the sump of a light duty automotive diesel engine. The samples were prepared for analysis by diluting with heptane. Individual tracking of soot agglomerates allows for size distribution analysis. The size of soot was compared with length measurements of projected two-dimensional TEM images of agglomerates. Both the techniques show that soot-in-oil exists as agglomerates with average size of 120 nm. NTA is able to measure particles in polydisperse solutions and reports the size and volume distribution of soot-in-oil aggregates; it has the advantages of being fast and relatively low cost if compared with TEM.

1. Introduction

Most of the particulate matter produced by the combustion process in a diesel engine is expelled with the exhaust gases into the exhaust system, but a small proportion is transferred to the lubricating oil. The routes by which this occurs include the transfer of soot into the oil film on the liners; themophoresis has been identified as an important transfer mechanism [1,2]. Over time the buildup of soot modifies the performance of the oil producing oil thickening, which increases the effective viscosity [3] and consequently raising CO_2 emissions and fuel consumption. Various investigators [4,5] have shown that soot build up in oil gives rise to increased engine wear rates; Gautam et al. [6] reported that wear increases with higher soot concentration. Soot reduces the effectiveness of anti-wear additives and its effect on wear depends upon the characteristics of the particles and agglomerates of soot. According to Li [5] abrasive wear occurs and wear scar width closely matches the primary particle size . As suggested by Yue et al. [7], soot aggregate morphology and size distribution can heighten the severity of fluid rheology. Timing chain elongation due to wear is enhanced by soot-in-oil, since wear between pins and bushings causes chain elongation [8].

Most of the soot-in-oil is present as carbon nanosized agglomerates, generally in chainlike and cluster shaped structures with a characteristic length of up to 200 nm [9]. The size distribution is of interest because of the potential influence on oil properties, and for the insight it gives to particle formation and growth. The understanding of soot in oil characteristics and the effects on oil properties and engine wear is impeded by the limitation of experimental techniques for soot analysis. To this end, it is essential to have a reliable characterisation technique. FTIR is widely used to determine soot-in-oil levels as a function of the reduction of light transmitted at a given wave length, but this technique does not provide information on the number, concentration or size distribution of particles. Cryogenic vitrification and imaging by Cryogenic TEM have been used by Kawamura et al. [10] and Liu et al. [11] to visualise soot agglomerates and their distribution in engine oil. The high viscosity of typical used engine oils lead to localised thick layers on the TEM grid and require specialized preparation equipment and expertise, making the technique unsuitable for routine analysis. Conventional TEM has been used to assess the size and shape of particle agglomerates extracted from the oil samples and HRTEM has been used to analyse the structure of the primary particles. Used engine oil is a contaminant for electron microscopes and leads to instabilities under the electron beam; a suitable sample preparation technique has to be employed to effectively remove lubricant from the soot particle. Li et al. [5] have used a solvent extraction technique and ultracentrifugation to prepare the specimen for conventional TEM

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to analyse soot primary particles from a heavy duty diesel test engine. Clague et al. [12] employed solvent extraction followed by centrifugation to extract soot from used engine oil and a similar technique was recently used by Esangbedo et al. [3]. However, a recent study on soot agglomerates shows that sample preparation can alter the distribution of size and shape of these [9]. Despite being an established analysis technique, TEM has the drawbacks of high running costs, analysis turnaround time, complex sample preparation procedures and the need for highly skilled operators.

Since its appearance on the market in 2006, Nanoparticle Tracking Analysis (NTA) has become an increasingly accepted tool for sizing nanoparticles and evaluating particle concentrations in liquid samples [13]. The system uses a laser beam to illuminate the particles, causing them to act as point scatterers, and an optical microscope with camera to visualise and record the path of the nanoparticles under Brownian motion. The centre of each identified particle is tracked and the hydrodynamic diameter of individual particles is calculated by analysing the particle's displacement over time. One of the advantages of this technique is the high sample throughput at relatively low cost compared with TEM. There are now examples of applications to particles ranging from 10 nm up to 1–2 μm in the medical, pharmaceutical, environmental and toxicological fields; NTA results are compared with more conventional techniques such as scattering techniques (SLS/DLS) and microscopy techniques (TEM/SEM) showing good agreement. NTA has been shown to reliably characterise a 40 nm viral vaccine [14] and polydisperse nanosized particles and proteins aggregates in which the presence of small amounts of large particles (1000 nm) did not compromise accuracy [15]. Hemmingsen et al. [16] compared the hazards of exhaust particles from combustion of biodiesel blends and conventional diesel. Particles emitted from the engine were collected from quartz filters in a raw gas tunnel filter and suspend them by sonication in Milli-Q water. The distribution of particle sizes in water was measured by nanoparticle tracking analysis.

In the work, the application of NTA to soot-in-oil sizing is described and compared with TEM results. The particle agglomerates examined are concentrated in the range of 30–150 nm. As far as the authors are aware, this is the first application of the NTA platform for the measurement of soot-in-oil agglomerates from automotive engines.

2. Experimental setup and sample preparation

The oil samples used in the study were drawn from a high pressure common rail (HPCR) direct injection diesel engine, which was a single cylinder variant of a multi-cylinder design meeting Euro 4 emissions requirements. The specifications of the engine and fuel injection system are provided in Table 1. The engine was installed on a test bed and filled with clean SAE 5W/30 lubricating oil at the start of a 10 day period during which the engine was run daily for typically 3 h. The two principal operating conditions were 2000 rpm at a gross IMEP of 11 bar and a fuel rail pressure of 1200 bar, and 1500 rpm at a gross IMEP of 3 bar and a rail pressure of 600 bar. The engine ran with EGR levels up to 20%. Although the mix of operating conditions covered was defined for other purposes, this was sufficiently varied to suggest the range of agglomerates formed would be representative of light duty diesel use. At the end of the 10 days, oil samples were drawn from the sump for the investigation of the soot content.

Table 1
Engine specifications.

Fuel injection system	HPCR max. 1800 bar
Injector type	Solenoid injector
Number of orifices	7
Engine type	Single cylinder
Cycle	Four stroke diesel
Valves per cylinder	4
Compression ratio	13.6
Con-rod length (mm)	160.0
Bore × Stroke (mm)	86.0 × 94.6
Displacement (cc)	549.5

2.1. NTA platform

NTA offers the capability to rapidly size nanoparticles contained in an oil sample diluted with heptane; NTA comprises 3 basic stages (i) video capture, (ii) setting of analysis parameters, (iii) tracking analysis. The Nanosight (LM14) was used in the present investigation. A thin laser beam illuminates the particles, from which the scattered light is visualised using an optical microscope. A camera aligned to the beam axis records a video of the movement of the particles at a rate of either 30 or 60 frame per second. Despite having a lower maximum resolution of 10–30 nm, the Nanosight offers advantages over other scattering techniques, due to the nature of the analysis it performs, in which it tracks the centre of each identified particle. A typical video is captured at 30 frames per second and the subsequent analysis compares the position of each particle on a frame-by-frame basis and tracks the displacement of each particle until the particle (i) moves out of the capture window, (ii) moves out of the place of focus (particles can sink or float) or (iii) crosses the path of another particle. Brownian particle displacement (D) is measured on a frame-by-frame basis. The hydrodynamic diameter of the particles tracked is calculated by applying the two dimensional Stoke–Einstein equation [13]:

$$d_h = \frac{K_B T t_s}{3\pi\eta D}$$

where D is the mean square displacement, K_B is the Boltzmann's constant, T is the temperature of the sample in Kelvin, t_s is the sampling time, η is the sample's viscosity and d_h is the hydrodynamic diameter of the tracked particle.

The high viscosity of the oil in the samples limited the movement of particles and prevented the value of d_h being determined. To overcome this, samples were diluted with heptane at a ratio of 5 μl of oil to 25 ml of heptane, giving a dilution of 5000 times. The heptane was mixed into the sample by gentle agitation. The reference value of viscosity used in this work is 0.4 mPa s at 20 °C; at the dilution ratio used the effect of oil viscosity is low and can be neglected. 1 ml of the resultant solution was loaded into a 1 ml glass syringe and this was added to the sample chamber of the Nanosight (LM14). The laser (404 nm) was turned on and the focus of the instrument set on a location where nanoparticles were present. Once particle identification and tracking were optimised, a series of automated batch capture experiments were performed to increase the sample size and reduce statistical errors. The data was analysed using the NTA (V2.3) software; attention was paid to achieving a particle concentration of between 10^5–10^{10}/ml in the sample, as suggested by Malloy and Carr [17], in order to balance the requirements of long particle track lengths and minimum numbers of particles analysed. Temperature was held constant at 20 °C during the experiment, using the temperature control on the LM14.

2.2. TEM analysis

Transmission Electron Microscopy allows for direct images of particle population. The solvent dilution technique was employed to minimise the stress on soot agglomerates during preparation for

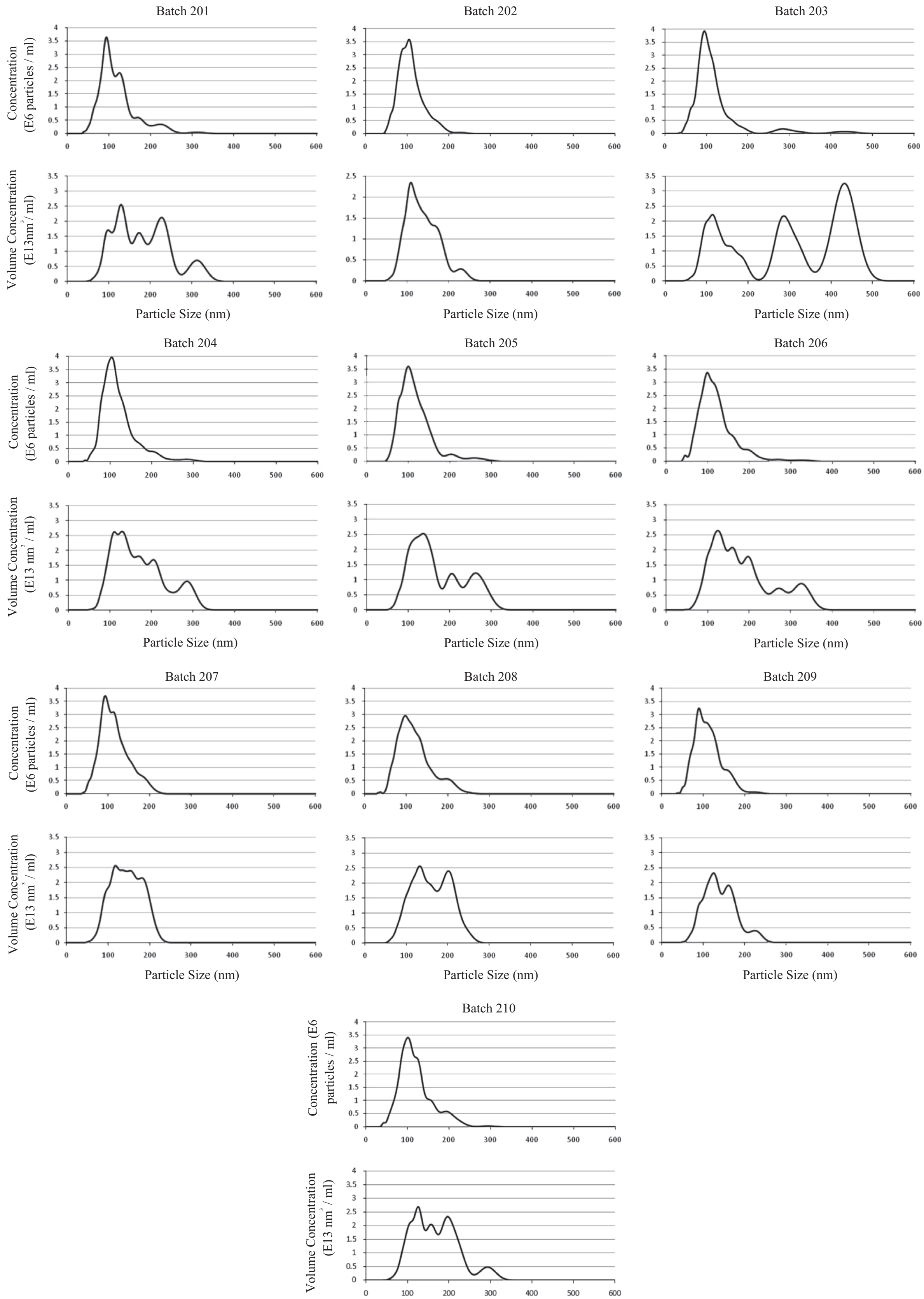

Fig. 1. Size distribution data and volume concentration of soot particles in oil/heptane solution (0.2 μl of oil in 1 ml heptane) measured by nanoparticle tracking analysis.

examination as described in La Rocca et al. [9]; it gave sufficient separation of oil and soot to allow conventional TEM results to be obtained. Oil was simply diluted in heptane (dilution ratio of 1:60) to produce a heptane solution that contained soot with a much lower oil content. The samples for TEM were prepared on a support film of carbon over a copper mesh grid. When deposited onto TEM grid the solvent evaporated rapidly to leave soot particles of varying sizes and degrees of aggregation. For optimum resolution, the material needs to be electron transparent, ideally less than 100 nm thick, and stable in high vacuum. Analysis of these samples was carried out at liquid nitrogen temperature, as the samples were found to be highly sensitive even to short exposures to the beam at lower magnifications and reduced beam intensity giving rise to significant levels of carbon contamination which rapidly obscured the region being analysed. Image quality was improved substantially by washing the deposited sample on the carbon grid with diethyl ether.

3. Results

The nanoparticle tracking analysis provides particle by particle analysis in liquids. One of the aims of this study was to demonstrate for the first time how this platform can be used in a routine process to measure the size distribution of soot-in-oil agglomerates. In order to verify the consistency of the NTA measurements with results of the more commonly used technique of TEM, both were applied to the same used engine oil samples. Results are presented in terms of concentration of particle per ml of solution.

The technique allows counting of the particles within the scattering volume; the particle number concentration refers to the unit volume of solution (0.2 μl of oil in 1 ml heptane). Dragovic et al. [13] report a good linearity between NTA measurements and actual particle concentration for monodisperse solutions; but advise that concentration measurements can be less precise in polydisperse solutions. Malloy and Carr [17] suggest that extending analysis time can help improve accuracy. In Fig. 1 individual particle size distributions are given for each of the batches data captured. The majority of peaks are around a 100 nm diameter. However, batches 203–206 contain several larger 300–400 nm particles. The vast majority of soot particles have a diameter lower than 200 nm though.

The Nanosight platform also offers option plots such as surface area in nm^2, as a simple extension of the estimated sphere diameter, and particle volume in nm^3 based on the estimated sphere diameter. Fig. 1 also shows the particle volume distribution for each of the 10 batches captured. The particle volume distribution versus size serves to highlight that the presence of even a low number of aggregates can represent a significant proportion of the total soot volume present in a sample; see for instance Fig. 1, batch 203. In this case a suspension of 95 nm particles was spiked with a low number of 300 nm and 400 nm particles (less than 0.08 E6 particles/ml). However, in this case, the peak soot volume occurs at 430 nm. The volume of a 95 nm particle is 93 times smaller than a 430 nm particle. The total soot mass in the sample has been evaluated from

$$m_{soot} = \rho \sum_{i=1}^{n} \left(\overline{V}_{c,i} \frac{1}{6} \pi d_i^3 \right)$$

where ρ is the soot density, and $\overline{V}_{c,i}$ is the volume concentration for particles of diameter d_i averaged over ten batches. For a spherical soot particle Heywood [18] suggests a density of $\rho = 2\ \text{g/cm}^3$. It follows that the 0.1 μl of used oil sample analysed contains 3.2×10^{-3} mg of soot; suggesting that 1 l of used oil drained from the engine after 30 h of engine operation contains 32 g of soot.

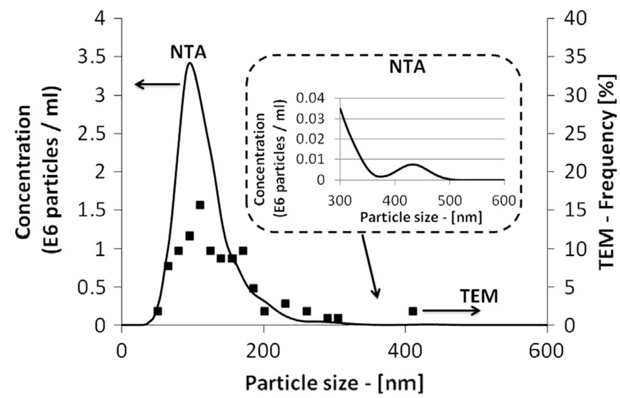

Fig. 2. Continuous line: average size distribution data (batches 201–210) of soot particles in oil/heptane solution (0.2 μl of oil in 1 ml heptane) measured by nanoparticle tracking analysis. Square marker (■): size frequency distribution of soot particles in heptane (dilution ration 1/60) analysed by Transmission Electron Microscopy.

Table 2
Measured particle size and statistical data from NTA and TEM.

	Number of particle analysed	Standard deviation (nm)	Mode (nm)	Mean (nm)
TEM	200	57.8	110	132
Batch201	241	46	94	121
Batch202	262	30	105	110
Batch203	250	67	95	122
Batch204	259	41	104	120
Batch205	269	40	100	118
Batch206	277	44	99	122
Batch207	274	34	93	116
Batch208	247	39	97	120
Batch209	218	32	89	112
Batch210	246	41	101	122

Fig. 2 shows the average size distribution of the ten batches. NTA successfully measures particle size in polydisperse used-oil/heptane solutions. The particle size distribution is well defined and clearly discriminate the particle concentration peaks in the range 93–105 nm for all the ten batches captured, see Table 2.

For conventional Transmission Electron Microscopy, one 2 μl drop of soot-in-oil suspension in heptane was deposited onto a support film of carbon mesh grid. TEM allows measuring the particle shape and size of projected two-dimensional images of agglomerates. It does not allow for the three-dimensional nature of agglomerates, and will generally underestimate the true maximum values of length of the agglomerate. This deficiency has been noted by Rogak et al. [19], and represents a common limitation of the imaging technique and equipment. La Rocca et al. [9] suggested skeleton length provides a more appropriate characterisation of soot-in-oil. To address this, the TEM particle size will be expressed in terms of length and compared with the particle size measured by the NTA platform. The particle length was measured using an open architecture image processing programme, ImageJ. Electron microscopy can only analyse the amount of agglomerates present in the measured area, i.e. the support grid, and requires extensive sample preparation and analysis. Approximately 200 agglomerates were isolated and examined [20] via TEM. Results are summarised in Fig. 2; for simplicity the NTA results have been presented in the same figure as an average of the 10 batches.

In Fig. 2, 90% of the particles analysed using TEM have a size less than 200 nm. The smallest particles are in the 35–45 nm range of lengths and accounted for the 2% of the total in the sample analysed. The frequency of particle with lengths between 50 and

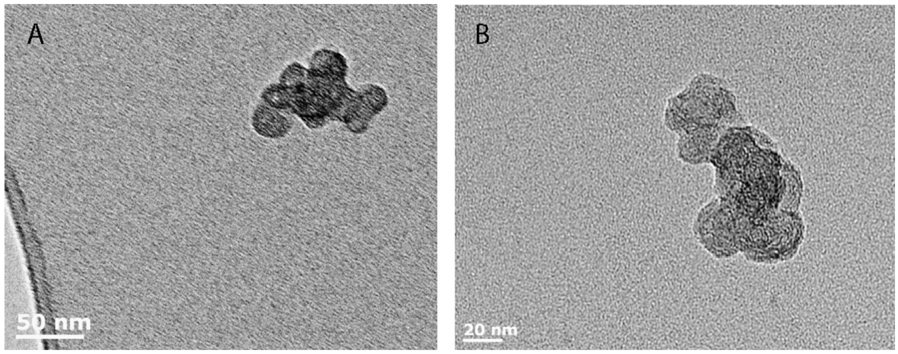

Fig. 3. TEM images of soot particles. Length of agglomerate A is $L_A = 98$ nm. Length of agglomerate B is $L_B = 102$ nm.

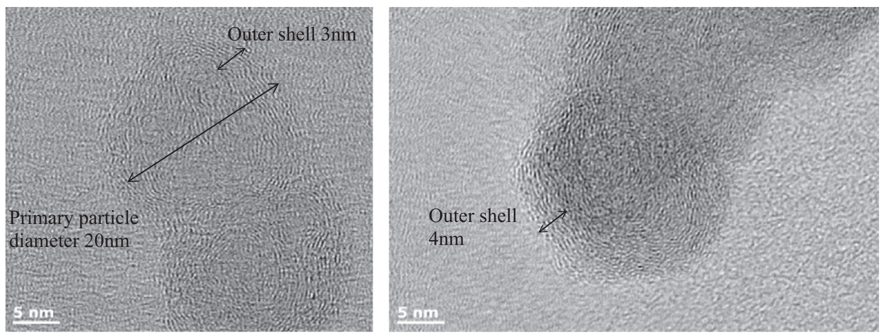

Fig. 4. TEM soot primary particles at high magnification level.

65 nm was 8%. TEM results also show a low number of 400 nm particles present in the suspension. The comparison between the two techniques shows that NTA can measure soot nanoparticles as small as 30 nm and there is a very good agreement between the particle sizes measured by the two techniques. Statistical information on the data presented in Fig. 2 are given in term of Mean (Avg), Mode and Standard deviation (StD) in Table 2. Both the mode and average are very similar. The NTA platform allows for a total of 2543 particles to be analysed in a very short period of time (20 min) and with results statistically more robust when compared to the 200 particles analysed using traditional TEM (few hours).

One of the drawbacks of NTA is that unlike TEM, it does not provide images of the particles. The images shown in Fig. 3 illustrate soot agglomerates from the TEM sample. These agglomerates have a modest branching structure and typically fall in the size range 30–130 nm.

TEM can also be employed to probe the structure of primary particles. Diesel exhaust soot has been reported having a bucky-onion structure [21], with core of around 13 nm and no shell in the majority of particles. Fig. 4 shows the structure of two particles analysed at high magnification. The inner core is 15 nm and it is surrounded by several graphitic layers. The fringes' planes are parallel to the surface. The outer shell is 3–8 nm composed by crystallites viewed edge-on on TEM projections.

4. Discussion

In this study the particle size distribution of soot from used engine oil was measured using two different techniques, TEM and NTA. TEM is more established than NTA as a technique to characterise soot-in-oil nanoparticles, but it has the drawback of high cost and does not provide particle concentration as number of soot particles per volume of oil. The NTA platform is a novel, rapid, low cost technique; it is simple to use to assess particle size distribution and generates data on the number of particles per ml of solution. Sample preparation is straightforward, requiring the dilution with heptane to the relevant concentration but without the measures required to protect instrumentation from oil contamination as in the TEM. Particles are analysed in suspension and therefore do not suffer from shrinkage due to solvent surface tension during drying. Soot-in-oil analysis is not an area in which NTA has been applied previously and the experience gained in the current study suggests size distributions and concentration information can be generated with relative ease. The most obvious limitations are the technique does not provide details of morphology and motion is recorded in two dimensions not three. The latter leads to some tracks being associated with a greater degree of motion and consequently with larger particles. The validity of two-dimensional measurement of three-dimensional Brownian motion is extensively discussed in [22,23]. Mixtures of different particle types of same diameter can be distinguished as two independent parameters are measured: particle scattering intensity and dynamic behaviour [17]. This allows for contaminating particles to be clearly identified.

Both NTA and TEM showed that soot agglomerate particles extracted from used engine oil range typically from 30 to 180 nm. The size distribution is remarkably similar. NTA confirmed the presence of larger agglomerates of 400 nm, although low in number compared to the major population below 180 nm. Both methods measured particles smaller than the 500 nm reported in [17]. One of the interesting advantages of NTA is the measurement of particle concentration per unit volume, something not available for TEM. This can be exploited to allow monitoring of changes in particle concentration in used engine oil samples, again not a measurement easily obtained by conventional TEM. Soot agglomerate size, their size distribution and concentration can be measured by Nanosight. In this work NTA has allowed an estimate of the volume of soot particles dispersed in engine oil and its mass.

The Nano Tracking Analysis requires only a few hours training to become familiar with the interface, the adjustment of apparatus and software settings, made more straightforward by recent updates to the software. It represents a new and reliable technique which opens to new interesting developments in the field of soot-from-oil analysis and beyond.

5. Conclusions

NTA has been evaluated for measuring particle size in poly-disperse used-oil/heptane solutions. Soot-in-oil size distribution results from traditional transmission electron microscopy and the novel nanoparticle tracking analysis were compared; the results for soot size distribution are closely similar. Soot agglomerates were found to be in the range of 50 and 300 nm, with an average size of 120 nm. NTA offers the possibility to monitor particle concentration per millilitre of sample measured which is a clear advantage over conventional TEM. NTA allows for particle visualisation but not imaging. TEM imaging is necessary to fully characterise soot particle shape and structure. Soot agglomerates show modest branching and are composed of spherical soot primary particles. The classic core–shell structure is clearly visible in all particles. Typically an inner core of 4–15 nm and a shell 3–8 nm thick can be observed.

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