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The Measurement of Ultrafine Particles: A Pilot Study Using a Portable Particle Counting Technique to Measure Generated Particles During a Micromachining Process

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The accurate measurement of airborne particles in the nanometer range is a challenging task. Because several studies have linked exposures to airborne ultrafine particles to elevated human health risks, the need to assess the concentrations of particles in the workplace that are below 100 nm in diameter is imperative. Several different techniques for monitoring nanoparticles are now available, and others are currently being tested for their merit. Laboratory condensation particle counters (CPC), field-portable CPC, nanometer differential mobility analyzers, electron microscopy, and other novel and experimental approaches to measuring nanoparticles have been recently used in investigations. The first part of this article gives an overview of these techniques, and provides the advantages and disadvantages for each. The second part of this article introduces a portable technique, coupling two particle measurement devices that are capable of characterizing microscale and nanoscale particles in the field environment. Specifically, this pilot study involved the use of a direct-reading CPC and a laser particle counter to measure airborne concentrations of ultrafine particles during a laboratory machining process. The measurements were evaluated in real time, and subsequently, decisions regarding human exposure could be made in an efficient and effective manner. Along with the results from this study, further research efforts in related areas are discussed.

Keywords micromachining, nanoparticles, particles, surface engineering

1. Introduction

Most definitions of nanotechnologies focus on size or scale, with "nano" indicating particles, molecules, or molecular structures of between 1 and 100 nm (Ref 1). With the recent advancements in nanotechnology and the commercialization of nanomaterials and products, additional concerns have been concentrated on the environmental and human health aspects of exposure to ultrafine particles that are generated during fabrication and manufacturing. Several epidemiologic studies have linked indoor and outdoor air pollution-related health risks associated with exposures to ultrafine particles smaller than 100 nm (Ref 2-5). In addition, most related studies have indicated that exposures to low-solubility nanoscale particles are more toxic to internal and external tissues and organs than are larger particles on a mass-for-mass basis (Ref 4-6).

While traditional particle-monitoring methods have concentrated mainly on determining the overall mass, several recent studies have indicated that particle number rather than mass may be more important in determining the health implications (Ref 6-8). However, the current best practice in measuring employee exposures to airborne particulate concentrations is to use a personal sampling device to collect, typically over an 8 h workshift, a representative volume of potentially contaminated air. The metric most often used to determine a relative exposure to microscale particles is the time-weighted mass concentration of each particular aerosol. Unfortunately, due to the inherent nature of the nanoscale particle, it is a widely accepted premise that the measurement of mass is not a sufficient worker health exposure metric (Ref 7). In contrast to traditional theories about the health effects from microscale particle exposures, the detriments from nanoparticles are likely to be dependent on the specific particle, its morphology, surface, composition, and size. Thus, ideally, a measurement of particle number or particle surface area would provide a more preferred means of biological relevance. Currently, the technology to provide one or both of these parameters is only in the developmental stages. A major challenge presented to current researchers is the accurate measurement of ultrafine particles by particle number. While several instruments and techniques that measure particles below 100 nm are currently being tested or recently have been commercialized, most of these lack the field portability and associated economics to make them practical for field use. The most promising methods available to measure particle number include optical particle counters, condensation particle counters (CPC), scanning mobility particle sizers (SMPS), and electrical low-pressure impactors (ELPI) (Ref 9-13). However, each of these has their associated limitations

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when used individually to measure particles in the nanoscale region. It has been argued that an economical technique that couples two or more of these technologies should be further investigated (Ref 7). This article begins with an overview of the current state of airborne nanoscale particle measurement. The various techniques that are currently in the commercial stage as well as in the developmental stages are presented along with their inherent advantages and disadvantages. Efforts are made to restrict the discussion to only those that are potentially viable for field applications. The merit of combining two or more of these techniques into an integrated system is also elucidated.

The second part of the article is dedicated to introducing a method of measuring nanoparticles that combines the use of a relatively inexpensive and field-portable CPC, capable of measuring ultrafine particles as small as 20 nm, with a portable and field-friendly laser optical counter. The advantage of this technique is that the laser particle counter (LPC) can only detect particles down to 300 nm in size. Thus, by using these two instruments in combination, a means for differentiating between particles of greater or smaller than this 300 nm detection limit value can be accurately realized. The technique was recently piloted under laboratory conditions and during an advanced machining process, which is known as *mechanical micromachining*, but it could also be used in other ultrafine particle-generating exercises such as surface-coating applications or device manufacturing. As a point of reference, mechanical micromachining is potentially an important manufacturing process due to its potential for machining microelectromechanical systems (MEMS) and nanotechnology components from engineering materials. To obtain acceptable machining results, engineering materials must be machined at their minimum recommended cutting speed. At the microscale and nanoscale, this speed can exceed 1 million rpm for an end-milling cutter of less than 250 μm in diameter. Due to the small depth of the cut and the high rotational speed, the amount of material removed by each tooth every revolution is very small; therefore, the chips produced are very small. For example, a micro 4 flute, 1.2 mm diameter, square end mill with a length of cut of ⅛ in. and a helix angle of 300°, produces a maximum chip size of 500 to 50 μm in width and 50 μm in diameter. When cutting conditions change (e.g., the depth of cut), the size of the particles produced will also change. Therefore, monitoring of the particles produced by micromilling can yield information about the cutting process. If particle size can be correlated to tool wear, then an in-process tool wear-monitoring system could be established for microscale high-speed milling. This is an important additional benefit of this technique.

2. Methods of Nanoparticle Measurement

Table 1 provides a summary of nanoparticle measurement techniques that are either currently in the developmental stages or have already been implemented in the workplace. The table includes the method, the metric measured, the sensitivity, and the major drawbacks or limitations of each technique.

The first method discussed is a personal sampling device that is size-selective. Currently, most analytical methods for particulate matter are based on the collection on a preweighed filter of any additional mass sampled at a known airflow rate. This is typically weighed on a laboratory balance, and the full production shift (i.e., 8 h) detection limit is approximately

Table 1 Summary of particle measurement techniques

Method or instrument	Measurement metric	Sensitivity, 10^{-9} m	Drawbacks and limitations
Personal sampler	Mass	0.02 mg/m^3	No size fraction cutoff in nm size
LPC	No. and concentration	300	Mainly for microscale use
CPC	No. and concentration	10	Not size selective
SMPS	No. and concentration	3	Not portable or user friendly and cost
Nanometer aerosol size analyzer	No. and concentration	3	Not portable and in development stage
MiPac Particulate Classifier	No. and concentration	10	No detection under 10 nm
ELPI	No. and concentration	7	Cost and not portable
Epiphaniometer	Surface area	NA (surface area)	Bulky, complex, and costly
Gas adsorption	Surface area	NA (surface area)	Large sample sizes needed for validity
SEM	No., size, and morphology	5	Sophisticated instrumentation
TEM	No., size, and morphology	1	Complicated sampling routine
Laser-induced plasma system	Composition	3	Composition information only

Note: NA, not applicable

0.02 mg/m^3. Obviously, this would present a problem in analyzing by mass an air sample composed mainly of nanoscale particles that would normally only weigh a fraction of this amount. However, with all of this said, it has still been suggested that a size-selective personal sampler could be developed with, for instance, a 100 nm cutoff point (Ref 7). This could provide some meaningful accuracy for measuring those coating aerosols above 50 nm or so.

The second through seventh methods provided in Table 1 are based on the number of particles counted. These methods include laser optical particle counters, condensation nuclei counters, SMPS, and electrical low-pressure impactors. These are primarily real-time counters, and range in relative portability and, subsequently, in their applicability to workplace exposure assessments. Also, several of these methods are still in the developmental stages. Due to its portability, versatility, and lower detection size limit, LPC have been traditionally used to measure particles down in the low-microscale range. However, particles that are less than 300 nm will not be detected by this method (Ref 9). This limits the applicability in the surface coatings industry, where particles are quite frequently found to be an order of magnitude smaller. There are more sophisticated optical samplers, but these are not currently portable devices, and, therefore, would not typically be used in industry to measure workplace exposures.

The most common instrument used to measure ultrafine particles employs condensation particle-counting technology. The CPC condenses vapor onto the sampled particles to "grow" them to a detectable size range. This type of instrument is usually very portable and easy to operate. The main disadvantage to using this type of instrument is that it is not size-

Fig. 1 A CPC (with permission from TSI, Inc)

Fig. 2 An ELPI (with permission from Dekati Ltd.)

selective and only provides the total particle counts above the detection limit, which ranges from 3 to 100 nm on commercially available units (Ref 13). Figure 1 shows an example of a typical CPC used to characterize ultrafine particles. The measurement methods that are currently available, which provide both size-selective information as well as number concentration, are inherently more complicated to use as well as not being very portable or versatile for field-exposure assessments. In addition, their higher costs typically eliminate applicability altogether in the workplace. The best instrument examples of these methods are the SMPS and the electrical low-pressure impactor. Both of these instruments can provide size-selective concentration data of particles all the way down to less than 10 nm in diameter (Ref 10, 13). Examples of both an ELPI and an SMPS are provided in Fig. 2 and 3.

Because the majority of nanoparticles generated agglomerate to some extent, it has been argued that the best way to characterize nanoscale particles is by the measurement of its surface area. The only instrument that is currently being used to measure surface area is called an *epiphaniometer* (Ref 11, 12). This instrument uses radioactive tagging to determine the surface area of the particle. Again, this instrument is very complicated and lacks versatility for field use. Gas adsorption techniques that require rather large sample sizes have also been used infrequently as a bulk method of ascertaining particle surface areas. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) also provide the means of determining ultrafine particle characteristics. While these instruments provide the morphology of the particles and excellent resolutions (e.g., TEM 1 nm; SEM 5 nm), these instruments are very expensive and usually require an expert technician or specialized training to be used effectively. However, recent studies point to the merit of this technique to characterize exposures in the workplace (Ref 14).

Nanoparticle composition measurement is normally an essential component for nanoscale particle studies. Not unlike many of the number, size-selective, and surface area techniques

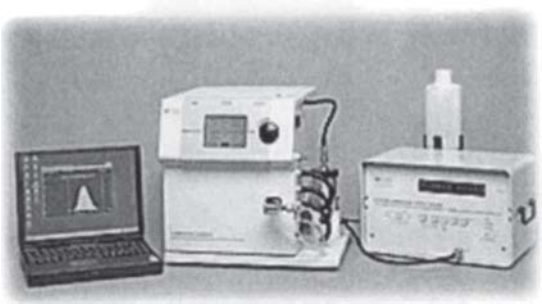

Fig. 3 An SMPS (with permission from TSI, Inc.)

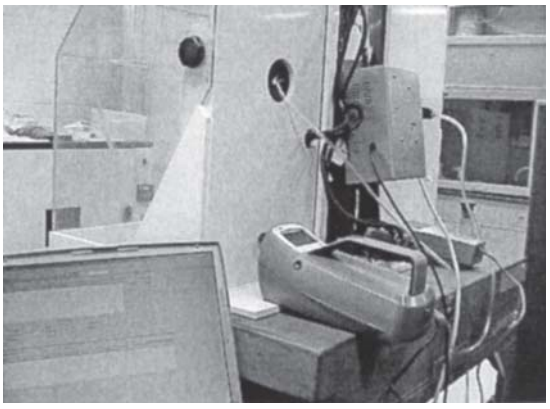

Fig. 4 Pilot set-up involving both the CPC and LPC

previously discussed, nanoparticle composition techniques are mainly in the developmental stages. The laser-induced plasma system and the high-temperature nanoparticle measurement systems can detect the composition of nanoscale particles as small as 3 nm (Ref 15). Each of the methods overviewed has its own set of merits and limitations. A possible solution to the dilemma at hand is the use of these instruments in combination. While the more sophisticated instruments have excellent resolution and many times both the concentration and size selectability, they are primarily limited to research settings due to their complexity, size, and costs.

However, the concerted use of portable techniques such as laser particle counting and condensation particle counting might eliminate or, at least, alleviate some of the major drawbacks of their individual usage for nanoscale aerosol characterization. In essence, a technique employing both an LPC, with size-selective information down to 300 nm, and several condensation nuclei counters with differing resolutions below 300 nm could provide relatively inexpensive exposure data to those working with nanoparticles in the coatings industry. The number of CPCs needed by a user would be as few as one, depending on how much information is already known about the size of the particles or their specific aggregate.

3. Pilot Study

Figure 4 provides an example of a pilot run involving the use of a CPC with a sensitivity of 20 nm coupled with a size-selective laser detection device with a sensitivity of 300 nm. It is worth noting that this methodology is inherently portable and economical as well as easily applicable to field aerosol exposure studies. A pilot study involving the use of two

Fig. 5 Pilot study experimental setup showing instruments

Fig. 6 The TSI P-TRAK CPC (with permission from TSI, Inc.)

of these techniques, laser detection and condensation nuclei counting, was recently attempted in the laboratory setting during a micromachining process. The two techniques were coupled to form an integrated, portable technique for ultrafine particle measurement. The following sections describes the methods, data, discussion, and conclusions from this effort.

4. Experimental Procedure

The experimental apparatus with associated monitors is shown in Fig. 5. The two portable monitoring devices were set up to collect data simultaneously and in real time. The CPC used for the study was the TSI P-TRAK Ultra Fine Particle Counter Model 8525 (TSI Incorp., Shoreview, MN). The P-TRACK is shown in Fig. 6. The sensitivity of the P-TRAK is 20 nm, and it can measure particles as large as 1 μm in size. The flow rate for the instrument defaults at 100 cc/min, and the instrument samples a reading per second. The second instrument used in this technique was the ARTI HHPC-6 Hand Held Particle Counter (Hach Ultra Analytics, Giants Pass, OR). Figure 7 shows the HHPC-6. This instrument has a laser detector and can provide the user particle size differentiation in ranges from 300 nm up to 5 μm. The ranges given were in concentrations of particles from 300 to 500 nm, 500 to 700 nm, 700 nm to 1 μm, 1 to 2 μm, 2 to 5 μm, and greater than 5 μm. The HHPC-6 has a flow rate of 2.83 L/min and is programmable to obtain different numbers of samples, according to the user's preference.

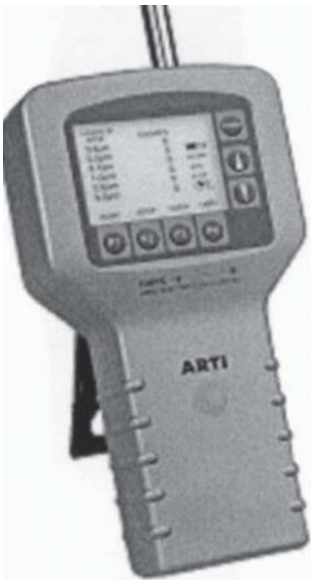

Fig. 7 The ARTI HHPC-6 LPC (with permission from ARTI)

The detectors were placed side by side, and at both 203 mm above and across from the cutting tool/piece and on the centerline of the traverse direction. The machining protocol involved a depth of cut of 12.7 μm, a feed rate of 25.4 mm/min, and a cut length of 40 mm. The machining process involved both a forward-cutting and a reverse-cutting protocol, and the total test time was set at 3.5 min. The ARTI laser counter was set to take a sample every 21 s, and the P-TRAK relied on its default setting of one sample per second. The sampling time window involved the actual cutting time, the background measurement time on both sides of the test duration, as well as a "machine turn-on" time sequence. These would be used as identifiable parameters for analyzing the data accurately. Data from both instruments were logged, and program software was used to graphically represent the findings. Several tests were run during the pilot study, and modifications to the protocol were made. Data were collected for determining the total particle number count per volume (concentration) and the differentiated counts per volume from 300 nm up to greater than 5 μm. Due to technique constraints and the inability of the CPC to differentiate particle size ranges, only the cumulative counts of particles per unit volume between 20 up to 300 nm were collected.

5. Experimental Data and Results

Figure 8 shows the data collected for the 3.5 min sampling duration for particles greater than 20 nm to just above 1 μm in size. Figure 9 represents the particle concentration measured above 300 nm during the sampling event. Particle number concentration is represented on the dependent axes of the two graphs as the number of particles per cubic centimeter. The independent axis of both graphs indicates the sampling event time duration. It should be further noted that Fig. 8 represents both the nanoscale and microscale data collected with the CPC,

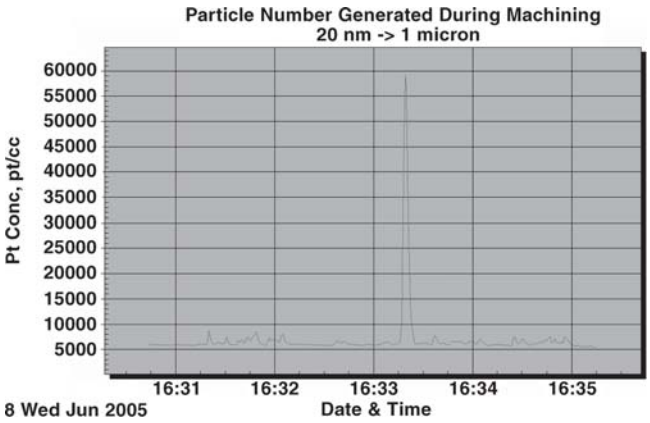

Fig. 8 Particle number from 20 nm to approximately 1 μm generated during machining

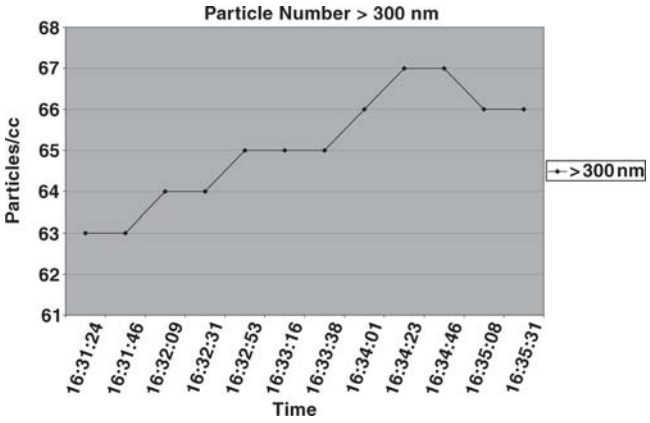

Fig. 9 Particle number >300 nm generated during machining

while Fig. 9 shows the microscale particle data collected with the laser counter. The data measured were collected simultaneously with both instruments.

Because proof is required that this technique has merit, further research is needed and a pilot study should conducted. The study should be conducted initially under controlled conditions in a laboratory and further tested for applicability in the field. The proposed study should begin with the use of an LPC and one CPC, and then should add CPC as the study becomes more involved. Ideally, a mathematical algorithm that relates the output from the instruments with each other as well as workplace exposures to nanoparticles would be one of the major outcomes. In addition, it is proposed that electron microscopy be used as a means of measurement quality assurance/control.

6. Discussion

The particle number data represented by Fig. 8 indicate initially that the background counts of particles of 20 nm to approximately 1 μm in size was around 6000 particles/cm^3. After the machining apparatus was turned on (but without traverse), the counts jumped up to approximately 9000 counts and then leveled out to a range of 6000 to 7500 counts during most of the machining process. However, the most noteworthy event during this run involved an increase in particle number concentration of nearly one order of magnitude, which occurred during a 5 s interval on the return pass. This resulted in the maximum particle number concentration for the sampling event of 59,000 particles/cm^3. This data aberration was accompanied by a "sparking" phenomenon originating at the interface between the cutting tool and the workpiece. In addition, at this point in time there was a significant change in the sound frequency generated due exclusively to the cutting action.

Figure 9 provides the data on cumulative concentration of particles greater than 300 nm. The background number concentration was found to be 63 particles/cm^3. There was a minor and insignificant increase in particle concentration in this size range during the total sampling event, with the maximum counts being 67 particles/cm^3. Thus, the data aberration that was observed by evaluating the data given in Fig. 8 was not encountered in the measurements taken for microscale-range particles by the LPC. The only conclusion that can be made from this observation is that during this time interval a dramatic increase in the number of particles of less than 300 nm was experienced.

The phenomenon experienced during the 5 s interval was most likely the result of the thermal oxidation of metal chips that were being generated by the cutting process. This would also help to explain why there was a sparking action realized at the same time as the tenfold increase in particles detected in the submicron region of the scale. While not quantified, a frequency change from a lower to a higher rate also would be expected during an event of higher energy levels and more cutting friction. In essence, the particles produced were more like those that would be generated during a grinding process rather than a micromachining process.

7. Conclusions

In conclusion, an overview was given of the currently available methods for segregating and measuring the concentrations of airborne nanoscale particles in the coatings industry. A few of these techniques could be somewhat useful in determining the worker exposure profiles, but when implemented alone have several additional limitations. A pilot run was conducted with a technique involving the combination of two of these portable methods for characterization. This technique proved to be an effective means for differentiating particle number concentrations generated during the mechanical micromachining process while under controlled laboratory conditions. The study showed that anomalies that occur during such processes can greatly increase the number of particles generated at sizes less than 300 nm. Intervals of increased particle generation in the lower microscale and nanoscale size ranges are significant to human health exposures. Portable techniques that combine the positive attributes of two or more available particle measurement technologies should be tested and subsequently used in field applications to assist in the determination of worker exposure. This technique demonstrated an effective, portable, and economical means for accomplishing this objective. Further studies will involve the researching of whether a strong correlation exists among sound frequency changes, particle size, and machining quality. A special emphasis will be placed on determining a relationship between the frequency-time domain and the particle size concentrations and distributions. The ultimate objective will be to determine an algorithm that relates sound frequency and particle concentration in the nanoscale

range. This could potentially provide helpful information for those trying to protect workers from the potential harmful effects of exposures to ultrafine particles during nanoscale and microscale machining processes.

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