Airborne Nanoparticle Detection By Sampling On Filters And Laser-Induced Breakdown Spectroscopy Analysis

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Abstract. Nowadays, due to their unique physical and chemical properties, engineered nanoparticles are increasingly used in a variety of industrial sectors. However, questions are raised about the safety of workers who produce and handle these particles. Therefore it is necessary to assess the potential exposure by inhalation of these workers. There is thereby a need to develop a suitable instrumentation which can detect selectively the presence of engineered nanoparticles in the ambient atmosphere. In this paper Laser-Induced Breakdown Spectroscopy (LIBS) is used to meet this target. LIBS can be implemented on site since it is a fast and direct technique which requires no sample preparation. The approach consisted in sampling Fe₂O₃ and TiO₂ nanoparticles on a filter, respectively a mixed cellulose ester membrane and a polycarbonate membrane, and to measure the surface concentration of Fe and Ti by LIBS. Then taking into account the sampling parameters (flow, duration, filter surface) we could calculate a detection limit in volume concentration in the atmosphere. With a sampling at 10 L/min on a 10 cm² filter during 1 min, we obtained detection limits of 56 µg/m³ for Fe and 22 µg/m³ for Ti. These figures, obtained in real time, are significantly below existing workplace exposure recommendations of the EU-OSHA and of the NIOSH. These results are very encouraging and will be completed in a future work on airborne carbon nanotube detection.

1. Introduction

Nowadays, due to their unique physical and chemical properties [1-4], engineered nanoparticles are increasingly used in a variety of industrial sectors, with more than 1000 products commercialized in the world. However, questions are now raised about the safety of workers who produce and handle these particles [5-7]. Indeed, the effect of nanoparticles on human health is not fully understood yet, and their toxicity is the subject of many researches [8-9]. In addition there is presently no regulation at the world level related to the synthesis and the safe handling of nanomaterials, nor any recommendation on the admissible exposure levels for workers [10]. Besides, to properly assess the
risk of nanoparticles, it is necessary to measure the exposure of workers. The main route of exposure is the inhalation of these particles [11], which are then distributed in the whole respiratory tract [12-13]. There is thereby a need to develop a suitable instrumentation to detect the presence of engineered nanoparticles in the ambient atmosphere.

Usual instruments for aerosol measurements were tested for that purpose [14-15]. Results show that aerosol particle sizers (mostly ELPI, SMPS, APS, FMPS) allow detecting in real time an increase of the particles concentration. However as the implemented techniques give no information on the particles shape or composition, it is sometimes difficult to ensure that the detected particles are those of interest. Therefore sampling and off-line analysis are often required. Furthermore, the natural background can be high ($10^4 - 10^6$ part/cm$^3$) compared to the concentration of engineered nanoparticles, and it can fluctuate a lot in time and in space, which makes their detection still more difficult.

In this context, we propose to use the Laser-Induced Breakdown Spectroscopy (LIBS) technique to meet this target [16]. The principle is to focus a high energy pulsed laser beam on a sample, causing its vaporization and a plasma formation. The plasma light is collected and spectrally analyzed. It is then possible to identify the chemical elements of the sample and their concentrations after calibration. The LIBS technique is fast and can be used directly for on-site measurements without sample preparation. It is very versatile and can be implemented on solids, liquids, gases and aerosols.

In this work we chose to sample airborne nanoparticles on a filter and to analyze the filter by LIBS to measure the particle mass surface concentration, and then their volume concentration in the ambient atmosphere. This approach has been already used by a few authors for particle measurements. Its first application was the detection of beryllium particles [17]. It was also implemented for environmental purposes to monitor heavy metals aerosols, with detection limits of the order of several tens to several hundreds of ng/cm$^2$ depending on the element [18-19]. In two interesting papers LIBS was used to analyze the particles collected on the stages of an ELPI to have a size-resolved quantitative chemical information [20-21]. And recently authors coupled LIBS to an aerodynamic lens depositing the particles on a rotating substrate, and they obtained a volume detection limit of 80 ng/cm$^3$ of copper for a 5 min sampling time [22].

This paper presents our first results obtained on Fe$_2$O$_3$ and TiO$_2$ nanoparticles. A known mass of these particles was deposited, respectively, on mixed cellulose ester membranes and on polycarbonate membranes, in order to make calibration samples. Then we traced calibration curves for both elements, Fe and Ti, and we determined the limits of detection.

2. Experimental

2.1. Filters enrichment

The experimental setup used to enrich filters with a controlled amount of Fe$_2$O$_3$ nanoparticles is shown on figure 1. A spark discharge aerosol generator was used (PALAS GFG-1000), producing nanoparticles with a mass median diameter around 100 nm. A flow splitter was placed after the generator to divide the aerosol in four lines. Two of them were used for sampling on filters, a third one enabled to do real-time mass deposition measurements with a tapered-element oscillating microbalance (TEOM 1105) and the excess flow was evacuated through the last one. The flow rate in the sampling lines and in the TEOM line was the same, equal to 3 L/min, so that the TEOM mass measurement was directly representative of the particles mass deposited on the filters. We made replicates of a series of filters and we checked that the TEOM data was consistent with ICP-OES measurements performed after complete dissolution of the filter. The particle surface concentration on the filters was changed by varying the exposure time. The filters used for Fe$_2$O$_3$ nanoparticles were mixed cellulose ester membranes (HAWP Millipore) with a diameter of 47 mm and a pore diameter of 0.45 µm.

The enrichment of filters with TiO$_2$ nanoparticles was performed differently. We used an atomizer which generated aerosols by atomization of a liquid dispersion of nanoparticles. The particle size distribution was measured with a Scanning Mobility Particle Sizer and the mass median diameter was
of the order of 100 nm. The particle mass concentration on the filters was controlled by subsequent TXRF measurements. The filters used were polycarbonate membranes (PC Osmonics) with a diameter of 37 mm and a pore diameter of 0.20 µm.

![Figure 1. Experimental setup for the enrichment of filters with Fe₂O₃ nanoparticles.](image)

2.2. LIBS setup

The LIBS setup is represented on figure 2. A Nd:YAG laser was used (Quantel Brio), delivering pulses of 5 ns duration and 25 mJ maximum energy at 355 nm. A shutter enabled to control the number of laser shots on the sample. The beam was then shaped by means of a home made optical system so that the energy profile at the sample surface was homogeneous ("top-hat" profile), for this configuration is well suited for surface, single-shot analysis. The spot diameter on the filter was 220 µm, the corresponding irradiance was 13 GW/cm². The working distance of the focusing lens was about 230 mm. The light emitted by the plasma was collected by a telescope and injected into a 3 m optical fiber transmitting the UV radiation, with a core diameter of 910 µm. This fiber was directly connected at the entrance of the spectrometer, a monochromator equipped with gratings of 2400 grooves/mm (for Fe₂O₃ nanoparticles) and 1200 grooves/mm (for TiO₂ nanoparticles). The detector used was an intensified CCD camera (Andor iStar). The gate delay of the detection was 1 µs for both types of particles, the integration time was 1.5 µs for Fe₂O₃ nanoparticles and 1 µs for TiO₂ ones.

The acquisition consisted in scanning the filter surface by performing a laser shot on one spot, without overlapping between two successive shots. The step between two shots was adjusted to 1 mm for that purpose. A spectrum was recorded for each shot. For Fe₂O₃ nanoparticles we recorded 529 spectra per filter, for TiO₂ ones, for which the filters used were smaller, we recorded 220 spectra.
3. Results and discussion

For Fe$_2$O$_3$ nanoparticles, figure 3 shows the spectra averaged over all laser shots for each filter, and the calibration line traced between 0 and 600 ng/cm$^2$ (Fe concentration). Figure 4 shows the same for TiO$_2$ nanoparticles, with a calibration line between 0 and 200 ng/cm$^2$ (Ti concentration). In both cases a good linearity was obtained. For the Fe and Ti elements, a limit of detection (LOD) of, respectively, 56 and 22 ng/cm$^2$ was determined.

To convert these figures into volume detection limits (in µg/m$^3$), let us consider for example a particle sampling at 10 L/min during 1 min on a 10 cm$^2$ surface filter. Then the volume LOD is 56 µg/m$^3$ for Fe and 22 µg/m$^3$ for Ti. These values, obtained in real time, are significantly below existing recommendations on workplace exposure: 330 µg/m$^3$ for Fe nanoparticles (EU-OSHA [23]) and 60 µg/m$^3$ for Ti nanoparticles (NIOSH [24]). These results are very encouraging and can be still improved by changing the sampling parameters. The LOD will be inversely proportional to the sampling duration for example. We deliberately took the case of real time monitoring here, but this can be discussed. In particular the technical implementation of a filter enrichment over such a short time (1 min) and at a high frequency has to be investigated. On the other hand if we accept a sampling over a day for instance, we can expect an improvement of more than two orders of magnitude in the sensitivity of the detection. LIBS can be implemented in various configurations to answer different types of problems. The results reported here show the possibility to perform real time quantitative measurements of workplace exposure to nanoparticles with a sufficient limit of detection, at least for Fe$_2$O$_3$ and TiO$_2$ nanoparticles, but this approach is not exclusive and can also be extended to other types of nanoparticles.
Figure 4. Average spectra for filters enriched with TiO$_2$ nanoparticles (left) and calibration line of the Ti surface concentration (right). The error bars represent one standard deviation calculated for 11 spectra accumulated over 20 laser shots.

4. Summary

In this paper Laser-Induced Breakdown Spectroscopy (LIBS) is used to make quantitative measurements of the concentration of Fe$_2$O$_3$ and TiO$_2$ airborne nanoparticles. This technique was chosen since it is fast, direct and requires no sample preparation. Nanoparticles were generated by a spark discharge generator or by nebulisation of a liquid dispersion. The approach consisted in sampling the particles on a filter, respectively a mixed cellulose ester membrane and a polycarbonate membrane, and to analyze the filter by LIBS. Then taking into account the sampling parameters (flow, duration, filter surface) we could calculate a detection limit in volume concentration in the atmosphere. With a sampling at 10 L/min on a 10 cm$^2$ filter during 1 min, we obtained detection limits of 56 µg/m$^3$ for Fe and 22 µg/m$^3$ for Ti. These figures, obtained in real time, are significantly below existing workplace exposure recommendations of the EU-OSHA and of the NIOSH. In addition the sampling parameters can be adjusted, particularly the sampling duration, to potentially decrease the detection limit of more than two orders of magnitude. This opens the way to the monitoring of workplace exposure over a longer time scale with a high sensitivity. These results are very encouraging and will be completed in a future work on airborne carbon nanotube detection.

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