

MICROFLUIDICALLY ENABLED HIGH-THROUGHPUT MONITORING OF ENVIRONMENTAL NANOPARTICLES

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ABSTRACT

Increased environmental exposure is an unavoidable consequence of the growing prevalence of nanomaterials, posing new and largely unknown risks to human health. A variety of detection methods allow nanoparticle concentrations to be sensitively measured offline, after sampling has already taken place. But few methods integrate both sampling and detection with sufficient throughput to perform continuous environmental monitoring of room-sized volumes. We describe a new approach that enables continuous environmental sampling of airborne nanoparticles with online detection and quantification of the collected species. Our method achieves orders of magnitude higher analytical throughput than is currently possible by uniquely combining the high flow rate sampling capability of wetted wall cyclone (WWC) collectors (up to > 1,000 L/min) with a microfluidic component that permits sensitive quantitative measurement of nanoparticle concentration. By coupling these components, we demonstrate detection of airborne ultrafine Al₂O₃ nanoparticles at environmental concentrations below 200 µg/m³ in air sampled at a 200 L/min, well within established toxicity limits.

KEYWORDS

Environmental monitoring, nanomaterials, detection.

INTRODUCTION

Efforts to assess safe environmental exposure limits for nanomaterials and establish correlations with potentially adverse health consequences critically depend on the ability to monitor the concentration of airborne nanomaterials. But the current generation of collection and monitoring technology is subject to limitations on throughput that do not permit continuous sampling of room-sized spaces, and analysis is performed offline using separate instrumentation. A key limitation of existing samplers is their ability to access only relatively low air inflow rates (below ~ 30 L/min), restricting analysis to small subsets of the total environment of interest. Rapid analysis is not achievable by these “personal samplers” because time resolution is constrained by the need to collect material over at least a full workday. Additional limitations emerge in terms of detection where a wide range of characterization tools are available but mostly involve methods are not readily adaptable for online use, often requiring a dedicated laboratory infrastructure. These issues suggest a need for integrated approaches capable of (1) continuously sampling large air volumes associated with a realistic workspace environment, and (2) performing real-time detection and analysis of nanoparticles in the sampled air.

EXPERIMENT

We have developed a new approach that overcomes these limitations by coupling the high flow rate air sampling capacity of a wetted wall cyclone (WWC) collector (hundreds to over 1,000 L/min) with a continuous-flow microfluidic component that provides online detection capability (Fig. 1a). The microfluidic approach harnesses the inherently steep chemical gradient established at the interface between co-flowing streams containing a nanoparticle-laden suspension and a fluorescent dye solution [1]. This sharp mismatch acts to localize adsorptive dye-nanoparticle complexation interactions within a narrow interfacial zone, instantaneously producing an intense and easily detectable fluorescence signature. WWC samplers operate by using an air blast atomizer to create a liquid spray that is directed through a rectangular inlet slot and into the cyclone body where the droplets impact on the cylindrical wall. The impacted liquid forms a film that interacts with the high velocity jet of environmental air drawn through the inlet and is transported along the wall to a skimmer. The liquid, containing the collected nanoparticles, is then aspirated by an external pump. The characteristic flow rate of this fluidic output from the WWC (0.04 – 0.2 mL/min) closely matches the operating flow rate of the microfluidic detector, thereby introducing the possibility to enable continuous detection by directly coupling both components. A correlation can then be established between interfacial intensity and the quantity of suspended nanoparticles so that the corresponding airborne environmental concentration can be inferred (Fig. 1b).

Microfluidic networks were constructed in poly(dimethyl siloxane) (PDMS) using standard soft lithography following a previously described procedure [1]. Nanoparticle suspensions were prepared by dispersing commercial nanomaterial powders in deionized water (Table 1) with an appropriate amount of stabilizing surfactant. Uniform dispersal was achieved by performing alternating cycles of 30 min sonication in an ultrasonic cleaner (Model 3510DTH; Branson Ultrasonics Corp.) followed by 20 s of agitation using a digital vortex mixer (Cat. No. 02215370; Fisher Scientific) for at least 3 h prior to each experiment. Standard test suspensions of Al₂O₃ (Fig. 3a) were prepared by dilution from a commercial suspension (NEI Corp., Somerset, NJ) to concentrations in the range of 0.02 – 0.2 wt%. Aqueous fluorescent dye solutions were prepared in deionized water at concentrations selected to provide adequate fluorescence but remain below the solubility limit.

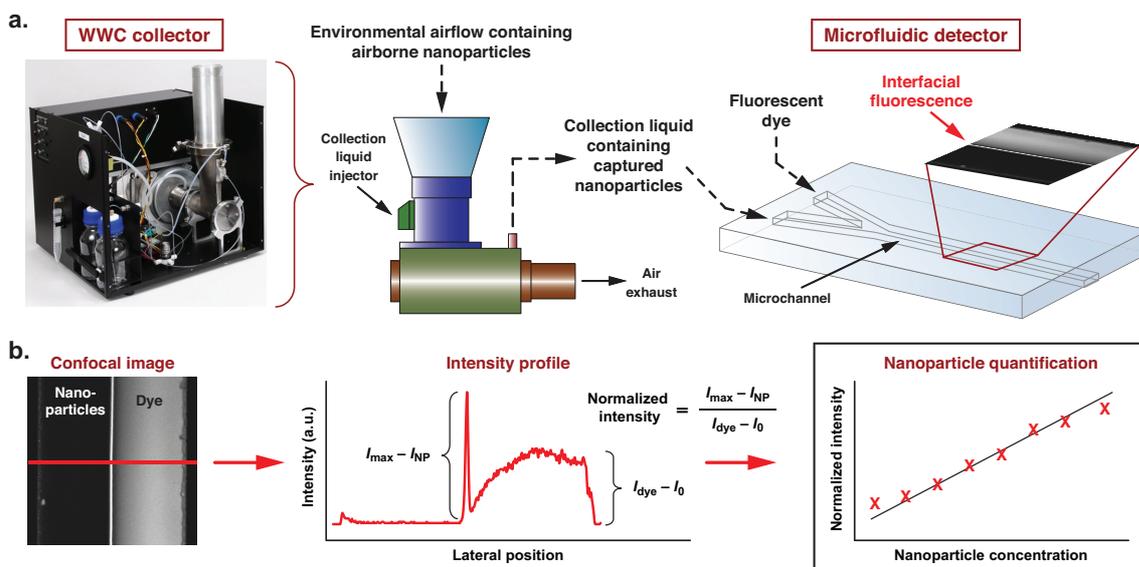


Figure 1. (a) Airborne environmental nanoparticles are collected and concentrated by a WWC, then co-injected into a microchannel in parallel with a tracer dye. A pronounced interfacial fluorescence signature emerges due to local dye-nanoparticle complexation between co-flowing streams in the microchannel. (b) The peak value in the lateral intensity profile is scaled with respect to baseline values in the nanoparticle and dye streams (I_{NP} and I_0 , respectively), yielding a normalized quantity that can be directly correlated with nanoparticle concentration.

Table 1. Summary of nanomaterials employed in our experiments.

Material	Composition	Particle size (nm)	Density (g/cm^3)
Al_2O_3	15 wt% suspension (aq) (Fig. 3)	< 100	4.0
Al_2O_3	Powder (Fig. 2b)	< 50	4.0
TiO_2	Powder	< 25	3.9
Fe_2O_3	Powder	< 50	5.1
CuO	Powder	23-37	~6.4
SiO_2	Powder	10-20	2.2-2.6
ZnO	Powder	< 100	5.6

The nanoparticle suspensions and tracer dyes were co-injected into the inlets of a y-shaped microchannel using a syringe pump (Model KDS-230, kd Scientific Inc.) at flow rates ranging from 0.002 to 0.2 mL/min. Fluorescence images were obtained several minutes after the flow was started to ensure that the flow reached steady state. Image acquisition was performed using a Zeiss LSM 5 Pascal Confocal Scanning Microscope with a Zeiss Plan-Neofluar 10X/0.3 numerical aperture objective interfaced with Canon PowerShot 640 digital camera (4x zoom) and Zeiss LSM 5 software (Release 3.2) as described previously [1]. Imaging was performed along the midplane of the microchannel to minimize sidewall effects.

RESULTS AND DISCUSSION

A surfactant (e.g., 0.1 mg/mL Tween 20) is typically added to the WWC collection liquid to promote uniform particle dispersal in the liquid film and to enhance particle recovery with minimal foaming. We selected fluorescein dye for use in the microfluidic detection component to maintain compatibility with Tween 20 surfactant in the WWC collection liquid. We next examined interfacial fluorescence as a function of particle composition by co-injecting fluorescein dye into the microchannel in parallel with Tween 20-stabilized suspensions of Al_2O_3 , TiO_2 , Fe_2O_3 , CuO , SiO_2 , and ZnO nanoparticles (Fig. 2). Here the molar concentration of each material is held constant based on the formula weight of its constituent molecules. Fluorescence from Al_2O_3 displays a characteristic pattern of focused interfacial intensity accompanied by an adjacent depletion zone in the dye stream, consistent with previous observations [1]. Since the depletion zone enables interfacial fluorescence to be clearly isolated, we selected this formulation for subsequent analysis. Even greater fluorescence enhancements were observed with TiO_2 and ZnO nanoparticles, suggesting the possibility to obtain more detailed characterization.

We characterized interfacial fluorescence intensity as a function of nanoparticle concentration using serial dilutions of a standard test suspension of Al_2O_3 nanoparticles (Fig. 3a). An approximately linear-relationship is maintained at concentrations up to 1.0 and 1.2 wt% at a flow rates of 0.2 and 0.02 mL/min, respectively, with fluorescence becoming saturated at concentrations beyond these limits. Interfacial fluorescence is enhanced at slower flow rates, yielding a detection limit of ~ 0.02 wt% at 0.02 mL/min. Since the standard test suspension is primarily composed of sub-100 nm nanoparticles, this fluorescence signature is attributed to particles in the ultra-fine size range.

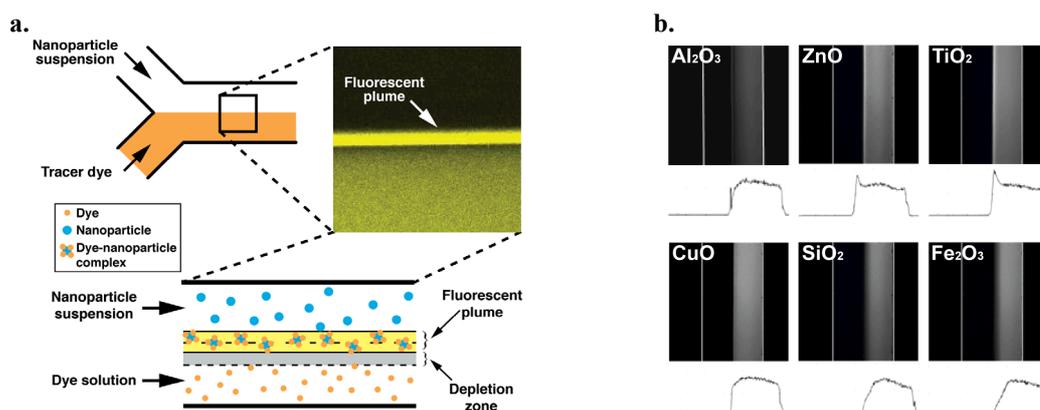


Figure 2. (a) Al_2O_3 nanoparticles (upper stream) exhibit intense interfacial fluorescence enhancement upon complexation with fluorescein (lower stream). This effect is governed by the rate of dye-nanoparticle complex formation relative to lateral dye diffusion. (b) Material dependence of the interfacial fluorescence between the nanoparticle suspension and tracer dye enables simultaneous online detection and speciation. Upper panels show images of co-flowing nanoparticle (left) and fluorescein (right) streams. Lower panels show the cross-sectional normalized intensity profile. The material-dependent nature of the interfacial fluorescence introduces the possibility of exploiting this phenomenon as a fingerprint to enable on-line speciation.

To demonstrate potential for integrated sampling and detection, we used the low cutpoint WWC to collect Al_2O_3 nanoparticles aerosolized from test suspensions and dispersed into an environmental chamber (Fig. 3b). Sampling was performed at a 200 L/min air inflow rate. The WWC collection liquid containing the sampled nanoparticles suspended in 0.01% Tween 20 was then co-injected into the microchannel in parallel with a 0.033 mg/mL fluorescein solution. The fluorescence images display the same characteristic features observed in the standard test solutions, and an approximately linear relationship between intensity and nanoparticle concentration is maintained. We used a scanning mobility particle sizer (SMPS) and gravimetry to quantify the concentration and size distribution of aerosolized nanoparticles inside the environmental chamber, and correlate them with the interfacial fluorescence intensity observed in the microchannel detector. These results indicate that the microfluidic approach is capable of detecting Al_2O_3 nanoparticles in the ultra-fine size range (4 – 160 nm) at environmental concentrations below $200 \mu\text{g}/\text{m}^3$, in the vicinity of established toxicity limits. This microfluidically enabled approach offers a useful tool to establish detailed occupational exposure profiles not easily obtainable using current-generation personal sampling instruments.

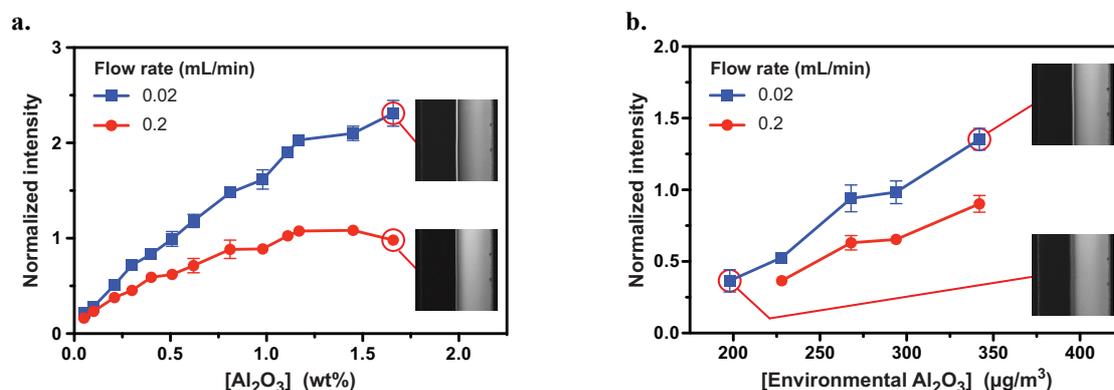


Figure 3. (a) Al_2O_3 concentration versus peak lateral intensity at dye nanoparticle interface in the microchannel detection component (mean particle size < 100 nm) (b) Correlation between interfacial fluorescence signal and environmental nanoparticle concentration in the sampled air using SMPS, indicating a detection limit below $200 \mu\text{g}/\text{m}^3$. Al_2O_3 samples were collected by the low cutpoint WWC at 200 L/min. All suspensions are mixed with 0.1 mg/mL Tween20 and co-injected in parallel with a 0.033 mg/mL fluorescein solution.

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