Lanthanide Doped Silica Nanospheres Surface Sampling in Deposition Studies

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Abstract

The overall objective of our research is to determine the degree of surface deposition resultant from the aerosolization of a solid or dusty material. Current methods for measuring the amount of deposited material require extraction of material from the surface, a process which involves manipulations that can disturb the settled material. In order to facilitate more reliable measurements of the amount of aerosol deposited, we have developed a model system of silica nanospheres, of known size and shape, with a lanthanide element incorporated into the spheres. The lanthanides we have chosen to work with are europium, terbium, and samarium, elements whose fluorescence spectra are well characterized. Addition of the lanthanides to the silica nanospheres allow fluorescence surface sampling to be performed after deposition, permitting measurement of the material without risk of disturbance or dislodging due to movement during traditional surface sampling techniques. Preliminary measurements of the 200 nm Eu-doped spheres have shown the fluorescence intensity to be linear (R = 0.9998) over 0.1 µM to 100 µM concentrations of the doped spheres in isopropyl alcohol. Results have also indicated that detection of the spheres is more sensitive for surface sampling than in solution. Use of multiple lanthanides allows for different doping for specific particle sizes. Based on particle size distribution data collected for agent aerosols, several different sizes of the lanthanide doped spheres can be mixed together to represent an aerosolized threat, with respect to the deposition hazard. Data collected from such experiments can be used in current hazard prediction models.

Motivation

Current methods for predicting the outcome of a release utilize data and source terms based on ***some*** similarities between traditional and emerging threats. The reality is that empirical data of very necessary parameters for emerging threats has yet to be measured. In fact, the data that is available for defining parameters is likely the byproduct of simulant studies that may or may not be relevant to the physical properties of the emerging threats. In order to perform meaningful deposition studies, especially above laboratory scale (e.g., wind tunnels, ambient breeze tunnels), a simulant must be identified. The intent of this work is to select such a simulant that matches the deposition properties of the agent, along with being differentiable from background species, and safe for outdoor/large scale releases.

Objectives

1. Perform agent studies to characterize the aerosol state with respect to pertinent physical properties (i.e., those which impact deposition).
2. Identify an appropriate simulant for wind tunnel and ambient breeze tunnel (ABT) releases.
    1. Selection was made based on properties measured of the agent aerosol.

Aerosol Characterization

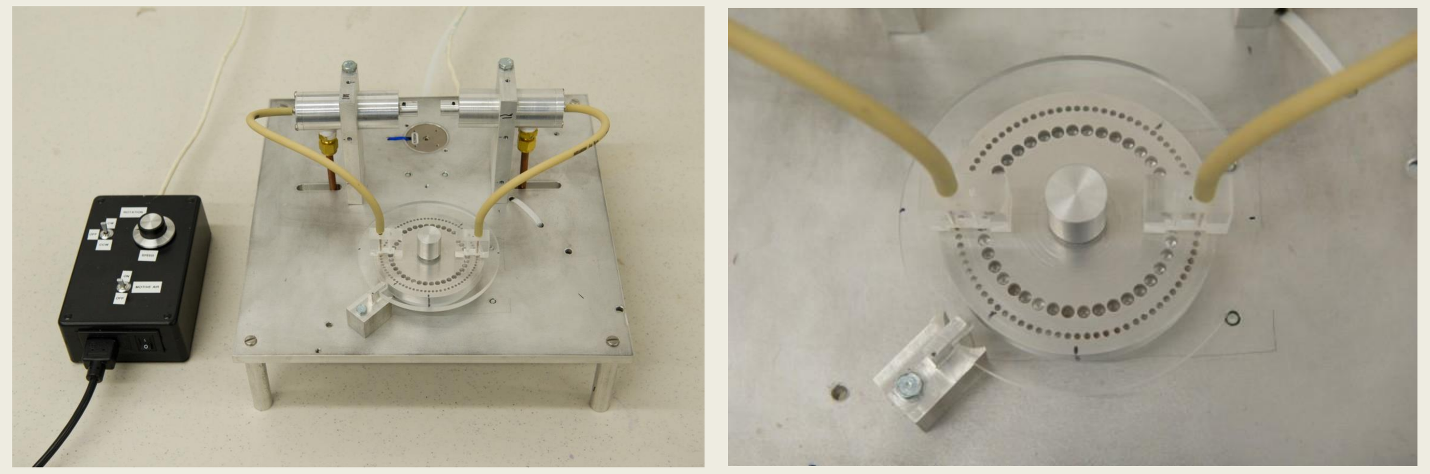


Figure 1. The device used for aerosol generation is shown above. The low volume powder disperser (LVPD) was designed and built at ECBC and creates an aerosol sample of either a solid or dusty sample via an expulsive technique.

The aerosol challenges were generated using a low volume powder disperser (LVPD). The internally designed device is very efficient at aerosolizing solid and dusty material. The two sonic jet nozzles use the Venturi effect to pick up the material from the sample wells in the spindle and expel it. The aerosols are generated via sheer forces applied in the nozzles. The sheer forces can be varied by adjusting the pressure of the compressed air through the device. The LVPD effectively deagglomerates the material, a feature that allows us to determine the native size of aerosol particles.

Simulant Selection

Based on the measured properties of the agent aerosols, a commercially available simulant was chosen for development. The simulant, Angströmspheres™, are silica spheres, produced in specific size ranges (0.1 to 10 µm), with < 10% variation in size and are perfectly spherical in shape. The material comes in dry powder form and so it can be aerosolized from this state, much like the solid/dusty material we are trying to simulate. The most appealing feature of this simulant is our ability to modify it. In order to perform deposition studies, we must be able to distinguish our deposited material from background signals, as well as determine the impact of particle size on the degree of deposition. In order to implicate this control, the simulant was modified with various lanthanides, imparting fluorescence properties on the silica spheres.

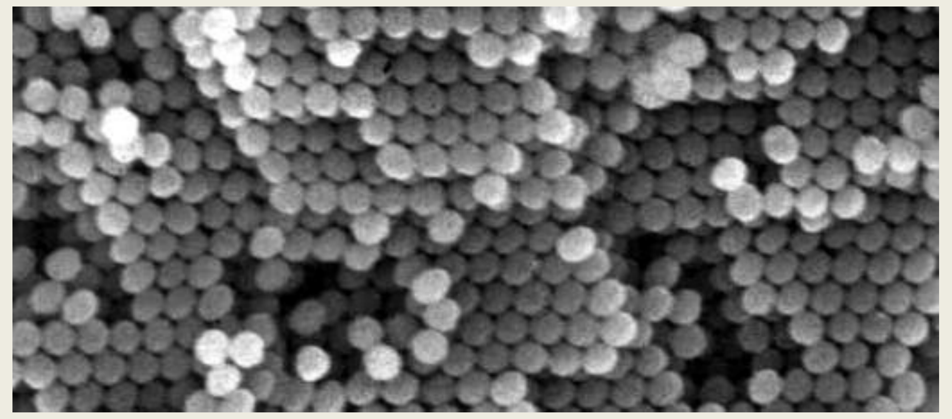


Figure 2. The simulant chosen for development is Angströmspheres™. The material is comprised of silicon dioxide providing the properties of amorphous silica along with unique control of duplication, both in form and particle size.

Simulant Characterization

Initial doping of the spheres was done with Europium (Eu). The intent was to ensure that incorporation of the lanthanide allowed us to distinguish the undoped silica spheres from the modified samples. Dry powder, of both the modified and unmodified spheres, was exposed to short wavelength UV excitation (254 nm). As shown in Figure 3 (top left), the spheres with Eu incorporated into the material exhibit two distinct bands, providing for easy distinction from the undoped material. The spheres were also investigated for their ease in surface sampling, a necessity for aerosol deposition studies. The surface detection, shown in the top right of Figure 3, displays all 3 peaks expected for the Eu 4f transition.

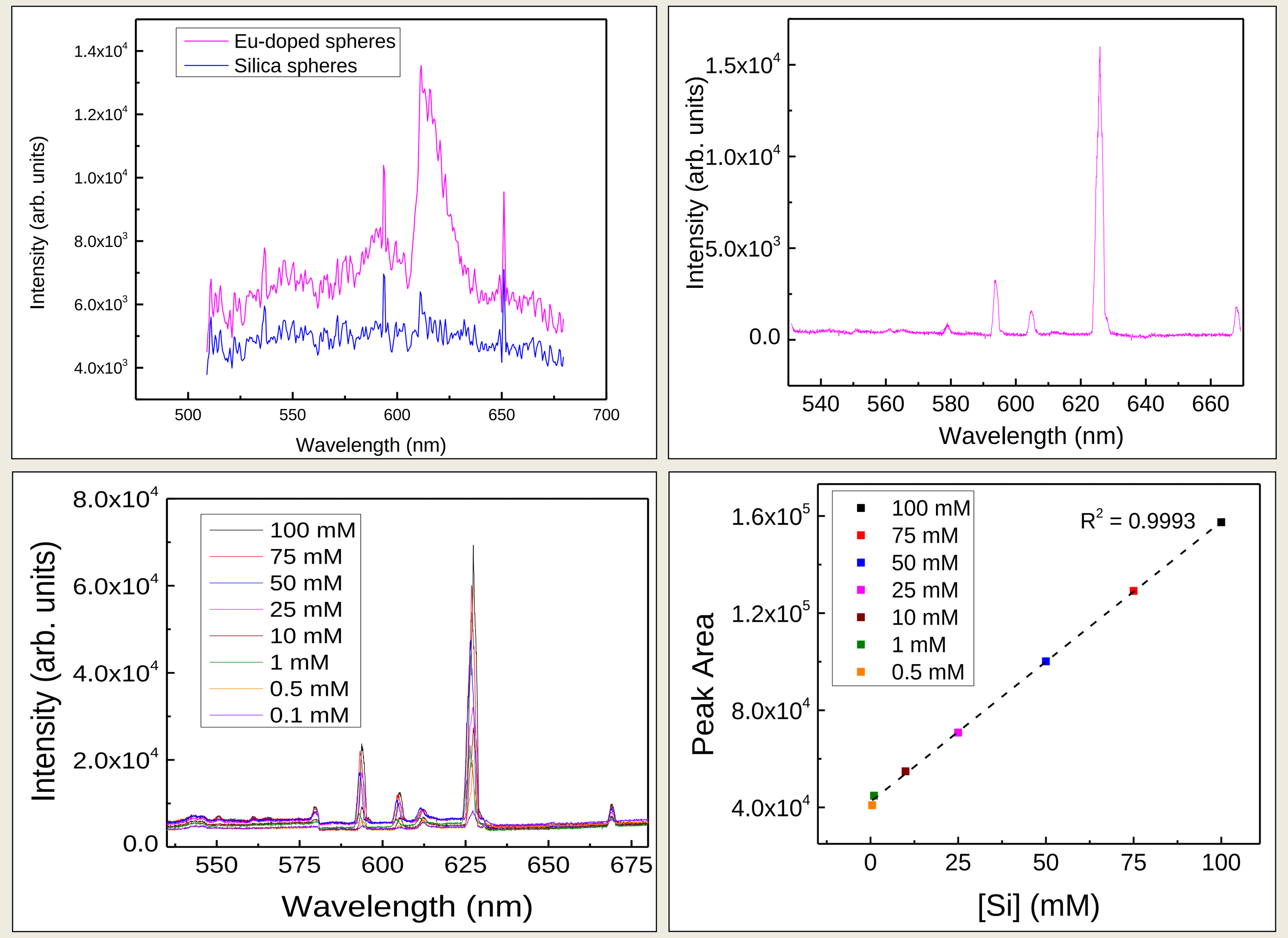
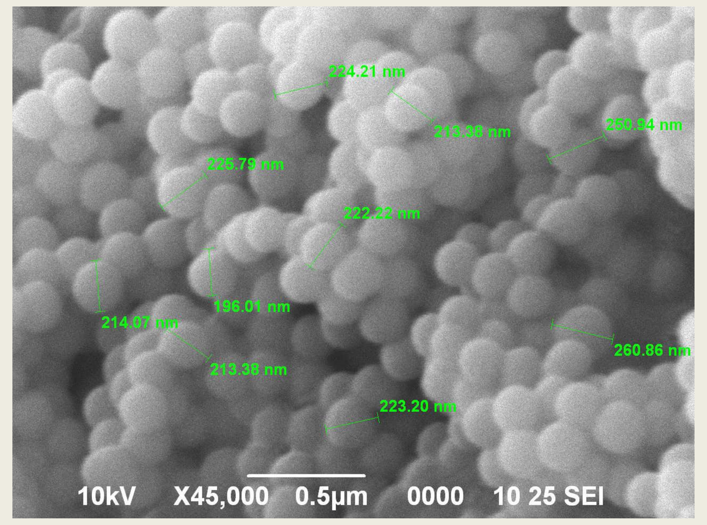


Figure 3. The top left displays the comparison of the Angströmsphere ™ dry powder, doped vs. undoped. The top right spectrum was collected from Eu-doped spheres deposited on a glass surface. The bottom graphs show the calibration curve created for the surface detection of the 200 nm Eu-doped spheres.

The final graphs in Figure 3 (bottom) represent the surface calibration curve for the 200 nm Eu-doped spheres. The LOD for these spheres on a surface is ~ 0.5 mM or several hundred ppb of Eu. Understanding the sensitivity of the spheres detection will be imperative for planning large scale disseminations; for example in wind tunnels and the ABT.

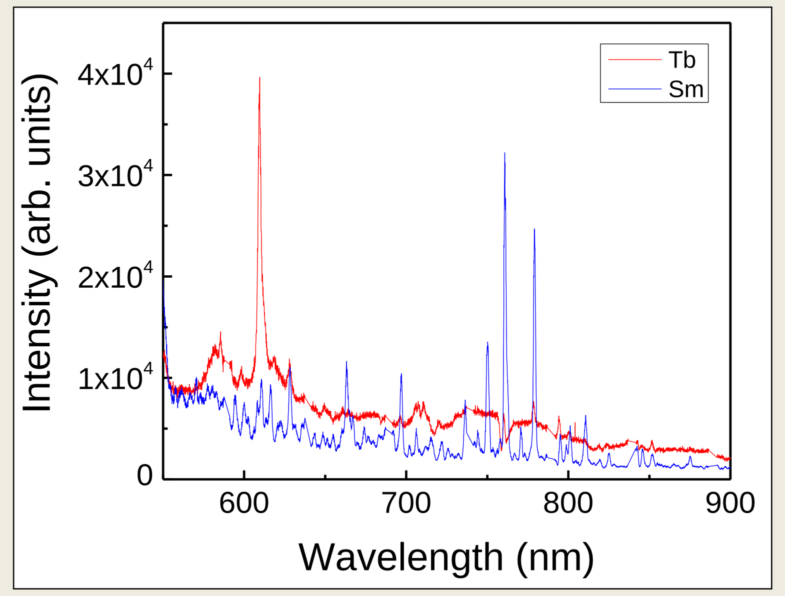
Particle Size and Varying Dopant

The size of the modified spheres was also considered. The size of the simulant was very important, as it had to replicate the size of the agent aerosols. To confirm that the lanthanide incorporation did not impact the overall size of the spheres, SEM was performed on the doped material. As shown in Figure 4, the lanthanide doped spheres do not deviate from the < 10% variation in size.



<-- Figure 4. SEM image of the 200 nm Eu-doped spheres. The inclusion of Eu does not appear to impact the overall size distribution of the material.

--> Figure 5. The spectra show the distinct differences in the fluorescence responses for Terbium and Samarium.



The spheres were also modified with Terbium and Samarium. Figure 5 shows not only the adequate incorporation of these lanthanides but also the distinctly different spectra associated with each one. The utilization of several lanthanides allows us to make a more realistic sample. While every material, once aerosolized, has a native particle size, the resultant aerosol always exhibits a distribution of particle sizes. With the ability to dope different size Angströmspheres™ with different lanthanides, we can create a mixed aerosol challenge and determine how different size particles deposit after a release. The impact of various factors can be explored; such as, material type, surface roughness, and wind speed.

Future Work

The final studies performed with these materials will involve their expulsive dissemination in wind tunnels and the ABT. They have also been utilized for test and evaluation purposes in order to assess a new technique for uniform deposition of aerosolized solid and dusty material. This technique will be vital in the work done to gauge currently fielded and newly developed decontamination methods.

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