

## Towards single particle surface analysis using fluorescence labelling

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In surface science there are a wide variety of methods used for identification and quantification of functional chemical groups. Xing and Borguet (2007) amass detection limits of different methods: fluorescence labeling  $10^{-5}$  molecules/nm<sup>2</sup>, X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy (IR)  $10^{-2}$  molecules/nm<sup>2</sup>, time-of-flight secondary ion mass spectrometry (ToF-SIMS)  $10^{-1}$  molecules/nm<sup>2</sup>. Our idea is to apply the fluorescence labeling method in real time aerosol particle surface analysis of the functional groups. One of the key questions is whether the fluorescent label material can be detected at low enough concentrations on the surfaces of airborne particles.

A laboratory setup was constructed to analyze the sensitivity of the method. A tailor-made optical chamber was used for scattering and fluorescence measurement from individual test particles. Wide collection solid angle optics with a dichroic mirror and a long-wave-pass optical filter enabled the measurement of scattering and low intensity fluorescence separately. The light detectors were photomultiplier tube modules (PMT). The excitation light source was a blue laser diode of 405 nm wavelength and 60 mW maximum output power. It was driven in the continuous wave mode. The signals from the PMTs were measured by two pulse height analyzers and saved to a PC. The test aerosol size distribution was measured by TSI APS 3321 aerodynamic particle sizer.

The test aerosol was made by coating monodisperse silica or polystyrene latex particles with different fluorescent dye surface concentrations using a custom-made ink jet aerosol generator. The silica particles were 1.2  $\mu\text{m}$  in diameter and polystyrene latex 5.0  $\mu\text{m}$ . The fluorescent dye was riboflavin-5'-phosphate monosodium salt (FMN). The dye surface concentration on the particles was varied from 1 to 200 molecules/nm<sup>2</sup>. The scattering and fluorescence signals were measured from 5 000 individual particles per each dye concentration.

In the figure 1 the fluorescence geometric mean signals are shown as a function of the dye surface concentration on the test particles. The error bars are the geometric standard deviations of the fluorescence signals. For the silica particles fluorescence signal depends on the dye concentration linearly in logarithmic scale. The slope given by the

least squares method is 1.2 as it was expected to be close to 1. The lower detection limit was 5 molecules/nm<sup>2</sup> and the highest measured concentration about 200 molecules/nm<sup>2</sup>.

For polystyrene latex particles the fluorescence signal depends on the dye concentration almost linearly in logarithmic scale. If seven of the highest dye concentrations are considered, the slope given by the least squares method is 0.9. The pure polystyrene latex particles absorb some blue light and fluoresce by themselves also. The effect of this autofluorescence can be seen on low surface concentrations. The lower detection limit was 1 molecules/nm<sup>2</sup> and the highest measured concentration about 200 molecules/nm<sup>2</sup>.

The detection limit was higher compared to the methods in surface science. However, if autofluorescence does not occur, it is possible to improve the sensitivity substantially e.g. using a more intense laser or even a pulsed laser as done by Agranovski *et al.* (2004) when testing the performance of the UVAPS using e.g. riboflavin dye. They were able to detect the amount of  $10^{-17}$  g riboflavin in particles of 1.7  $\mu\text{m}$  in diameter compared to  $10^{-14}$  g FMN detected on the surface of 1.2  $\mu\text{m}$  particles in this work.

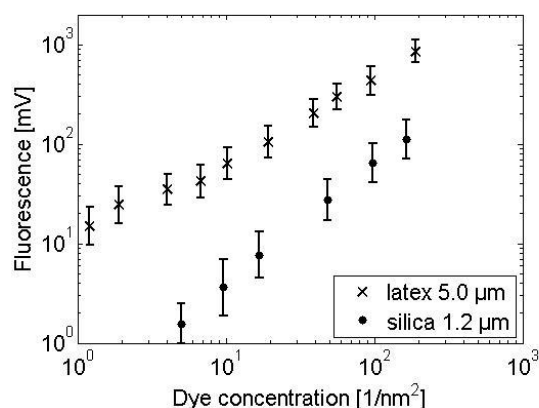


Figure 1. Fluorescence signal as a function of the dye surface concentration on the test particles.

Xing, Y. & Borguet, E. (2007). *Langmuir*, 23, 684-688.

Agranovski, V., Ristovski, Z. D., Ayoko, G. A. & Morawska, L. (2004). *Aerosol Science and Technology*, 38, 354-364.