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X-ray absorption measurements on an ultrasonic spray aerosol

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Spray deposition of thin films and coatings is a widely used manufacturing process owing to its low cost, versatility and simple implementation. The objective of the presented experiments was to investigate whether X-ray absorption measurements on solutes carried by aerosols are possible, and what count rates can be achieved depending on solution flow through and the resulting mass density in the interrogation volume. The investigated prototypical spray aerosol was $InCl_3$ dissolved in water or ethanol dispersed *via* an ultrasonic nebulizer. $InCl_3$ spray is essential for the ion layer gas reaction process used for the deposition of In_2S_3 buffer layers for highly efficient chalcopyrite solar cells. The discussed experiments demonstrate that measurements are possible, but that the achievement of good signal-to-noise ratios requires extended sampling times and concentrated solutions.

Keywords: X-ray absorption; spray deposition; solute signal; aerosol.

1. Introduction

Spray processes are a versatile, cost-effective and relatively simple manufacturing method in many industries. Most materials that can be dissolved in a compatible solvent can be sprayed. Rational optimization of spray processes requires a detailed understanding of the spray aerosol. Optical techniques are the obvious choice for spray characterization owing to the easy interaction of photons and aerosols. There have been a number of investigations of spray plumes in the past using techniques like high-speed photography (Shao *et al.*, 2003; Esmail *et al.*, 2010; Kostas *et al.*, 2011), anemometry (Sommerfeld, 1998; Liu *et al.*, 2010) or laser fluorescence spectroscopy (Zhou *et al.*, 1999). In such experiments one needs to distinguish between the investigation of the kinetic physical behavior of entire droplets (*e.g.* size reduction, velocity, spray pattern *etc.*) *versus* processes that affect the solute (*e.g.* chemical reactions, adductions, *etc.*) and occur inside droplets. The experiments presented here aimed to assess the potential of X-ray absorption spectroscopy measurements to characterize processes occurring within droplets, with a focus on the solute. The investigated system was $InCl_3$ dissolved in water or ethanol. This material system was selected on one hand owing to the relatively strong absorption of the In *K*-edge at about 28 keV, well suited for the X1 beamline at DESY Hamburg, while also being a system of particular interest owing to the demonstrated success of the ion layer gas reaction (ILGAR) spray technique for the deposition of In_2S_3 buffer layers for $CuInS_2$ solar cells (Fischer *et al.*, 2011).

2. Experimental

Details of the experimental set-up are provided as supplementary material.[1] In short, the experiments were performed at the Hamburger Synchrotronstrahlungslabor (HASYLAB) at the Deutsches Elektronen-Synchrotron (DESY). The bending-magnet-based X1 beamline was used for the experiments. It has a photon flux of the order of 10^9 photons s^{-1}. The ultrasonic spray system has been described elsewhere in detail (Allsop *et al.*, 2006). The inset in Fig. 1 shows a schematic of the essential parts. Briefly, a commercial household nebulizer was used to nebulize the $InCl_3$ solution. Three solution concentrations of 50, 100 and 200 mmol L^{-1} were used for the experiments. The aerosol formed in the nebulizer chamber was extracted through a continuous N_2 flow. A 1.7 cm-long section of a plastic tube channeling the aerosol to the beam path was partially removed to create an unobstructed path for the X-ray beam uninhibited by aerosol condensate, which usually forms on the inner tube walls. The nebulizer transducer amplitude could be adjusted on a scale from 1 to 10 (arbitrary units), which had a strong influence on the aerosol formation rate. The XAFS spectra were measured in fluorescence yield mode. Scans were made between 27.8 keV and 28.1 keV with varying step size (pre-edge: 5 eV; edge: 0.5 eV; post-edge: 1.0 eV). The accumulation time per point was 1 s. The resulting

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: HF5194). Services for accessing these data are described at the back of the journal.

Table 1
Nebulization rate of solution, In mass flow and In mass density in aerosol depending on N_2 gas flow and nebulizer setting.

All mass values are based on a solution concentration of 100 mmol L^{-1} InCl.

	N_2 gas flow					
	1.0 L min^{-1} (= 16.7 cm^3 s^{-1})			1.9 L min^{-1} (= 31.7 cm^3 s^{-1})		
Nebulizer amplitude (a.u.)	Nebulization rate of solution (cm^3 min^{-1})	In mass flow (μg s^{-1})	In mass density (μg cm^{-3})	Nebulization rate of solution (cm^3 min^{-1})	In mass flow (μg s^{-1})	In mass density (μg cm^{-3})
1	0.15	28.6	1.72	0.5	95.7	3.02
4	0.25	47.8	2.87	0.75	144	4.55
8	0.45	86.1	5.16	1.05	201	6.35

data were evaluated using the *Athena* program within the *iXAFS* package (Newville, 2011). The spectra measured on a particular sample were added up, then normalized and the background removed following standard procedures.

3. Results and discussion

The objectives of the experiments were to demonstrate measurements on aerosol plumes, and to determine quantitative fluorescence photon count rates depending on the incident primary photon flux, as well as the mass density of the solute dispersed in the aerosol. Fig. 1 shows two exemplary spectra measured on the $InCl_3$ aerosol at minimum and maximum In mass density conditions in the aerosol. The bottom spectrum was integrated for about 1 h on a 50 mmol L^{-1} solution dispersed at the lowest nebulizer and N_2 gas flow settings (nebulizer: 1; N_2: 1.0 L min^{-1}). The top spectrum was achieved using a 200 mmol L^{-1} solution and running the nebulizer at level 8 near the maximum of its output range. The same gas flow of 1.0 L min^{-1} was used for this experiment. The integration time was about 4:45 h.

The In mass density in the aerosol can be estimated by calculating the In mass introduced into the N_2 gas flow, and dividing it by the gas volume flowing through the system per time unit. Table 1 gives the nebulization rates depending on the nebulizer setting (1, 4 and 8) and the N_2 gas flow (1 and 1.9 L min^{-1}). The six combinations enabled the investigated nebulization rates ranging from 0.15 to 1.05 ml min^{-1}. In combination with the three solution concentrations these rates led to an investigated In mass density range of 0.86 to 10.3 μg cm^{-3}.

Fig. 2 shows the fluorescence count rates at the absorption edge depending on the In mass flow. The circles, squares and triangles correspond to measurements made on aerosols generated from the 50, 100 and 200 mmol L^{-1} solutions under the three nebulizer settings and the two N_2 gas flows (200 mmol L^{-1} experiments were only carried out at 1.0 cm^3 min^{-1} N_2 flow). The rates are given normalized to an incident primary photon flux of 1×10^9 photons s^{-1}. The graph shows a directly linear dependence between In mass density and fluorescence count rates, as would be expected. The line fit yielded an average count rate of 293 Hz per 1 μg cm^{-3} density increment at a standard deviation of 25.5 Hz. The two deviating count rates at 3.4 and 5.16 μg cm^{-3} mass density are probably a result of the variability of the pump flow adjustment, which was adjusted on sight to obtain a smooth-looking aerosol flow across the measurement gap in the delivery tube. An estimation of the theoretically expected count rate assuming a detector area that subtended approximately 1.4% of the solid angle of a sphere at the given probe volume-to-detector distance of 5.6 cm yielded a maximally possible count rate of 958, *i.e.* the measured count rate is about three times weaker than this estimation. The reasons for this discrepancy lie mostly in the semicircular cross section of the probed aerosol stream (the above calculation assumed a 1.7 cm-long path through a homogeneous medium of constant mass density), the fact that a small fraction of the beam covered a volume

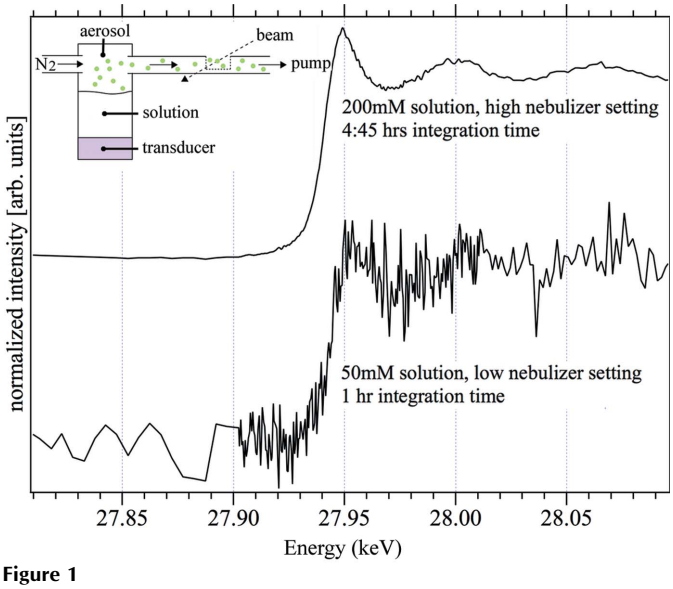

Figure 1
X-ray absorption spectra measured on $InCl_3$ solution-based aerosol produced *via* ultrasonic nebulization combined with a N_2 gas flow. The two spectra show the extremes encountered during the exploration of a range of In mass densities in the aerosol. The bottom spectrum corresponds to the lowest density investigated. The aerosol was produced at the lowest nebulizer setting, lowest gas flow, and a 50 mmol L^{-1} solution concentration. The top spectrum was measured on the aerosol with the highest density, which was produced at the highest nebulizer setting, the highest gas flow, and a 200 mmol L^{-1} solution concentration. Inset: schematic of the experimental set-up.

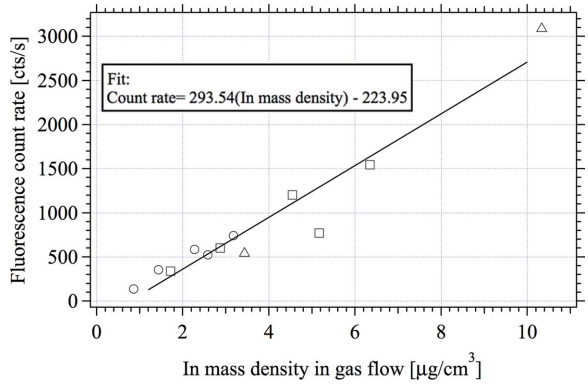

Figure 2
Fluorescence count rates depending on the In mass density measured in 12 experiments covering a variety of nebulizer settings and gas flows. Solution concentrations covered 50 (circles), 100 (squares) and 200 mmol L^{-1} (triangles). The data points confirm a linear dependence of the absorption on the mass density. The fit showed that a fluorescence signal of 293 Hz resulted per incremental 1 μg cm^{-3} of In density. This signal is about two times lower than the expected intensity, which is probably related to aerosol dispersion after leaving the feeding tube.

outside the tube cross section, and the fact that the higher gas flow at the exit of the tube cut-out draws in air from the surrounding volume, hence diluting the aerosol in the probed volume.

The described experiments suggest that a count-rate increase is desirable for future experiments. In this context the use of higher X-ray intensities immediately comes to mind. However, the experiments indicate that this may be problematic owing to the scattering background from the air and solvent matrices. It was not possible to position the fluorescence detector as close to the interrogated volume as spatially possible since detector overload would occur. The detector had to be retracted until the overload was reduced to a normal signal. This indicates that simply using higher-intensity X-ray beams will not yield a better signal-to-noise ratio. It appears that the only way to improve the signal would require the use of band-pass filters suitable for the edge to be measured, or the use of a detector coupled with a monochromator to block most of the background signal. It can be expected that such a set-up can increase the signal-to-noise ratio by a factor of ten or better.

4. Conclusions

XAFS measurements were performed on aerosols dispersed *via* ultrasonic nebulization from $InCl_3$ solutions. A range of solution concentrations and gas flows were explored, and the absorption at the In *K*-edge was measured *via* fluorescence detection. A linear correlation between the determined In mass density in the aerosol stream and the measured fluorescence signal was found. A comparison with theoretical absorption rates indicated that the measured signal is about three times weaker than would be expected solely based on the aerosol mass density. This discrepancy is mainly a result of the dilution of the aerosol stream by ambient air in the interrogation volume. These experiments demonstrated that solutes in aerosols can be investigated with X-ray absorption measurements using fluorescence detectors. However, owing to the very low mass density of the solutes in aerosols the signal is weak and requires fairly long integration times and high solution concentrations combined with substantial aerosol densities. It is reasonable to assume that a magnitude or more signal-to-noise improvement could be achieved by using band-pass filtered detectors.

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