Supplementary information: Surface composition of size-selected sea salt particles under the influence of organic acids studied in situ using synchrotron radiation X-ray photoelectron spectroscopy

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1   Aerosol size distribution

Figure presents the number size distributions of the studied aerosol particles with log normal fit results. Figure 2 shows a collection of photos presenting the experimental setup used in the experiment.
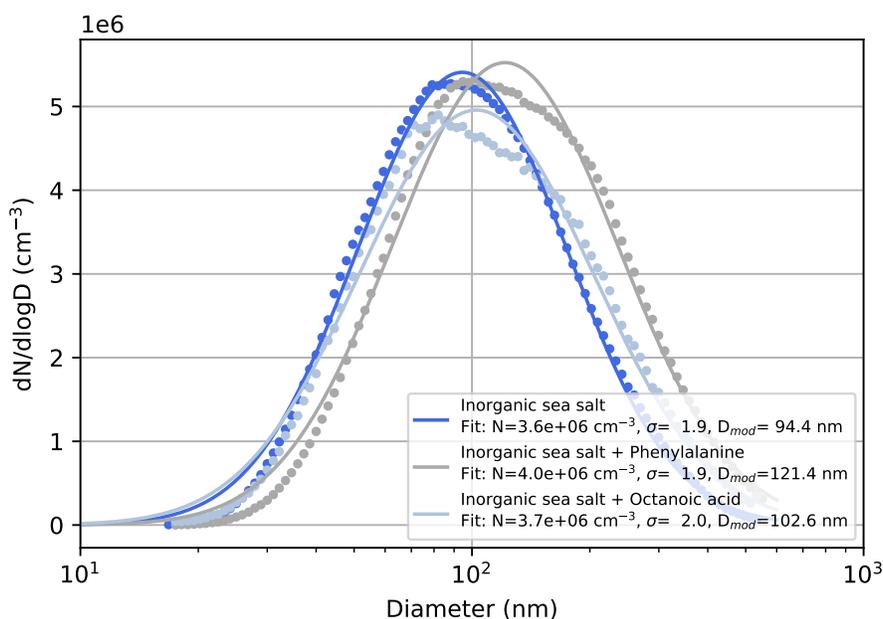
Figure 1 Number size distribution vs. electrical mobility diameter measured by the scanning mobility particle sizer (SMPS) of sea spray particles generated by the TSI 3076 aerosol generator. Single lognormal fits to these data are also presented.
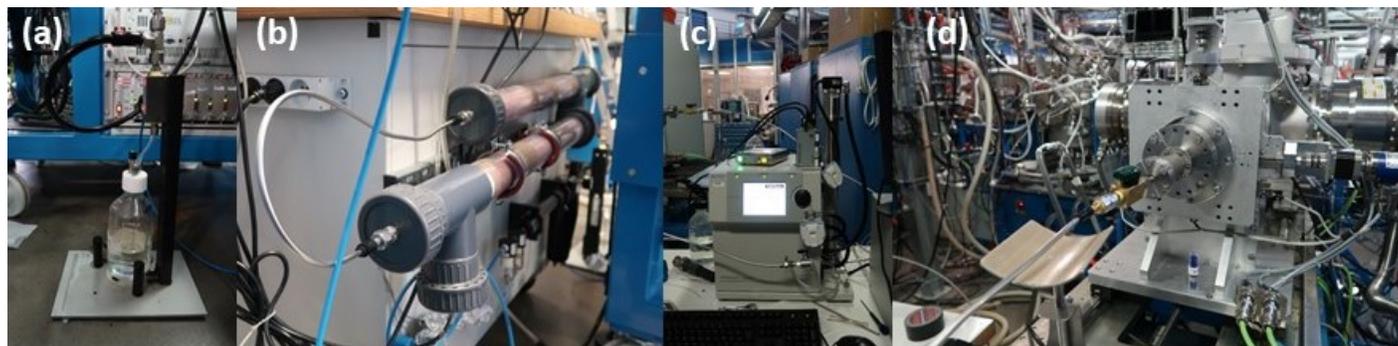
Figure 2 Images of the experimental set-up at the PLEIADES beamline used during the experiment. **(a)** Aerosol generator **(b)** Silica gel diffusion driers **(c)** Aerosol classifier **(d)** Entrance to XPS detection chamber.

2   Details of XPS measurements and data analysis

Table 1 presents an overview of the collected spectra and number of individual acquisitions (sweeps) the XPS measurements consist of. Each sweep took approximately 30 s. The photoelectron spectra were recorded in short sequences of 2 to 12 sweeps per level so that possible fluctuations in the intensity of the nanoparticle beam would not affect the final intensity ratios between the levels. Figure 3 gives an overview of the photoelectron spectra of studied core levels from measurement of aerosol particles generated from pure sea salt solution. The O 1s level (Fig. 3 (c)) shows a signal mostly from gas phase water, which we can separate from the particle signal by looking at the electron analyser's detector image (Fig. 3 (d)). In the detector image, aerosol particles focused by the aerodynamic lens appear in the center of the detector (in y-direction) while non-focused gas phase molecules result in a line over the whole detector[1]. Si 2p level was measured to confirm that there is no contamination from silica dryer or conductive silicone tubing[1]. We mostly used stainless steel tubing and the length of the conductive silicone tubing was kept minimal, and no contamination was observed.

Table 1 Number of sweeps in each of the samples per core levels.

Aqueous solutions	Levels measured	Particle size			
		Polydisperse	350 nm	250 nm	150 nm
Pure sea salt	Mg2p	10	80	47	52
	Cl2p	10	160	83	98
	C1s	10	80	47	52
	O1s	12			
	Ca2p	8			
	S2p	8			
	Si2p	8			
	Na2s	8			
Sea salt + phenylalanine	Mg2p	10	150	70	39
	Cl2p	20	150	70	130
	C1s	20	150	70	39
	Na2s	10			
Sea salt + octanoic acid	Mg2p	10	74	35	39
	Cl2p	10	178	84	130
	C1s	10	80	35	39
	Ca2p	10			
	Na2s	10			
	S2p	10			

XPS spectra were analysed using the Igor Pro software (WaveMetrics), with a least-squares curve fitting package SPANCF[2–4]. An independent analysis was carried out also using routines developed by Stephan Thürmer. Figure 4 presents examples of the fits performed with SPACNF for polydisperse particles. The energy difference of spin-orbit components $2p_{1/2}$ and $2p_{3/2}$ (1.60 eV and 0.28 eV for Cl and Mg, respectively) and their intensity ratio (1:2) were kept fixed in all fits. For the analysis of C 1s spectra, the highest statistics polydisperse particle spectra were fitted first, determining the energy

separation of C 1s signal from different functional groups for the fits of size selected particles. It was noticed that there was some small gas phase C-containing contamination in the experimental chamber, independent from the particle beam (shown in Fig. 6. The contamination spectrum was fitted with two peaks and these peaks with the same intensity ratio and energy separation were also fitted to all particle spectra. There was a non-linear background in the Mg 2p spectra due to overlapping transitions in the N_2 carrier gas. This background was recorded without particles by adding a filter before the flow limiting orifice. The background was then subtracted from the Mg 2p spectra before the curve fitting.

References

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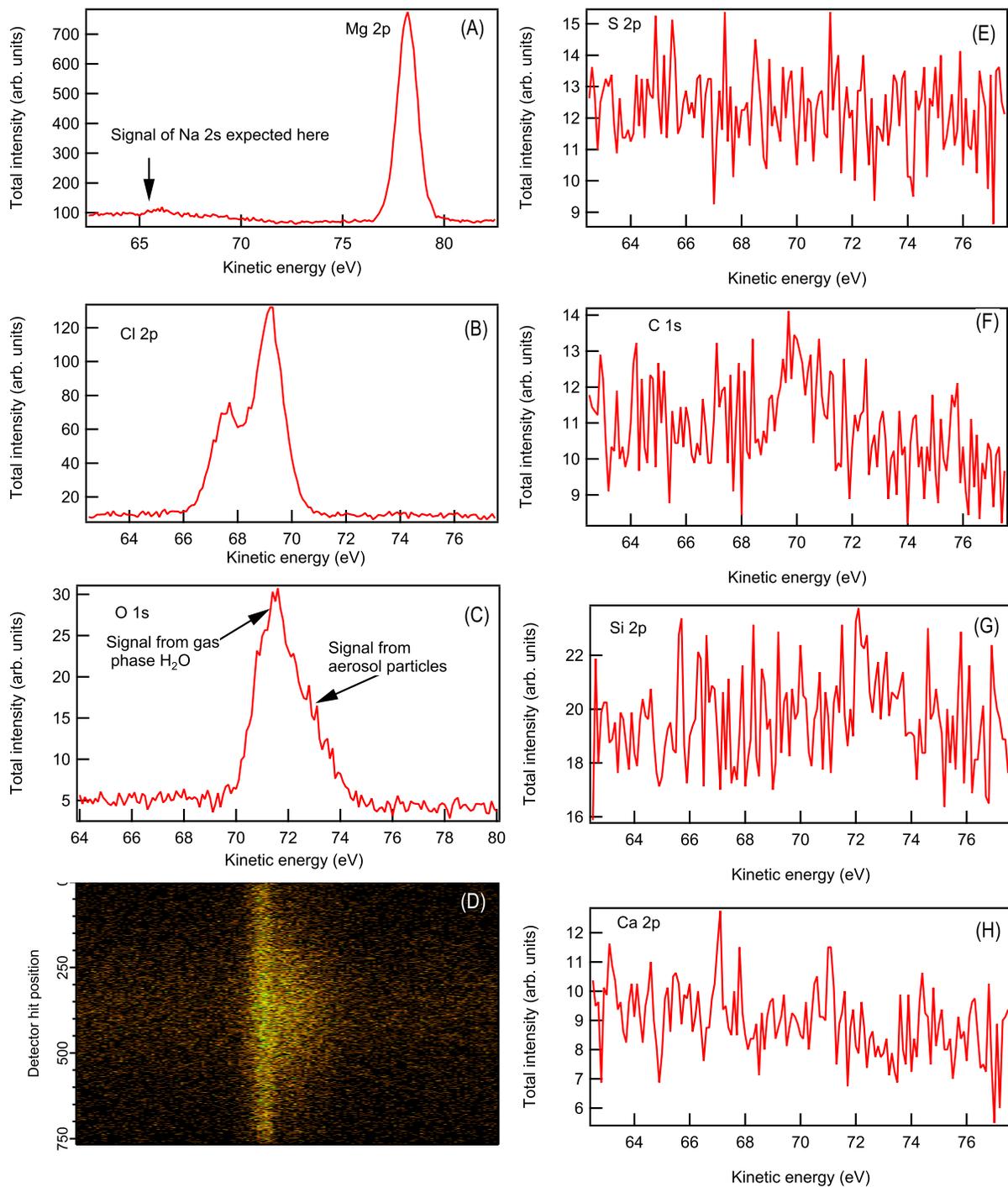
Figure 3 Total photoelectron spectra of different core levels of polydisperse sea salt experiment. **(a)** Na 2s and Mg 2p (recorded with photon energy $h\nu = 135$ eV) **(b)** Cl 2p ($h\nu = 273$ eV) **(c)** O 1s with contributions from gas phase water and particles indicated ($h\nu = 610$ eV) **(d)** Detector image of the O 1s acquisition showing the gas phase signal extended over the whole detector in y-direction, while particle signal is centered. **(e)** S 2p ($h\nu = 230$ eV) **(f)** C 1s ($h\nu = 360$ eV) **(g)** Si 2p ($h\nu = 180$ eV) **(h)** Ca 2p ($h\nu = 424$ eV).

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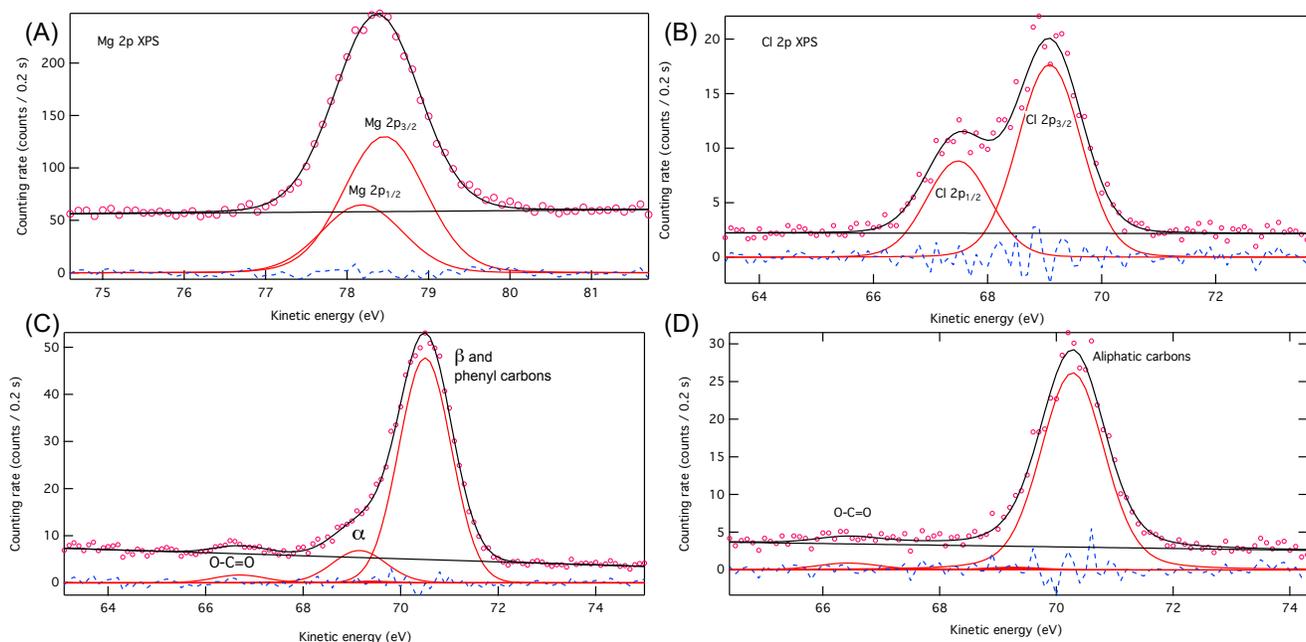
Figure 4 Examples of fitted photoelectron spectra of polydisperse aerosol particles. Circles, experimental data points; solid black line, fitted spectrum; red solid lines, fitted individual peaks; black linear curve, fitted background; dashed blue line, residual of the fit. (A) Mn 2p (B) Cl 2p photoelectron spectra of pure sea salt aerosols showing two spin-orbit components. Total area of both fitted peaks was taken into account for enrichment calculations. (C) C 1s photoelectron spectrum of aerosol particles from sea salt water solution with phenylalanine. Signals from carboxyl carbon (O-C=O), α carbon and combined signal from β carbon and phenyl carbons are indicated. Area of β and phenyl carbons peak was taken into account for enrichment calculations. (D) C 1s photoelectron spectrum aerosol particles from sea salt water solution with octanoic acid. Signals from carboxyl carbon (O-C=O) and aliphatic carbon chain are indicated. Area of aliphatic carbon chain signal was taken into account for enrichment calculations.

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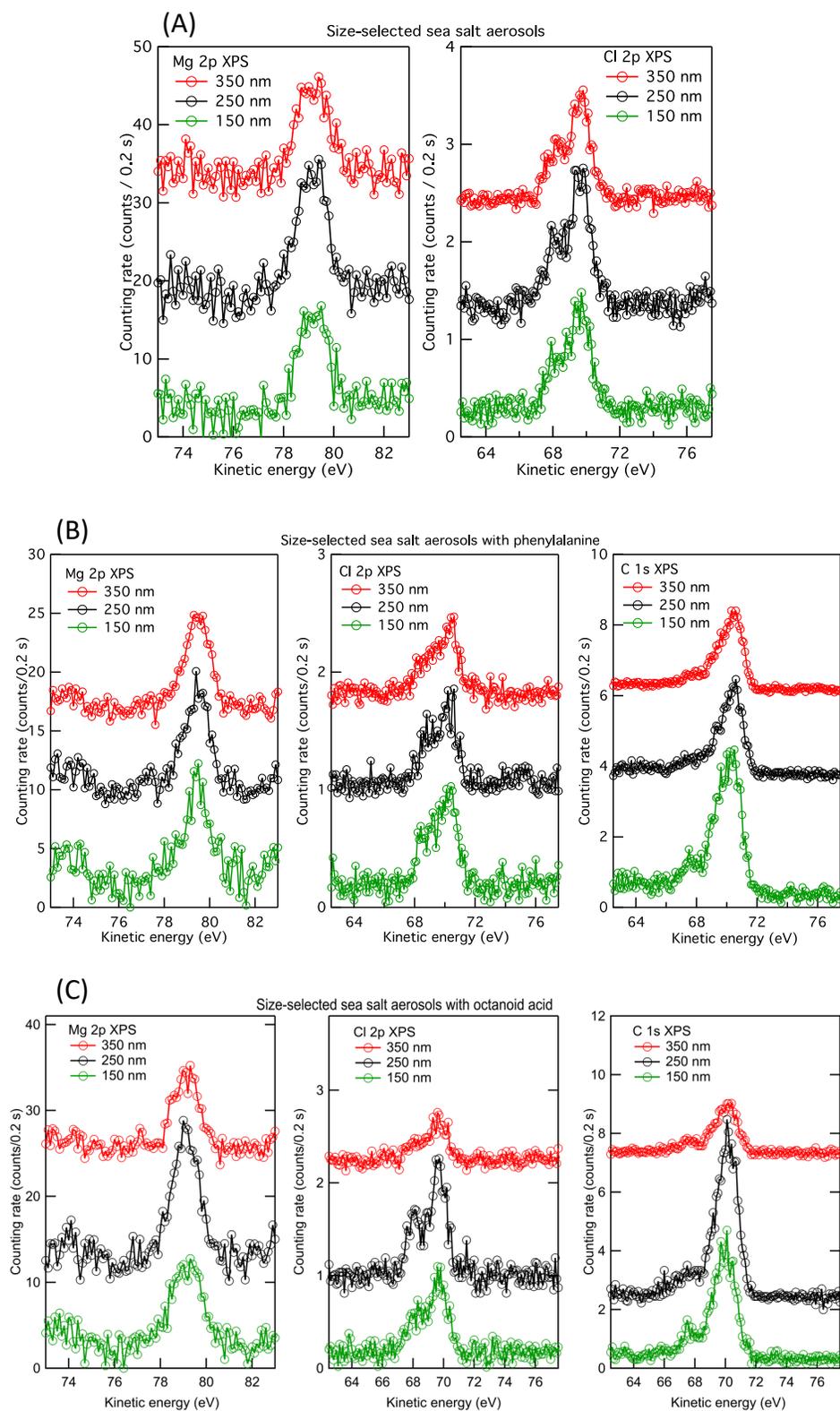
Figure 5 Examples of normalized photoelectron spectra of size-selected aerosol particles. (A) Pure inorganic sea salt (B) Phenylalanine + inorganic sea salt (C) Octanoic acid + inorganic sea salt
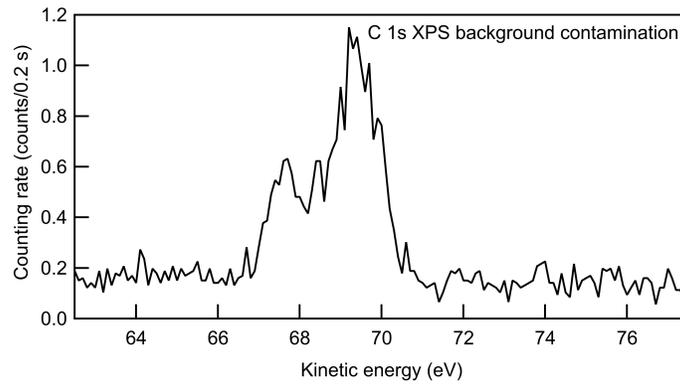
Figure 6 C 1s XPS spectrum of the gas phase contamination observed in the experimental chamber (measured without particle beam).