

Novel approach to identifying size dependent losses of semivolatile compounds during room temperature storage of sampled aerosol matter

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In recent studies we have discussed negative artefacts associated with the loss of semivolatile compounds of aerosol matter. It is well known – but not often fully appreciated – that the processes leading to such artefacts during sampling are in most cases quite significant (Wittmaack and Keck, 2004; Keck and Wittmaack, 2005). Less well studied are losses that can occur during subsequent storage of aerosol matter on filters or on collection plates of impactors. Unpublished data suggest that even after several years of storage the losses might not be complete.

This study was performed to explore a novel ‘soft’ approach to identifying the total amount of matter that can be lost due to volatilisation during sample storage. In order to determine the size dependence of the effect, sampling was performed in impactors. Two essentially identical 8-stage cascade impactors (Berner type) were operated in parallel at flow rates of 30 L/min. PM_{2.5}, PM₁₀ and TSP mass concentrations were also determined by filter sampling. Particle size distributions in the range above 0.3 µm were recorded using an optical counter (Grimm model 1108). The results discussed here relate to 24-h sampling in late winter with temperatures around 0°C.

The collected masses were first determined by gravimetry. Thereafter one set of impactor samples was transferred into a vacuum chamber and stored at < 10⁻⁶ hPa. The mass losses that occurred in vacuum were determined at storage times between 18 h and three weeks, at which point the losses had stabilized.

The water soluble fractions of the impactor deposits were carefully extracted and analysed by ion chromatography. Size distributions of SO₄²⁻ and NH₄⁺, measured with as-sampled and vacuum treated impactor deposits, are presented in Figs. 1(a) and (b). Within experimental uncertainty the results for SO₄²⁻ are the same, indicating that this component did not suffer from any losses in vacuum. By contrast, NH₄⁺ was lost very significantly throughout the whole spectrum, with possible exceptions at the lower and upper end of the spectra. Large losses were also observed with NO₃⁻, see Fig. 1(c) and, to a lesser extent, for Cl⁻ (not shown).

Interpretation of the results was assisted by measuring the time dependence of mass losses in vacuum for the pure salts NH₄NO₃ and NH₄Cl.

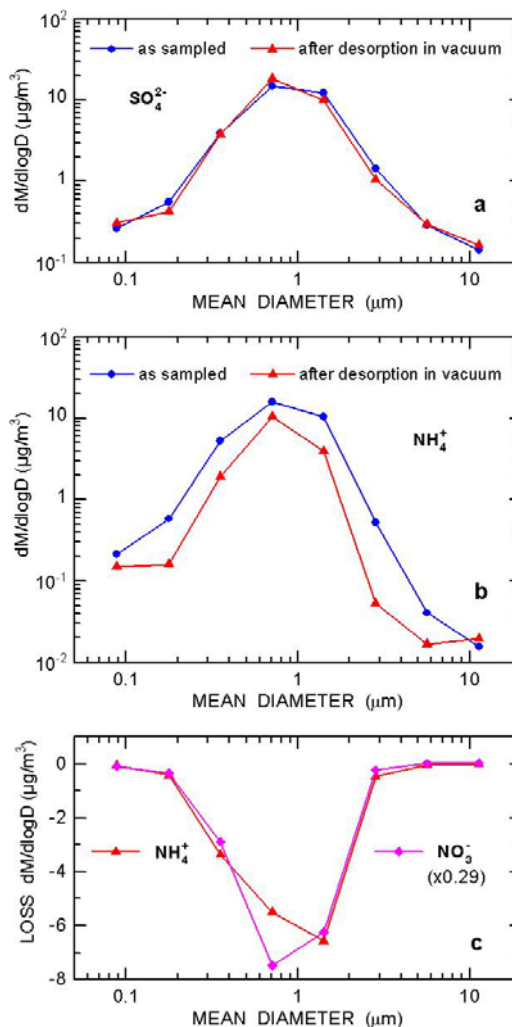


Figure 1. Comparison of the mass spectra of (a) SO₄ and (b) NH₄ ions in impactor deposits without and with long-term storage in vacuum. (c) Comparison of mass losses for NH₄ and NO₃.

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