# The influence of functional groups on organic aerosol hygroscopicity

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Organic aerosols in the atmosphere are composed of a wide variety of species, reflecting the multitude of sources and growth processes of these particles. Especially challenging is predicting how these particles may act as cloud condensation nuclei (CCN). Köhler theory relates the particle's dry diameter to its critical supersaturation. A hygroscopicity parameter, kappa, parameterizes this relationship in terms of the particle's chemical composition. Previous studies have characterized kappa values for a range of organic model compounds. Here we extend these studies by designing new model systems that allow systematic investigation of the influence of the number and location of particular functional groups on the organic aerosols' kappa value. Organic compounds were synthesized via gas-phase and liquid-phase reactions. Aerosol products from gas-phase reactions were collected on filters, extracted using ethyl acetate, and fractionated by reversed-phase high-performance liquid chromatography using gradient elution with acetonitrile and water. The eluate was atomized, the solvent was removed by evaporation, and the residual aerosol particles were analyzed as a function of retention time using high-resolution scanning flow CCN analysis. Individual organic compounds eluting from the synthesized mixture were identified using thermal desorption particle beam mass spectrometry. These experiments yielded changes in kappa that can be attributed to the addition of one or more hydroxyl, nitrate, carboxyl, aldehyde, hydroperoxide, and methylene functional groups while otherwise maintaining the structure of the organic molecule. Our results show that the addition of hydroxyl and carboxyl groups can significantly increase a particle's kappa value, while the addition of hydroperoxide, nitrate, and methylene groups does not. We anticipate that our results contribute to a mechanistic understanding of chemical aging and will help to guide input and parameterization choices in models that rely on simplified treatments such as the atomic oxygen-to-carbon ratio to predict the evolution of organic aerosol hygroscopicity.

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# LA-ICP-MS: a success story of in-situ element & isotope ratio analysis

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LA-ICP-MS has become the method of choice for in-situ trace element analysis, recently expanding into applications traditionally dominated by other analytical techniques. In its beginning ~30 years ago [1], fundamental problems arising from poorly controlled LA of material to element ionization from dry particles orders of magnitude larger than dried liquid aerosol to sensitive and representative transient signal recording dominated research initiatives (Longerich and co-workers [2]). High-UV LA combined with MS detection has since become the preferred instrumental combination [3].

And where are we today? Studies on technical parameters have greatly improved our understanding of fundamental processes occurring at various sites in the instrumentation. Hand in hand goes prominent progress achieved in "fitting LA-ICP-MS for purpose", by developing new or significantly refining analyical protocols. However, praised seminal instrumental developments have not resulted in quantum leaps; hence, neither LA-ICP-MS analytical protocols nor instrumentations have changed radically in the past decade.

This contribution outlines the interplay between fundamental instrumental parameters for successful LA-ICP-MS measurement of element concentration and isotope ratio data and addresses components critical to analytical accuracy, including calibration materials [4]. Emphasis will be put on the quantification of the bulk composition of phase mixtures (e.g., fluid inclusions [5,6]) for which LA-ICP-MS is the undisputed analytical instrument of choice. Precise and accurate isotope ratio and radiometric age determinations are now feasible from ever decreasing sample amounts, emphasizing the relevance of analytical sensitivity.

Common perception is that instrumental possibilities (e.g., sensitivities, resolution in space and time, signal detection, element and isotope ratio fractionation) dictate the progress in LA-ICP-MS applications. However, no modern equipment can compensate for lack of sound instrumental and geoscientific understanding of how to employ LA-ICP-MS for solving analytical problems.

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