



Compound specific ^{13}C - and ^{18}O -isotope analysis of organic aerosols

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The wide ranging environmental and health effects of aerosols are increasingly coming to light. Various studies have further highlighted the complex nature of organic aerosols, particularly oxidised organics with multiple functional groups. Source apportionment studies on aerosols are crucial to successful implementation of mitigation strategies, but this is complicated by their complex nature. Ideally, individual components of aerosols can be tracked from their source to their atmospheric sink. However, chemical alteration and the formation of secondary aerosols in the atmosphere often preclude this direct tracking on a compound specific basis. Compound specific isotope analysis could overcome these problems, as certain processes and sources impose characteristic isotope ratios on products, which may be retained even after chemical alteration in the atmosphere. Progress has been made over the past decades in the separation and identification of individual compounds that contribute to aerosol formation. Compound separation by gas chromatography (GC), coupled to mass spectrometry (MS), has enabled identification of organic compounds of various sources. On the other hand, only few studies have addressed the isotopic composition of these compounds. For successful isotopic analysis of specific compounds, using GC coupled to isotope ratio MS (GC-irMS), several challenges must be faced that go beyond the requirements for GC-MS-based compound identification. Sample extraction and handling techniques must avoid isotope fractionation. This is especially important in the light of sample extraction by e.g. thermal desorption, which may impose a temperature-induced fractionation on complex organics. Furthermore, derivatisation techniques, necessary for adequate GC compound separation, must not lead to exchange reactions of the element of interest, which would alter the measured isotope ratio. So far most studies have dealt with carbon, and other elements have been neglected. Elements other than carbon may provide valuable additional information. Here we report on the development of methods for the analysis of stable carbon and oxygen isotope ratios of organic compounds in aerosols, through GC-combustion-irMS and GC-pyrolysis-irMS. We apply these analyses to environmental aerosol samples and samples of smog-chamber experiments, with the aim of identifying isotopic signatures of sources and pathways. We will pay special attention to derivatisation techniques – notably alternatives to the often-used trimethylsilyl derivatives in GC-pyrolysis-irMS for $\delta^{18}\text{O}$ analysis – and to compound separation and identification. We present initial data of combined $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ studies on (secondary) organic aerosol samples, and their added value for source apportionment studies.