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Development of a Low-Mass, High-Precision Multi-Isotope Method for Sulfate ($\delta^{34}S$, $\Delta^{33}S$, $\delta^{18}O$, $\Delta^{17}O$) Using ESI-Orbitrap Mass Spectrometry

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Multiple sulfur and oxygen isotope measurements of sulfate (SO_4^{2-}) are powerful tools for constraining atmospheric oxidation chemistry and biogeochemical sulfur cycling. However, conventional isotope ratio mass spectrometry (IRMS) techniques typically require several micromoles of SO_4^{2-} and involve extensive chemical conversion, limiting applications in low-mass environmental systems. Here we present a refined electrospray ionization–Orbitrap (ESI-Orbitrap) method for direct isotopologue analysis of intact SO_4^{2-}, achieving precisions of ±0.2‰ ($\delta^{34}S$), ±0.3‰ ($\Delta^{33}S$), ±0.3‰ ($\delta^{18}O$), and ±0.4‰ ($\Delta^{17}O$). Method development required systematic evaluation of solvent composition, SO_4^{2-}concentration effects, dehydration and resuspension protocols, fragmentation behavior, and Orbitrap resolution settings. Optimized sample preparation includes offline cation exchange resin pretreatment, chromatographic sulfate isolation and collection, quantitative water removal, and reconstitution in 90:10 methanol:water to enhance ionization efficiency and minimize matrix effects. Using this workflow, we demonstrate reliable sulfate isotope analysis from as little as ~100 nmol of SO_4^{2-}, with analytical limits governed by purification efficiency rather than instrumental sensitivity. This represents an order-of-magnitude reduction in sample size relative to traditional IRMS approaches. We apply the method to diverse environmental systems, including fine-mode aerosol collected by aerosol impactors, atmospheric oxidation experiments of reduced sulfur gases, and wastewater treatment samples. The ability to obtain coupled $\delta^{34}S$–$\Delta^{33}S$–$\delta^{18}O$–$\Delta^{17}O$ measurements from low-mass sulfate opens new opportunities for investigating sulfur cycling in atmospheres, hydrospheres, and engineered systems where material is limited.