Accurate and rapid determination of silver, sulfur, selenium and tellurium in geological reference materials by inductively coupled plasma-tandem mass spectrometry (ICP-MS/MS)

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As chalcophile elements, Ag, S, Se, and Te serve as crucial tracers for various geological and cosmochemical processes, providing critical insights into core-mantle differentiation, the delivery of volatiles, and crust-mantle magmatic evolution [1]. However, their accurate quantification in geological samples remains analytically challenging due to severe spectral interferences, ultralow abundances in general geological reservoirs, and potential volatile loss during sample preparation. Conventional approaches requiring additional chemical purification or auxiliary devices (e.g., membrane desolvator or hydride generator) are time-consuming, reagent-intensive and costly [2]. Inductively coupled plasma tandem mass spectrometry (ICP-MS/MS) has emerged as one of the most effective techniques for suppressing spectral interferences due to its groundbreaking capability for online separation of analytes and interferents [3]. But, its application in geological elemental analysis remains underexplored. This work developed a novel ICP-MS/MS method utilizing reactive gases (NH₃, O₂ or N₂O) to achieve rapid and accurate determination of Ag-S-Se-Te in complex geological matrices without chemical separation or other redundant operations. Acid-digested samples were directly introduced into the instrument, and Ag was readily determined via "on-mass" mode (Ag⁺) and "mass-shift" mode (Ag(NH₃)₂⁺) under NH₃-filled cell conditions. S-Se-Te quantification required isotope dilution to compensate for volatile loss during digestion, and O₂/N₂O was applied as reaction gas to overcome their spectral interferences. S and Se were detected as oxide species while Te was analyzed in the natural m/z. Systematic optimization of reaction gas flow rate, octopole bias voltage (controlling the ion kinetic energy), and integration time was conducted to determine optimal analytical conditions. The proposed method demonstrated excellent agreement with conventional ID-ICP-MS results across international reference materials spanning ultramafic to felsic lithologies. Notably, the digested samples could be directly analyzed after a 1000-fold dilution, significantly simplifying sample preparation procedures and enhancing the analysis efficiency. This approach establishes robust strategies for quantifying low-abundance and interferenceprone elements in geological matrices, offering great potential for high-throughput geochemical studies.

[1] Wang & Becker (2013) *Nature* 499, 328-331; [2] Wang et al (2015) *GGR* 39, 185-208; [3] Bolea-Fernandez et al (2017) *JAAS* 32, 1660-1679.