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Method Validation for the Determination of Sulfur Isotope Ratio: A Case Study in Organic Shale

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The sulfur isotope ratio ($d^{34}S$) is a valuable tool in paleogeochemistry, providing additional insights when carbon and nitrogen isotope analysis yield inconclusive or uncertain results. To ensure the reliability of $d^{34}S$ determination in organic shale samples, we performed a method validation following ISO/IEC 17025, using an Elemental Analyzer coupled to the Isotope Ratio Mass Spectrometer (EA-IRMS). The following performance characteristics of the method were evaluated: linearity, trueness, precision (repeatability and reproducibility), selectivity, measurement uncertainty, and robustness. Linearity was evaluated by constructing a three-point calibration curve (n=5) using Certified Reference Materials (CRM) of inorganic compounds produced by the International Atomic Energy Agency: IAEA-SO-6 (-34.1 ± 0.2‰), IAEA-S-1 (-0.30 ± 0.06‰) and IAEA-S-2 (22.62 ± 0.16‰). Analytical curves exhibited linear behavior in a wide working range ($d^{34}S$ from -34.1 to 22.62‰, VCDT) with a coefficient of determination greater than 0.9999. To evaluate trueness and precision, a second source of CRM, the IAEA-S-3 (-32.49 ± 0.16‰), was assessed by two different analysts (n=7). The trueness of the method was proved by an error of 0.05‰. The method showed good precision for both matrices evaluated, namely silver sulfide and organic shale: the coefficient of variation (CV) in 7 replicates of analysis was 0.85% and 0.67%, respectively, and the difference between analysts was 1% and 0.65%. The method is selective as there is no difference in the variance between the analysis of silver sulfide and organic shale. The expanded uncertainty (U) was 3.5%. Method robustness was evaluated using an organic shale sample that underwent the combustion process with and without vanadium peroxide catalyst. T-test showed a significant difference ($p<0.05$) between the use of the catalyst ($d^{34}S$= -42.27‰) and its absence ($d^{34}S$= -40.22‰), indicating that the addition of vanadium pentoxide is necessary for matrices containing carbon and nitrogen. Furthermore, the use of a catalyst presented a lower variation (CV=0.7%) compared to non-use (CV = 4%). In conclusion, vanadium pentoxide is critical for total sulfur conversion in organic shale samples, avoiding isotopic fractionation. The validated method demonstrated satisfactory performance and the accreditation by ISO/IEC 17025 ensure that the results generated by the laboratory are internationally accepted.