Analysis of low abundance trace metals and $^{51}V/^{50}V$ isotope ratios in crude oils: New methods for characterization and exploration

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Many studies have illustrated the application of a limited number of high abundance trace or minor elements (e.g., V, Ni, S) in crude-oil classifications, source rock characterization, oil-oil correlation, and oil-source rock correlation, and as environmental tracers and refining catalyst poisons, but many of the trace metals in crude oils remain generally poorly known, often below detection limits using conventional sample preparation and analytical techniques, and plagued by interferences and complex organic matrices. Abundances and stable isotope ratios of trace metals in crude oil remain relatively unexplored. Here we present new techniques for rapid digestion and analysis using a single microwave digestion technique with large volume samples that allow destruction of the heavy organic matrices and direct high precision analyses of ~50 trace metals and S with combined ICP-OES and a recently developed QQQ-ICP-MS method that can help to mitigate interferences. Significant variations in a wide range of elemental abundances in natural crude oil samples are documented. The same digestion techniques used with multi-step cation and anion exchange columns to purify V have achieved precise and accurate (+0.3‰, 2σ) analysis of $^{51}V/^{50}V$. Each isotope ratio analysis is bracketed by 1000 ng/g in-house V single element standard prepared from the V ICP standard from Inorganic Ventures (USA). Isotope compositions are reported relative to this in-house standard in parts per 1000: $\delta^{51}V = 1000 \times [(^{51}V/^{50}V_{sample}/^{51}V/^{50}V_{in\text{-}house})-1]$. Better than 0.2 ‰ internal and 0.3‰ external precision on the $^{51}V/^{50}V$ ratio for a 1000 ng/g V solution is achieved. BDH and AA vanadium standards recently certified were tested successfully. A Venezuelan crude oil standard (NIST RM8505) was developed as a crude oil reference standard for isotope measurements, and analysis of several crude oils were conducted showing significant variation in $\delta^{51}V$ relative to the bulk silicate Earth value of -0.7± 0.2 ‰. Coupled investigations of a wider range trace element abundances and vanadium isotope fractionation effects in natural crude oils have important exploration implications, such as in fingerpring biodegraded oils, oil-oil correlation, maturation, and typing source rock biomass.