Gas-source mass-spectrometry "strikes back": multi-isotopic composition of selenium and their mass-independent fractionation.

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Selenium is a chalcogen element with properties similar to sulfur. Its isotopic composition is generally presented as a powerful tracer of redox conditions. So far, isotope measurements (masses 74, 76, 77, 78, 80 and 82) implied 2 isotopes by gas-source IRMS (Krouse & Thode 1962) or up to 5 by MC-ICP-MS (Stüeken et al. 2013), yet requiring corrections. Here we present the first measurements for the 6 isotopes in multicollection on the gaseous molecule SeF6 using the new high-resolution Mat253 Ultra spectrometer. Zero enrichments are good with a typical precision of 0.005‰ for 76,77,78 and 82, without any correction and little possible interferences (as checked with high resolution) compared with precision of ±0.2‰ by MC-ICP-MS. Even though amounts are greater than what needed for ICP-MS, this level of precision can allow detection of small but significant mass-independent fractionation.

The protocol developed here starts with selenite ions SeO_3^{2-} converted to solid Ag_2Se, before being converted to a gaseous SeF_6 being subsequently cryogenically purified before analysis by IRMS. Standard measurements showed consistent results for 76, 77, 78, 80 and 82 isotopes whereas the $^{74}SeF_5^+$ (m/z 169), is interfered by another compound, likely $C_3F_7^+$ ions. Either further purification is needed e.g. through a gas chromatography or the sample has to be analyzed at higher resolution.

Partial reduction experiments of selenite ion to hydrogen selenide reveal mass independent fractionation for ^{77}Se [$\Delta^{77}Se \approx 0.2$‰ for 70% reduction, where $\Delta^{77}Se = \delta^{77/80}Se - 1000*((\delta^{78/80}Se/1000+1)^{1.519}-1)$], well distinct from standard deviation. More experiments are currently undertaken to better characterize this effect. Since ^{77}Se is the only odd-numbered isotope, this anomaly may result from either nuclear field shift effect or magnetic effect.

Krouse, H.R. & Thode, H.G., 1962. *Can. J. Chem.*, **40**, pp.367–375.

Stüeken, E.E. et al., 2013. *J. Anal. At. Spectrom.*, **28(11)**, p.1734.