Single column extraction of Ge and Si from natural samples allows reliable Ge analysis by ICP-MS

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Germanium (Ge) exists at trace levels in the earth's crust and is a powerful geochemical tracer of silicon (Si) cycle. However, Ge content is often overlooked in the array of analyzed elements. This arises from the analytical difficulties to obtain reliable data because Ge concentrations in natural samples are generally below the detection limit of many modern analytical methods. In addition, Ge isotopes are affetcted by multiple interferences in ICP-MS techniques. Then, the majority of studies published so far on Ge have been carried out using the isotope-dilution hydride-generation ICP-MS technique (ID-HG-ICP-MS) developed by Mortlock and Froelich (1996). This technique is reliable and precise but has the disadvantage of requiring a hydride generation system, not widespread in laboratories while isotope dilution is tedious and time consuming. The objective of this study is to propose an alternative simple and reliable method to determine Ge contents in natural soils and plant samples using ICP-MS. As Si and Ge have very similar chemical properties, we investigated the applicability of the chemical preparation procedure developed for silicon isotopes (Georg et al., 2006) to the analysis of Ge in environmental samples. This allows precise determination of Ge concentrations in environmental samples down to a limit of quantification of about 12 ng l^{-1}. Analyses performed on ^{74}Ge, the most abundant isotope, show the best external reproducibility of about 3%. Accuracy, difficult to assess given the scarcity of reliable data available for comparison, was estimated to be about 6%. This method provides a cost effective procedure to determine accurate and precise Ge concentrations in natural samples and has the great advantage of coupling two Si tracers in one chemistry. A systematic coupling of Ge/Si ratios and δ^{30}Si compositions is a great asset in the interpretation of Si cycle as both tracers are very complementary. This work is supported by the BIOSiSOL project (ANR-14-CE01-0002).

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