A precise and less hazardous method to determine chlorine stable isotope composition in aqueous samples

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The differentiation between the two stable isotopes of chlorine ³⁵Cl and ³⁷Cl represents a powerful analytical tool and enables the reconstruction of the evolution of saline waters. The isotopic signatures provide precise insights into the origin and fate of dissolved chloride, as well as the transport pathways of water. Previously, environmental chlorine isotope ratios have been measured after conversion to chloromethane with Dual Inlet Isotope Ratio Mass Spectrometry [1]. To avoid highly toxic iodomethane as reagent, phosphoric acid and ethanol can be used to measure chloroethane isotope ratios via purge and trap gas chromatography-continuous flow-isotope ratio mass spectrometry (P&T-GC-CF-IRMS) [2].

We developed a novel sample preparation and measurement technique and combined the simplicity of the chloromethane formation with the advantages of the less toxic chloroethane preparation. In our approach, the formation of chloroethane occurs in a single step by reacting crystallized chloride with iodoethane in a sealed headspace vial, which is then directly injected into the headspace-gas GC-CF-IRMS. Measurements were performed with a Finnigan-MAT Delta-S, equipped with a CNOS/MEMCO collector system (6-cup version) set to the masses m/z = 64 for C₂H₅³⁵Cl and m/z = 66 for C₂H₅³⁷Cl.

The precision of our new method was assessed using the standard material ISL-354 yielding an $\delta^{37}Cl_{ISL-354}$ value of +0,05 ± 0,04 ‰ for n = 15. This standard deviation is significantly more precise compared to values of ± 0,07 ‰ 1 and ± 0,09 ‰ [2]. No memory effects were observed during the measurement of six different isotope standards ranging from -0,55 ‰ to +1,84 ‰. Moreover, the reaction and measurement accuracy were maintained after adding various ions. This clearly demonstrates that determining chlorine isotope ratios via chloroethane using HS-GC-CF-IRMS, offers distinct advantages in terms of handling, occupational safety and the quality of the measurement results compared to previous studies.

References

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