

## Comparison of different evaluation schemes and optimization of instrumental parameters for chlorine isotope analysis of organic compounds using GC-qMS

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Compound specific chlorine isotope analysis is a valuable tool to detect and quantify biodegradation processes and abiotic transformation of chlorinated organic compounds in the subsurface. The new GC-qMS method avoids tedious off-line sample pretreatments and offers a quick and sensitive method for on-line determination of chlorine isotope ratios. In this study, the GC-qMS method for chlorine CSIA of chlorinated hydrocarbons was evaluated and validated. We compared the existing evaluation schemes to determine chlorine isotope ratios with newly proposed and/or modified ones. Besides, we tested the important instrumental settings such as split ratio, ionization energy and dwell times. Chlorinated ethenes were selected as model organic contaminants. Headspace sample of tetrachloroethene (PCE), trichloroethene (TCE) and cis-dichloroethene (cisDCE) at aqueous concentrations in the range of 20-500  $\mu\text{g/L}$  were analyzed using GC-qMS. The results showed good precisions (relative standard deviation: 0.4% - 2.1%, n=5). We also found that the precision of the GC-qMS method depends on the applied evaluation schemes, instrumental parameters and target compounds. A systematic test and evaluation of these important factors enabled us to optimize the GC-qMS technique to determine the chlorine isotope ratios of chlorinated organic contaminants.

## *In situ* Pb and U isotope analysis of single ostracod shells from Nam Co, Tibet

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We have developed a new LA-ICP-MS technique for combined *in situ* trace element, Pb and U isotope analysis of single ostracod shells. High spatial resolution is achieved by using spot sizes of 12 - 100  $\mu\text{m}$ . We analyzed very small (ca. 0.5 mm) and thin (about 0.05 mm) shells from eight levels of a Holocene lake sediment core from Nam Co, Central Tibetan Plateau, deposited within the last 7700 a BP [1]. *In situ* measurements of  $(^{234}\text{U}/^{238}\text{U})$ ,  $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$  yielded a precision (RSD) of about 2 % for U = 10 - 20  $\mu\text{g g}^{-1}$  and 0.2 % for Pb = 10 - 40  $\mu\text{g g}^{-1}$ .

Our results show identical ratios for ostracods from the same core depth indicating that they reflect the composition of the lake water.  $(^{234}\text{U}/^{238}\text{U})$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  show significant variability with age: Ostracods from the upper core section show uniform isotope ratios ( $1.42 \pm 0.01$  and  $2.134 \pm 0.003$ , respectively). The older samples show lower and more variable isotope ratios. These findings are in agreement with investigations of the sediments [1] and suggest that the isotope ratios of the ostracod shells reflect past climate variability: reduced precipitation and runoff, low lake level and maximum salinity since ca. 800 a BP, more humid conditions and a positive precipitation/evaporation balance between 5400 and 7200 a BP [1]. The lowest ratios ( $(^{234}\text{U}/^{238}\text{U}) = 1.13$ ,  $^{208}\text{Pb}/^{206}\text{Pb} = 2.112$ ) are observed in a 6000 a old ostracod shell, where a high intensity of monsoonal precipitation, associated with elevated lake levels in Tibet, is recorded [1].

[1] Mügler *et al.* (2010) *J. Paleolimnol.* **43**, 625–648.