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Chemical characterization of lipids in speleothems and cave drip water by organic trace analysis (HPLC-ESI-IT/MS) and its potential for the investigation of palaeoenvironmental changes

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Cave drip water, speleothems and the proxies preserved within them have significant potential to record palaeoenvironmental changes in the regional vegetation [1]. The use of stalagmites provides valuable information because they form a chemically closed system which does not change much after lithification, they grow continuously and are amenable to precise Th/U-dating [2]. The most common proxies measured in speleothems are inorganic proxies, in particular oxygen isotopes, but more recently the importance of organic matter analyses in this field is examined. This study focuses on the research of lipid biomarkers. The lipids contained in stalagmites originate from the overlying soil and different plants, bacteria and fungi. Therefore different compositions of lipids may provide records of environmental changes [3].
In the following the development of a new method for the extraction of saturated free fatty acids from cave drip water and their measurement by RP-HPLC-ESI-IT/MS (reversed phase high performance liquid chromatography coupled to electrospray ion trap mass spectrometry) is presented. Four different fatty acids (myristic acid, palmitic acid, stearic acid and arachidic acid) with chain lengths from C14 to C20 were applied as analytical standards. A mixture of these was used to optimize the separation by HPLC. The analytes were measured in MRM mode (multiple reactions monitoring) and negative polarity (m/z: 227, 255, 283, 311) therefore a time consuming derivatisation of the fatty acids was not necessary. By using a certain gradient program an adequate separation of the standards was accomplished. Likewise the realization of calibration curves of the different fatty acids showed that quantitative analyses are possible as well. To simulate the extraction of the analytes from cave drip water a spiking experiment with the analytical standards was performed. Three water samples were spiked with the same amount of the fatty acids to test the reproducibility of the extraction. The extraction was carried out using a SPE (solid phase extraction) procedure in which the elution of the analytes was assured by using a rather apolar solvent like dichloromethane. Measurements of water blanks which were treated the same way as the spikes showed high amounts of palmitic acid and stearic acid which were reduced by heating the glass ware to 400 °C before usage. To achieve an improvement of the reproducibility of the spiking experiment different amounts and compositions of organic solvents were added to the water samples to function as a modifier. These parameters are optimized to obtain a sufficient reproducibility of the extraction procedure in order to extract the actual cave drip water samples.

References:

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