^{39}Ar ATTA @ Heidelberg - Preparation of Water and Ice Samples

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With its half-life of 269 yr, the rare Ar radioisotope ^{39}Ar is an ideal dating tracer in the age range between 50 and 1000 years, which is of interest in various fields of environmental sciences such as hydro(geo)logy, oceanography, paleoclimatology, and glaciology, but hardly accessible by any other dating tool [1]. However, the classical analytical method of ^{39}Ar detection by low-level counting requires very large sample sizes (on the order of 1 L STP of Ar), limiting the practical applicability of this tracer. Recently, progress has been made towards using atom trap trace analysis (ATTA) to detect ^{39}Ar [2,3], opening the prospect of measuring ^{39}Ar on much smaller samples. Here we present preparation (gas extraction and Ar separation) methods for groundwater and ice samples for later analysis by the ATTA technique.

For groundwater, the sample size is less of a limitation for applications of ^{39}Ar than in oceanography or glaciology. Large samples are furthermore needed to enable a comparison of ^{39}Ar results from ATTA with ^{39}Ar measurements by low-level counting. Therefore, a system was built that enables gas extraction from several thousand liters of water using membrane contactors. This system provides degassing efficiencies greater than 80 % and has successfully been tested in the field. Gas samples are further processed to separate a pure Ar fraction by a gas-chromatographic method based on Li-LSX zeolite as selective adsorber material at very low temperatures, following a method developed at the University of Bern [4]. The gas separation achieved by this system is controlled by a quadrupole mass spectrometer. It has successfully been tested and used to separate Ar from real large-volume groundwater samples. The separation efficiency was found to be strongly temperature dependent in the range of -118 to -130 °C.

Since ATTA should enable the analysis of ^{39}Ar on samples of less than 1 ccSTP of Ar (corresponding to about 100 ml of air, 2.5 l of water or 1 kg of ice), a simpler method to separate Ar from small amounts of gas was developed. For gas samples in that size range, chemisorption on hot titanium surfaces (gettering) is an effective method to separate noble gases from the reactive components. Titanium sponge was found to absorb 60 ccSTP of reactive gases per g of the getter material with reasonably high absorption rates at high operating temperatures (about 800 °C). Good separation (higher than 92 % Ar content in the residual gas) was achieved by this gettering process. The other main remaining component is H_2, which can be further reduced by operating the Ti getter at lower temperature. Analysis of ^{39}Ar on small gas samples opens in particular the possibility to date glacier ice. A system was therefore designed to degas ice samples, followed by Ar separation by gettering. Ice from an alpine glacier was successfully processed on this system.

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