Groundwater dating with Atom Trap Trace Analysis of ^{39}Ar

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Abstract We report on the realization of Atom Trap Trace Analysis for ^{39}Ar and its first application to dating of groundwater samples. The presented system achieves an atmospheric ^{39}Ar count rate as high as 3.58 ± 0.10 atoms/h allowing for the determination of the ^{39}Ar concentration in less than a day. We demonstrate that the measured count rates are proportional to the ^{39}Ar concentration by intercomparison with Low-Level Counting results and by measurements on prepared argon samples with defined concentration. For a geophysical application, we degas three different groundwater samples and gas chromatographically extract the argon. The ^{39}Ar ages inferred from the count rates extend over the accessible dating range and are in agreement with the Low-Level Counting results as well as with complementary isotope data.

1. Introduction

The radioisotope ^{39}Ar with a half-life of 269 years can be used for the dating of water and ice in the time range of 50–1000 years, in which no other reliable dating method exists [*Loosli*, 1983]. This time range is relevant for groundwater management as well as ocean circulation and climate archives [*Corcho Alvarado et al.*, 2007; *Schlosser et al.*, 1994; *Corcho Alvarado et al.*, 2009]. ^{39}Ar has ideal properties as a tracer in hydrology since, as a noble gas, it is not involved in geochemical processes and has a well-defined atmospheric source. However, its routine application in environmental sciences is hampered by its extremely low atmospheric abundance of ^{39}Ar/Ar = 8.23×10^{-16} [*Loosli*, 1983] corresponding to merely ~8000 ^{39}Ar atoms in a liter of modern water. So far, it has been accessible only by Low-Level Counting (LLC) in the underground laboratory at the University of Bern, requiring 8–60 days of measuring time and 1–3 metric tons of water. The latter requirement mainly limits the applicability of ^{39}Ar dating with LLC to groundwaters, where degassing several tons of water from a well is typically feasible. Applications to ocean water have only been realized when large ocean water samples were collected for ^{14}C analysis [*Loosli*, 1989; *Schlitzer et al.*, 1985; *Schlosser et al.*, 1994, 1995]. With the advent of Accelerator Mass Spectrometry (AMS) for ^{14}C analysis, requiring only 1 L samples, oceanographic ^{39}Ar measurements practically ceased. The few ^{39}Ar studies with LLC on ice have been conducted on samples from Greenland, Antarctica, and Devon Island between 1969 and 1974 where ^{39}Ar ages were compared to ages obtained from δ^{18}O stratigraphy [*Loosli*, 1983].

Accelerator Mass Spectrometry for ^{39}Ar analysis has been successfully demonstrated [*Collon et al.*, 2004]. However, since ^{39}Ar as a noble gas does not form negative ions and is difficult to separate from its isobar ^{39}K, a complex and large accelerator facility is necessary which hinders routine ^{39}Ar measurements. Further efforts to establish AMS for ^{39}Ar analysis are currently not anticipated [*Collon et al.*, 2012].

Atom Trap Trace Analysis (ATTA) is an atom optical technique that has been developed for rare krypton isotopes [*Chen et al.*, 1999]. It is now available for routine analysis [*Jiang et al.*, 2012] and several environmental studies based on radiometric krypton dating with ATTA have been conducted [*Sturchio et al.*, 2004; *Buizert et al.*, 2014; *Lu et al.*, 2013]. The method makes use of the high selectivity of resonant photon scattering involved in laser cooling in order to distinguish the desired rare isotope from the abundant isotopes. Since it is not bound to radioactivity, it allows for a fast analysis while requiring only comparatively small sample sizes independent of the isotope's half-life.

The applicability of ATTA to ^{39}Ar has been demonstrated in a proof of principle experiment [*Jiang et al.*, 2011]. However, the achieved ^{39}Ar count rate of 0.22 atoms/h is too low for practical dating of groundwater. Here we report on the significant improvement of the count rate allowing for the explicit application of this method to the dating of groundwater samples.
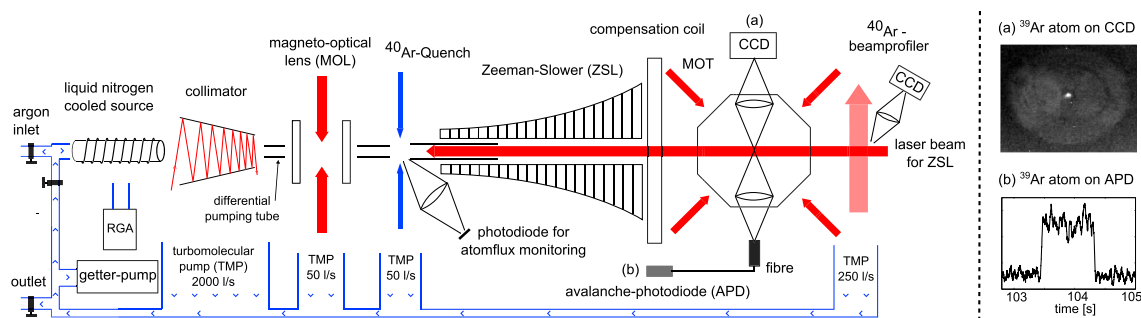
Figure 1. Schematic of the ^{39}Ar-ATTA apparatus including the vacuum system. The single atom CCD and APD signal are depicted on the right.

2. ^{39}Ar-ATTA System

A schematic of our apparatus for ^{39}Ar-ATTA is depicted in Figure 1. The setup follows the same concepts as the ones described in *Jiang et al.* [2011, 2012]. The argon atoms are excited to a metastable state by an RF discharge in a liquid nitrogen-cooled source leading to a metastable flux of $\sim 5 \times 10^{14}$ atoms/sr/s with a mean velocity of ~ 280 m/s. The divergent atom beam is collimated by transverse laser cooling in a tilted mirror setup enhancing the flux in the magneto-optical trap (MOT) by a factor of ~ 130. The collimated atom beam is focused with a magneto-optical lens (MOL) enhancing the metastable flux in the MOT by another factor of ~ 1.4. In the following differential pumping stage, the ^{40}Ar atoms are removed from the metastable level via a quenching transition at 802 nm in order to avoid background light in the MOT, originating from off-resonant excitation of ^{40}Ar atoms. The 843 nm light, which the ^{40}Ar atoms emit upon deexciting to the ground state, is continuously monitored with a photodiode as a measure for the metastable atom flux. The atom beam is longitudinally slowed down in a Zeeman slower (ZSL) from a maximum velocity of ~ 500 m/s down to about 50 m/s. A second frequency in the ZSL laser beam forms an additional slowing stage with the rising slope of the MOT magnetic field, where the atoms are slowed down to the capture velocity of the MOT (~ 10 m/s). Due to this two-stage Zeeman slowing design, the divergence of the atom beam at the end of the Zeeman slower is reduced. Finally, the atoms are captured in the MOT where the scattering light is imaged onto a CCD camera on one side, and onto a fiber connected to an avalanche photodiode (APD) on the opposite side. In the chamber behind the MOT, further fluorescence imaging is used to profile the ^{40}Ar beam allowing for precise alignment of the collimator and the MOL. A single ^{39}Ar atom is identified from the APD signal with a threshold that is adapted to the lifetime of the particular atom in the trap. This threshold is derived based on Bayesian analysis [*Ritterbusch*, 2014] such that the total probability for counting a false atom is less than 10^{-6} while 96% of all atoms captured in the MOT are detected.

The nonvanishing nuclear spin of ^{39}Ar leads to a hyperfine splitting of the cooling transition that has been measured previously [*Welte et al.*, 2009; *Williams et al.*, 2011]. Thus, for each laser cooling stage (except ZSL) up to three additional repumping frequencies are employed. Generally, the laser system allows a quick change between the isotopes, which is important for optimization and control of performance.

A crucial problem for dating of groundwater with ATTA lies in translating a measured count rate for a sample into a concentration. ATTA for krypton has the advantage of possessing the abundant and stable isotope ^{83}Kr which exhibits similar hyperfine structure as the rare radioisotopes ^{81}Kr and ^{85}Kr. The concentration of ^{81}Kr and ^{85}Kr can therefore be determined by normalization with the ^{83}Kr MOT loading rate [*Cheng et al.*, 2013; *Jiang et al.*, 2012]. For ^{39}Ar such a reference isotope is not available. We therefore employ the ^{39}Ar count rate of argon samples derived from atmospheric air (commercial bottle argon) as a standard for normalization. This approach requires a constant and reproducible ^{39}Ar detection efficiency, which we achieve with measures such as active stabilization of laser powers and frequencies. Moreover, we perform control measurements of the stable argon isotopes before and after each ^{39}Ar measurement to ensure that all components not specific to ^{39}Ar operate on the assigned efficiency. Besides the metastable atom flux we monitor laser frequencies, laser powers, and laser locking signals during an ^{39}Ar measurement.

In the time span of 13 weeks, during which all samples considered in this study have been analyzed, we performed a total of 28 atmospheric ^{39}Ar measurements which are compiled in Figure 2. The histogram of
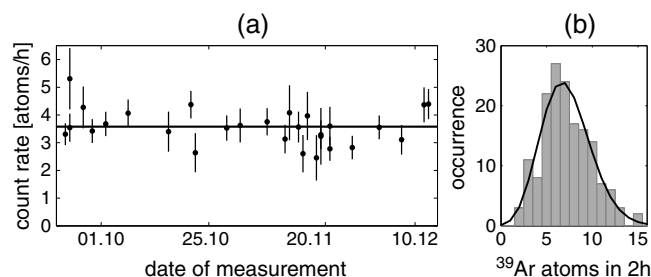
Figure 2. Compilation of all 28 atmospheric ^{39}Ar measurements each lasting between 3–21 h. Altogether 1162 ^{39}Ar atoms have been counted in 324 h distributed over 13 weeks. (a) The error bars shown for each measurement correspond to a statistical 1σ confidence level given by the number of detected atoms. The solid line corresponds to the mean value over all measurements. (b) The histogram of the data in 2 h frames indicates a Poissonian distribution which is represented by the solid line.

all atmospheric measurements indicates a Poissonian distribution with a mean atmospheric ^{39}Ar count rate of 3.58 ± 0.10 atoms/h, where the statistical 1σ error of the mean value is stated. Binning three data points reveals a long-term drift from the mean value of about 15%, which we can correlate with the deterioration of the source as identified with our atom beam diagnostics. However, the apparatus was operating with the mean efficiency for all samples considered in the following except for one specific sample for which the atom beam diagnostics indicate a source efficiency that is 14% lower than the mean value. We therefore correct the measured count rate accordingly.

Our apparatus can operate with less than 0.1 mL STP of argon in recycling mode (i.e., the gas circulates in a closed vacuum system, see Figure 1). However, a detectable background level of ^{39}Ar is embedded in our vacuum system due to previous optimization and characterization of the apparatus with enriched ^{39}Ar samples. The accumulating ^{39}Ar background currently precludes the analysis in recycling configuration. Nevertheless, we can deduce from the accumulated background in recycling mode that the contribution of the contamination in throughput configuration (i.e., the inserted argon sample is pumped out of the apparatus) is maximally 2% of the atmospheric ^{39}Ar count rate. In this study, we therefore measured the ^{39}Ar concentrations in throughput configuration leading to 0.5–1 L STP of argon being consumed for an ^{39}Ar measurement within 15–30 h. The performance of the apparatus is the same in throughput as in recycling configuration.

3. Samples

The groundwater samples analyzed in this study were taken at different locations based on previous isotope data, with the aim to cover a range of ^{39}Ar ages (Table 1). In the following we shortly discuss the details of the three groundwater wells sampled for this study.

F18/2 is an observation borehole about 10 km southwest of the city of Heidelberg, Germany, tapping the upper part of the second (middle) aquifer in the sediments of the Upper Rhine Graben. Samples for ^{3}H, ^{14}C, noble gases, and other tracers were taken in October 2011 in the framework of a local isotope hydrological study. The sampling for ^{39}Ar took place in June 2012. The ^{3}H and ^{14}C concentrations measured in F18/2 (Table 1) are only slightly lower than the values found in the young (about 20 years based on SF$_6$ data) groundwater of the overlying upper aquifer in this area. These data indicate an intrusion of young water into the generally old (^{3}H-free) groundwater of the middle aquifer at this location. ^{39}Ar is the ideal tracer to investigate the age distribution of such mixed samples.

Table 1. Groundwater Samples Measured With ^{39}Ar-ATTA in Comparison With LLC Measurements and Complementary Isotope Data[a]

	F18/2	Uster404	HR544259
NGT[b] (°C)	7.8 ± 0.6	7.3 ± 0.5[c]	4.3 ± 1.1
^{3}H (TU)[d]	7.40 ± 0.16	0.4 ± 0.1[c]	0.6 ± 0.9
^{14}C (pmC)[e]	84.03 ± 0.24	22.1 ± 0.4[c]	0.025 ± 0.02
^{39}Ar LLC (pmAr)[f]	87 ± 10	29 ± 8	9 ± 8
^{39}Ar-ATTA (pmAr)	89 ± 16	23 ± 6	13 ± 6
^{39}Ar age LLC (a)	54 ± 45	480 ± 107	> 688
^{39}Ar age ATTA (a)	44 ± 71	572 ± 95	> 644

[a]The statistical 1σ errors are indicated.
[b]NGT = noble gas temperature.
[c]Values are from 1998 as published in *Beyerle et al.* [1998].
[d]TU = tritium units.
[e]pmC = percent modern carbon.
[f]pmAr = percent modern argon.

The borehole *HR544259* in the Hessian Ried is located about 30 km northwest of the city of Heidelberg and taps the lower aquifer in the sediments of the Upper Rhine Graben. It was sampled in September 2011 for ^{3}H, ^{14}C, noble gases, and ^{39}Ar. It contains no ^{3}H and has a very low ^{14}C content (Table 1), indicating an age on the order of 30 ka. The cool noble gas temperature (NGT) of about 4°C, derived using the methods described by *Aeschbach-Hertig et al.* [2000], supports the conclusion that this groundwater was recharged during the last glacial period, i.e., more than 11 ka ago. The near-zero ^{14}C activity of this well rules out the presence of a significant young component. In the absence of ^{39}Ar subsurface production, this sample can therefore be expected to be free of ^{39}Ar. Subsurface production has especially been observed in low-porosity fractured crystalline rock formations but may also occur in sandstone aquifers [*Loosli et al.*, 1989; *Andrews et al.*, 1991; *Lehmann and Purtschert*, 1996]. The sandy sediments of the Hessian Ried aquifer are expected to show a low subsurface production, due to the low U/Th content and the high porosity.

The well *Uster404* was sampled in July 2013. It is situated in the upstream part of a confined aquifer in the Glatt Valley near Zurich, Switzerland, and corresponds to borehole 1 in the study of *Beyerle et al.* [1998]. In that study a low but nonzero ^{39}Ar activity of 9 ± 5 pmAr (percent modern argon) measured by LLC was reported. Nevertheless, the sample was interpreted as about 5 ka old based on its ^{14}C content (Table 1). Other wells further downstream yielded even higher ^{39}Ar contents and were interpreted as binary mixtures of an old and a young component.

For water degassing, up to about 2500 L of groundwater were pumped by a submersible pump with a flow rate of about 30 L/min through a membrane contactor (Liqui-Cel 6 × 28 Extra Flow, Membrana). The gas side of the contactor was evacuated to ∼50 mbar, and the extracted gas was compressed into a sample gas cylinder for transport and storage. A maximum of 63 L STP of gas can be sampled in the 9 L stainless steel sample cylinders at the achievable compression of 7 bar. Depending on the gas content of the groundwater and the degassing efficiency, this corresponds to about 1000 to 3000 L of water being degassed. The degassing efficiency of the setup strongly depends on the pressure at the gas ports of the contactor and ranged between 84% for helium and 90% for argon. Although the degassing therefore slightly fractionates between elements, the isotope fractionation for argon is negligible, as determined by mass spectrometric analyses of the ^{36}Ar/^{40}Ar ratio on water and gas samples, using procedures as described by *Aeschbach-Hertig et al.* [2008].

Argon was separated from the extracted gas by a gas chromatographic system similar to that developed at the University of Bern [*Riedmann*, 2011], consisting of nine columns filled with zeolite Li-LSX as selective adsorbent, a quadrupole mass spectrometer to observe the composition of the gas leaving the columns and an activated charcoal trap to catch the argon fraction. Helium is used as a carrier gas. Argon leaves the columns first as its interaction with the Li-LSX zeolite is weaker than that of O_2 or N_2. The efficiency of the separation is optimal at column temperatures between −130 and −135°C, which are achieved by immersing the columns in liquid nitrogen vapor and electrical heating to control the temperature. The setup achieves argon purities better than 98% and argon recoveries above 96% [*Reichel*, 2013], without inducing isotope separation, as tested by mass spectrometric analyses of the ^{36}Ar/^{40}Ar ratio. The argon collected on the activated charcoal trap is finally transferred to a container for the transport of the argon sample to the ATTA setup.

The samples Uster404 and HR544259 have been degassed and purified for the ATTA as well as the LLC measurement with the described system in Heidelberg. The sample F18/2 instead was prepared independently by the groups at the universities of Heidelberg and Bern.

In order to cover the full dating range of ^{39}Ar, we prepared further argon samples with ^{39}Ar concentrations of 56 ± 5 pmAr and 78 ± 3 pmAr by a defined mixture of atmospheric argon and the Uster404 sample based on its ^{39}Ar concentration measured by LLC (Table 1).

For a defined blank measurement, we furthermore employ a sample from the Great Artesian Basin, Australia, which has an ^{39}Ar concentration of 1 ± 8 pmAr according to the LLC measurement. This groundwater sample, in the following named *GAB*, has been degassed and purified by the group at the University of Bern. For the ATTA measurement the methane admixture necessary for LLC analysis has been removed by the Heidelberg purification system.

4. Results

Our ^{39}Ar results for the described samples are compiled in Table 2. The count rates are compared with the corresponding LLC/mixture results in Figure 3. We find a general agreement over the whole concentration

Table 2. ^{39}Ar-ATTA Counting Results[a]

Sample	Counting Time (h)	Counted ^{39}Ar Atoms	^{39}Ar Count Rate R (atoms/h)	R/R_{100} (%)
GAB	17.5	8	0.52 ± 0.18	15 ± 5
HR544259	8.85	4	0.45 ± 0.23	13 ± 6
Uster404	19.5	16	0.82 ± 0.21	23 ± 6
56 pmAr	9.23	21	2.28 ± 0.50	64 ± 14
78 pmAr	14	42	3.00 ± 0.46	84 ± 13
F18/2	9.68	31	3.20 ± 0.58	89 ± 16
100 pmAr	325	1162	3.58 ± 0.10	100

[a]The mixed samples with 56 ± 5 pmAr and 78 ± 3 pmAr are prepared from the Uster404 sample and the 100 pmAr (atmospheric) reference. The ^{39}Ar count rate R is calculated by dividing the number of counted ^{39}Ar atoms by the counting time. The count rate of the GAB sample is corrected by +14% taking into account the lower source efficiency. In the last column, the count rate R divided by the atmospheric count rate R_{100} is given.

range with the ideal calibration line given by the origin and the atmospheric standard. Only the GAB sample exhibits a difference exceeding the 1σ error between the LLC and our ATTA measurement which nevertheless is consistent within a 2σ confidence level. An ^{39}Ar contamination from the ATTA setup which could explain the elevated concentration is very unlikely as discussed in section 2. Performing the extraction routine on prepared gas with a composition similar to a groundwater sample, but free of argon, showed that a maximum contamination of only 1% atmospheric argon may have occurred during extraction. In order to resolve the difference between the LLC and the ATTA result for the GAB sample, further studies specifically devoted to this low concentration regime are necessary.

The proportionality in Figure 3 justifies the inference of the ^{39}Ar concentration of a sample as $c^{ATTA} = R/R_{100}$, where R represents the measured ^{39}Ar count rate and R_{100} the atmospheric count rate. The resulting concentrations for the groundwaters that were sampled in the course of this study are listed in Table 1 together with the corresponding ^{39}Ar ages as well as complementary isotope data.

The ATTA as well as the LLC result for the ^{39}Ar concentration of the F18/2 sample are consistent with the quasi modern ^{3}H and ^{14}C content. The ^{39}Ar result supports the interpretation that this sample is a mixture resulting from intrusion of young groundwater into the generally old middle aquifer and indicates that the young component is dominant. The ^{39}Ar concentration of the Uster404 sample is higher both in the LLC and the ATTA measurement than the 9 ± 5 pmAr reported in *Beyerle et al.* [1998]. This finding hints at a shift toward a higher proportion of younger water components in this well during the last two decades. This indicates that the exploitation rate exceeds the recharge rate in this important pristine water resource. The ^{39}Ar data of wells F18/2 and Uster404 emphasize the relevance of ^{39}Ar for recovering the age distribution of samples that have a mean age in the time range of 50–1000 years.
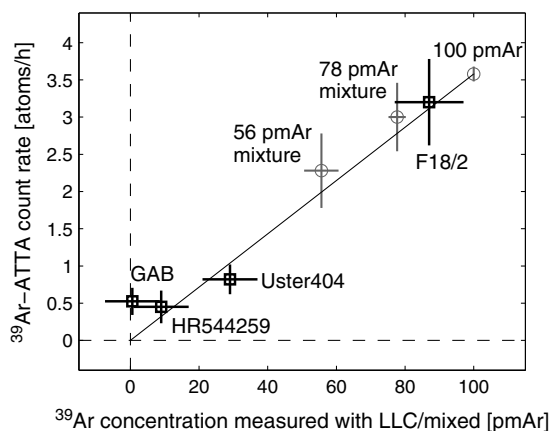
The sample HR544259 exhibits a very low ^{39}Ar concentration both in the LLC and the ATTA measurement in agreement with the very low ^{14}C activity and the absence of ^{3}H in the sample. The detected ^{39}Ar in the sample (on the 1σ confidence level) might either be the result of underground production [*Loosli et al.*, 1989; *Yokochi et al.*, 2012; *Edmunds et al.*, 2014; *Mei et al.*, 2010] or contamination during sampling and/or the purification process. Since the latter is very unlikely, this result indicates that a measurable underground production of ^{39}Ar is not only limited to U/Th rich-fractured formations but may also occur in sandy sediments as in the Hessian Ried. ^{39}Ar-ATTA has the potential to address this low-level regime and can thus contribute in a methodical way

Figure 3. ^{39}Ar count rates measured with ^{39}Ar-ATTA versus the corresponding LLC/mixture result. The samples GAB, HR544259, Uster404, and F18/2 (bold square symbols) were measured in intercomparison with LLC. The mixed samples (grey circle symbols) are prepared from the Uster404 sample and atmospheric argon. The line is defined by the origin and the atmospheric standard.

to groundwater dating with ^{39}Ar. With the previous considerations we interpret the ATTA result as giving a lower bound for the ^{39}Ar age of 644 years within 1σ confidence.

5. Conclusion and Outlook

The agreement of the ^{39}Ar-ATTA results with the LLC measurements as well as with the prepared concentrations demonstrate that now dating of groundwater with ^{39}Ar-ATTA is feasible. We use this method for dating three different groundwater samples demonstrating that it can be applied to environmental systems.

Current developments on the ATTA setup, including the implementation of more elaborate laser cooling techniques such as bichromatic cooling, aim at increasing the ^{39}Ar count rate in order to reduce the necessary counting time and the statistical uncertainties. Due to the contamination embedded in the vacuum system, several tons of water were needed for the ^{39}Ar measurements shown in this work. However, reducing the necessary sample size should only require replacing the contaminated vacuum components. With this upgrade, we expect that the apparatus can operate with 0.1 mL STP of argon, corresponding to about 0.25 L of water or 0.1 kg of ice, which is sufficient for practical dating of ocean water and glacier ice.

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