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Key Points:

- Krypton-85 is a useful tracer for young groundwater in the age range of 5–50 years
- Throughput of krypton-85 abundance measurements increased twelvefold from previous state of the art

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Rapid processing of $^{85}\text{Kr}/\text{Kr}$ ratios using Atom Trap Trace Analysis

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Abstract We report a methodology for measuring $^{85}\text{Kr}/\text{Kr}$ isotopic abundances using Atom Trap Trace Analysis (ATTA) that increases sample measurement throughput by over an order of magnitude to six samples per 24 h. The noble gas isotope ^{85}Kr (half-life = 10.7 years) is a useful tracer for young groundwater in the age range of 5–50 years. ATTA, an efficient and selective laser-based atom counting method, has recently been applied to $^{85}\text{Kr}/\text{Kr}$ isotopic abundance measurements, requiring 5–10 μL of krypton gas at STP extracted from 50 to 100 L of water. Previously, a single such measurement required 48 h. Our new method demonstrates that we can measure $^{85}\text{Kr}/\text{Kr}$ ratios with 3–5% relative uncertainty every 4 h, on average, with the same sample requirements.

1. Introduction

The noble gas isotope ^{85}Kr is a radioactive nuclide with a half-life of 10.739 ± 0.014 years [Singh and Chen, 2014]. It occurs naturally in the atmosphere, produced by cosmic radiation, but at a rate 4 orders of magnitude lower than current global emission from nuclear fuel reprocessing [Ahlsweide *et al.*, 2013]. Due to this anthropogenically increased abundance in the atmosphere and a precise understanding of its input function, ^{85}Kr can be applied as a tracer to date young groundwater on the order of 5–50 years old.

Tracers in this age regime are crucial to water resource management given the global increased dependency on groundwater, including instances of complete dependency on young, shallow groundwater for drinking water [Moran *et al.*, 2005]. ^{85}Kr provides an excellent complement for determining ages when taken with other existing tracers in this age regime, such as chlorofluorocarbons (CFCs) [Cook and Solomon, 1995] and $^3\text{H}/^3\text{He}$, which have both independent input functions and corrections from ^{85}Kr [Loosli *et al.*, 1999; Visser *et al.*, 2007]. Moreover, CFCs are subject to local contamination [Plummer *et al.*, 2006] and $^3\text{H}/^3\text{He}$ dating is highly sensitive to natural degassing [Visser *et al.*, 2007]. In contrast, ^{85}Kr is steadily released into the atmosphere in a manner that is both monitored and well understood [Ahlsweide *et al.*, 2013], making it a robust tool for dating. ^{85}Kr also has a number of applications beyond groundwater dating, such as monitoring air for nuclear fuel processing activities [Kalinowski *et al.*, 2004; Klingberg *et al.*, 2010], monitoring gas transport in the unsaturated zones (which can differ significantly from water transport) [Cook and Solomon, 1995], and as a tracer of ocean water ventilation and shallow mixing [Schröder, 1975].

As a tracer for dating groundwater, ^{85}Kr has been successfully applied on many occasions using low-level gas proportional counting (LLC), both on its own [Smethie *et al.*, 1992] and in conjunction with other isotopic tracers for deconvolving the age distributions of mixed groundwater [Corcho Alvarado *et al.*, 2007; Althaus *et al.*, 2009; Visser *et al.*, 2013; Mayer *et al.*, 2014; Delbart *et al.*, 2014; Alikhani *et al.*, 2016]. ^{85}Kr samples are collected by degassing groundwater samples in the field, and then separating krypton from the bulk gas in the laboratory [Purtschert *et al.*, 2013]. Recent developments have both decreased separation times and increased krypton yields of groundwater samples. Ten microliters of krypton gas (STP) can be purified in the laboratory from 10 L of air in approximately 75 min. In the field, this amount of air can typically be degassed from 100 L of groundwater in 30–60 min [Yokochi, 2016].

However, despite these improvements, ^{85}Kr dating has not been applied routinely at a large scale due to the slow processing time and comparatively large sample volume requirements of LLC [Plummer and Friedman, 1999; Loosli and Purtschert, 2005]. The development of Atom Trap Trace Analysis (ATTA), a laser-based

atom counting method [Chen *et al.*, 1999], has sought to provide the necessary tool to make large-scale analysis of ^{85}Kr viable. The ATTA-3 instrument at Argonne National Laboratory (ANL), has been used to routinely measure isotopic abundances of ^{81}Kr and ^{85}Kr in groundwater samples [Jiang *et al.*, 2012] using 5–10 μL of krypton gas at STP extracted from 50 to 100 L of water or 5–10 L of air at STP. In the past, a single sample measurement required 48 h.

We report here on a new methodology for ^{85}Kr analysis through ATTA. We demonstrate that, by using this method on a newly improved ATTA-3 system described in Zappala *et al.* [2017], we now have the ability to continuously measure $^{85}\text{Kr}/\text{Kr}$ ratios with 3–5% error every 4 h, on average, increasing the sample throughput by a factor of 12 from Jiang *et al.* [2012]. We do so with no increase in sample size requirements. We show this method to be linear and repeatable, and present an understanding and control over systematic effects due to cross-sample contamination on the 0.8% level.

2. Atom Trap Trace Analysis Method

The ATTA technique is described fully in Chen *et al.* [1999], Jiang *et al.* [2012], and Zappala *et al.* [2017], but summarized here briefly: krypton gas is injected into a vacuum system and passes through a liquid-nitrogen-cooled, radio-frequency plasma discharge. The cooling slows the atoms and the plasma transfers a fraction of the atoms into a metastable electronic state. From this state, the atoms are resonantly excited with 811 nm lasers used throughout the system to further slow and trap the atoms in a magneto optical trap (MOT). By measuring the loading rates of both the radioactive (^{81}Kr and ^{85}Kr) and stable (^{83}Kr) isotopes into the trap, we can obtain an isotopic ratio. Furthermore, in order to remove any systematic effects from changes in efficiency that may occur in the system, we also measure a krypton reference gas immediately after measuring the sample that same day. With the isotopic ratios in both the sample and the reference, we ultimately report a “superratio” (SR) defined for ^{85}Kr as

$$^{85}\text{Kr}_{\text{SR}} = \frac{^{85}\text{Kr}_{\text{Sample}} / ^{83}\text{Kr}_{\text{Sample}}}{^{85}\text{Kr}_{\text{Reference}} / ^{83}\text{Kr}_{\text{Reference}}} \quad (1)$$

Such a routine analysis of both the sample and the reference requires 6 h of total atom trapping. At current, however, the improved ATTA-3 system described in Zappala *et al.* [2017] requires 24 h to complete a single measurement. Sixteen hours of this time is devoted to “washing” the system to decrease cross-sample contamination caused by our plasma discharge, which implants krypton ions from the sample into our vacuum chamber walls. To remove this implanted krypton the plasma discharge is run using argon gas. This process requires that the system return to room temperature to completely remove frozen krypton, meaning 2 h of the time are spent warming and later recooling the liquid-nitrogen source.

However, for measuring only ^{85}Kr , we can employ a new method. Since $^{85}\text{Kr}/\text{Kr}$ isotopic abundances are 10 times higher than $^{81}\text{Kr}/\text{Kr}$, a routine measurement would have sufficient statistics to reach a level of 2–3% error in 0.25 h, subsequently reducing the amount of krypton being embedded in the system during such a short run. In addition, we can also remove the liquid-nitrogen cooling. This will increase the mean velocity of the atoms, reducing the efficiency of our trap by a factor of 4, lengthening the measurement time to 1 h; however, it saves 2 h by removing the heating/cooling cycle.

Here we present a new measurement procedure without liquid-nitrogen cooling for rapid-processing of $^{85}\text{Kr}/\text{Kr}$ ratios using the ATTA system. First, we describe a contamination model for this new method that allows us to control the systematic effects caused from the residual cross-sample contamination. Then we apply that model to six calibration samples measured in a 24 h period. Samples for this experiment were prepared at the University of Bern and ANL. Their activities were measured using LLC at the University of Bern, and their ^{85}Kr superratios, defined in equation (1), were measured using the routine ATTA technique that includes liquid-nitrogen cooling and is described at the beginning of this section. These results are reported in first two columns of Table 1. The reference gas is represented by the sample J3.

For the proceeding sections, we perform all experiments under our liquid-nitrogen-free “rapid-processing” conditions. Measurements are conducted in the manner illustrated in Figure 1: a sample is measured for $^{85}\text{Kr}/\text{Kr}$ for 1 h, followed by a 2.25 h argon wash, another 1 h sample measurement, a 1 h reference measurement, and finally another 2.25 h argon wash before the cycle is repeated. This timing permits us to measure

Table 1. Krypton Calibration Samples Measured Using LLC, ATTA, and the New Rapid-Processing Procedure^a

	LLC Activity ^b	ATTA ⁸⁵ Kr _{SR}	Rapid ATTA	
			⁸⁵ Kr _{SR} (Raw)	⁸⁵ Kr _{SR} (Corrected) ^c
J5	269 ± 13	8.0 ± 0.5 ^d	7.7 ± 0.3	7.8 ± 0.3
J4	36.2 ± 3.1	1.04 ± 0.03	1.09 ± 0.05	1.09 ± 0.05
J3	32.1 ± 1.2	0.94 ± 0.01	0.95 ± 0.05	0.95 ± 0.05
J2	18.2 ± 0.6	0.53 ± 0.02	0.54 ± 0.03	0.54 ± 0.03
J1	8.9 ± 0.4	0.25 ± 0.01	0.26 ± 0.02	0.25 ± 0.02
J0	<1.0 (90% C.L.)	<0.013 (90% C.L.)	0.032 ± 0.006	<0.021 (90% C.L.)

^aAll ATTA results are expressed using the superratio (SR) defined in equation (1).

^bReported in decays per minute per cm³ of Kr gas at STP, adjusted to 3 March 2016.

^cCorrected values include adjustment from the contamination model. Raw values do not.

^dMeasured using 1 μL of Kr gas to prevent extensive contamination of ⁸⁵Kr.

the ⁸⁵Kr/Kr ratio of one sample every 4 h, on average. To define a shorthand for the following sections, a measurement of “S₁-S₂-R,” would mean a measurement of S₁ as the first sample and S₂ as the second, followed by a reference measurement R. During the sample measurements, gas is recirculated in the system (as it is for a typical ATTA measurement) due to the small size of the samples. During the washes and the reference measurements, the gas is flowed continuously and discarded. Due to this systematic difference between measurements made with and without gas recirculation, the ⁸⁵Kr superratio of our reference gas measured as a sample (J3) on ATTA is 0.94. However, this systematic difference is found to be consistent and is taken into account as a constant calibration factor. Thus, it does not affect the linearity or reliability of our measurements.

3. Contamination Model

Due to the significantly reduced wash times in this rapid-processing procedure, it is crucial that we develop a model for the cross-sample contamination effects on our system. The goal of this section is to develop a relatively simple but reliable empirical model that quantitatively describes the data without going into the complexities of the cross-contamination mechanism such as specific implantation sites and chamber volumes.

Following the diagram in Figure 1, we consider the collective surfaces of ATTA-3 affected by implantation and the volume of sample gas to be two distinct reservoirs. The former is filled with contaminant from previous samples and the latter is filled with our sample to be measured. The contaminant has its own ⁸⁵Kr/Kr ratio, which we define as C. Due to the plasma discharge there is an exchange: sample gas enters the surface reservoir and contaminant leaks into the volume of the sample gas. The contamination that leaks into the sample becomes part of our measured value. The sample which enters into the surfaces replaces some fraction x of the current contaminant in the reservoir, reducing the influence of each previous sample’s contribution to the contaminant by some fraction 1 – x. The wash procedure afterward reduces the overall number of contaminating krypton atoms by replacing them with argon atoms. However, the wash does not alter the ⁸⁵Kr/Kr ratio of the contaminant since it affects all implanted krypton isotopes equally.

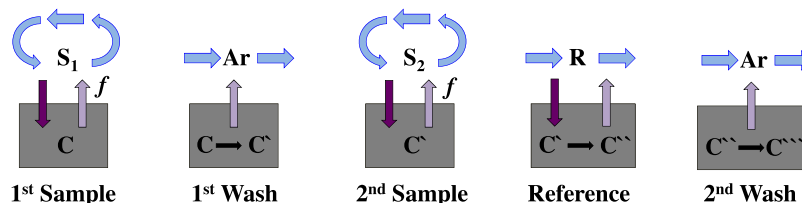


Figure 1. A diagram for the sequence S₁-S₂-R. During sample measurements, there is gas exchange between the contaminant in the chamber wall and the sample gas, which is being recirculated. During washes, argon gas is flowed through the system without recirculation, removing some contaminant. During the reference measurements, reference gas is flowed without recirculation. It enters the chamber walls and reduces the presence of the previous contaminant simultaneously. The contaminant changes in each step as described by our model (see text for details).

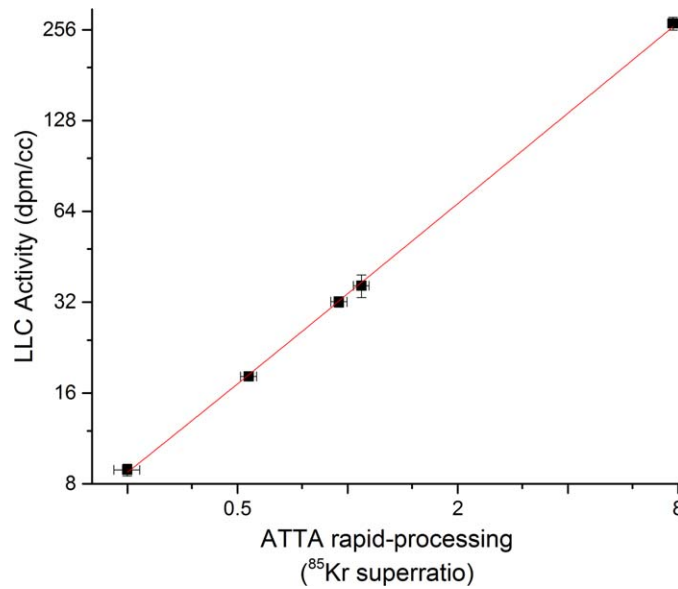


Figure 2. A demonstration of linearity for rapid-processing superratio measurements on ATTA via comparison with LLC results. Both axes are drawn on a log₂ scale. J0 was measured to have a superratio of <0.021 (90% C.L.), but is not shown due to the log scale. The fit has a reduced chi-square of 0.2.

Thus, if there is some contaminant C before S_1 is measured, then after the wash we now have a contaminant

$$C' = C(1-x) + S_1x \quad (2)$$

We test such a model by attempting to find a repeatable value for x . This x is particular to our current vacuum system and will require reevaluation if changes are made to the chamber.

To find x , we first need to know how much contamination we have in our system. We define f , the average portion of the sample (S) volume that is replaced by the contaminant (C) during a measurement of the sample (M_S) as

$$M_S = (1-f)S + fC \quad \text{where} \quad f = \frac{\frac{1}{2}tR_{Kr}}{P_{avg}} \quad (3)$$

Here t is the length of the measurement, R_{Kr} is the linear outgassing rate of the contaminant, and P_{avg} is the average partial pressure of krypton during the run. The factor $\frac{1}{2}tR_{Kr}$ gives us the integrated contamination injected into the gas volume, which is normalized by the partial pressure of krypton, P_{avg} . The only unknown here is the outgassing rate. To determine the rate, we regularly conduct an outgassing test prior to each measurement: the system is filled with argon gas and the gas is recirculated with the plasma active. We then measure how much krypton leaches out of the wall over a few minutes using a SRS Residual Gas Analyzer and extrapolate a krypton outgassing rate due to the argon discharge, R_{Ar} . However, we need to determine the krypton outgassing rate in the presence of a krypton discharge, which should be proportional, but not equal to the rate we have measured, i.e., $R_{Kr} = bR_{Ar}$.

To determine b , we first clean the system for longer than the normal wash period such that the outgassing rate is more than a factor of 4 lower than the typical rates we expect in these measurements. In this "clean start," if we measure S_1 - S_2 - R , then the contaminant $C \approx S_1$ when we measure S_2 . Accordingly, we obtain

$$M_{S_2} = (1-f)S_2 + fC = (1-f)S_2 + fS_1$$

Using our calibration samples, we start with a clean system and then measure J5-J0-R. This simplifies the above equation even further, since J0 is devoid of ⁸⁵Kr ("85Kr-dead") and thus $S_2 = 0$. With only the second term, we can solve for b . We used three such measurements to determine that $b = 2.4 \pm 0.3$.

Now that we know the value of f , we can work to find x by applying the model. If we consider measuring S_1 - S_2 - R - S_3 with our clean start, the model gives us the following for the third sample measurement

$$\begin{aligned} M_{S_3} &= S_3(1-f) + fC'' \\ &= S_3(1-f) + f(C'(1-x) + Rx) \\ &= S_3(1-f) + f(S_1(1-x) + S_2x)(1-x) + Rx \end{aligned}$$

From here, we can solve for x . We ran two separate sequences, J2-J5-R-J0 and J5-J0-R-J0-J0, to solve for x and found that $x = 0.60 \pm 0.02$. Note that we have considered the reference to both be a sampling and a wash procedure. Yet despite it only being 1 h instead of 2.25, we still found consistent results. The reason is that, as shown by solving for b , a krypton wash is ~ 2.4 times more effective at extracting krypton than an argon wash. As such, we could increase the efficiency of the wash by using ⁸⁵Kr-dead krypton gas as our wash gas. However, sufficient amounts of ⁸⁵Kr-dead krypton gas are not readily available.

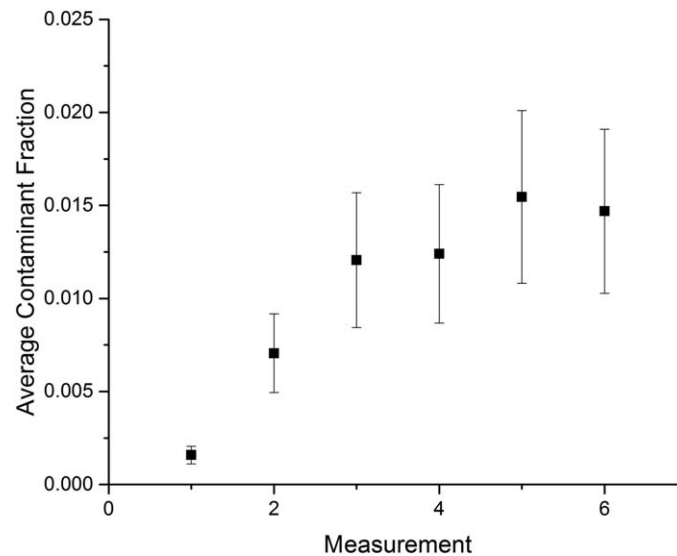


Figure 3. Average contamination during each measurement over six sequential measurements during a 24 h period.

With this repeatable value for x we have determined a simple and consistent model for describing our contamination in this rapid-processing mode.

4. Rapid Processing Results

We measured six calibration samples in a 24 h period (measured in the order J2-J5-R-J0-J4-R-J1-J3-R). The ^{85}Kr superratios determined from these measurements are listed in Table 1 in the third column, and listed with corrections from the contamination model in the fourth column. The LLC activities of the samples are plotted against these corrected values in Figure 2 and fit to a line. The measurement of J0 does not appear in the figure due to the \log_2 scaling, but is included in the fit. The reduced chi-square of the fit is 0.2 We also see that in the six samples we measured the contamination fraction per sample saturated below the 2.5% level, as seen in Figure 3. Based on this saturation level and the errors of our contamination model, the correction will add a maximum error of below 0.8% to the $^{85}\text{Kr}/\text{Kr}$ isotopic abundance measurements, which typically have 3–5% statistical error.

The rapid-processing measurements' agreement with typical ATTA measurements and their linear relationship with LLC activities, demonstrates the validity of this approach. This method increases the throughput of $^{85}\text{Kr}/\text{Kr}$ isotopic abundance measurements on a single ATTA system by a factor of twelve. The agreement of this calibration over such a large range of activities (J5 being nearly 4 times higher than the typical 75 dpm/cm³ activity in the atmosphere of the northern hemisphere [Ahlsweide et al., 2013]) also shows that our contamination model can even handle enrichment levels we would normally wish to avoid in the standard ATTA system. With this rapid-processing procedure validated, ATTA is ready to increase the capacity for ^{85}Kr -dating in the geoscience community.

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