



LAWRENCE  
LIVERMORE  
NATIONAL  
LABORATORY

# California GAMA Special Study: Development of a Capability for the Analysis of Krypton-85 in Groundwater Samples

A. Visser, R. Bibby, J. Moran, M. Singleton, B.  
Esser

January 6, 2015

## **Disclaimer**

---

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.



# GAMA: AMBIENT GROUNDWATER MONITORING & ASSESSMENT PROGRAM SPECIAL STUDY



## **California GAMA Special Study: Development of a Capability for the Analysis of Krypton-85 in Groundwater Samples**

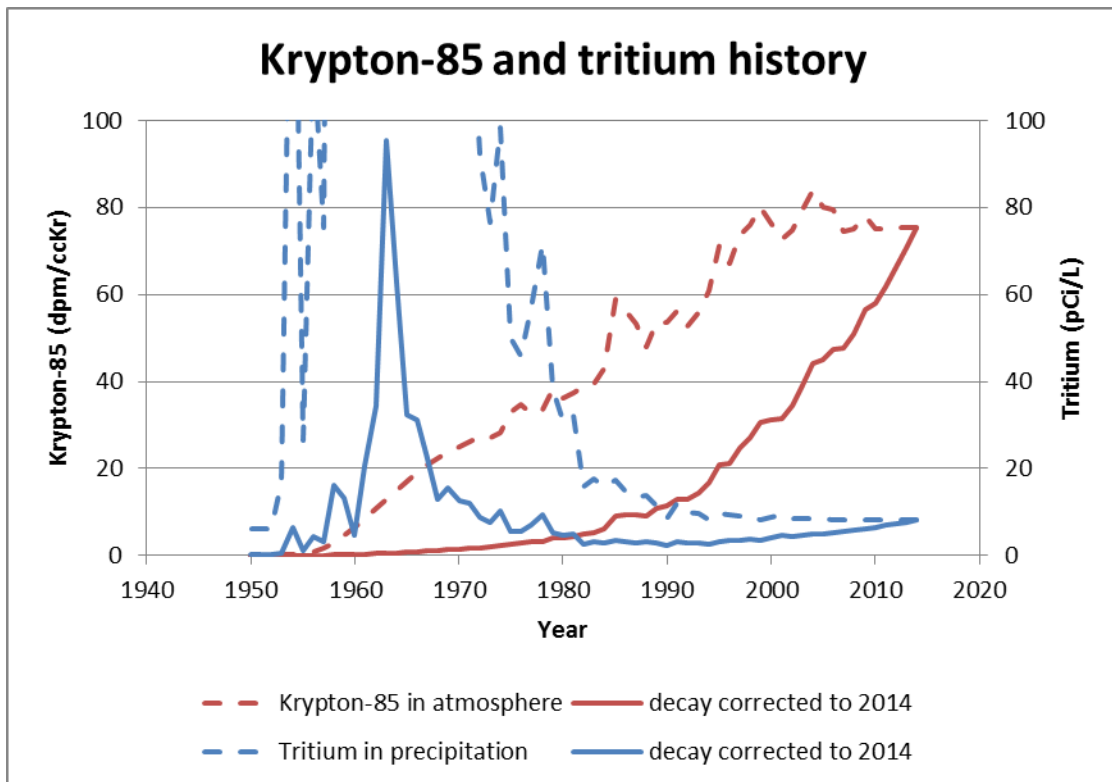
*Ate Visser, Richard K. Bibbey, Jean E. Moran\*, Michael J. Singleton,  
and Bradley K. Esser*

*Lawrence Livermore National Laboratory*

*\*California State University, East Bay*

Prepared in cooperation with the  
California State Water Resource Control Board  
LLNL-TR- 665865

June 2015



***Suggested citation:***

*Ate Visser, Richard K. Bibby, Jean E. Moran, Michael J. Singleton, and Bradley K. Esser (2015)*  
**California GAMA Special Study: Development of a Capability for the Analysis of Krypton-85 in Groundwater Samples.** Lawrence Livermore National Laboratory LLNL-TR-665865, 25 pp.

## **California GAMA Special Study: Development of a Capability for the Analysis of Krypton-85 in Groundwater Samples**

A. Visser, R. K. Bibby, J. E. Moran\*, M. J. Singleton, and B. K. Esser:

*Lawrence Livermore National Laboratory, \*California State University-East Bay*

*Prepared in cooperation with the State Water Resources Control Board*

### **Key Points**

- A capability for the analysis of krypton-85 in groundwater samples was developed.
- Samples are collected by extracting gas from 2000-4000 L of groundwater at the well, yielding approximately 0.2 cm<sup>3</sup> krypton. Sample collection takes 1 to 4 hours.
- Krypton is purified in the laboratory using a combination of molecular sieve and activated charcoal traps, and transferred to a liquid scintillation vial.
- The <sup>85</sup>Kr activity is measured by liquid scintillation on a Quantulus 1220 liquid scintillation counter from PerkinElmer.
- Liquid scintillation counting performance was verified using present day air samples of different size.
- The detection limit for a typical 0.2 cm<sup>3</sup>Kr sample size is 11% of the present day activity in air, corresponding to the decay-corrected activity in air in 1987.
- The typical measurement uncertainty is below 10% for recently recharged samples.
- Six groundwater samples were collected, purified and counted.
- <sup>85</sup>Kr concentrations in the groundwater samples were below the LLNL LSC detection limit. The low concentrations of <sup>85</sup>Kr were confirmed by the low level counting laboratory of Bern University, where the samples concentrations were quantified at 1.5 and 6.6 decays per minute per cm<sup>3</sup> krypton, corresponding to decay corrected activities in air between 1971 and 1985.

## Table of Contents

1	Introduction .....	3
2	Methods .....	4
2.1	Gas Extraction.....	4
2.2	Krypton Purification.....	4
2.2.1	Components.....	4
2.2.2	Procedure.....	5
2.3	Liquid Scintillation Counting.....	6
2.4	Calibration, Uncertainty Propagation and Groundwater Samples.....	7
2.4.1	Calibration .....	7
2.4.2	Uncertainty Propagation.....	8
2.4.3	Groundwater Samples.....	8
3	Results .....	9
3.1	Krypton Purification from Air .....	9
3.2	Liquid Scintillation Counting of Air Standards .....	10
3.3	Groundwater Samples.....	11
4	Summary .....	12
5	Tables .....	13
6	Figures .....	15
7	References.....	21

## **California GAMA Special Study: Development of a Capability for the Analysis of Krypton-85 in Groundwater Samples**

A. Visser, R. K. Bibby, J. E. Moran\*, M. J. Singleton, and B. K. Esser:

*Lawrence Livermore National Laboratory, \*California State University-East Bay*

*Prepared in cooperation with the State Water Resources Control Board*

### **1 INTRODUCTION**

LLNL has successfully applied  $^3\text{H}/^3\text{He}$  groundwater dating in many settings in California to determine groundwater ages. This experience and the large number of samples have highlighted a number of settings where accurate  $^3\text{H}/^3\text{He}$  ages are impossible to determine, for example where terrigenous or mantle helium ( $^3\text{He}$  and/or  $^4\text{He}$ ) is present. Previous GAMA Special Studies have also demonstrated that low  $^3\text{H}$  concentrations are imparted on recent recharge when old groundwater is recycled, typically through irrigation return flow. Both cases call for an additional age tracer for the young (0-30 year) age range.

For this age range, the radioisotope krypton-85 ( $^{85}\text{Kr}$ , half-life = 10.76 years) is ideal. The production and processing of nuclear fuel releases  $^{85}\text{Kr}$  into the atmosphere, and atmospheric concentrations of  $^{85}\text{Kr}$  have increased steadily since the advent of the nuclear age (Figure 1). Groundwater studies have demonstrated that  $^{85}\text{Kr}$  is a reliable age tracer and an excellent complement to tritium [Loosli *et al.*, 1989; Smethie *et al.*, 1992] to constrain complex age distributions [Corcho Alvarado *et al.*, 2007; Visser *et al.*, 2013].  $^{85}\text{Kr}$  has a similar half-life as tritium but has dramatically increased in the atmosphere over the last fifty years, while tritium concentrations in precipitation peaked in the 1960s. A  $^{85}\text{Kr}$  capability at LLNL will expand the existing age dating tools available to the GAMA program, and provide additional insight into travel time distributions in complex mixed groundwater systems

Collecting and preparing samples and analyzing  $^{85}\text{K}$ , however, is complicated because of its low isotopic abundance ( $10^{-15}$  of total krypton) and the low concentration of total krypton in water. The process involves extracting and collecting dissolved gas from several cubic meters of groundwater at the point of collection, followed by the separation of Kr from hundreds of liters of collected gas. Analysis involves counting  $^{85}\text{Kr}$  on special low-level scintillation counters.

LLNL has developed and tested a  $^{85}\text{Kr}$  capability at LLNL. LLNL now has the ability (1) to collect a large volume of dissolved gases extracted from groundwater, (2) to purify the Kr from the large volume gas sample, and (3) to analyze the  $^{85}\text{Kr}$  activity of the sample in existing low level liquid scintillation counting facilities at LLNL. The capability was tested by collecting, purifying and analyzing a number of groundwater samples for multiple age tracers, including  $^{85}\text{Kr}$ , and verifying the  $^{85}\text{Kr}$  activity by analysis of sub-samples at the established, low level counting facility of the University of Bern.

## 2 METHODS

### 2.1 Gas Extraction

LLNL has adapted the Gas Extraction System (GES) that was previously developed with GAMA funding [Moran *et al.*, 2008] so that gas from large volumes of water can be compressed into a reasonably-sized container in the field. Details of the GES have been reported previously. In short, water is pumped through a gas permeable membrane contactor. Gases are extracted by applying a vacuum to the membrane. Collected gases are compressed into pre-evacuated portable air tanks (10-20 L) typically used for compressed air tools. The progress of the gas extraction is monitored by tracking the volume of water processed and the pressure in the air tank. The target quantity of krypton is typically between 0.1 and 0.4 cubic centimeters at standard temperature and pressure ( $\text{cm}^3\text{STP}$ ). The concentration of krypton in groundwater is primarily controlled by the recharge temperature and to a lesser extent by the concentration of excess air. Subsurface production of dissolved gases (e.g. nitrogen from denitrification, carbon dioxide or methane) would increase the total dissolved gas concentration without increasing the Kr concentration. The volume of water processed is therefore a more reliable measure for the quantity of Kr collected than the pressure in the tank. The target water volume to be processed is calculated using the target Kr concentration and the local recharge temperature or mean annual air temperature. Typically, between 500 and 1200 gallons of water (2000-4000 L) need to be processed, yielding 55 to 90 L of gas. The gas is compressed to a maximum of 3.4 bar (50 psi). The rate at which water is processed varies between 3 and 15 gallons per minute depending on the available water pressure. Gas extraction at the wellhead can take between 1 and 4 hours.

### 2.2 Krypton Purification

Several methods for the purification of krypton from air or extracted gas samples have been published in literature [Janssens *et al.*, 1986; Loosli *et al.*, 1989; Momoshima *et al.*, 2010; Ohta *et al.*, 2009; Okai *et al.*, 1984; Yokochi *et al.*, 2008]. Krypton can be purified by a combination of sorption traps for water and carbon dioxide, sorption of Kr to activated charcoal or stainless steel at cryogenic temperatures, gas chromatography and/or reactive metal getters removing nitrogen and oxygen. The system developed at LLNL closely resembles that published by Momoshima, which was based on an earlier publication by Okai. This section first describes the components of the system and secondly the procedure to process air or extracted gases from groundwater extracted gases.

#### 2.2.1 Components

The LLNL system is built from stainless steel tubing with  $\frac{1}{4}$ " VCR and  $\frac{1}{8}$ " Swagelok fittings (Figure 2). Air or groundwater extracted gas is introduced into the system using a Pfeiffer diaphragm pump (MVP-100). The flow rate of introduced gas is limited by a mass flow controller (MKS GE50A) which also tracks the total volume of gas processed.

The purification is achieved using three traps. The first two traps are stainless steel cylinders (5cm diameter, 40 cm long) with the inlet at the top and the outlet dropped down to 1 inch above the bottom. The first trap (labeled 13X) contains molecular sieve 13X (Sigma Aldrich), which traps water vapor and carbon dioxide. The second trap (labeled AC1) contains ~100g of activated charcoal (Sigma Aldrich DARCO, 12-20 mesh). The third trap (AC2) is a 50 cm long  $\frac{1}{4}$ " stainless steel tube containing 1 g of activated charcoal. The tube is coiled to fit in a glass vacuum insulated beaker. 5 pellets of 13X molecular sieve are present in the outlet side of the third trap to further capture water vapor and carbon dioxide.



Helium is used to transfer gases through the system, at rates varying from 10 to 1000 cubic centimeters at standard temperature and pressure per minute (sccm). The helium flow rate is controlled by two mass flow controllers (MKS GE50A). The process of purification is monitored by a residual gas analyzer (RGA200, SRS systems) attached to the system via a variable leak valve (Pfeiffer Gas Dosing Valve EVN 116). The purified krypton is transferred into a 20 mL liquid scintillation counting (LSC) vial (Perkin Elmer) through thin silicone tubing reaching the bottom of the vial. The vial contains 3 g of silica beads to facilitate the trapping of krypton. After the transfer, a 30 mL syringe is used to add scintillation cocktail (Ultima Gold LLT, Perkin Elmer) to the LSC vial.

### **2.2.2 Procedure**

The krypton purification procedure consists of 7 steps. Each step is described in detail below. An additional clean up step is described separately.

1. Sample introduction and trapping on AC1 at -195 °C
2. Venting AC1 with helium at -78 °C
3. Transfer of gases to AC2
4. Venting AC2 with helium at -78 °C
5. Venting AC2 with helium at 0 °C
6. Transfer of krypton to liquid scintillation counting vial
7. Addition of scintillation cocktail

Step 1: Sample introduction and trapping on AC1 at -195 °C

Trap AC1 is cooled to -195 °C using liquid nitrogen (LN). The gas (helium) inside AC1 is pumped away using the diaphragm pump to a pressure of less than -25 inHg. Once the trap is cooled and evacuated, the sample is introduced through the mass flow controller at a rate of 5000 sccm. Water vapor and carbon dioxide are trapped on trap 13X. All krypton and a large fraction of the nitrogen, oxygen, and argon are trapped on AC1. Sample collection can take between 10 to 100 minutes, depending on the required sample size

Step 2: Venting AC1 with helium at -78 °C

After the entire sample is introduced, the gases in the head space of traps 13X and AC1 are pumped away to -25 inHg. AC1 is separated from 13X by closing the valve in between. The valve to the pump is closed. The headspace of AC1 is filled with helium at a rate of 500 sccm, controlled by the mass flow controller. Once the pressure in AC1 reaches 1 atmosphere, the gas is directed towards the leak valve by switching the first 3-way valve, bypassing AC2 using the 4-way valve. The composition of the gases passing the leak valve is monitored on the residual gas analyzer (RGA). Once the flow rate has stabilized, it is increased to 1000 sccm. Then, AC1 is warmed to -78 °C by removing the liquid nitrogen and packing AC1 on dry ice. Desorbing gases (N<sub>2</sub>, O<sub>2</sub> and Ar) are vented off with helium for 2 hours.

Step 3: Transfer of gases to AC2

The helium flow rate is reduced to 250 sccm and the gas flow is directed through AC2 by switching the 4-way valve. AC2 is cooled to -195 °C by immersion in liquid nitrogen. The dry ice is removed from AC1 and AC1 is warmed to 200 °C with two electric band heaters, powered by a Variac voltage controller, monitored using a thermocouple. Once AC1 reaches 200 °C, the gases are transferred for 30 minutes.

Step 4: Venting AC2 with helium at -78 °C

The helium flow rate is reduced to 100 sccm. The first three way valve is switched and helium is supplied by the second mass flow controller at 100 sccm. The liquid nitrogen is removed and AC2 is immersed in a dry ice – isopropanol slush. Desorbing gases (N<sub>2</sub>, O<sub>2</sub> and Ar) are vented off with helium for 30-45 minutes.

#### Step 5: Venting AC2 with helium at 0 °C

The dry ice slush is removed and AC2 is immersed in a beaker with water and water ice. The helium flow rate is maintained at 100 sccm. At 0 °C, N<sub>2</sub>, O<sub>2</sub> and Ar desorb from activated charcoal, along with krypton. Due to the length of the trap, it acts as a gas chromatograph and N<sub>2</sub>, O<sub>2</sub> and Ar are released from the trap before Kr is released. To avoid losing the krypton, the composition of the gas effluent is closely monitored. Once Kr is detected, AC2 is bypassed by switching the 4-way valve and krypton remains trapped as a gas in AC2. AC2 is then warmed to 35 °C by immersion in warm water.

#### Step 6: Transfer krypton to liquid scintillation counting vial

The second 3-way valve is switched to direct the helium from the second mass flow controller (100 sccm) through the liquid scintillation counting (LSC) vial. The vial is flushed for 2 minutes to remove atmospheric gases. The bottom 2 cm of the LSC vial is slowly immersed in liquid nitrogen to cool the glass and silica beads to -195 °C. The vial is cooled for 5 minutes under 100 sccm helium. The syringe is filled with 15 mL LSC cocktail.

The aperture of the variable leak valve is increased to bleed more gas into the RGA and increase the signal. The helium flow rate is reduced to 10 sccm and the 4-way valve is switched. Helium carries the krypton from AC2, by the leak valve, and into the bottom of the LSC vial through thin silicone tubing. The concentration of krypton in the helium flow is closely monitored on the RGA because this quantifies the volume of krypton trapped in the vial. Transfer typically takes 10-15 minutes. Transfer is complete when the concentration of krypton is reduced to background (or < 1% of the peak concentration). The second 3-way valve is switched to direct the helium flow way from the vial. The LSC cocktail is added to the vial, covering the silica beads. The cocktail freezes to the vial and traps the silicone tube. The liquid nitrogen is removed from the vial and the glass vial is removed from the cap, leaving the tube in. The vial is quickly capped to prevent escape of krypton. It takes 6 hours to purify one krypton sample.

Split samples for analysis at Bern were separated by bypassing AC2 after the krypton signal had decreased to  $\sim 2.5 \times 10^{-8}$ . The amount of krypton remaining in AC2 was approximately 0.015 cm<sup>3</sup>STP. After the main sample was transferred to the LSC vial, scintillation cocktail was added and the vial was capped, the split sample was transferred to a U-shaped 25 cm long ¼" OD copper tube containing 0.3 gram activated charcoal. The U-shaped trap was cooled to liquid nitrogen and the krypton was transferred in 10 sccm helium flow. After the transfer, the ends of the copper tube were pinch-clamped, in the way that groundwater samples are collected for noble gas analysis.

## 2.3 Liquid Scintillation Counting

The Krypton 85 samples were counted as-is on a Quantulus 1220 liquid scintillation counter from PerkinElmer. The instrument is located in a count room several stories underground in a specially designed facility to minimize cosmic ray and environmental background contributions. Additionally, the Quantulus is equipped with chilling unit to maintain a stable temperature during counting. Liquid scintillation counting depends on the beta emission from Kr85 (maximum energy 0.687 MeV, average energy 0.251 MeV). Interaction of the beta emission with the scintillation cocktail produces

photons which are captured by photomultiplier tubes (PMT) on the liquid scintillation counter. On the Quantulus, the default “High Energy Beta” settings were used on the instrument with channels 150-750 used as the counting window. Samples were counted for 200 minutes a piece for two cycles; prepared blank samples were used to determine a background subtraction and were counted for 200 minutes.

## 2.4 Calibration, Uncertainty Propagation and Groundwater Samples

### 2.4.1 Calibration

The two laboratory components of the  $^{85}\text{Kr}$  analytical capability (purification and counting) were tested and calibrated using air samples and pure, commercial Kr. The composition of dissolved gases in groundwater samples can vary due to variations in recharge temperature and elevation, excess air, and subsurface gas production. Therefore, the amount of Kr transferred to the LSC vial is determined from the RGA.

First, the RGA peak area ( $A_{\text{RGA}}$ ) was calibrated against the volume of 10 purified air samples ( $V_{\text{air}}$ ), varying in volume between 57 and 479 L-STP. The concentration of krypton in air is constant ( $[\text{Kr}_{\text{air}}] = 1.14 \text{ ppm}$ ) and the amount of Kr transferred to the vial is directly related to the processed air volume (assuming a 100% retention of Kr during the purification steps). After this calibration, the amount of Kr transferred to the LSC vial can be determined from the RGA peak area (referred to as  $\text{Kr}_{\text{RGA}} [\text{cm}^3\text{STP}]$ ).

$$([\text{Kr}_{\text{air}}] \times V_{\text{air}}) \sim \text{Kr}_{\text{RGA}} = f(A_{\text{RGA}}) \quad [\text{Eq 1}]$$

As noted previously, the composition of dissolved gases in groundwater samples can vary significantly due to variations in recharge temperature and elevation, excess air, and subsurface gas production, so the volume of processed gas extracted from groundwater cannot be used as a measure of the amount of Kr transferred to the LSC vial.

Second, the sensitivity of the liquid scintillation counting ( $s_{\text{LSC}}$ ) was calibrated by a linear regression of the count rate ( $\text{CR}_{\text{LSC}}$ ) of the 10 purified air samples to the amount of Kr transferred to the LSC vial, derived from the RGA peak area ( $\text{Kr}_{\text{RGA}}$ ). From the slope of the regression line ( $\text{CPM}/\text{cm}^3\text{Kr}$ ) and the activity of air, measured by the University of Bern ( $\text{DPM}/\text{cm}^3\text{Kr}$ ), the sensitivity – or counting efficiency – was calculated, expressed as counts per minute per decays per minute ( $\text{CPM}/\text{DPM}$ ). The background count rate ( $\text{CR}_{\text{LSC,background}}$ ) of the vial, silica beads, silicone tubing and scintillation cocktail was established by counting 8 vials with no krypton.

The  $^{85}\text{Kr}$  activity of unknown samples, expressed as a percentage of present day air, is derived from the ratio of the count rate and the RGA-derived Kr amount in the vial, referenced against the ratio of the count rate and RGA-derived Kr of standard Kr samples, divided by the LSC sensitivity.

$$A_{85\text{Kr}} = [ (\text{CR}_{\text{LSC, sample}} - \text{CR}_{\text{LSC,background}}) / \text{Kr}_{\text{RGA,sample}} ] / s_{\text{LSC}} \quad [\text{Eq 2}]$$

It should be noted that the efficiency of the purification or the liquid scintillation counting do not need to be known precisely since  $^{85}\text{Kr}$  dating depends upon the ratio of  $^{85}\text{Kr}/\text{Kr}$ .

In addition,  $^{85}\text{Kr}$  activities were analyzed in small ( $\sim 0.02 \text{ cm}^3 \text{ Kr}$ ) subsamples by low level gas proportional counting in the Deep Laboratory of the Physics Institute, University of Bern, Switzerland [Loosli, 1983; Loosli et al., 1989]. These samples included the pure Kr standard (Linde Electronic & Specialty Gases), a purified air sample, and 6 well samples.

### 2.4.2 Uncertainty Propagation

The uncertainty of the calculation  $^{85}\text{Kr}$  activity of unknown samples is derived by propagating the uncertainty of the calibration of the separate steps: the uncertainty of the Kr amount transferred to the vial derived from the RGA signal ( $\sigma_{\text{Kr\_RGA}}$ ), the uncertainty of the count rate of the sample ( $\sigma_{\text{CR\_LSC, sample}}^2$ ) and the instrument background ( $\sigma_{\text{CR\_LSC, background}}^2$ ), the uncertainty of the liquid scintillation counting efficiency ( $\sigma_{\text{s\_LSC}}$ ) and the uncertainty of the  $^{85}\text{Kr}$  standard ( $\sigma_{\text{A\_85Kr, standard}}$ ). These sources of uncertainty are assumed to be independent and the combined uncertainty is calculated as the square root of the sum of squared relative uncertainties of each of the variables in the calculation:

$$\sigma_{\text{A\_85Kr, sample}} = \text{A}_{85\text{Kr, sample}} \times \left\{ \left( \frac{\sigma_{\text{Kr\_RGA}}}{\text{Kr}_{\text{RGA}}} \right)^2 + \left( \frac{[\sigma_{\text{CR\_LSC, sample}}^2 + \sigma_{\text{CR\_LSC, background}}^2]^{1/2}}{[\text{CR}_{\text{LSC, sample}} - \text{CR}_{\text{LSC, background}}]} \right)^2 + \left( \frac{\sigma_{\text{s\_LSC}}}{\text{s}_{\text{LSC}}} \right)^2 \right\}^{1/2} \quad [\text{Eq 3}]$$

The uncertainty of the RGA-derived Kr amount ( $\sigma_{\text{KrRGA}}$ ) was calculated as the standard deviation of the differences between the Kr amounts derived from the peak area and the processed air volume, for the samples used in developing the calibration curve.

$$\sigma_{\text{Kr\_RGA}} = \left\{ \sum ([\text{Kr}_{\text{air}}] \times V_{\text{air},i} - \text{Kr}_{\text{RGA},i})^2 / n \right\}^{1/2} \quad [\text{Eq 4}]$$

The uncertainty of the background count rate ( $\sigma_{\text{CR\_LSC, background}}$ ) was calculated as the standard deviation of 4 blank LSC vials. The uncertainty of the sample count rate ( $\sigma_{\text{CR\_LSC, sample}}$ ) is calculated from the sample count rate (counts per minute) and the counting time (t) in minutes.

$$\sigma_{\text{CR\_LSC, sample}} = (\text{CR}_{\text{LSC, sample}} / t)^{1/2} \quad [\text{Eq 5}]$$

The standard error of the slope of the linear regression calibration was used as the uncertainty of the liquid scintillation counting sensitivity ( $\sigma_{\text{s\_LSC}}$ ). The uncertainty of the standard activity was obtained from the Bern analysis of the standard.

From the uncertainty propagation calculations, the uncertainty of measured  $^{85}\text{Kr}$  activities was predicted for various sample sizes (Kr amounts) and activities.

### 2.4.3 Groundwater Samples

Groundwater samples were collected from six public drinking water supply wells in the City of Turlock on 30 June and 1 July 2014 (Table 1). The processed volume of water varied between approximately 2100 and 4300 liters (550 to 1130 gallons). The extracted gas samples varied in size between 57 and 82 liters STP. Based on the dissolved noble gas analyses performed at the LLNL Noble Gas Mass Spectrometer facility, the collected gas samples contain 0.16 to 0.33  $\text{cm}^3 \text{STP Kr}$ , assuming 100% gas extraction efficiency.

## 3 RESULTS

### 3.1 Krypton Purification from Air

Figure 3a shows the RGA signal for helium ( $m/z=4$ ), water ( $m/z=18$ ), nitrogen ( $m/z=28$ ), oxygen ( $m/z=32$ ), argon ( $m/z=40$ ) and krypton ( $m/z=84$ , the most abundant isotope of Kr) during the entire process of purifying one sample. Measurements are made every 4 seconds. Step 1 is not monitored by the RGA. During Step 2 (Venting AC1 with helium at  $-78\text{ }^{\circ}\text{C}$ ) the signal peaks of nitrogen, oxygen and argon first sharply increase before steadily decreasing over the course of 2 hours. While the remaining gases are transferred to AC2 in Step 3, all gases are trapped in AC2 and the RGA measures only helium. Nitrogen, oxygen and argon are released from AC2 in Step 4 (Venting AC2 with helium at  $-78\text{ }^{\circ}\text{C}$ ) and the signals decrease over the course of 30 minutes (Figure 3b). After AC2 is warmed to  $0^{\circ}\text{C}$  (Step 5) the trap acts as a chromatographic column. Krypton is not fixed to activated charcoal at  $0^{\circ}\text{C}$ , but the transport of krypton through the column is retarded resulting in a nearly complete separation of krypton from the remaining nitrogen and oxygen. (The sharp increase in  $\text{N}_2$  and  $\text{O}_2$  preceding the krypton release at the end of Step 5 is the result of opening the aperture of the leak valve to obtain a higher sensitivity to the krypton signal.) Once the krypton signal exceeds  $10^{-9}$ , trap AC2 is bypassed to retain the krypton and then warmed to  $30^{\circ}\text{C}$ . After the LSC vial is prepared and cooled to LN, the krypton is transferred to the vial using a helium flow of 10 standard cubic centimeters per minute (sccm). The concentration of krypton in the 10 sccm helium flow is monitored to calculate the amount of krypton transferred. The shaded area underneath the krypton signal (RGA peak area) represents the amount of krypton transferred, and is calculated by summing all measured RGA values during the transfer period (arbitrary units). The peak krypton signal is reached after  $\sim 4$  minutes and the entire transfer takes  $\sim 10$  minutes. For the sample shown in the figure, AC2 was bypassed during the Kr transfer when the RGA signal reached  $2.5 \times 10^{-8}$ . The second shaded peak area represents the transfer of the remainder of the Kr trapped in the volume of AC2 to a LN-cooled U-shaped copper tube containing 0.3 gram activated charcoal for gas proportional counting analysis in Bern.

The entire sample purification takes approximately one day, including cleaning the traps by heating to  $200^{\circ}\text{C}$  under helium flow for 30-60 minutes.

The RGA peak area correlates with the amount of Kr processed (calculated from the volume of processed air), showing a non-linear relationship (Figure 4). A 2<sup>nd</sup> order polynomial with zero offset was fitted to the 10 data points, resulting in an  $R^2$  value of 0.979. Four data points are visible outliers. These were removed to avoid the polynomial being biased towards the outliers. Outliers are defined as data points that are significantly ( $P < 5\%$ ) different from the rest of the data set, assuming a normal distribution. The outliers were identified by calculating the difference between the outlier value and the polynomial fitted to the remaining data points. If this difference was more than 1.96 times the standard deviation of the residuals of the remaining data points to the polynomial (equivalent to a two-tailed probability of 5%) the outlier was removed. Four outliers were significant. The  $R^2$  of the polynomial fitted to the remaining 6 data points was 0.9997. The polynomial is described by

$$A_{\text{RGA}} = 6.12 \times 10^{-5} \times \text{Kr}^2 + 1.53 \times 10^{-5} \times \text{Kr} \quad [\text{Eq 6}]$$

The transferred krypton volume is calculated by inverting the quadratic equation:

$$Kr_{RGA} = [ -b + ( b^2 - 4 \times a \times -A_{RGA} )^{1/2} ] / 2a \quad [Eq 7]$$

with  $a = 6.12 \times 10^{-5}$  and  $b = 1.53 \times 10^{-5}$

The root mean squared error of the residuals between the RGA-derived Kr amount and the air-derived Kr amount is  $0.007 \text{ cm}^3\text{STP}$ , which is used as the uncertainty of the RGA-derived krypton amount ( $\sigma_{Kr\_RGA}$ ).

The cause of the non-linearity in the RGA peak area response is suspected to lie in variations in the efficiency of the source and/or detector of the RGA. During the purification procedure, the RGA is operated near the maximum operating pressure in order to maximize the sensitivity to very small concentrations of krypton in the helium flow. During the transfer of the krypton, the helium signal varies, positively correlating with the krypton signal, indicating increased sensitivity for the presence of krypton. While the maximum concentration of krypton in the helium stream never exceeds 2%, the variations in helium signal are up to 10%. However, correcting for the variation in helium signal did not remove the non-linearity and the empirical 2<sup>nd</sup> order polynomial was deemed best for calibrating the RGA peak area.

### 3.2 Liquid Scintillation Counting of Air Standards

The background count rate, determined as the average of ten vial with beads, silicone tubing and liquid scintillation cocktail, without krypton, is  $4.16 \pm 0.28$  counts per minute (CPM). The standard deviation of the ten blanks (0.28 CPM) is used as the uncertainty of the background count rate ( $\sigma_{CR\_LSC, \text{background}}$ ).

The count rate of air samples correlates linearly with both the air derived krypton amount and the RGA-derived krypton amount (Figure 5). The slope of a linear regression line represents the sensitivity of the liquid scintillation counting method. Four outliers are visible. Considering the counting uncertainty ( $\sigma_{CR} = (CR/t)^{1/2}$ ), all four outliers are significant, following the outlier identification procedure described above. The slope of the regression line fitted to the remaining 6 data points and 4 blanks is  $21.6 \text{ CPM/cm}^3\text{Kr}$  with  $R^2 = 0.9986$ . The uncertainty of the slope of the calibration line is  $0.357 \text{ CPM/cm}^3\text{Kr}$ . The sensitivity of the liquid scintillation counting method ( $S_{LSC}$ ) was calculated to be  $(21.6 \text{ CPM/cm}^3\text{Kr} / 75.4 \text{ DPM/cm}^3\text{Kr}) = 0.286 \text{ CPM/DPM}$ . The uncertainty of the sensitivity ( $\sigma_{s\_LSC}$ ) is  $0.013 \text{ CPM/DPM}$ , incorporating both the uncertainty of the slope and the uncertainty of the activity of the air sample measured by the University of Bern.

The detection limit is determined by the variation of the ten blank samples. The 95% one-tailed confidence interval ( $1.64 \sigma$ ) corresponds to a detection limit of  $0.46 \text{ CPM}$  above the background count rate of  $4.16 \text{ CPM}$ . For a  $0.2 \text{ cm}^3\text{STP Kr}$  sample, this corresponds to a detection limit of 11% of the present day  $^{85}\text{Kr}$  activity, or the activity in air in 1987. ( $0.2 \text{ cm}^3\text{STP} \times 21.6 \text{ CPM/cm}^3\text{STP} = 4.3 \text{ CPM}$ ;  $0.46 \text{ CPM} / 4.3 \text{ CPM} = 11\%$ )

Table 3 summarizes the parameters used in the calculation of the measured  $^{85}\text{Kr}$  activity (Eq 2) and the propagated analytical uncertainty (Eq 3) with the values derived in the calibration. With these parameters, the propagated analytical uncertainty was calculated for future samples with an activity between 10% and 100% of present day air and sample sizes of 0.1, 0.2 or  $0.3 \text{ cm}^3\text{STP Kr}$  (Figure 6).

The relative measurement uncertainty is smaller for larger samples with a higher activity, and larger for smaller samples with a lower activity. For a typical sample of 0.2 cm<sup>3</sup>STP Kr, the relative uncertainty increases from 10% for a present day activity to 38% for an activity of 20% of present day (recharged in 1993).

### **3.3 Groundwater Samples**

Purified dissolved gas from the six groundwater samples are between 0.168 and 0.240 cm<sup>3</sup>STP Kr. The RGA-derived Kr amounts vary between 70% and 107% of the Kr sample sizes estimated from the processed water volume and the dissolved krypton concentration. Low apparent recovery might be the result of gas escape from the sample containers during storage. Samples were stored for 5 months awaiting the completion and calibration of the Kr purification system. Gas pressure in the tanks was recorded at time of sampling but not subsequently when the samples were processed. Loss of pressure was noted on some samples, but not recorded.

Sample count rates vary between 3.95 and 4.43 counts per minute. The count rate did not exceed the 95% confidence detection limit of approximately 11% of the present day air activity for any of the samples. The non-detectable <sup>85</sup>Kr activity in five of the samples is consistent with the results of <sup>3</sup>H/<sup>3</sup>He dating indicating residence times of more than 40 years. The period in which these samples recharged was thus before the sharp increase of atmospheric <sup>85</sup>Kr. The <sup>3</sup>H/<sup>3</sup>He age of sample 110958 (Well 20) is 23±18 years, the estimated recharge year is 1991, and it was expected that <sup>85</sup>Kr would be detected. The concentration of terrigenous helium in this sample indicates a component of pre-modern water. Dilution with pre-modern water has lowered the <sup>85</sup>Kr activity below the LLNL detection limit.

<sup>85</sup>Kr was detected by Bern in all samples between 1.5 and 6.6 decays per minute per cm<sup>3</sup> krypton. The detection of <sup>85</sup>Kr was surprising given the <sup>3</sup>H/<sup>3</sup>He ages of the collected samples. While all detections are below the LLNL detection limit (within uncertainty) and therefore do not point directly to a contamination of groundwater samples with present day air, further testing of the GES to examine the possibility of atmospheric contamination during sampling will be performed. The detected activities in the groundwater samples correspond to decay corrected activities in air between 1971 and 1985. The activity in sample 110958 corresponds to a recharge year of 1985 (± 0.85 years), 6 years before the estimated <sup>3</sup>H/<sup>3</sup>He recharge year, but well within the uncertainty of the <sup>3</sup>H/<sup>3</sup>He age (18 years). The difference between the apparent <sup>3</sup>H/<sup>3</sup>He recharge year (1991) and the apparent <sup>85</sup>Kr recharge year (1985) could also be the result of a groundwater age distribution with a fraction of pre-modern groundwater (recharged before 1950). The fraction pre-modern groundwater lowers the <sup>3</sup>H and tritiogenic <sup>3</sup>He concentrations as well as the <sup>85</sup>Kr activity. The sample appears to be older due to the lower <sup>85</sup>Kr activity, while the <sup>3</sup>H/<sup>3</sup>He ratio (and therefore the <sup>3</sup>H/<sup>3</sup>He age) reflect the age of the modern groundwater component. The fraction pre-modern groundwater is also reflected in the sum of <sup>3</sup>H and tritiogenic <sup>3</sup>He when compared to the concentration of tritium in historical precipitation. The detection of <sup>85</sup>Kr in the other samples indicates that a fraction of the sampled groundwater has recharged later than the <sup>3</sup>H/<sup>3</sup>He ages indicate.

## 4 SUMMARY

A capability for the analysis of krypton-85 ( $^{85}\text{Kr}$ ) in groundwater samples was developed at LLNL. Samples are collected by extracting gas from 2000-4000 L of groundwater at the well, yielding approximately  $0.2\text{ cm}^3$  STP krypton. Sample collection takes 1 to 4 hours. Krypton is purified in the laboratory using a combination of molecular sieve and activated charcoal traps, and transferred to a liquid scintillation vial. The  $^{85}\text{Kr}$  activity is measured by liquid scintillation on a Quantulus 1220 liquid scintillation counter from PerkinElmer. The detection limit for a typical  $0.2\text{ cm}^3$  Kr sample size is 11% of the present day activity in air, corresponding to the decay corrected activity in air in 1987. The typical measurement uncertainty is below 10% for recently recharged samples. Six groundwater samples were collected, purified and counted.  $^{85}\text{Kr}$  was not detected in any of the samples counted at LLNL.

$^{85}\text{Kr}$  was detected by the low level counting laboratory of Bern University in all samples between 1.5 and 6.6 decays per minute per  $\text{cm}^3$  krypton, corresponding to decay corrected activities in air between 1971 and 1985.

The new capability is an excellent complement to tritium-helium, expanding the existing suite of age dating tools available to the GAMA program ( $^{35}\text{S}$ ,  $^3\text{H}/^3\text{He}$ ,  $^{14}\text{C}$  and radiogenic helium).  $^{85}\text{Kr}$  can replace  $^3\text{H}/^3\text{He}$  in settings where  $^3\text{H}/^3\text{He}$  ages are impossible to determine (for example where terrigenous helium overwhelms tritogenic helium) and provides additional insight into travel time distributions in complex mixed groundwater systems.



## 5 TABLES

**Table 1: Groundwater samples collected from public drinking water supply wells.**

Sample	Collection Date	Well	Kr concentration	Processed water volume	Gas sample	Estimated Kr sample size
			cm <sup>3</sup> STP/g	L	L STP	cm <sup>3</sup> STP
110956	6/30/2014	Well 8	$7.67 \times 10^{-8}$	3142	78	0.24
110957	7/1/2014	Well 39	$7.61 \times 10^{-8}$	4280	82	0.33
110958	7/1/2014	Well 20	$7.71 \times 10^{-8}$	2707	63	0.21
110959	7/1/2014	Well 29	$7.79 \times 10^{-8}$	3853	79	0.30
110960	7/1/2014	Well 36	$8.06 \times 10^{-8}$	3141	88	0.25
110961	6/30/2014	Well 14	$7.54 \times 10^{-8}$	2082	57	0.16

**Table 2: Processed air samples for calibration of the RGA-derived sample size and liquid scintillation sensitivity.**

Sample Number	Type	Air Volume	Kr <sub>air</sub>	RGA Peak Area	Kr <sub>RGA</sub>	Count Rate	Count Time	σ <sub>CR_LSC</sub>
		L	cm <sup>3</sup> STP	×10 <sup>-6</sup>	cm <sup>3</sup> STP	CPM	minutes	
18	blank	0	0.000	-	-	4.05	200	0.14
19	blank	0	0.000	-	-	4.09	200	0.14
20	blank	0	0.000	-	-	4.17	200	0.14
21	air	386	0.440	18.3	0.437	13.52	200	0.26
22	blank	0	0.000	-	-	4.32	200	0.15
23	air	272	0.311	8.3	0.264	12.48	200	0.25
24	air	208	0.237	8.7	0.273	10.17	200	0.23
25	air	479	0.546	26.7	0.547	15.00	200	0.27
26	air	292	0.333	11.9	0.333	11.67	200	0.24
27	air	115	0.131	3.9	0.158	7.45	200	0.19
28	air	455	0.519	20.2	0.463	15.63	200	0.28
29	air	216	0.246	7.9	0.255	11.57	200	0.24
30	air	57	0.065	1.5	0.075	5.77	200	0.17
31	air	185	0.211	0.0	0.201	8.11	200	0.20

Kr<sub>air</sub>: air volume-derived sample size;

Kr<sub>RGA</sub>: RGA peak area-derived sample size;

σ<sub>CR\_LSC</sub>: count rate uncertainty.

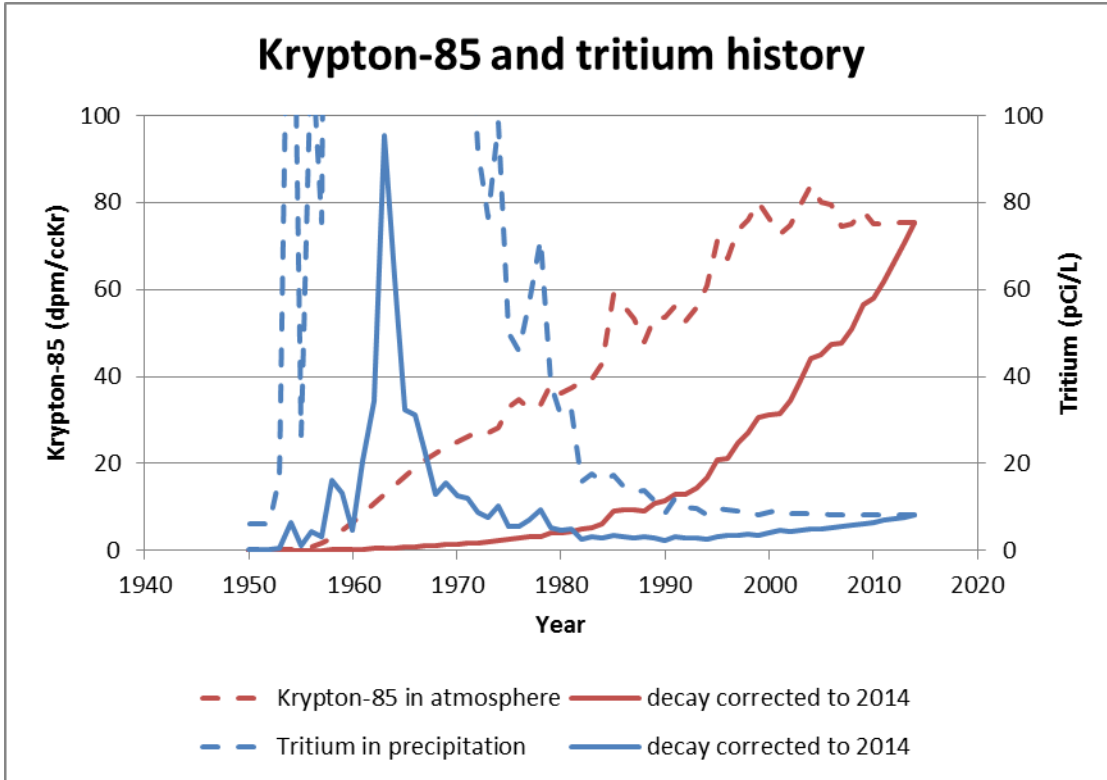
**Table 3: Parameter values used in Equations 2 and 3 for calculating the measured activity and the propagated analytical uncertainty.**

Parameter	Value	Unit	Description
$A_{85\text{Kr, sample}}$	-	DPM/cm <sup>3</sup> Kr	Measured <sup>85</sup> Kr activity
$\sigma_{A_{85\text{Kr, sample}}}$	-	DPM/cm <sup>3</sup> Kr	Uncertainty of measured <sup>85</sup> Kr activity
$Kr_{\text{RGA, sample}}$	-	cm <sup>3</sup> STP	RGA derived Kr amount
$\sigma_{Kr_{\text{RGA}}}$	0.007	cm <sup>3</sup> STP	Uncertainty of RGA derived Kr amount
$t$	200-400	minutes	Sample count time
$CR_{\text{LSC, sample}}$	-	CPM	Sample count rate
$\sigma_{CR_{\text{LSC, sample}}}$	$= (CR_{\text{LSC, sample}} / t)^{1/2}$	CPM	Uncertainty of sample count rate
$CR_{\text{LSC, background}}$	4.16	CPM	Background count rate
$\sigma_{CR_{\text{LSC, background}}}$	0.28	CPM	Uncertainty of background count rate
$A_{85\text{Kr, air, Bern}}$	75.4	DPM/cm <sup>3</sup> Kr	<sup>85</sup> Kr activity of present day air, measured by the University of Bern
$\sigma_{A_{85\text{Kr, air, Bern}}}$	3.1	DPM/cm <sup>3</sup> Kr	Uncertainty of <sup>85</sup> Kr activity of air
$S_{\text{LSC}}$	0.286	CPM/DPM	LSC sensitivity
$\sigma_{S_{\text{LSC}}}$	0.013	CPM/DPM	Uncertainty of LSC sensitivity

**Table 4: Krypton purification, liquid scintillation counting and gas proportional counting results of six well samples and one air sample.**

Sample	Process Date	RGA Peak Area	Kr Sample	Count Time	Count Rate	<sup>85</sup> Kr Activity (LLNL)	<sup>85</sup> Kr Activity (Bern)
		$\times 10^{-6}$	cm <sup>3</sup> STP	minutes	CPM	% present day air	DPM/cm <sup>3</sup> STP Kr
110956	12/1/2014	4.51	0.175	200	4.28	<12.2%	4.8±1.7
110957	12/5/2014	6.56	0.226	200	4.34	<11.8%	6.6±1.3
110958	12/3/2014	5.84	0.209	200	3.95	<10.2%	6.4±1.3
110959	12/4/2014	7.16	0.240	200	4.31	<8.9%	2.2±1.7
110960	12/2/2014	4.71	0.180	200	4.43	<9.4%	6.6±1.1
110961	12/9/2014	4.29	0.168	200	4.27	<12.7%	1.5±1.3
air	1/12/2015	11.66	0.329	200	11.28	100.2%±5.8%	75.4±3.1

## 6 FIGURES



**Figure 1: Historical (dashed) activities of krypton-85 in air (red) and tritium in precipitation (blue), and decay corrected to 2014 (continuous).** Tritium time series compiled from IAEA Global Network of Isotopes in Precipitation data from Ottawa (Canada), Portland (Oregon) and Menlo Park (California). The time series of the <sup>85</sup>Kr activity in the atmosphere collected and measured at Freiburg im Breisgau (Institute of Atmospheric Research (IAR), Freiburg, Germany) and adjusted to the activity in an air sample ( $75.4 \pm 3.1$  DPM/cm<sup>3</sup>Kr) collected in 2014 in Livermore and analyzed by Bern University.

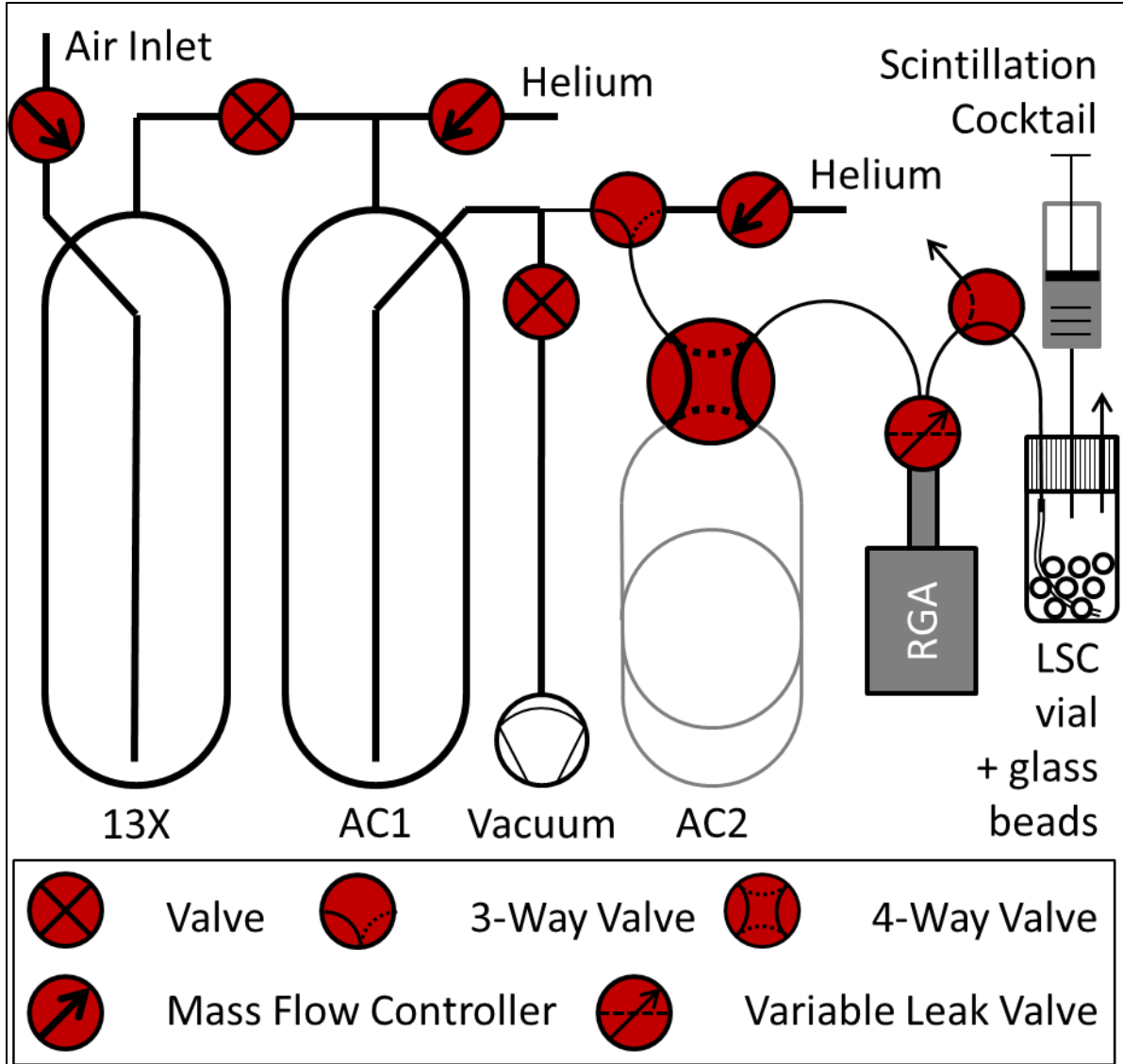


Figure 2: Schematic of the krypton purification system.

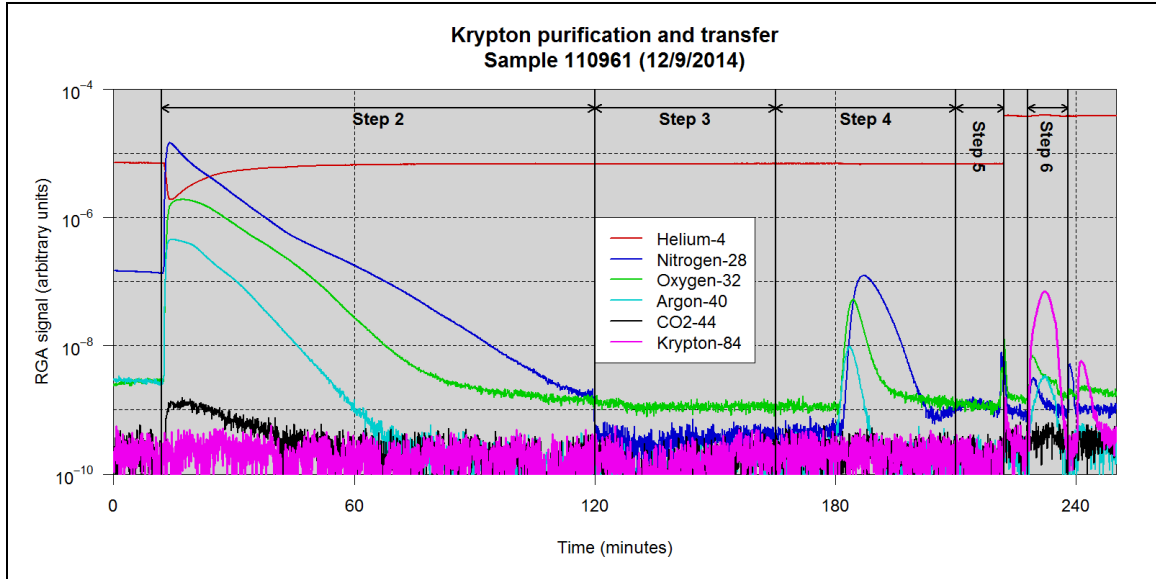


Figure 3a: RGA signals during purification and transfer of sample 110961.

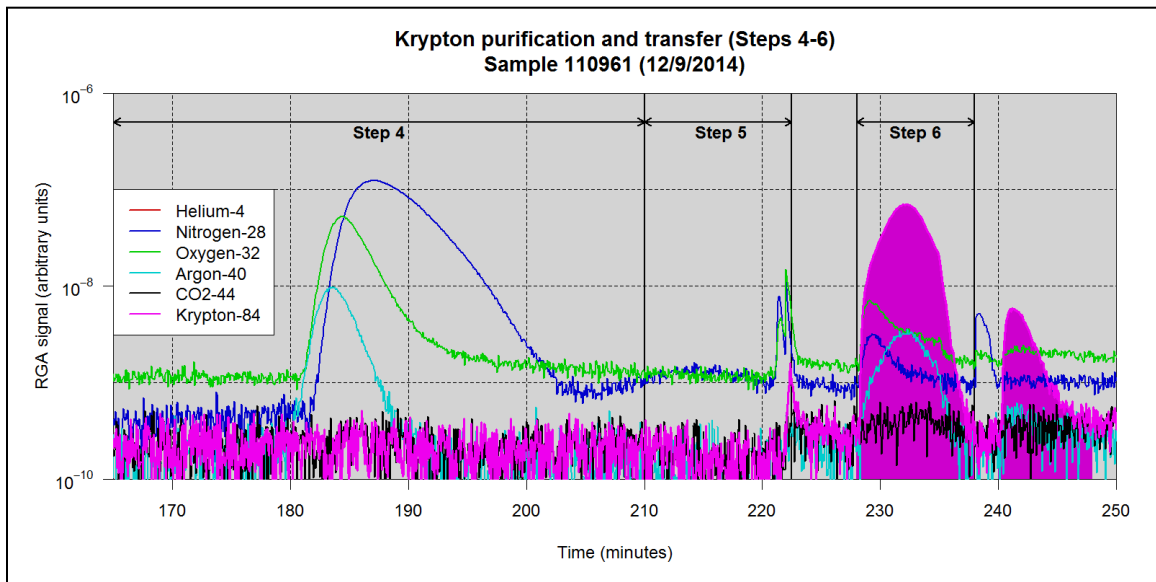


Figure 3b: RGA signals during Steps 4-6 of the purification and transfer of sample 110961.

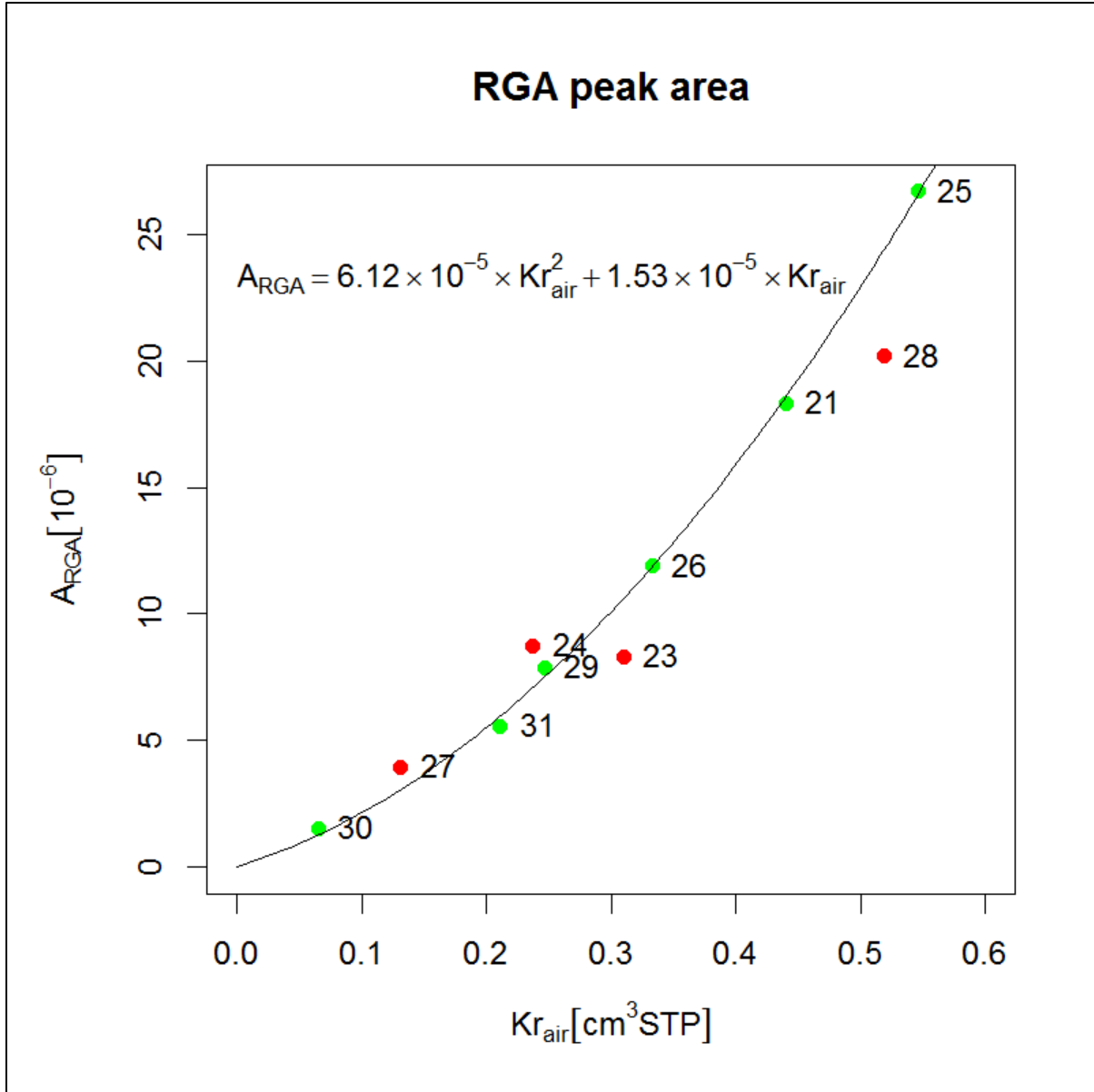
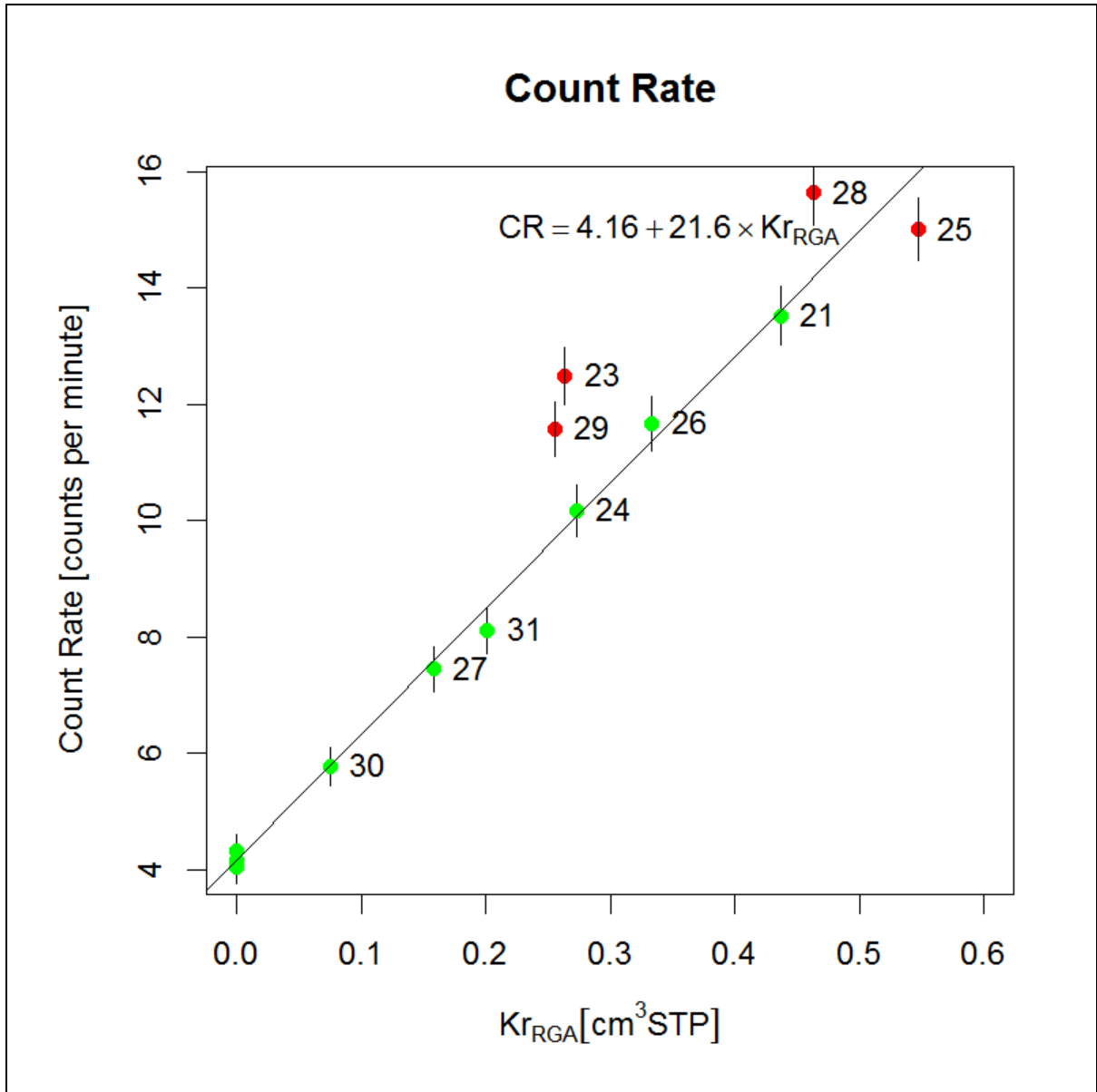


Figure 4: A second order polynomial fitted to the non-linear relationship between RGA peak area ( $A_{RGA}$ ) and air volume-derived Kr amount ( $Kr_{air}$ ), omitting four outliers (in red).  $R^2 = 0.9997$ .



**Figure 5: Liquid scintillation count rate calibrated against the RGA-derived krypton amount ( $Kr_{RGA}$ ) using a linear regression, omitting four outliers (in red). Error bars indicate the 1 sigma counting uncertainty.  $R^2 = 0.9986$ .**

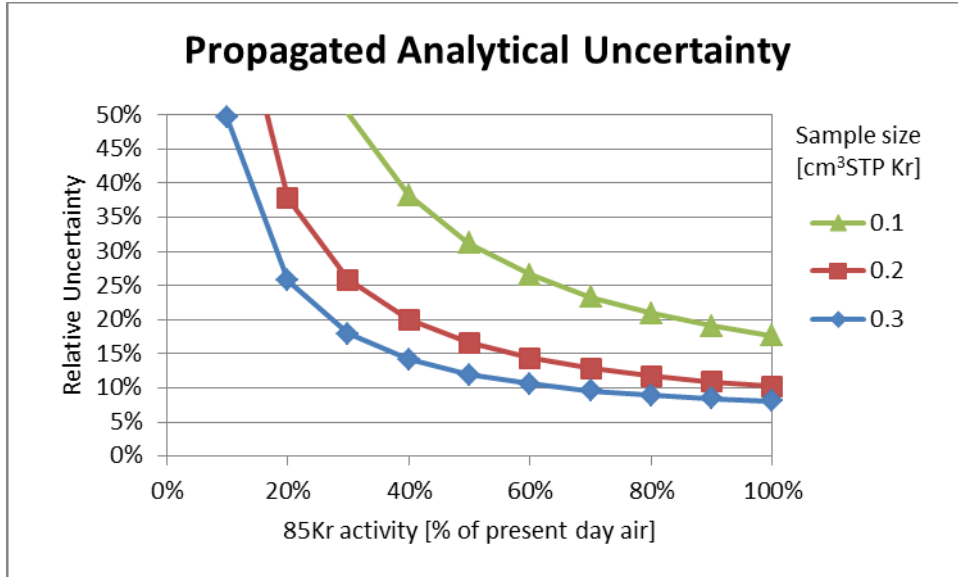


Figure 6: Propagated analytical uncertainty, relative to measured <sup>85</sup>Kr activity, for samples of different size.



## 7 REFERENCES

GAMA Project reports are available on the State Water Board GAMA website:

[http://www.swrcb.ca.gov/water\\_issues/programs/gama/report\\_depot.shtml](http://www.swrcb.ca.gov/water_issues/programs/gama/report_depot.shtml)

- Corcho Alvarado, J. A., R. Purtschert, F. Barbecot, C. Chabault, J. Rueedi, V. Schneider, W. Aeschbach-Hertig, R. Kipfer, and H. H. Loosli (2007), Constraining the age distribution of highly mixed groundwater using  $^{39}\text{Ar}$ : A multiple environmental tracer ( $^3\text{H}/^3\text{He}$ ,  $^{85}\text{Kr}$ ,  $^{39}\text{Ar}$ , and  $^{14}\text{C}$ ) study in the semiconfined Fontainebleau Sands Aquifer (France), *Water Resour Res*, 43(3), W03427.
- Janssens, A., J. Buysse, F. Raes, and H. Vanmarcke (1986), An improved method for the sampling of atmospheric  $^{85}\text{Kr}$ , *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 17(5-6), 564-567.
- Loosli, H. H. (1983), A dating method with  $^{39}\text{Ar}$ , *Earth and Planetary Science Letters*, 63(1), 51-62.
- Loosli, H. H., B. E. Lehmann, and W. Balderer (1989), Argon-39, argon-37 and krypton-85 isotopes in Stripa groundwaters, *Geochim Cosmochim Acta*, 53(8), 1825-1829.
- Momoshima, N., F. Inoue, S. Sugihara, J. Shimada, and M. Taniguchi (2010), An improved method for  $^{85}\text{Kr}$  analysis by liquid scintillation counting and its application to atmospheric  $^{85}\text{Kr}$  determination, *Journal of Environmental Radioactivity*, 101(8), 615-621.
- Moran, J., R. Ruiz, T. Ford, M. Singleton, B. K. Esser, G. T. Soto, C. Velsko, and D. Hillegonds (2008), California GAMA Program: Development of a Field Deployable Dissolved Gas Extraction Apparatus. Lawrence Livermore National Laboratory. UCRL-TR-407175 Rep.
- Ohta, T., Y. Mahara, N. Momoshima, F. Inoue, J. Shimada, R. Ikawa, and M. Taniguchi (2009), Separation of dissolved Kr from a water sample by means of a hollow fiber membrane, *Journal of Hydrology*, 376(1-2), 152-158.
- Okai, T., Y. Takashima, N. Shiraishi, and N. Matsuoka (1984), Measurement of krypton-85 in the atmosphere with a portable apparatus, *Journal of Radioanalytical and Nuclear Chemistry*, 81(1), 161-165, doi:10.1007/bf02132931.
- Smethie, J. W. M., D. K. Solomon, S. L. Schiff, and G. G. Mathieu (1992), Tracing groundwater flow in the Borden aquifer using krypton-85, *Journal of Hydrology*, 130(1-4), 279-297.
- Visser, A., H. P. Broers, R. Purtschert, J. Sültenfuß, and M. de Jonge (2013), Groundwater age distributions at a public drinking water supply well field derived from multiple age tracers ( $^{85}\text{Kr}$ ,  $^3\text{H}/^3\text{He}$ , and  $^{39}\text{Ar}$ ), *Water Resour Res*, 49(11), 7778-7796, doi:10.1002/2013WR014012.
- Yokochi, R., L. J. Heraty, and N. C. Sturchio (2008), Method for Purification of Krypton from Environmental Samples for Analysis of Radiokrypton Isotopes, *Analytical Chemistry*, 80(22), 8688-8693, doi:10.1021/ac801804x.