Measuring the diffusion of noble gases through a porous medium using prompt gamma activation analysis

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Abstract Detection of anthropogenic noble gas isotopes in the atmosphere is an important indication that a below ground nuclear-test has taken place. Diffusion plays a critical role in the transport of these gases through the geological media to the surface where they can be detected. Better techniques are need with which to study the diffusion of noble gases through porous systems. Here we demonstrate the suitability of using prompt gamma activation analysis to measure the time dependent concentration of argon as a result of its diffusion through a porous medium that is saturated with nitrogen at atmospheric pressure. The experiments were conducted in a 1 m long tube, 10 cm diameter, and packed with fine SiO_2 sand. Prompt gamma activation analysis was used to measure the concentration of argon within the experimental system as a function of time.

Keywords Noble gas · Diffusion · Prompt gamma activation analysis · Concentration

Introduction

The presence of anthropogenic radioisotopes provides the only definitive evidence that a clandestine nuclear weapon

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test has taken place [1]. Noble gas isotopes are particularly useful in this regard as their non-reactive nature allows them to migrate to the surface after a below ground detonation. The International Monitoring System of the Comprehensive Nuclear-Test Ban Treaty Organization often uses the presence of anthropogenic xenon in the atmosphere [1, 2] to determine whether a below ground test has taken place. Recently, it has been suggested that anthropogenic argon could be also be used for this purpose. The detection of anthropogenic noble gas isotopes can also be useful as an indicator for underground contamination from buried radioactive materials [3]. In both cases, subsurface gas transport will affect the quantities of gas that reach the surface and the time required to do so [2, 4].

The time dependent concentration of a gas moving through a porous medium can be described using:

$$\frac{\partial C_A}{\partial t} = -\nabla \times (C_A V - D_{AB} \nabla C_A) + R_A \tag{1}$$

Here C_A is the concentration (moles m^{-3}), v is the bulk velocity (m s^{-1}), D_{AB} is the binary diffusion coefficient (m^2 s^{-1}) of A through B, and R_A is the rate at which A is produced or lost at a given location (moles m^{-3} s^{-1}) [5, 6].

All experimental techniques that are used to study the diffusion of gases through a porous medium require the ability to measure the time dependent concentration of the gas [7–13]. Common methods for doing this include gas chromatography and mass spectroscopy [8, 10, 14], photothermal deflection [15], neutron radiography [16], and nuclear magnetic resonance [17, 18]. The selection of one or another technique is based on a consideration of its availability, precision, the way the measurement needs to be conducted (invasive or non-invasive), and the type of gas under study [19]. Mass spectroscopy (sometimes combined with gas chromatography analysis) is arguably

the most popular technique to analyze noble gas concentrations. The principal advantages of this technique (in a inductively coupled plasma mass spectrometer) are the small detection limits (parts per trillion), high sensitivity, and the ability to measure the elemental isotopic content of the analyte [20–22]. However, this analytical technique is invasive (requires the extraction of a sample form the system), destructive (the sample will be destroyed) and may necessitate a time-consuming sample preparation (extraction, purification and separation of the noble gas are needed previous to the analysis) [20, 21].

Prompt gamma activation analysis (PGAA) is a technique suitable for making non-invasive measurements of noble gas concentrations in porous and non-porous systems. This technique can be used to make non-invasive measurements on the concentration of noble gases as well as differentiate isotopes of the same chemical species [23, 24]. Unlike standard neutron activation analysis, PGAA is able to quantify the concentrations of non-radioactive isotopes. Here, prompt gamma photons of distinctive energy are produced in the stable isotope nucleus after it interacts with an incident neutron. These prompt gammas are detected, analyzed, and registered based on their energies using a semiconductor crystal detector in conjunction with a signal amplifier and a multichannel analyzer [25]. The gamma intensity at specific energies is proportional to the concentration of a particular non-radioactive isotope in the sample.

In this paper we demonstrate that use of PGAA for measuring time dependent argon concentrations as a result of diffusion through a homogeneous porous media.

Methodology

Diffusion experiments with high purity argon in nitrogen within a uniform porous media were conducted at the Nuclear Engineering Teaching Laboratory at The University of Texas at Austin. The diffusion experiments were conducted in a 1 meter long steel pipe with an internal diameter of 10.3 cm (4 in diameter ANSI Schedule 40) packed with 20/30 sieve Ottawa sand. On each end of this body, a 10 cm long by 10 cm internal diameter cylindrical aluminum chamber is added. These two chambers allow for a uniform diffusion front during the experiments. Two OMEGA® PX653-05D5 V differential pressure transducers were connected at the inlet and outlet of the aluminum chambers to guarantee measure pressure differentials and guarantee a diffusion-dominant process during the experiments. Figure 1 shows a schematic of the experimental set-up.

The neutron source for this work was a 1.1 MW TRIGA Mark II nuclear research reactor. A parabolic focusing element at the end of the horizontal neuron guide allows an equivalent thermal neutron flux of 5.3×10^6 cm^{-2} s^{-1} at the sample location when the reactor operates at 950 kW [26, 27]. The 65 % relative efficiency p-type ORTEC high purity germanium detector with a resolution of 1.95 keV at 1,332 keV was used for this work and was shielded with a combination of different materials from lead bricks to a borated foam and cadmium sheets. A Tennelec TC 702 amplifier and a 16 k Canberra 8713 analog to digital convertor with a Multiport II Canberra multichannel analyzer was employed for the signal processing. Genie™ 2000 software was used to analyze the gamma photon spectrum obtained.

Calibration and detection limits

For the present study, the detection limits of argon and natural xenon were estimated. First, the total counting efficiency and energy calibration of the PGAA system were performed using a ^{152}Eu source from the National Institute of Standards and Technology. Equation (2) shows the least square curve fit equation obtained for the counting efficiency e as a function of energy E (keV). Equation (3) gives the relationship between gamma energy and detector channel:

$$ln(e) = -0.0827ln(E)^3 + 1.5323ln(E)^2 - 9.6935ln(E) + 14.565 \tag{2}$$

where:

$$E = 0.6813 \times X + 8.4788 \tag{3}$$

with X denoting the detector channel.

The counting and pressure detection limits ($L_{D(counts)}$ and $L_{D(pressure)}$) were determined to evaluate the viability to use this nuclear analysis technique to track the argon and xenon concentrations in the gas sample aluminum cylinder. The counting detection limits $L_{D(counts)}$ (minimum amounts of xenon and argon gases that will be detected using the current measuring process) were calculated from the critical limit, L_C, following Currie's method [28–30]. The critical limit is defined by Currie as the minimum significant value that discriminates a net signal from the
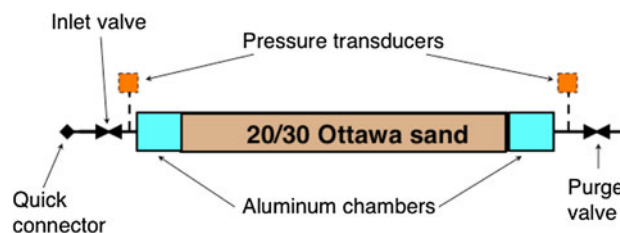
Fig. 1 Experimental set-up schematic

background [28, 29]. Equation (4) gives the statistical calculation of the critical limit. In this expression, k is the abscissa of the standardized normal distribution corresponding to the desired error probability, and μ_C is the background continuum at the channels where the peak of interest would be located. Using a false positive and false negative error probability of 5 %, the abscissa of the normal distribution, k, equals 1.624. To determine the counting detection limits, a background sample (gas sample cylinder vacuum up to 0.667 kPa (abs)) was analyzed during a 4 h live-time period with the nuclear reactor operating at 950 kW, i.e., with a 5.3×10^6 cm^{-2} s^{-1} neutron flux approximately:

$$L_C = k\sqrt{2 \times \mu_C} \qquad (4)$$

$$L_{D(counts)} = k^2 + 2 \times L_C \qquad (5)$$

$$L_{D(pressure)} = \frac{L_{C(counts)} \times p}{1000 \times \text{net counts}_{sample}} \qquad (6)$$

$$L_{D(concentration)} = \frac{L_{D(pressure)} \times 10^{-9}}{R \times T} \qquad (7)$$

$$CR = \frac{0.6023 \times e \times \phi \times \sigma_\gamma \times V_{eff} \times p}{R \times T}. \qquad (8)$$

The pressure and concentration detection limits, and the prompt gamma counting rates were calculated using Eqs. (6, 7, and 8) respectively, and assuming an ideal gas behavior of the sample. These equations give an estimation of the pressure detection limit $L_{D(pressure)}$ (kPa), the molar concentration detection limit $L_{D(concentration)}$ (mol cm^{-3}) and the counting rate CR (s^{-1}) for a detector efficiency e, a neutron flux ϕ (cm^{-2} s^{-1}), a neutron-gamma isotopic cross section $\sigma\gamma$ (barns), an ideal gas constant R (8.31446 J mol^{-1} K^{-1}), a reference sample pressure p (Pa) and temperature T (K), and an effective volume V_{eff} (16 cm^{-3} were estimated from the geometry of the beam and sample cylinder). The net peak area or net number of counts [net counts$_{sample}$ in Eq. (6)] were obtained from the spectra of a 99.9999 % high purity argon, and a natural xenon samples at 106.92 kPa (abs) and 298 K analyzed during a 4 h live-time period with the nuclear reactor operating at full power (950 kW). The sample spectra were evaluated using the second difference peak locator and the peak area analysis tools from Genie^{TM} 2000. Part of the spectrum acquired for each noble gas sample is shown in Fig. 2. The estimated counting rates and the calculated detection limits are tabulated in Table 1. This table also shows the counting rates obtained for these two gases using Genie^{TM} 2000 for comparison with their estimated values. It is important to mention that the neutron-gamma cross sections listed in Table 1 for the xenon isotopes match the values reported by the International Atomic Energy Agency and published by Molnar [31]. However, the cross sections used for the argon

nuclides correspond to those listed by Molnar and reduced by a factor of 0.417. This factor was estimated from the comparison between the argon mass concentrations ρ_{Ar} (g cm^{-3}) calculated using the sample pressure and Eq. (9):

$$\rho_{Ar} = \frac{p \times M_{Ar} \times 10^{-6}}{R \times T}, \qquad (9)$$

and the one estimated using the net peak area from the PGAA energy spectrum netcounts$_{sample}$, the analysis live-time t (s), and Eq. (10):

$$\rho_{Ar} = \frac{\text{net counts}_{sample} \times M_{Ar}}{0.6023 \times e \times \phi \times \sigma_\gamma \times V_{eff} \times t}. \qquad (10)$$

Diffusion experiments

The procedure followed for this work is divided in three major steps: porous media column venting, argon sample preparation, and diffusion of argon in nitrogen. The porous media column was vented flowing nitrogen at 25 cm^3 s^{-1} during 1 h, and at 8.3 cm^3 s^{-1} during at least another hour
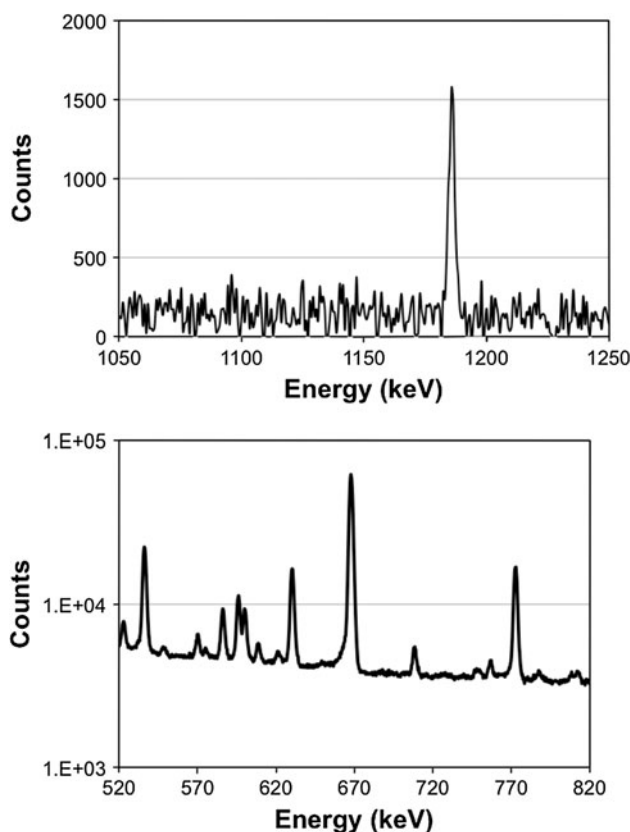
Fig. 2 Argon spectra and counts. *Top* 1186.8(3) keV peak of a PGAA spectrum obtained from a pure argon sample at 106.9 kPa (abs) and 298 K. *Bottom* PGAA spectrum of a natural xenon sample at 107.1 kPa (abs) and 296 K

Table 1 Prompt gamma counting rates and detection limits for ^{40}Ar, ^{129}Xe and ^{131}Xe (*^{131}Xe and ^{129}Xe also present peaks at 670.02 and 668.59 keV with neutron-gamma cross sections of 0.22 and 0.17 barn respectively)

Isotope	Energy (keV)	σ_Υ (b)	Efficiency (4.02 % error)	Counting rate predicted (s^{-1})	Counting rate measured (s^{-1})	Detection limit × 10^6 (mol cm^{-3})	Detection limit (kPa)
^{40}Ar	167.3	0.22	0.002494	1.209 ± 0.18	1.26 ± 0.01	3.681 ± 0.22	8.87 ± 0.07
	1186.8	0.14	0.001353	0.418 ± 0.06	0.44 ± 0.01	6.367 ± 0.38	15.36 ± 0.19
^{129}Xe	536.17	1.71	0.001724	6.49 ± 1.16	6.69 ± 0.02	0.436 ± 0.03	1.05 ± 0.004
	586.17	0.48	0.001688	1.79 ± 0.33	1.81 ± 0.01	1.708 ± 0.10	4.12 ± 0.03
	1482.06	0.112	0.001215	0.30 ± 0.05	0.28 ± 0.01	10.889 ± 0.66	26.25 ± 0.42
^{131}Xe	630.29	1.41	0.001658	5.15 ± 0.70	5.01 ± 0.02	0.607 ± 0.04	1.45 ± 0.005
	667.79*	6.7	0.001635	25.58 ± 3.43	26.25 ± 0.04	0.113 ± 0.01	0.28 ± 0.001
	772.72	1.78	0.001572	6.17 ± 0.85	6.24 ± 0.02	0.476 ± 0.03	1.15 ± 0.004

to remove the traces of argon from previous experiments. Then, the ball purge valve was closed and the experimental set-up is pressurized up to about 100 kPa.

The argon sample preparation consist of a series of vacuum-fill cycles using a Argon 6.0 Research gas from Praxair to ensure that more than 99.5 % of the gas molecules in the sample correspond to the high purity argon (Batch number W476720701). The gas sample cylinder was then pressurized up to 105 kPa (abs). Since the experimental set-up and the argon cylinder were pressurized in different rooms, the pressure of the argon sample need to be lower to match the one of the experimental set-up with a pressure excess lower than 70 Pa using a SS low-flow metering valve from Swagelok®, and a PX653-05D5V differential pressure transducer from OMEGA®. The sample was then analyzed using PGAA with the reactor operating at 950 kW.

The aluminum cylinder is connected to the experimental set-up through a full-flow quick connector from Swagelok® and the argon is allow to diffuse within the porous media for a desired amount of time. The argon concentration left within the sample cylinder was measured using PGAA and a neutron flux of about 5.3×10^6 cm^{-2} s^{-1}

Error propagation

The experimental uncertainties reported in this paper were calculated following the error propagation formulae [25] and a least-squares regression analysis [32] as applied to each of the equations used to estimate the results listed in Table 1. In general, for every count net peak area used, its variance was obtained from the Genie^{TM} 2000 peak area analysis tool after fitting a Gaussian distribution to the peak of interest in the gamma spectrum. The standard deviations for the neutron-gamma cross sections were those reported by Molnar [31] for the xenon isotopes. For the argon nuclides cross sections, the values listed in Table 1 were assumed to have an error of 10 % (close to the relative

error on the values tabulated by Molnar for these isotopes). Also, the background counts and neutron flux were assumed to be the mean values and therefore equal to their variance. The error for the effective sample volume was assumed to equal 10 % (1.6 cm^3). In the case of pressure and temperature, the reading accuracies (0.25 % and 0.5 °C respectively) were taken as the dominant error. The variance in the detector efficiency was determined from a least-squares regression analysis.

Results and discussion

Various diffusion experiments were conducted as described in the previous section. A gas sample cylinder was prepared and analyzed using PGAA before and after the nine diffusion experiments listed in Table 2. This table shows the live-time of prompt gamma analyses, and the percentage of argon concentration that remains within the cylinder after each test. The percentage of the remainder argon in the sample container was obtained from the ratio of the net areas of the 1186.6 keV peaks in the pre- and post-diffusion spectra. The spectrum peaks at this energy were selected despite their smaller neutron-gamma cross

Table 2 Diffusion experiment results

Diffusion time (h)	Prompt gamma counting live-time (h)	C/C_o measured (%)
4.0	4.0	94.3 ± 4.49
6.0	5.0	95.5 ± 4.76
8.0	4.0	81.7 ± 4.05
16.0	3.0	71.5 ± 4.44
20.0	4.0	67.9 ± 4.20
23.5	4.0	63.2 ± 4.28
42.5	4.0	48.4 ± 3.37
66.0	5.0	34.6 ± 2.67
89.5	5.0	27.0 ± 2.63
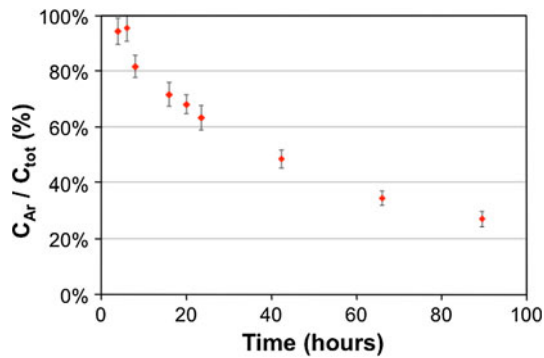
Fig. 3 Argon concentration ratio. Ratio of argon concentration within the gas sample cylinder to its initial molar concentration after diffusing through the experimental set-up for different periods of time

sections because of the higher Compton and more background peaks near-by 167.3 keV. The results recorded in this table are also depicted in Fig. 3.

Conclusions

An experimental set-up, and a test procedure have been developed to demonstrate the suitability of using PGAA to evaluate the time dependent concentration of argon as a result of its diffusion through a porous media. The results demonstrate that PGAA can be used to study the time varying concentrations of argon and xenon that would result from their diffusion through a porous medium.

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