Extraction and quantification system for environmental radioxenon sample analysis

M. Sabzian[a], M.N. Nasrabadi[a,*], M. Haji-Hosseini[b]

[a] Department of Nuclear Engineering, Faculty of Advanced Sciences & Technologies, University of Isfahan, HezarJerib Street, 81746-73441, Isfahan, Iran
[b] Materials and Nuclear Fuel Research School, Nuclear Science and Technology Research Institute, Iran

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ABSTRACT

A xenon dynamic adsorption setup based on granular activated carbon packed column was developed. The adsorption behavior of xenon under different experimental conditions was studied and the results used to design an appropriate adsorber column for specific conditions. The resulting radioxenon gas extraction and quantification setup was evaluated based on an inter-comparison exercise and standard sample analysis results. The results showed that the quantification setup achieves experimental rules with uncertainty of ± 3%.

1. Introduction

Environmental radioxenon gas monitoring is a major technique for the detection of underground or underwater nuclear explosions (Carrigan et al., 1996; De Geer, 1996; Ringbom et al., 2014). The International Monitoring System (IMS) has been established to verify compliance with the Comprehensive Nuclear-Test-Ban Treaty (CTBT). Once completed, the radionuclide monitoring network of IMS will consist of 80 stations located worldwide for sampling, processing and measurement of airborne radioactive fission products. This network shall also include 40 stations that are planned to be capable to sample, process and analyze relevant airborne radioxenon isotopes, namely ^{131m}Xe, ^{133}Xe, ^{133m}Xe, and ^{135}Xe. In order to meet the requirements for IMS noble gas stations, four systems have been developed yet, namely SAUNA: Swedish Automatic Unit for Noble gas Acquisition (Ringbom et al., 2003), ARSA: Automated Radioxenon Sampler and Analyzer (Bowyer et al., 2002), ARIX: Analyzer of Xenon Radio Isotopes (Dubasov et al., 2005) and SPALAX: Système de Prélèvement Automatiqueen Ligneavecl' Analysedu Xénon atmosphérique (Fontaine et al., 2004).

Besides these IMS stations, there are 16 radionuclide laboratories that would support radionuclide network for further analysis of specific samples. These laboratories are also used for calibration of quality assurance reference spikes at the stations (Karhu and Clawson, 2001). Precise determination of the xenon activity concentrations at laboratories has two separate steps. In the first step, the xenon in a sample has to be extracted and then the volume of xenon in the sample determined. Then, the xenon activity of sample would be measured in an appropriate radiation detector (Cagniant et al., 2014; Schroettner et al., 2010;

Xie et al., 2013). Xenon extraction is usually performed based on chromatographic processes and the xenon volume measurement is performed with a thermal conductivity detector. Conformity of the measured values at the noble gas station and at the laboratory depends on several factors, such as potential loss of gas, lack of volume measurement accuracy, and traceability of the actual measurements. Laboratory measurements have essential rule in quality assurance/quality control (QA/QC) program of IMS noble gas systems. This program includes regular proficiency test exercises (PTE) to assess the accuracy and traceability of the actual measurements of a laboratory against pre-established criteria. Currently six IMS radionuclide laboratories have developed radioxenon gas measurement capabilities (Gohla et al., 2016). In addition to the above mentioned laboratories, three more laboratories improved their competence for the measurement of radioxenon samples from noble gas stations, namely the Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA) has established a noble gas system (Nava et al., 2013); the Swedish Defense Research Agency laboratory (FOI) (Ringbom et al., 2009), and the German Federal Office for Radiation Protection (Bundesamt für Strahlenschutz, BfS) (Schlosser et al., 2017).

Here, the endeavor is to develop a gas extraction system based on xenon adsorption on activated carbon at room temperature. Development of such a system demands several requirements to attain quantitative measures. To meet the requirements of CTBT, a precise volume measurement system has to be included (CTBT/PTS/INF.96/Rev9, 2012). In this work, xenon dynamic adsorption on a granular activated carbon (GAC) packed bed absorber is discussed and the method to calculate the appropriate parameters from xenon breakthrough curve involving the Wheeler-Jonas equation (WJ equation) is

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Table 1
Characteristics of GAC obtained from BET analysis.

BET surface area $(m^2 \, g^{-1})$	BJH method $(m^2 \, g^{-1})$	BJH method pore volume CC/g	BJH method pore diameter (nm)
1074	683.4	40.36	1.220

presented. Hence, the amount of GAC required to absorb and isolate a certain amount of xenon gas was estimated. Afterwards, the gas extraction and volume measurement setup was equipped with GAC packed column absorber. Then a gas chromatographic system was developed and its performance was investigated based on the inter-comparison exercise and standard sample analysis.

2. Material and methods

The adsorbent test bed in this study is a GAC packed column with average particle nano-pore diameter is 1.22 nm that was purchased from Merck Company (Darmstadt, Germany). The characteristics of GAC obtained from BET analysis are shown in Table 1. Natural helium and xenon gases were purchased with 99.999% purity (Air Products, China). The GAC was heated at 473 K for at least 2 h to remove moisture and then it was cooled in a desiccator to room temperature. The mixture of xenon in helium with 500 parts per million by volume (ppmv) concentration was employed to study dynamic adsorption by the adsorbent. Collection of xenon from the gas chromatographic system output was performed using 0.5 g of carbon molecular sieve (CMS) contained in a 10-cm-long, by 3-mm-diameter stainless steel column.

2.1. Xenon dynamic adsorption setup

The schematic diagram of experimental system to characterize the GAC column is shown in Fig. 1. The GAC was weighted and properly packed into a 100-cm-long stainless steel column with an inner diameter of 0.325 cm resulting to the internal volume of 33.16 mL. Total mass of the packed GAC was 20.99 g. A glass wool filter (Merck, Darmstadt, Germany) was placed at both ends to prevent loss of GAC during sample loading stage. Before performing the experiments, GAC packed column was conditioned by heating up to 443 K for 2 h in an oven (Memert GmbH, Germany). Helium gas was supplied at a volumetric flow rate of 60 mL min⁻¹ while the GAC packed column cooled down to the room temperature. After each adsorption experiment the bed was regenerated by the same procedure. As illustrated in Fig. 1, the

Fig. 1. Schematic diagram of GAC column characterization experimental system.

GAC packed column was placed in a thermostatic water circulator to keep constant temperature of the column. A solenoid valve regulated gas flow from two gas cylinders, one filled with the helium gas that was used to vent through the GAC packed column at beginning of process and the other one was filled with 500 ppmv helium-xenon gas mixture. A needle valve (Swagelok, USA) and a digital mass flow controller (FC-2900V, Mykrolis, TX, USA) were used to read and control the gas flow. The mixed gas that passed through GAC packed column transferred to a 6-port rotary valve placed inside the sampling section of gas chromatographic system (680, Buck scientific, USA) to collect samples for analysis. All eluted xenon at the end of GAC packed column was analyzed using the GC system equipped with a thermal conductivity detector (TCD) and a rotary valve with a 1 mL sampling loop. A stainless steel tube packed with Propak Q (80-100 mesh) was used as GC column. Oven temperature was fixed in isothermal mode at 200 °C. Detector temperature was held at 170 °C and carrier gas pressure in the column was 1.5 bar. The eluted xenon concentration from GAC packed column was monitored every 5 min by TCD. The vacuum pump (VP25, PRO-SET, USA) was used to remove air from setup at early stage.

The effects of operating temperature and volumetric flow rate were considered as state variables, while taking into account the adsorption isotherms and breakthrough curves regarding xenon dynamic adsorption on GAC adsorbent. The experiments were designed to study the effect of each state variable. The flow rate was changed between 50 and 387 mL min⁻¹ keeping the temperature constant at 298 K. Another set of experiments was designed at constant flow rate of 180 mL min⁻¹ as temperature varied from 268.15 K to 328 K.

In dynamic adsorption processes the breakthrough times, midpoint (equilibrium), and saturation were found (Wood, 2002). Combined with the flow rate, gas concentration, packed bed volume and GAC mass, the following quantities can be calculated: dynamic adsorption coefficient (k_d), gravimetric capacity (q), length of mass transfer zone (L_{MTZ}) and length of unused bed (LUB). At low concentrations, the nonlinear Langmuir is displayed in Henry equation form as:

$$q = K_d C_0 \tag{1}$$

The GAC adsorption capacity is described by k_d that can be derived from mass balance of a packed bed absorber (Adams et al., 1959; Siegworth et al., 1972). The adsorption capability involves the quantity q that can be calculated approximately from breakthrough curve as below (Chongyang et al., 2010):

$$q = \frac{F \, t_{0.05} \, C_0}{W} \tag{2}$$

where F, $t_{0.50}$, W and C_0 are the inlet gas volumetric flow rate, the equilibrium time (defined as the time when the outlet concentration is at 50% of the inlet concentration), GAC mass in grams and equilibrium concentration of inlet gas, respectively.

The length of the packed bed related to the breakthrough curve is defined as L_{MTZ} which governs the reasonable depth of the packed bed. After the mass transfer zone is formed, its length remains unchanged for constant velocity conditions; and it moves forward in the direction of the gas stream. Practically, the depth of the packed bed is chosen to be more than twice L_{MTZ}. According to (Pota and Mathews, 2000), L_{MTZ} could be calculated as:

$$L_{MTZ} = \frac{2(t_{0.95} - t_{0.05})}{(t_{0.95} + t_{0.05})} \times h \tag{3}$$

where $t_{0.95}$, $t_{0.05}$ and h refer to saturation time, breakthrough time and the bed length, respectively. Saturation and breakthrough times are defined as the times when the outlet concentrations are at 95% and 5% of inlet concentrations respectively.

The part of the bed length with no adsorption is defined as LUB which is used to depict the front spreading of the concentration. As flow rate affect LUB but bed length does not, it is used to scale up packed bed from experimental size to real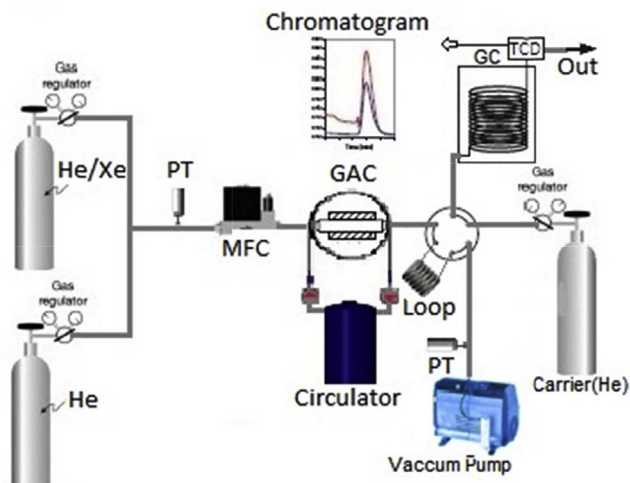 applications (Ruthven, 1984). An