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RESEARCH PAPER

Determination of Atmospheric Krypton and Xenon by Gas Chromatography-Mass Spectrometry in Direct Injection Mode

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Abstract: Volume concentration determination of atmospheric krypton and xenon is very important for krypton-85 and radioactive xenon isotopes monitoring. An injection set-up integrated adjustable quantity sample injection and quantitative dilution function was designed. The effects of electron impact (EI) source parameters on the sensitivity of MS detector were studied. Optimal values were as follows: ionization energy of 70 eV, emission current of 40 mA, cathode voltage of 27 mV, ion focus voltage of 85 mV and lens compensation voltage of 20 V. A GC-MS method for the determination of krypton and xenon in atmosphere without sample pretreatment was developed. Minimal detected concentrations for krypton and xenon were 3.3×10^{-8} (*V*/*V*) and 2.6×10^{-9} (*V*/*V*) respectively. Moreover, krypton and xenon concentrations in the ground level air were measured with the results of 1.1×10^{-6} (*V*/*V*) and 9.3×10^{-8} (*V*/*V*). The related combined standard uncertainties for krypton and xenon results were 2.38% and 3.15%, respectively.

Key Words: Gas chromatography-mass spectrometry; Atmosphere; Krypton; Xenon

1 Introduction

Nuclear explosion generates large quantities of fission gases. Due to their attributes, noble gases may readily escape into ambient air. The xenon isotopes ^{131m}Xe ($\tau_{1/2}$=11.9 d), ^{133}Xe (5.2 d), ^{133m}Xe (2.2 d) and ^{135}Xe(9.1 h) have large fission yields and moderate half-lives, and their ambient atmospheric concentrations are relatively low, therefore the radioxenons can be used as sensitive indicators of nuclear detonations[1]. Actually, xenon isotopes (^{131m}Xe, ^{133m}Xe, ^{133}Xe and ^{135}Xe) monitoring became one of the most effective techniques for disclosing clandestine tests of nuclear weapons, and was included in the verification regime for the Comprehensive Nuclear-Test-Ban Treaty (CTBT)[2]. Radioxenons also released from nuclear reactor operation as well as from medical and industrial uses. Therefore, atmospheric xenon monitoring is very important for emergency monitoring of nuclear accidents and safe operation of nuclear reactors[3,4].

^{85}Kr exists in large amount in spent fuel rods of nuclear reactors, and it will leak from the rods during the reprocessing of spent fuel. Therefore, by monitoring of ^{85}Kr, important information of some nuclear event may be obtained, such as operation conditions of post-treatment facilities for spent fuel, irradiation time of spent fuel and reactor type. The information is very useful for Fissile Material Inspection (FMI)[5]. Moreover, temporary ^{85}Kr activity concentration increase in atmosphere with unknown causes indicates that a nuclear leakage accident may have occurred, which is very important for safety of nuclear facilities and safety of environmental radiation[6]. US research institutes have continued to monitor ^{85}Kr which is generated in fission reaction and leaks into the atmosphere, to detect reprocessing

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activities of plutonium around the globe since the 1940s[7]. From 1975, ^{133}Xe in atmosphere in the US was sampled and monitored for nearly 20 years, and many background data of radioactive xenon were collected[8–10]. Swedish researchers started to monitor ^{133}Xe in the atmosphere in 1971[11,12]. Japanese institutes started to study activity concentration of ^{85}Kr in atmosphere around its nuclear fuel treatment plant and its irradiation effect thereof. In 1995, the Japanese institutes evaluated ^{85}Kr contribution for their annual irradiation dosage comprehensively[13]. From 1995 to 1998, Japanese Meteorological Institute and German institutes continuously monitored ^{85}Kr and ^{133}Xe in atmospheric in Japan[14]. In 1996 WHO included irradiation effects of ^{85}Kr in the atmosphere into its scientific research fields, and ^{85}Kr was adopted as a tracer agent for regional and global atmospheric circulation research[15].

Currently, trace quantity of xenon and krypton in the atmosphere is enriched and concentrated as the first step for monitoring radioactive xenon isotopes and ^{85}Kr. Secondly, high-purity germanium γ spectrometer, β-γ coincidence method or proportional counter is utilized to test the activity of radioxenon isotopes and ^{85}Kr. And eventually total amount of xenon and krypton in the enriched samples is tested by chromatography to calculate effective air sampling volume by substituting the atmosphere concentration of stable xenon and stable krypton with reference values 8.7×10^{-8} (V/V) and 1.14×10^{-6} (V/V), respectively. In our previous study, helium ionization detector was used to measure atmospheric concentration of xenon and krypton[17,18]. In this paper, an analysis method for atmospheric xenon and krypton by GC-MS in direct injection mode was established. The volume concentrations of xenon and krypton in atmosphere were tested, and the result was matched perfectly with reference values.

2 Experimental

2.1 Design of injection setup

The so-called direct injection means that air samples are not pretreated and enter directly into chromatograph for separation. On the basis of the adjustable quantity sample injection setup[19], a quantitative dilution function was added with the injection setup for convenient quantitative dilution of standard gas, so that standard reference samples at lower concentration levels could be obtained. Schematic diagram of the setup is illustrated in Fig.1.

Main pipeline of the setup was made up by 1/8" stainless steel valve pipe fittings. The vacuum system was composed of a molecular pump unit, and the vacuum degree may reach 0.01 Pa. Pressure measurement system was a set of MSK high-precision pressure sensor and the measuring range was 5.00–1.33×10^5 Pa with less than 0.5% of pressure uncertainty. Effective dead volume of the setup was approximately 10 mL.

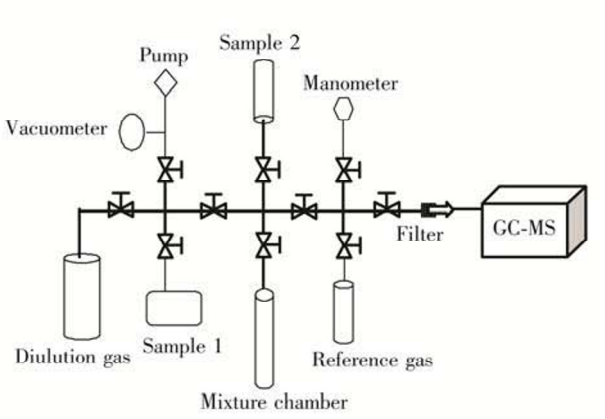

Fig.1 Schematic illustration of a direct injection setup for GC-MS

Volume of mixing chamber for dilution was about 500 mL. Diluents gas was high-purity nitrogen or high-purity helium.

2.2 Instrument, experiment condition and reagent

7980A/5975C GC-MS (split/splitless inlet, Agilent) and 5 Å molecular sieve capillary column (HP-PLOT-Molesieve-5A, 30 m × 0.32 mm × 0.25 μm, Agilent) were used in this experiment. The operation temperature of electron impact (EI) ion source was set at 230 °C, and the operation temperature of quadrupole mass analyzer was 150 °C; chromatography carrier gas flow was 0.92 mL min^{-1}; split ratio was 50:1; column temperature was 100 °C; sample ring volume was 5 mL.

1.0×10^{-6} (V/V) xenon standard gas, 1.1×10^{-5} (V/V) krypton standard gas and 99.999% (V/V) high-purity helium (as balance gas) were purchased from Beijing ZG Special Gases Science and Technology Co., Ltd.

2.3 Experiment methods

2.3.1 Optimization of MS detector parameter

Due to the structure of EI ion source and MS operation principle, the parameters such as EI ionization energy, filament emission current, cathode voltage, ion focus voltage and lens compensation voltage could influence the MS detector response. Xenon standard samples were used to evaluate the impact on MS response as the parameters were adjusted. The experiment method was that while other parameters were constant, xenon response factor with one changing parameter was tested. Subsequently, MS detector operation parameters were optimized in accordance with variation rules of response curves.

2.3.2 Quantitative dilution of standard gas and calibration of standard curve

Background concentrations of xenon and krypton in the atmosphere are respectively in the orders of 10^{-8} and 10^{-6}