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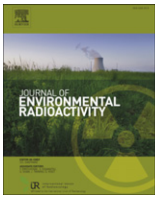

^{3}He mass spectrometry for very low-level measurement of organic tritium in environmental samples

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ABSTRACT

The design, setup and performance of a mass spectrometric system for the analysis of low to very low-level tritium in environmental samples are described. The tritium concentration is measured indirectly by the ^{3}He ingrowth from radioactive decay after complete initial degassing of the sample. The analytical system is fully computer-controlled and consists in a commercial helium isotope mass spectrometer coupled with a high vacuum inlet system. A detection limit of 0.15 Bq/kg is routinely obtainable for sample sizes of 20 g of water equivalent and an accumulation time of three months. Larger samples (and/or longer accumulation time) can be used to obtain lower detection limits. In addition to the benefit of a lower detection limit, another advantage of this non-destructive method lies in the simplicity of the analytical procedure which strongly limits the risk of contamination. An inter-comparison was successfully performed with the conventional beta counting technique on lyophilized grass samples, in a range of tritium concentrations of environmental interest. It shows that the ^{3}He mass spectrometry method yields results that are fully consistent with the conventional liquid scintillation technique over a wide range of tritium concentrations.

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1. Introduction

Tritium (^{3}H) is present in the environment as a result of both natural and anthropic sources. Owing to its low natural production by cosmic radiations in the upper atmosphere (Table 1) and to its relatively short half-life of 4500 days (Lucas and Unterweger, 2000), natural tritium levels in precipitation and surface waters, as determined from early tritium (pre-nuclear) measurements (Libby, 1955) and from polar ice cores (Jouzel et al., 1982; Fourré et al., 2006 and references therein) were quite low, not exceeding a few Bq/L. In the fifties and early sixties however, this low background has been multiplied by a factor of one thousand due to the release of tritium in considerable amounts by the atmospheric tests of nuclear weapons. Tritium is also released in various amount by industrial activities (Table 1), including the nuclear industry, nuclear weapons production facilities, and the luminous compounds industry (tritium being used as a radiation source in luminous paints and GTLS – Gaseous Tritium Light Sources – for clocks, watches and various devices including emergency signs and military equipments). Although these tritium sources may be significant locally, at the global scale tritium levels are steadily declining (IAEA, 2009), so that present-day levels are usually at or near minimum detectable concentrations by conventional liquid-scintillation counting systems.

Over the last three decades, an alternative method based on the detection of its radioactive daughter ^{3}He by mass spectrometry (the so-called ^{3}He ingrowth method – Clarke et al., 1976) has been extensively used for routine measurements of very low to ultra-low levels of tritium (in the range 0.1–0.01 Bq/L) in oceanography and hydrology (see Jenkins, 2007; Phillips and Castro, 2007; Jenkins, 2009 and references therein).

Our group has been involved since the early 80's in the measurement of tritium in oceanic and continental waters by the ^{3}He ingrowth method (Jean-Baptiste et al., 1992). The principle of the method is to remove the ^{3}He initially dissolved in the water sample by degassing under vacuum, then to store it in a closed container (usually a glass bulb) to allow for the accumulation of tritiogenic ^{3}He. The tritium content of the sample is subsequently deduced from the mass spectrometric determination of the amount of ^{3}He produced during the storage period. Since ^{3}He is sparingly soluble in organic compounds and readily enters the gas phase (Tremblay et al., 2006), the technique is adaptable to a wide variety of sample matrices such as food items, vegetation, etc. Hence, ^{3}He mass spectrometry appears as a promising option for

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Table 1
Tritium production and inventory.

	Release rate (PBq/an)	Tritium inventory (PBq)	References
Natural production	75	1370	Craig and Lal (1961), Nir et al. (1966), Jouzel et al. (1982)
Bomb tests	–	186,000[b]	UNSCEAR, 2000
Weapons installations	–	>720	Traub and Jensen (1995)
Nuclear power plants[a]			UNSCEAR (2000)
Airborne releases	4.9		
Liquid effluents	9.5		
Reprocessing[a]			
Airborne releases	0.5		
Liquid effluents	12.7		
Total nuclear industry	27.6	423[c]	
Commercial products[d]	10–20	–	Krejci and Zeller (1979), Combs and Doda (1979) and Okada and Momoshima (1993)

[a] 1995–1997 Average.
[b] Cumulated releases of atmospheric tests.
[c] Cumulated releases (1950–1997).
[d] Estimate based on available data for the year 1978.

environmental tritium studies and monitoring. However, in spite of this, this technique has remained largely ignored so far by the environmental tritium community, with only a few studies reported in the litterature based on this technique (Surano et al., 1992; Brown, 1995; Kotzer et al., 1998). Here, we describe the application of this mass spectrometric method to biological samples, with the aim of providing essential elements for those interested in evaluating or comparing measurement techniques for environmental tritium studies.

2. Experimental procedure

2.1. Samples collection, packaging and preparation

Since Tissus Free Water Tritium (TFWT) and exchangeable Organically Bound Tritium (OBT) tend to equilibrate with their local environment in a matter of hours or less (Mann, 1971), measurement of environmental tritium samples requires precaution to avoid contamination.

In the field, the samples (sediment, soil, grass, moss, vegetable, fish, etc.) are stored in plastic boxes sealed in polyethylene bags and then placed in a refrigerator at −20 °C within 24 h after sampling.

In the lab, each frozen sample (still in its box and polyethylene bag) is placed in a vacuum-oven (at ambient temperature) connected to a lyophilizer (Alpha 1–2 LD, Martin-Christ Gesellschaft, Germany) already under vacuum at −50 °C. While the oven is being flushed with argon, the polyethylene bag and the box cover are quickly removed and the oven is immediately evacuated with a primary pump to avoid contamination by ambient air moisture. Then the valve between the oven and the lyophilizer is opened to start lyophilization. At the end of drying procedure (typically 48 h), the temperature of the oven is raised to 40 °C for 12 h to eliminate any remaining trace of water. Then the oven is flushed with argon and the plastic box is quickly closed and sealed again in a polyethylene bag filled with argon. The lyophilizer is stopped and filled with argon as well. Once melted, the water is collected through a valve at the bottom of the lyophilizer in a 500 ml Pyrex bottle for Tissus Free Water Tritium (TFWT) analysis using our standard procedure for tritium in water (Jean-Baptiste et al., 1992). To avoid cross-contamination, the lyophilizer is rinced with tritium-“free” water and dried with an hair drier between each sample (for tritium-“free” water, we use groundwater from the Paris basin aquifer - commercial name “Chantereine”, whose tritium content is 0.07 ± 0.01 Bq/L).

Dried sediments and soils are first sieved at 2 mm, and biological samples are finely ground before being transferred into a 100 ml low helium diffusivity Corning 1724 glass bulb (previously weighed). To minimize ^{3}He blank, the bulbs are previously baked in a flow of argon at 600 °C for 24 h to remove the helium dissolved in the glass. All manipulations are undertaken in a glove-box flushed with argon to minimize contamination by ambient air moisture. The bulb is attached to a high vacuum line and evacuated down to $<10^{-5}$ Torr, then it is flame-sealed and weighed again to determine the mass of the sample. After sealing, the samples are stored at −20 °C to further minimize helium diffusion through glass (Jean-Baptiste et al., 1989).

Whenever larger samples are needed, either due to the very low organic matter content of the sample (such as soils and sediments whose organic content can be less than 1%) or because the time storage needs to be shortened, glass bulbs can be replaced by 1 L metal cylinders closed with two high vacuum valves mounted in series.

2.2. Mass spectrometry analysis

After a period of storage of typically 100–150 days, the bulbs are connected to the inlet line of a mass spectrometer for ^{3}He analysis. The instrument is a MAP-215-50 noble gas mass spectrometer equipped with a stainless steel low blank inlet system (^{3}He blank $< 3\times10^{-20}$ mol) – Fig. 1. The pressure gauges, pneumatic Nupro valves and breaking devices for glass bulb reopening are computer-controlled so that up to 12 samples can be processed in a row without any manual intervention. The measurements are calibrated against an air standard (He = 5.24 ppm, ^{3}He/^{4}He = 1.38×10^{-6}) drawn from a 5 L tank filled with clean air at known pressure, temperature and relative humidity conditions, through a precisely calibrated volume $V = 122.2 \pm 0.1$ (2σ) mm^3. The ^{3}He$^+$ ion beam (typically in the range 1–250 ions/s) passes through an electrostatic filter before impinging the detector (a 16-stages electron multiplier connected to a pulse counting system). Thanks to this filter, the ^{3}He background, which constitutes the ultimate limit for ^{3}He detection, is very low (<0.05 count/sec). ^{4}He$^+$ is measured on a Faraday cup. The ^{4}He signal is usually very low ($<4 \times 10^{-14}$ mol) and corresponds to the small helium residue left behind at the end of the degassing step (plus the blank of the mass spectrometer inlet system). The corresponding ^{3}He signal ($<5 \times 10^{-20}$ mol) can be calculated by applying the ^{3}He/^{4}He ratio of the blank component (see below).

The mass spectrometer is operated in a static mode. Five series of ten 10-seconds integrations are performed on the ^{3}He$^+$ peak and

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