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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.

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 $= 1.38 \times 10^{-6}$) 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

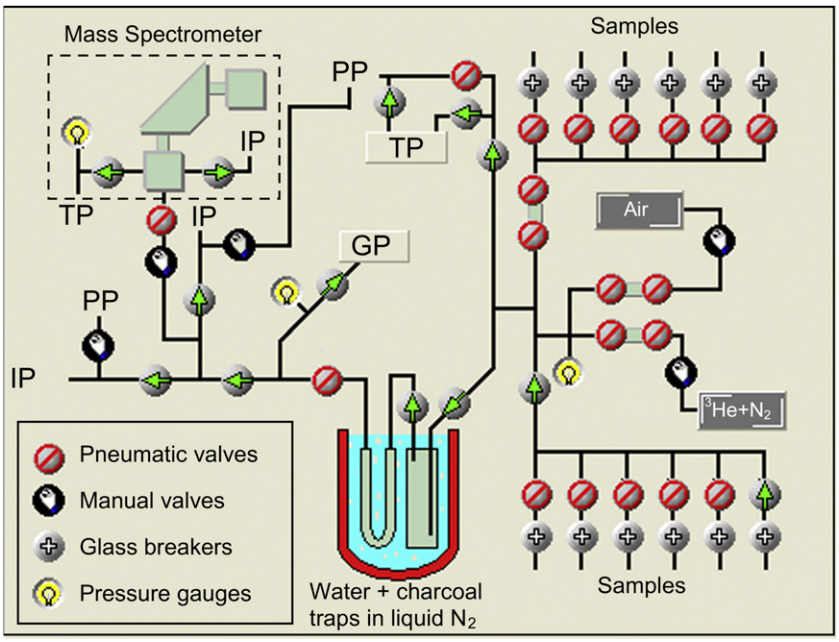

Fig. 1. Schematic diagram of the mass spectrometer inlet system (PP, primary pump; TP, turbomolecular pump; IP, ion pump; GP, getter pump).

on the baseline. Each series is interspaced by five measurements of the $^4He^+$ peak and baseline. Each sample measurement is followed by a standard air aliquot measured in the same conditions. However, whereas the sample contains some 10^{-14} mol of gas only, the air aliquot contains about 10^{-10} mol of helium and neon (neon is not quantitatively retained by the charcoal trap at 77 K – Fig. 1). Hence, the pressure in the ion source is different for the standard and for the sample, with potential effect on the ion source sensitivity (Burnard and Farley, 2000). This means that although the ^{3}He response of the mass spectrometer remains linear, the slope will depend on the pressure in the source. The magnitude of this pressure effect is determined by comparing the ^{3}He signals for an aliquot of a ^{3}He–N_2 mixture (with no ^{4}He and no neon) and for the same aliquot added to the standard air aliquot. The measured pressure correction factor, F_P, is in the range 0.85–0.95, depending on the tuning of the mass spectrometer (a correction factor of 0.968 was reported in Clarke et al., 1976), and has to be closely monitored through time (every week).

The amount of ^{3}He accumulated in the sample (typically in the range 5×10^{-19}–10^{-17} ^{3}He mol) is calculated by direct comparison to the standard air aliquot. The ^{3}He blank is inferred from the measurement of the $^4He^+$ residue and is subtracted from the measured ^{3}He signal to give the tritiogenic component ^3He_T:

$$^3He_T = [(N3_{sample}/N3_{standard}) - (N4_{sample}/N4_{standard}) \times (R_{blank}/R_a)] \times {}^3He_{standard} \times F_P$$

where $^3He_{standard}$ is the ^{3}He amount in the air standard aliquot, $N3_{sample}$, $N4_{sample}$, $N3_{standard}$ and $N4_{standard}$ are the ^{3}He and ^{4}He peaks height for the sample and for the standard air aliquot respectively. R_a is the atmospheric ^{3}He/^{4}He ratio and R_{blank} is the ^{3}He/^{4}He ratio of the blank component. In theory, R_{blank} can differ from R_a by up to ±15% ($=4/3^{0.5}-1$) due to isotope fractionation during the degassing step. Our own statistics of blank measurements on samples analysed immediately following degassing (i.e., with no tritiogenic ^{3}He contribution) shows that R_{blank} is identical to R_a within 10%.

3. Activity and *T*/*H* isotopic ratio calculations

The specific tritium activity of the sample, A_T (in Bq/kg of dry sample), is directly deduced from the tritiogenic ^{3}He component $(^3He)_T$ (in mol) by the following formula:

$$A_T = \frac{\lambda N(^3He)_T}{m(1-e^{-\lambda\tau})} \quad (1)$$

where m represents the mass of the dry sample (in kg), λ is the tritium radioactive constant, N is the Avogadro number, and τ the storage time.

It follows that the T/H ratio of the sample is given by:

$$T/H = \frac{A_T}{\lambda} \times \frac{M_H}{N[H]} \quad (2)$$

where [H] is the hydrogen mass fraction of the analysed dry material and M_H is the mass of one mole of hydrogen ($M_H = 10^{-3}$ kg). For TFWT, the hydrogen mass fraction [H] is directly deduced from the composition of the water molecule (hence $[H] = 2/18 = 0.11$). The hydrogen mass fraction [H] of organic materials is measured on a CHN analyser at the Micro-Analysis Laboratory (CNRS/ICSN – Gif/Yvette). Plants usually have an organically-bound hydrogen mass fraction in the range 0.05–0.07. Fats have higher [H] contents up to ~0.12. A comprehensive database on elemental composition of food items and biological tissus is available in the Handbook of Biological Data (1956) and in the Geigy Scientific Tables (1981).

3.1. Tritium activity of the non-exchangeable OBT

Depending on authors, OBT values reported in the literature may either represent the total organically-bound tritium or the non-exchangeable fraction only. However, since the non-exchangeable hydrogen pool is the only hydrogen fraction that faithfully records the history of environmental tritium seen by a living organism during its growing period, a consensus seems to

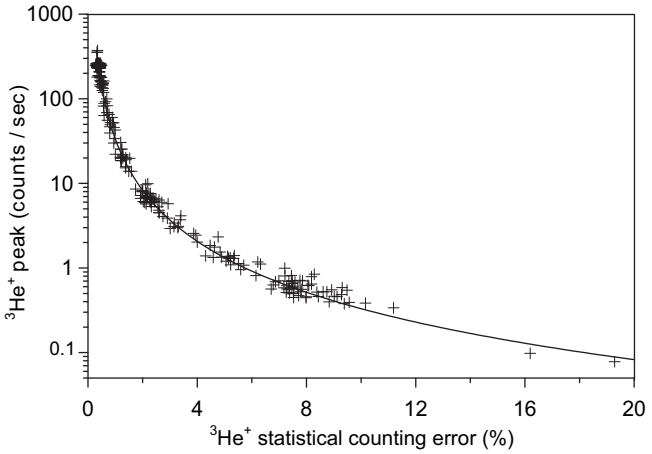

Fig. 2. Plot of the ^{3}He statistical counting error (in %) vs ^{3}He peak height (in counts/s) for mass spectrometer data collected over several months.

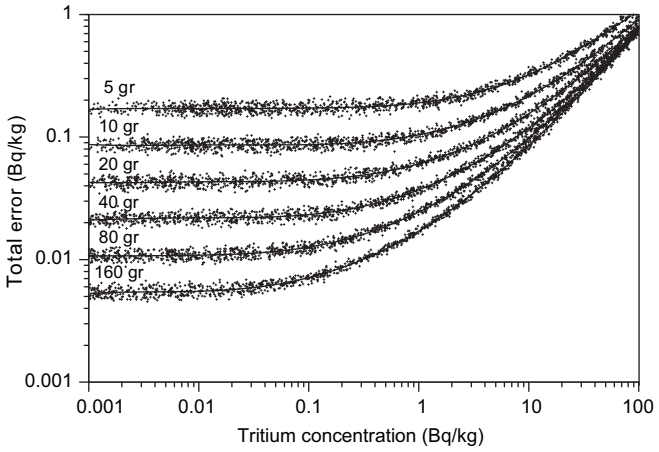

Fig. 3. Monte-Carlo simulation of the total error (1σ + systematic) vs tritium concentrations for various sample sizes (5, 10, 20, 40, 80 and 160 g of water equivalent) and a storage time of three months.

exist from now on over the idea that reported data should correspond to this non-exchangeable fraction. If the TFWT and total OBT content of a sample are known, the T/H value of the non-exchangeable hydrogen pool $(T/H)_{nex}$ can be deduced from the T/H ratio of the total OBT, $(T/H)_{OBT}$ and of the tissue-free water $(T/H)_{TFWT}$ by assuming that the exchangeable hydrogen pool was at equilibrium with the tissue free-water:

$$(T/H)_{nex} = \left[(T/H)_{OBT} - \alpha (T/H)^*_{TFWT}\right] \Big/ (1-\alpha) \quad (3)$$

where α is the fraction of exchangeable hydrogen (typically between 0.2 and 0.3). $(T/H)^*_{TFWT}$ is the T/H value of the tissue free-water corrected for the tritium enrichment by Raleigh distillation during lyophilization (Kim and Baumgartner, 1991):

$$(T/H)^*_{TFWT} = (T/H)_{TFWT} \times (1-r)^{(1-\beta)/\beta} \quad (4)$$

where r is the ratio of the tissue free-water hydrogen pool to the total exchangeable hydrogen pool (tissue free-water + exchangeable OBT). The value of the isotope fractionation factor β corresponding to the lyophilization conditions was determined to be $\beta = 1.1$ from special experiments performed on crushed ice of known tritium concentration.

In a similar way, the specific activity of the non-exchangeable tritium, $(A_T)_{nex}$ (in Bq/kg of dry sample), can be determined from the total specific tritium activity of the sample $(A_T)_{OBT}$ (in Bq/kg of dry sample) and the specific tritium activity of the Tissue Free Water $(A_T)_{TFWT}$ (in Bq/kg of water):

$$(A_T)_{nex} = (A_T)_{OBT} - \alpha \times WEF \times (A_T)_{TFWT} \times (1-r)^{(1-\beta)/\beta} \quad (5)$$

where WEF is the water equivalent factor of the dry material (i.e., the ratio of the hydrogen mass fraction of the sample to the hydrogen mass fraction of water).

In our opinion, this procedure is preferable to the alternative method which consists in eliminating the exchangeable organic tritium by isotopic exchange with tritium-free water for about 48 h (Pointurier et al., 2003). For non-aquatic samples, the isotopic exchange technique (either in the liquid or the vapour phase) usually causes significant losses of organic matter by dissolution and/or degradation of the sample (Pointurier et al., 2004) and leads to less reproducible results. For aquatic samples, which are not significantly altered when soaked in water, from our own experience, both methods are suitable and give consistent results. Note however that suppressing the isotopic exchange step makes the sample treatment less time-consuming and avoids risks of contamination. In the case of isotopic exchange with tritium-"free" water, $(T/H)_{TFWT}$ in Eq. (4) is the T/H value of the tritium-"free" water.

The main problem with non-exchangeable OBT determination is that the exact proportion of the exchangeable hydrogen pool, determined from equilibration experiments with deuterium or tritium, is not always known with the desired accuracy. Although the fraction of tritium that is readily exchangeable is known with a good precision for some well documented terrestrial species from replicated experiments (Lang and Mason, 1960; Guenot and Belot, 1984; Kim and Baumgartner, 1991), we do not know which values could be used in the case of aquatic sedimentary and biota samples for instance, due to the lack of experimental work that could serve of reference in that matter. Also, experimental results for a given species often reveal substantial discrepancies, depending on the experimental procedure (Mann, 1971; Grinsted and Wilson, 1979). In fact, organic hydrogen appears to be distributed over several sub-fractions with different kinetics of isotopic exchange, thus raising the question of the definition of the exchangeable pool of organic hydrogen (Baumgartner and Gonhaerl, 2004). Note that this serious limitation to the overall precision of the non-exchangeable OBT determination is independent of the technique used for measuring tritium, and is a general concern for the entire environmental tritium community.

4. Results and discussion

In the ^{3}He ingrowth method, the main source of uncertainty relates to the $^3He^+$ detection. Fig. 2 shows a plot of the statistical error on $^3He^+$ counting as a function of the size of the $^3He^+$ peak, for a number of analysis performed during the past few months. For $^4He^+$, statistical error is much smaller, ranging from 0.01% for the standard air aliquot to 1% at the blank level. The overall uncertainty in the tritium concentration, including counting statistics and all other factors (^{3}He and ^{4}He content of the air standard aliquot, blank correction, pressure correction, mass of the sample, etc.) is shown in Fig. 3 for various sample sizes. For a typical sample size of 20 g (of water equivalent) and a storage time of three months, it follows that the limit of detection (defined as the minimum concentration of a substance being analysed that has a 99% probability of being identified – EPA, 1997) is ~0.15 Bq/kg. Fig. 3 shows that the technique is essentially "open-ended" in that larger samples (and/or longer accumulation time) can be used to obtain lower detection limits.

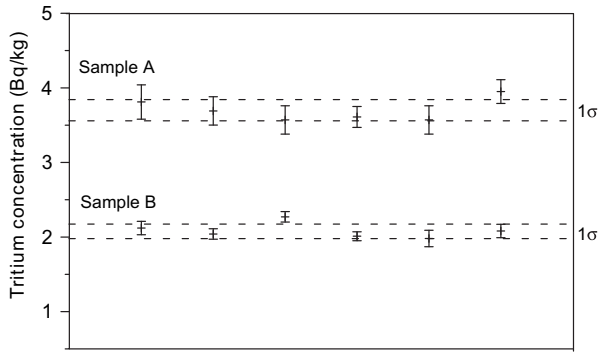

Fig. 4. Reproducibility of measured tritium concentrations for two lyophilized grass samples of ~30 g of dry matter (equivalent to ~16 g of water) stored 44 days (sample A) and 90 days (sample B). The error bars correspond to 1-sigma errors of the individual measurements.

As an illustration of the overall reproductibility of the method, the results of total OBT concentrations measured on two series of replicates from two different lyophilized grass samples are shown in Fig. 4. The standard deviations of the tritium concentrations are almost identical to the total errors of the individual measurements, indicating that the error calculation of the individual measurement includes all major sources of uncertainty.

An intercomparison exercise (Fig. 5a) was carried out on lyophilized grass samples with a conventional liquid scintillation system (Pointurier et al., 2004) in a range of tritium concentrations typical of environmental samples (between 1 and 40 Bq/kg of dry material). Since the exercise was specifically designed to compare the two analytical techniques, the measurements were carried out on total OBT. For higher tritium concentrations, we participated to an intercalibration with seven other labs of the french CETAMA group (Comité d'ETAblissement des Méthodes d'Analyse) operating conventional beta counting systems. The sample distributed among the participants was a lyophilized grass sample collected downwind of a stack releasing tritiated effluents. Fig. 5a and b shows that the tritium results obtained by ^{3}He mass spectrometry are consistent with the conventional liquid scintillation technique over a wide range of tritium concentrations.

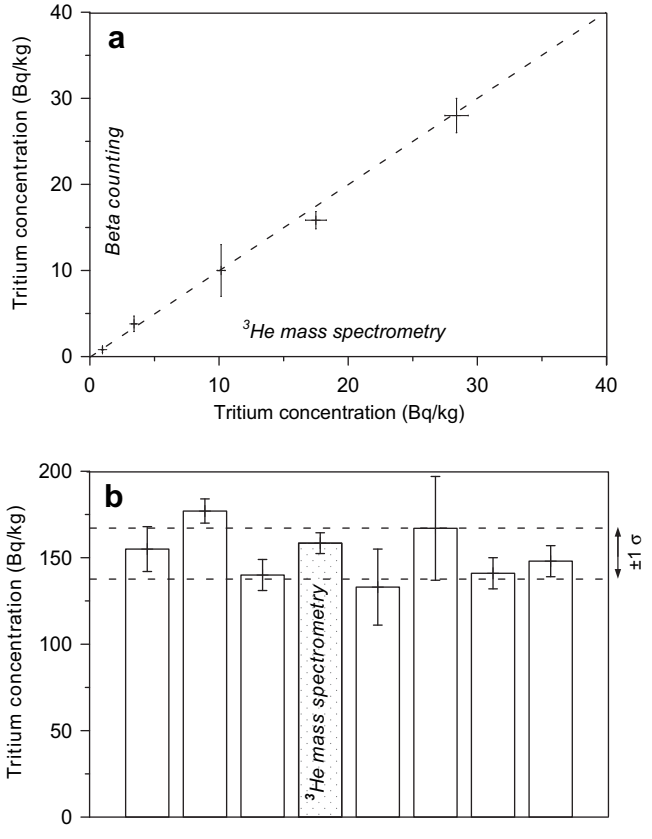

Fig. 5. (a) Comparison of total OBT concentrations in lyophilized grass samples measured by liquid scintillation (Pointurier et al., 2004) and ^{3}He mass spectrometry. The error bars correspond to 1-sigma errors of the individual measurements. (b) Result of an inter-comparison exercise on a lyophilized grass sample between seven conventional beta counting laboratories and our ^{3}He mass spectrometric system. The error bars correspond to 1-sigma errors of the individual measurements.

5. Concluding remarks

The ^{3}He ingrowth method is very effective in determining low to very low-level tritium concentrations in environmental samples. The main advantage of this non-destructive technique over the methods of beta counting is its lower detection limit. A typical detection limit of 0.15 Bq/kg is routinely obtainable for a sample size of 20 g (of water equivalent) and an accumulation time of 3 months. This tritium detection limit can be pushed further down (or the accumulation time reduced) with larger samples. Counting time of the $^3He^+$ peak can also be extended to improve counting statistics.

Another major advantage lies in the simplicity of the analytical procedure which requires only two steps, e.g., complete degassing of the sample and ^{3}He measurement. Processes such as combustion, distillation, isotopic enrichment are not necessary, therefore it is less susceptible to contamination. The only disadvantage is that every measurement involves a mandatory storage period to allow ^{3}He to accumulate. However, this accumulation time can be reduced using larger samples and can also be adjusted based on desired detection limits.

Therefore, in face of the globally declining tritium levels, ^{3}He mass spectrometry may become the method of choice for routine low-level environmental tritium monitoring and research in the future, applicable to a wide variety of samples of radio-ecological interest.

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