

# Indirect Tritium Determination by an Original $^3\text{He}$ Ingrowth Method Using a Standard Helium Leak Detector Mass Spectrometer

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**A traditional helium leak detector mass spectrometer is applied in analytical chemistry. We report its straightforward use for the precise quantification of  $^3\text{He}$  and  $^4\text{He}$  concentrations at a sub-ppb level. Repetitive external calibrations with certified gases demonstrate long-term stability, reproducibility of 3% at the ppb range, and linearity versus helium concentration over 5 orders of magnitude. The mass spectrometric determination of  $^3\text{He}$  takes into account a  $\text{H}_3^+$  contribution and has a  $^3\text{He}$  detection limit of 2 ppb. Since  $^4\text{He}$  induces an attenuation effect of the mass 3 signal, this apparatus is only suitable for the measurement of  $^3\text{He}/^4\text{He}$  ratio greater than  $10 R_a$  (atmospheric ratio  $R_a = 1.38 \times 10^{-6}$ ). This mass spectrometric technique has found novel application in the determination of tritium concentrations with an original  $^3\text{He}$  ingrowth method. Here, samples are first purified cryogenically onto activated charcoal to eliminate tritium interfering during the  $^3\text{He}$  mass spectrometric determination step. Helium is also preconcentrated, and  $^3\text{He}$  is routinely determined around 0.05 ppb with a 20% relative uncertainty. This  $^3\text{He}$  measurement technique has been successfully applied in the field of tritiated waste drums as a nondestructive method. The total amount of tritium present in these 200-L drums can be determined as low as  $\sim 1 \text{ GBq}$ .**

Measurements of the two stable helium isotopes  $^3\text{He}$  and  $^4\text{He}$  are mainly performed in the context of environmental studies.<sup>1</sup> Values of the isotopic ratio ( $R = ^3\text{He}/^4\text{He}$ ) vary to a large extent around the atmospheric ratio  $R_a = 1.384 \times 10^{-6}$  ( $\pm 0.4\%$ ),<sup>2</sup> from  $0.001 R_a$  up to  $200 R_a$ .<sup>3,4</sup> This ratio is well known as a reliable marker for tritium because  $^3\text{He}$  is the stable product of its

radioactive decay ( $^3\text{H} \rightarrow ^3\text{He} + \beta^- + \nu$ , half-life  $12.32 \text{ yr}^{-1}$ ).<sup>5</sup> The  $^3\text{He}$  ingrowth method is now widely used to detect the presence of very-low-level tritium in water samples.<sup>2,6,7</sup> It is also used for measuring the chemical shift effect of the tritium decay constant.<sup>8</sup> Most of the existing analytical techniques dealing with  $^3\text{He}/^4\text{He}$  measurements use expensive and especially designed high-resolution isotope ratio mass spectrometers with two collectors in order to record simultaneously both the  $^3\text{He}^+$  (electron multiplier) and  $^4\text{He}^+$  (Faraday cup) ionic currents. Their complex use requires not only powerful conventional pumping systems but also specific charcoals and getter materials to improve vacuum in the mass spectrometer. In addition, the extraction and purification of the gaseous samples must precede the introduction into the mass spectrometer.

However, in nuclear plants particularly, there is an increasing need for techniques able to measure  $^3\text{He}$  at significant higher concentrations. This paper describes a novel technique based on a straightforward use of a readily available helium leak detector mass spectrometer (HLD-MS). Although such detectors are widely used only for qualitative purposes, here we demonstrate a quantitative determination of the isotopic ratio via consecutive and precise measurements of both  $^3\text{He}$  and  $^4\text{He}$  concentrations. In addition, the application of this technique in a tritium waste management context is described. The determination of the amount of tritium in a radioactive waste drum can be deduced from its  $^3\text{He}$  content.<sup>9</sup> Indeed, the nondestructive analysis of a radioactive tritiated drum is based on a correlation between the  $^3\text{He}$  outflow of the drum and its internal tritium activity. Actually, the drum is placed into a hermetically sealed chamber and the  $^3\text{He}$  outflow is quantified by sampling the chamber's atmosphere. Before the helium mass spectrometric determination, the samples are purified in order to overcome isobaric problems due to tritium. The performances of our analytical technique are discussed in terms of sensitivity, detection limit, precision, and accuracy derived from repeated measurements on standard gaseous mixtures. The

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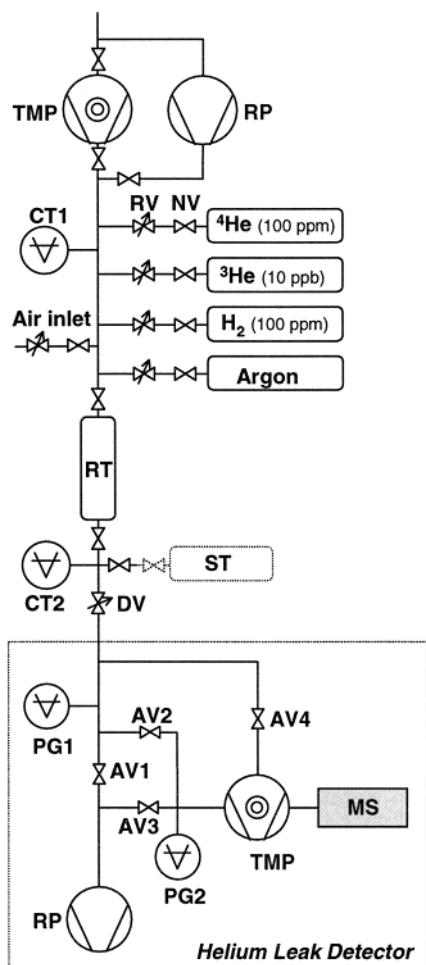


Figure 1. Schematic view of the mobile apparatus used for the quantitative determination of  $^4\text{He}$ ,  $^3\text{He}$ , and  $\text{H}_2$ . It comprises a standard helium leak detector mass spectrometer linked to a gas handling system including the standard gas mixtures. Key: AV1–AV4, automated valve in the detector; NV, Nupro valve; RV, regulate valve; DV, dosing valve; RP, rotary pump; TMP, turbomolecular pump; MS, mass spectrometer cell; PG1, PG2, Pirani gauge in the detector; CT1, CT2, capacitance transducer; RT, reference tube; ST, sample tube.

application of the technique to radioactive waste drums is finally shown and discussed.

## EXPERIMENTAL SECTION

**Instrumentation. (1) Helium Leak Detector Mass Spectrometer.** A commercially available version of a HLD-MS (UL200, Inficon, Köln, Germany) is used. The vacuum scheme of the detector is shown in Figure 1. It operates in a dynamic mode based on a counterflow phenomenon: the He reaches the MS cell against the pumping flow created by the turbomolecular pump.<sup>10</sup> When the inlet pressure measured by the Pirani gauge PG1 is less than 0.3 mbar, the sensitivity is enhanced and the response time is shortened because the gas flow is directly admitted into the upper part of the turbomolecular pump through the automated valve AV4.

The main characteristics of the mass spectrometer cell are summarized in Table 1. In the mass spectrometer cell, ionization occurs due to the impact of constant-energy electrons. After a 180°

Table 1. Principal Characteristics Given by the Manufacturer of the Helium Leak Detector Mass Spectrometer (UL200, Inficon) Used Here for Quantitative Purposes

parameter	value	unit
pressure in the ion source	$10^{-4}$	mbar
magnetic field	0.240	T
magnetic deflection radius	7	cm
electron energy	80	eV
tuneable accelerating potential	400–1000	V
detectable mass	2–4	uma
sensitivity versus He	$10^{-3}$	$\text{A} \cdot \text{mbar}^{-1}$
faraday cup detection limit	$10^{-15}$	A
leak rate detection limit	$5 \times 10^{-11}$	$\text{mbar} \cdot \text{L} \cdot \text{s}^{-1}$

magnetic deflection, the ionic current for each mass value is collected on a unique Faraday cup, by way of a scanning accelerated voltage. An electrometer measures and converts the current into a 0–10 V signal with a resolution of 0.1 mV. For example, the highest value of the electrometer resistance is  $5 \times 10^{11} \Omega$  so that the ionic current is measured with a precision of  $2 \times 10^{-16} \text{ A}$  in the  $1 \times 10^{-15}$ – $2 \times 10^{-11} \text{ A}$  range. Taking into account a calibration step with an internal  $^4\text{He}$  calibrated leak, the current is finally translated into a leak rate signal ranging from  $1 \times 10^{-11}$  to  $1 \times 10^{-1} \text{ mbar} \cdot \text{L} \cdot \text{s}^{-1}$ .

The leak rate output signal is assumed to be proportional to the partial pressure of helium applied above the detector. For a fixed conductance of the inlet system, and for a given value of the total pressure in the sample or reference tube measured by the capacitance transducer CT2, the helium leak rate delivered by the detector ( $Q_{\text{He}}$  in  $\text{mbar} \cdot \text{L} \cdot \text{s}^{-1}$ ) is directly proportional to the helium concentration in the tested gas, according to the eq 1

$$Q_{\text{He}} = C p_{\text{He}} = C P x_{\text{He}} \quad (1)$$

where  $C$  is the conductance of the inlet system ( $\text{L} \cdot \text{s}^{-1}$ ),  $p_{\text{He}}$  is the helium partial pressure,  $P$  is the total pressure (mbar), and  $x_{\text{He}}$  is the helium concentration expressed in volumic fraction (ppm or ppb).

**(2) Gas Handling System.** The gas handling system linked to the detector is schematically shown in Figure 1. A capacitance transducer CT1 1–2000 ( $\pm 1.0$ ) mbar is connected to the gas introduction line and used to measure pressure during the preparation steps. High-purity argon and three different reference gaseous mixtures (Carboxique) are connected to the line. Each includes one light element at trace level in an  $\text{N}_2/\text{O}_2$  matrix:  $100 \pm 1 \text{ ppm}$  ( $^4\text{He}$ ),  $10 \pm 1 \text{ ppb}$  ( $^3\text{He}$ ), or  $104 \pm 1 \text{ ppm}$  ( $\text{H}_2$ ). In the line, the vacuum is generated by a rotary pump (Trivac S4B, Inficon) and a turbomolecular pump (TV141 Navigator, Varian). The HLD-MS is linked to the gas handling system with a dosing valve (VDH016-X, Inficon). The analyzed gases are pumped into the detector through the adjustable opening of the dosing valve that has been optimized. To measure the pressure of the gaseous mixture during the mass spectrometric measurements, a capacitance transducer gauge CT2 0.02–10 ( $\pm 0.02$ ) mbar (Effa) is connected close to the sample tube ST and to the reference tube RT (identical to ST).

**Procedures. (1) Sample Intake.** Sample tubes are 2-L stainless steel 316L cylinders closed by vacuum valves (Nupro

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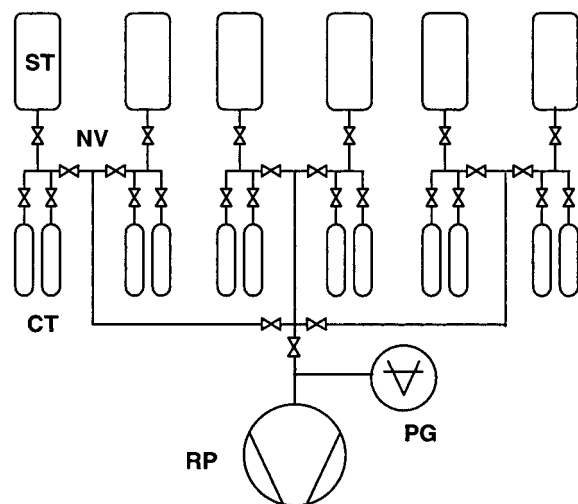


Figure 2. Schematic view of the apparatus used before the mass spectrometric step for the helium purification of six samples onto activated charcoals ( $T = 77$  K). Purification results from a selective and preferential adsorption of the matrix and hydrogen, whereas helium is not trapped. Key: ST, sample tube; CT, charcoal trap; NV, Nupro valve; RP, rotary pump; PG, Pirani gauge.

SS-4H-TW). Initially, they are pumped down to a pressure less than  $10^{-2}$  mbar. Two sample tubes are connected onto a hermetically sealed chamber into which a waste drum has been placed. First, 99% of the 70 L inner air (between the drum and the chamber) is eliminated after 10 min of a  $13 \text{ L}\cdot\text{s}^{-1}$  argon flow.<sup>11</sup> Then, the valve of the sample tube is opened to take an aliquot of the chamber's atmosphere. About 24 h later, the second sample tube is filled in the same way. The increase in  $^3\text{He}$  concentration inside the chamber  $\Delta x_{^3\text{He}}$  (ppb) allows the drum  $^3\text{He}$  outflow ( $\text{Pa}\cdot\text{m}^3\cdot\text{s}^{-1}$ ) to be estimated using the eq 2

$$Q_{^3\text{He}} = 10^9 P_C V_C \Delta x_{^3\text{He}} / \Delta t \quad (2)$$

where  $P_C$  and  $V_C$  are the pressure (Pa) and the volume ( $\text{m}^3$ ) of the inner space between the drum and the upper chamber, respectively, and  $\Delta t$  is the time (s) between both intakes. The mass spectrometric procedure was developed to quantify the  $^3\text{He}$  increase inside the chamber.

**(2) Purification Procedure.** Because samples include tritium, they are purified before the  $^3\text{He}$  mass spectrometric determination. A separate apparatus schematically shown in Figure 2 can purify six samples simultaneously. Two identical traps are dedicated to each sample. A trap consists of a stainless steel cylinder (2 cm inner diameter by 20 cm long) that contains precisely 33 g of granular activated charcoal (AC35, Prolabo). After their intake at a pressure around 950 mbar, the samples are connected to the purification system. The traps, preevacuated and kept at room temperature, are submerged into liquid nitrogen. Then, the samples are cryogenically pumped and adsorbed for 10 and 15 min in the first and second traps, respectively. After all, the noncondensed part of the initial mixture is isolated in the sample tube at a pressure of  $\sim 0.05$  mbar. To regenerate the traps, the adsorbed gases are finally pumped for 24 h at room temperature.

During purification, a selective adsorption occurs and allows for the preferential elimination of the argon matrix and the hydrogen species. Only helium is assumed not to be adsorbed onto charcoals. The helium concentration in the gas phase of purified samples is therefore significantly enhanced.

**(3) Mass Spectrometric Determinations.** Each purified sample is connected to the air inlet of the gas handling system and is systematically completed with a constant aliquot of pure argon, so the sample pressure reaches finally 7 mbar. Then, the sample valve linked to the measurement line is opened. Because the detector is continuously pumping the sample through the dosing valve, the sample pressure decreases during the measurement step. In addition, the time response of the detector is a few seconds when the  $m/z$  ratio is scanned. So concretely, the sample pressure and the mass spectrometer signal are both recorded simultaneously. Each mass-to-charge ratio is measured at a specific value of the decreasing sample pressure. In practice, for each sample initially introduced around 7 mbar, the  $m/z = 3, 4$ , and 2 stabilized ionic currents are recorded successively when the CT2 pressure indicates 6, 5, and 4 mbar, respectively. The complete analysis of  $^3\text{He}$ ,  $^4\text{He}$ , and  $\text{H}_2$  concentrations in a tube requires  $\sim 2$  min. The quantitative determination needs an external calibration obtained from the measurements of three certified mixtures and the argon blank. All are introduced and measured in the same way.

**Calculation of Sample Concentrations.** Since the preparation reduces the sample pressure, and assuming that helium is not trapped during purification, the final helium concentration will be enhanced compared to the initial one. These final concentrations  $\tilde{x}_j^S$  ( $j = ^3\text{He}, ^4\text{He}, \text{H}_2$ ) are calculated from the mass spectrometric measurements according to eq 3

$$\tilde{x}_j^S = \frac{I_k^S - I_k^B}{\beta_j} \quad \text{with} \quad \beta_j = \frac{I_k^R - I_k^B}{x_j^R} \quad (3)$$

where  $k$  ( $k = 2, 3, 4$ ) refers to the  $m/z$  ratio,  $I_k^S$ ,  $I_k^R$ , and  $I_k^B$  (A) are the ionic currents recorded respectively for sample, reference, and blank measurements, and  $x_j^R$  (ppm) is the concentration of the species  $j$  in the reference mixture. The sensitivity  $\beta_j$  ( $\text{A}\cdot\text{ppm}^{-1}$ ) is derived from reference mixture measurements. Sample or reference measurements are systematically corrected by subtracting the signal given by the argon blank measurements.

The initial concentrations in the sample  $x_j^S$  are deduced from the measured ones according to the eq 4

$$x_j^S = \tilde{x}_j^S / \alpha_j \quad (4)$$

where  $\alpha_j$  is the preconcentration factor. It takes into account three independent effects: the adsorption efficiency onto charcoals that varies to a large extent with the chemical nature of the  $j$  species, the dilutions during preparation steps, and the pressure reduction between the intake and the measurement stage. A high value of  $\alpha_j$  indicates an elevated enrichment factor resulting from a low adsorption efficiency of charcoals toward the  $j$  species. In practice,  $\alpha_{^3\text{He}}$ ,  $\alpha_{^4\text{He}}$ , and  $\alpha_{\text{H}_2}$  are determined experimentally by comparing the measurements of reference mixtures before and after the purification procedure.

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Table 2. Results of Repeated Mass Spectrometric Calibrations over 80 days ( $n = 33$ )

$m/z$	blank		reference		sensitivity	
	mean <sup>a</sup> (A)	RSD <sup>b</sup> (%)	mean <sup>a</sup> (A)	RSD <sup>b</sup> (%)	mean <sup>d</sup> (A·ppm <sup>-1</sup> )	RSD <sup>b</sup> (%)
4	$7.46 \times 10^{-15}$	6.7	$5.45 \times 10^{-11}$	1.9	$5.45 \times 10^{-13}$	1.9
3	$9.17 \times 10^{-15}$	6.2	$2.51 \times 10^{-14}$	2.4	$1.60 \times 10^{-12}$	3.5
2	$1.84 \times 10^{-11}$	18.8	$8.01 \times 10^{-10}$	2.3	$7.48 \times 10^{-12}$	2.3

<sup>a</sup> Peak high measured at a total introduction pressure of 6, 5, and 4 mbar for  $m/z$  3, 4, and 2, respectively, with gases introduced at 7 mbar.  
<sup>b</sup> RSD, relative standard deviation. <sup>c</sup> ppm, part per million in volume.  
<sup>d</sup> Calculated using eq 3.

## RESULTS AND DISCUSSION

**Mass Spectrometric Measurements. (1) Blank Measurement.** The results of 33 blank measurements over 80 days are shown in Table 2. It is observed that the presence of pure argon not only stabilizes but also reduces the residual ionic currents under values of  $1 \times 10^{-14}$  A for helium ( $m/z$  4 and 3) and  $2 \times 10^{-11}$  A for hydrogen. The standard deviations are  $5.0 \times 10^{-16}$ ,  $5.7 \times 10^{-16}$ , and  $3.4 \times 10^{-12}$  A for  $m/z$  4, 3, and 2, respectively.

Figure 3 shows that the blank measurement is relatively stable over a period of several months, even if some daily discrepancies can emerge. It also appears that these deviations in the  $m/z$  3 blank are strongly correlated to those of the  $m/z$  2 blank. No similar correlation was found with the  $m/z$  4 variations. This suggests that the  $m/z$  3 residual signal is mostly due to hydrogen via the contribution of molecular  $\text{HD}^+$  or hydrogen trimmer  $\text{H}_3^+$ . Indeed, the  $m/z$  2 blank is 3 orders of magnitude higher than that of helium. This is explained by two additional facts: hydrogen is the most desorbing species inside the mass spectrometer and also possesses the lowest compression factor ( $2 \times 10^3$  for  $\text{H}_2$  compared to  $5 \times 10^4$  for  $^4\text{He}$  or  $1 \times 10^9$  for Ar) that limits its evacuation by the turbomolecular pump.

**(2) External Calibration.** The values of the sensitivity, calculated using eq 3, are given in Table 2. It is observed that the sensitivity is enhanced for the lightest species: the HLD-MS is respectively 3 and 15 times more sensitive with  $^3\text{He}$  and  $\text{H}_2$  than with  $^4\text{He}$ . This is in accordance with the turbomolecular pump compression factors, but the drop between  $^3\text{He}$  and  $\text{H}_2$  is attributed to the difference in their ionization efficiency in the mass spectrometer cell.

The relative standard deviation of the external calibration, over 80 days, is around 2% for  $\text{H}_2$  and  $^4\text{He}$  and 3.5% for  $^3\text{He}$ . In addition, sensitivities remain extremely constant over several months as shown in Figure 4. This is of great importance for routine use, since the calibration frequency can be drastically reduced to weekly or monthly verification, for example. The mass spectrometric reproducibility and stability is the consequence that we record the electrometer signal directly on the MS electronic card, instead of the traditional output leak rate. With this simple adaptation, the possible variations of the internal calibrated leak cannot affect our measurements. Earlier studies demonstrated that, when using the leak rate signal and taking into account a systematic internal calibration, the deviations of the external calibration are  $\sim 3$  times higher (10%).

**(3) Detection Limit.** The detection limit is the minimal measurable concentration that corresponds to the lowest signal

that is assumed to be different from the blank with a probability of 95%. According to our protocol including a blank subtraction, the calculation of the detection limit  $\text{DL}_j$  (ppm or ppb) gives

$$\text{DL}_j = 4\sqrt{2}\sigma_k^B/\beta_j \quad (5)$$

where  $\sigma_k^B$  is the standard deviation of the blank measurements. The detection limits calculated with eq 5 are 5.2 ppb for  $^4\text{He}$ , 2.0 ppb for  $^3\text{He}$ , and 2.6 ppm for  $\text{H}_2$ . Even without any preconcentration, it is demonstrated that concentrations as low as ppb for helium isotopes and ppm for hydrogen can be determined.

**(4) Linearity.** The HLD-MS linearity has been verified with the reference mixtures diluted in blank argon. The ionic current plotted versus the  $^4\text{He}$  concentration gives a good linear correlation ( $R^2 = 0.998$ ) from 1 ppb up to 100 ppm. This has also been verified for  $^3\text{He}$  ( $R^2 = 0.990$ ) between 1 and 10 ppb. Then, only one standard mixture per analyzed species can be used to cover the entire range of measurable concentrations.

**(5) Accuracy.** The accuracy of the technique has also been studied. Therefore, the  $^4\text{He}$  concentration in ambient air was determined from comparison to our  $^4\text{He}$  reference mixture. The results of seven determinations give  $5.20 \pm 0.05$  ppm (2 $\sigma$ ). It lets us verify that the weak bias of 0.8% according to the theoretical value of 5.24 ppm is smaller than the uncertainty (1%) of the reference mixture. So, the accuracy of  $^4\text{He}$  determinations is demonstrated. In addition, 20 measurements of two certified  $^3\text{He}$  mixtures containing respectively 80 and 8500 ppb have been performed. One of these gas mixtures was taken as a reference in order to determine the concentration of the other one. This procedure leads to the same conclusion for the accuracy, given a bias of 8.4%, lower than the uncertainty ( $\pm 10\%$ ) on the reference mixtures.

**(6) Resolution of the Mass Spectrometer.** A mass spectrum of each mixture connected to the apparatus was recorded. They are superimposed in Figure 5a, and the  $m/z$  4, 3, and 2 peaks appear from left to right. We note first the very broad shape of the peaks and second the large difference between their intensities. From the peak width measurement, the resolution of the mass spectrometer is calculated as 3 (no dimension) using the "5% peak high" definition.<sup>12</sup> The  $m/z$  3 peak is too weak on the linear representation shown Figure 5a. So, the  $m/z$  3 region has been magnified in Figure 5b and it can be observed how the  $m/z$  3 peak is affected by the presence of other elements at adjacent  $m/z$  ratio. On one hand, according to the resolution, the peak is the addition of many contributions that comprise not only the  $^3\text{He}^+$  but also the  $\text{HD}^+$ ,  $\text{H}_3^+$ , and  $\text{T}^+$  ionic currents. That is why the appearance of an intense  $m/z$  3 peak is observed when the  $\text{H}_2$  reference mixture is measured. On the other hand, the  $^4\text{He}$  reference mixture induces a negative contribution. It is suggested, contrary to the hydrogen contribution, that the  $^4\text{He}$  perturbation is not in relation with the poor resolution of the mass spectrometer.

**(7)  $\text{H}_3^+$  Contribution.** The formation of the  $\text{H}_3^+$  trimmer results from ion/molecule reactions that occur in the mass spectrometer.<sup>13</sup> Since the residual hydrogen induces a  $m/z$  3

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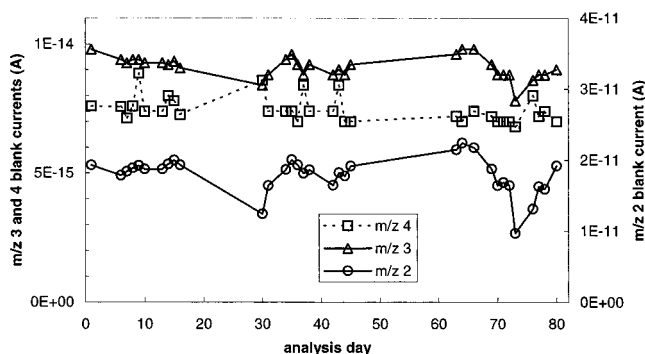


Figure 3. Results of 33 measurements of the blank over 80 days showing the correlation between the  $m/z$  2 and 3 residual ionic currents whereas no relation is found with the  $m/z$  4 ionic current.

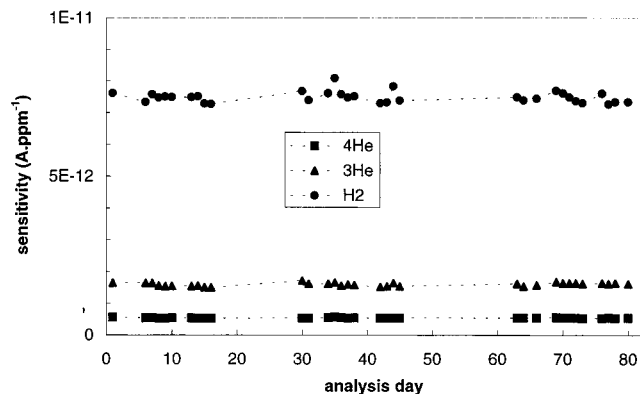


Figure 4. Reproducibility and stability over 80 days of the sensitivity coefficients derived from repeated external calibrations with the references and blank gaseous mixtures.

contribution, it must be taken into account for the accurate determination of very small  $^3\text{He}$  concentrations. To quantify the  $\text{H}_3^+$  contribution, the  $\text{H}_2$  reference mixture was diluted between 1 and 100 ppm. Then, the  $m/z$  2 and 3 ionic currents were consecutively measured, and Figure 6 shows their linear correlation ( $R^2 = 0.998$ ). Therefore, the proportionality factor, with a value of  $6.1 \times 10^{-5}$ , is used to quantify the  $\text{H}_3^+$  contribution. The  $^3\text{He}$  concentration is finally calculated using the following equation, which corresponds to eq 3 including the subtraction of the  $\text{H}_3^+$  contribution derived from the  $m/z$  2 signal:

$$\bar{x}_{3\text{He}}^S = \frac{(I_3^S - I_3^B) - 6.1 \times 10^{-5}(I_2^S - I_2^B)}{\beta_{3\text{He}}} \quad (6)$$

Note that a linear production of  $\text{H}_3^+$  versus the  $\text{H}_2$  abundance is observed, in contrast with a quadratic dependence reported in papers dealing with hydrogen isotopic studies.<sup>14,15</sup> It could be due to the fact that here  $\text{H}_2$  is only present at a trace level. Then it is not the only neutral species present in significant quantities, as is supposed in the cited works.

**(8)  $^4\text{He}$  Perturbation.** A significant presence of  $^4\text{He}$  leads to a broad  $m/z$  4 peak that induces a  $m/z$  3 negative contribution

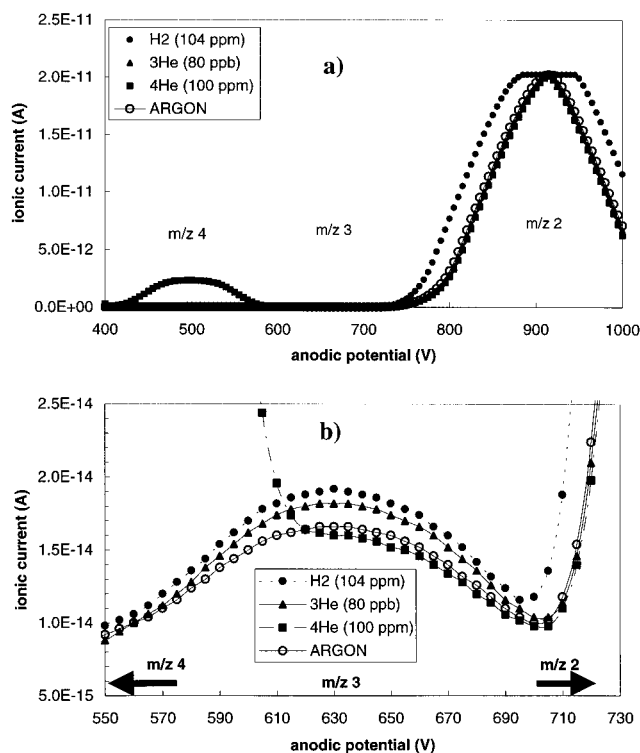


Figure 5. Mass spectra of the gas mixtures used for the blank and calibration measurements. (a) Total scan showing the both  $^4\text{He}^+$  and  $\text{H}_2^+$  peaks whereas the  $^3\text{He}^+$  peak is too weak to be observed. (b) Magnification of the  $m/z$  3 peak region showing not only the  $\text{H}_3^+$  contribution resulting from hydrogen ion/molecule reactions but also the attenuation (compared to the argon blank) of the  $m/z$  3 signal due to the presence of  $^4\text{He}$ .

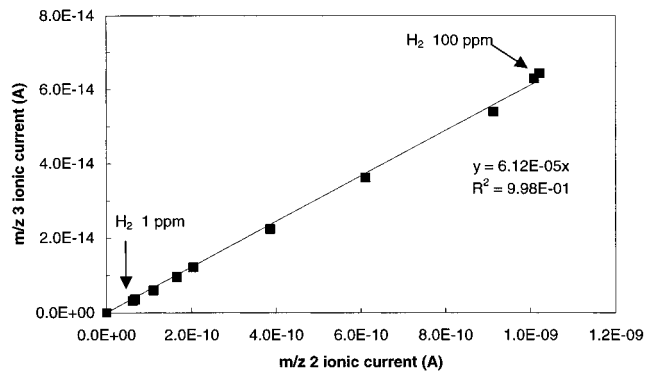


Figure 6. Linear relationship between the  $m/z$  3 ( $\text{H}_3^+$ ) and 2 ( $\text{H}_2^+$ ) ionic currents resulting from measurements between 1 and 100 ppm  $\text{H}_2$ . It is used for subtraction of the  $\text{H}_3^+$  contribution in the  $^3\text{He}$  quantitative determination.

by reducing the  $m/z$  3 ionic current under the blank value, implying a scattering effect.<sup>16</sup> This tends to underestimate the  $^3\text{He}$  determination for the lowest values of the isotopic ratio, and consequently, the analysis need the correction of this effect for a ratio under  $10R_a$ . Contrary to the hydrogen contribution, this effect is not corrected here because, in practice,  $^3\text{He}$  is analyzed in an argon matrix. In this case,  $^4\text{He}$  in samples is always under a value that could disturb the  $^3\text{He}$  determination even for concentrations as low as 0.05 ppb.

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**Measurement of Preconcentration Factors.** The preconcentration factor is a parameter that reflects the adsorption efficiency onto activated charcoals. Theoretically, the highest value of the preconcentration factor  $\alpha_{\max}$  corresponds to a nontrapped element. It is calculated with the eq 7 that takes in account the volume and pressure changes induced by the purification step

$$\alpha_{\max} = \frac{V_s}{V_s + V_d} \frac{P^i}{P^f} \quad (7)$$

where  $V_s$  and  $V_d$  are the sample and the purification line volumes, respectively, and  $P^i$  and  $P^f$  the initial and final pressures. The calculation yields  $\alpha_{\max} = 125$ .

Experimentally, the preconcentration factor of each species was measured. Sample tubes filled with reference mixtures at atmospheric pressure were submitted to the purification procedure including the Ar refilling step. These preconcentrated reference mixtures were compared to the initial gases with known concentrations. According to eq 4, the values of the preconcentration factors are  $\alpha_{\text{H}_2} = 2.5$ ,  $\alpha_{\text{He}} = 91.3$ , and  $\alpha_{\text{He}} = 75.6$  with relative standard deviations ( $n = 4$ ) around 4%. Helium is  $\sim 33$  times more preconcentrated (less trapped) than hydrogen. From the  $\alpha$ ,  $P^i$ , and  $P^f$  values, the efficiency of hydrogen trapping and helium recovery are calculated according to the eq 8

$$\tilde{p}_j/p_j = \alpha_j(P^i/P^f) \quad (8)$$

where  $\tilde{p}_j$  and  $p_j$  are respectively the preconcentrated and the initial partial pressure of the  $j$  species derived from the concentration and the total pressure measurements. The ratio expresses for each considered species the relative quantity that is recovered in the sample tube after a purification step. It is demonstrated that hydrogen is close to being totally eliminated since only 1.5% is recovered, whereas the helium recovery is between 55 ( $^4\text{He}$ ) and 67% ( $^3\text{He}$ ). Measurements with reference mixtures denote a 20% relative difference between  $\alpha_{\text{He}}$  and  $\alpha_{\text{He}}$ . This could either result from an isotopic effect in helium adsorption, according to the boiling temperatures of 3.19 ( $^3\text{He}$ ) and 4.22 K ( $^4\text{He}$ ), or either arise from an influence of the initial concentration which is 5 orders of magnitude smaller for  $^3\text{He}$  than for  $^4\text{He}$ .

In addition, the  $^3\text{He}$  standard mixture was submitted to dilutions before the purification step. When pure argon is used for the dilutions, Figure 7 shows the measured  $\alpha_{\text{He}}$  values with initial  $^3\text{He}$  concentrations comprised between 0.05 and 10 ppb. Although the results show an apparent increasing  $\alpha_{\text{He}}$  mean value from 91 (10 ppb) to 106 (0.05 ppb), the corresponding uncertainties also increase from 4% up to 20%. Thus, the preconcentration factor is considered as a constant, whatever the helium concentrations are. Compiling all the determinations,  $\alpha_{\text{He}} = 98.5 \pm 16$  ( $2\sigma$ ,  $n = 16$ ) is finally the retained value. The experimental results show that 0.05 ppb  $^3\text{He}$  in argon is easily detected with no bias and a precision of  $\sim 20\%$ .

In contrast, when air is used for the dilutions, the results have shown that, under 0.1 ppb  $^3\text{He}$ , the presence of the 5.24 ppm atmospheric  $^4\text{He}$  produces a notable  $^3\text{He}$  underestimation. The atmospheric helium isotopic ratio is close to being measured, but actually, the detector is adequate for the determination of  $^3\text{He}/^4\text{He}$  ratios greater than  $2 \times 10^{-5}$ .

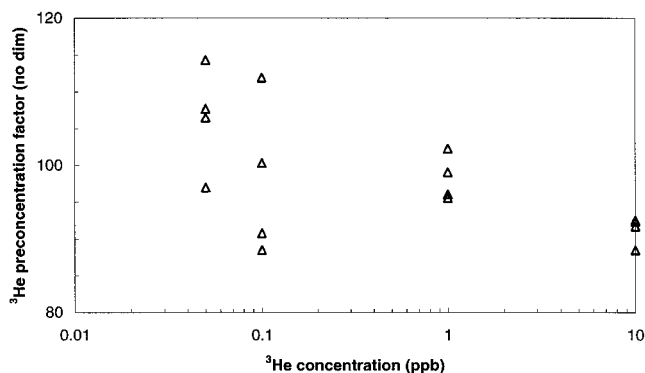


Figure 7. Plot of the 16 measurements of the  $^3\text{He}$  preconcentration factor measured four times for four different initial concentrations ranging from 0.05 to 10 ppb.

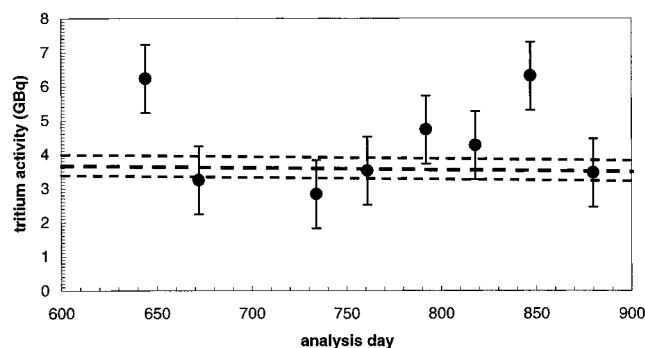


Figure 8. Example of eight activity measurements on a homemade reference drum containing initially  $4.1 \pm 0.4$  GBq. The theoretical values of 3.71 (644 day) and 3.59 GBq (880 day) are presented in dotted lines. Experimental results deduced from the determination of the  $^3\text{He}$  outflow are in agreement with the theoretical value. The two highest points are discussed in the text.

**Tritium Activity Determination in Drums.** Many reference drums were measured following the described procedures. They were custom-made by filling drums with various noncontaminated organic materials and adding a small and accurate quantity of tritiated water. After they were closed, they were stored for more than 1 year, so it is assumed that the drum has reached an equilibrium. In this condition, the loss of  $^3\text{He}$  equals the  $^3\text{He}$  production due to tritium. That is why the internal tritium activity  $A$  (Bq) is directly determined from the  $^3\text{He}$  outflow measurement according to eq 9

$$A = Q_{\text{He}}(N_A/RT) \quad (9)$$

where  $N_A$  is the Avogadro number ( $\text{mol}^{-1}$ ),  $R$  the perfect gas constant ( $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ), and  $T$  the absolute temperature (K).

The lowest active reference drum contained initially  $4.1 \pm 0.4$  GBq of tritiated water that corresponds to  $\sim 1 \times 10^{-5}$  g of tritium in 200-L sample. Consequently, the reference activity corrected with the tritium decay (Figure 8) is 3.71 and 3.58 GBq after 644 and 880 days of storage, respectively. The drum was measured 8 times during this period, and the results are shown in Figure 8. The mean value of the measured activity is 4.33 GBq and corresponds to a deviation of  $\sim 20\%$  from the theoretical value. The reproducibility of the drum determination is under 30% with the respective standard deviation of 1.34 GBq. It is on the order of the uncertainty of 1 GBq on each activity measurement.

When detailing the results, it appears that two measurements (644 and 847 days) gave too high results with biases up to +70% whereas no low value was measured. This can be explained with a model of the drum outflow<sup>17</sup> that implies a laminar gaseous flow arising from the variations of the atmospheric pressure superimposed on a <sup>3</sup>He steady-state permeation. In fact, the pressure inside the drum follows the variations of the atmospheric pressure, but the large inner volume of the drum induces a retarding effect. That is why intense atmospheric variations can cause imbalance between inner and atmospheric pressures. Therefore, when the atmospheric pressure falls significantly before putting the drum into the measurement chamber, the drum outflow is greatly enhanced, giving an overestimated activity. On the other hand, with the present drum, we did not obtain any value lower than the value corresponding to the constant <sup>3</sup>He permeation flow. This is in accordance with the model predictions.

The detection limit is calculated around 10<sup>9</sup> Bq according to 25 h of confinement and <sup>3</sup>He mass spectrometric performances. This is 10<sup>5</sup>-fold lower than the concurrent calorimetric determination<sup>18</sup> that has a detection limit of  $2 \times 10^{14}$  Bq. It should be noted that 1 GBq of tritium is a very low activity that corresponds to as low as  $3 \times 10^{-6}$  g of tritium that has to be measured inside a sample as large as 200 L.

## CONCLUSIONS

It was demonstrated that a helium leak detector mass spectrometer can be used to precisely determine the helium isotopes at the ppb level and hydrogen at the ppm level. The measurement procedure was optimized through a simple adaptation that gives stability in external calibration. The technique is easy to use since software (L2I) was developed. It assists the analysis by taking into account the following: the computer command of the mass spectrometer, the simultaneously recording of the pressure, and the mass spectrometer signals, the calculation of concentrations,

and finally the management of a database of all analyses and calibrations. The weakness of the apparatus is the impossible measurement of helium isotope ratio around the atmospheric value. Therefore, certified gaseous mixtures are required for the external calibration. Advanced modifications in the mass spectrometer or in the pumping system should be performed to use air for calibration.

When the leak detector is combined with a cryogenic adsorption, helium in samples can be preconcentrated and freed from hydrogen. Then, <sup>3</sup>He determinations can be used for indirect tritium measurement with a <sup>3</sup>He ingrowth method. The advantages of the technique are, the mobility of the apparatus, the simplicity and reliability that routine measurements require, and the low cost of such a portable MS compared with large-scale calorimeters.

This work has found an original and significant application in the nondestructive determination of tritium in radioactive waste drums. Currently, the <sup>3</sup>He outflow method is the only way to manage a nondestructive and reliable analysis of wastes containing low tritium activity. The measurable values in a 200-L drum range from ~10<sup>9</sup> Bq to the detection limit of calorimetric determination. Based on this work, an industrial device was designed to measure systematically all tritiated waste drums before their reconditioning.

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