

Hot vacuum extraction-isotopic dilution mass spectrometry for determination of hydrogen isotopes in zircalloys

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Abstract A hot vacuum extraction-isotope dilution mass spectrometry (HVE-IDMS) was studied for determination of hydrogen isotopes in zirconium metal and alloys as nuclear reactor materials. A theoretical assessment of the completeness of the extraction of hydrogen isotopes under the chosen condition was carried out based on the hydrogen and deuterium solubility data for zirconium. The optimal isotopic spiking condition for conventional IDMS was further explored for the special case IDMS where the isotope abundance of the samples is varied and non-natural. Applying the optimal conditions, the accurate IDMS determination was realized. The agreement between the measured values and the certified or prepared values of standard reference materials and homemade standard materials validate the method developed.

Keywords Hot vacuum extraction · Isotopic dilution · Mass spectroscopy · Hydrogen · Deuterium · Zirconium · Zircaloy

Introduction

The pressure tubes in CANDU[®] reactors are comprised of Zr-2.5wt% Nb alloy based on its desired low neutron capture cross section and good chemical and mechanical properties. In the reactor core, pressure tubes are exposed to high temperature and high pressure heavy water coolant as well as high nuclear radiation. Corrosion causes the

ingress of deuterium into the materials which, at high concentration, may lead to hydride formation and delayed hydride cracking [1]. Hence, monitoring the concentration of hydrogen isotopes in the pressure tube materials is required to assess the integrity of the components by both the nuclear power plant operators and nuclear safety regulators. Since the concentration of hydrogen isotopes is usually low and the test specimen sampled from the highly radioactive pressure tube material is generally small (~0.1 g), a sensitive and accurate analytical method is essential. In addition, the heavy water reactor industry requires the determination of the concentration of both hydrogen isotopes, H and D, separately.

A number of techniques, including isotopic equilibration [2, 3], hot vacuum extraction (HVE) [4–6], spark source mass spectrometry [7], laser ablation mass spectrometry [8], and ultrasound-based non-destructive evaluation [9] have been researched or developed to determine hydrogen or hydrogen isotopes in zircaloy. Among these methods, HVE coupled with mass spectrometry (MS) is the most widely used method for its excellent accuracy and sensitivity. Over the decades, a hot vacuum extraction-isotope dilution mass spectrometry (HVE-IDMS) has been developed and used at Canadian Nuclear Laboratories (CNL), formerly Atomic Energy of Canada Limited (AECL), Chalk River Laboratories (CRL) for the determination of hydrogen isotopes in zirconium metal and alloy materials [6]. This method is based on the hot vacuum extraction of the hydrogen isotopes as gases from the samples and the quantitative determination of the extracted gases by isotope dilution mass spectrometry. Experimental development of the method, including gas extraction, procedure blanks, analysis of standards, method uncertainties, and bias, has been discussed previously [6]. The method meets the requirements for surveillance examination of the Zr-2.5wt% Nb pressure tubes of CANDU

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reactors and post-irradiation examination of zircaloy cladding materials of reactor fuel elements. This paper reports some continuing development of the HVE-IDMS methodology for the purpose of improving the accuracy and minimizing the uncertainty. One emphasis is the theoretical assessment of the completeness of the gas extraction based on available hydrogen and deuterium solubility data for zirconium. The second emphasis is to establish the optimized isotopic spike for this special case IDMS where the isotopic ratios of the sample (or the target) and spiked sample (or the blend) are to be measured, as opposed to the conventional IDMS where only the spiked sample isotopic ratio is to be measured.

Experimental

The system design and procedures for both analysis and standard preparation is similar to what was previously reported [6]. Details will not be repeated here, only the more recent upgrades to equipment are described here. The specimens are heated in a quartz tube using a SpotIR Spot Heater (Model 4085, Research Inc. Eden Prairie, USA). The transfer pump is a Turbovac 151 turbo molecular pump with ceramic bearing (Leybold Vacuum Products Inc., Mississauga, ON, Canada), that replaced the magnetically coupled turbo molecular pump Turbovac 340 M (Leybold Vacuum Products Inc., Mississauga, ON, Canada).

Of the two systems in our laboratory, one utilizes a VG Micromass 8-80 mass spectrometer with the mass resolution ($M/\Delta M$) set at ~ 50 . The other system utilizes a Prima dB process mass spectrometer with an $M/\Delta M$ at ~ 20 (Thermo Scientific, UK). The two spike gases are compressed UHP natural hydrogen and UHP deuterium. The isotopic composition of the hydrogen gas is taken from the hydrogen natural abundance of 99.9885 % H and 0.0115 % D. The two deuterium spike gases installed on the two HVEMS systems have slightly different isotopic composition; either 0.28 % H and 99.72 % D, or 0.18 % H and 99.82 % D. The relative sensitivities of H_2 , HD and D_2 , measured in the mass spectrometers at the atomic mass units of 2, 3, and 4, respectively, are predetermined by analyzing a comprehensive combination of gas mixtures of H_2 , HD and D_2 . The directly measured H to D atomic ratio, H/D, is corrected for relative sensitivity to give the “true” ratio. In addition, factors for spectral interfering ion species, mainly D^+ with H_2^+ , and H_3^+ with HD^+ , are also predetermined and applied to correct the measured H/D ratio.

Results and discussion

Hot vacuum extraction

The determination of hydrogen and deuterium in zirconium by HVEMS is based on the quantitative hot vacuum extraction of the hydrogen isotopes as gases from the samples followed by IDMS determination of the extracted gases. An accurate determination requires either the complete extraction of the hydrogen isotopes from the sample, or application of a valid recovery correction if the extraction is not complete. An estimation using hydrogen solubility in zirconium described by Sievert's Law [10] can shed some light on the completeness of the extraction. The equilibrium between the hydrogen partial pressure, p , surrounding the specimen and the hydrogen concentration in solid solution in the specimen, c , is described in Eq. (1). The Sieverts' constant, k , having a relationship with temperature, T , shown in Eq. (2), can be experimentally determined.

$$c = k\sqrt{p} \quad (1)$$

$$\ln k = a + \frac{b}{RT} \quad (2)$$

There have been a number of reported values of the Sieverts' constants for hydrogen-zirconium system (metal and alloys) measured at temperatures close to 1100 °C [11–15]. In these studies, very little differences in the hydrogen isotope solubility have been observed between Zr metal and Zr alloys. Based on these values, the equilibrium concentrations of H or D in the metal phase (or alloy), under the normal achievable hydrogen partial pressures in the specimen tube of about 4×10^{-6} Pa [6] in the HVEMS apparatus, and at a temperature of 1100 °C, were calculated. These values were taken as an estimate of the amount of H or D remaining in the specimen after extraction. The results (Table 1) show that, after HVE under the chosen conditions, the maximum unextracted residual H and D concentration remaining in the metal could only be about 0.026–0.035 ppm and 0.053–0.070 ppm, respectively. This estimate of unextracted H and D remaining in the samples are considered to be either less than the uncertainty or below the method detection limits for H and D; the possible bias due to incomplete extraction is insignificant compared to the measurement uncertainties and the detection limits. Experimentally, the quantitative extraction of hydrogen isotopes from zirconium materials is validated by the agreement between the measured values and the certified or prepared values of the hydrogen isotope concentration in analyzing the standard reference materials (SRM) or

Table 1 Estimated equilibrium concentrations of H and D after HVE in Zr at 1100 °C and under a partial pressure of 4×10^{-6} Pa

Solubility data source	Temperature range (°C)	k, H/Zr atomic ratio Pa ^{-1/2}	Equilibrium concentration (ppm)	
			H	D
Ells and McQuillan [11]	500–950	0.00119	0.026	0.053
Watanabe [12]	870–940	0.00124	0.027	0.051
Moalem and Olander [13]	950–1400	0.00129	0.029	0.057
Yamanaka et al. [14]	925–1050	0.00153	0.034	0.067
Steinbruck [15]	957–1457	0.00158	0.035	0.070

homemade standard materials (RM). Detailed information is given later within this paper.

Optimal spiked isotopic ratio

For a two isotopic system, such as H and D, the equations to calculate the amount of H and D isotopes in the extracted gas (or the target) can be written as Eqs. (3) and (4) according to the principle of IDMS [16, 17]. In the equations, N_H , N_D , and N_s stand for the amount (moles) of H isotope, D isotope in the target, and the amount of the enriched isotopic spike, respectively. R_t , R_s , and R_b are the H-to-D isotopic ratios of the target, the spike, and the blend (the spiked gas), respectively.

$$N_H = N_s \frac{R_t(R_b - R_s)}{(1 + R_s)(R_t - R_b)} \tag{3}$$

$$N_D = \frac{N_H}{R_t} = N_s \frac{(R_b - R_s)}{(1 + R_s)(R_t - R_b)} \tag{4}$$

Following the uncertainty propagation law, the uncertainty of the measured target isotopic amount is composed of the uncertainties attributed from each of the variables with multiplication factors as shown in Eq. (5) and (6).

$$\begin{aligned} \left(\frac{\sigma_{N_H}}{N_H}\right)^2 &= \left(\frac{\sigma_{N_s}}{N_s}\right)^2 + \left(\frac{R_b}{(R_t - R_b)}\right)^2 \left(\frac{\sigma_{R_t}}{R_t}\right)^2 \\ &+ \left(\frac{(1 + R_b)R_s}{(1 + R_s)(R_b - R_s)}\right)^2 \left(\frac{\sigma_{R_s}}{R_s}\right)^2 \\ &+ \left(\frac{(R_t - R_s)R_b}{(R_t - R_b)(R_b - R_s)}\right)^2 \left(\frac{\sigma_{R_b}}{R_b}\right)^2 \end{aligned} \tag{5}$$

$$\begin{aligned} \left(\frac{\sigma_{N_D}}{N_D}\right)^2 &= \left(\frac{\sigma_{N_s}}{N_s}\right)^2 + \left(\frac{R_t}{(R_t - R_b)}\right)^2 \left(\frac{\sigma_{R_t}}{R_t}\right)^2 \\ &+ \left(\frac{(1 + R_b)R_s}{(1 + R_s)(R_b - R_s)}\right)^2 \left(\frac{\sigma_{R_s}}{R_s}\right)^2 \\ &+ \left(\frac{(R_t - R_s)R_b}{(R_t - R_b)(R_b - R_s)}\right)^2 \left(\frac{\sigma_{R_b}}{R_b}\right)^2 \end{aligned} \tag{6}$$

Extensive studies have concluded that, for conventional IDMS, a theoretical optimum spike amount exists resulting in a theoretical optimum spiked isotopic ratio of the blend,

$R_{b,opt}$ (Eq. (7)), which leads to a minimal uncertainty for the measured isotope amounts of the target [16, 18–20].

$$R_{b,opt} = \sqrt{R_s R_t} \tag{7}$$

There are two assumptions in conventional IDMS that lead to this optimized spike condition. The first assumption is that the uncertainty from the target isotopic ratio (R_t) is small and can be ignored because it is usually not measured but taken from the commonly accepted and accurate natural isotopic abundance. The second assumption is that the uncertainty from the isotopic ratio of enriched isotopic spike (R_s) is also small and to be ignored because the spike is either a well characterized SRM (with very small uncertainty) or its isotopic ratio can be determined accurately before use. However, in analyzing an isotopically non-natural target, such as the hydrogen isotopic gas extracted from CANDU® reactor pressure tube materials, R_t needs to be measured and the associated uncertainty from that measurement cannot be ignored. Introducing the term $R_b/R_{b,opt}$ as an indicator of the degree of agreement of the actual blend isotopic ratio to the theoretical optimal blend isotopic ratio, and for convenience, expressing the uncertainty multiplication factors in Eqs. (5) and (6) as $A = \frac{R_b^2}{(R_t - R_b)^2}$ or $\frac{R_t^2}{(R_t - R_b)^2}$, $B = \frac{(1 + R_b)^2 R_s^2}{(1 + R_s)^2 (R_b - R_s)^2}$, and $C = \frac{(R_t - R_s)^2 R_b^2}{(R_t - R_b)^2 (R_b - R_s)^2}$, the variation of each uncertainty multiplication factor with respect to $R_b/R_{b,opt}$, choosing $R_t = 1$ and $R_s = 0.002$ for example, are plotted and shown in Figs. 1 and 2. From the plots, it is clearly shown that even considering the uncertainty contribution from R_t , the optimal spiking condition given by Eq. (7) still holds; the minimum uncertain is reached when $R_b = R_{b,opt}$.

As expected, a more enriched spike (very large or small R_s), or an isotopically purer target sample (very large or small R_t) would result in a smaller uncertainty multiplication factor and a wider range for the optimum spiked ratio (Fig. 3). In the HVE-IDMS method, isotopic composition of the target gas varies depending on the sample nature. To minimize the uncertainty, natural hydrogen ($R_s \approx 8695$) and highly enriched deuterium ($R_s \approx 0.002$) are selected as spikes.

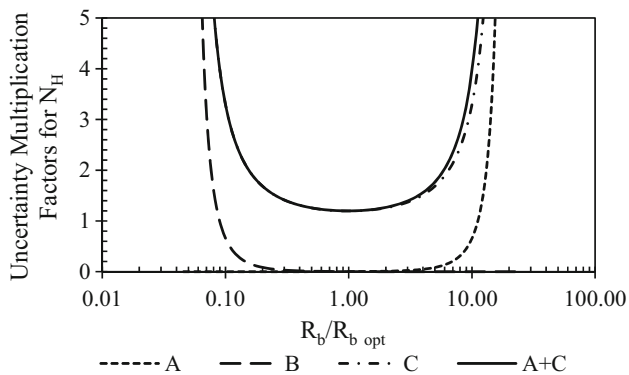


Fig. 1 Uncertainty multiplication factors for N_H against $R_b/R_{b,opt}$ ratio ($R_t = 1$, $R_s = 0.002$)

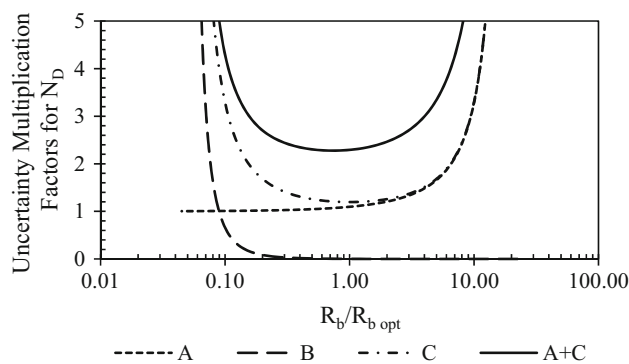


Fig. 2 Uncertainty multiplication factors for N_D against $R_b/R_{b,opt}$ ratio ($R_t = 1$, $R_s = 0.002$)

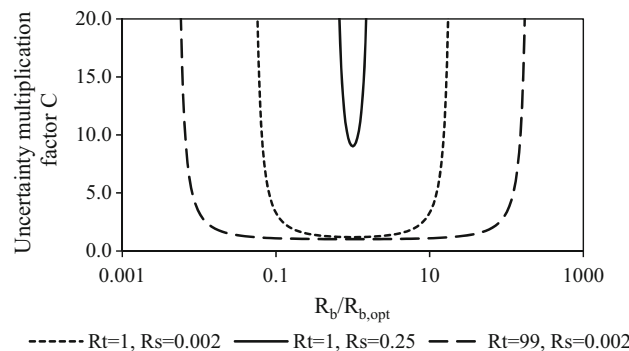


Fig. 3 Uncertainty multiplication factors C against $R_b/R_{b,opt}$ under different R_t and R_s

Over the years, a larger number of samples, procedure blanks, and standards have been analyzed by HVE-IDMS and the relative standard uncertainties and the $R_b/R_{b,opt}$ were calculated for each of the analyses. They are presented in Fig. 4 and 5 in 3-D graphs. These graphs clearly show that at approximately the same H and D amount, lower uncertainty was observed for the analyses performed at $R_b/R_{b,opt}$ closer to 1. These figures also show that the

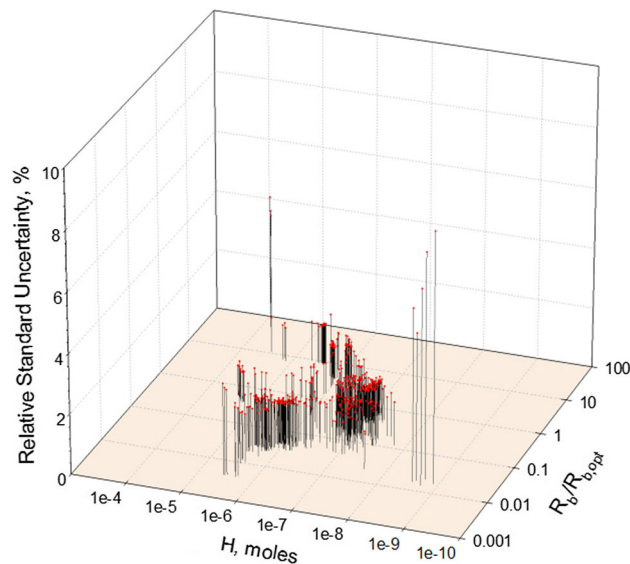


Fig. 4 Measured standard uncertainty of H at different $R_b/R_{b,opt}$ and amount of H

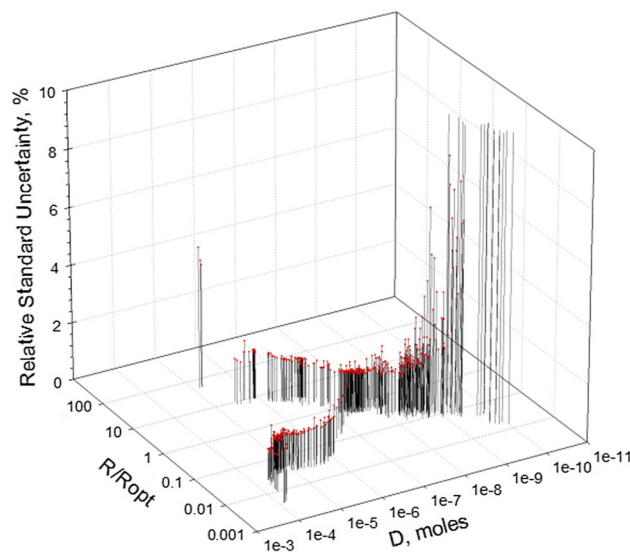


Fig. 5 Measured standard uncertainty of D at different $R_b/R_{b,opt}$ and amount of D

uncertainty was higher at lower H or D amounts (lower concentration) regardless of the agreement between R_b and $R_{b,opt}$. This is expected since the uncertainty of the isotopic ratio measurement, R_t , is higher when the ion current intensity is low (hydrogen isotopic amount to be measured is low).

Blanks

The blank refers to the hydrogen and deuterium measured by the HVE-IDMS procedure in a given specimen from which all the hydrogen and deuterium have been

previously extracted. As expected, the deuterium blank is expected to be low, in contrast there are many factors, including the condition of the sample tube, humidity of the lab, geometry of the specimen, which could contribute to hydrogen blank. The blank subtraction results in an additional uncertainty component to the overall uncertainty of the measured concentration of hydrogen isotopes in samples. The significance of the uncertainty contribution from the blanks varies depending on the H and D amount extracted from the samples. The uncertainty contribution from the H blank subtraction could be a significant component of the overall uncertainty of the measured H concentration, when the H concentration is low.

Over the years, many blanks have been analyzed along with the sample analyses. Figure 6 shows approximately 1900 blanks measured from November, 2006 to October, 2012. Individual values of the H and D blanks are plotted with times and dates when they were measured. Also in the figure, the moving averages of 50 successive measurements are presented as lines. It appears that there could be a seasonal variation of the hydrogen blank, especially visible from the line of the moving average. In general, the H blank appeared higher in the summer time and lower in the winter time. A similar variation is less visible for the D blanks.

Based on the above analyses, the typical D blank was estimated as approximately $0.0015 \mu\text{mol}$ with a standard deviation of around $0.0018 \mu\text{mol}$. This level of blank is very low compared to the D content in most of the samples analyzed. Hence, the D blank correction did not introduce significant uncertainty to the overall uncertainty of the analysis except when analysing samples with a natural hydrogen source or when the D concentration was very low. The typical H blank, on the other hand, varies between 0.18 and $0.36 \mu\text{mol}$ over the 12 months with standard deviations between 0.12 and $0.18 \mu\text{mol}$. The uncertainty of the H blank correction is the dominant contributor to the

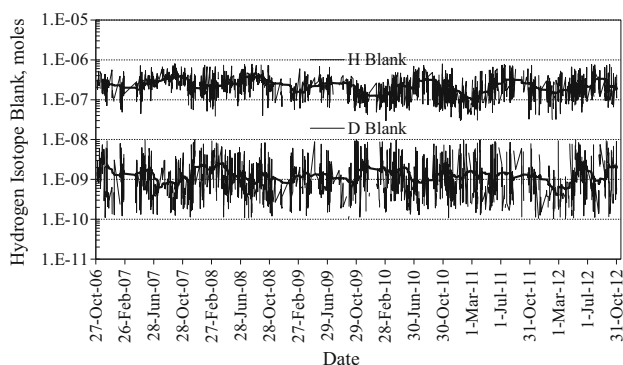


Fig. 6 Procedure blanks measured from Nov. 1, 2006 to Oct. 31, 2012

overall uncertainty for analyzing the H concentration in CANDU[®] pressure tube samples.

Analysis of standard reference materials (SRM) and homemade standard materials

When it was available, a hydrogen-in-zirconium standard reference material (SRM), NBS 358 was analyzed repeatedly for QC purpose. This SRM, in form of wires, had a certified nominal H concentration of 105 ± 3 (1 s) $\mu\text{g g}^{-1}$, which was based on the best estimate of the “true” value determined by hot vacuum extraction on samples weighing 0.20 – 0.23 g. Hydrogen inhomogeneity might have existed within the materials [4]. In our lab, 47 measurements were performed from 2007 to 2008. The average sample weight used in these 47 measurements was 0.13 g which might have been subjected to issues of inhomogeneity. Nevertheless, the measured H values along with the uncertainty are plotted according to the order of the measurement numbered from 1 to 47 and shown in Fig. 7. The overall measured average was calculated to be $103 \mu\text{g g}^{-1}$ with a standard deviation of $3 \mu\text{g g}^{-1}$, which is considered in agreement with the certified value in consideration of the possible inhomogeneity and the uncertainties.

To further validate the method for determination of both H and D, in-house standard materials (SM) were prepared according to a previous publication [6]. These SM were made to have prepared concentrations of one or both isotopes, H and D. The mass of the specimen was varied but most of them had a sample mass of approximately 0.2 g. The hydrogen concentration ranged from 0 to 100 ppm and the D concentration from 0 to 69 ppm with the majority at about 10 and 20 ppm. Figures 8 and 9 show the plots of the measured H and D concentration against the prepared concentration for approximately 800 in-house SM prepared and analyzed over the years. The good agreement between the prepared value and the measured value can be visually seen from the plots.

A linear regression analysis was performed between the measured hydrogen values against the prepared concentrations.

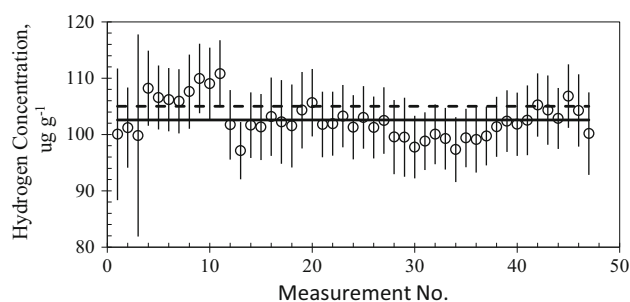


Fig. 7 Measured H concentrations in NBS 358

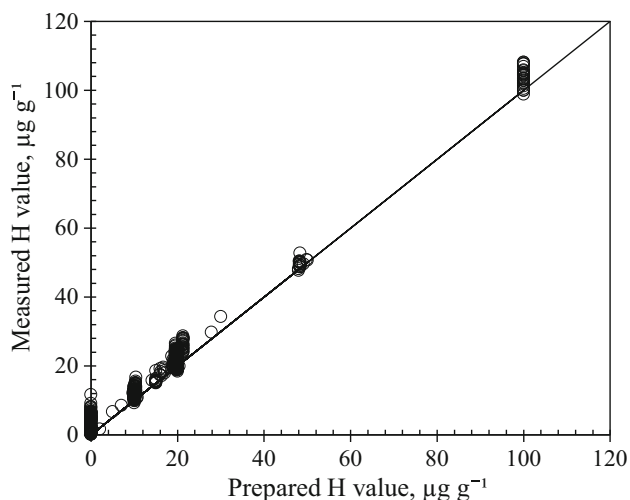


Fig. 8 Measured versus prepared H concentration values from homemade reference materials; Note the diagonal line is the 1:1 line

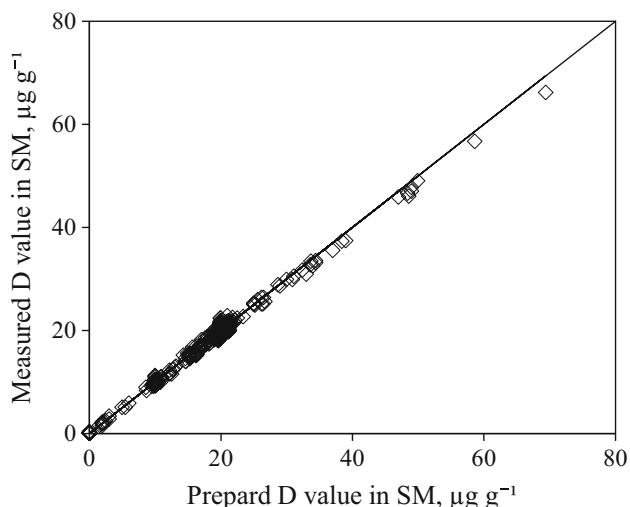


Fig. 9 Measured versus prepared D concentration values from homemade reference materials; Note the diagonal line is the 1:1 line

The slope of the regression was 1.003 ± 0.004 (1 s). A *t* test indicates that this slope is not significantly different from 1 ($t = 0.86$ or $p = 0.19$, $t_{799, 0.05} = 2.25$). The intercept, 2.35 ± 0.09 was found to be significantly different from 0 ($t = 27.1$ or $p = 2.8 \times 10^{-115}$, $t_{799, 0.05} = 2.25$). This systematic deviation of 2.35 ppm above the added hydrogen is believed to be introduced as a background during the preparation of the standard materials.

The linear regression for the deuterium measured values against the prepared values gave a slope of 0.98 ± 0.02 ($t = 0.92$ or $p = 0.18$, $t_{799, 0.05} = 2.25$) and an intercept of 0.25 ± 0.34 ($t = 0.74$ or $p = 0.23$, $t_{799, 0.05} = 2.25$), which cannot be distinguished from 1 and 0, respectively.

These results show that within the uncertainty of the analysis, the measured concentration of the hydrogen isotopes of the in-house standard materials agreed well with the expected prepared values.

Conclusions

The completeness of the hot vacuum extraction of hydrogen isotopes from zirconium metal or alloy was investigated through the solubility. Calculations show that the extraction of hydrogen isotopes from zirconium materials was complete at around 1100 °C temperature and under 4×10^{-6} Pa pressure. The excellent agreement between the measured and the certified or prepared concentration values in the analysis of standard reference materials and many in-house standard materials validated the theoretical investigation. The theoretical optimal isotopic spiking condition derived from conventional IDMS was found applicable to samples with non-natural isotopic composition theoretically and experimentally. Use of natural hydrogen gas and high purity deuterium gas as the isotope spike for IDMS resulted in a wider range of spike amount that minimized the uncertainty of the IDMS determination. The typical procedural blanks of the HVE-IDMS for both hydrogen isotopes were evaluated statistically from a large number of measurements and found that in general H blank contributed more than the D blank to the overall uncertainty of the determination.

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