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The determination of hydrogen and deuterium in Zr–2.5Nb material by hot vacuum extraction mass spectrometry

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Abstract

An analysis method for the determination of H and D concentrations in Zr–2.5Nb material has been established based on hot vacuum extraction and isotope dilution mass spectrometry. Hot vacuum extraction enables complete removal of the hydrogen isotopes from the sample. The isotope dilution technique is used to determine quantitatively the amount of hydrogen isotopes in the extracted gas. Methods for preparing standards of H, D or H and D in Zr–2.5Nb have also been established. These 'in-house' standards are used to assess the performance of the analysis method. The analysis uncertainty, based on the determined content relative to the dosed H or D isotope content of each standard, is 1% (at a level of confidence of 95%) for samples containing greater than ~5 μmoles H or D. The uncertainty increases to 5% as the sample content decreases to 0.5 μmoles H or D. The uncertainty of this analysis method is well within the requirements for surveillance examinations of CANDU® reactors and post-irradiation examinations of reactor components.

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1. Introduction

Zirconium alloys are used extensively by the nuclear industry in reactor core components. The CANDU® reactor utilizes Zr–2.5wt%Nb (Zr–2.5Nb) pressure tubes with D_2O as the primary heat transport fluid. Corrosion reactions enable ingress of deuterium into these components. Deuterium ingress must be monitored and controlled because high deuterium/hydrogen concentrations may lead to deuteride/hydride formation and the possibility of delayed hydride cracking. Hence, surveillance of CANDU® reactors require analyses of Zr–2.5Nb for both hydrogen and deuterium (i.e., the as manufactured hydrogen content, and the deuterium content due to ingress). The H and D concentration range of interest for Zr–2.5Nb pressure tubes is between 1 and 100 μg isotope per g alloy (μg/g). Apart from station surveillance, many research programs within the nuclear industry require 'state-of-the-art' determinations of H and D content in Zr–2.5Nb and other Zr alloy material. While station surveillance needs can be met with an analysis uncertainty of 5% (at a level of confidence of 95%), even lower uncertainties are required to meet the needs of some research programs.

The first reported method for the determination of H in Zr involved an isotope balancing procedure, in which the sample was heated in vacuum and equilibrated with a known amount of D_2 [1]. The resulting gas mixture was analyzed with an optical spectrograph [1] or a mass spectrometer [2]. In later developments [3–7], complete

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extraction of hydrogen from the metal was achieved by use of a Toepler pump to transfer gas from the hot sample to a mass spectrometer inlet. That method, known as hot vacuum extraction mass spectrometry (HVEMS), allows determination of both H and D in the same sample, and avoids fractionation of the hydrogen isotopes between the metal and gas phases.

Commonly, the inert gas fusion (IGF) method with thermal conductivity detection is used to measure H content in Zr alloys [8,9]. IGF instruments are commercially available for this purpose. However, IGF instruments cannot differentiate between H and D, and standard reference materials are required for calibration. For these reasons, we chose to develop the HVEMS method for determination of H and D in Zr alloys.

In this work, the HVEMS method utilizes a high vacuum apparatus featuring a turbomolecular pump for transfer of the gas from the sample to the mass spectrometer inlet [10]. The isotope dilution technique is used to determine quantitatively the amount of hydrogen isotopes in the extracted gas. This method is considered to be absolute, and no empirical factors are used to obtain agreement between measured and known values. Significant effort has been devoted to establish optimum conditions and procedures to minimize the analytical uncertainty. Computer automation ensures the high level of reproducibility required to maintain analysis precision.

Standards of H, D or H and D in zirconium alloys are required to test the performance of the HVEMS method. The availability of hydrogen-in-metal standards is limited, particularly for H in Zr. The National Institute for Standards and Technology (NIST) no longer produces H-in-zirconium standards. In our experience, surrogate metal standards (e.g., H-in-Ti) have not worked well as reference material for Zr. The most widely distributed H-in-Zr standard is NBS 358 (nominal concentration of 105 μg/g), which is still available as Zr wire (Wah Chang, Albany, Oregon). There are some uncertainties in the H content of NBS 358 due to the inhomogeneity of H throughout the wire. Other zirconium wires of ‘known’ H concentrations, close to 15 μg/g, are also available from Wah Chang, but these are not certified reference materials and are also susceptible to heterogeneity problems. Deuterium-in-Zr standards have not been commercially available. Moreover, a wide range of standards is desirable, containing H or D or comparable amounts of H and D, with the size and weight of the standard matching those of the samples. For these reasons, procedures have been established in our laboratory to produce discrete standards with chosen size, concentration and isotopic composition. The specimen and a known quantity of hydrogen gas are introduced into a custom built high vacuum chamber, and heating of the specimen to >850 °C causes the gas to be taken up by the metal. Standards containing either H or D, or both, can be prepared in this way. The assigned hydrogen concentration in these standards is based on the method of preparation, rather than on the results of analyses.

2. Experimental

2.1. Analysis apparatus and procedures

The analysis apparatus is constructed with high vacuum stainless-steel tubing, connections and pneumatic valves. All-metal seals are used throughout to ensure high vacuum integrity. The essential features of the HVEMS analysis apparatus are shown in Fig. 1. A high-vacuum carousel can be used for pre-evacuating the samples and for subsequent transfer to the sample tube without exposure to air. Extraction of the gas is accomplished by heating the samples under vacuum to

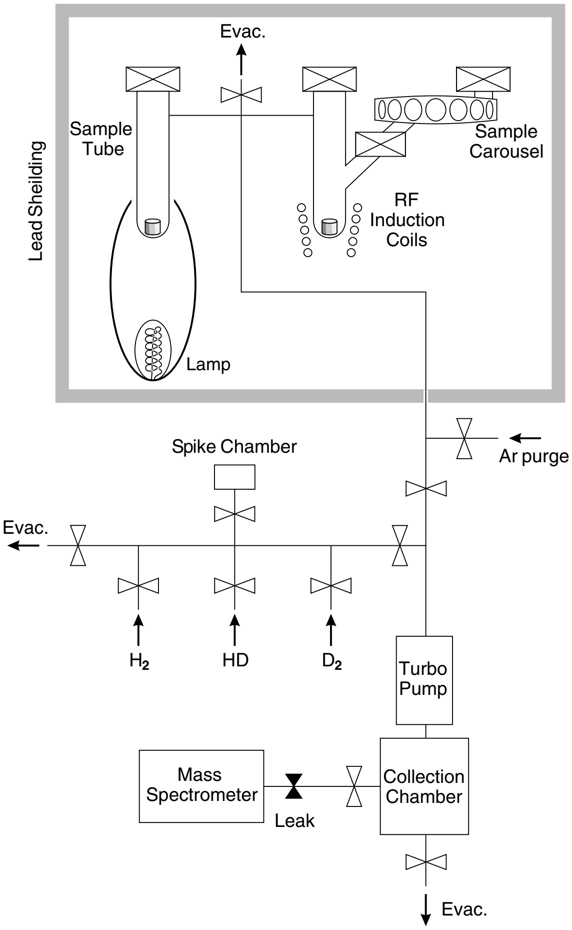

Fig. 1. Schematic diagram of HVEMS apparatus for the determination of H and D in zirconium specimens.

≈1100 °C in quartz tubes using either radiant energy from an ellipsoidal spot lamp (Research Inc., Hotspot, model 4085) or RF induction heating. An 11 kW RF induction generator (Phillips, model PH1004-10-11), with a 5 turn resonant load coil surrounding the bottom of the sample tube, is used for direct RF induction heating of the sample. The sample temperature is monitored with an optical pyrometer (The Pyrometer Instrument Co. Inc., Northvale, NJ). A magnetically coupled turbomolecular pump (Leybold Vacuum Products Inc., Turbovac 340M) is used to extract the hydrogen gases from the heated samples and transfer them to the collection chamber. To ensure that backstreaming and hence, isotopic fractionation across the turbomolecular pump are insignificant, the gas pressure in the collection chamber never exceeds 10 Pa. The gas is leaked into the source region of a Vacuum Generators MicroMass 8–80 mass spectrometer for the isotopic measurements. A calibrated spike chamber (~17 ml) is available for preparation of the isotope spike. A capacitance manometer (Edwards, 600 Barocell, 10 Torr full scale) is integral to the spike chamber for an accurate pressure measurement of the spike. Gas is transferred from the spike chamber to the collection chamber by the extraction turbomolecular pump. The sample tube, an analytical balance, and portions of the vacuum system are located in a shielded hot cell to permit the analysis of radioactive specimens. All vacuum, heating, and timing operations are fully computer automated to ensure that the analysis procedures are performed in a reproducible manner.

The loading of a sample and extraction of its gases are performed in the shielded hot cell. When low H backgrounds are required, a series of samples are cleaned and then loaded into the carousel and evacuated overnight to minimize adsorbed water vapor. Samples can then be loaded into the specimen tube without breaking vacuum, heated by RF induction, and the hydrogen gas extracted. When low H backgrounds are not required, samples are cleaned and then directly loaded into an alternate specimen tube and heated with the spot lamp for extraction. After the extraction, the mass spectrometer leak is opened, and the H_2^+, HD^+ and D_2^+ mass peaks are recorded in sequence, several times, in a peak-jumping mode. The isotopic spike (either H_2 or D_2) is added to the collection chamber and the mass analysis is repeated.

2.2. Standards apparatus and procedures

A diagram showing the essential features of the standards apparatus is given in Fig. 2. The standards apparatus is constructed from high-vacuum stainless-steel tubing, connections and pneumatic valves. All-metal seals are used throughout to ensure high vacuum integrity. A turbomolecular pump is used to evacuate the system to 4×10^{-6} Pa between specimen and gas additions. Zirconium alloy specimens are heated in a quartz tube with radiant energy from an ellipsoidal spot lamp. Pure H_2 and D_2 gases are metered into the dose chambers via needle valves. These calibrated dose chambers are constructed identically to the spike chamber on the analysis apparatus. All vacuum, heating, and timing operations are fully computer automated, and a robotic sample-changer arm (CRS, model M1A) is used for unattended production of many standards.

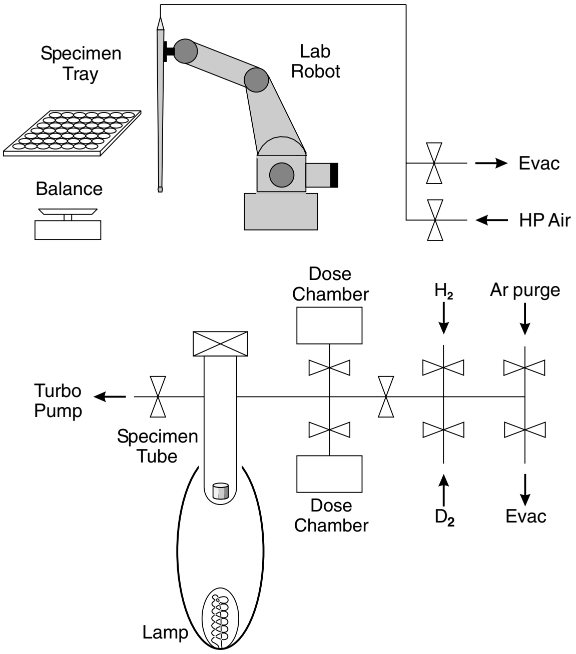

Fig. 2. Schematic diagram of apparatus for the preparation of hydrogen-in-zirconium standards. The robotic arm uses suction to transfer specimens between the specimen tray, balance and specimen tube.

Four different types of zirconium alloy specimens are prepared. Pellets are cylindrical with a diameter of 0.4 cm, height of 0.4 cm, and weight of ~0.5 g. Buttons are punched from 1 mm thick material and have a diameter of either 0.2 cm (~0.1 g) or 0.5 cm (~0.2 g). Scrapes are pared from the surface of zirconium alloy components and are ~5 cm long, ~0.5 cm wide, and ~0.01 cm thick (~0.1 g). Each specimen is ultrasonically cleaned in acetone and methanol, dried and placed in the sample tray. During the automated run, the robot arm acquires and weighs the next specimen in the sequence. The specimen tube and connecting region, which is normally maintained at a vacuum of 4×10^{-6} Pa, is pressurized with argon to allow for the removal of a previously prepared specimen and insertion of the next specimen by the robot arm. After re-evacuation of the specimen tube, a pre-selected pressure of the chosen gas (H_2, D_2 or both) is added to the dose chamber(s). The specimen is then pre-heated to 950 °C while the specimen tube is open for evacuation by the turbomolecular pump. This removes the initial, as-received quantity of hydrogen from the specimen before dosing. Next, the specimen tube is isolated from the turbomolecular pump, and the hot specimen is exposed to the pre-selected amount of hydrogen gas in the dose chamber(s). The hot specimen consumes the hydrogen and remains isolated in the tube to cool before this 'in-house standard' is removed.

This procedure is applicable to standards containing H, D or both H and D. System blanks are obtained by using the same procedure, but without supplying any hydrogen dose. The initial pre-heat may be omitted for standards for which only the D concentration is assigned.

3. Results and discussion

3.1. Pressure and volume calibration

Accurate pressure and volume measurements are key to the analysis of samples and preparation of standards. Very low levels of uncertainty on the quantity of spike gas or dose gas, also ensures the success of these methods. The dose or spike quantities of H_2 or D_2 are determined from the ideal gas equation. Pressure is measured with capacitance manometers ($\approx$1.3 kPa full scale for this work), specified with 'an accuracy of 0.15% of reading and a repeatability of $\pm$0.13 Pa'. We have determined from calibration procedures that the valid working range of these capacitance manometers is between 0.03 and 1.3 kPa. The volume of an evacuated enclosed section is determined by expansion of a gas from a vessel with a known volume, and recording the pressure before and after the expansion. A glass bulb was calibrated as a primary known volume by weighing when filled with water. The dose and spike chambers have a nominal volume of 17 ml and when calibrated by replicate determinations, show a typical standard deviation of 0.04 ml.

3.2. Hydrogen background

Both the measurement of background H during analysis and the uptake of background H during preparation of standards are concerns. Special precautions must be taken to minimize background levels of H. The major sources of H are leaks, out-gassing from hot components, and water vapor. Leaks and out-gassing are controlled by the use of high vacuum construction techniques and by minimal heating of structural components. Good high vacuum practices are followed at every step for both the analysis of samples and the production of standards. Argon flushes are used during specimen loading to prevent atmospheric water vapor from entering and adsorbing onto the exposed vacuum surfaces.

The background levels of H and D in the analysis system, and their associated uncertainties, are determined by multiple analyses on pre-extracted specimens (blanks). Using the high vacuum sample carousel with RF heating, blank levels of 0.050 μmoles H (with a standard deviation of 0.009 μmoles) and 0.0005 μmoles D (with a standard deviation of 0.0002 μmoles) are obtained. The carousel permits in vacuo placement of samples into the sample tube, after overnight evacuation to remove surface water vapor. RF induction enables direct heating of the sample during analysis with minimal heating of the sample tube. These efforts are particularly important for small samples, e.g. <0.2 g, with H concentrations of <10 μg/g.

For the alternate analysis approach, based on use of the sample tube with the spot lamp heater and without the vacuum carousel, background H levels are typically 0.20 μmoles (with a standard deviation of 0.07 μmoles). The same procedures are used in this case, except that: (1) the sample is exposed to the atmosphere immediately before loading and analysis; (2) the sample tube is exposed to the radiant heat of the lamp during extraction; and (3) the extraction time is generally longer. These analysis background levels are acceptable for many of the sample types analyzed and the spot lamp heater was used for most of the measurements reported here.

Removal of the initial hydrogen in the metal is an essential first step for production of standards with an accurately assigned H content. The pre-heat step is effective in extracting nearly all of the initial H (typical initial H concentration ranges from 3 to 15 μg/g). Blanks processed through the standards apparatus are found to contain less than 0.2 μmoles of excess H upon analysis. This blank value can be quite variable and is highest for heavier and thicker samples. Blanks are prepared along with the standards, analyzed to determine the residual H contribution, and used to correct the assigned dose if necessary.

3.3. Extraction

Complete extraction of hydrogen gases from the metal is necessary for quantitative analysis. For hot Zr material (>850 °C), hydrogen prefers to remain in solution while only a small fraction will be present in the gas phase. Continuous pumping of the gas-phase fraction shifts the equilibrium so that all of the hydrogen can be removed from the sample. Extraction occurs more rapidly at higher temperatures, but a practical upper limit is 1100 °C because of the softening of the quartz tube and the vaporization of zirconium that occur at higher temperatures. Extraction times are established based on the sample weight and shape, and the heating method. To determine optimum extraction times, several specimens of a particular weight and shape are prepared with known D content. Each specimen is heated and extracted for different time periods. The residual gas remaining in each specimen is analyzed with a subsequent exhaustive (20 min) extraction. For example, 4 min of heating at 1100 °C with the spot lamp heater, will allow extraction of >99% of the hydrogen from 0.5 g Zr–2.5Nb pellet specimens (see Fig. 3). Smaller specimens and specimens heated by RF induction require less extraction time.

A test to confirm completeness of extraction is to compare results using either the induction furnace or spot lamp heater. A small batch of Zr–2.5Nb wires were obtained which were found to exhibit a fairly homogeneous D distribution (19.4 μg/g D with a standard deviation of 0.3 μg/g). Twenty-nine random sections (0.1 g specimens) from these wires were analyzed over a period of one year using either of the two extraction methods; 14 samples with the induction furnace using a 2 min extraction, another 15 samples with the spot lamp heater using a 5 min extraction. Table 1 shows the analysis results. The results for the two sets of data are reasonably consistent with normal distributions (the Shapiro–Wilk test for normality [11] yields $p = 0.3$ for induction heating and $p = 0.5$ for spot lamp heating). The mean and standard deviation are similar for both extraction methods. A formal F-test to compare the standard deviations of the two distributions gives $F = 1.25$ ($p(F, 13, 14) = 0.341$ that F could be this large by chance). A t-test on the difference of the two means gives $t = 0.133$ ($p(t) = 0.896$ that t could have a value this large by chance). Therefore, there is no strong evidence of bias between the two different extraction methods.

Table 1
Analysis results for homogeneous wire (~0.1 g samples)

RF induction heating	Spot lamp heating
19.51 (μg/g)	19.40 (μg/g)
18.97	19.59
19.86	18.91
19.40	19.41
19.09	19.65
19.50	19.83
19.51	19.12
20.09	19.15
19.39	19.61
19.41	19.34
19.56	19.36
19.44	19.10
19.46	19.46
19.21	19.53
	19.66
Avg = 19.46, sd = 0.28	Avg = 19.41, sd = 0.25

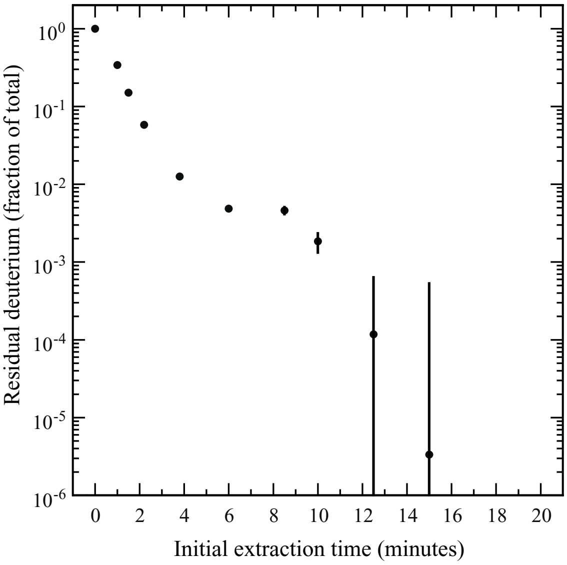

Fig. 3. Residual deuterium gas in 10 identical standards using different initial extraction times. The standards are 0.5 g Zr–2.5Nb pellets with a concentration of 100 μg/g deuterium and heated with the spot lamp heater (1100 °C).

3.4. Isotope dilution mass spectrometry

Quantification of the hydrogen isotopes is achieved by the isotope dilution technique using pure H_2 or D_2 as the spike. The isotope dilution method relies on accurate mass spectrometric measurements of the H/D ratios in both the extracted gas mixture and the spiked gas mixture. The H/D ratio is determined by

$$\frac{\mathrm{H}}{\mathrm{D}} = \frac{i_2 + 0.5 i_3}{i_4 + 0.5 i_3}, \tag{1}$$

where i_k are the ion currents measured at masses 2, 3 or 4. The mass spectrometer source voltages are carefully tuned so that the relative sensitivity (mass bias) between the hydrogen species (H_2^+, HD^+, D_2^+) is near unity and is essentially independent of inlet pressure and isotopic composition. The relative sensitivity is measured over a wide range of inlet pressures and isotopic composition with known gas mixtures prepared using the calibrated spike chambers. The dependence of the relative sensitivity on isotopic composition is negligible, and there is typically a slight dependence on the mass spectrometer inlet pressure (see Fig. 4). The D^+ interference at mass 2 and the H_3^+ interference at mass 3 are also determined from this measurement. The relative sensitivity, as a function of inlet pressure, is applied as a correction to the measured isotopic ratios. The D^+ interference at mass 2 is also applied as a correction. Tracking the temporal decay of the signals for H_2, HD and D_2, and extrapolating back to the time at which the leak valve

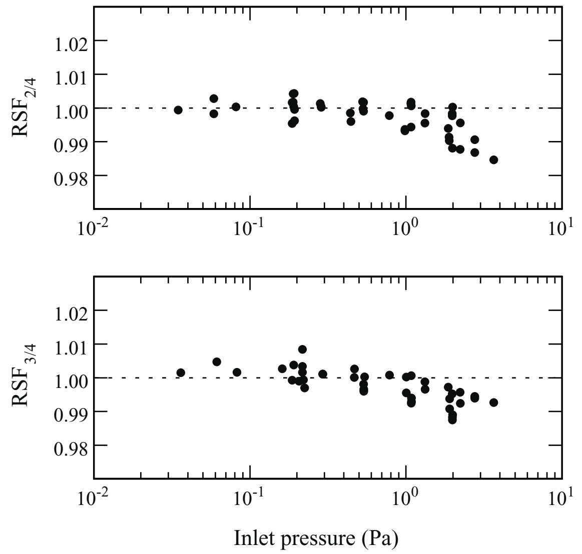

Fig. 4. Relative sensitivity factor (RSF) determination for the hydrogen isotopes at masses 2 and 3 relative to mass 4 (H_2 and HD relative to D_2). $RSF_{2/4} = (i_2/n_2)/(i_4/n_4)$ and $RSF_{3/4} = (i_3/n_3)/(i_4/n_4)$, where i is the measured ion current and n is the quantity of the isotopic species added to the calibration mix.

was opened, accounts for the isotopic fractionation that occurs as the gas mixture flows through the leak into the mass spectrometer.

The amount of H and D in the sample is determined from the H/D ratio in the extracted gas, the H/D ratio after spiking, and the known amount of spike added. For a system containing two isotopes (a and b), and a spike containing the isotope b, the following two isotope dilution equations apply:

$$n_a = n_{b(\mathrm{spike})}\frac{((a/b)_{\mathrm{extd+spike}} - (a/b)_{\mathrm{spike}})}{\left(1 - \dfrac{(a/b)_{\mathrm{extd+spike}}}{(a/b)_{\mathrm{extd}}}\right)}, \qquad (2)$$

$$n_b = \frac{n_a}{(a/b)_{\mathrm{extd}}}, \qquad (3)$$

where n_a and n_b are the unknown quantities of the two isotopes in the extracted gas, $n_{b(\mathrm{spike})}$ is the quantity of b isotope in the added spike, $(a/b)_{\mathrm{extd}}$ is the measured isotopic ratio of the extracted gas, $(a/b)_{\mathrm{spike}}$ is the known isotopic ratio of the spike gas, and $(a/b)_{\mathrm{extd+spike}}$ is the measured isotopic ratio of the extracted gas combined with the spike. Each result is corrected for the analysis background levels.

3.5. Results on analysis of in-house standards

The HVEMS results are considered to be absolute; they are not dependent on standards to provide empirical correction factors. However, standards are routinely analyzed to monitor the performance of the analysis apparatus. They are especially useful for confirming that the extractions are complete. Standards are also used to reveal and diagnose other problems with the analysis apparatus. Moreover, the standards serve to validate the HVEMS analysis method.

A comparison of the measured results and the dosed D content is shown in Fig. 5(a). These standards were either pellets or scrapes and were dosed to produce concentrations between 1 and 40 μg/g D. Some of these were combined standards with varying amounts of H (concentrations between 2 and 50 μg/g), and some (dosed with D only) did not undergo the pre-extraction cycle. The data in Fig. 5(a) can be fitted by a weighted linear regression [12]. Each datum is weighted by the inverse square of the associated experimental error, which is comprised of two parts (constant error and relative error) and determined by analysis of the residuals. The intercept was indistinguishable from zero and the final fit was constrained to pass through the origin. The slope of the final regression analysis is 1.0003 (with a standard deviation of 0.0005). A t-test indicates that

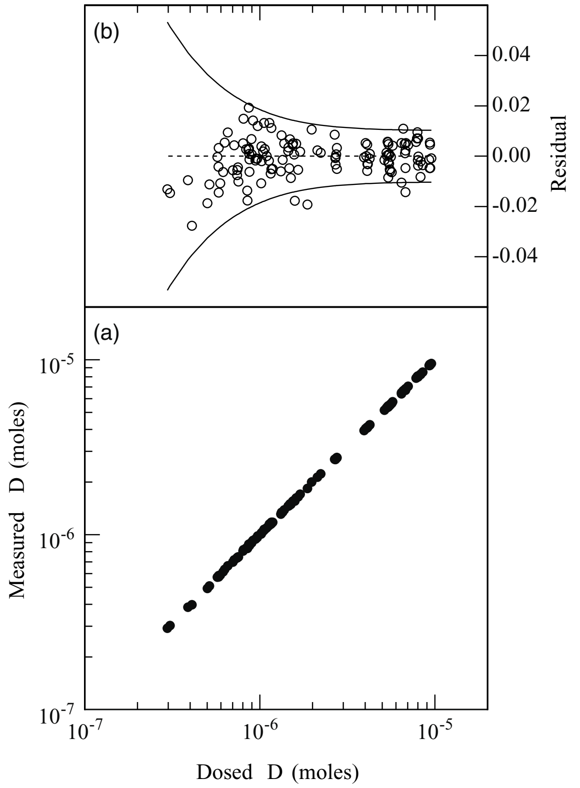

Fig. 5. (a) Comparison of analyzed D content with the dosed D content in Zr–2.5Nb. (b) The relative linear regression residuals; (analyzed D content/predicted D content) − 1. The solid lines in (b) are the 95% PIs computed from the linear regression.

the slope cannot be distinguished from unity ($t = 0.568$ for 129 degrees of freedom, $p(t) = 0.57$), so that a bias cannot be discerned between the dosed and measured D content of these standards. The normalized residuals ((measured/predicted) − 1) are plotted for the D standards in Fig. 5(b). The computed 95% prediction intervals (PIs) are also overlaid on the residuals in Fig. 5(b). The 95% PI is comprised of a relative component having a value approximately 1% of the D content, and a constant component having a value of 0.016 μmoles. For D content below 5 μmoles, Fig. 5(b) seems to show some systematic deviations. This behavior is found at dosed pressures <0.04 kPa, where pressure measurement accuracy begins to degrade.

Fig. 6(a) shows analysis results for H in combined H and D standards. The dosed H values have been corrected to include the system blank (background H from the standards apparatus). These standards are scrapes, 0.1, 0.2 g buttons, and pellets, with concentrations ranging from 2 to 50 μg/g H and 1–40 μg/g D. Again, a weighted linear regression analysis was used to fit the data. The slope from the regression analysis is 1.0007 (with a standard deviation of 0.0024). As was the case for D standards, the slope does not differ significantly from unity ($t = 0.273$ for 80 degrees of freedom, $p(t) = 0.79$) so again; there is no evidence for bias. The absolute residuals (measured − predicted) are plotted in Fig. 6(b). The computed 95% PIs are also overlaid on the residuals in Fig. 6(b). The 95% PI is comprised of a relative component having a value approximately 1.7% of the H content, and a constant component having a value of 0.16 μmoles. The constant component of the 95% PI is similar to the uncertainty of the H background value. As mentioned in Section 3.2, multiple determinations of analysis blanks show a standard deviation of 0.07 μmoles (an uncertainty of ∼0.14 μmoles at the 95% level of confidence).

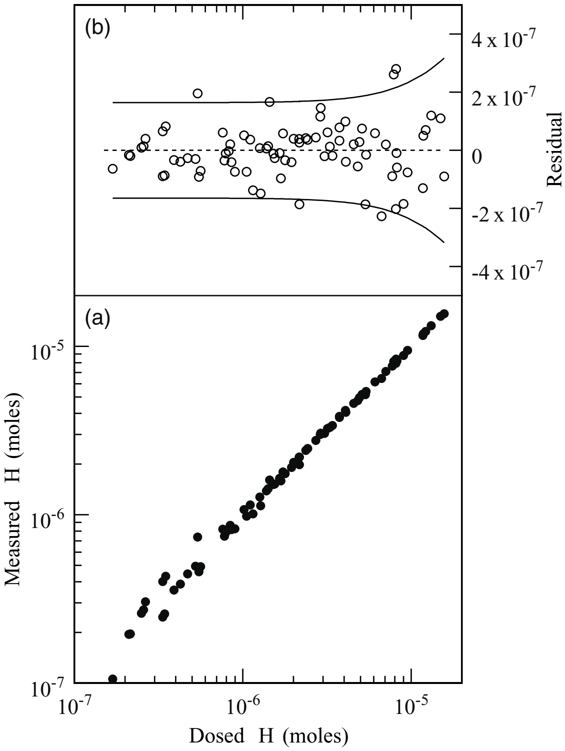

Fig. 6. (a) Comparison of analyzed H content with the dosed H content in Zr–2.5Nb. (b) The absolute linear regression residuals; analyzed H content minus the predicted H content in units of moles. The solid lines in (b) are the 95% PIs computed from the linear regression.

3.6. Analysis uncertainty and bias

The uncertainty (at a 95% level of confidence), assigned to the measured H or D content of any particular standard, is given by the PI shown in Figs. 5(b) and 6(b). The 95% PI defines a region, between which, 95% of all future measurements of standards are predicted to lie provided that no systematic biases are introduced. This is a combined uncertainty; it includes the uncertainty of the dose assigned to the standard and the uncertainty of the analyzed content. However, an assignment of the analysis uncertainty for blind samples is the ultimate goal. A propagation of errors evaluation can be used to shed more light on the true magnitude of the analysis uncertainty. For production of standards, all of the uncertainty in the size of the dose is brought in by a single pressure/volume/temperature measurement (i.e., the pressure reading repeatability, dose chamber volume uncertainty, and temperature uncertainty). The contribution of this dose uncertainty is found to be more than an order of magnitude smaller than the 95% PI shown in Fig. 5. On the other hand, a propagation of errors on the measured isotopic content requires the inclusion of several mass spectrometric determinations, corrections for fractionation and consumption of the analyte, and a pressure/volume/temperature determination of the spike quantity. The analysis uncertainties (at a 95% level of confidence) predicted from propagation of errors are about 1% at high molar content and increase to about 3% at 0.3 μmoles D. These predicted analysis uncertainties agree remarkably well with the measured 95% PI in Fig. 5. Therefore, the uncertainties observed from the measurements in Fig. 5 are reasonably insensitive to the dose uncertainty and can be taken as a good estimate of the analysis uncertainty for unknown samples.

The uncertainty for analysis of D in unknown samples, estimated as the measured 95% PI for analysis of D standards, is plotted in Fig. 7 (curve A). The measured H blank uncertainties can be combined with curve A to provide estimates of the uncertainty for analysis of H in unknown samples. Curve B of Fig. 7 is the estimated

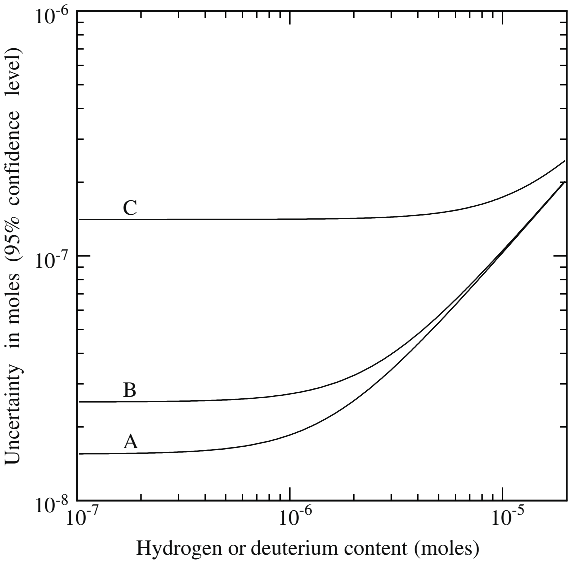

Fig. 7. Analysis uncertainty (95% confidence level) for the determination of H and D in Zr–2.5Nb: curve A: estimated uncertainty for deuterium, curve B: estimated uncertainty for hydrogen using the vacuum sample carousel with RF heating for extraction, curve C: estimated uncertainty for hydrogen using the spot lamp heater for extraction.

uncertainty for analysis of H using the low-background vacuum carousel with RF induction heating (H blank uncertainty is ~0.02 µmoles at a 95% level of confidence). Curve C of Fig. 7 is the estimated uncertainty for analysis of H using the spot lamp heater (H blank uncertainty is ~0.14 µmoles at a 95% level of confidence).

The lack of any bias on the data presented in Figs. 5 and 6 indicates a high degree of accuracy. However, the analysis of standards is not completely independent of the production of standards and some correlated systematic errors may exist. For example, the dose chambers and associated capacitance manometers on the standards apparatus are replicas of the spike chamber and capacitance manometer on the analysis apparatus. A bias on both the spike chamber and the dose chambers may be offsetting; the resulting bias on the measured content may be the same as the bias on the dosed content. Such possible systematic errors have been minimized by proper pressure and volume calibrations and a thorough analysis of the procedures. Furthermore, the data presented in Figs. 5 and 6 were taken from a large number of samples with varying sizes, thicknesses and dosed content. It is unlikely that any significant systematic errors would remain hidden under these wide-ranging conditions. Support for the analysis accuracy is also provided by the results of analysis of the NBS-358 certified reference material. A concentration of 100 µg/g with a standard deviation of 3 µg/g is obtained from our long-term analysis of this standard as compared to the quoted H content of 102 µg/g and a standard deviation of 4 µg/g (Wah Chang).

3.7. Limits on production of standards

The concentration range of H and D standards presented in this paper is that of most interest for surveillance of CANDU® reactor components, and are not indicative of the range or limits of the method. The range of the capacitance manometer and the volume of the chamber used for gas dosing determine the upper limit to the concentration ranges for these standards. For this work, using a capacitance manometer with 1.3 kPa full scale and a 17 ml dose chamber, the upper limits are 35 and 70 µg/g for H and D, respectively, in 0.5 g samples. Higher concentrations may be prepared by using smaller specimens, higher range capacitance manometers, or larger dose chambers. An ultimate upper limit is imposed by the formation of fully hydrided Zr–2.5Nb (H concentration ≈16 000 µg/g), but the dosing process is slow and not practical at such high concentrations.

The uncertainties from the pressure/volume measurement and from background H determine the lower concentration limit for these standards. A more sensitive capacitance manometer or smaller chamber volume could be used to lower the dose quantity for D considerably. H standards face a more severe limitation because of the inherent high H background in the vacuum systems and the ability of the Zr–2.5Nb to pick up H from corrosion reactions when exposed to humid air. Standards have not been verified with H or D content outside the range shown in Fig. 7.

4. Conclusions

An absolute analysis method for H and D in zirconium alloys has been established based on HVEMS and isotope dilution mass spectrometry. By using the special procedures and components described in this paper, very low analysis uncertainties can be achieved. These capabilities exceed the routine requirements for surveillance of zirconium components in nuclear reactors. The analysis uncertainty (at a level of confidence of 95%) is 1% for Zr–2.5Nb samples containing >3 µmoles D and increases to 5% as the sample content decreases to 0.3 µmoles D (or 6 µg/g in a 0.1 g sample). For H, the analysis uncertainty is 1% for samples containing >5 µmoles H and increases to 5% as the sample content decreases to 0.5 µmoles H (or 5 µg/g in a 0.1 g sample).

Standards of H, D or H and D in Zr–2.5Nb can be prepared as small, 0.05–0.5 g, specimens. The problem of heterogeneity of the H concentration throughout a wire standard (or batch of standards) is avoided by the preparation of discrete, individual specimens, which are to be analyzed whole. The lower limit for preparation of D standards could be extended with the use of appropriate capacitance manometers or smaller dose chambers. Saturation of the metal with hydrogen/deuterium imposes an ultimate upper concentration limit. These standards are used routinely for performance testing of our HVEMS instruments and are commercially available for use in other laboratories.

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