

## Determination of H<sub>2</sub> and D<sub>2</sub> content in metals and alloys using hot vacuum extraction

Y. Sessa Sayi, K. L. Ramakumar, Rajendra Prasad, C. S. Yadav, P. S. Shankaran, G. C. Chhapru, H. C. Jain

Fuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

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A hot vacuum extraction technique for the determination of hydrogen in metal and alloy samples has been standardised. After measuring the total pressure of the evolved gases, individual hydrogen and deuterium intensities are measured using an on-line quadrupole mass spectrometer. Synthetic mixtures of H<sub>2</sub> and D<sub>2</sub>, in known concentrations, have been analysed by QMS and an analytical expression correlating the measured [D<sub>2</sub>]/[HD] intensity ratio with the mole fraction of deuterium in the synthetic mixture has been arrived at. The precision and accuracy in the measurement of hydrogen is about 10% at 50 ppmw level.

### Introduction

Presence of gaseous elements even in trace amounts in metals and alloys, either in free state or in combined form, has profound effect on their structural, mechanical and other properties. The presence of hydrogen in certain metals (e.g., titanium, vanadium, zirconium) and alloys (e.g., steel, zircaloy) beyond certain limit leads to embrittlement resulting in loss of structural integrity of the material.<sup>1–3</sup> Some of the techniques identified for the determination of hydrogen in solid samples include inert gas fusion (IGF),<sup>4,5</sup> differential scanning calorimetry (DSC),<sup>6</sup> nuclear techniques involving neutron scattering<sup>7</sup> as well as heavy ion induced reactions<sup>8</sup> on hydrogen targets, hot vacuum extraction (HVE),<sup>4,5,9</sup> and mass spectrometry.<sup>10,11</sup> The IGF technique has been the most commonly employed method for the determination of hydrogen in metals. In this technique hydrogen is separated from other released gases using gas chromatography and the amount of hydrogen is determined by thermal conductivity measurement. Now a days dedicated “hydrogen determinators” based on this principle are commercially available. This method is simple and fast. However, its accuracy is affected if hydrogen contains the higher isotope, deuterium. This is because in these instruments the entire gas being measured is assumed to be only hydrogen gas with molecular weight equal to 2. No allowance is made for the presence of deuterium and its molecular weight. Also no correction is allowed for the differences in thermal conductivities of H<sub>2</sub> (g) and D<sub>2</sub> (g). Since thermal conductivity of hydrogen gas is about 30% higher than that of deuterium gas,<sup>12,13</sup> these dedicated hydrogen determinators give unreliable results whenever deuterium is present in the samples. The DSC technique is based on the functional relationship between the hydride dissolution temperature and the hydride content in the matrix. The method is simple, fast, non

destructive, requires only small amounts (≈10–50 mg) of samples and depends only on the combined hydrogen content and not on the free occluded species. Moreover, isotopic information on hydrogen cannot be deduced. This technique has to be validated by established methods for hydrogen determination. Nuclear techniques are by far the most sensitive of all the methods available for hydrogen determination, but the requirement of nuclear reactors or other neutron sources for neutron scattering or accelerators for heavy ion induced nuclear reactions is not always possible to realise.

In contrast to these limitations, hot vacuum extraction (HVE) technique has been reported to be a viable alternative for the determination of gases in metals and alloys.<sup>5</sup> The technique is straightforward and is generally based on simple gas laws for the calculation of hydrogen concentration. In fact, if hydrogen is the only impurity to be determined, HVE has generally been preferred over other techniques.<sup>14,15</sup> Mainly two variations of this technique are available in the literature. In one,<sup>9</sup> the evolved hydrogen is preferentially absorbed in a Pd filter while all other gases are removed. Subsequently the Pd foil is heated and the pressure due to evolved hydrogen is measured. In another variation,<sup>14</sup> first the total pressure of the evolved gases is measured. Then hydrogen is oxidised to water on heated CuO and the moisture is preferentially absorbed in an anhydron trap. The decrease in pressure is due to the hydrogen removed as moisture. These two variations, though simple, cannot be used for differentiating the liberated hydrogen as protium or its heavier counter part deuterium. Such an information is useful in nuclear technology to identify the exact cause of corrosion as due to water or heavy water so that the appropriate corrective measures can be undertaken. A mass spectrometer coupled to a HVE system is an ideal combination for the determination of gases and their

isotopic composition in metals and alloys. Isotopic composition of hydrogen, for instance would be useful in expressing the hydrogen+deuterium content as total hydrogen equivalent given as  $[H]+[D]/2$ . This paper gives the details of a hot vacuum extraction technique coupled to an on-line quadrupole mass spectrometer for the determination of hydrogen and deuterium in different metal and alloy samples.

## Experimental

### Hot vacuum extraction apparatus

A high vacuum system has been built and set up for hydrogen extraction and determination. Figure 1 gives a sketch of the system. The sample weighing about 20 mg or above is taken in an alumina boat and is introduced into a quartz tube. The entire system is evacuated to a vacuum better than  $10^{-6}$  mbar. The quartz tube and the sample are heated by a resistance furnace employing a temperature programmer. Degassing of the sample is carried out at 450 °C for 15 minutes. The outlet valve at the quartz tube end is closed and the temperature is slowly raised at the rate of 10 °C/min to a temperature of 1050 °C and then heated at 1050 °C for 15 minutes. The valve is then opened and the evolved gases are extracted out of the quartz tube by an ejector pump and allowed to expand to a known volume. Pressure measurement is done either by using a McLeod gauge (for pressures  $\leq 0.1$  mbar) or an oil manometer (for pressures  $>1$  mbar). The gases enter the on-line quadrupole mass spectrometer through a microleak valve. The gases enter the on-line quadrupole mass spectrometer through a microleak valve.

### Quadrupole mass spectrometer (QMS)

A commercial quadrupole mass spectrometer has been used for on-line measurements. It consists of a 8 cm quadrupole analyser and a constant energy electron impact ion source. Both faraday cup and secondary electron multiplier (SEM) detectors are available. All the functions of mass spectrometric analysis namely the selection of the detector, relative gain factors for ion intensities, mass scanning mode (Bar graph), or the measurement of different  $m/z$  ion intensities, (Peak select), are carried out through a microprocessor control unit. Upto sixteen  $m/z$  values can be selected at a time for the measurement of intensities. The control unit is connected to a personal computer for recording mass spectra and the ion intensities of selected  $m/z$  values. These data are used to calculate the background corrected ion intensities for the selected  $m/z$ 's.

### Samples and materials

Zirconium samples weighing between 20 to 500 mg and containing known amounts of hydrogen and also a Ti steel standard for hydrogen were used in the initial experiments and for the system calibration.

Synthetic mixtures with known mole fractions of deuterium were prepared from mixtures of quartz distilled H<sub>2</sub>O and high purity D<sub>2</sub>O (>99.99%). High purity calcium metal freshly taken out of an inert glove box was used to reduce the water/heavy water synthetic mixture to H<sub>2</sub>(g) and D<sub>2</sub>(g). The evolved gaseous mixture was dried by passing through anhydrous magnesium perchlorate column.

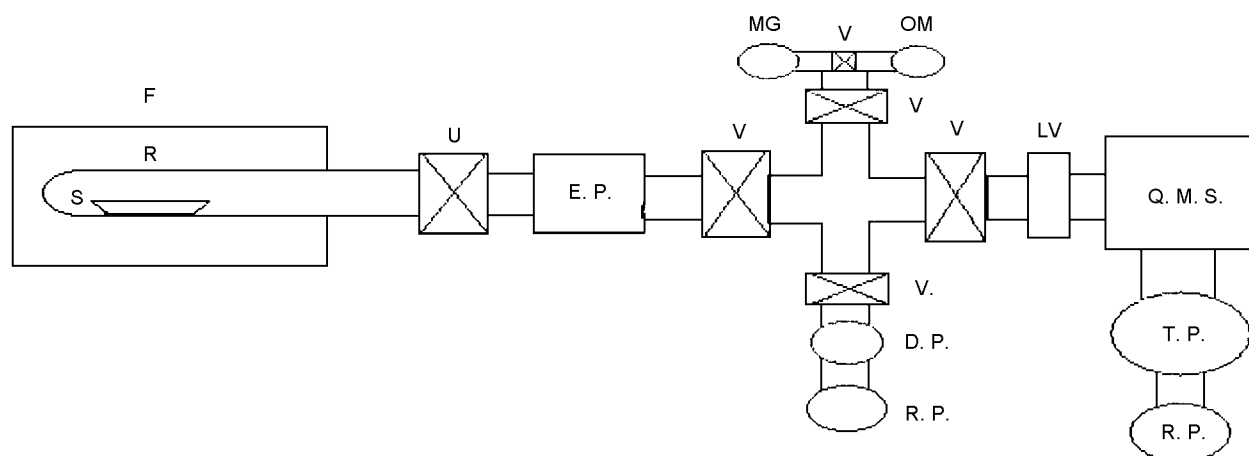


Fig. 1. Schematic of hot vacuum extraction system for hydrogen determination: F – furnace, R – quartz tube, S – sample, V – valves, E.P. – ejector pump, MG – McLeod gauge, D.P. – diffusion pump, R.P. – rotary pump, OM – oil manometer, LV – microleak valve, Q.M.S. – quadrupole mass spectrometer, T.P. – turbo pump

### Calibration of the system volume

About 100 mg of zirconium samples containing known hydrogen concentration were analysed. From evolved gas pressures and the composition of gases, the partial pressure of hydrogen was calculated. From a knowledge of the number of moles of hydrogen present in the sample taken, assuming ideal gas behavior for hydrogen, and employing Boyle's gas law, volume of the extraction system was calculated and found to be  $1.0 \pm 0.1$  l. Table 1 gives the results of volume calibration from replicate analyses. The accuracy in volume calibration was confirmed by determining hydrogen concentration in a Ti steel standard (LECO standard for hydrogen,  $28.1 \pm 5.1$  ppmw). It should be mentioned that these LECO calibration standards are traceable to National Institute of Standards and Technology (NIST) standards, other government reference materials or gas dosing methods. The value obtained for this LECO standard in the present work was  $29 \pm 2$  ppmw.

### Construction of a calibration plot for calculating mole fraction of deuterium from intensity ratio of $[D_2]/[HD]$

Mixtures of hydrogen and deuterium gas were introduced into the QMS system through a microleak valve. The mole % of D<sub>2</sub> in the synthetic mixture was varied between 2.5 and 100. Mass spectra for  $m/z$ 's 1(H), 2(H<sub>2</sub>+D), 3(HD) and 4(D<sub>2</sub>) were monitored and the intensity ratios of  $[D_2]/[HD]$  were calculated. The data are shown in Table 2. The mole fraction of D<sub>2</sub>(g) could be expressed in terms of  $[D_2]/[HD]$  intensity ratio  $[R]$ . A regression analysis has been carried out by fitting the data to a polynomial to obtain the calibration plot. The mole fraction of deuterium  $X(D_2)$  could be expressed as

$$X(D_2) = A_0 + A_1[R] + A_2[R]^2 + A_3[R]^3 + A_4[R]^4 \quad (1)$$

where the values of coefficients are:  $A_0 = -0.0024$ ,  $A_1 = 1.8733$ ,  $A_2 = -1.5769$ ,  $A_3 = 0.6116$  and  $A_4 = -0.0859$ . This relationship is shown in Fig. 2. This graph constituted the calibration plot for obtaining the mole fraction of D<sub>2</sub>(g) in the hydrogen gas liberated from the sample from which total hydrogen content could be calculated.

Table 1. Volume calibration of hot vacuum extraction system

Sample No.	Weight of sample, g	System volume, l
1	0.2315	0.98
2	0.3355	1.0
3	0.1285	1.15
4	0.0950	0.95
Average:		$1.02 \pm 0.08$

Table 2. Mole fraction of deuterium in synthetic water mixtures and the intensity ratio  $[R]$  of  $[D_2]/[HD]$

$X(D_2)$	$[R]$
0.009	0.020
0.023	0.013
0.045	0.023
0.068	0.052
0.091	0.037
0.137	0.072
0.184	0.103
0.231	0.129
0.278	0.179
0.375	0.270
0.474	0.339
0.626	0.531
0.730	0.667
0.836	1.520
0.945	1.588

## Results and discussion

Initial experiments were carried out to optimise the temperature of extraction. The gases started extracted out from the sample even at  $900^\circ\text{C}$  onwards, but the quantitative extraction as measured by the constancy in pressure measurement took almost 60 minutes. When the temperature was  $1200^\circ\text{C}$  or more, the extraction was over in less than 10 minutes, but the structural integrity of quartz tube deteriorated rapidly. As a compromise, a temperature of  $1050^\circ\text{C}$  and an extraction time of 15 minutes was found to be optimum.

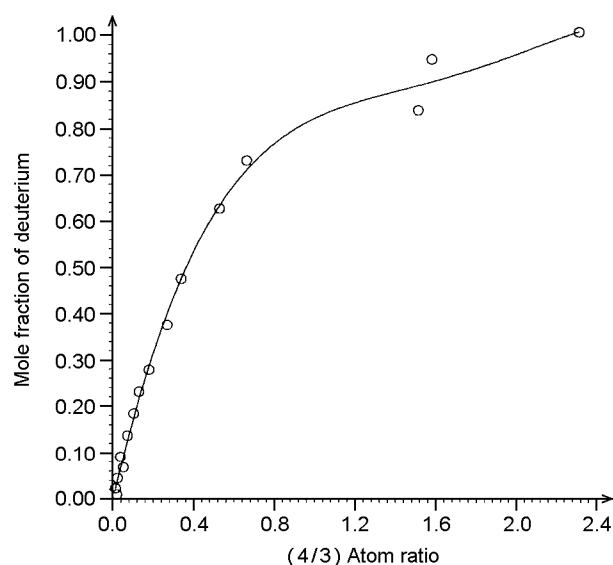


Fig. 2. Calibration plot of mole fraction of deuterium vs. (4/3) atom ratio

Table 3. Typical intensities obtained during QMS analysis of evolved gases

Mass	Average intensity	Abundance, %
1	6.06·10 <sup>-8</sup>	0.696
2	1.20·10 <sup>-6</sup>	13.783
3	3.20·10 <sup>-9</sup>	0.037
4	7.80·10 <sup>-11</sup>	0.001
18	3.00·10 <sup>-6</sup>	34.457
28	3.54·10 <sup>-6</sup>	40.659
32	9.06·10 <sup>-8</sup>	1.041
44	7.32·10 <sup>-7</sup>	8.408

### Composition of evolved gases

Even though the present investigation has been aimed at determining hydrogen concentration, a typical mass spectrum of the evolved gases indicated the presence, in addition to hydrogen peaks ( $m/z=1, 2, 3,$  and  $4$ ), of moisture ( $m/z=18$ ), CO+N<sub>2</sub> ( $m/z=28$ ), O<sub>2</sub> ( $m/z=32$ ) and CO<sub>2</sub> ( $m/z=44$ ). Ion intensities obtained in a typical mass spectrum are given in Table 3. It should be mentioned that appropriate traps could have been incorporated in the vacuum line (such as magnesium perchlorate for moisture, ascarite for CO<sub>2</sub> etc.) to selectively trap the undesired gases leaving only hydrogen for measurement. The selective trapping was not resorted to because of possible uncertainties that might creep in the system volume calibration. Moreover the behavior of these chemical traps in vacuum needs careful scrutiny. Indeed, in some of the initial experiments, a magnesium perchlorate trap was incorporated in the vacuum line just after the ejector pump to selectively absorb moisture, but during the course of experiment it was observed that the vacuum in the system deteriorated frequently. This was traced to a constant release of moisture by the magnesium perchlorate trap. MCGEARY<sup>9</sup> also observed constant diffusion of oxygen from CuO trap during his experiments on hydrogen determination by HVE method. Further, the possibility of adsorption of H<sub>2</sub>, HD and D<sub>2</sub> on these traps can also not be ruled out. Subsequently the remaining experiments were carried out without incorporating any chemical traps. The total pressure due to all the evolved gases and all the individual ion intensities have been considered in calculations.

### Mass spectra of H<sub>2</sub>+D<sub>2</sub>

Whenever both hydrogen and deuterium are present together, the mass spectrum reveals peaks at  $m/z$ 's 1 (due to H), 2 (H<sub>2</sub>+D), 3 (HD) and 4 (D<sub>2</sub>). This is because of the well known equilibrium reaction



It can be shown that at equilibrium the molecular ratio  $[\text{D}_2]/[\text{HD}]$  would vary between 0 and  $\infty$  when the mole fraction of deuterium ( $X(\text{D}_2)$ ) is changed from 0 to 1. Hence a correlation can be constructed between  $[\text{D}_2]/[\text{HD}]$  vs.  $X(\text{D}_2)$ . A 4th degree polynomial equation gave the best regression fit for the correlation (c.f. Fig. 2). For Reaction (2), the atom fraction of deuterium  $[\text{D}]$  under the equilibrium conditions can also be calculated using the expression  $[\text{D}] = [\text{D}_2] + 1/2[\text{HD}]$ .<sup>16</sup> It was seen that there was no significant difference between the mole fraction values obtained by these two modes of calculations. The polynomial correlation was preferred as it would reflect the actual experimental conditions and most of the uncertainties during the measurement would get averaged out.

It may be mentioned that while calculating the total intensity due to hydrogen isotopes, it was assumed that the intensity at  $m/z=2$  is completely due to H<sub>2</sub> and the contribution from the atomic D is ignored. It is justified because in diatomic molecular species, molecule is the more stable species. In fact, the ratio of intensities between the molecular ion and the corresponding atomic ion, at least in the case of hydrogen, was found to be about 200 (see Table 3). Hence the uncertainty associated while ignoring the contribution from D at  $m/z=2$  is expected to be negligible.

Another possible uncertainty in the measurements could come from the formation of molecular ion H<sub>3</sub><sup>+</sup> which interferes at HD peak with same  $m/z$ . The intensity at  $m/z=3$  would therefore depend on the formation of H<sub>3</sub><sup>+</sup> ion. The intensity ratio of  $m/z$ 's 2 and 3 or 3 and 4 would change accordingly. The intensity of H<sub>3</sub><sup>+</sup> ion is a function of square of the pressure in the system.<sup>17</sup> During the mass spectrometric analysis of the evolved gases, the pressure in the analyser region was better than 10<sup>-6</sup> mbar. The system employed in the present work is an integral electron impact ioniser type. Both the ion source and the mass analyser (QMS) are integrated. Hence, the pressure in the ion source could also be assumed to be 10<sup>6</sup> mbar. The intensity ratio of  $m/z$ 's at 2 and 3 was monitored at controlled leak rates without significantly disturbing the pressure in the analyser region. The ratio of intensities of  $m/z$ 's 2 and 3 was found to be constant indicating negligible contribution from H<sub>3</sub><sup>+</sup> ion at  $m/z=3$  corresponding to HD mass peak.

### Concentration of hydrogen in zirconium samples

Prior to each sample analysis, a blank spectrum was recorded for all the  $m/z$ 's of interest. The data collection during the sample analysis consisted of recording a minimum 5 sets of mass spectra each set consisting of 5 scans. The signal intensities at different  $m/z$  values were corrected for the corresponding blank contribution. The total intensity of hydrogen ( $I(\text{Hydrogen})$ ) is simply sum

Table 4. Concentration of hydrogen in zirconium samples determined by hot vacuum extraction followed by quadrupole mass analysis

Sample weight, g	Total pressure, mbar	Total intensity	Relative H <sub>1</sub> /2+H <sub>2</sub> intensity, %	p(H <sub>2</sub> ), atm	Amount of H <sub>2</sub> , µg	Concentration of H <sub>2</sub> , ppmw
0.10838	4.8·10 <sup>-2</sup>	9.44·10 <sup>-5</sup>	27.03	1.20·10 <sup>-5</sup>	0.98	9*
0.12961	6.0·10 <sup>-2</sup>	9.89·10 <sup>-6</sup>	28.55	1.69·10 <sup>-5</sup>	1.37	10.6
0.11720	6.5·10 <sup>-2</sup>	2.61·10 <sup>-6</sup>	22.66	1.45·10 <sup>-5</sup>	1.18	10.1
0.12466	6.3·10 <sup>-2</sup>	6.78·10 <sup>-6</sup>	28.71	1.79·10 <sup>-5</sup>	1.46	11.7
0.12625	6.5·10 <sup>-2</sup>	1.77·10 <sup>-6</sup>	29.35	1.89·10 <sup>-5</sup>	1.52	12
0.13571	6.7·10 <sup>-2</sup>	3.90·10 <sup>-6</sup>	25.34	1.68·10 <sup>-5</sup>	1.37	10.1
0.04775	3.3·10 <sup>-2</sup>	4.19·10 <sup>-6</sup>	16.45	5.30·10 <sup>-6</sup>	0.43	9.0
0.12986	6.5·10 <sup>-2</sup>	7.88·10 <sup>-6</sup>	27.41	1.80·10 <sup>-5</sup>	1.43	11.0

Mean: 10.4±1.1

\* The value given is the average of five sets of data with an RSD of 3%. Concentration from inert gas fusion 10±1 ppmw.

of the individual intensities of hydrogen isotopes at  $m/z$  values 1, 2, 3 and 4. ( $[I_1]/2 + [I_2] + [I_3] + [I_4]$ ). Relative intensity of hydrogen to the total intensity ( $I(\text{Hydrogen}) + I(\text{H}_2\text{O}) + I(\text{CO}) + I(\text{O}_2) + I(\text{CO}_2)$ ) was used to obtain the actual pressure due to hydrogen isotopes as a fraction of total pressure of the evolved gases as measured by the McLeod gauge or oil manometer. (Partial pressure of hydrogen isotopes = relative intensity of hydrogen isotopes multiplied by the total pressure). From the measured intensity ratio of  $[D_2]/[HD]$  and the calibration plot constructed, the mole fractions of hydrogen and deuterium were computed. Table 4 gives the hydrogen content in a zirconium sample in replicate analyses employing HVE-QMS. The same sample has been analysed by employing IGF method using a dedicated hydrogen determinator, the results of which are also given in the same table. It is clearly seen that the agreement in results is good.

### Conclusions

The hot vacuum extraction technique can overcome the limitations of other conventional techniques such as inert gas fusion. With the HVE coupled to an on-line quadrupole mass spectrometer, it is possible to get isotopic information and also the composition of evolved gases. The isotopic information is useful for correcting, particularly the results obtained from IGF-TCD technique. From the evolved gas composition, it may be possible to determine other gases as well along with hydrogen in a single analysis. The method is fast, simple, cost effective and requires only small sample amounts. Using the method standardised it is possible to analyse one sample in one hour. The absolute sensitivity of the technique is 0.05 µg which is limited only on the lowest pressure measurement capability.

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