

# Determination of hydrogen in titanium, zirconium and its alloys by isotope-equilibration mass spectrometry – verification of certified values

Kazuo Watanabe, Misao Ouchi, and Katsubumi Gunji

Analytical Chemistry Laboratory, Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Japan

## Bestimmung von Wasserstoff in Titan, Zirkonium und dessen Legierungen mit Hilfe der Isotopenäquilibrierungs-Massenspektrometrie; Prüfung zertifizierter Werte.

**Zusammenfassung.** Die Probe wird bei diesem Verfahren mit einer bekannten Menge Deuterium bei 850°C 20 min lang in einem einfachen Glasgerät äquilibriert. Mehr als 90% des äquilibrierten Wasserstoffs wurden wiedergefunden und so die systematischen Fehler eliminiert, die sich aus dem Isotopeneffekt auf die Wasserstofflöslichkeit in den Metallen ergeben. Die relative Standardabweichung betrug 0,5–1% bzw. 2–10% für Wasserstoffkonzentrationen von 50–120 µg/g bzw. 7–20 µg/g. Das Verfahren wurde auf NBS- und JAERI-Standardsubstanzen angewendet und gute Übereinstimmung mit den zertifizierten Werten erhalten.

**Summary.** A procedure has been developed for the accurate determination of hydrogen in metals by isotope equilibration mass spectrometry. The sample was equilibrated with a known quantity of deuterium at 850°C for 20 min in a simple vacuum apparatus. More than 90% of the resulting equilibrated hydrogen gas was recovered in order to eliminate systematic errors caused by the isotope effect on hydrogen solubilities in the metals. The relative standard deviations were 0.5–1% and 2–10% for hydrogen concentrations of 50–120 µg/g and 7–20 µg/g ranges, respectively. Application of this technique to NBS and JAERI standard samples yielded results that were in good agreement with the certified values.

Hydrogen which is present in such metals as titanium, zirconium and its alloys in excess of the terminal solid solubility forms metal hydrides and causes serious embrittlement of the metals and alloys [1, 2]. The maximum permissible value for hydrogen in zirconium and its alloys for nuclear applications is 0.0025% by weight [3]. Therefore, an accurate determination of hydrogen is of considerable industrial importance. Hot extraction methods are commonly used for the purpose [4]. However the results obtained are highly dependent upon the extraction conditions. Complete extraction of hydrogen from titanium becomes difficult when the pressure within the vacuum system approaches the equilibrium pressure of hydrogen in titanium [5]. From the solubility data of hydrogen in  $\beta$ -phase of titanium and zirconium [6], about 0.6 µg/g of hydrogen

in these metals are estimated to be in equilibration with  $1.3 \times 10^{-3}$  Pa of gaseous hydrogen at 1,200°C, the temperature employed in the ASTM method [7], hence complete extraction can not be attained. The particle size of sample can sometimes be an important factor in the extraction of particular alloys [8].

In order to test the accuracy of the hot extraction results, independent analysis techniques are required. Recently, the isotope equilibration method has been investigated for the absolute determination of hydrogen in metals. The results were found to be dependent upon the recovery of the isotopically equilibrated hydrogen because of the isotope effect on the solubilities of hydrogen and deuterium in the solid samples, i. e., hydrogen is more soluble than deuterium. In order to overcome this isotope effect, the recovery must exceed 70% of the equilibrated hydrogen [9].

In the present paper the isotope equilibration procedure was modified for the accurate and precise determination of hydrogen in titanium, zirconium and its alloys. The equilibrated hydrogen gas was recovered almost quantitatively for the isotopic composition measurements, thus eliminating the systematic errors resulting from the isotope effect. The procedural blank which has been a major source of uncertainty in determination at low µg/g levels is reduced by more than an order of magnitude compared with previous work.

## Experimental

**Apparatus.** An Atlas-Werke CH4 mass spectrometer equipped with a Cary 401 vibrating read electrometer and a strip chart recorder was employed. Utilizing a mass selector which steps the magnet field to sweep the masses 2, 3 and 4, ion current ratio measurements (five sets of ion peaks) could be made in less than 5 min with little isotope fractionation among three masses. This gave replicate  $i_2/i_4$  (mass2/mass4) and  $i_3/i_4$  (mass3/mass4) ratio measurements with a relative standard deviation of 0.5% and 0.2%, respectively.

The vacuum system developed for the isotope equilibration between deuterium and hydrogen in metal samples is shown schematically in Fig. 1. The system was constructed of borosilicate glass except for the silica isotope equilibration tube, and was evacuated to  $\sim 10^{-5}$  Pa with a 100 l/s oil-diffusion pump. The pressure of gas admitted was measured with one of two Baratron capacitance manometers (MKS Instruments, Inc.), which covered the pressure ranges 0–133 Pa (1-Torr sensor) and 0– $1.33 \times 10^4$  Pa (100-Torr sensor). A mercury transfer diffusion pump was used for transference of the equilibrated hydrogen gas to a 5 l gas

Offprint requests to: K. Watanabe

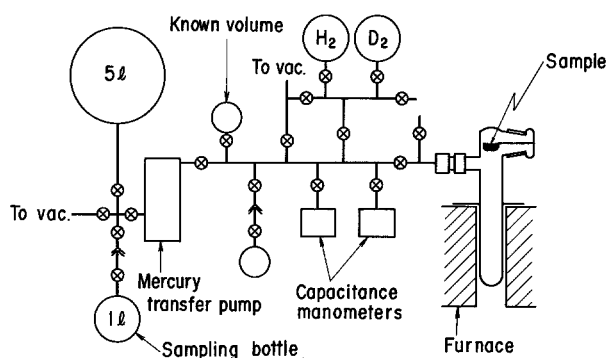


Fig. 1. Vacuum apparatus for hydrogen isotope equilibration

collecting volume. This large volume enabled the back pressure of the transfer pump to be kept low enough for it to operate.

Research grade deuterium gas (99.69 at. %D; 0.31 at. %H) in an 1 l glass cylinder was used without further purification.

**Procedure.** The equilibration temperature of ca. 850°C was selected from the results of the previous study [9]. The equilibrium hydrogen pressure over the  $\alpha$ -phase of titanium and zirconium showed maximum values at that temperature.

Typically 0.5 g of sample was loaded on the sample holder, which was attached to the vacuum system. The system was evacuated to about  $1 \times 10^{-4}$  Pa. The silica tube was outgassed for 30 min by heating at 900°C. Then the temperature of the tube was lowered to 850°C. The tube was isolated from the evacuating diffusion pump. Deuterium gas was admitted to the known-volume-vessel and the pressure was recorded. The sample was dropped into the silica tube (850°C) by rotating the sample holder. The deuterium in the known-volume vessel was expanded into the silica tube and reacted with the sample hydrogen for 20 min. The equilibrated hydrogen gas was then transferred to the 5 l gas-collecting vessel by the mercury transfer diffusion pump. The collected hydrogen gas was transferred to 1 l sampling bottle for subsequent mass spectrometric analysis.

Five sets of ion currents at mass peaks 2, 3 and 4 are measured consecutively. The deuterium concentration in the sample gas is calculated from the ion current ratios ( $i_2/i_4$  and  $i_3/i_4$ ):

$$X_D = \frac{(1/2) b(i_3/i_4) + 1}{a(i_2/i_4) + b(i_3/i_4) + 1} \quad (1)$$

where  $X_D$  is the deuterium concentration in the atomic fraction and  $a$  and  $b$  are the ratios of the sensitivities:  $S_4/S_2$  and  $S_4/S_3$ , respectively. From the deuterium concentrations of the spike ( $X_{sp}$ ), the equilibrated hydrogen ( $X_{eq}$ ) and the hydrogen in the sample ( $X_x$ ), a quantity of hydrogen detected in numbers of atoms is calculated:

$$n_x = n_{sp}(X_{sp} - X_{eq})/(X_{eq} - X_x) \quad (2)$$

where  $n_{sp}$  is the quantity of the spike admitted in numbers of atoms. When hydrogen in the sample metals has a natural isotopic composition ( $X_x = 1.5 \times 10^{-4}$ ),  $X_x$  can be negligible compared with  $X_{eq}$ .

**Ratios of the sensitivities.** The accuracy of the results of the present technique was directly affected by the accuracy of

Table 1. Reproducibility of the hydrogen determination for NBS SRM 358 (zirconium wire; certified value:  $107 \pm 3$   $\mu\text{gH/g}$ )

Sample (g)	Spike (No. of atoms)	$X_{eq}$ (atomic fraction)	H found ( $\mu\text{g/g}$ )
1. 0.5852	$2.544 \times 10^{-4}$	0.8005	107.9
2. 0.4798	$2.272 \times 10^{-4}$	0.8137	107.4
3. 0.4509	$2.266 \times 10^{-4}$	0.8234	106.7
4. 1.0413	$2.114 \times 10^{-4}$	0.6552	106.7
		Mean value	$107.2 \pm 0.58$

Table 2. Determination of hydrogen in titanium, zirconium and its alloy standard samples

Sample <sup>a</sup>	Hydrogen ( $\mu\text{g/g}$ )		
	Certified value	Present study	$n$
NBS SRM			
357, zirconium	$19 \pm 3$	$19.7 \pm 0.4^b$	4
358, zirconium	$107 \pm 3$	$107.2 \pm 0.6$	4
1086, titanium	$116 \pm 3$	$113.8 \pm 1.1$	4
1087, titanium	$57.5 \pm 2.5$	$56.1 \pm 0.4$	5
JAERI			
Z-8, zircaloy-2	—	$7.5 \pm 0.7$	6
Z-10, zircaloy-2	$(8.2 \pm 1.1)^c$	$9.3 \pm 0.4$	5
Z-17, zircaloy-2	—	$15.8 \pm 0.5$	4
Z-18, zircaloy-4	—	$13.4 \pm 0.6$	4

<sup>a</sup> Sample sizes were 0.3–1.0 g

<sup>b</sup> Standard deviation

<sup>c</sup> Mean value obtained at the Sub-Committee on Reactor Materials, JAERI. Nine laboratories participated in the determination; all used the vacuum hot extraction method

the deuterium concentration analysis in the equilibrated hydrogen by mass spectrometry. Since the mass spectrometric sensitivities of pure gases ( $\text{H}_2$ , HD and  $\text{D}_2$ ) varied appreciably daily while the ratio of them did not, the ratios of the sensitivities were used for the deuterium concentration determination. The ratios of the sensitivities were determined from the ion current ratio measurements of the standard mixtures (0.2–0.9 D atomic fraction; 16 samples) of  $\text{H}_2$ , HD and  $\text{D}_2$  which were prepared by equilibrating known amounts of hydrogen and deuterium gases at 850°C with a platinum catalyst in the vacuum system. Linear regression analysis of the ion current ratios on reciprocals of deuterium atomic fractions of the standard mixtures yielded the sensitivity ratios as slopes:  $a = 1.371 \pm 0.012$  ( $2\sigma$ ) and  $b = 1.130 \pm 0.004$  ( $2\sigma$ ) [10]. Using these values, the determination of the deuterium concentration could be made with a relative standard deviation of 0.2%.

## Results

The major source of the blank in the present method is considered to be caused by isotope exchange between deuterium and hydroxyl groups on the wall of silica tube. This contribution could be minimized in two ways: (1) rapid sample changing while exposing the inside of the silica tube to dried air; (2) outgassing the silica tube under vacuum for 30 min by heating to 900°C just before the equilibration

step. However, when new silica tubes were used, it was necessary to precondition them by heating under vacuum at about 1,000°C for more than 4 h prior to use so as to obtain low and consistent blank values. Blanks were determined by carrying out the entire procedure; the value of  $(0.93 \pm 0.46) \times 10^{-8}$  mole  $H_2$  ( $n = 6$ ; 1s) was obtained. If the detection limit is defined as three times the standard deviation of the blank, about  $1.5 \times 10^{-8}$  mole of hydrogen should be detectable.

Table 1 shows the reproducibility of the present technique on an actual sample: NBS SRM 358, zirconium wire. A summary of hydrogen results on the standard samples is shown in Table 2. Although it is stated in the certificate for NBS wire samples that "the sample should be washed in acetone or trichloroethylene prior to use", no significant difference between the results for each sample (as received and washed) was found. In all cases values obtained in this study are in good agreement with the existing certified values within experimental error.

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