Preparation and Certification of Hydrogen in Titanium Alloy Standard Reference Materials

Rick L. Paul and Richard M. Lindstrom, Analytical Chemistry Division, Materials Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899

A series of three hydrogen in titanium alloy Standard Reference Materials (SRMs 2452, 2453, and 2454) were prepared with hydrogen mass fractions bracketing the hydrogen specification limit of 125 mg/kg. Commercial titanium alloy Ti6Al4V (6 % aluminum, 4 % vanadium) was heated under vacuum in a furnace to remove native hydrogen, then doped with a measured quantity of hydrogen. Prompt gamma-ray activation analysis was used to determine hydrogen in the degassed material and finished SRMs. A combination of preparation data and PGAA measurement was used to certify the hydrogen mass fraction of each. The certified hydrogen mass fractions are 62.5 mg/kg ± 1.6 mg/kg for SRM 2452, 114 mg/kg ± 5 mg/kg for SRM 2453, and 211 mg/kg ± 4 mg/kg for SRM 2454.

INTRODUCTION

Commercial grades of titanium alloys require hydrogen to be present at levels below about 125 mg/kg as specified in ASTM B348-83.[1] Above this level, the solubility limit for hydrogen is exceeded, and hydride formation occurs, which may lead to structural failure. Control of quality in manufacturing requires reliable determination of hydrogen in the product. Analysis is typically performed using hot vacuum or inert gas extraction of hydrogen followed by measurement of hydrogen by gas chromatography or mass spectrometry, for example the ASTM Standard Test Method E1447 for hydrogen in

titanium alloys.[2] Independently produced standards for calibration are required as well as reference materials for continued validation of the analytical procedure.

Standard Reference Materials (SRMs) at the National Institute of Standards and Technology are usually certified using two or more independent methods of analysis, i.e., methods that have few or no significant sources of bias in common.[3] Another approach to certifying reference materials is to use certification by preparation, where synthesis of the material takes the place of one of the methods of analysis. A known quantity of the doping constituent is homogeneously added to a known quantity of matrix material that contains a negligible or blank amount of the dopant. As an example, solution SRMs are prepared by dissolving a measured mass of a metal or stoichiometric compound of known assay in high-purity acid and then diluting to a measured volume.   Analysis of the product by an independent method validates the preparation.

In this investigation, three hydrogen in titanium alloy Standard Reference Materials (SRMs) were prepared, at levels bracketing the specification limit of 125 mg/kg, by doping a weighed quantity of degassed titanium alloy (Ti6Al4V) with a measured volume of hydrogen.   Prompt gamma-ray activation analysis (PGAA) was used to assess the amount of hydrogen in the degassed alloy as well as to measure the hydrogen mass fraction of the final product. The prompt gamma measurements were used in combination with the preparation data to certify the hydrogen mass fraction of each SRM.

MATERIALS AND METHODS

The procedure used in this investigation for preparing titanium alloy reference materials containing low mass fractions of hydrogen, is based on the reversible reaction:

$$Ti + H_2 = TiH_2; \qquad \Delta G_f^0 = -80.3 \text{ kJ/mole} \qquad (1)$$
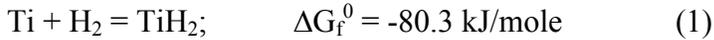
where the equilibrium pressure of H_2 is below 10^{-8} Pa ($< 10^{13}$ atm) at room temperature, and above 10 MPa (>150 atm) at 1173 K (900 °C). The reaction is rapid above 773 K (500 °C). The product is stable at room temperature. This procedure has been used elsewhere to prepare specimens of known hydrogen content for mechanical testing.[4] It has also been used in our laboratory to fabricate H in Ti alloy standards for nondestructive assay by neutron incoherent scattering (NIS)[5, 6] and for neutron tomography.[7]

Prototype experiments

Prior to preparation of the SRMs, a prototype system was set up to produce hydrogen doped titanium alloy on a scale of a few grams.[8] The prototype system for the initial experiments was made of copper tubing and glass (Figure 1). A quartz furnace tube was used, with valves and fittings suitable for intermediate vacuum ($\approx$ 0.01 Pa). The pressure of the dopant hydrogen was measured using a capacitance manometer, nominally accurate to $\pm$ 0.5 % of the reading. Titanium alloy Ti6Al4V (containing mass fractions of $\approx$ 90 % Ti, 6 % Al and 4 % V) was selected as the matrix material because it

is the most commonly used titanium alloy, with extensive applications in aerospace (for example in manufacture of gas turbine compressor blades), medicine, and other industries. The alloy, which typically contains about 50 mg/kg of hydrogen as received, was degassed prior to doping, by heating in the evacuated furnace tube overnight at a temperature above 1073 K (800 °C), but below the 882 °C (1155 K) α-β Ti transition temperature, with continuous pumping to remove evolved H_2.

After returning the system to room temperature, specimens were removed for blank measurement by PGAA, and the system re-evacuated. The pump and furnace were then closed off, and a measured pressure of hydrogen was admitted from the storage cylinder to the calibrated volume at a measured room temperature. The furnace valve was opened, and the temperature of the closed system raised until the reaction was seen to take place, as revealed by a drop in pressure. After absorption of hydrogen was complete, several hours of annealing was performed to make the hydride distribution more uniform.

The quantity of hydrogen in the products was determined in 100 mg specimens by cold neutron PGAA. Duplicate measurements of materials doped at three different mass fractions (Table 1) showed that the quantity measured agreed with the quantity added, as calculated from pressure-volume-temperature measurements.

Preparation of SRM 2453

SRM 2453, with a nominal H mass fraction of 100 mg/kg, was the first of the three SRMs prepared. For preparation of the SRM, twelve 10 cm x 30 cm x 0.1 cm sheets of Ti6Al4V alloy (Goodfellow) were cleaned, weighed, and degassed by heating to

1073 K (800 °C) in a vacuum system consisting of a large quartz furnace tube and stainless-steel high-vacuum components. The degassed material was sampled by systematically taking 300 mg punchings from alternate sheets (the hydrogen mass fraction of the punchings being analyzed by prompt gamma-ray activation analysis and by neutron incoherent scattering), and the remaining material was then reweighed and returned to vacuum. A measured quantity of hydrogen was added to the system from a calibrated volume, and the material was heated to 673 K (400 °C). The reaction was completed by raising the temperature to 773 K (500 °C) for 6 h. Diffusion was encouraged by annealing at 673 K (400 °C) overnight, then the material was cooled to room temperature, whereupon the pressure dropped to 10^{-2} Pa (10^{-7} atm). The sheets were reweighed and alternate sheets sampled again by punching. Analysis of these samples by PGAA and also by neutron incoherent scattering (NIS) indicated nonuniform loading, so the batch was chipped with an electric nibbler to a particle size of approximately 15 mg. Particles less than 0.425 mm were removed by shaking on a stainless steel sieve. The chipped material was cleaned by extraction with methanol, dried, blended, and bottled.

Preparation of SRM 2452 and SRM 2454

SRM 2452 and SRM 2454, doped with approximately 50 mg/kg and 200 mg/kg hydrogen respectively, were prepared using a procedure similar to that used for SRM 2453. In order to minimize problems due to non-uniform loading of hydrogen encountered with the first SRM, these SRMs were prepared by doping of material that had already been chipped. Each SRM was prepared using the following procedure. A total mass of 2.2 kg of Ti6Al4V for SRM 2452 or 2.8 kg for SRM 2454 was weighed,

and the total was divided in half for processing. Each portion was weighed and degassed

at 973 K (700 °C) in a vacuum system consisting of a quartz furnace and stainless-steel

high-vacuum components for 4 d to 5 d, by which time the hydrogen pressure shown by a

residual gas analyzer (RGA) was less than 10^{-4} Pa. The degassed material was sampled

and analyzed by PGAA. After cooling to room temperature, a measured quantity of dry

hydrogen was added to the system from a calibrated volume, and the material was heated

to 773 K (500 °C). The reaction was completed by raising the temperature to 873 K (600

°C) for 4 d to 5 d. After cooling, the residual hydrogen pressure was less than 10^{-7} Pa.

The two batches were combined and passed through a No. 4 (4.75 mm) stainless-steel

sieve. The material was then blended and bottled.

Determination of Hydrogen by Prompt Gamma-ray Activation Analysis

Prompt gamma-ray activation analysis is a non-destructive[†], multielement

technique that has proven useful for determination of hydrogen and other elements in a

wide variety of materials.[9] Samples are irradiated by neutrons, inducing nuclei of most

elements to undergo neutron capture. The capture nucleus, which is in an excited state

several MeV above ground, then de-excites within 10^{-14} s by emission of prompt gamma

rays. For example, hydrogen captures a neutron via the $^1H(n,\gamma)^2H$ reaction (thermal

neutron capture cross section of 0.3 b), de-exciting by emission of a characteristic

2223.23 keV gamma ray. The emitted prompt gamma rays are measured by a high-purity

germanium detector, and comparison with standards yields quantitative measurement.

[†] In practice the measurement is not always totally nondestructive, since small quantities of residual
radioactivity may be present after analysis.   However, irradiation of the Ti6Al4V alloy analyzed here
yields only the short-lived nuclides ^{51}Ti, ^{28}Al, ^{52}V, with half-lives of 5.76 min, 2.25 min, and 3.76 min
respectively, hence any residual radioactivity is essentially gone after a few hours.

The use of cold neutrons (energies <5 meV) in the analysis results in higher capture rates and better sensitivity.

In this investigation, cold neutron PGAA was used to measure the H/Ti ratio in degassed blanks and final SRMs. A combination of thermal neutron PGAA and instrumental neutron activation analysis (INAA) was then used to confirm the Ti content of the alloy so that mass fraction of H in the alloy could be determined. The procedure is detailed below.

Preparation of samples, standards, controls, and blanks. SRM measurements were carried out on aliquots taken from randomly culled bottles of each material. Eight bottles of SRM 2453 and six bottles each of SRM 2452 and 2454 were sampled, with one aliquot from each bottle analyzed. Approximately 300 mg of metal was removed from each bottle and pressed into a 12.7 mm diameter pellet using a stainless steel die and hydraulic press. Each pellet was then weighed and heat-sealed into a bag of FEP (fluorinated ethylene propylene) Teflon.

To complete the characterization of the SRMs, portions of degassed alloy were also analyzed. For SRM 2453, blanks were in the form of punches; for SRMs 2452 and 2454, ≈ 300 mg portions were taken from two batches of the chipped degassed material and were pressed into pellets as described above. Measurement of the degassed blanks was necessary to correct the volumetric measurements of hydrogen added to the blank for residual hydrogen remaining in the blank after degassing.

A 235 mg single piece of SRM 354 (Unalloyed Titanium for Hydrogen, certified at 215 mg/kg ± 6 mg/kg H) and a 150 mg piece of SRM 352c (Unalloyed Titanium for

Hydrogen, certified at 49 mg/kg ± 0.9 mg/kg), both sealed in Teflon bags, were used as controls. These control SRMs had been certified for hydrogen using hot gas extraction vacuum fusion.[10, 11]

In order to minimize uncertainties due to the effects of neutron scattering, neutron self absorption, and variations in irradiation geometry, the ratio of hydrogen to titanium in the samples was measured rather than the absolute quantity of hydrogen.[11] Standards for analysis were therefore prepared from mixtures of urea (Eastman Kodak, ACS grade), graphite (Spectrographic Services, 100 mesh), and titanium powder (Spex Industries, Hi-Pure, TMI 1000, 99.9 %), and urea, graphite, and titanium dioxide (TiO_2, Fisher Certified Reagent) so that a hydrogen to titanium sensitivity ratio could be determined. Mixtures were prepared by weighing components into a plastic vial and shaking for at least 20 minutes in a mixer mill. Compositions of the mixtures were calculated to be 12.55 % Ti ; 3.193 % H (urea/graphite/titanium) and 11.45 % Ti ; 2.679 % H (urea/graphite/titanium dioxide) based on the masses of the individual components, and assuming compositions of 100 % Ti for the titanium powder, 59.95 % Ti for the TiO_2, and 6.713 % H for the urea. PGAA analysis of the graphite, titanium powder, and titanium oxide confirmed that no additional hydrogen was introduced by these materials. A stainless steel die and hydraulic press were used to press each mixture into four 250 mg pellets.

Measurement of H and Ti by cold neutron PGAA. Measurements were performed using the cold neutron PGAA spectrometer at the NIST Center for Neutron Research.[12, 13] Because of its hydrogen-free construction, compact geometry, and higher neutron capture rate, the hydrogen detection limit (< 5 mg/kg for most materials) for this instrument is

significantly better than that of the University of Maryland/NIST thermal neutron PGAA instrument, also located at this facility.[14] Targets were irradiated in an evacuated magnesium box sample chamber. Irradiation times were chosen to obtain counting statistics better than 2.5 % (1s) when possible. Approximate irradiation times were 24 h to 48 h for SRM samples, 48 h to 72 h for degassed blanks, and < 30 minutes for standards. Changes in neutron fluence throughout the course of the measurements were monitored by repeated irradiations of the same titanium foil flux monitor (12.7 mm diameter, 147.5 mg), with the foil irradiated before and after each sample. In order to account for the hydrogen background signal resulting from neutron capture by hydrogen present in the detector, shielding, mounting materials, and surrounding environment an empty Teflon bag was irradiated in the evacuated chamber for two days.

Hydrogen and titanium gamma-ray peaks at 2223 keV and 1381 keV respectively were integrated and fitted using the Hypermet-PC program.[15, 16] This program was needed to resolve the hydrogen peak at 2223 keV from an interference peak from titanium at 2219 keV (Figure 2).[17] Count rates for all targets were corrected for pulse pileup and for a hydrogen background count rate of (0.072 ± 0.005) counts per second (equivalent to ≈ 5 μg of hydrogen). The mass fraction of hydrogen in each sample (in mg/kg) was then calculated as:

$$\frac{(C_H - C_{bkg}) \cdot S_{Ti/H} \cdot F_{Ti}}{C_{Ti}} \qquad (2)$$

where C_H and C_{Ti} are the pileup corrected count rates (counts per second) for H and Ti in the samples, C_{bkg} is the pileup corrected hydrogen background count rate, $S_{Ti/H}$ is the average Ti/H sensitivity ratio determined from the standards (equal to 0.459×10^6 counts per second per kilogram Ti / counts per second per milligram H), and F_{Ti} is the fraction of titanium in the alloy. The value for F_{Ti} (nominally 0.9 for Ti6Al4V) was confirmed by a combination of thermal neutron PGAA and instrumental neutron activation analysis (INAA) as described below.

Determination of Ti fraction of Ti6Al4V. Five 300 mg pellets of SRM 2454 were analyzed for major element composition of Ti using the Maryland /NIST thermal neutron PGAA instrument. The thermal neutron (TN) PGAA instrument was used for these measurements because corrections for neutron self-shielding are smaller and more accurately determined for thermal neutrons (average energies = 0.025 eV) than for cold neutrons. Samples were irradiated for 8 h to 16 h. A thin disk of titanium was used as a standard.

Titanium was also measured by INAA in 100 mg pellets of Ti alloy. Samples were packed into two rabbits (polyethylene irradiation vessels) along with Ti disk standards. Rabbits were irradiated for 1 minute each, with each rabbit flipped (rotated end over end) after 30 seconds in order minimize errors due to a flux gradient in the reactor tube. Samples were allowed to cool for 30 min to 45 min to allow for decay of ^{27}Al ($t_{1/2} = 2.2$ min) and ^{52}V ($t_{1/2} = 3.8$ min). ^{51}Ti ($t_{1/2} = 5.8$ min) was measured using a high purity germanium detector. Samples and standards were counted for approximately

3 minutes each; count rates were corrected for all known sources of bias: radioactive decay, pileup, and dead time.

Titanium values measured by TNPGAA were in agreement with those measured by INAA. A mean Ti mass fraction of 0.896 ± 0.005 ($1s$ uncertainty), in agreement with the nominal value of 0.9, was used as the value of F_{Ti} in Equation (2).

Neutron incoherent scattering

Neutron incoherent scattering (NIS) was used to provide measurement of hydrogen in the degassed alloy for SRM 2353 preparation and H in the hydrogenated SRM 2353 material solely for the purpose of homogeneity assessment. The method, described in detail elsewhere[5, 6], takes advantage of the large incoherent scattering cross section of ^{1}H (80 b for thermal neutrons). The sample is irradiated in a neutron beam, and neutrons scattered from the sample are measured by two ^{3}He detectors mounted at 45° to the sample. Thin films of polyethylene are used as H standards. Although the NIS method is more sensitive to H than PGAA, because the neutron scattering cross section is more than 200 times the neutron capture cross section, the signal is less specific to hydrogen because other elements in the sample scatter neutrons. Hence with the exception of measurement of H in degassed material for SRM 2353, NIS measurements were not used for SRM certification.

RESULTS AND DISCUSSION

Hydrogen Determination by PGAA

Table 2 gives hydrogen mass fractions measured in each SRM by PGAA, along with sources of uncertainty and the contributing uncertainty from each source. Individual sources of uncertainty were added in quadrature to obtain a combined standard uncertainty (u_c), which was then multiplied by a coverage factor of 2 to obtain the expanded uncertainty (U).[18] Uncertainties were evaluated from measurement replication, background subtraction contribution, normalization of H/Ti ratios to Ti content, uncertainties in the measurement and preparation of standards, and from differences in gamma-ray attenuation, pulse pileup correction, and neutron fluence rate between samples and standards. A detailed explanation of evaluation of uncertainties in PGAA is given elsewhere[9, 19], the discussion here will focus on the most significant sources of uncertainty. Measurement replication uncertainties for both samples and standards were determined as $1/\sqrt{n}$. For standards, replication was based on measurement of eight standards, four from each mixture – titanium/graphite/urea or TiO_2/graphite/urea. Reagent purity uncertainties were calculated based on manufacturers specifications of the urea, TiO_2, and Ti powder. Most likely, the uncertainty here is somewhat underestimated, because both Ti powder and TiO_2 are likely to contain impurities not mentioned on the bottle. However, Ti/H sensitivity ratios measured from pellets in both mixtures agree within calculated uncertainties. Moreover, determination of H in titanium control materials SRM 352c and SRM 354 by PGAA yields values that agree with certified values within the uncertainty of the method (Figure 3), indicating that there is no significant bias introduced by the measurement of the standards. Uncertainties arising from normalization of the H/Ti ratio to the Ti content of the alloy are based on uncertainty in the measured Ti content of the alloy by TNPGAA/INAA. The uncertainty

from background subtraction was determined by adding in quadrature counting statistics from H peaks in sample spectra and background spectra. For SRM 2453, prepared and certified more than a year before the other two SRMs, this uncertainty also included the uncertainty due to an interference correction for a Ti interference peak at 2219 keV. This peak represents the single escape peak of the Ti 2230 keV gamma-ray line, and is difficult to correct for if the peak is not resolved from the hydrogen peak at 2223 keV. For analysis of SRMs 2452 and 2454, the 2219 keV and 2223 keV peaks were fitted and resolved using Hypermet-PC, which has proven effective for fitting overlapping peaks as singlets. The use of this program eliminated the need to perform an interference correction, and the uncertainty in the background correction was much diminished.

The final PGAA value and expanded uncertainty are given for each SRM at the bottom of Table 2. Relative expanded uncertainties for the PGAA measurements are 10 % for SRM 2354, 3.2 % for SRM 2452, and 2.4 % for SRM 2454, reflecting the improvement of the PGAA measurements for the final two SRMs.

Hydrogen Determination from Preparation Data and Blank Measurement

The determination of total H in the SRMs from the preparation data and blank measurement is illustrated in Table 3. The uncertainty on the mg/kg H determined by volumetric addition is the combined 1s uncertainty from pressure, volume, and temperature measurements. The blank H values for SRMs 2452 and 2454 represent the mean of four different portions of degassed blank. The blank value for SRM 2453 is the weighted mean of measurements of two portions of degassed material by PGAA and four measurements of the same material by neutron incoherent scattering. The total H

measured by preparation and blank was calculated by adding volumetrically measured H and blank values, with the uncertainties added in quadrature. H mass fractions measured in this manner are in all cases in agreement with total hydrogen measured by PGAA.

The two methods used to determine total hydrogen mass fractions of the SRMs are not totally independent, because PGAA was used in the measurement of the blank as well as to measure total H in the final products. Of particular concern is the fact that PGAA analysis of the blanks did not yield "zero" hydrogen within the uncertainty of the method, implying that not all hydrogen was removed from the alloy by degassing at 1073 K (800 °C), despite the fact that heating was performed until no more evolved H_2 was measured with the residual gas analyzer. There are three possible hypotheses to explain this: either the temperature was not high enough to expel all hydrogen from the alloy, some hydrogen was reintroduced into the metal after degassing but before PGAA measurement, or all hydrogen was in fact removed and the PGAA measurements are simply biased high by 11 mg/kg. If we assume that the latter hypothesis is the correct one, then the bias would have to affect both the blank and SRM measurements by the same amount because the sum of added hydrogen plus residual hydrogen measured in the blank was equal to the total amount of hydrogen measured in the SRM by PGAA for all materials. However, measurement of hydrogen in both control materials (H in Unalloyed Titanium) that were previously certified by hot gas extraction methods revealed no bias, as PGAA measurements were in agreement with certified values (Figure 3). The most likely source of high bias for PGAA would be an underlying interference peak by a matrix element at 2223 keV. If the bias is only present in measurement of Ti6Al4V, and

not unalloyed titanium, then the interference would have to come from an alloying element, aluminum and/or vanadium, and not the titanium itself.

To test this theory, 100 mg to 133 mg disks of high-purity aluminum and vanadium were analyzed for several hours by cold neutron PGAA. Integration of the 2223 keV gamma ray, followed by subtraction of background hydrogen and comparison with standards yielded apparent H mass fractions of (41 ± 7) mg/kg in aluminum and (8 ± 5) mg/kg in vanadium (uncertainties are 1s from counting statistics/background subtraction). However, Al and V make up only 6 % and 4 % of the mass of the alloy, respectively. Therefore, even if we assume that 100 % of the 2223 keV gamma ray in the spectrum of each element was due to an interference peak and not hydrogen itself, the maximum contribution from interference peaks in the Ti6Al4V alloy would be (2.47 ± 0.40) mg/kg for aluminum and (0.33 ± 0.21) mg/kg from vanadium. The total contribution with 1s uncertainties added in quadrature is therefore (2.80 ± 0.45) mg/kg (1s uncertainty), yielding an upper limit of $2.8 + 0.9$ (2s), or < 3.7 mg/kg for the magnitude of any possible interference correction for these two elements. This is only about a third of the observed blank value. Therefore, we can conclude that there is insufficient contribution from spectral interferences to account for apparent bias of the magnitude observed.

Another hypothesis to explain the non-zero blank is that not all hydrogen was extracted from the alloy at 1073 K (800 °C). Although thermodynamics calculations indicate that all hydrogen should be extracted, the kinetics might be too slow at this temperature to allow complete degassing in the time allotted. One further note: although our samples were degassed at < 1155 K (882 °C) to stay below the α-β Ti transition

temperature, hot vacuum extraction for determination of hydrogen is normally performed at a much higher temperature. The certificate of analysis for SRM 354 indicates that the certification measurements were performed by vacuum extracting the material at 1623 K (1350° C) to 1673 K (1400 °C).[10] In fact, five measurements by vacuum extraction at these temperatures yielded hydrogen mass fractions from 209 mg/kg to 219 mg/kg, while vacuum fusion at 2223 K (1950 ℃) yielded the highest value of 223 mg/kg hydrogen. It is possible that reaction kinetics at these temperatures allow for faster removal of the hydrogen.

A third possible explanation is that some hydrogen was reintroduced into the metal after degassing but before analysis by PGAA. If the surface oxide layer is depleted upon heating in a vacuum, then it is possible that some hydrogen could be absorbed into the metal after degassing upon exposure to humid air, before the protective oxide layer had a chance build up again. This behavior was noted by high purity niobium metal used for superconducting cavities that had been treated by heating after removal of the surface oxide layer.[20] It was found that much less hydrogen re-absorption occurred if the metal was first exposed to dry nitrogen gas upon removal from the vacuum furnace rather than immediately exposing it to humid air.   A systematic analysis of degassed titanium alloy exposed to air upon removal from the furnace vs. degassed titanium alloy removed from the chamber after first flushing the chamber with nitrogen might help to shed some light on this question.

Certified Values

The certified value for each SRM was calculated as the mean of the values obtained by PGAA and by preparation. The certified value and expanded uncertainty for each SRM is given in Table 3.

CONCLUSIONS

Certification by preparation and independent measurement by prompt gamma-ray activation analysis proved to be a reliable method for preparation of titanium alloy SRMs with hydrogen certified at mg/kg levels. Good agreement was obtained between hydrogen mass fractions measured using the two methods. The non-zero blank observed after degassing does not appear to be the result of a high PGAA bias due to spectral interferences, but rather represents either hydrogen remaining in the metal after heating or reintroduced after degassing. The methods used here may be modified to produce reference materials for other metals (e.g. zirconium and its alloys) certified for hydrogen mass fraction.

The identification of certain commercial equipment, instruments, or materials does not imply recommendation or endorsement by the National Institute of Standards and Technology. These identifications are made only in order to specify the experimental procedures in adequate detail.

Table 1. Comparison of hydrogen added to the amount found by PGAA for the prototype material.

H added (mg/kg)	H measured by PGAA (mg/kg ± 1s)
306	294 ± 11
	305 ± 10
208	194 ± 11
	218 ± 11
92	100 ± 11
	101 ± 11

Table 2. Hydrogen mass fractions measured in SRMs 2452, 2453, and 2454 by PGAA.

	SRM 2452 H (mg/kg)	SRM 2453 H (mg/kg)	SRM 2454 H (mg/kg)
1	62.8	111	211
2	64.8	105	214
3	64.5	108	217
4	62.6	118	203
5	60.9	109	207
6	59.5	126	207
7	----	125	----
8	----	114	----
Mean ± 1s	**62.5 ± 2.1**	**114 ± 8**	**210 ± 5**
Type A Uncertainty measurement replication (s/√n)	0.85	2.6	2.1
background subtraction	0.34	5.9	0.33
normalization to Ti	0.16	1	0.53
measurement replication (standards) (s/√n)	0.26	1.5*	0.88
weighing (standards)	0.004	---	0.014
reagent purity (standards)	0.3	---	1.0
Combined Type A	**1.0**	**6.8**	**2.4**
Type B Uncertainty gamma-ray attenuation	0.02	0.1	0.06
pulse pileup correction	0.12	0.12	0.12
neutron fluence variation	0.04	0.04	0.04
Combined Type B	**0.12**	0.12	0.13
Combined Standard Uncertainty (u)	**1.0**	**6.8**	**2.4**
Coverage Factor	**2**	2	**2**
Expanded Uncertainty	**2.0**	**14**	**5.0**
Final PGAA value (U)	**62.5 (2.0)**	**114 (14)**	**210 (5)**

* Sum of all standards' uncertainties.

Table 3. Summary of H in SRMs 2452 and 2454 by PGAA and by volumetric addition of H_2 along with the final certified value. Uncertainties are 1s, combined standard uncertainty (u_c) or expanded uncertainty (U) as indicated.

SRM	mg/kg H by PGAA (u_c)	mg/kg H by volumetric addition (1s)	mg/kg H degassed alloy (1s)	Total H mg/kg volumetric addition + blank (u_c)	Certified H value (mg/kg) (U)
2453	114 (6.8)	100.3 (0.5)[1]	11 (8)[2]	111 (8)	**114 (5)**
2452	62.5 (1.0)	50.9 (0.09)	11.6 (1.2)[3]	62.5 (1.2)	**62.5 (1.6)**
2454	210 (2.4)	200.4 (0.34)	11.6 (1.2)[3]	212.0 (1.2)	**211 (4)**

[1]An independent value of (111.6 ± 7.7) mg/kg (1s uncertainty) was measured by gravimetry: 12 portions of Ti alloy were weighed after degassing and again after H doping. This value was not used in the calculation of certified value.

[2]Mean and standard deviation of measurements made by PGAA and NIS

[3]Mean and standard deviation of measurements made on 4 degassed portions of Ti alloy by PGAA.

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