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Calibration of Thermal Desorption System (TDS) Response to Hydrogen for Analysis of Titanium Subhydride and Titanium Hydride

Bernice E. Mills

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

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Bernice E. Mills
Materials Chemistry Department, org. 8223
Sandia National Laboratories
P.O. Box 94551-0969
Livermore, California 94550-MS9403

Abstract

The equipment and method for and results of calibration of the Sandia/CA TDS system for hydrogen quantification is presented. The hydrogen quantity Q in Torr-liters per second can be expressed as

$$Q(\text{Torr-l/s}) = 29.995 \cdot I_{2\text{AMU}} (\text{A})$$

where $I_{2\text{AMU}}$ is the intensity of the mass 2 (hydrogen) signal in the mass spectrum measured in Amps. This is valid for $I_{2\text{AMU}} (\text{A}) \leq 0.00017 \text{ A}$ or about 0.005 Torr-l/s.

This technique for calibration can be used to quantify the hydrogen content titanium subhydride, titanium hydride, and any other hydrogen-containing material that desorbs its hydrogen in the form of molecular hydrogen below 1450°C.

ACKNOWLEDGMENTS

Thanks to Robert Anderson (I think) for his original construction of the TDS, Kristin Hertz for permitting the author to use the system, Josh A. Whaley for modifying the LabVIEW virtual instrument to indicate how long the pressure had been stable for each calibration step, and Michael E. Malinowski for modifying the gas calibration manifold system to accommodate higher gas flow rates than could be achieved with a calibrated leak.

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NOMENCLATURE

AMU	atomic mass unit
BAG	Bayard-Alpert ionization gauge, a vacuum gauge
CEM	continuous-dynode electron multiplier, also known as channel electron multiplier
DASYLab	a commercial software program used to collect pressure data during calibration
FY	fiscal year
$I_{2\text{AMU}}$	current (in Amps) of the mass 2 AMU (hydrogen) peak recorded by the RGA
I	the time integral of the 2 AMU peak signal (in A-s)
k	constant relating partial pressure to current (in Torr/A)
k1	constant relating k and pumping speed (in Torr-l/A-s)
k2	relates the change in mass to the time integral of the 2 Amu signal (in mg/A-s)
l	liters
l/s	pumping rate
LabVIEW	a commercial software suite used to control the RGA and collect data
m	mass (in mg)
P	vacuum system pressure (in Torr)
p	calibration system pressure (in Torr)
P_{H_2}	partial pressure of hydrogen
Q	input gas flow rate (in Torr-l/s)
Q	the time integral of the gas desorbed (in Torr-l)
Q₀	the time integral of the gas desorbed at STP (in Torr-l)
Q_{H_2}	flow rate of hydrogen (in Torr-l/s)
RGA	residual gas analyzer, in this case a quadrupole mass spectrometer
s	seconds
S	vacuum pumping speed (in liter/second or l/s)
S(P)	vacuum pumping speed (in l/s), a function of pressure
S_{H_2}	pumping speed for hydrogen (in l/s),
STP	standard temperature, pressure for an ideal gas (0 °C, 760 Torr)
T	time (in seconds)
TC	thermocouple
TDS	thermal desorption spectroscopy
TiH _x	titanium subhydride (also can refer to titanium hydride, the dihydride)
TMP	turbomolecular (vacuum) pump
Torr	a unit of pressure
UHV	ultra-high vacuum
V _{1,v}	volume of input gas system after calibration using vc and capacitance manometer
vc	calibrated volume as calibrated by Sandia standards lab
V	volume of vacuum system including quartz thimble and RGA

1. INTRODUCTION

When Mound was part of the nuclear weapons complex, it was responsible for the production of titanium subhydride TiH_x powder for use as the fuel component of energetic materials. Mound also analyzed the product for both water and hydrogen content. When Sandia assumed the responsibility for this material, it was necessary to reestablish this analysis capability, either in house or at an outside vendor. Repeated attempts to get analyses to the desired 1% accuracy showed that 10% accuracy was the best that could be expected from existing procedures, both at Sandia/NM and at vendors. Sandia/CA was then asked to develop a technique using thermal desorption spectroscopy (TDS), reported to be one of the methods used at Mound, to analyze TiH_x . To interpret the data from a TDS experiment, the system must be calibrated for the mass of interest: in this case mass 2 for molecular hydrogen.

The calibration technique chosen for this work was based the American Vacuum Society Recommended Practice for the Calibration of Mass Spectrometers for Partial Pressure Analysisⁱ. Their method #4 addresses calibration of the partial pressure analysis to a known gas flow rate. It is done *in situ* so that the pumping speed during calibration is the same as that during use. It entails the introduction of a gas at a known low pressure via a molecular leak. Pressures are measured with a capacitance manometer. This is further based on the work of Ellefson *et al* at Mound^{ii,iii}.

Heretofore, we have been able to rely on batches of titanium subhydride manufactured either at Mound or by the same personnel who made it at Mound. The latter batches had been manufactured per the Mound procedure but had not been analyzed. It was necessary to redevelop the analysis process. Recently, the stockpile of titanium subhydride has been depleted to the extent that more must be manufactured from the stockpile of titanium hydride (nominally the dihydride). The calibration process shown here is applicable to both compounds as well as hydrogen in other materials. It can also be used for calibrating any other gas that does not condense.

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2. THERMAL DESORPTION SPECTROSCOPY

This TDS is performed in a vacuum system located in the accelerator laboratory, Building 916, room 104. A schematic of the system is shown in Figure 1.

The TDS uses a Quad Elliptical Heating Chamber Model E4 (5528-02). This is powered by a Research Inc. single phase, phase angle controlled 240VAC 25A power controller. The temperature ramps and holds are generated using an Omega CN3000 controller and the internal thermocouple (TC) shown in Figure 1. That temperature measurement is not used in the calibration process. The entire vacuum system is pumped by a Pfeiffer TMU 071 YP high compression ratio, 60 l/s (nominal) turbomolecular pump (TMP) backed by a rotary vane (RV) pump (not shown) and has a base pressure of $\sim 2 \times 10^{-9}$ Torr. The sample chamber can be isolated from the RGA and the TMP by a valve to change the sample in the quartz thimble. When samples are introduced, the RV pump is temporarily repurposed to rough the sample chamber. The total pressure in the system is measured with a Granville-Phillips Series 370 STABIL-ION® gauge, a highly stable Bayard-Alpert ionization gauge (BAG) with a NIST-traceable, nitrogen calibration. Also on the system is a Stanford Research System (SRS) 300 quadrupole residual gas analyzer (RGA), used to detect the different gas species desorbed. The RGA response to hydrogen was measured using a custom-made gas calibration inlet system with a capacitance manometer; this gas inlet system is described in the next section.

The system had been calibrated at lower hydrogen flow rates in FY2006. The current work was performed to redo the calibration of the response of the RGA 2 AMU signal at the higher flow rates expected when analyzing a bulk hydride, rather than hydrogen dissolved into a metal. More accurate values of the hydrogen content of a material can be obtained if the amount of material used and the RGA signal can be maximized. However, it is necessary to remain in the linear region of the response curve and to avoid signal saturation.

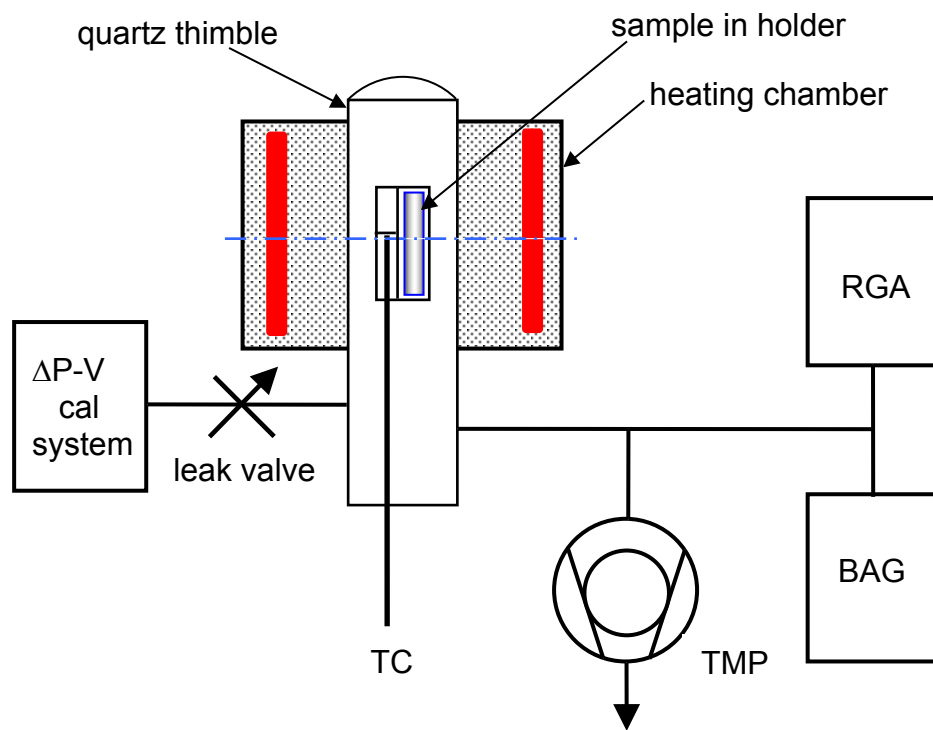


Figure 1. Schematic of thermal desorption system (TDS).

3. GAS CALIBRATION SYSTEM

This system was based on determining gas flow input to the vacuum system by measuring the pressure drop in a calibrated, fixed volume using a capacitance manometer connected to a known volume. Such an arrangement was used instead of a commercially available calibration leak because such leaks could not be used to calibrate the higher flow rates encountered in the current work. A sketch of the gas inlet system as configured for the current work is shown in Figure 2. This inlet system was slightly different from that used in the FY2006 work in the size and placement of both the calibration volume and the hydrogen gas source volume. All other equipment – including the leak valve, calibrated 100 Torr Baratron capacitance manometer, and the other valves – were the same as used in FY2006.

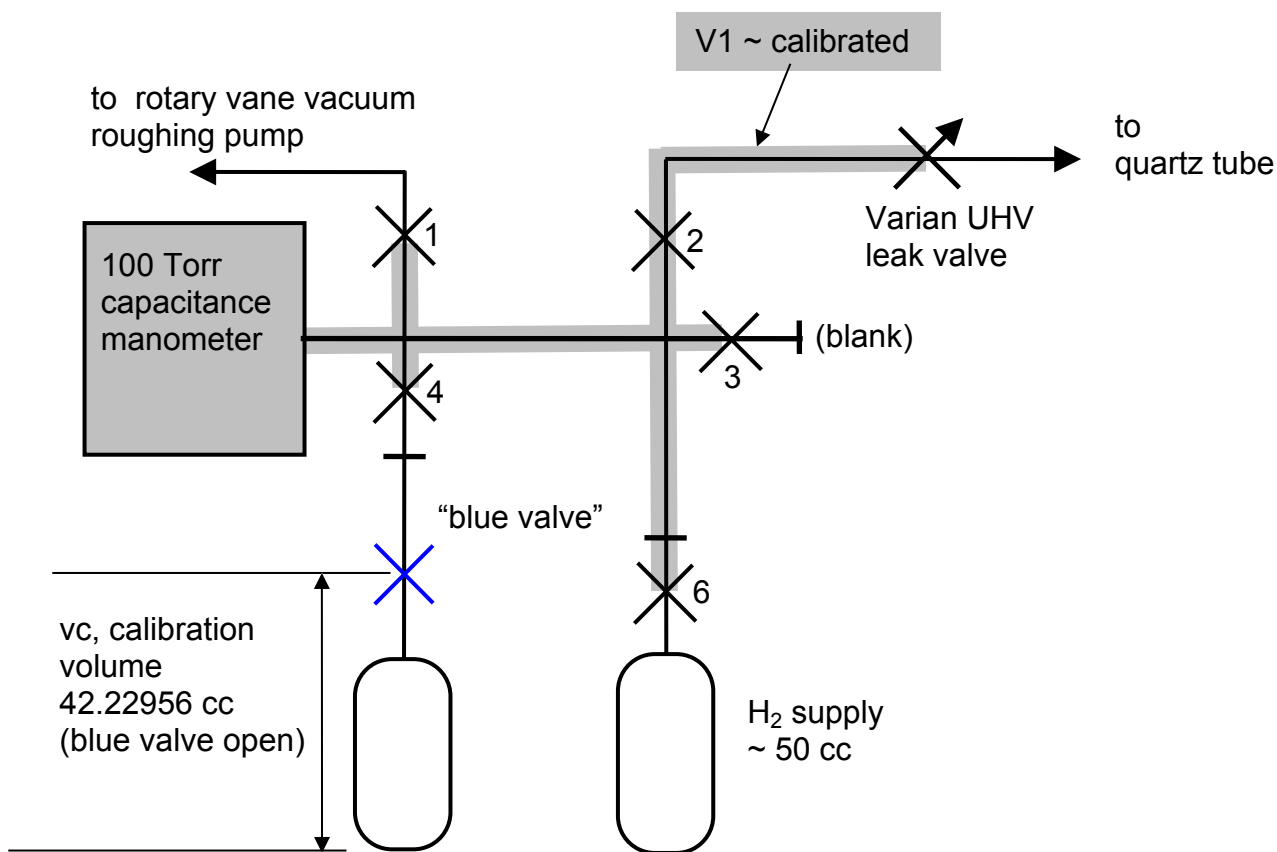


Figure 2. Schematic of gas inlet system for calibration.

Gas was admitted to the vacuum system by an all-metal, manual leak valve, and the input gas flow rate, Q , in Torr-l/s was related to the capacitance manometer pressure (p) and volume (v) of the input gas system by

$$(1) Q = v \cdot (dp/dt)$$

In the current calibration work, the volume of the input gas system either included or excluded the known calibration volume. This allowed flexibility to accommodate very different flow rates with tractable rates of pressure drop. Both p and P , the vacuum system Bayard Alpert gauge pressure, were recorded with one computer running DASyLab software. (dp/dt) was determined for each gas flow calibration point and Q calculated by equation (1).

The RGA output during calibration was recorded with a second computer using LabVIEW based programs; one program was named “trend5.vi,” the second program, “trend6.vi.” These programs recorded four, different mass peaks at 2 s intervals: AMU 2(H_2^+), 7(background), 18(H_2O^+) and 28(N_2^+ / CO^+). The RGA was run in the Faraday cup mode; each mass peak was recorded as a current (A). This mode was found to be the most stable operation mode of the RGA. The other mode uses a continuous-dynode electron multiplier, also known as a channel electron multiplier or CEM. The CEM mode can detect lower levels of signal, but can change with time. This may be due to the changes in the glass surface of the multiplier due to ion bombardment. When analyzing hydrides, however, a low signal level is not a concern.

The basis of the linear relationship between the 2 AMU RGA output and the input hydrogen flow rate originates in the gas flow equation for vacuum systems:

$$(2) Q = S(P) \cdot P + V \cdot (dP/dt),$$

with V = the vacuum system volume

P = the vacuum system pressure.

$S(P)$ = the (possibly pressure dependent) pumping speed.

When $S \cdot P \gg V \cdot (dP/dt)$, the system pressure is approximately constant, and

$$(3) Q \approx S(P) \cdot P, \text{ or}$$

(4) $P_{H_2} \approx Q_{H_2} / S_{H_2}(P)$, where the H_2 subscripts refer to H_2 values. If the pumping speed is constant and if the 2 AMU RGA peak current, $I_{2AMU} = (1/k) \cdot P_{H_2}$, with k a constant, then

$$(5) Q_{H_2} \approx (1/S_{H_2}) \cdot k \cdot I_{2AMU}, \text{ or}$$

$$(6) Q_{H_2} \approx k1 \cdot I_{2AMU}, \text{ with } k1 \equiv (1/S_{H_2}) \cdot k.$$

Given the above assumptions, a plot of Q_{H_2} versus I_{2AMU} should therefore yield a straight line. If Q_{H_2} is expressed in Torr-l/s and I_{2AMU} is measured in amps, the units of $k1$ are (Torr-l/s-A or Torr-l/A-s).

When desorption experiments are performed, the time integral of I_{2AMU} , in A-s, gives the total amount of molecular hydrogen desorbed, if signal saturation is not occurring in the RGA. Sample mass measurements, before and after desorption, with a sensitive balance can determine the mass change due to the loss of hydrogen. The above relation between Q and I_{2AMU} can be related to the total mass loss in the sample if all the hydrogen in the sample were desorbed only

as molecular hydrogen (H₂) and if only hydrogen is desorbed. This mass change determined by weighing should be equal to that measured by the time integral of I_{2AMU}:

$$(7) \Delta m = k_2 \cdot \int dt,$$

where Δm = the mass loss measured by the microbalance, and
 $\int dt$ = the time integral of the 2 AMU peak signal, and
 k_2 = a constant.

If Δm is expressed in mg, $\int dt$ in A-s, k_2 has units of mg/(A-s). k_1 and k_2 are related; this relationship can be determined by integrating (6) above

$$(8) \int P dt = k_1 \cdot \int dt, \text{ where } \int P dt = \text{the time integral of the gas desorbed (in Torr-l)}.$$

At standard temperature and pressure (STP) conditions, one mole (gram molecular weight) of gas occupies a volume of 22.414 l at a pressure of 760 Torr and temperature of 0 °C. Since one mole of hydrogen weighs 2 g, the mass of $\int P dt$ Torr-l of gas at a temperature T (°C) is

$$\Delta m = 2 \cdot \left(\frac{\int P dt}{760} \right) \cdot \left(\frac{273.15}{T+273.15} \right). \text{ Using (8),}$$

$$(9) \Delta m = \left(\frac{2}{760} \right) \cdot \left(\frac{273.15}{T+273.15} \right) \cdot k_1 \cdot \int dt.$$

Comparing (7) and (9),

$$(10) k_2 = 1000 \cdot \left(\frac{2}{760} \right) \cdot \left(\frac{273.15}{T+273.15} \right) \cdot k_1.$$

Where the factor of 1000 converts from g to mg. In the experiments run on the desorption chamber, $T \approx 20$ °C. Explicitly evaluating (10) yields the following numerical relationship between k_2 and k_1 :

$$k_2 [\text{mg/A-s}] = 1000 \cdot \left(\frac{2}{760 \cdot 22.414} \right) \cdot \left(\frac{273.15}{293.15} \right) \cdot k_1 [\text{Torr-l/s-A}], \text{ or}$$

$$(11a) k_2 [\text{mg/A-s}] = 0.109396 \cdot k_1 [\text{Torr-l/s-A}].$$

For most gas flow rates, the hydrogen pumping speed is constant. When not conductance limited, the hydrogen pumping speed for the Pfeiffer TMU 071 YP TMP is 42 l/s. When performing calibrations at high gas flows, the effective pump speed of the TMP can decrease. In addition, at high enough pressures, the relationship between I_{2AMU} and P_{H₂} will no longer be linear because the mean free path of the ions will not be as long as the path length in the RGA from the ionizer to the detector. Either of these effects will be evident in a departure from linearity.

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4. RESULTS

To check the purity of the hydrogen gas to be used for calibration, hydrogen was admitted to the vacuum system at a pressure of 10^{-6} Torr (a high pressure for the RGA) and an analog RGA spectrum of the gas was acquired at a resolution of 0.1 AMU between 0 to 100 AMU. The 1 to 50 AMU portion of that spectrum is shown as the red trace in Figure 3 along with a background spectrum taken at a pressure of 6×10^{-9} Torr shown in blue. No peaks above noise level were detected between 50 to 100 AMU.

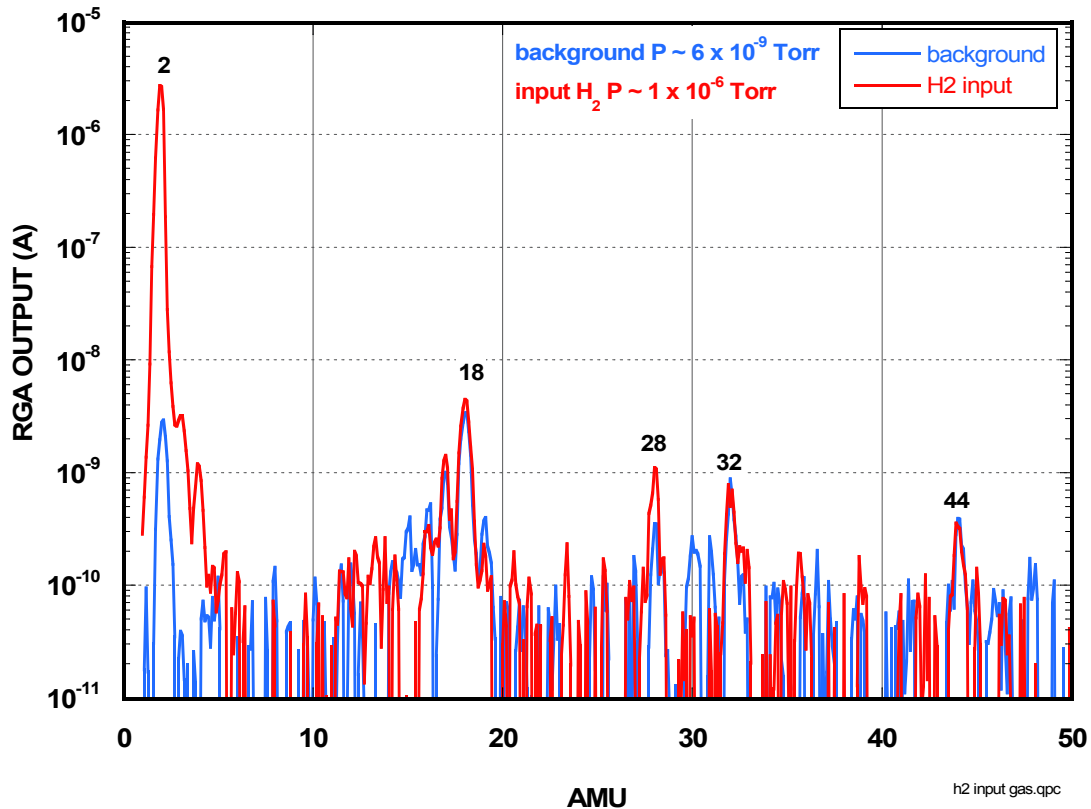


Figure 3. Analog RGA spectrum of background (blue) and hydrogen gas (red).

Most of the calibration gas was hydrogen at 2 AMU. However, there is an increase in the 28 AMU peak (nitrogen/carbon monoxide) above the background level. The 18 AMU (water), 32 AMU (oxygen), and 44 AMU (carbon dioxide) peaks are not detectably different from the background. If the sensitivity for the 28 AMU peak is the same as that for hydrogen and we neglect fractionation through the leak valve, the amount of contamination in the calibration gas is on the order of 0.02%

The results of the calibration are summarized in Figures 4 and 5. Figure 4 shows hydrogen flow rate Q_{H_2} vs. mass 2 current I_{2AMU} . The Q values were calculated at 20°C, and the results from acquiring the RGA peaks with two different LabVIEW virtual instruments trend5.vi (red circles)

and trend6.vi (blue squares) are shown. The fit to the linear range shown in black used both sets of data. The calibration from FY2006 is shown in grey for comparison.

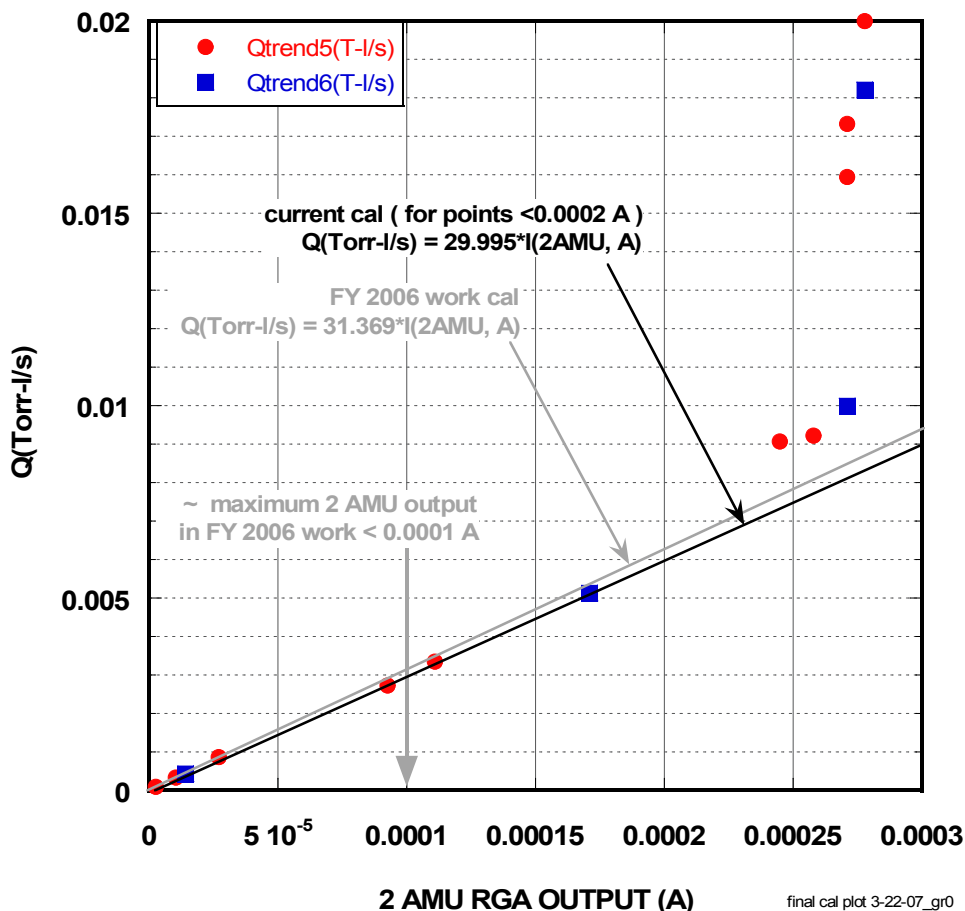


Figure 4. Current calibration results (colored) compared with previous calibration (grey).

The following observations regarding these results can be made:

1. Results obtained with both trend5.vi and trend6.vi are consistent with each other.
2. Q_{H_2} and I_{2AMU} are linearly related for $I_{2AMU} \leq 0.00017$ A. This relationship is approximately Q (Torr-l/s) = $29.995 \cdot I_{2AMU}$ (A). From equation (11a) the relationship between sample mass loss and time-integrated I_{2AMU} signal, \square , would be Δm (mg) = $3.2764 \cdot \square$ (A-s).
3. This relationship compares with Q (Torr-l/s) = $31.37 \cdot I_{2AMU}$ (A) from the FY2006 calibration where the RGA current was always < 0.0001 A and extends it to higher flow rates.
4. At even higher hydrogen flow rates, the linear relationship between Q_{H_2} and I_{2AMU} breaks down: Non-linear behavior occurs for I_{2AMU} (A) > 0.00017 A, with saturation of the RGA output occurring at I_{2AMU} (A) ~ 0.00027 A. This may happen because of the higher hydrogen pressures in the RGA and subsequent loss of ion signal due to reduced ion mean free path.

In contrast to the RGA signal, the BAG pressure signal is linear to higher hydrogen flow rates. Figure 5 shows RGA signal (I_{2AMU} (A)) and vacuum pressure P(BAG (Torr)) plotted versus Q. The fact that the linear range of the BAG response continues to a much higher flow rate, Q, allows us to salvage data when we have underestimated the hydrogen content of some unique materials samples.

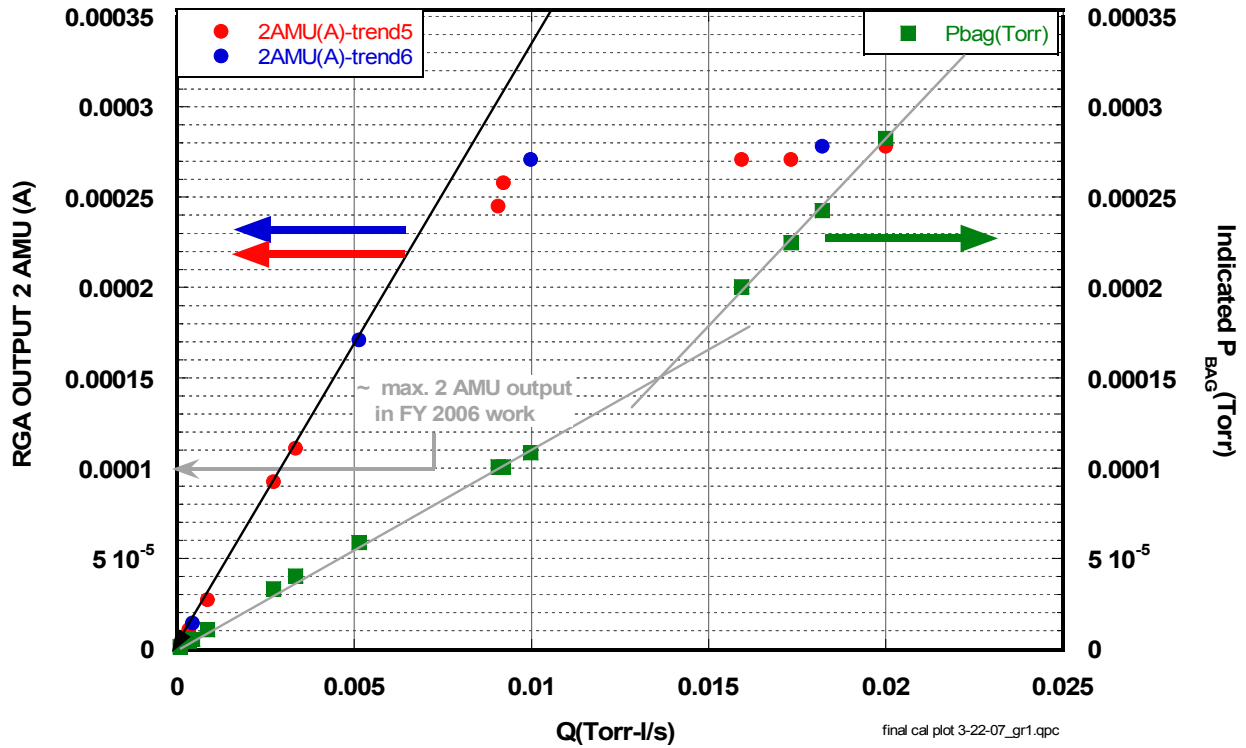


Figure 5. Mass 2 RGA signal and indicated BAG pressure versus hydrogen gas flow rate.

The indicated BAG pressure is the nitrogen equivalent pressure. The manual for the Series 370 STABIL-ION® gauge shows the scale factor to get from the indicated pressure for nitrogen to the pressure for hydrogen is 2.17^{iv} .

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5. CONCLUSIONS

The hydrogen response of the RGA and the BAG in the vacuum system used for desorption of titanium subhydride and titanium hydride (TiH_x) samples was measured *in-situ* using the gas inlet/calibration system on the TDS vacuum system. Response was measured at hydrogen flow rates up to 0.02 Torr-l/s. A linear response of the RGA signal with flow was detected up to a flow rate of more than 0.005 Torr -l/s, corresponding to a 2 AMU RGA signal of about 0.00017 A; the LabVIEW virtual instrument programs “trend5.vi” and “trend6.vi” were used for RGA data acquisition. A linear fit to these lower flow rate data resulted in the following relationship between hydrogen flow rate (Q) and the 2 AMU peak amplitude (I_{2AMU}) in the RGA scan:

$$Q(\text{Torr-l/s}) = 29.995 \cdot I_{2\text{AMU}} (\text{A}), \text{ for } I_{2\text{AMU}} (\text{A}) \leq 0.00017 \text{ A.}$$

This result was independent of the RGA data acquisition program used. The previous calibration of the RGA in FY 2006 resulted in a factor of 31.37 instead of 29.995 in the Q-I relation. At flow rates above about 0.005 Torr-l/s the RGA response deviated from linearity, with a saturation of the RGA output occurring at ~ 0.01 Torr-l/s, corresponding to an RGA output of about 0.00027 A. It is likely that this saturation was a result of the higher pressures in the RGA sensor head. The ions of interest have a sufficiently reduced mean-free-path so that fewer of the ions generated at the source get to the detector without suffering a collision that removes them from the path to the detector. The path of ions in a quadrupole is convoluted and longer than the length of the quadrupole elements.

The above relation between Q and I_{2AMU} can be related to the total mass loss in the sample if all the hydrogen were desorbed only as molecular hydrogen (H₂) and if no other species was desorbed. Given this assumption, the corresponding relationship between sample mass loss (Δm) and time-integrated I_{2AMU} signal (∫) would be

$$\Delta m[\text{mg}] = 3.2764 \cdot \int [\text{A}\cdot\text{s}].$$

The response of the Bayard-Alpert ionization gauge (BAG) to hydrogen is linear to double the pressure that the RGA response is linear. In addition, the BAG signal appears not to saturate.

Since the calibration constant, though similar, has changed from one calibration to another. Therefore it is recommended, for the most accurate measure of hydrogen content, that the system be recalibrated for each experiment. Since the linear range is now known, it should be possible to use only one or two pressures to correct the calibration.

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6. REFERENCES

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- ⁱ J. A. Basford, M. D. Boeckmass, R. E. Ellefson, A. R. Filippelli, D. H. Holkeboer, L. Lieszkovszky, and C. M. Stupak, American Vacuum Society Recommended Practice for the Calibration of Mass Spectrometers for Partial Pressure Analysis, in *J. Vac. Sci. Technol. A* 11(3), pp. A22-A40, May/June 1993.
- ⁱⁱ R. E. Ellefson, W. E. Moddeman, and H. F. Dylla, Hydrogen isotope analysis by quadrupole mass spectroscopy, in *J. Vac. Sci. Technol.*, 18(3), pp. 1062-1067, April 1981.
- ⁱⁱⁱ R. E. Ellefson, D. Cain, and C. N. Lindsay, Calibration of Mass spectrometers for quantitative gas mixture analysis, in *J. Vac. Sci. Technol. A* 5(1), pp. 134-139, January/February 1987.
- ^{iv} Granville-Phillips, *Series 370 STABIL-ION® Vacuum Measurement System Installation, Operation, and Maintenance Instructions*, p. 4-9, June 1999.

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