Inorganic Application Note

Hydrogen Determination in Reactive and Refractory Metals*

Instrument

RHEN600/602

Introduction

Titanium is a metal that can be combined with elements such as aluminum and iron to produce high strength, low density, and corrosion resistant alloys. Titanium alloys are used by the military, medical device, sporting goods, and aerospace industries because of these properties, and due to the precise nature of these industries, effort needs to be taken to assure that the material meets high quality standards.

One of the most critical chemical specifications of titanium alloys is the hydrogen content. Too high of a hydrogen content can cause hydrides to precipitate, which can lead to embrittlement and subsequent cracking when the alloy is stressed.

The LECO RHEN600 and RHEN602 are hydrogen determinators that utilize an electrode furnace, an argon carrier gas, and thermal conductivity detection to meet the analytical needs of the ferrous, refractory, and inorganic material industries. The RHEN602 has the added ability to differentiate between surface and bulk hydrogen when analyzing aluminum and aluminum alloys.

This application note was written for use with the LECO RHEN600 or RHEN602 Hydrogen Determinator.

Method Reference

ASTM E1447

Sampling and Sample Preparation

A clean representative sample is required for proper hydrogen determination. Solid samples should be sectioned in such a manner as to avoid overheating, preferably by shearing. If necessary, abrade sample surfaces with a clean file, rinse in acetone, and air dry to remove surface contamination. Cleaned samples must be handled with tweezers or forceps to prevent contamination.

Accessories

619-895 Graphite Crucibles, 761-739 Tin Pellets, 501-059 or 502-040 Tin Capsules, 617-997 Funnel

Calibration Samples

LECO 502-135, 762-741 Titanium Calibration Samples, NIST or other suitable refractory metal reference materials.

**Reactive and Refractory metals include: Ti, Zr, W, Mo, Ta, Nb, Hf, and their alloys.*

RHEN600/602

Method Parameters

Analysis Parameters

Outgas Cycles	3
Analysis Delay	90 seconds
Analysis Delay Comparator	1.000000
Analysis Type	Semi- Auto Analysis
Pre-Analysis Purge Time	15 seconds
Sample Drop Delay	0 seconds
Auto Analyze on Mass Entry	Disabled
Preliminary Crucible Outgas (mass not required)	Disabled
Standards require separate bulk and surface parameters	Enabled
Bulk/Surface Separation	Disabled

Element Parameters	*Hydrogen*	*Standards*[1]
Minimum Analysis Time	90	90 seconds
Significant Digits	7	7
Conversion Factor	1.000000	1.000000
Integration Delay	32	32 seconds
Comparator Level	2.000000	2.000000 %

Gas Dose Parameters	*Hydrogen*
Minimum Gas Dose Time	90 seconds
Integration Delay	32 seconds
Comparator Level	1.000000 %
Gas Dose Cycles	1

Furnace Parameters

Furnace Control Mode	Current	Current
Purge Time	15 seconds	15 seconds
Outgas Time	30 seconds	30 seconds
Outgas Cool Time	5 seconds	5 seconds
Outgas Low Current	900 amps*	900 amps*
Outgas High Current	900 amps*	900 amps*
Outgas Ramp Rate	0 amps/sec	0 amps/sec
Analyze Low Current	825 amps*	825 amps*
Analyze High Current	825 amps*	825 amps*
Analyze Ramp Rate	0 amps/sec	0 amps/sec
Sample Prep Time	0 seconds	0 seconds
Sample Prep Current	0 amps	0 amps
Furnace On Time	60 seconds	60 seconds

Temperature Sustain	None
Temperature Sustain Standards	None
Peak Find Parameters	Hydrogen
Look for Shoulders	No
Peak Threshold	0.000000

Calibration Parameters

Hydrogen $y = +1.0x + 0$ (default setting)

**May vary depending on line voltage. Level can be adjusted to facilitate recovery and/or reduce crucible burn-through.*

[1] *RHEN602 Only*

Procedure

1. Prepare instrument for operation as outlined in the operator's instruction manual.
2. Determine Blank.
   a. Enter 1.0000 g mass into Sample Login (F3) using Blank as the sample name.
   b. Press Loader Switch on front of furnace, after a short delay the loading head slide block will open.
   c. Press Loader Switch again, the loading head slide block will close and the lower electrode will open.
   d. Place two 761-739 tin pellets into a 619-895 graphite crucible.
   e. Place crucible on electrode pedestal.
   f. Press Loader Switch, the lower electrode will close and the analysis sequence will start and end automatically.
   g. Repeat steps 2a through 2f a minimum of three times.
   h. Set the blank following the procedure outlined in the operator's instruction manual.
3. Calibrate/Drift Correct.
   a. Weigh 0.15 to 0.35 g of a calibration sample, enter mass, and sample identification into Sample Login (F3).
   b. Press Loader Switch on front of furnace, the loading head slide block will open.
   c. Place sample into open port at top of loading head.
   d. Press Loader switch again, the loading head slide block will close and the lower electrode will open.
   e. Place two 761-739 tin pellets into a 619-895 graphite crucible.
   f. Place crucible on the electrode pedestal.
   g. Press Loader Switch, the lower electrode will close and the analysis sequence will start and end automatically.
   h. Repeat steps 3a through 3g a minimum of three times for each calibration/drift sample used.
   i. Calibrate or Drift Correct the instrument following the procedure outlined in the operator's instruction manual.
4. Analyze Samples.
   a. Weigh 0.15 to 0.35 g sample, enter mass, and sample identification into Sample Login (F3).
   b. Proceed as directed in steps 3b through 3g.

Typical Results—Solid Samples

Sample	*Mass g*	*H ppm*
LECO	0.2509	43.6
762-741	0.2491	41.4
Titanium	0.2514	42.6
@ 42.2 ±3.3	0.2523	41.1
ppm H	0.2486	41.5
	0.2521	42.4
	0.2455	42.8
	0.2507	43.6
	0.2480	41.7
	0.2491	42.5
	***X* =**	***42.3***
	***s* =**	***0.87***

Alternate Procedure—Powder/Chip Samples

If powder or chip samples are to be analyzed, they cannot be placed directly in the loading head. Samples can be weighed into tin capsules and be analyzed in the Semi -Auto Analysis mode. There are issues related to blank, limited volume/sample weight and the increased time and manipulation to weigh samples in a capsule. However, good results and precision are obtainable using this method. In addition, there are two methods of manually loading a sample available to the RHEN600/602 user.

Manual Analysis – The electrodes are opened after outgas and the sample is inserted into the crucible. This method will result in higher and more erratic hydrogen blanks and is generally not recommended.

Manual Top Load – After outgas, loading head is opened and the sample is dropped into the crucible. For powder samples, a LECO 617-997 funnel can be inserted through loading head into crucible and the sample is transferred to crucible via the funnel.

This option will limit the outgassed crucible's exposure to the atmosphere, reducing blank variability, subsequently improving precision. Therefore, the Manual Top Load function of the RHEN602 can be used to obtain good and precise hydrogen results.

Procedure—Tin Capsule

1. Determine Blank.
   a. Enter 1.0000 g mass into Sample Login (F3) using Blank as sample name.
   b. Press Loader Switch on front of furnace, after a short delay the loading head slide block will open.
   c. Place an empty tin capsule into open port at top of loading head.

   Note: Use same part number and lot number of capsules that will be used for the analysis of samples, leave capsule open.

   d. Press Loader Switch, the lower electrode will open.
   e. Place two 761-739 tin pellets into a 619-895 graphite crucible.
   f. Place crucible on electrode pedestal.
   g. Press Loader Switch, the lower electrode will close and the analysis sequence will start and end automatically.
   h. Repeat steps 1a through 1g a minimum of three times.
   i. Set the blank following the procedure outlined in the operator's instruction manual.
2. Calibrate/Drift Correct.
   a. Weigh 0.15 to 0.35 g of calibration sample into a tin capsule, enter mass, and sample identification into Sample Login (F3).

   Note: Leave capsule open.

   b. Press Loader Switch on front of furnace, after a short delay the loading head slide block will open.
   c. Place capsule into open port at top of loading head.
   d. Press Loader Switch, the lower electrode will open.
   e. Place two 761-739 tin pellets into a 619-895 graphite crucible.
   f. Place crucible on electrode pedestal.
   g. Press Loader Switch, the lower electrode will close and the analysis sequence will start and end automatically.
   h. Repeat steps 2a through 2g a minimum of three times for each calibration/drift sample used.
   i. Calibrate or Drift Correct the instrument following the procedure outlined in the operator's instruction manual.
3. Analyze Samples.
   a. Weigh 0.15 to 0.35 g sample into a tin capsule, enter mass, and sample identification into Sample Login (F3).

   Note: Leave capsule open.

   b. Proceed as directed in steps 2b through 2g.

Typical Results—Tin Capsule-Powder Samples

Sample	*Mass g*	*H ppm*
Tantalum	0.2567	190
Powder	0.2456	194
(H not certified)	0.2615	193
	0.2669	201
	0.2622	192
	0.2616	183
	0.2515	186
	0.2398	193
	0.2583	193
	0.2763	186
	***X* =**	***191***
	***s* =**	***5.3***

Procedure—Manual Top Load

1. Set Method Parameters as noted above with the following exceptions.
   a. Under Analysis Parameters set Analysis Type to: Manual Top Load.
   b. Under Analysis Parameters set Pre-Analysis Purge Time to: 50 seconds.
2. Determine Blank.
   a. Enter 1.0000 g mass into Sample Login (F3) using Blank as sample name.
   b. Press Loader Switch on front of furnace, after a short delay the lower electrode will open.
   c. Place two 761-739 tin pellets into a 619-895 graphite crucible.
   d. Place crucible on electrode pedestal.
   e. Press Loader Switch, the lower electrode will close and the outgas sequence will start automatically.
   f. When the outgas sequence is complete, an add sample message will appear in the lower left-hand corner of the instrument display. Press the Loader Switch and the loading head slide block will open.
   g. Place the 617-997 funnel into the open loading head.
   h. Remove the funnel, press the Loader Switch, the loading head slide block will close and the analysis sequence will start and end automatically.
   i. Repeat steps 2a through 2h a minimum of three times.
   j. Set the blank following the procedure outlined in the operator's instruction manual.
3. Calibrate/Drift Correct.
   a. Weigh 0.15 to 0.35 g of a calibration sample, enter mass, and sample identification into Sample Login (F3).
   b. Press Loader Switch on front of furnace, after a short delay the lower electrode will open.
   c. Place two 761-739 tin pellets into a 619-895 graphite crucible.
   d. Place crucible on electrode pedestal.
   e. Press Loader Switch, the lower electrode will close and the outgas sequence will start automatically.
   f. When the outgas sequence is complete, an add sample message will appear in the lower left-hand corner of the instrument display. Press the Loader Switch and the loading head slide block will open.
   g. Place the 617-997 funnel into the open loading head and add sample taking care to make sure that all of the sample material is transferred into crucible.
   h. Remove funnel, press Loader Switch, the loading head slide block will close and the analysis sequence will start and end automatically.
   i. Repeat steps 3a through 3h a minimum of three times for each calibration/drift sample used.
   j. Calibrate or Drift Correct the instrument following the procedure outlined in the operator's instruction manual.
4. Analyze Samples.
   a. Weigh 0.15 to 0.35 g of sample, enter mass, and sample identification into Sample Login (F3).
   b. Proceed as directed in steps 3b through 3h.

Typical Results Manual Top Load Procedure – Chip Sample

Sample	*Mass g*	*H ppm*
NIST 176	0.2449	61.5
Ti Alloy	0.2409	60.1
Chip	0.2569	58.1
(H not certified)	0.2381	56.5
	0.2412	53.1
	0.2398	57.5
	0.2712	56.8
	0.2345	59.0
	0.2386	63.8
	0.2380	60.4
	X **=**	***58.7***
	s **=**	***3.0***

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