

ARGONNE
NATIONAL
LABORATORY

INTRA-LABORATORY MEMO

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TAB

ET-IPS

SUBJECT: Procedure for Hydrogen Analysis of Refractory Metals

1. SCOPE

This procedure is to be used for the determination of the hydrogen content of refractory metals using the LECO RH-404 hydrogen determinator that is located in glovebox #13 in Building 212, room DL-114. This procedure is based on the standard procedures in the instruction manual for the LECO RH-404 and specific methods recommended for refractory metals (ASTM E-1447, Standard Test Method for Determination of Hydrogen in Titanium and Titanium Alloys by the Inert Gas Fusion Thermal Conductivity Method).


This procedure supersedes the old procedure AGHCF-PROG-205, which is a subset of IPS-448-00-00.

2. SAMPLE SIZE

The maximum amount of hydrogen that can be processed by the RH-404 is 250 micrograms. Therefore, if the sample contains more than 250 wppm of hydrogen the sample must be smaller than the normally recommended 1 gram size. If smaller samples are used the samples should be weighed more accurately than the normal three-places if the same accuracy is to be achieved. Table 1 provides a guide for the sample size and weighing accuracy recommended for materials containing a wide range of hydrogen contents.

Estimated hydrogen content, wppm	Sample size, g	Weighing accuracy, g
10,000 (1 wt%)	0.005 to 0.02	± 0.00002
5000 (0.5 wt%)	0.01 to 0.04	± 0.00005
1000 (0.1 wt%)	0.05 to 0.2	± 0.0002
500	0.1 to 0.5	± 0.0005
100	1 to 2	± 0.002

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3. PROCEDURES

3.1. Sample Preparation

Samples are to be prepared in such a way that the true hydrogen content of the sample is not biased by the sample preparation method. For most metal samples with a homogeneous hydrogen content it is only necessary to make sure that sample surfaces haven't oxidized and the sample is dry. Usually filing the surfaces just before the analysis will provide an adequately clean sample.

3.2. LWR Cladding Samples

Hydrogen analysis of samples of cladding from irradiated fuel rods require special care to prevent loss of material from the ID and OD of the cladding that may contain hydrogen. The cognizant engineer should be consulted as to the sample preparation technique that is required for a particular sample. Samples from LWR cladding that have been subjected to high temperature oxidation tests may require a very detailed procedure such as that in IPS-377-01-00, "Work Plan for Preparing Samples for Oxygen Analysis from Zry Cladding after Steam Oxidation Tests at High Temperature."

3.3. Hydrogen Analysis Procedure

It is assumed that the operator of the LECO RH-404 is trained in the operation of the instrument. It is also assumed that the instrument has been properly setup to perform analyses on the type of material in question. For Zircaloy samples a channel titled "Titanium" has been set up with the proper parameters to analyze refractory metals. This channel should be used for the analysis of Zircaloy samples. It is also important to calibrate the instrument with a standard material of the proper type and hydrogen content. If possible a zirconium standard with a hydrogen content within about 100 wppm of the hydrogen content of the samples to be analyzed is preferred. The pedigree of the material used to calibrate the instrument will depend on the level of quality assurance required for the results. The person requesting the analysis should specify the level of QA required.

1. Check to make sure the power is on to the furnace and that the gas is on. If the gas has been turned off, do not perform analyses until the gas has been turned for at least one hour. The power to the analyzer (left portion of the equipment) should only be turned off if the instrument malfunctions.
2. Make sure the oven is on and up to operating temperature.
3. Perform analysis on three blanks using the channel associated with the type of material you are analyzing.
4. Enter an ID code for each blank (a minimum of three is required). [See page 5-5 of the LECO Manual for instruction on creating an ID Code.].
5. Enter a weight of 1 gram for each blank sample to be analyzed.
6. Place two tin flux tablets into a graphite crucible.
7. Perform an analysis using the manual analysis method.

3.4. Manual Analysis Method–Blanks

1. While the Analyze Menu is displayed, press the F7 key to highlight the MAN mode. (MAN should be in all capital letter: i.e. MAN/Auto.)
2. If the gas is OFF press the GAS key on the determinator to start gas flow.
3. Select an ID Code and press ENTER.
4. Press the LOADER CONTROL key on the furnace to open the sliding block and dispose of the used crucible. Place the crucible in a proper container if it is radioactive.
5. Clean the upper and lower electrodes using the 774-649 Brush and the throat using the 782-942 Brush.
6. Wipe the dust from the brush (plate near handle of the brush) and the general area of the electrode using an alcohol dampened wipe. Place the wipe in the radioactive waste barrel.
7. Select a new crucible containing two tin flux (accelerator) tablets and place the new crucible on the lower electrode.
8. Press the LOADER CONTROL key and the lower electrode closes.
9. Press the F5 (START ANALYSIS) key. The monitor will display the remaining outgas time (in seconds) behind the line "Manual Outgas Time-".
10. When the furnace completes outgasing, press the LOADER CONTROL key and the electrode will open.
11. Press the LOADER CONTROL key to close the electrode (no sample or standard is inserted for blank analyses).
12. Press the F5 (START ANALYSIS) key and the analysis will begin.
13. The results of the analysis will print automatically at the end of the analysis cycle.
14. Repeat steps (c) through (m) until the analyses of all the blanks are complete.
15. After all the blanks have been analyzed calculate the average blank value.
16. Press the F8 key to display the System Update Menu.
17. Press the F2 (BLANKS) key to enter the Blanks procedure.
18. Press the F1 (MANUAL BLANK) key to open the Manual Blank procedure. The display will prompt for the entry of the hydrogen blank value.
19. Enter the average hydrogen blank value calculated in step 6.
20. After entry of the new blank value, the display will prompt for recalculation of analysis results using the new blank value.
21. Press F8 to return to the System Update Menu.
22. Press F8 to return to the Analyze Menu.

3.5. Calibrate the System Using the Standard Sample Method

1. Enter the ID code information for a minimum of three standard samples. [See page 5-5 of the LECO Manual for instruction on creating an ID Code.]
2. Weigh the standard samples to be analyzed.
3. Analyze the standard samples using the manual analysis procedure.

3.6. Manual Analysis Method —Standard Sample

1. While the Analyze Menu is displayed, press the F7 to highlight the MAN mode. (MAN should be in all capital letter: i.e. MAN/Auto.)
2. If the gas is OFF press the GAS key on the determinator to start gas flow.
3. Create ID codes for all of the samples that are to be run in a batch
4. Select an ID Code and manually enter the weight of the sample by pressing the F2 (TARE) key, place standard sample on the balance. Enter the sample weight by pressing ENTER.
5. Press the LOADER CONTROL key on the furnace to open the sliding block and dispose of the used crucible. Place the crucible in a proper container if it is radioactive.
6. Clean the upper and lower electrodes using the 774-649 Brush and the throat using the 782-942 Brush.
7. Wipe the dust from the brush (plate near handle of the brush) and the general area of the electrode using an alcohol dampened wipe. Place the wipe in the radioactive waste barrel.
8. Add one tin flux (accelerator) tablet to a new crucible and place the new crucible on the lower electrode.
9. Press the LOADER CONTROL key and the lower electrode closes.
10. Press the F5 (START ANALYSIS) key. The monitor will display the remaining outgas time (in seconds) behind the line "Manual Outgas Time-".
11. When the furnace completes outgasing, press the LOADER CONTROL key and the electrode will open.
12. Place the standard sample in the crucible and then press the LOADER CONTROL key to close the electrode.
13. Press the F5 (START ANALYSIS) key and the analysis will begin.
14. The results of the analysis will print automatically at the end of the analysis cycle. You may also want to review the shape of the analysis curve at this time.
 - a. Bring up the diagnostic menu by pressing F8.
 - b. Press F3, Data Buffers.
 - c. Press F1, Screen Plot
 - d. Press F2, Print.
 - e. Press F8 to return to the Analyze Menu.
15. Repeat steps 4 through 14 until the analyses of all the standard samples are complete.
16. After all the standard samples have been analyzed, press the F8 (MORE) key to display the System Update Menu.
17. Press the F1 (CALIBRATION) key to enter the Calibration Procedure.
18. Press the F1 (STANDARD CALIBRATION) key to open the Standard Calibration routine. The display will prompt for entry of the hydrogen standard value.
19. To select a standard result which will be used in calculation the new calibration:
 - a. Press the F3 (INCLUDE RECORD) key to accept a result for calibration. Each time the F3 (INCLUDE RECORD) key is pressed, the standard result is highlighted and the cursor moves up one line.
 - b. To move the cursor to a standard to be included, press the F2 (NEXT LINE) key. Each time the F2 (NEXT LINE) key is pressed the cursor moves up one line.
 - c. Press the F1 (NEXT PAGE) key to display the next sixteen results in the Answer Stack.

- d. To view additional standard analysis information before choosing standards, press the ←(Shift/4) and →Shift/6) keys to view the following information:
 - i. ID Code, Hydrogen, Weight, Calibration, Blank, Analysis Time, Peak.
 - ii. ID Code, Hydrogen, Weight, Channel Time & Date.
 - iii. ID Code, Weight, Classification, Operator.
20. If a standard result is included in error:
 - a. Press the F5 (UP/DOWN) key and the F2 (NEXT LINE) key to line the highlight cursor up with the result to be removed.
 - b. Press the F4 (EXCLUDE RECORD) key to exclude the highlighted result.
21. Once all of the desired standard results have been selected, press the F7 (PROCESS RESULTS) key. The instrument uses the selected results to calculate the new calibration.
22. After the calculation of a new calibration, the display will prompt for recalculation of analysis results using the new calibration
23. Press F1 (ALL OF TODAY'S) key.
24. Press F8 (EXIT) key to return to the System Update Menu.
25. Press F8 to return to the Analysis Menu.
26. At this point laboratory samples can be analyzed on this channel.
27. It is assumed that the samples will be pre-weighed and properly prepared for analysis.

3.7. Manual Analysis Method

1. While the Analyze Menu is displayed, press the F7 key to highlight the MAN mode. (MAN should be in all capital letter: i.e. MAN/Auto.)
2. If the gas is OFF press the GAS key on the determinator to start gas flow.
3. Create ID codes for all of the samples that are to be run in a batch. [See page 5-5 of the LECO Manual for instruction on creating an ID Code.]
4. Select an ID Code and manually enter the weight of the sample by pressing the F3 (MANUAL WEIGHT) key. Enter the sample weight using the keyboard (the internal balance is not monitored) and then press ENTER.
5. Press the LOADER CONTROL key on the furnace to open the sliding block and dispose of the used crucible. Place the crucible in a proper container if it is radioactive.
6. Clean the upper and lower electrodes using the 774-649 Brush and the throat using the 782-942 Brush.
7. Wipe the dust from the brush (plate near handle of the brush) and the general area of the electrode using an alcohol dampened wipe. Place the wipe in the radioactive waste barrel.
8. Add tin flux (accelerator) to a new crucible and place the new crucible on the lower electrode.
9. Press the LOADER CONTROL key and the lower electrode closes.
10. Press the F5 (START ANALYSIS) key. The monitor will display the remaining outgas time (in seconds) behind the line "Manual Outgas Time-".
11. When the furnace completes outgasing, press the LOADER CONTROL key and the electrode will open.
12. Place the sample in the crucible and then press the LOADER CONTROL key to close the electrode.

13. Press the F5 (START ANALYSIS) key and the analysis will begin.
14. The results of the analysis will print automatically at the end of the analysis cycle. You may also want to review the shape of the analysis curve at this time.
 - a. Bring up the diagnostic menu by pressing F8.
 - b. Press F3, Data Buffers.
 - c. Press F1, Screen Plot.
 - d. Press F2, Print.
 - e. Press F8 to return to the Analyze Menu.
15. Repeat steps 4 through 14 until the analyses of all the samples are complete.

4.0 RECORD

1. All parameters and results must be entered into the Hydrogen Analysis Log book.
2. A copy of printed results shall be placed in the data books.