Simultaneous Oxygen, Nitrogen and Hydrogen Determination of Metals

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The inert gas fusion (IGF) principle has been used to determine oxygen, nitrogen and hydrogen contents of a variety of metals for many years. Simultaneous oxygen and nitrogen, as well as hydrogen only, analytical instruments are currently in use in a variety of laboratories throughout the World. Significant advancements in technology and method development by LECO Corporation has led to the introduction of the TCH600, a simultaneous oxygen, nitrogen and hydrogen determinator. A brief description of the IGF principle along with key features of the TCH600 is presented. Simultaneous oxygen, nitrogen and hydrogen data obtained on a variety of metals is illustrated. Sampling and sample preparation, as well as proper analytical techniques are explained.

Inert Gas Fusion

The inert gas fusion (IGF) principle was introduced in the mid-twentieth century. This method is also referred to as gas fusion analysis (GFA), or carrier gas hot extraction method (CGHE). The principle of operation is based on the fusion of a sample in a high-purity graphite crucible at temperatures up to, or in some cases exceeding, 3000° C in an inert gas such as helium. The typical IGF instrument is computer controlled and consists of an alloy-tipped water-cooled electrode furnace and a measurement unit containing the bulk of the electronics and detectors. A pre-weighed sample [nominal 1-gram for steel] is placed in a loading chamber located above the graphite crucible in the electrode furnace. After a short purge cycle, electric current is passed through the crucible heating it up to 3000° C while the carrier gas is flowing over it in order to "out-gas" [remove contaminants] the crucible. Following this out-gas cycle, the crucible temperature is lowered by reducing the current and the sample is transferred to the hot crucible by a sample drop mechanism. The sample melts and any oxygen in the sample reacts with carbon from the crucible to form carbon monoxide (CO), some carbon dioxide (CO_2) may also be released depending on the sample type and crucible temperature. Nitrogen in the sample is released as molecular nitrogen (N_2) while hydrogen elutes as hydrogen gas (H_2). These gasses are swept out of the furnace and on to the detectors by the carrier gas.[1] A cut-away view of a typical electrode furnace can be found in figure 1.
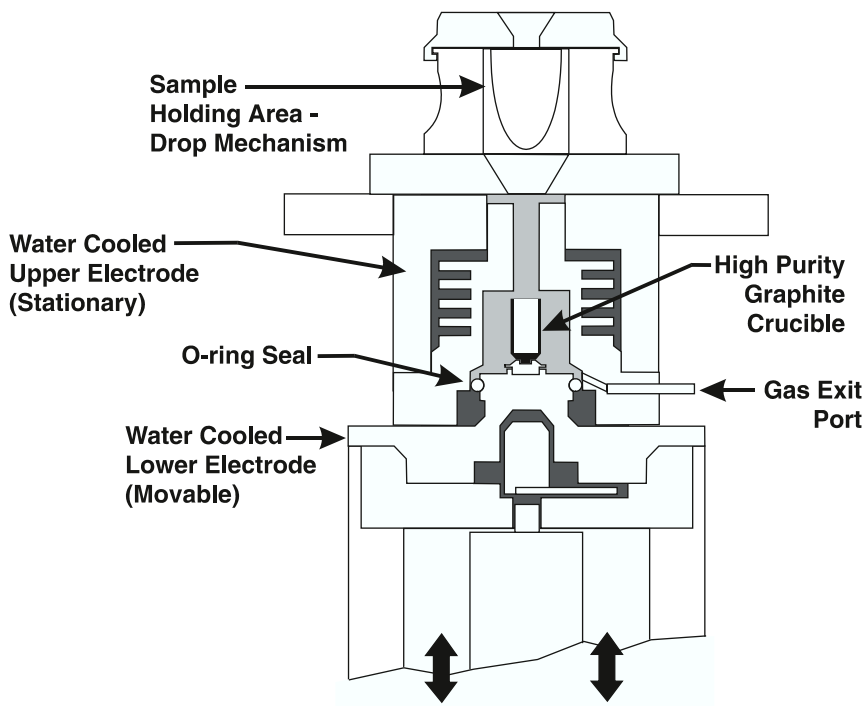
**Figure 1.** Cut Away of Electrode Furnace Crucible Area.

Detection

Oxygen is typically detected as CO, CO_2, or both using infrared (IR) detectors. CO and CO_2 absorb IR energy at specific wavelengths within the IR spectrum. Nitrogen, as N_2, and hydrogen, as H_2, normally are detected using a thermal-conductivity (TC) detector. A TC detector is a universal detector, responding to any gas that has a different thermal conductivity than the carrier gas.[2] Therefore separation or removal of gases other than the gas being measured and the carrier gas itself, is required. Dipolar gases such as N_2 and H_2 do not absorb IR energy, therefore, TC detectors are used for nitrogen and hydrogen measurement. The sensitivity of a TC detector is dependent on the thermal conductivity difference between the carrier gas and the analyte gas. Helium is used as a carrier gas for nitrogen measurement because of the large thermal conductivity difference between He and N_2. Helium and H_2 have similar thermal conductivity, therefore argon (Ar) is typically used as a carrier gas in an instrument designed to measure hydrogen. Since Ar and N_2 have similar thermal conductivity, low levels of nitrogen cannot be accurately determined using Ar as a carrier gas. A TC cell is a very sensitive and generally linear detection device, however it is a universal detector that cannot tell the difference between various gases unless they are separated (or removed) by some means. Gases such as CO, CO_2 and N_2, must be either removed or separated from the H_2 for proper hydrogen measurement. In a typical hydrogen determinator using Ar as a carrier gas, the CO released from a sample is converted to CO_2 by passing it over Schutze reagent (iodine pentoxide on treated silica gel). This conversion takes place at room temperature and does not effect either H_2 or N_2 released from a sample. The CO_2 is subsequently removed

using sodium hydroxide (on a clay base). The N_2 cannot be removed; therefore it is separated from the H_2 by passing the gas stream through a long column. The H_2 elutes from the column first and is measured by the TC cell. The N_2 elutes from the column approximately 45 seconds after the hydrogen has been measured and is not measured. For these reasons, simultaneous nitrogen and hydrogen determination using TC detectors is not feasible. Figure 2 contains a cut-away diagram of a typical TC detector cell. In contrast, IR detectors used to determine oxygen, as CO or CO_2, will function well in a variety of carrier gases. A typical IR detection cell is illustrated in figure 3. A modern simultaneous oxygen and nitrogen determinator uses both IR and TC detectors and a helium carrier gas. Oxygen is measured as CO, CO_2, or both, using IR detectors, while nitrogen is measured using a TC detector. The CO is converted to CO_2 using heated copper oxide (CuO) which also converts any H_2 to water (H_2O). The CO_2 and H_2O are removed with sodium hydroxide (on clay) and magnesium perchlorate (Anhydrone) respectively, while the N_2 passes through to the TC cell for measurement.
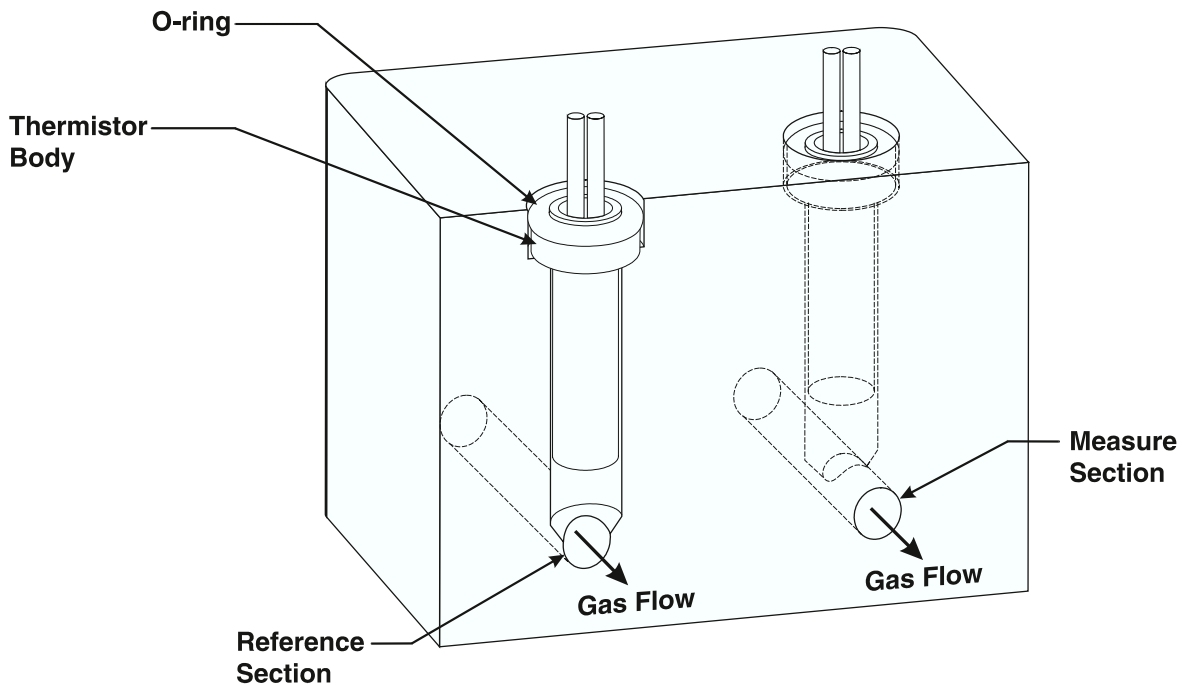

Figure 2. Typical Thermal Conductivity Detection Cell.
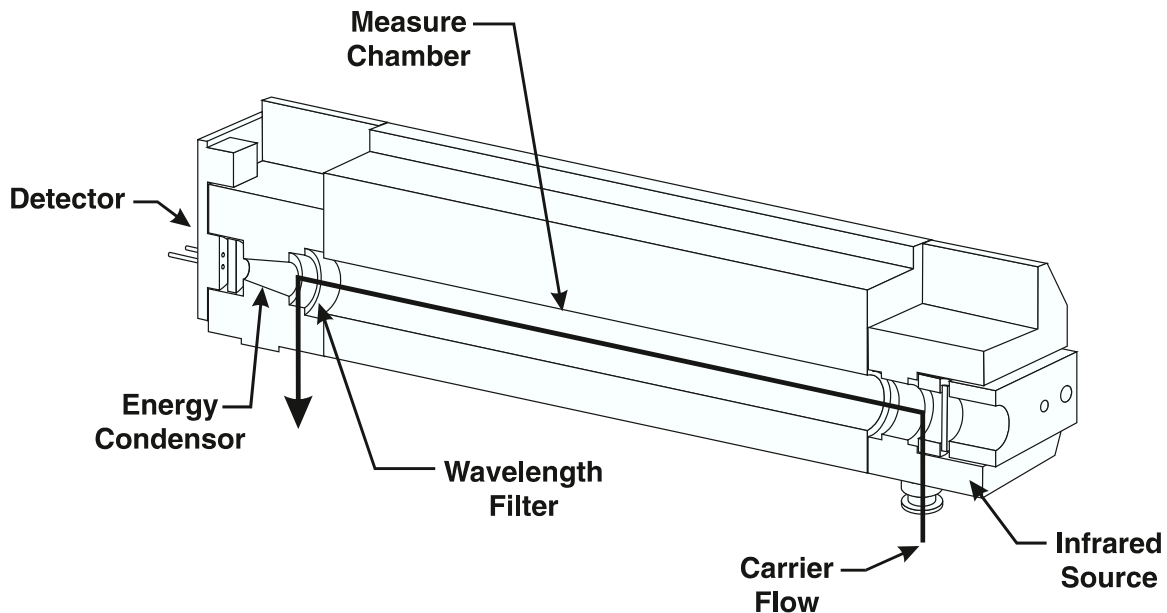
Figure 3. Typical Infrared Detection System.

New Detection Scheme

LECO Corporation, St. Joseph, MI, USA, has introduced the TCH600 simultaneous oxygen; nitrogen and hydrogen determinator based on the IGF principle. This instrument incorporates newly designed IR detectors to measure oxygen as CO and CO_2, hydrogen as H_2O, while nitrogen as N_2 is measured using a TC detector. Other notable features include; mass flow control, a dynamic flow compensation system designed to maintain flow system integrity when high oxygen samples are analyzed, improved signal-to-noise ratios on all detectors, and increased dynamic range capability. Helium is used as the carrier gas to maintain good nitrogen detection sensitivity. In this system, oxygen is measured as CO and CO_2 using three separate IR detectors that communicate through the computer which selects the appropriate combination of detectors depending on the level of oxygen. The CO is converted to CO_2 by passing it over heated CuO, likewise, the H_2 released from a sample is converted to H_2O. An IR detector measures the H_2O and appropriate traps remove the CO_2 and H_2O while the N_2 passes on to a TC cell for measurement. This detection scheme eliminates the need for a column to separate H_2 from N_2. Total analysis time on the TCH600 for simultaneous O, N, and H determination is 2 – 3 minutes. A simplified flow diagram for the TCH600 is illustrated in figure 4.
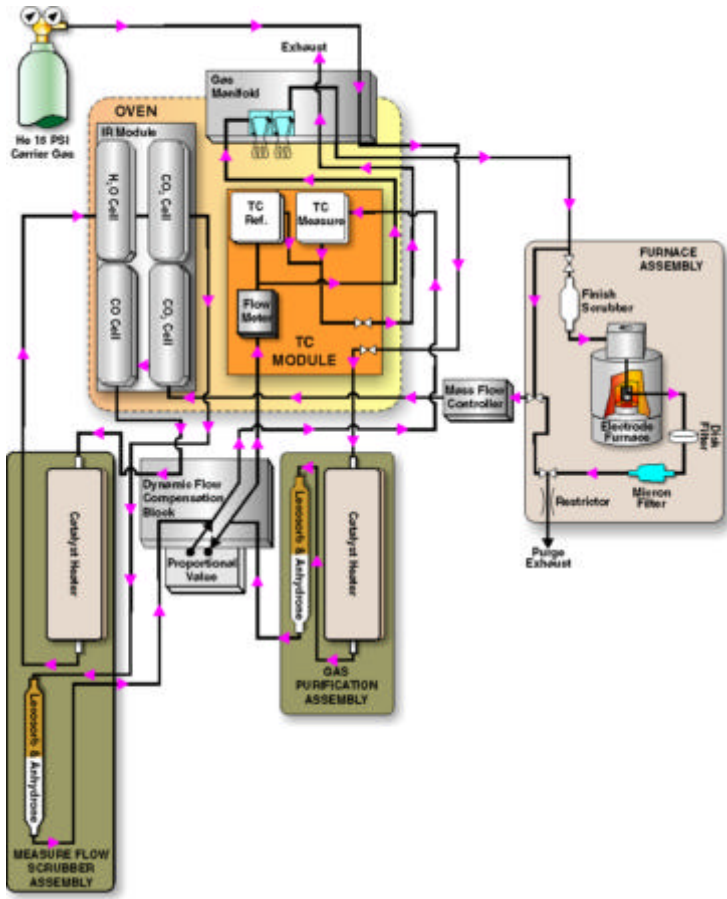
Figure 4. TCH600 Flow Diagram

Calibration

Inert gas fusion instruments must be calibrated with samples of known concentrations of the analytes of interest. Calibration is a comparison of a measurement standard with another standard to report or eliminate, by adjustment, any variation or deviation in the accuracy in the item being compared.[3] The LECO TCH600 is factory linearized making single-point linear (fixed-at-origin) calibrations possible. The TCH600 also has the ability to use multi-point calibrations as well. This permits the operator to use multiple calibration standards at various levels of analyte concentration. The accuracy of the instrument is greatly influenced by the accuracy of the standard(s) used. Accuracy is defined as the closeness of a measured value to the true value. An example of a multi-point calibration is illustrated in figure 5.
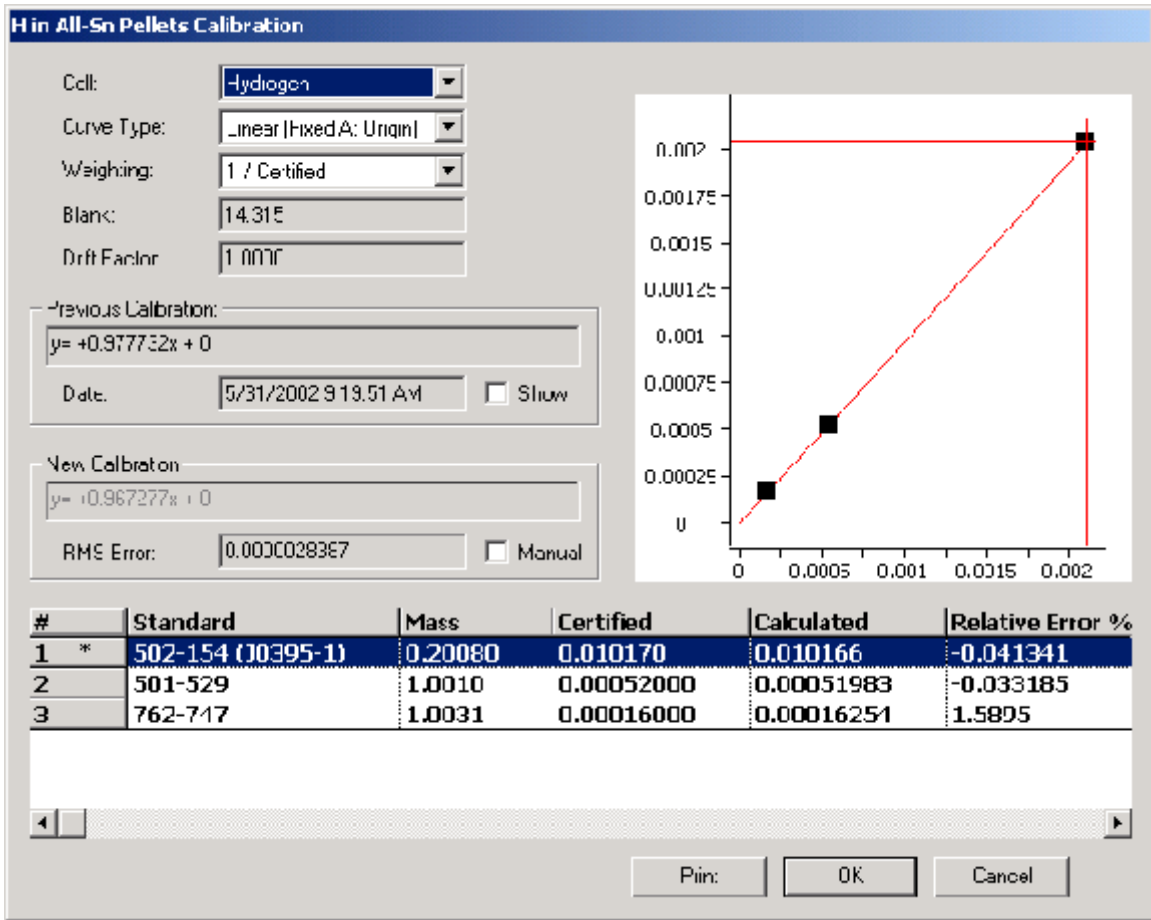
Figure 5: Example of Multipoint Calibration

Sampling and Sample Preparation

Sampling and sample preparation are very important factors for proper analysis. A variety of sample shapes and forms such as; pins, cubes, balls, chips, granular and powdered materials can be analyzed by the IGF method. However, solid samples are the preferred sample form especially for oxygen and hydrogen determination. The sample must be representative of the material being analyzed. ASTM E 1806 [4] and ISO 14284 [5] are sampling and sample preparation documents for steel and iron that are excellent sources of information. Traditional methods used for sampling of molten steel and iron for oxygen and nitrogen determination are not suitable for hydrogen determination because of the mobile nature of hydrogen. Special precautions must be taken when sampling molten steel and iron for hydrogen determination. The sample must be immediately quenched in cold water and stored in liquid nitrogen, a mixture of acetone and solid carbon dioxide (dry ice), or dry ice in order to minimize losses of hydrogen from diffusion. Losses of oxygen and nitrogen are typically not a problem. The sample that is taken for hydrogen and stored in a refrigerant can also be used for oxygen and nitrogen determination. However, the sample that is typically taken for oxygen and/or nitrogen is generally allowed to cool slowly and as such is not suitable for hydrogen determination due to hydrogen loss. In any event, the surface of the sample must be prepared by filing (abrading) or light grinding using care not to overheat the sample.

After the surface of the sample has been has been prepared it is washed in acetone and dried with warm air. The sample should be analyzed immediately after preparation. Table 1 contains data comparing O, N and H results obtained using a LECO TCH600 on samples taken from molten steel using a 6 mm evacuated glass pin tubes. The samples were immediately quenched in water and stored in a refrigerant until analysis. One set of data is from samples removed from the refrigerant, abraded with a file, washed in acetone and analyzed. The other set is from the same samples, however they were removed from the refrigerant and allowed to remain at room temperature for two days before sample preparation and analysis. You will note the lower hydrogen content of the samples that were analyzed after two days at room temperature. This illustrates the mobility of hydrogen in steel and the subsequent losses over time. The oxygen and nitrogen contents did not change. Sample weights were 1-g (nominal).

Sample	PPM O	PPM N	PPM H	Comments
Steel # 1	75	126	6.29	Stored in refrigerant
	79	129	5.27	"
Steel # 1	85	131	2.42	After 2 days at room temperature
	79	129	1.90	"
Steel # 2	64	129	4.88	Stored in refrigerant
	66	128	4.59	"
Steel # 2	61	129	3.60	After 2 days at room temperature
	66	129	3.14	"
Steel # 3	73	127	5.02	Stored in refrigerant
	77	129	4.90	"
Steel # 3	78	129	1.04	After 2 days at room temperature
	78	127	2.09	"

Table 1 – Example of hydrogen mobility in steel

The importance of sample surface preparation is illustrated in table 2. This table compares data from a 1018 steel rod sample analyzed as received and after surface preparation (abrading with file). A LECO TCH600 was used to obtain this data. You will note a significant difference in the oxygen and hydrogen data indicating surface contamination. Oxides and drawing lubricants are present on the surface of many wire and rod samples. The nitrogen results are comparable however.

	As Received			**Abraded**		
Sample	**PPM O**	**PPM N**	**PPM H**	**PPM O**	**PPM N**	**PPM H**
1018 steel	136	96	16.7	31	96	0.25
Rod	144	93	15.1	30	95	0.16
	160	94	15.7	30	93	0.16
	150	89	14.9	30	94	0.15
	140	94	13.4	29	92	0.16
X =	*146*	*93*	*15.2*	*30*	*94*	*0.18*
s =	*9.1*	*2.4*	*1.21*	*0.7*	*1.6*	*0.04*

Table 2 – Importance of surface preparation on steel

Sampling and sample preparation of reactive/refractory metals such as titanium and zirconium is somewhat different than that for steel and iron. Hydrogen is not mobile in titanium and zirconium; therefore storage of samples in a refrigerant is not required. However, it is important to keep the sample cool during machining, cutting or sectioning. Sample preparation for titanium and zirconium has been somewhat different for oxygen, nitrogen and hydrogen determination primarily since each element has been determined separately. Typically titanium and zirconium samples are chemically etched to remove surface contamination when oxygen and nitrogen determination are performed. In certain cases, chemical etching may introduce hydrogen into some samples. ASTM E 1409, Standard Test Method for Determination of Oxygen in Titanium and Titanium Alloys by the Inert Gas Fusion Technique[6], allows either chemical etching or filing (abrading) the test specimen. ATSM E 1937, Standard Test Method for Determination of Nitrogen in Titanium and Titanium Alloys by the Inert Gas Fusion Technique[7], requires etching the test specimen. ASTM E 1447, Standard Test Method for Determination of Hydrogen in Titanium and Titanium Alloys by the Inert Gas Fusion Thermal Conductivity Method[8], indicates that the test specimen can be abraded with a clean file followed by rinsing in acetone and air-drying. This difference in sample preparation does raise some question when simultaneous O, N and H determination is performed. However, filing the surface of the test specimen will yield appropriate O, N and H results. Table 3 contains data obtained on a titanium sample comparing sample preparation techniques. A LECO TCH600 was used for this test. The "abraded" sample was filed with a flat mill file, rinsed in acetone and dried with warm air. The "etched" sample was immersed in a solution of 15 ml of 1:1 HNO_3: H_2O + 10 drops of 49% HF, for 5 minutes, rinsed in H_2O, followed by acetone and air drying. The as received samples were not prepared. Sample weights of ~ 0.15 grams were used. Although there is only a slight improvement, the samples that were abraded yielded the best results.

	Abraded			Etched			As Rec'd		
Sample	PPM O	PPM N	PPM H	PPM O	PPM N	PPM H	PPM O	PPM N	PPM H
Titanium	1152	31	21.6	1154	27	30.3	1172	36	25.1
	1139	34	23.5	1185	32	31.2	1183	35	23.8
	1157	33	22.6	1144	27	21.7	1167	31	23.9
	1149	31	21.6	1153	30	21.4	1160	28	22.0
	1157	31	23.3	1156	34	22.5	--	--	--
X =	*1151*	*32*	*22.5*	*1158*	*30*	*25.4*	*1171*	*33*	*23.9*
s =	*7*	*1*	*0.9*	*16*	*3.1*	*4.9*	*10*	*4*	*1.1*

Table 3 – Comparison of sample preparation techniques on Titanium

Additional Results From The LECO TCH600

Table 4 contains results obtained on a LECO 502-416 plated steel pin sample with O, N and H values established. Note the excellent precision obtained on all three elements determined simultaneously on the TCH 600.

Sample	Weight	PPM O	PPM N	PPM H
LECO 502-416	1.0026	30	447	3.0
Steel Pin	1.0006	31	454	3.2
@ 29 ppm O	1.0024	28	448	3.3
450 ppm N	1.0013	30	453	3.3
3.2 ppm H	1.0005	29	452	3.2
	1.0004	30	454	3.1
	1.0007	29	453	3.1
	1.0034	30	446	3.2
	1.0008	29	451	3.1
	0.9989	30	451	3.3
	X =	*30*	*451*	*3.2*
	s =	*0.6*	*3*	*0.09*

Table 4 – Typical data on a steel calibration sample analyzed on a TCH600

Table 5 includes data obtained from a LECO 762-741 titanium calibration standard. This material is typically used to calibrate LECO hydrogen determinators. Oxygen and nitrogen values have not been established. The samples were analyzed using 1-g nickel flux to facilitate nitrogen recovery. Approximately 0.12-g sample weights were used.

Sample	Weight	PPM O	PPM N	PPM H
LECO 762-741	0.1369	462	108	20.9
Titanium	0.1419	468	109	20.4
@ 21 ppm H	0.1244	476	115	21.8
	0.1122	480	120	20.9
	0.1310	469	121	20.3
	0.1154	468	116	21.4
	0.1253	475	119	20.7
	0.1206	470	124	21.7
	0.1159	473	115	20.4
	0.1037	485	131	21.8
	X =	*473*	*118*	*21.0*
	s =	*7*	*7*	*0.6*

Table 5 – Typical data on titanium analyzed on a TCH600

The results found in Table 6 are from a zirconium pin sample with a known oxygen value of 0.13 %. The procedure was the same as that used for the titanium sample illustrated in table 5.

Sample	Weight	PPM O	PPM N	PPM H
LECO 502-047	0.1086	1312	28	19.1
Zirconium Pin	0.1111	1308	28	19.8
@ 1300 ppm O	0.1103	1305	29	19.6
	0.1141	1313	28	20.0
	0.1110	1301	25	18.6
	0.1096	1313	29	20.0
	0.1125	1309	29	19.7
	0.1052	1310	27	19.3
	0.1003	1308	27	19.6
	0.1132	1316	29	20.4
	X =	*1310*	*28*	*19.6*
	s =	*4*	*1.2*	*0.49*

Table 6 – Typical data on zirconium analyzed on a TCH600

Summary
The IGF method is an effective method for accurate determination of O, N, and H in a variety of metals. Recent developments by LECO Corporation have resulted in the introduction of the TCH600, a simultaneous O, N and H determinator that offers significant analytical advantages. Likewise, a single determinator reduces costs, improves throughput, as well as saves valuable bench space.

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