Carbon and Sulfur Determination—LECO Induction Furnace Instruments

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General Overview

The majority of metals and their alloys will burn in oxygen if heated to a high enough temperature. The carbon in the sample is oxidized to carbon dioxide (CO_2) while the sulfur is converted to sulfur dioxide (SO_2). CO_2 and SO_2 can then be measured by infrared (IR) detectors. Early combustion methods utilized the resistance heated furnace, but by the mid-1900s it had been replaced by the high frequency (HF) induction heated furnace for increased speed and accuracy.

Often, combustion of inorganic materials can be hastened through the use of an ***accelerator***. The purpose of the accelerator is to ignite or set fire to the sample. It can also double as a ***flux*** to dissolve any oxide skins making the melt thoroughly fluid. A completely fluid melt is essential in order to oxidize the carbon and sulfur in the sample in a relatively short time frame.

The use of an induction furnace is the preferred method of heating and combusting metals for carbon and sulfur analysis. In an induction furnace, induced electrical currents heat the sample and accelerator; this transfer of power is commonly referred to as ***coupling*** with the electric field. Most metals couple well; however, most oxides do not. As combustion proceeds and the metals are transformed to oxides, the combustion temperature will drop significantly resulting in poor recovery. Certain metals such as copper and iron, as well as their oxides, will couple in an HF furnace thereby maintaining sufficient temperature to permit complete oxidation of the carbon and sulfur present in a sample.

Accelerators

Several metals have been used as accelerators over the years, however only a few have been adopted for routine use. Certain advantages are found with each accelerator and in many cases they are combined for optimum performance. When analyzing nonconductive materials such as ceramics and many other nonferrous samples, the use of an accelerator with good inductive capabilities, such as iron, is essential.

Following is a description of various accelerators commonly used on an induction furnace.

Accelerator	**Application**
Copper Chip	Excellent accelerator/flux for carbon determination (particularly in ultra low carbon determination) in steel, nonferrous metals and alloys. Usually combined with iron chip when nonferrous materials are analyzed. Copper accelerator is normally not recommended for sulfur determination in ferrous materials, but it can be used for sulfur determination using the low temperature technique described in the Analytical Procedures and Special Applications (Copper base, page 16) section of this document.
Iron Chip	Used for both carbon and sulfur determination in some ferroalloys as well as nonferrous materials. Usually combined with tungsten, copper, or tin accelerators.
Tungsten	Good accelerator for plain carbon steels providing excellent combustion characteristics when combined with tin.
Tin	Typically used as an additive to tungsten, copper and iron. Burns readily producing a lot of heat. It can lower the ***liquidus*** temperature of the melt.

Accelerator	**Application**
Vanadium Pentoxide	Excellent accelerator for difficult to burn materials. It will produce very high combustion temperatures while also contributing oxygen to the combustion process. It may be used in conjunction with tungsten metal.

LECO supplies a variety of high purity accelerators for use in induction furnace carbon and sulfur determinators. Following is a description of the most commonly used accelerators.

Part No.	**Description**	**Application(s)**
501-263	**Copper Chip,** -20 to +30 mesh	General use in carbon determination.
502-492	**High Purity Copper Chip,** -20 to +30 mesh	High purity copper for low carbon determination.
501-457	**Tin Coated Copper Chip,** -20 to +30 mesh	Carbon determination for hard to burn samples such as materials containing refractory carbides.
501-076	**Tin Metal,** -20 to +30 mesh	General application, typically used with tungsten, iron or copper accelerators.
501-077	**Iron Chip,** -6 to +20 mesh	General application, typically used with tungsten or tungsten/tin accelerators.
502-231	**High Purity Iron Chip,** -6 to +20 mesh	Ultra low carbon and sulfur determination; lower and more consistent blanks than the 501-077 accelerator.
501-078	**Low Sulfur Iron Powder**	Low sulfur determination on LECO iodate titrators. Normally not used for carbon determination due to higher carbon content of this accelerator.
763-266	**Lecocel,** -20 to +40 mesh tungsten metal	Carbon and sulfur determination of plain carbon steels. Can be used in conjunction with iron or other accelerators when nonferrous and/or poor coupling materials are analyzed.
763-263	**Lecocel III,** -12 to +20 mesh tungsten metal	Carbon and sulfur determination in plain carbon steels and copper base materials. This was the original Lecocel used on older LECO induction furnace instruments. Its coarser mesh will couple better on lower frequency HF furnaces.
501-008	**Lecocel II,** -12 to +40 mesh tungsten/tin mixture	General application in carbon and sulfur determination for steel alloys and nickel and cobalt base alloys. Can be used in conjunction with iron chip accelerator for nonferrous or hard to burn materials.
502-173	**Lecocel II HP,** -12 to +40 mesh high purity tungsten/tin mixture	Ultra low carbon and sulfur determination; lower and more consistent blanks than the 501-008 accelerator. Can be used in conjunction with high purity iron chip for nonferrous or hard to burn materials.

Ceramic Crucibles and Covers

Ceramic crucibles are used to contain the sample and accelerators during the combustion process. Ceramic covers are used to reduce combustion ***splatter***. LECO supplies several types of these crucibles and covers, which are described next.

528-018 Ceramic Crucible, standard: This is the most commonly used crucible in LECO induction furnace units for carbon and sulfur determination. This crucible can be used with LECO autoloaders.

528-018HP Ceramic Crucible, high purity: High-purity crucible with ultra-low sulfur content. Recommended for ultra-low sulfur determination.

528-038 Ceramic Crucible, heavy duty: These crucibles incorporate a heavy side-wall and bottom design to prevent crucible burn through due to extended burn times. They are typically used on older LECO induction furnace units such as titrators. They can be used on modern LECO induction furnace units, however, they will not work well with LECO autoloaders.

528-028 Filtering Crucible, standard: This filtering crucible has the same dimensions as the 528-018; however, it is porous enough to filter aqueous solutions and trap graphitic carbon. This crucible can be used with LECO autoloaders.

528-030 Filtering Crucible, larger and tapered: These are the original filtering crucibles used for graphitic carbon determination in cast iron. They are larger than the 528-018 or 028 crucibles and are tapered to facilitate filtration. Due to their larger size and taper they are not designed to work with LECO autoloaders.

619-880 Ceramic Cover, 10 mm hole: This cover has a 10 mm hole in the center to allow for improved gas flow to and from the sample while minimizing splatter and sample blow-out. They can be used with 528-018, 018HP, 028, and 038 ceramic crucibles.

528-040 Ceramic Cover, 4 mm hole: This cover has a 4 mm hole in the center. It is used on older LECO combustion instruments where extended burn times were common. It is not recommended for modern combustion/IR detection systems since the small hole restricts the combustion process.

528-042 Porous Ceramic Cover: This cover is designed for older LECO titrators and is not applicable to newer combustion units. It restricts the combustion too much to be used on modern carbon and sulfur determinators.

529-036 Crucible Liner: This liner is made of alumina (Al_2O_3) and is intended to be used for acid treatment of soils, rocks and ore type materials where acid is added directly to the sample to remove carbonates. The liner does not absorb much acid and after acid treatment of the sample and drying, it is inserted into the 528-018 crucible where accelerator is added and the analysis proceeds. The liner will crack upon heating, but because it is inside of the 528-018, it will not cause any problems. The standard LECO crucible cannot be used alone because it will absorb too much acid. LECO filtering crucibles are not normally used for this application because they may filter some of the noncarbonate carbon in soils through the crucible.

Analytical Considerations

There are several areas of the analytical process that need to be controlled in order to best determine carbon and sulfur by combustion. Most of the methodology has been documented in various published works including ASTM E1019 and ISO procedures 9556 & 4935. In this section we will review the techniques that are important to achieve the most accurate and precise results when performing combustion carbon and sulfur determination.

Detection Capability (instrumental)

A major analytical consideration is the ability of the analytical instrument to accurately measure the CO_2 and SO_2 produced during the combustion of samples. This ability can be determined by ***dosing*** known volumes of CO_2, SO_2 or mixtures of these gases directly into the instrument. LECO carbon and sulfur determinators such as the CS-444 and CS600 have built-in gas dosing capabilities. Additionally, dosing can routinely be used for diagnostic purposes. Gas dosing facilitates the evaluation of a particular instrument's detection capabilities apart from the influence of other parameters such as crucibles, gas supply, accelerators, combustion characteristics, sample homogeneity and the like. Data obtained from gas dosing has been used to confirm instrumental performance specifications.

Oxygen (combustion and carrier gas)

The oxygen is used to fuel the combustion process and act as a carrier gas, but it is an important aspect of the analytical scheme that is often overlooked. Normal grades of oxygen contain impurities that will affect accurate carbon and, to a lesser extent, sulfur determination. Impurities such as CO_2 are easily removed at ambient temperatures with reagents such as Lecosorb (sodium hydroxide/clay). However, a more common impurity is methane. Methane cannot be removed as easily and during the combustion process it will be oxidized to CO_2 and H_2O. The amount of oxidation varies depending on the temperature of the crucible and sample, and the time of analysis. This effect is very problematic for accurate low carbon and sulfur determination. During the determination of the analytical ***baseline***, oxygen is passing through the instrument's gas system over a cold crucible and through the IR cells. If this oxygen contains methane, the IR cells do not detect it. During the combustion of the sample, the crucible, sample and accelerator reach temperatures in excess of 1500 C°. These temperatures are capable of oxidizing some of the methane to CO_2 and H_2O. This CO_2 will be detected by the carbon IR detector biasing the results high. The contribution of the methane cannot be blanked out because it varies depending on the temperature, burn time and methane concentration in the oxygen. The two alternatives to this problem are: 1) use higher grades of oxygen such as zero grade, or 2) pass the incoming oxygen over a heated catalyst furnace to oxidize the methane (as well as other hydrocarbon gasses) to CO_2 and H_2O which can be readily removed with Lecosorb and Anhydrone (magnesium perchlorate). Option one is easily done; however, the cost per analysis will be somewhat higher due to increased cost of higher purity grades of oxygen. The second option is more cost effective in the long run requiring the installation of an in-line gas purifier on the oxygen supply, such as the LECO CF-10. On some LECO models like the CS-444 and CS600, the gas purifier is built into the instrumentation. These purifiers require little if any maintenance and the copper oxide used in them will last for several years.

Ceramic Crucibles

The ceramic crucibles (covers) used during the combustion of samples can add to analytical variability if they are not properly prepared. The standard 528-018 ceramic crucible, weighs ~18 g on average. The samples analyzed typically weigh 1 g or less. This means only 1 ppm of carbon (or sulfur) in or on the crucible will result in 18 µg of carbon (or sulfur) being added to the analytical result. However, the contamination is not consistent. Some crucibles will have no carbon or sulfur in (or on) them, while others will have up to 25 micrograms. If the crucibles are handled with bare hands, contamination will be increased, resulting in even more erratic results. To account for this, ASTM and ISO procedures call for preheating or baking off of the crucibles. This is typically done in a muffle or tube furnace at temperatures of at least 1000 C° for 2 hours or at more than 1250°C for at least 15 minutes. Then they are removed from the heat, allowed to cool on a tray, and placed in a desiccator. The crucibles are then handled with clean tongs and removed individually from the desiccator for use. They must not be allowed to remain in an open-air environment too long as they can be contaminated with air-born particulate (dust). Table 1 illustrates carbon and sulfur data obtained on ceramic crucibles used in the nonbaked, baked and handled condition. You can easily see the importance of baking off the crucibles. Although this procedure is typically reserved for low carbon (<0.1%) and sulfur (<0.01%) determination, the effects can be noticed on high carbon results when smaller sample weights are used. For example, customers who need to accurately determine carbon in tungsten carbide (WC) routinely require absolute precision (1 sigma) of <0.01%. Since the nominal sample weight of WC analyzed is ~0.25 g, any variation in the crucible (determined at 1 g) is magnified four times. If the non-baked crucible blank has deviations of 0.0015% at a 1 g weight entry, this variation will be +/- 0.006% when 0.25 g samples are analyzed. This variation due to the crucible is 60% of the desired precision! Baking off the crucibles eliminates the variation caused by the crucible. However, not all crucibles are created equal. We have come across some ceramic crucibles produced by competitors that even after baking off, have high and erratic blanks.

Table 1—Impact of Preheating Crucibles on Carbon/Sulfur Results

	Baked		**Not Baked**			
			Not Touched		**Touched**	
	C PPM	S PPM	C PPM	S PPM	C PPM	S PPM
CS444LS High Purity Iron Standard @ 5 PPM C 2 PPM S	4.6	2.5	13.5	3.1	40.1	3.9
	4.6	2.0	12.3	3.8	24.4	3.7
	4.8	1.8	11.5	3.2	24.6	3.5
	4.9	1.5	12.5	3.2	22.9	3.8
	5.8	2.7	12.8	3.8	34.4	3.3
	4.8	2.5	12.6	3.8	22.8	4.4
	4.5	2.2	11.6	4.1	41.5	3.8
	3.6	1.5	18.5	2.3	21.6	3.7
	6.0	2.0	12.0	3.9	32.5	4.2
	6.0	1.6	16.0	4.2	31.4	4.3
Average (PPM)	5.0	2.0	13.3	3.5	29.6	3.9
Std Dev	0.75	0.45	2.20	0.59	7.40	0.34

Accelerators

As was discussed in an earlier section, accelerators play an important role in proper combustion by an induction furnace. The purity and consistency of the accelerator is very important. An accelerator should be low in both carbon and sulfur content, as well as have any carbon and/or sulfur impurity evenly distributed. This will allow for proper blanking of the accelerator. We will discuss the blank issue in a later section. Another area of concern is the handling and storage of accelerators. Accelerators can be packaged in a variety of containers in a variety of sizes. It is important to protect the accelerators from inadvertent contamination. A subtle but common source of contamination is leaving the lid of the accelerator container off for extended periods of time, allowing airborne particulate (dust) to contaminate the accelerator. This contamination is typically more evident for carbon than sulfur, but any variability contributed by the accelerator will be added to the variability inherent in the sample. The amount of accelerator used for each analysis should be kept consistent within the method. Normally, 1 g amounts of each accelerator are used. In rare cases, it may be possible to adequately combust a sample without accelerator. In ultra low sulfur determination of high temperature nickel base alloys, it may be possible to analyze turnings of these alloys without accelerator. The main desire is to reduce variation due to the sulfur variability in the accelerator. Accurate sulfur determination at or below 1 ppm is of interest in these specialty alloys. This is indeed the exception rather than the rule, as extreme care must be used to assure that complete oxidation of the sulfur in the sample is achieved.

Sampling and Sample Preparation

In order to obtain suitable results, a representative sample must be analyzed. Sampling can be quite involved and a thorough understanding of sampling techniques is a prerequisite for obtaining a usable and representative sample. There are two comprehensive sampling documents containing valuable sampling information for steel and iron; ASTM E 1806 and ISO 14284. LECO induction furnace carbon and sulfur determinators can combust solid, chunk, drillings, millings, chip and powdered samples. This makes the sampling issue somewhat less complicated. However, two areas of concern are: 1) surface contamination in ultra low carbon determination and 2) carbon and sulfur determination in as-cast iron. First, samples with large surface areas, such as chips and drillings, can contribute to erratic results due to surface contamination. This makes solid samples the preference. In the second case, as-cast (Grey) iron has a significant amount of graphitic carbon content that is separated from samples during drilling, milling, and crushing. It is essential that ascast samples of cast iron be from solid “slices” at least 3 mm thick. For more information refer to Appendix A, “Comparison of Sample Preparation Techniques used for Combustion of Cast Iron Samples As-cast vs. Chilled.” Sample preparation can be an important aspect of the analytical scheme. Surface contamination can have a significant impact on the data obtained. Solid samples can be abraded either with a flat file or ***linishing*** using abrasive rotating disk or continuous belt type grinder/polishers. Samples may be washed in alkaline cleaners, rinsed in solvents, vapor degreased, chemically etched, or a combination of any of these. For ultra low carbon determination in automotive body steel, different forms of sample preparation have been shown to make a difference. Table 2 contains carbon data comparing various surface treatments applied to automotive body steel.

Table 2—Evaluation of various sample preparation methods on low carbon steel sheet for carbon analysis

Sample Preparation	**n**	**C ppm (avg.)**	**Std. Dev.**
Rinsed in acetone	10	16.89	0.91
Abraded+acetone	10	15.97	0.3
Etched*	10	15.2	0.42
Pre-heated**	10	16.8	0.62

**Etched in mixture of* H_2O_2 *(30%) and HF (48%), (14:1)*
***Pre-heated for 10 minutes at* 450^oC *in air.*
Results based on 1 gram samples analyzed on the LECO CS-444.

Blank

A ***blank*** is the signal obtained during an analysis that cannot be attributed to the sample. The blank is due primarily to impurities in the oxygen supply, accelerator and crucible. In order to properly account for this blank, the average amount of contribution from these sources must be determined. It should be noted that while the average contribution of carbon and sulfur can be compensated for, the variability due to inconsistencies in these sources cannot be removed. It is the variability that is the most detrimental to accurate low carbon and sulfur determination. There are basically two ways in which the blank is determined; accelerator and crucible only, and accelerator, crucible and a standard sample. Normally a 1 g weight entry is made into the weight compensation portion of the instrument. In the first case, the proper amount of accelerator is added to the crucible and analyzed. In the second case, the proper amount of accelerator along with a 1 g sample of a low carbon and/or sulfur standard is analyzed. An advantage of the second case is to provide the same combustion temperature and crucible penetration as a normal sample analysis. A disadvantage of the second case is that the variability associated with the standard is transferred to the blank. LECO’s Technical Services Laboratory has found that when crucibles have been properly baked off and high purity accelerator is utilized, the use of a low carbon and sulfur standard material to determine the blank is not needed. This procedure does not necessarily apply when crucibles are not baked off. Without a 1 g sample of steel or iron in the crucible, there is less heat and virtually no penetration into the crucible which could cause the blank to be understated or inaccurately determined. In either case, a minimum of three replicates is analyzed to determine the blank. The blank is calculated by determining the difference between the total and the certified, or expected carbon and/or sulfur content of the standard. The crucibles must be handled with clean tongs to avoid recontamination. The blank should be checked several times throughout the day to verify it has not drifted.

Calibration

Combustion carbon and sulfur instruments must be calibrated with samples of known carbon and sulfur concentrations. Calibration, as defined in NIST Special publication 260-100, is a comparison of a measurement standard or instrument with another standard or instrument to report or eliminate, by adjustment, any variation or deviation in the accuracy of the item being compared. All LECO combustion carbon and sulfur instrumentation can utilize single point linear (fixed-at-origin) calibration. This is possible because LECO instruments are linearized at the factory. Some instruments can also use multi-point linear or linear fixed-at-origin calibrations. The calibration process is based on analyzing calibration samples of known carbon and sulfur content. The calibration factor is determined by comparing the % ***Analyte*** obtained by the analysis and the known % Analyte of the standard. Analyte is defined as the substance whose physical or chemical properties are measured and correlated, directly or indirectly, to the desired information. A standard should be selected with a known analyte concentration in the middle to upper portion of the operating analyte concentration range. A ratio is taken of the known and observed analyte concentration. The resultant ratio is taken as the calibration factor. The calibration is then a line drawn from the origin having a slope equal to the calibration factor. Instrument calibration should be checked throughout the day to assure it is within the expected range.

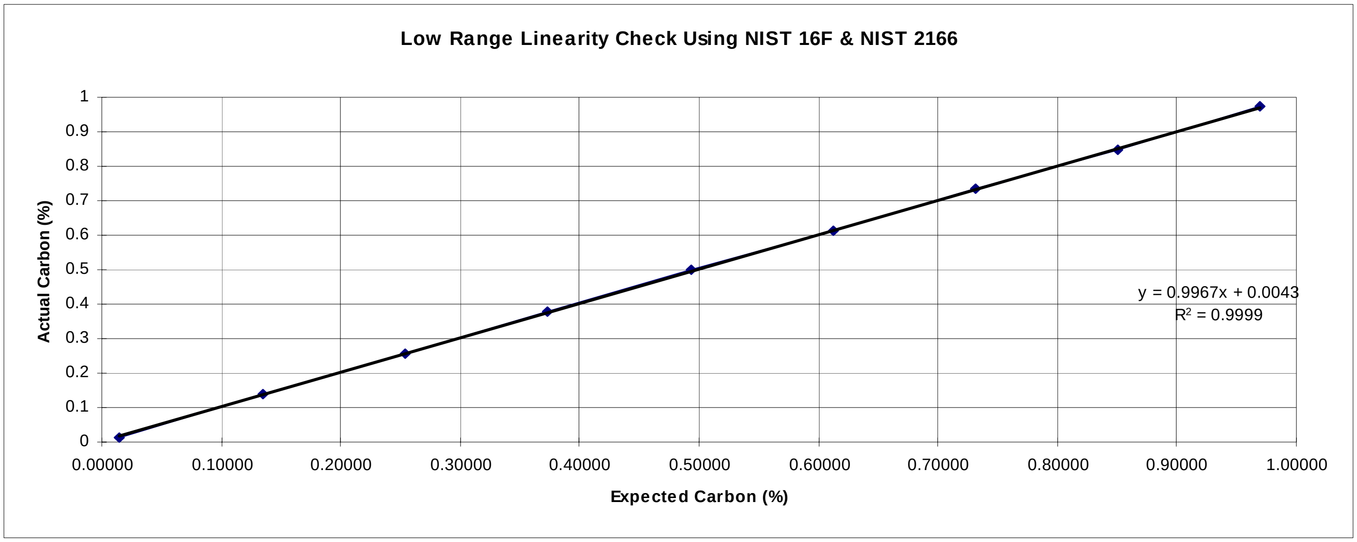
Accuracy/Precision/Linearity

Since these instruments must be calibrated with samples of known carbon and sulfur content, the accuracy of the instrument is directly related to the accuracy of the calibration sample used. A fairly large variety of standards are available for use as calibration samples. These include: certified reference materials (CRM), standard reference materials (SRM), and reference materials (RM). The majority of these standards are consensus standards. This means the analyte concentrations are determined by sending samples to several laboratories for analysis to determine the analyte(s) of interest. ***Accuracy*** is defined as the closeness of a measured value to the true value. Accuracy includes the concepts of bias and precision. A measurement process must be unbiased and sufficiently precise to obtain accurate data. The concept of ***bias*** is concerned with whether or not the value obtained by the measurement process differs from the true or accepted value. The concept of ***precision*** relates to the variability of the individual results of replicate measurements. The smaller the variability, the greater the precision. It is possible to have a set of very precise but inaccurate data. Each laboratory will have a different measurement system increasing the potential for bias. When reference standards are determined using the multi-laboratory procedure, the potential for differences between reference standards is an issue. Therefore, when several CRMs, SRMs, or RMs are analyzed on the same calibration curve of a LECO carbon and sulfur determinator, they may not all line up on the calibration curve. In some cases, a reference material will have a stated ***uncertainty***, in other cases this information may not be available. Regardless, the typical reaction of the instrument operator is to suspect their instrument is nonlinear. Instrument ***linearity*** is the ability of an analytical instrument to obtain accurate analyte measurement throughout the specified analytical range.

In LECO carbon and sulfur determinators, we can verify instrument linearity by analyzing two steel samples, one of high carbon (or sulfur) content and one of low carbon (or sulfur) content and then mixing portions of each to simulate different concentrations. The expected (calculated) results are compared to the actual obtained results to verify instrument linearity. An example of results obtained by using this technique can be found in Table 3.

Table 3—Linearity of Carbon Utilizing the LECO CS-200 Carbon Sulfur Determinator

	NIST 16F @ 0.97%C		NIST 2166 @ 0.015%C						
Sample	**Approx. Weight (g)**	**Actual Weight (g)**	**Approx. Weight (g)**	**Actual Weight (g)**	**% C (approx)**	**% C (theoretical)**	**% C (actual)**	**Difference (actual - theoretical)**	**% Relative Error**
1	1.0000	0.9999	0.0000	0.0000	0.970	0.970	0.973	0.0027	0.28
2	0.8750	0.8758	0.1250	0.1257	0.851	0.850	0.846	-0.0045	0.53
3	0.7500	0.7501	0.2500	0.2500	0.731	0.731	0.735	0.0037	0.51
4	0.6250	0.6258	0.3750	0.3742	0.612	0.613	0.614	0.0017	0.27
5	0.5000	0.5006	0.5000	0.4991	0.493	0.493	0.499	0.0062	1.26
6	0.3750	0.3748	0.6250	0.6253	0.373	0.373	0.378	0.0049	1.31
7	0.2500	0.2504	0.7500	0.7493	0.254	0.254	0.259	0.0044	1.74
8	0.1250	0.1252	0.8750	0.8752	0.134	0.135	0.140	0.0054	3.99
9	0.0000	0.0000	1.0000	1.0004	0.0150	0.0150	0.0150	0.0000	0.30



Another method of verifying linearity is to analyze a series of fractional weights of pure compounds such as calcium carbonate ($CaCO_3$) for carbon and/or barium sulfate ($BaSO_4$) for sulfur. This method is used in some ISO procedures, however the main problem is in weighing relatively small amounts of these samples.

Yet another procedure which has been adopted as part of ASTM method E 1915 incorporates $CaCO_3$ and $BaSO_4$ mixed with silica sand to produce synthetic standards of different levels of carbon and sulfur. This method is written for determination of carbon and sulfur in metal bearing ores. In any event, some labs would prefer to use software programs to correct for the apparent nonlinear response. If the linearity of the instrument is verified, using software calculations to correct something related to the accuracy of a standard and not the instrument is the wrong approach.

An additional area of concern is related to recovery of the analyte being measured. During the combustion process there is a possibility not all of the analyte is being converted to a form that can be measured. This can be a problem when the recoveries are different for different sample matrices. We will address this issue in more detail in the Analyte Recovery and Related Issues section relating to different types of accelerators.

LECO Calibration Samples/Traceability

LECO manufactures a complete line of calibration samples designed for use in LECO carbon and sulfur determinators. LECO produces several 1 g steel carbon and sulfur samples, typically as pins or rings, that are very easy to use as well as cost effective. These samples are traceable to certified reference materials such as those produced by the National Institute of Standards and Technology (NIST). ***Traceability*** as defined by ISO is "the property of a result of a measurement whereby it can be related to appropriate standards, generally international or national standards, through an unbroken chain of comparisons." The designation of primary or secondary standards is used frequently. According to NIST definition, a primary standard can be defined as one whose value is accepted without further verification by the user. It can also be used to establish a value for a secondary standard. In the case of LECO calibration samples, the primary standard is the NIST SRM (or other certifying body CRM) and the LECO sample is the secondary standard. It should be noted in some cases a secondary standard, once its value is established, could become a primary standard for other users. It should also be noted ISO definitions of primary and secondary are different. ISO defines a primary standard as a pure compound or other constant of nature, while CRMs or SRMs are considered secondary standards. LECO carbon and sulfur calibration standards have a +/- value assigned. Normally, this value represents two times the standard deviation obtained on a minimum of three sets (n=10 for each set) of data. This means 19 out of 20 results should fall within the stated range on a LECO carbon and sulfur determinator which is operating properly following the appropriate analytical procedures: baked off crucibles, Lecocel II accelerator, etc., and calibration of the instrument with the same standard. Note that a few of the newer standards, at lower levels of analyte concentration, have standard deviations of only one sigma. Accuracy of such a standard is only as good as the accuracy of the primary standard used for calibration.

Analyte Recovery and Related Issues

In order to obtain accurate carbon and sulfur results, it is imperative complete combustion of a sample is obtained. Sometimes, this may be difficult to determine. In most cases, a general observation of the plate current of the induction furnace is made to determine adequate combustion. This is a measure of the coupling of the sample and accelerator in the high frequency (HF) furnace and is a good indicator of the combustion of a sample. However, it is subjective and may not be completely accurate. LECO analysts typically look for a plate current of at least 350 mA, which can be sustained for at least 15 to 20 seconds. Even so, there are times when this is the case and the results are still not suitable. The best way to verify proper combustion is to analyze calibration samples with known carbon and sulfur contents. There can be a slight difference in carbon and sulfur recovery when different types and amounts of accelerator are used. For example, LECO carbon and sulfur steel ring and pin samples assigned values are determined using Lecocel II (tungsten/tin) as accelerator. There is a slight difference in the carbon and sulfur recovery on some of these standards when Lecocel (tungsten only) is the accelerator. Typically, slightly lower carbon and slightly higher sulfur results are obtained when tungsten only is used in lieu of tungsten-tin on some (not all) standards. Many customers prefer to use tungsten only because less oxide dust is generated when compared to tungsten-tin accelerator. Table 4 illustrates the difference in carbon and sulfur recoveries in steel standards comparing Lecocel II and Lecocel accelerators. Although these differences are subtle, they are enough to cause some concern, which may mislead the operator into blaming instrument linearity, or question the accuracy of a particular standard. In some cases, particularly for sulfur, losses can occur after combustion. This is often associated with oxide dust build-up in the dust filter. This dust can act as a column (to retard CO_2 or SO_2 delivery) or a trap (to retain CO_2 or SO_2). Typically this problem is associated with sulfur recovery. As the dust builds up in the dust filter and surrounding areas, SO_2 released from the combustion of a sample can be retained in this dust. The amount of this retention will depend on the amount of dust and type of oxide. Several LECO carbon and sulfur instruments have special autocleaner/dust removal systems either standard or offered as optional equipment. These systems help to reduce the dust build-up problem.

Table 4—Analyte Recovery Comparing Lecocel II and Lecocel Accelerators

Carbon %			
Standard	**Expected (or Certified)**	**Lecocel II**	**Lecocel**
TRP 1043	0.0005	0.00053	0.00021
NIST 2168	0.00075	0.00066	0.00038
NIST 131f	0.00351	0.00394	0.00163
NIST 125b	0.028	0.0291	0.0257
NIST 344	0.069	0.0707	0.0694
NIST 15h	0.076	0.0774	0.0747
NIST 362	0.16	0.165	0.163
NIST 32E	0.409	0.414	0.409
NIST 13g	0.613	0.619	0.611
NIST 364	0.87	0.873	0.867
NIST 16f	0.97	0.971	0.969
501-674	0.017	0.0175	0.0177
501-675	0.069	0.0709	0.0713
501-676	0.199	0.205	0.202
501-677	0.391	0.397	0.392
501-678	0.575	0.580	0.571
501-679	0.897	0.904	0.892
502-148	0.0103	0.0104	0.0079
501-501	0.0346	0.0355	0.0351
501-502	0.052	0.0537	0.0511
501-503	0.162	0.168	0.165
501-504	0.447	0.454	0.447
501-505	0.556	0.564	0.557
501-506	0.814	0.819	0.803

Sulfur %			
Standard	**Expected (or Certified)**	**Lecocel II**	**Lecocel**
TRP 1043	0.0002	0.00032	0.00022
131f	0.00043	0.00038	0.00039
2168	0.0010	0.00090	0.00083
125b	0.008	0.0076	0.0070
344	0.019	0.0179	0.0173
15h	0.019	0.0185	0.0181
32E	0.021	0.0178	0.0187
364	0.025	0.0230	0.0228
16f	0.026	0.0221	0.0214
13g	0.031	0.0284	0.0276
362	0.036	0.0361	0.0367
501-679	0.0051	0.0050	0.0050
501-678	0.0084	0.0085	0.0082
501-677	0.0092	0.0087	0.0084
501-676	0.0122	0.0116	0.0110
501-675	0.0117	0.0113	0.0104
501-674	0.0211	0.0209	0.0206
501-504	0.0074	0.0072	0.0077
501-505	0.0076	0.0072	0.0077
501-506	0.0077	0.0075	0.0079
502-148	0.0091	0.0086	0.0082
501-502	0.0092	0.0089	0.0086
501-501	0.0131	0.0123	0.0118
501-503	0.0178	0.0183	0.0178

Lecocel II–A tungsten/tin accelerator
Lecocel–A tungsten only accelerator

Water and Sulfur Recovery

Sulfur recovery losses are magnified when water is present; however, trace amounts of water are not going to be a problem. Water can be in a sample either in residual or crystalline (hydrated,$\bullet H_2O$) forms and may be present in weight % quantities. Residual water can be removed by drying the sample at 105° C for one hour. However, crystalline water is not easily removed since the sample must be subjected to much higher temperatures (up to 1300° C). Unfortunately this will also remove some or all of the carbon and sulfur in a sample. It should be noted the water released from a sample has little if any effect on carbon recovery. Water produced, as opposed to released, during the combustion of metal hydrides (titanium hydride, zirconium hydride, $-H_x$) or hydroxides (calcium or magnesium hydroxides, $(-OH)_x$) will have the same effect of reducing sulfur recoveries. Hydrated, hydride or hydroxide samples are typically analyzed for sulfur using LECO resistance furnace IR systems such as the SC632.

During a series of analyses, if sulfur results appear to be decreasing within a set of samples and analysis of a check standard is also lower than expected, chances are that water is the culprit. Reducing the sample weight may help, as it also decreases the amount of water released. Additionally, if the moisture levels are not too high, combusting several ***conditioners*** such as LECO ring standards will be enough to allow the sulfur results to return to their expected levels. In some cases, you can alternate between sample and conditioner, and achieve the same effect. The conditioner should be of higher sulfur content such as a LECO 502-271 steel ring sample.

Organic Materials

An induction furnace carbon and sulfur determinator is not suited to analyze organic, organometallic, or inorganic samples that contain certain quantities of organic matter. The problems associated with combustion of organic samples are incomplete combustion due to volatilization of the sample and large amounts of water produced during the combustion of some of the organic matter. Analysis of organic samples such as coal, oil, plastic, etc., can cause damage to the instrument, and it is imperative that they not be analyzed on an induction furnace IR detection carbon and sulfur determinator. This is because the ***hot zone*** of an induction furnace during the combustion process is limited to an area immediately adjacent to the crucible. The sample and accelerator, as contained in the crucible, are positioned on the furnace pedestal at near ambient temperature. When the HF current is applied to the accelerator and sample, it takes several seconds for the maximum furnace temperature to be obtained. During this period, a good portion of an organic matrix sample will ***volatilize*** without combusting. These volatilized products may contain methane (CH_4) which may cause an explosion in the combustion tube, or may blow out the internal glass tube in the sulfur IR cell. The latter occurrence will result in a very costly repair bill. Samples with smaller amounts of organic content such as metal powders coated with paraffin wax may not cause any harm to the instrument, but may cause sulfur recovery problems as stated earlier. In any event, it is very important to know what the sample matrix is prior to analyzing it.

Other Problematic Materials

Induction furnace carbon and sulfur determinators can be used on a variety of inorganic materials with success. There are, however, some inorganic materials that cause some difficulties. These materials present difficulties for a variety of reasons and in most cases the problem will be associated with sulfur recovery. Some can be analyzed for carbon, but not for sulfur. Some will combust with too much volatility, and some produce oxide dusts that plug the dust filter area causing flow problems. We will examine some of these problem materials and discuss which procedures are best suited for a particular material or group of materials. This information does not include all materials that may cause problems, but it does relate to variety of materials that we have attempted to analyze.

Reactive Materials

Samples that cannot be analyzed using this technique because they combust too vigorously or are otherwise too reactive include the metals: calcium (Ca), magnesium (Mg), lithium (Li), sodium (Na) and potassium (K). The last two will react with oxygen in the air and are usually stored in liquid. The oxides of these materials (CaO, MgO, etc.) can be analyzed for carbon and sulfur; however, Li, Na, and K oxides will cause analytical problems for sulfur. Beryllium (Be) has been analyzed successfully by some people, but due to its toxic nature, extreme caution must be used and only those trained in handling this material should attempt to analyze it (this also includes alloys containing Be).

Materials Causing Sulfur Recovery Problems

Certain metals and their alloys have been shown to cause sulfur recovery problems including manganese (Mn), platinum (Pt), iridium (Ir), palladium (Pd), silver (Ag), and lead (Pb). The exact reasons for the recovery problems are not completely understood; however, there are a few theories that have been proposed. Low sulfur recoveries have been noticed when analyzing Pt, Ir and Pd. This effect is very noticeable when iron chip and Lecocel II are used as accelerators because of their higher sulfur content. The blank is determined and set for the accelerators, compensating for it electronically. When analyzing Pt, Ir, or Pd, the sulfur from the accelerator does not reach the detector, resulting in a negative sulfur value. It is possible that these materials or their oxides are acting as catalysts and converting SO_2 to SO_3, which would not be measured by the sulfur IR cell. Lead and silver also present similar analytical problems for sulfur determination in an induction furnace. Lead dioxide (PbO_2) heated to about 250°C will effectively remove SO_2. Therefore it is likely that PbO_2 formed during the combustion of lead samples outside of the hot zone may contribute to low sulfur recovery. Likewise, silver and/or silver oxides have a similar effect on sulfur recovery. In the case of Mn, it is well documented that manganese dioxide (MnO_2) will absorb SO_2 at room temperature. In fact, it is a principal reagent in LECO thermal-conductivity (TC) detection carbon instruments such as the WR-12 and WR-112. During the combustion of Mn metal or alloy, MnO_2 will form and be trapped in the dust filter above the combustion chamber. It is likely that some of the SO_2 produced during the combustion will be retained by this MnO_2 in the dust filter. The interesting phenomenon is that we are able to analyze MnO_2 materials without a great deal of difficulty. This could be because the MnO_2 stays in the crucible hot zone where the high temperatures prevent absorption of SO_2. In the case of Mn and alloys such as ferromanganese, MnO_2 is forming above the crucible and is carried to the dust filter.

Analytical Procedures and Special Applications

In this section we will cover a variety of analytical procedures that can serve as a guide for obtaining the best performance from your LECO carbon and sulfur instrument. In many cases there is more than one procedure that can be followed on a given sample and still produce suitable results. The original design of the induction furnace carbon and sulfur instruments was to analyze steel and iron samples, and this application is the most widely used. There are many other materials for which this instrumentation has been found suitable; however, modifications in the analytical procedures are generally required. We will address these in the following paragraphs.

Steel and Iron

This is the most common application for LECO induction furnace line of carbon and sulfur determinators. ASTM E 1019, “Determination of Carbon, Sulfur, Nitrogen and Oxygen in Steel, and in Iron, Nickel, and Cobalt Alloys,” is applicable to steel and iron analyzed on LECO induction furnace combustion instruments. Typically 1 g samples of steel or iron are analyzed with approximately 1 g of Lecocel II or Lecocel accelerators for simultaneous carbon and sulfur determination. When carbon only is being determined, copper accelerator will suffice and is more cost effective.

Cast Iron

Cast iron is another common application for LECO induction furnace carbon and sulfur determinators. ASTM E 1019 covers carbon and sulfur determination in cast iron using LECO induction furnace-combustion instruments. Since cast iron is higher in carbon (>2%) than steel, LECO typically recommends that ~0.5 g samples be analyzed with ~1 g of Lecocel or Lecocel II and ~0.5 g of iron chip. The iron is added to sustain the burn, while the sample weight is reduced to facilitate complete combustion in less than 40 seconds. Note that sulfur release is delayed when higher carbon content is present in a sample, increasing the overall combustion times. As mentioned in the section on sample preparation, as-cast (Grey iron) samples must be handled carefully to avoid carbon loss. A solid slice or chunk of an as-cast sample must be used rather than a pulverized or crushed sample. A chilled sample (white iron) can be analyzed as a solid single piece or as drillings, chips, or powder.

Nickel and Cobalt Base

This group of materials include high purity nickel and cobalt, as well as nickel base, iron nickel base and cobalt base superalloys (high temperature alloys). They are typically analyzed using the same procedure as steel. In some cases, they will not burn readily and may require the addition of extra accelerator. Combustion is more difficult when analyzing solid, single-piece samples. Samples of chunks, chips, drillings, shavings, and powders will combust more readily than solid single piece samples. Normally, 1 g samples are analyzed using ~1 g of Lecocel II HP. If difficulty in combustion is encountered, then ~2 g of Lecocel II HP can be used. If this still is not effective, ~1 g of Lecocel II HP and ~1 g of HP iron chip may be a better alternative. Sulfur detection is of critical importance in many of these alloys. Detecting sulfur at levels less than 2 ppm may be required. At these low levels, the best method is to use only Lecocel II HP instead of Lecocel II HP and HP iron chip, due to the added sulfur content and variability of the iron chip. The LECO CS-444LS and CSLS600 are the instruments of choice for ultra low sulfur detection in nickel and cobalt base alloys. They have a special sulfur trap mode which effectively pre-concentrates the sulfur during the combustion phase of a sample. During the detection phase, the trap is heated and the collected sulfur is purged from the trap into the sulfur IR cell for measurement. Table 5 illustrates the improved sulfur results of the trap mode of a CS-444LS. ASTM methods E 1019 and E 1587 “Chemical Analysis of Refined Nickel” are both applicable for these samples.

Table 5–Sulfur in UHP Nickel analyzed on CS-444LS

Sample	Weight (g)	S (ppm)
UHP Ni	1.0069	0.40
	1.0075	0.42
	1.0078	0.32
	1.0134	0.36
	1.0012	0.33
	1.0110	0.34
	1.0056	0.29
	1.0004	0.29
	1.0027	0.48
	1.0099	0.32
		X = 0.35
		s = 0.062

Lecocel II HP used as accelator

Refractory or Reactive Metals

This group of metals and alloys include zirconium (Zr), titanium (Ti), hafnium (Hf), niobium (Nb), vanadium (V), chromium (Cr), molybdenum (Mo), tungsten (W), and tantalum (Ta) based materials. They are typically analyzed for carbon using LECO induction furnace, IR detection carbon determinators. ASTM E 1941 “Carbon in Refractory and Reactive Metals and Their Alloys” covers this group of materials analyzed on LECO induction furnace-combustion instruments. ASTM E 1941 dictates using copper and Fe chip as accelerators. This applies to carbon only analysis, since copper oxide dust will permeate the system and cause sulfur recovery losses in subsequent analyses. Refer to LECO Application Note #203-821-308, "CS600—Carbon in Refractory & Reactive Metals and their Alloys" for details regarding determining carbon in this group of metals.

Carbides

Carbon determination in carbides is a common application for LECO induction furnace carbon determinators. Tungsten carbide and silicon carbide are the most commonly analyzed carbides. Other carbides such as chrome carbide, niobium carbide, tantalum carbide, titanium carbide, zirconium carbide, halfmium carbide, cobalt carbide, vanadium carbide, boron carbide, and cemented carbides (tungsten carbide based sintered products) can also be analyzed.

Tungsten carbide producers normally require one sigma carbon precision of less than 0.015% (absolute) at the 6% carbon level. This is a relative standard deviation (RSD) of less than 0.25%. The majority of LECO induction furnace carbon determinators have precision specifications of 0.5% RSD. The LECO WC600 is designed for improved precision when analyzing carbides. It is capable of consistently producing RSDs of less than 0.2% on tungsten carbide. Refer to LECO Application Note #203-821-281, "WC600—Carbon in Tungsten Carbide" for details regarding carbon determination in this group of metals.

Copper Base

Sulfur determination in copper and copper base alloys is a common application for LECO induction furnace combustion carbon and sulfur determinators. Calibration with a copper base sample is the preferred procedure. NIST SRM 885, a refined copper pin sample with a certified sulfur content of 18 ±3 ppm, is a popular standard used by LECO customers and LECO's Technical Services Laboratory. Carbon is determined as well, but it is not requested as much as sulfur determination in these materials. The main difficulty with determination of sulfur in copper base materials relates to the dust build-up in the dust filter area. It is very important to keep the filter and surrounding area clean. The original procedure was to analyze 0.8 to 1 g samples using ~1 g of Lecocel or Lecocel III (tungsten only) accelerator. Iron chip accelerator is not recommended, as there will be a sulfur recovery problem associated with the iron and copper.

A new procedure developed by the Technical Services Laboratory at LECO uses reduced furnace power to analyze copper base samples at lower temperatures. It is applicable to all LECO induction furnace units with furnace power limit circuitry. This circuitry is standard on newer LECO induction furnace based carbon and sulfur determinators such as the CS-200, CS230, CS-400, CS-444, and CS600-series, and can be found on later CS-244 series instruments. The CS600-series has an advanced furnace control system controlled through the PC, making the CS600-series an excellent choice for this application. The key to this procedure is to set the furnace limit control to the correct setting. This is done by trial and error. If the 2 g samples are chips, drillings or finely divided, they can be analyzed without accelerator. If the samples are pins or other solid pieces, 1 g of the material should be analyzed with ~1 g of high purity copper chip accelerator. The furnace limit control is set at the minimum setting and increased as needed to melt the sample. Solid samples require the most time in determining the appropriate furnace power set point. The critical aspect of this is to set the furnace power limit high enough to melt the sample, but low enough to prevent significant portions of the sample from vaporizing and depositing in the dust filter area. Using this procedure, tests have shown that the dust filter shows little sign of accumulated dust even after as many as 30 determinations. This method is now the preferred procedure for sulfur determination in copper since it is cleaner, offers improved sulfur recovery, and is applicable to a wide variety of copper alloys varying in sulfur content from the ppm level to tenths of a percent on a 1 g basis. More information on this method can be found in LECO Application Note #203-821-109.

Battery Materials

There are many materials that are encompassed in this group, those most typically analyzed for carbon and sulfur are: $Mn/MnO/MnO_2$ and $PbO/PbSO_4$. Carbon analysis is relatively straightforward for these applications and typically up to 0.5 g samples are combusted with ~1 g of copper or Lecocel II (W/Sn) and Iron chip accelerator. However, as noted in the section on Materials Causing Sulfur Recovery Problems, there are problems associated with sulfur analysis in the presence of manganese, lead, hydrogen, and cadmium. LECO has made improvements in technique to increase sulfur recoveries. When analyzing MnO_2, ~0.25 to 0.35 g samples can be analyzed for carbon and sulfur simultaneously using ~1 g Lecocel II HP and ~1 g iron chip as accelerators.

For lead based samples there are two methods that have been used for sulfur analysis. In both methods ~0.10 to 0.15 g samples are analyzed. Past attempts at using Lecocel III and iron chip have resulted in low recovery when analyzing lead oxides, and virtually no recovery when analyzing pure lead samples. The low temperature method described in the copper section is the preferred procedure for the analysis of battery plates. Sulfur recoveries are improved and carbon can be done simultaneously with this method. Refer to LECO Application Note #203-821-209 for details.

Metal Bearing Ores and Related Materials

Carbon and sulfur determination in this group of materials is used to classify ores for processing and classify waste materials from the mining and processing of ores according to their potential to generate acid in the environment. Either induction or resistance based IR carbon and sulfur determinators can be used for these sample types. Induction furnace systems are preferred due to their relative speed and robustness. ASTM method E1915 “Analysis of Metal Bearing Ores and Related Materials by Combustion Infrared Absorption Spectrometry” was written specifically to cover carbon and sulfur determination of these material types. The typical carbon level of materials in this group ranges from 0.03 to 10% carbon, while sulfur levels range from 0.04% to 9%. Nominal sample weights of 0.2 g are combusted using ~1 g of tungsten or tungsten/tin plus ~1 g of iron chip accelerators. Sample weights may be reduced when samples contain higher concentrations of sulfur (>1.75%). Standard LECO carbon and sulfur induction furnace units have a sulfur range of up to 0.4% based on a one gram sample or a range of up to 1.75% sulfur using a 0.2 g sample. High sulfur versions such as the CSHS600, SHS600, and SDR600 have a range of up to 1.75% sulfur based on a one gram sample, or 8.75% sulfur at a 0.2 g sample weight. LECO 502-318, 502-319, 502-320 and 502-372 are ore tailing samples from mining operations which are recommended for calibration and/or verification of either induction or resistance furnace carbon and sulfur determinators. Refer to LECO Application Note #203-821-309 for more information.

Soil, Clay, and Rock

Carbon and sulfur (with some exceptions) determination in this group of materials can be performed on either an induction or resistance based furnace IR detection system. Soil samples that contain large amounts of organic matter and/or water should be analyzed using a resistance furnace based system. Likewise, clay, soil or rock samples containing high amounts of crystalline water will not yield accurate sulfur determination when analyzed on an induction furnace based system (refer to “Water and Sulfur Recovery” section p. 12). Samples can be dried at 105°C for approximately one hour to remove residual water. The recommended analytical procedure is to analyze sample weights of between 0.2 to 0.5 g using ~1 g of Lecocel II and ~1 g of iron chip accelerator.

In some cases, total carbon along with Total Organic Carbon (TOC) is required. The organic carbon can be determined by acid-treating the sample and analyzing the residue. A weighed sample of ~0.5 g is treated with dilute acid (1:1, $HCl:H_2O$) to remove carbonates; the treated sample is then analyzed to determine the non-carbonate carbon. The non-carbonate results are typically referred to as “Total Organic Carbon.” The difference between the averages of the total carbon and noncarbonate carbon is considered carbonate carbon. We do not recommend acid treating samples directly in the ceramic combustion crucibles because too much residual acid will be left in the crucible. LECO 529-036 Crucible Liners which are designed for this application are typically used. Alternately, samples can be acid treated in a "watch glass" or similar container, dried, and transferred to the ceramic crucibles.

Aluminum Base

Carbon determination in aluminum and aluminum alloys is a common application. Aluminum combusts very vigorously, consequently the sample weights should be reduced to facilitate accurate and reproducible analyses. Combustion of chips, chunks, drillings, millings and granular aluminum is more controlled than attempting to burn a sample that is a single piece. Single piece samples will splatter vigorously, causing combustion tube damage and erratic results. This phenomenon appears to be caused by the ***dross*** (oxide) layer formed on larger single-piece samples during the heating of the sample and melting of the aluminum on the inside which bursts out of the crucible about midway into the burn cycle. LECO 619-880 ceramic crucible covers are recommended for this application. The most common procedure is to use ~1 g of Lecocel II HP and ~1 g of HP iron chip accelerator with a 0.2 to 0.5 g sample. Alternately, ~1 g of copper + ~1 g of HP iron chip may be used as accelerators. Carbon contents of high-purity aluminum are typically extremely low and special care should be exercised when setting the blank. In order to obtain the most accurate results, LECO recommends that at least 10 replicate blank analyses be performed. This will allow for an accurate blank level to be set, as well as determine the detection limit based on the standard deviation of the blank. The LECO CS600-series of instruments are the best suited for high purity aluminum because of the detection capability of the furnace "power ramping" feature.

Ferroalloys

This group of steel-making alloys includes ferrosilicon (regular and high purity grades), ferrochromium (low and high carbon grades), ferromanganese, ferrophosphorus, magnesium ferrosilicon, and ferrochromium silicon. These materials are commonly analyzed for carbon and sulfur using LECO induction furnace instrumentation. Carbon determination is less complicated than sulfur determination on these products. Ferromanganese, as mentioned earlier, can exhibit sulfur recovery problems. Ferrosilicon samples combust much more vigorously than do the other ferroalloys, requiring analysis of reduced sample weights. This in turn, causes a loss in precision. The typical analytical procedure is to analyze between 0.2 to 0.5 g of sample (0.1 to 0.2 g for ferrosilicon) with ~1 g of Lecocel II HP and ~1 g of HP iron chip. Ferroalloy samples will typically be in the form of large chunks or irregular pieces, and should be crushed to a fine powder in order to obtain suitable results.

Mold Powders

This group of materials is used in steel making as flux material or solid lubricant for continuous casting. They consist of a mixture of oxides as well as added carbon (carbon black, graphite and carbonates) and fluorides. Carbon determination is important because the carbon content controls the melting rate of the flux. The total carbon contents of mold powders range from approximately two to eight percent. Several LECO customers use either induction or resistance furnace carbon determinators to analyze these sample types. Due to the fluoride content of these samples, a fluoride trap is recommended. Typically a trap assembly (LECO 769-641) is installed between the furnace and measurement unit. This trap is filled with 502-351 halogen scrubber. When the furnace and measurement unit is in the same cabinet, such as in the CS-200/230/600-series, the halogen scrubber material can be placed in the bottom two-thirds (2/3) of the anhydrone tube (the top 1/3 is filled with anhydrone). Depending on the carbon content of a particular mold powder, the sample weight analyzed is around 0.1 g, with ~1 g of Lecocel II and 1 g of iron chip is used as accelerator.

Slag

Generally, the term slag is used in the steel industry and it applies to the fusible material formed by the chemical reaction of a flux with the oxides of an ore. Slag functions as an insulator for liquid iron and as the primary means of removing impurities such as sulfur and phosphorus in basic oxygen and electric furnace steel making processes. Slag can also be recycled in blast furnaces. In any event, determination of the sulfur content is an important analytical consideration. The analytical procedure is the same as ferroalloys (refer to the Ferroalloy section). In some cases, slag will contain elevated levels of fluorine from fluorspar (CaF_2) that may have been used in the steel making process. If this is the case, LECO recommends installing a fluorine trap (refer to Mold Powder section). The sample should be ground to a relatively fine powder in order to obtain a suitably representative sample.

Limestone, Dolomite, Burnt Lime and Burnt Dolomite

This group of materials is used in iron and steel production as basic fluxes. Determination of the sulfur content of these materials is very important. Historically, both resistance furnace and induction furnace sulfur determinators have been utilized. Resistance furnace units are generally better suited for limestone, while burnt lime is most accurately analyzed on induction furnace instrumentation. This is partially due to the tendency of limestone to have higher water content (free and crystalline) than burnt lime. Quicklime can contain some water in either residual or crystalline form, and will pose sulfur recovery problems on an induction furnace unit (refer to Water and Sulfur Recovery section). We also have found that even when there is not any water present, as in pure calcium and magnesium carbonate, sulfur release is delayed in an induction furnace. This could be because the decomposition reaction of calcium and magnesium carbonates are endothermic; however, this has not been proven. Limestone is analyzed on an induction furnace by combusting approximately 0.075 g of sample with ~1 g of Lecocel II + ~1 g of Iron Chip accelerators. As a precaution, limestone should be dried at 105° C for at least one hour prior to analyzing. Burnt lime usually requires no drying prior to analysis. Refer to LECO Application Note #203-821-135 for details on analysis of burnt lime.

Cement and Fly Ash

Portland cement and fly ash are routinely analyzed for sulfur and carbon content. These materials have been successfully analyzed using either resistance or induction furnace instrumentation. The analytical procedures are the same as those used for burnt lime (refer to Limestone, Burnt Lime, Dolomite and Burnt Dolomite section).

Ceramics, Sand and Glass

This group of materials is readily analyzed on induction furnace carbon and sulfur instrumentation. Typically the carbon and sulfur contents are low. The recommended analytical procedure is to analyze sample weights of 0.2 to 0.5 g using ~1 g of Lecocel II + ~1 g of iron chip accelerator. The samples can be dried at 105° C for one hour. One exception is the analysis of foundry sands containing organic binders. These sands should be analyzed using a resistance furnace instrument instead of the induction furnace instrumentation because of reduced sulfur recoveries and/or possible instrument damage as outlined previously in the organic materials section.

Cracking Catalysts

This group of materials is made up of various substrates, such as alumina, alumina/silicate, zirconia and zeolite, doped with metal catalysts. They are used as hydrocarbon cracking catalysts and the determination of carbon and sulfur is very important. They are typically categorized as new, depleted or regenerated catalysts. New catalysts are materials that have not been used yet. The depleted catalysts are used to the point where they no longer function as intended. The regenerated catalysts are those that have been reprocessed to remove carbon and sulfur deposits. Carbon and sulfur determination is a valuable tool in producing and using these materials. Some of the substrates, such as zeolite, are hydrated and will not yield accurate sulfur data on an induction furnace instrument. These samples must be analyzed using a resistance furnace based unit. Some of the depleted catalyst might also contain elevated levels of organic material, which will produce low sulfur recovery and must also be analyzed on a resistance furnace unit in order to obtain suitable sulfur results. Refer to earlier sections on samples containing water and organic materials for additional information. The analytical procedure for catalyst materials is to use ~0.1 to 0.5 g samples with ~1 g of Lecocel II + ~1 g of iron chip as accelerators. The larger sample weights are used on the lower carbon and sulfur levels found in new and regenerated catalysts. The smaller weights are used when high levels of carbon and sulfur are present as is typical in depleted catalysts. Many of these materials are extruded or have somewhat non-uniform particle sizes. Since most of the carbon and sulfur are deposited on the surface, this can lead to very erratic results on the depleted catalyst samples. It may be necessary to grind the sample material into a uniform powder to obtain repeatable results.

Abbreviations

ASTM: American Society for Testing and Materials

CRM: Certified Reference Material; RM issued and certified by an organization generally accepted to be technically competent to do so - NIST Special Publication 260-100

g: Gram

HF: High Frequency

IR: Infrared

ISO: International Organization for Standardization

NIST: National Institute of Standards and Technology

RM: Reference Material; A substance for which one or more properties are established sufficiently well for use to calibrate a chemical analyzer or to validate a measurement process - NIST Special Publication 260-100

SRM: Standard Reference Material; a CRM issued by NIST - NIST Special Publication 260-100

TC: Thermal Conductivity

Glossary of Terms

Accelerator (Induction Furnace): Material with good coupling capabilities that is added on top of the sample before sample analysis to set fire or ignite the sample.

Accuracy: Closeness of a measured value to the true value.

Analyte: Substance whose physical or chemical properties are measured and correlated, directly or indirectly, to the desired information.

Baseline: electronic line determined as the zero or reference line which is used to differentiate the actual analyte concentration.

Bias: Deviation of a measurement process from the true or accepted value.

Blank: The signal obtained during an analysis that cannot be attributed to the sample.

Calibration: A comparison of a measurement standard or instrument with another standard or instrument to report or eliminate, by adjustment, any variation or deviation in the accuracy of the item being compared (Taylor, John K. “Standard Reference Materials Handbook for SRM Users.” NIST Special Publication, 260-100, 1993 Edition.)

Conditioners: Samples analyzed to condition or stabilize the system either at the beginning of the day, or in the presence of samples containing water.

Consensus (standards): Determination of analyte concentration by several laboratories utilizing more than one technique when applicable.

Coupling: Induced electric current in a sample used to heat a sample and accelerator.

Dosing: Injecting known volumes of a specific analyte directly into an instrument.

Dross: Oxidized impurities that float to the top of a molten metal.

Flux: A material that renders refractory impurities more easily fusible and also preferentially combines with such impurities.

Hot Zone (Induction furnace): The crucible and the area immediately adjacent to the crucible that reaches temperatures in excess of 1500^{0}C during the combustion process.

Linearity: Measure of the ability of an analytical instrument to obtain accurate analyte measurement throughout the specified analytical range.

Linishing: Removal of surface contamination using an abrasive rotating disk or continuous belt type grinder/polisher.

Liquidus: On an phase equilibrium diagram, the liquidus line is the line separating the boundary between a liquid system and a liquid/solid system.

Precision: Variability of the individual results of replicate measurements.

Splatter: Material, either sample accelerator or both, which escapes the crucible and deposits on the sidewall of the combustion tube.

Traceability: The property of a result of a measurement whereby it can be related to appropriate standards, generally international or national standards, through an unbroken chain of comparisons (International Organization for Standardization. ISO Guide 34 Quality System Guidelines for the Production of Reference Materials. Nov. 1994.)

Uncertainty: The range of values within which the true value is estimated to lie. It is the best estimate of the possible inaccuracy due to both random and systematic error (Taylor, John Keenan. Statistical Techniques for Data Analysis. Chelsea, Michigan: Lewis Publishers, Inc., 1990.)

Volatilize: A change from solid or liquid to gas at relatively low temperatures and pressures.

Appendix A

Comparison of Sample Preparation Techniques Used for Combustion of Cast Iron Samples

As-Cast vs. Chilled

June 29, 1998

LECO Corporation
3000 Lakeview Ave
St. Joseph, MI 49085

Purpose

To demonstrate the differences which can come about in thermal analysis due to the differing techniques of sample preparation for various iron samples.

Procedure

Sample Preparation

Three samples and a NIST SRM grey cast iron were selected for this experiment: cast iron rotor, a chilled grey iron coupon, a chilled ductile iron coupon, and NIST SRM chips. The LECO LSM-250 was used to section the samples. Preliminary sample sectioning can be seen in Figure 1 and 2.

Figure 1:

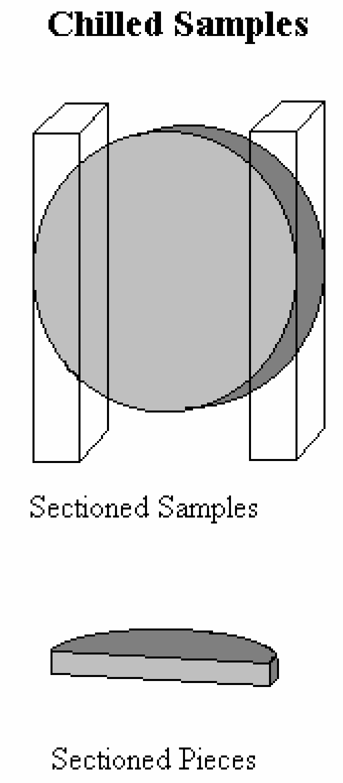
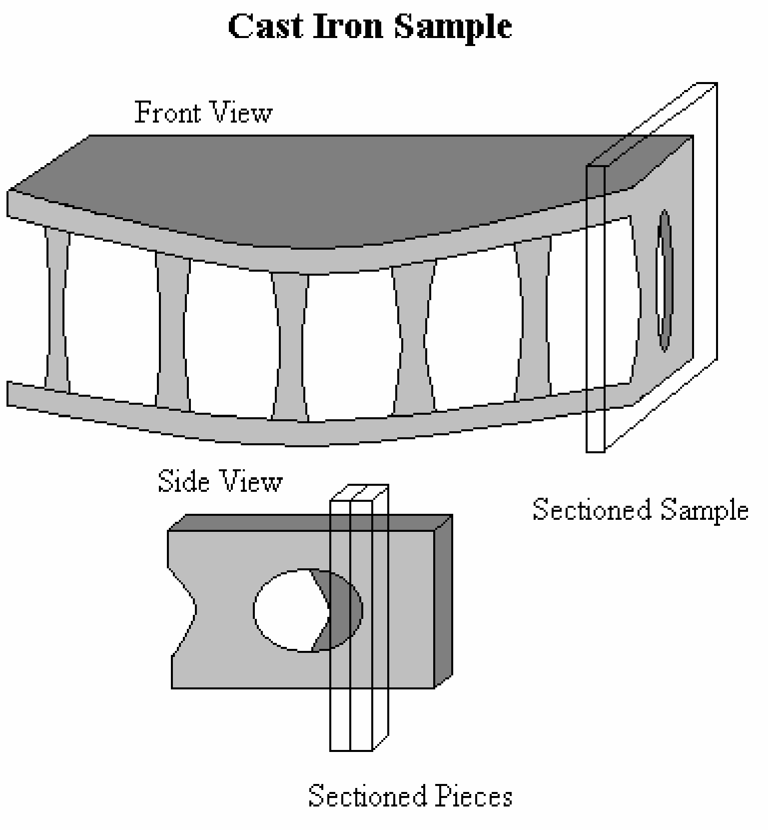


Figure 2:



The preliminary samples ranged from five to seven grams in weight. Two segments were cut from each of the selected irons. All of the selected samples, except the NIST SRM which is a chip, were surface abraded using a flat file. One section was then cut into 0.5 gram solid chunks using shears, while the other section was pulverized for 40 seconds using a ring and puck mill. A portion of the cast iron sample was pulverized for 5 seconds for comparison. The mill was cleaned between every sample to avoid contamination of the other samples.

Instrumentation

The LECO CS-200 Carbon Sulfur Determinator was used to run analyses. The parameters for the analysis channel are contained in Table 1.

Table 1–Channel Parameters for CS-200

Method Name	Method 1
Purge Time	10 sec
Delay Time	20 sec
Carbon: Significant Figures	4
Minimum Timeout	50 sec
Comparator Level	1.00
Calibration	1.0367
Blank	0.00023
Answer Format	% Carbon
Sulfur: Significant Figures	4
Minimum Timeout	60 sec
Comparator Level	2.00
Calibration	1.0111
Blank	0.00059
Answer Format	% Sulfur

Standards

NIST 338, a white cast iron powder, was used for the calibration of carbon. NIST 334, a grey cast iron chip, was used for the calibration of sulfur.

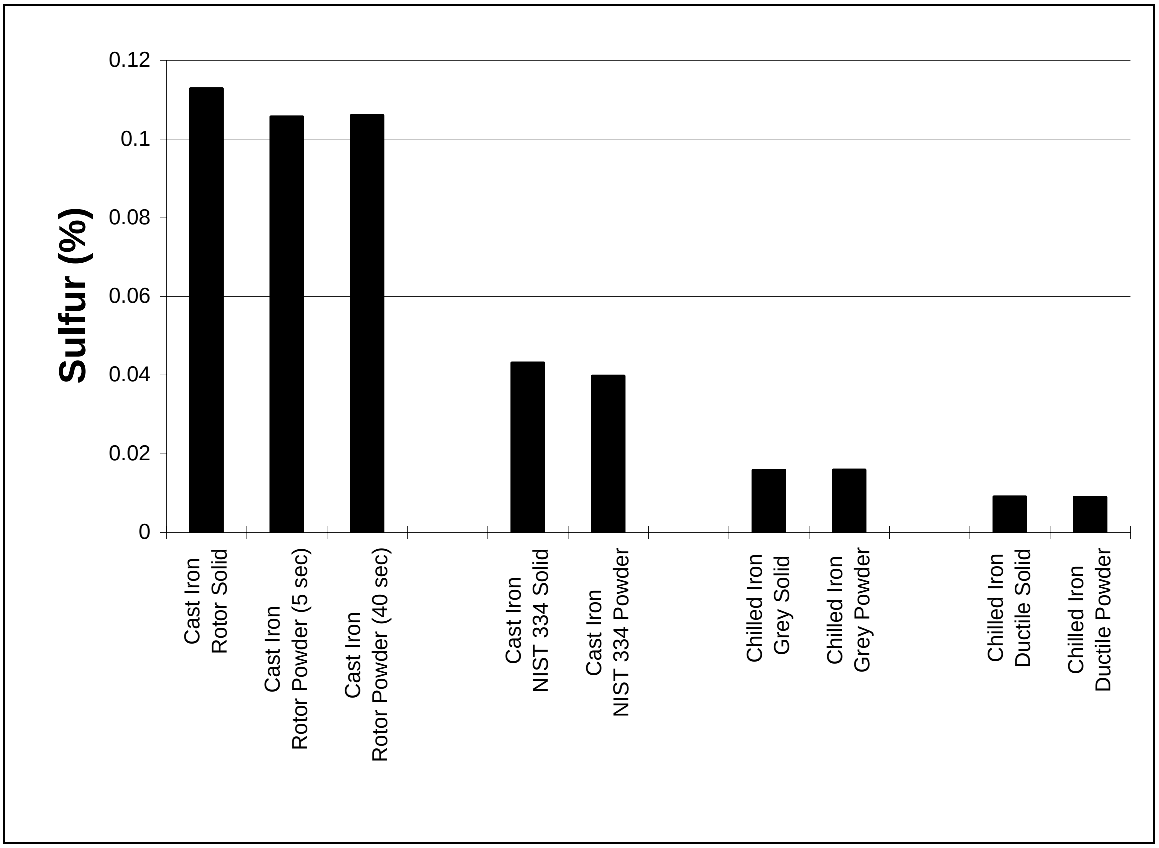
Analyses

The samples were each analyzed five consecutive times. Standards were analyzed every ten analyses to ensure that the instrument was working properly. Lecocel (-20 to +40 mesh Tungsten) and High Purity Iron Chip were used as accelerators to aid in the combustion process.

Results

The results for sulfur analysis for all of the selected samples appears in Figure 3.

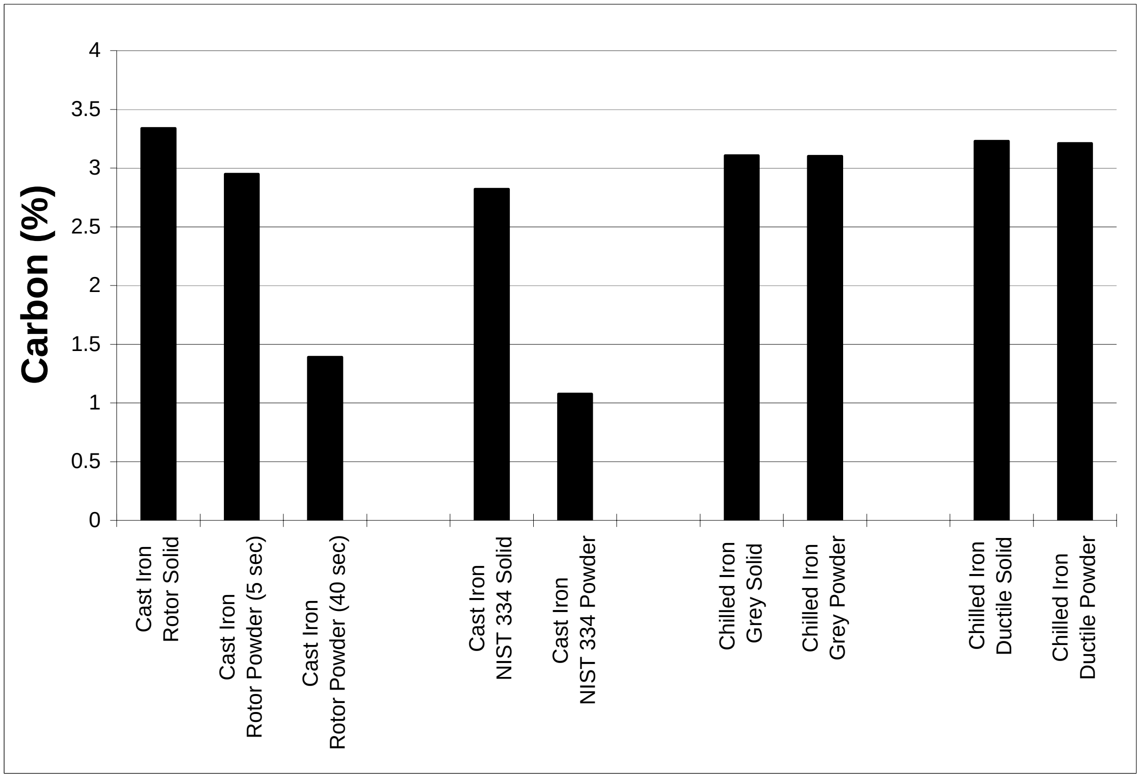
Figure 3–Comparison of Sulfur Results Using Differing Techniques



All of the values above are average values over the five completed analyses. The as-cast rotor averaged 0.113 %S in solid form. This value decreased to 0.106% when it was pulverized, both for 5 seconds and for 40 seconds. This can also be seen in the standard as NIST 334 dropped from 0.0431% S as chips down to 0.0398% S in powdered form. The chilled samples did not appear to have the same reaction when pulverized. The grey iron sample averaged 0.0159% S as a solid and a powder. And the chilled ductile iron averaged 0.0091% S as a solid, and averaged 0.0090% S as a powder.

While preparation styles seemed to affect sulfur results in the as-cast samples, it is even more prevalent when comparing carbon results in the selected samples. The carbon results using the different techniques of preparation are shown in Figure 4.

Figure 4–Comparison of Carbon Results Using Different Techniques



The as-cast rotor sample in solid form averaged 3.33% C. When pulverized for 5 seconds, the carbon level dropped down to 2.95% C. However, when the sample was pulverized for 40 seconds this value was reduced even further to 1.39% C. This same phenomenon can be seen in the NIST standard. NIST 334, as bottled, averaged 2.82% C. But when the sample was pulverized, the carbon level dropped to an average of 1.08% C. However, as seen before in sulfur comparison, both the chilled pieces stayed at relatively the same level for carbon. The chilled grey iron averaged 3.11% C as sectioned into 0.5 g chunks, and averaged 3.10% C when pulverized. The chilled ductile iron averaged 3.23% C in 0.5 g chunks, and averaged 3.21% C when pulverized.

Conclusions and Recommendations

It can be derived that sample preparation is key to getting a correct evaluation of carbon and sulfur content in cast iron samples. While pulverizing the sample allows for a more consistent sample size for combustion, carbon losses of up to 2/3 of the original sample content may be found. There also appears to be a loss of sulfur in the pulverization process. However, this does not tend to be the case with chilled iron samples.

LECO suggests that further study be done as to the actual reason for component loss in the cast iron samples when none is evident in the chilled iron samples. This should cover as many different types of cast iron as feasible.

Until then, laboratories should follow ISO 14284 and ASTM E1806 requirements for sampling and sample preparation of cast iron samples when doing thermal analysis. The sample should be in the form of a solid mass no less than 0.3 grams in weight when doing analysis using thermal methods. This should alleviate any problems which could come about due to varying sample techniques.

Application Notes

{Insert Application Notes Here}

203-821-004, 060, 109, 135, 198, 209, 261, 281, 308, 309

Inorganic Application Note

Ultra-Low Carbon and Sulfur Analysis in Steel, Nickel-Base, and Cobalt-Base Alloys

Approval

Carbon/Sulfur combustion method - ASTM E1019

Sample Preparation

Surface contamination on the sample can cause significant errors in the analytical data; therefore, care must be taken to ensure a clean, representative sample is analyzed. Solid samples should be abraded with a clean file, rinsed in acetone and dried with warm air prior to analysis. Samples that cannot be abraded due to irregular shapes should be rinsed in acetone and dried. Care must be taken to remove all traces of the solvent. If a sample is porous, it is advisable not to use solvents as it will be difficult to remove all traces.

Accessories

528-018 Crucibles (preheated); 502-173 LECOCEL® II HP; 502-231 Low C/S Fe Chip*

Calibration Standard

NIST or or other suitable standard

Program Settings

Pre-Analyze Purge:	5 seconds
Pre-Analyze Delay:	25 seconds
C IR Cell Range:	Low
C Minimum Timeout:	45 seconds
S Minimum Timeout:	55 seconds
C Comparator Level:	0.5%
S Comparator Level:	0.5%

Procedure

1. Preheat ceramic crucibles in a muffle or tube furnace at least 1250°C for not less than 15 minutes, or at 1000°C for not less than 40 minutes. The crucibles are removed from the furnace, allowed to cool for 1 to 2 minutes, and then placed in a desiccator for storage. If the crucibles are not used within four hours, they should be re-baked.
2. Prepare the instrument for operation as outlined in the operator's instruction manual.
3. Determine blank as follows:
   a. Enter a 1.000 g weight into weight stack.
   b. Add 1.000 g (±0.005 g) of 502-173 LECOCEL II HP to a preheated crucible.
   c. Place the crucible on furnace pedestal and analyze.
   d. Repeat steps 3a through 3c a minimum of 3 times.
   e. Enter blank following routine outlined in operator's instruction manual.

CS-444

4. Calibrate as follows:
    a. Weigh ~1.000 g calibration standard into a preheated 528-018 Crucible and enter the weight into weight stack.
    b. Add 1.000 g (±0.005 g) of 502-173 LECOCEL II HP to the crucible.
    c. Place the crucible on furnace pedestal and analyze.
    d. Repeat steps 4a through 4c a minimum of three times and calibrate the instrument following the auto calibration procedure as outlined in the operator's instruction manual.
    e. Verify the calibration by analyzing the calibration standard again. It should fall within the expected tolerance. If not, repeat steps 4a through 4d again.
5. Analyze samples as follows:
    a. Weigh ~1.000 g sample into a preheated 528-018 Crucible and enter the weight into weight stack.
    b. Add 1.000 g (±0.005 g) of 502-173 LECOCEL II HP to the crucible.
    c. Place crucible on furnace pedestal and analyze.

**NOTE: For some samples which are difficult to burn, it may be necessary to use ~0.75 g 502-231 Iron Chip and 1.0 g LECOCEL II HP to obtain a suitable combustion. (Generally, a peak plate current of 380 to 400+ milliamps obtained 15 to 25 seconds into the analysis indicates a good combustion.) The blank is determined by analyzing ~0.75 g 502-231 Iron Chip and 1.0 g LECOCEL II accelerators following steps 3b through 3e. Only 0.5 g samples should be analyzed, otherwise the burn will be too vigorous.*

Typical Results

Sample	Weight (g)	ppm C	ppm S
LECO 502-254 High Purity Iron @ 8 ±2 ppm C 5 ±1 ppm S	1.1089	7.8	5.6
	1.1013	8.0	4.3
	1.0058	7.6	4.9
	1.0003	7.6	5.5
	1.0150	7.4	4.7
	1.0075	8.4	4.9
	1.0674	8.2	4.9
	1.0231	8.2	4.1
	1.0102	7.3	4.4
	1.0152	7.1	5.1
		$\bar{x}$ = 7.8	**$\bar{x}$ = 4.8**
		s = 0.43	**s = 0.49**

Sample	Weight (g)	ppm C	ppm S
Nickel Base Chips	1.0020	32.0	3.1
	1.0068	31.0	3.0
	0.9971	30.0	3.1
	0.9967	30.0	2.5
	0.9949	31.0	1.9
	0.9974	29.0	2.2
	1.0006	32.0	1.8
	0.9968	29.0	1.9
	0.9970	29.0	1.7
	1.0282	31.0	2.6
		$\bar{x}$ = 30.4	**$\bar{x}$ = 2.4**
		s = 1.2	**s = 0.56**

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Form No. 203-821-004
8/07—REV6

Inorganic Application Note

Carbon in Tungsten Carbide Powder

Instrument

WC-200 Carbon Determinator

Calibration Standard

NIST 276b, BCS 352, LECO 501-123 Tungsten Carbide, or other suitable standards

Accessories

528-018 Ceramic Crucibles (preheated), 619-880 Ceramic Covers (preheated), 501-263 Copper, 502-173 Iron Chip, 773-579 Metal Scoop

Program Settings

Pre-Analyze Purge	20 seconds
Pre-Analyze Delay	0 seconds
Collect Time	50 seconds
Trap Purge Time	65 seconds
Carbon Minimum Time-Out	35 seconds
Carbon Comparator Level	1.0%

Sample Weight

~0.25 ±0.005 grams

Sample Preparation

Uniform powder

Method

1. Preheat ceramic crucibles and covers in a muffle or tube furnace at 1350°C for not less than 15 minutes or at 1000°C for not less than 40 minutes. Remove the crucibles from the furnace, cool for 1-2 minutes and place in a desiccator for storage. If the crucibles are not used within four hours, they should be rebaked.
2. Prepare the instrument as outlined in the operator's instruction manual.
3. Determine the instrument blank.
   a. Enter 1.000 gram weight into weight stack.
   b. Add 1.00 (±0.005 g) of 501-263 Copper and 1.000 (±0.005 g) of 502-231 Iron Chip.
   c. Place crucible cover on crucible.
   d. Place crucible on furnace pedestal and analyze.
   e. Repeat steps 3a through 3d a minimum of three times.
   f. Enter blank following routine outlined in operator's instruction manual.

WC200

4. Calibrate instrument.
    a. Weigh ~0.250 g (±0.005 g) Tungsten Carbide calibration standard into a preheated 528-018 Crucible and enter weight into weight stack.
    b. Add 1.000 g (±0.005 g) of 501-263 Copper and 1.000 g (±0.005 g) 502-231 Iron Chip to the crucible.
    c. Place crucible cover on crucible.
    d. Place crucible on furnace pedestal and analyze.
    e. Repeat steps 4a through 4d a minimum of three to five times and calibrate the instrument following the auto calibration procedure as outlined in the operator's instruction manual.
    f. Verify the calibration by analyzing the calibration standard again. It should fall within the expected tolerance. If not, repeat steps 4a through 4e.
5. Analyze samples.
    a. Weigh ~0.250 g (±0.005 g) sample into a preheated 528-018 Crucible and enter weight into weight stack.
    b. Add 1.000 g (±0.005 g) of 501-263 Copper and 1.000 g (±0.005 g) 502-231 Iron Chip to the crucible.
    c. Place crucible cover on crucible.
    d. Place crucible on furnace pedestal and analyze.

NOTE: For optimum results, a five-place balance is recommended. Crucibles and covers should be handled with crucible tongs.

Typical Results

Sample	Weight	% Carbon
BCS 352 Tungsten Carbide 6.116%C	0.25800	6.107
	0.25120	6.122
	0.25636	6.118
	0.25728	6.114
	0.25972	6.113
	0.25792	6.117
	0.25425	6.114
	0.25845	6.111
	0.25483	6.108
	0.25584	6.108
	0.25734	6.116
	0.25308	6.120
	0.25061	6.118
	0.25515	6.121
	0.25034	6.126
	Average	***6.1155***
	Std. Deviation	***0.00557***
	RSD (%)	***0.091%***

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Inorganic Application Note

Sulfur in Copper Base Materials

Instrument

CS-200, 300, 400, 444, and 600-Series Determinators
(Differences in instrument setup for the 600-Series are noted in parenthesis.)

Calibration Standard

LECO 502-403 Copper Pin, NIST SRM 885 refined copper pin, or other suitable standards

Accessories

Preheated LECO 528-018 Ceramic Crucibles, 773-579 Metal Scoop, 502-403 Copper Pin or other similar-sized copper solid, 501-263 Copper Accelerator

Sample Weight

~1.0 gram

Sample Preparation

Surface contamination on the sample can cause significant errors in the analytical data and care must be taken to ensure a clean representative sample is analyzed.

Program Settings

Pre-Analyze Purge:	10 seconds
Pre-Analyze Delay:	25 seconds
Sulfur Minimum Time-Out:	60 seconds
Sulfur Comparator Level:	1.00%
Clean Interval:	Every 50 analyses
Power Level:	Refer to Instrument Set-up for details; typically the Power Level Knob is set between the 12 and 3 o'clock position. (*CS600-Series:* Typically the Furnace Power is set between 30 and 40.)

Notes

1. Solid samples burn less aggressively than chips or powders. Care should be given to setting up the instrument with the most dense sample. It is suggested that 502-403 Copper Pin Samples or a similar solid copper sample weighing ~1.0 g be used when setting up the instrument. Place the sample in the crucible on top of the accelerator.
2. A clean combustion tube and dust filter are essential before starting this procedure.

Instrument Setup

This method lowers the power level from the maximum set in a typical method in order to decrease the dust produced from combustion of the sample.

1. Turn the Power Level knob counterclockwise to a twelve o'clock position. The knob is located on the front panel. (*CS600-Series:* Set the Furnace Low and High Power to 30 in method parameters.)
2. Add ~1.0 g—one level 773-579 Metal Scoop—501-263 Copper Accelerator to a pre-heated 528-018 Crucible so that it is evenly distributed on the bottom of the crucible.
3. Place the LECO 502-403 Copper Pin or ~1.0 g copper solid into the crucible.
4. Enter a 1.0 g weight into the instrument.
5. Place crucible on furnace pedestal and analyze.
6. For a complete combustion, the following plate currents should be observed:
   Maximum: ~250 to 300 mA; 20 seconds into combustion cycle: ~180 to 220 mA
   (*CS600-Series:* Maximum: ~280 to 320 mA; 20 seconds into combustion cycle: ~220 to 260 mA)
7. The sulfur peak should start between 15 and 25 seconds after the combustion cycle begins. (*CS600-Series:* For solids, sulfur peak should start between 10 and 20 seconds after the combustion cycle begins. For powders and chips, the sulfur peak should start between 5 and 15 seconds.)
8. Immediately following the combustion cycle, open the furnace and remove the crucible using the tongs. Look at the sample while it is still red hot. It should visually be a flat smooth melt with no dark spots at the bottom of the crucible.
   Caution sample may be liquid and will be extremely hot!

CS-Series

Instrument Setup (continued)

9. If the plate current exceeds 320 mA (*CS600-Series:* 360 mA) for most of the analysis then dust has probably been generated which will more than likely cause sulfur recovery losses.
10. a. If steps 6 through 8 are satisfied, proceed to step 1 of Method.
    b. If plate current exceeds 320 mA (*CS600-Series:* 360 mA) for most of the analysis—step 9, turn power level control slightly counter-clockwise to reduce the power level. (*CS600-Series:* Reduce the Furnace Low and High Power settings in method parameters.) Manually brush dust filter and cleaner head to remove all dust that has been generated then repeat steps 3 through 8.
    c. If steps 6 through 8 are not satisfied, continue until desired plate current in achieved.

Method

1. Preheat ceramic crucibles in a muffle or tube furnace at 1250°C for not less than 15 minutes or at 1000°C for not less than 40 minutes. The crucibles are removed from the furnace, allowed to cool for 1 to 2 minutes and placed in a desiccator for storage. If the crucibles are not used within four hours, they should be rebaked.
2. Determine the blank:
    a. Enter 1.000 gram weight into weight stack.
    b. Add ~1.0 g—one level 773-579 Metal Scoop—501-263 Copper Accelerator to a preheated 528-018 Crucible so that it is evenly distributed on the bottom of the crucible.
    c. Place crucible on furnace pedestal and analyze.
    d. Repeat steps 2a through 2c a minimum of five times.
    e. Enter blank following routine outlined in operator's instruction manual.
3. Calibrate:
    a. Add ~1.0 g—one level 773-579 Metal Scoop—501-263 Copper Accelerator to a preheated 528-018 Crucible so that it is evenly distributed on the bottom of the crucible.
    b. Weigh ~1.0 g calibration standard and place into the center of the crucible entering the weight into the weight stack.
    c. Place crucible on furnace pedestal and analyze.
    d. Repeat steps 3a through 3c a minimum of five times and calibrate the instrument following the auto calibration procedure as outlined in the operator's instruction manual.
    e. Verify the calibration by analyzing the calibration standard again. It should fall within the expected tolerance. If not repeat steps 3a through 3e.
4. Analyze samples:
    a. Add ~1.0 g—one level 773-579 Metal Scoop—501-263 Copper Accelerator to a preheated 528-018 Crucible so that it is evenly distributed on the bottom of the crucible.
    b. Weigh ~1.0 g sample and place into the center of the crucible entering the weight into the weight stack.
    c. Place crucible on furnace pedestal and analyze.

Typical Data *Obtained on a LECO CS-444*

Calibrated with BAM NR 227@0.122% S

Sample	*Weight (g)*	*Sulfur (%)*
BAM NR 227	0.9511	0.123
@ 0.122% S	0.9668	0.123
	0.9806	0.122
BCS 183/4	0.9768	0.110
Leaded Gunmetal	0.9549	0.110
Chips @0.11% S	0.9460	0.110
BCS 180/2	0.9287	0.0058
Copper-Nickel Chips	1.0416	0.0059
@0.006% S	0.9293	0.0056

Calibrated with NIST 885 @0.0018% S

Sample	*Weight (g)*	*Sulfur (%)*
NIST 885	0.8989	0.0018
Refined Copper	0.8803	0.0019
Pin @ 0.0018% S	0.8959	0.0018
LECO 502-403	0.9991	0.00093
Copper Pin	0.9930	0.00096
@0.00093% S	0.9957	0.00091

NOTE: If carbon analysis is required simultaneously; this same technique applies.

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Inorganic Application Note

Carbon and Sulfur in Lime

Instrument

CS-200, CS-300, CS-400 and CS-444 Series Carbon and Sulfur Determinators

Calibration Standard

NIST or other suitable standards
Suggestions: LECO 502-319 @ 1.36% C and 1.53% S,
NIST SRM 2690 Fly Ash @ 0.15% S

Accessories

LECO 528-018 Ceramic Crucibles (preheated), LECO 773-579 Metal Scoop, 763-266 LECOCEL or 763-263 LECOCEL III, and 502-231 or 501-077 Iron Chip Accelerators (for carbon-only instruments substitute 501-263 Copper Accelerator for LECOCEL or LECOCEL III)

Sample Weight

~0.20 to 0.25 grams

Sample Preparation

Sample should be uniform powder.

Instrument Settings

Power Level:	maximum
Pre-analyze Purge*:	5 seconds
Pre-analyze Delay*:	10 seconds
Carbon Minimum Time-out:	50 seconds
Carbon Comparator Level:	1.00%
Sulfur Minimum Time-out:	60 seconds
Sulfur Comparator Level:	1.00%

**For improved precision at low carbon levels (<0.1%), a pre-analyze purge of 10 and delay of 25 seconds is recommended.*

Note

Samples containing water of hydration (crystallization) or hydroxides could experience diminished sulfur recovery.

Carbon/Sulfur

Method

1. Preheat ceramic crucibles in a muffle or tube furnace at 1200 to 1300°C for not less than 15 minutes or at 950 to 1050°C for not less than 40 minutes. Remove the crucibles from the furnace, cool for 1 to 2 minutes, and place in a desiccator for storage. If the crucibles are not used within four hours, they should be rebaked.
2. Determine the blank.
    a. Enter 1.000 g weight into weight stack.
    b. Add one level 773-579 Metal Scoop of LECOCEL followed by one level metal scoop of iron chip accelerator to a preheated crucible.
    c. Place crucible on furnace pedestal and analyze.
    d. Repeat steps 2a through 2c a minimum of five times.
    e. Enter blank following routine outlined in operator's instruction manual.
3. Calibrate.
    a. Weigh ~0.20 to 0.25 g calibration standard into the center of the preheated crucible. Enter the weight into the weight stack.
    b. Add one level 773-579 Metal Scoop of LECOCEL followed by one level metal scoop of iron chip accelerator covering the calibration sample.
    c. Place crucible on furnace pedestal and analyze.
    d. Repeat steps 3a through 3c a minimum of five times and calibrate the instrument following the calibration procedure as outlined in the operator's instruction manual.
    e. Verify the calibration by analyzing the calibration standard again. It should fall within the expected tolerance. If not repeat steps 3a through 3e.
4. Analyze samples.
    a. Weigh ~0.20 to 0.25 g sample into the center of the crucible. Enter the weight into the weight stack.
    b. Add one level 773-579 Metal Scoop of LECOCEL followed by one level metal scoop of iron chip accelerator covering the sample.
    c. Place crucible on furnace pedestal and analyze.

Typical Results

	Weight (g)	**Carbon (%)**	**Sulfur (%)**
LECO 502-319	0.2056	1.36	1.53
Ore	0.2035	1.36	1.53
@1.36% C,	0.2024	1.36	1.53
1.53% S	0.2175	1.36	1.54
	0.2130	1.36	1.52
NIST 2690	0.1966	0.393	0.151
Fly Ash	0.2072	0.392	0.150
@ 0.15% S	0.2000	0.386	0.150
Carbon is	0.2019	0.383	0.149
not certified	0.1960	0.383	0.151

	Weight (g)	**Carbon (%)**	**Sulfur (%)**
Quicklime	0.1951	1.914	0.0168
Sample A	0.2120	1.842	0.0174
	0.2120	1.910	0.0161
Quicklime	0.2020	0.606	0.0220
Sample B	0.1993	0.653	0.0213
	0.2072	0.595	0.0218
Dolomitic Lime	0.2171	0.209	0.0249
Sample A	0.2067	0.235	0.0240
	0.1951	0.213	0.0232
Dolomitic Lime	0.2217	0.0952	0.0149
Sample B	0.2040	0.0918	0.0151
	0.2173	0.0914	0.0152

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Inorganic Application Note

Carbon and Sulfur in Potassium Heptafluorotantalate Materials

Sample Preparation

Contamination on the sample can cause significant errors in the analytical data, therefore care must be taken to ensure a clean representative sample is analyzed.

Accessories

528-018 Crucibles (preheated); 502-173 LECOCEL® II HP, 502-231 Iron Chip, 502-351 Halogen Trap Material, 773-579 Metal Scoop, 781-420 Manual Cleaner, 769-641 Fluorine/Chlorine Trap Kit

Calibration Standard

NIST (steel) or other suitable standard

Sample Weight

~0.1 g

Program Settings

Pre-Analyze Purge:	15 seconds
Pre-Analyze Delay:	25 seconds
C Minimum Timeout:	50 seconds
C Comparator Level:	0.5%
S Minimum Timeout:	60 seconds
S Comparator Level:	1.0%

NOTE: *The oxides of Potassium Heptaluorotantalate produced during combustion may cause a flow restriction with the auto cleaner, therefore it is necessary to use the MANUAL CLEANER. The down stream pressure on the furnace will decrease if there is a restriction from these oxides.*

Procedure

1. Install a 769-641 Trap in the measure line between the furnace and determinator, following instructions found in the trap kit. Pack the trap with 502-351Halogen Trap Material or equivalent.
2. Preheat ceramic crucibles in a muffle or tube furnace at 1250°C for not less than 15 minutes or at 1000°C for not less than 40 minutes. The crucibles are removed from the furnace, allowed to cool for 1 to 2 minutes and placed in a desiccator for storage. If the crucibles are not used within four hours, they should be re-baked.
3. Prepare instrument as outlined in the operator's instruction manual.
4. Determine the blank.
   a. Enter 1.000 g weight into the weight stack.
   b. Add 1.000 g (±0.005 g) of 502-173 LECOCEL II HP and 1.000 g (±0.005 g) of 502-231 Iron Chip to a preheated 528-018 Crucible.
   c. Place the crucible on furnace pedestal and analyze.
   d. Repeat steps 4a through 4c a minimum of three times.
   e. Enter blank following routine outlined in operator's instruction manual.

CS-444
CS-400

Procedure (continued from page 1)

5. Calibrate.
   a. Weigh ~0.5 g (steel) calibration standard into a preheated 528-018 Crucible and enter weight into the weight stack.
   b. Add 1.000 g (±0.005 g) of 502-173 LECOCEL II HP and 1.000 g (±0.005 g) 502-231 Iron Chip to the preheated crucible.
   c. Place the crucible on furnace pedestal and analyze.
   d. Repeat steps 5a through 5c a minimum of three times and calibrate the instrument following the auto calibration procedure as outlined in the operator's instruction manual.
   e. Verify the calibration by analyzing the calibration standard again. It should fall within the expected tolerance. If not, repeat steps 5a through 5d.
6. Analyze samples.
   a. Weigh ~0.1 g sample into a preheated 528-018 Crucible and enter weight into the weight stack.
   b. Add 1.000 g (±0.005 g) of 502-173 LECOCEL II HP and 1.000 g (±0.005 g) 502-231 Iron Chip to the preheated crucible.
   c. Place the crucible on furnace pedestal and analyze.

Typical Results

Sample	Weight	% Carbon	% Sulfur
K_2TaF_7	0.1071	0.0046	0.0174
	0.1059	0.0053	0.0204
	0.1058	0.0054	0.0185

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ISO-9001:2000 No. FM 24045

Inorganic Application Note

Sulfur in Battery Paste (PbO/$PbSO_4$)

Instrument

CS-200, 300, 400, 444, and 600-Series Determinators (Differences in instrument setup for the 600-Series are noted in parenthesis.)

Calibration Standard

502-319 LECO Pulp, or other suitable standards

Accessories

528-018 Ceramic Crucibles (preheated), 773-579 Metal Scoop, 502-403 Copper Pin or other similar sized copper solid, 501-263 Copper Accelerator

Sample Weight ~0.05 to 0.15 grams

Sample Preparation None

Program Settings

Power Level:	See Instrument Setup
Pre-Analyze Purge:	10 seconds
Pre-Analyze Delay:	25 seconds
Sulfur Minimum Time-Out:	60 seconds
Sulfur Comparator Level:	1.00%
Clean Interval:	Every 50 analyses

Notes

1. Solid samples burn less aggressively than chips or powders. Care should be given to setting up the instrument with the most dense sample. It is suggested that 502-403 Copper Pin samples or a similar solid copper sample weighing ~1.0 g be used when setting up the instrument.
2. This method may be utilized for simultaneous carbon analysis.

Instrument Setup

This method lowers the power level from the maximum set in a typical method in order to decrease the dust produced from combustion of the sample.

1. Turn the Power Level knob counterclockwise to a twelve o'clock position. The knob is located on the front panel. Typically the power level knob is set between the 12 and 3 o'clock position. (*CS600-Series:* Set the Furnace Low and High Power to 30 in method parameters.)
2. Add ~ 1 g—one level 773-579 Metal Scoop—of 501-263 Copper Accelerator to a preheated 528-018 Crucible so that it is evenly distributed on the bottom of the crucible.
3. Place the LECO 502-403 Copper Pin or a ~1.0 g copper solid into the crucible.
4. Enter a 1 gram weight into the instrument.
5. Place crucible on furnace pedestal and analyze.
6. For a complete combustion the following plate currents should be observed:
   Maximum: ~250 to 300 mA; 20 seconds into combustion cycle: ~180 to 220 mA
   (*CS600-Series:* Maximum: ~280 to 320 mA; 20 seconds into combustion cycle: ~220 to 260 mA)
7. The sulfur peak should start between 15 and 25 seconds after the combustion cycle begins. (*CS600-Series:* For solids, sulfur peak should start between 10 and 20 seconds after the combustion cycle begins. For powders and chips, the sulfur peak should start between 5 and 15 seconds.)

CS-Series

8. Immediately following the combustion cycle, open the furnace and remove the crucible using the tongs. Look at the sample while it is still red hot. It should visually be a flat smooth melt with no dark spots at the bottom of the crucible. ***Caution: Sample may be liquid and will be extremely hot!***
9. If the plate current exceeds 320 mA (*CS600-Series:* 360 mA) for most of the analysis then dust has probably been generated which will more than likely cause sulfur recovery losses.
10. a. If steps 6 through 8 are satisfied proceed to step 1 of Method.
    b. If plate current exceeds 320 mA (*CS600-Series:* 360 mA) for most of the analysis—step 9—turn power level control slightly counter-clockwise to reduce the power level. (*CS600-Series:* Reduce the Furnace Low and High Power settings in method parameters.) Manually brush dust filter and cleaner head to remove all dust that has been generated then repeat steps 3 through 8.
    c. If steps 6 through 8 are not satisfied, continue until desired plate current is achieved.

Method

1. Preheat ceramic crucibles in a muffle or tube furnace at 1250°C for not less than 15 minutes or at 1000°C for not less than 40 minutes. The crucibles are removed from the furnace, allowed to cool for 1 to 2 minutes and placed in a desiccator for storage. If the crucibles are not used within four hours, they should be rebaked.
2. Determine the blank.
    a. Enter 1.000 gram weight into weight stack.
    b. Add two level 773-579 Metal Scoop of 501-263 Copper Accelerator to a preheated 528-018 Crucible so that it is evenly distributed on the bottom of the crucible.
    c. Place crucible on furnace pedestal and analyze.
    d. Repeat steps 2a through 2c a minimum of five times.
    e. Enter blank following routine outlined in operator's instruction manual.
3. Calibrate.
    a. Weigh ~0.15 g calibration standard into the center of a preheated 528-018 Crucible entering the weight into the weight stack.
    b. Add two level 779-579 Metal Scoop of 501-263 Copper Accelerator to the crucible covering the sample.
    c. Place crucible on furnace pedestal and analyze.
    d. Repeat steps 3a through 3c a minimum of five times and calibrate the instrument following the auto calibration procedure as outlined in the operator's instruction manual.
    e. Verify the calibration by analyzing the calibration standard again. It should fall within the expected tolerance. If not repeat steps 3a through 3e.
4. Analyze samples.
    a. Weigh ~ 0.10 g sample and place into the center of the crucible entering the weight into the weight stack.
    b. Add two level 779-579 Metal Scoop of 501-263 Copper Accelerator to the crucible covering the sample.
    c. Place crucible on furnace pedestal and analyze.

Typical Results ***Obtained on a LECO CS-200; Low Temperature Method***

Sample	A	B	C	D	E	F
Sulfur %	0.446	2.081	2.170	1.485	0.971	1.562
	0.451	2.080	2.168	1.504	0.971	1.553
	0.465	2.081	2.146	1.487	0.972	1.563
	0.444	2.085	2.173	1.493	0.976	1.552
	0.440	2.056	2.151	1.495	0.973	1.565
Average S %	***0.449***	***2.077***	***2.162***	***1.493***	***0.973***	***1.559***
Std Dev.	***0.010***	***0.012***	***0.012***	***0.007***	***0.002***	***0.006***

Note: If carbon analysis is required simultaneously, this same technique applies.

Delivering the Right Results

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Inorganic Application Note

Carbon and Sulfur in Steel, Nickel-Base, and Cobalt-Base Alloys

Instrument

CS600-Series

Sampling and Sample Preparation

Surface contamination on the sample can cause significant errors in the analytical data; therefore, care must be taken to ensure a clean, representative sample is analyzed. Solid samples should be abraded with a clean file, rinsed in acetone and dried with warm air prior to analysis. Samples that cannot be abraded due to irregular shapes should be rinsed in a suitable solvent such as acetone, and dried with warm air. Care must be taken to remove all traces of the solvent. If a sample is porous, refrain from using solvents, as it will be difficult to remove all traces of the solvent by drying. Refer to ASTM E1806 for additional sampling and sample preparation information.

Accessories

528-018 or 528-018HP Ceramic Crucibles (preheated)*; LECOCEL II (501-008) or LECOCEL II HP (502-173) accelerator.

**Ceramic crucibles are baked in a muffle or tube furnace (LECO TF-10) at 1250°C for a minimum of 15 minutes, or at 1000°C for 40 minutes. The crucibles are removed from the furnace, allowed to cool for 1 to 2 minutes, and are transferred to a desiccator for storage. If the crucibles are not used within four hours, they should be re-baked.*

Calibration

There are several suitable calibration samples available from LECO. Likewise, NIST, JK, JSS, and BCS are certified bodies that have a variety of certified reference materials (SRM/CRM) available as well. It is important that both high- and low-carbon ranges are calibrated. Single or multipoint calibration curves can be utilized. Refer to the operator's instruction manual for details.

Method Parameters

Purge Time (seconds):	1**
Delay Time (seconds):	8**
Furnace Low Power (%):	100
Furnace High Power (%):	100
Furnace Ramp Rate:	0

	Carbon	*Sulfur*
Minimum Timeout (seconds):	40	40
Comparator Level:	1.00	1.00
Significant Digits:	4 or 5	4 or 5
Integration Delay:	0	0

***For optimum analytical performance on samples with low carbon and sulfur content (≤0.05%), a purge time of 10 seconds and a delay time of 20 seconds is recommended.*

CS600

Procedure

1. Prepare instrument for operation as outlined in the operator's instruction manual.
2. Determine blank.
    a. Enter 1.0000 g weight into weight stack.
    b. Add ~1.5 g of accelerator to crucible.
    c. Place the crucible on the furnace pedestal (or appropriate autoloader position if so equipped), and analyze.
    d. Repeat steps 2a through 2c a minimum of five times.
    e. Enter blank following procedure outlined in the operator's instruction manual.
3. Calibrate.
    a. Weigh ~1.0 g calibration sample into crucible and enter weight into weight stack.
    b. Add ~1.5 g of accelerator on top of sample.
    c. Place the crucible on the furnace pedestal (or appropriate autoloader position if so equipped), and analyze.
    d. Repeat steps 3a through 3c a minimum of five times for each calibration sample intended for calibration.
    e. Calibrate using the procedure outlined in the operator's instruction manual.
4. Analyze Samples.
    a. Weigh ~1.0 g sample into crucible and enter weight into weight stack.
    b. Add ~1.5 g of accelerator on top of sample.
    c. Place crucible on furnace pedestal (or appropriate autoloader position if so equipped), and analyze.

Note: *Some "solid" samples, notably nickel and/or cobalt-base alloys, are difficult to combust and may require additional accelerator. Likewise, reducing the sample to small chunks, chips, or pieces will facilitate combustion. For additional information on Carbon and Sulfur Determination using an Induction Furnace IR detection instrument, request LECO's Application Tips CD (209-050-055).*

Typical Results

Sample	Weight (g)	C %	S %
LECO	1.0	0.605	0.0176
501-505		0.605	0.0172
Steel Ring		0.605	0.0169
0.607 % C		0.607	0.0171
0.0172% S		0.607	0.0174
		0.605	0.0176
		0.606	0.0178
		0.604	0.0173
		0.606	0.0173
		0.605	0.0168
	X =	***0.606***	***0.0173***
	s =	***0.001***	***0.0003***
LECO	1.0	0.0375	0.0223
501-501		0.0380	0.0221
Steel Ring		0.0375	0.0222
0.0377 % C		0.0377	0.0222
0.0220 % S		0.0376	0.0223
		0.0376	0.0222
		0.0373	0.0221
		0.0376	0.0222
		0.0377	0.0223
		0.0377	0.0222
	X =	***0.0376***	***0.0222***
	s =	***0.0002***	***0.0001***

Sample	Weight (g)	C %	S %
LECO	1.0	0.00089	0.00062
502-348		0.00089	0.00067
Low C and S		0.00094	0.00068
Steel Pin		0.00095	0.00060
0.0009 % C		0.00085	0.00064
0.0007 % S		0.00085	0.00061
		0.00090	0.00062
		0.00090	0.00060
		0.00090	0.00065
		0.00089	0.00055
	X =	***0.00090***	***0.00062***
	s =	***0.00003***	***0.00004***
LECO	1.0	0.0414	0.0025
501-933		0.0414	0.0027
Ni-Base Alloy		0.0413	0.0027
Chip Sample		0.0414	0.0028
0.042 % C		0.0415	0.0027
0.003 % S		0.0413	0.0028
		0.0414	0.0028
		0.0415	0.0028
		0.0412	0.0027
		0.0414	0.0029
	X =	***0.0414***	***0.0027***
	s =	***0.0001***	***0.0001***

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Form No. 203-821-261
8/07-REV1

Inorganic Application Note

Carbon Determination in Tungsten Carbide

Instrument

WC600

Sampling and Sample Preparation

Typically, samples should be in the form of fine powder (- 200 mesh).

Accessories

528-018 or 528-018HP Ceramic Crucibles (preheated)*, 619-880 Crucible Covers (optional), 763-266 LECOCEL and 501-263 Copper Chip accelerator; Five place (0.01 mg) balance (recommended).

**Ceramic crucibles and covers are baked in a muffle or tube furnace (LECO TF10) at 1250°C for a minimum of 15 minutes, or at 1000°C for 40 minutes. The crucibles are removed from the furnace, allowed to cool for 1 to 2 minutes, and are transferred to a desiccator for storage. If the crucibles/covers are not used within four hours, they should be re-baked.*

Calibration

LECO 502-123 Tungsten Carbide (WC). NIST and BCS are certified bodies that have tungsten carbide reference materials (SRM/CRM) available as well.

Method Parameters

Purge Time (seconds)	50
Delay Time (seconds)	30
Sample Cool Time (seconds)	20
Furnace Low Power (%)	90
Furnace High Power (%)	90
Furnace Ramp Rate (%)	0

Carbon

Minimum Timeout (seconds)	90
Comparator Level	100.00
Significant Digits	5
Integration Delay	0

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.
   b. Add 1.2 g (±0.010 g) of LECOCEL and 1.8 g (±0.010 g) of copper accelerator to crucible.
   c. Place the crucible on the furnace pedestal (or appropriate auto-loader position if so equipped) and analyze.
   d. Repeat steps 2a through 2c a minimum of five times.
   e. Enter blank following procedure outlined in operator's instruction manual.

WC600

3. Calibrate.
    a. Weigh 0.25 g (±0.005 g) WC calibration sample (to the nearest 0.01 mg) into crucible and enter mass into Sample Login.
    b. Add 1.2 (±0.010 g) of LECOCEL followed by 1.8 (±0.010 g) of copper accelerator on top of sample (take care to evenly cover sample with accelerator).
    c. Place the crucible on the furnace pedestal (or appropriate auto-loader position if so equipped) and analyze.
    d. Repeat steps 3a through 3c a minimum of five times for each calibration sample intended for calibration.
    e. Calibrate using the procedure outlined in the operator's instruction manual.
4. Analyze Samples.
    a. Weigh 0.25 g (±0.005 g) WC sample (to the nearest 0.01 mg) into crucible and enter mass into Sample Login.
    b. Follow steps 3b through 3c.

    Note: Using a 619-880 Ceramic Cover in conjunction with the 528-018 or 528-018HP Crucibles may help reduce splatter of the products of combustion onto the combustion tube. This in-turn can improve the usable life of the combustion tube. The 619-880 Covers must be baked off using the same procedure as used for the 528-018 Crucibles.

Typical Results

Sample	**Mass g**	**C %**	**Sample**	**Mass g**	**C %**
NIST	0.24995	6.1023	Production	0.25198	5.9912
SRM 276b	0.25042	6.1001	Tungsten	0.25011	5.9935
Tungsten	0.25091	6.0986	Carbide	0.25196	5.9889
Carbide	0.24945	6.1035		0.25218	5.9968
@ 6.10% C	0.25156	6.1058		0.25216	5.9955
	0.25081	6.0974		0.25055	5.9992
	0.24972	6.1034		0.25101	5.9981
	0.25223	6.0957		0.25118	5.9956
	0.24973	6.0955		0.25048	5.9981
	0.25056	6.0978		0.25174	5.9931
	***X* =**	***6.1000***		***X* =**	***5.9950***
	***s* =**	***0.00356***		***s* =**	***0.00331***
LECO	0.24989	6.1954	BS 107	0.25035	6.1355
501-123	0.25368	6.1954	Tungsten	0.24978	6.1431
Tungsten	0.25102	6.2030	Carbide	0.24952	6.1304
Carbide	0.25338	6.2015	@ 6.14% C	0.25026	6.1457
@ 6.20% C	0.25287	6.1948		0.25238	6.1353
	0.25001	6.2023		0.25129	6.1409
	0.25162	6.1979		0.25122	6.1403
	0.25084	6.2033		0.25223	6.1479
	0.25221	6.2026		0.24971	6.1399
	0.25299	6.2040		0.25113	6.1410
	***X* =**	***6.2000***		***X* =**	***6.1400***
	***s* =**	***0.00371***		***s* =**	***0.00515***

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Form No. 203-821-281
8/07-REV1

Inorganic Application Note

Carbon in Refractory and Reactive Metals and Their Alloys[†]

Instrument

CS600-Series

Sampling and Sample Preparation

Surface contamination on the sample can cause significant errors in the analytical data; therefore, care must be taken to ensure a clean, representative sample is analyzed. Solid samples should be abraded with a clean file, rinsed in acetone, and dried with warm air prior to analysis. Samples that cannot be abraded due to irregular shapes should be rinsed in a suitable solvent such as acetone and dried with warm air. Care must be taken to remove all traces of the solvent. If a sample is porous, it is advisable to avoid using solvents, as it will be difficult to remove all traces of the solvent by drying.

Method Reference

ASTM E1941

Accessories

528-018 or 528-018HP Ceramic Crucibles and 619-880 Ceramic Crucible Covers (preheated)*; 502-492 High Purity Copper Accelerator and 502-231 High Purity Iron Chip Accelerator

**Ceramic crucibles and covers are baked in a muffle or tube furnace (LECO TF10) at 1250°C for a minimum of 15 minutes, or at 1000°C for 40 minutes. The crucibles/covers are removed from the furnace, allowed to cool for 1 to 2 minutes, and transferred to a desiccator for storage. If the crucibles/covers are not used within four hours, they should be re-baked.*

Calibration Samples

NIST or other suitable reference materials.

Note: Due to limited availability of refractory/reactive reference materials, steel calibration samples can be used to calibrate.

Method Parameters

Purge Time (seconds)	10
Delay Time (seconds)	20
Furnace Low Power (%)	100
Furnace High Power (%)	100
Furnace Ramp Rate	0

	Carbon
Minimum Timeout (seconds)	40
Comparator Level	1.00
Significant Digits	4 or 5
Integration Delay	0

CS600

[†] Ti, Zr, W, Ta, Mo, Nb, Hf, and Re

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. Add ~1.0 g of iron chip and ~1.5 g of copper accelerator to a prepared crucible.
    c. Place a prepared crucible lid on the crucible.
    d. Place the crucible on the furnace pedestal (or appropriate autoloader position if so equipped) and initiate Analyze (F5).
    e. Repeat steps 2a through 2d a minimum of five times.
    f. Set blank following procedure outlined in operator's instruction manual.
3. Calibrate/Drift Correct.
    a. Weigh ~0.5 g calibration/drift sample into a prepared crucible, enter mass and sample identification into Sample Login (F3).
    b. Add ~1.0 g of iron chip accelerator and ~1.5 g of copper accelerator on top of sample.
    c. Place a prepared crucible lid on the crucible.
    d. Place the crucible on the furnace pedestal (or appropriate autoloader position if so equipped) and initiate Analyze (F5).
    e. Repeat steps 3a through 3d a minimum of five times for each calibration/drift sample intended for calibration/drift.
    f. Calibrate/drift correct using the procedure outlined in the operator's instruction manual.
4. Analyze Samples.
    a. Weigh ~0.5 g sample into prepared crucible, enter mass and sample identification into Sample Login (F3).
    b. Add ~1.0 g of iron chip accelerator ~1.5 g of copper accelerator on top of sample.
    c. Place a prepared crucible lid on the crucible.
    d. Place crucible on furnace pedestal (or appropriate autoloader position if so equipped) and initiate Analyze (F5).

Typical Results*

Sample	**Mass g**	**C %**
Titanium Wire	0.5353	0.0247
	0.5215	0.0246
	0.5106	0.0252
	0.5377	0.0245
	0.4677	0.0244
	0.4969	0.0246
	0.4590	0.0246
	0.4981	0.0245
	0.5281	0.0245
	0.4285	0.0246
	X =	***0.0246***
	s =	***0.0002***
NIST SRM 173a Titanium alloy Chip @ 0.025% C	0.5005	0.0250
	0.4989	0.0251
	0.5031	0.0251
	0.4973	0.0249
	0.4988	0.0251
	0.5041	0.0249
	0.5010	0.0249
	0.4986	0.0249
	0.4996	0.0250
	0.5023	0.0251
	X =	***0.0250***
	s =	***0.0001***

Sample	**Mass g**	**C %**
NIST SRM 360a Zircaloy-2 Chip (C not certified)	0.4983	0.0156
	0.5032	0.0158
	0.5056	0.0158
	0.5061	0.0157
	0.4983	0.0154
	0.5094	0.0156
	0.5015	0.0156
	0.5032	0.0156
	0.5099	0.0154
	0.5091	0.0160
	X =	***0.0157***
	s =	***0.0002***
Tantalum Powder	0.5029	0.0022
	0.4962	0.0020
	0.5024	0.0022
	0.5069	0.0021
	0.4974	0.0021
	0.4977	0.0022
	0.5060	0.0024
	0.5092	0.0022
	0.5066	0.0022
	0.5004	0.0022
	X =	***0.0022***
	s =	***0.0001***

**Based on single-standard calibration using NIST SRM 173a*

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Inorganic Application Note

Carbon and Sulfur in Metal-Bearing Ores and Related Materials

Instrument

CS600-Series

Introduction

The determination of carbon and sulfur levels in metal-bearing ores is a necessary quality control, environmental monitoring, and cost-saving step in the metals recovery process. These levels are used as a means of ore classification for process selection, and waste classification for the determination of potential environmental impact. For example, the amount of sulfur present in gold-bearing ores gives an indication of the level of sulfides present, which are refractory in nature. The sulfur level helps determine the optimal type of oxidative pretreatment process, and the potential for harmful environmental effects like acid rock/mine drainage. The amount of carbon present in gold-bearing ores is relative to the amount of carbonaceous material present. These materials adsorb gold during processing, thus reducing the recovery rate. Other ores, such as copper-bearing ores, are also analyzed for similar reasons.

Sampling and Sample Preparation

Samples should be uniform powder of <100 mesh (150 micron). Samples should be dried at 105°C to constant weight.

Method Reference

ASTM E1915

Accessories

528-018 or 528-018HP Ceramic Crucibles*; LECOCEL (763-266 or 763-263) or LECOCEL II (501-008 or 502-173) accelerator, and Iron Chip accelerator (501-077 or 502-231)

**For best precision, ceramic crucibles should be baked in a muffle or tube furnace (LECO TF10) at 1250°C for a minimum of 15 minutes, or at 1000°C for 40 minutes. The crucibles are removed from the furnace, allowed to cool for 1 to 2 minutes, and transferred to a desiccator for storage. If the crucibles are not used within four hours, they should be re-baked. Handle crucibles with clean tongs only.*

Calibration

NIST reference materials and/or LECO 502-318, 502-319, 502-320, 502-372 Ore samples.

Method Parameters

Purge Time (seconds)	5**
Delay Time (seconds)	10**
Furnace Low Power (%)	100
Furnace High Power (%)	100
Furnace Ramp Rate	0

	Carbon	*Sulfur*
Minimum Timeout (seconds)	40	40
Comparator Level	1.00	1.00
Significant Digits	4 or 5	4 or 5
Integration Delay	0	0

***For optimum analytical performance on samples with low carbon and sulfur content (<0.05%), a purge time of 10 seconds and a delay time of 20 seconds is recommended.*

CS600

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. Add ~1.5 g of LECOCEL (or LECOCEL II) and ~1 g of Iron Chip accelerator to crucible.
    c. Place the crucible on the furnace pedestal (or appropriate autoloader position if so equipped), and initiate analyze (F5).
    d. Repeat steps 2a through 2c a minimum of five times.
    e. Set blank following procedure outlined in operator's instruction manual.
3. Calibrate/Drift Correct.
    a. Weigh ~0.2 to 0.3 g calibration/drift sample into crucible and enter mass and sample identification into Sample Login (F3).
    b. Add ~1.5 g of LECOCEL (or LECOCEL II) and ~1 g or Iron Chip accelerator on top of sample.
    c. Place the crucible on the furnace pedestal (or appropriate autoloader position if so equipped), and initiate Analyze (F5).
    d. Repeat steps 3a through 3c a minimum of five times for each calibration/drift sample intended for calibration/drift.
    e. Calibrate/drift correct using the procedure outlined in the operator's instruction manual.
4. Analyze Samples.
    a. Weigh ~0.2 to 0.3 g sample into crucible and enter mass and sample identification into Sample Login (F3).
    b. Add ~1.5 g of LECOCEL (or LECOCEL II) and ~1 g of Iron Chip accelerator on top of sample.
    c. Place crucible on furnace pedestal (or appropriate autoloader position if so equipped), and initiate Analyze (F5).

Note: Samples with high carbon and sulfur content may require reduced sample mass to prevent saturation of the IR detection cells.

Typical Results*

Sample	Mass g	C %	S %	Sample	Mass g	C %	S %
LECO	0.2236	1.38	1.39	NIST	0.2516	5.63	1.48
502-319	0.2212	1.38	1.39	SRM 886	0.2515	5.73	1.46
Ore Tailing	0.2229	1.38	1.39	Gold Ore	0.2512	5.70	1.47
1.38% C	0.2222	1.39	1.36	(5.7)% C	0.2504	5.65	1.46
1.36% S	0.2249	1.39	1.37	1.466% S	0.2538	5.66	1.44
	0.2261	1.38	1.38		0.2495	5.60	1.48
	X =	***1.38***	***1.38***		***X =***	***5.66***	***1.46***
	s =	***0.01***	***0.01***		***s =***	***0.05***	***0.02***
LECO	0.2526	0.519	0.733	NIST	0.2513	3.36	0.347
502-318	0.2545	0.522	0.739	SRM 8704	0.2503	3.35	0.356
Ore Tailing	0.2532	0.520	0.737	River Sediment	0.2513	3.35	0.359
0.50% C	0.2521	0.520	0.725	3.351% C	0.2541	3.35	0.359
0.73% S	0.2502	0.521	0.733	(sulfur not	0.2536	3.32	0.361
	0.2512	0.518	0.738	certified)	0.2502	3.33	0.372
	X =	***0.520***	***0.734***		***X =***	***3.34***	***0.360***
	s =	***0.001***	***0.005***		***s =***	***0.02***	***0.008***

**Carbon results based on single-standard calibration with NIST SRM 8704, sulfur results based on single-standard calibration with NIST SRM 886.*

Delivering the Right Results

LECO Corporation **• 3000 Lakeview Ave. • St. Joseph, MI 49085**
Phone: 800-292-6141 • Fax: 269-982-8977
info@leco.com • www.leco.com • ***ISO-9001:2000 No. FM 24045***