SciAps ApNotes

September 2017

Carbon Analysis in Low-alloy and Carbon Steels with Handheld LIBS

Introduction

Presented here is a method to analyze carbon content in carbon and stainless steels, utilizing the technique of handheld laser induced breakdown spectroscopy (HH LIBS). The method specifies the SciAps Z-200 C+, the world's only handheld analyzer capable of analyzing carbon content in alloys. The Z-200 uses a pulsed, 1064 nm laser, operating at 5.5 mJ/pulse and 50 Hz repetition rate. The onboard spectrometer spans 190 nm – 620 nm. A dedicated high resolution spectrometer (0.06 nm FWHM) spans the 193 nm carbon range. The analyzer also uses an on-board, user replaceable argon purge gas. The argon canister located in the handle provides about 125-150 carbon analyses before replacement. For general alloy analysis, the argon canister lasts 600 tests.

What's Included with The Carbon App

Model Z-200 C+:

- Stainless base, carbon, and other elements Si, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, Se, W.
- Iron-base alloy calibration for elements including Si, Al, Ti, V, Cr, Mn, (Fe by difference), Co, Ni, Cu, Nb, Mo, W, Pb.
- Carbon calibration from 0-1%. User may extend range or create additional calibrations for cast irons, for example
- Carbon Equivalent (CE) formulas and calculations, Mn:C ratios and residual element sums.
- ProfileBuilder desktop/tablet software for user-generated carbon calibrations on different bases or ranges.
- Carbon calibration check and drift correction standards (3).

Any existing Z-200 may be updated to the Model Z-200C or Model Z-200 C+. Customers may optionally add additional calibration bases such as Ni, Ti, Al, Cu, Co and others at time of purchase or any time after delivery.

Parameter	Value (% absolute)	Comment
Limit of Detection	0.015	3-sigma detection level for C.
Precision @ 0.02% C (absolute)	± 0.005%	
Precision @ 0.2% C (absolute)	0.01%	
Iron base: Test time, properly ground materials.	10-15 s	Includes pre-burn and purging time. Typically average of 3 tests, 3 s/test, plus pre-burn, pre-purge time.
Stainless base: Test time, properly ground materials.	15-20s	Includes pre-burn, purging time. Typically average 4-5 tests, 3 s/test plus pre-burn and pre-purge time.

Table 1. Summary Performance Parameters Z-200 C or LGC for Carbon

Performance Summary

Carbon data have been obtained from multiple analyzers, on stainless steels and low alloy steels (LAS). The Z also measures cast irons. For properly ground materials, the test times for all analysis range between 10-20 seconds total, depending on the level of shot rejection performed by the method algorithm (more later). Users that are separating steels that differ by 0.1% carbon or more can generally complete tests in 10 seconds or less. The performance results are summarized in Table 1.

Stainless Base Materials

Calibration for L-grade Stainless:

The global stainless calibration is currently performed with a variety of 304, 304L, 316, 316L and 317L standards of carbon concentrations between trace up to 0.15% C. A representative calibration curve is shown in Figure 1. Users may expand the calibration matrix if desired or create additional more type-specific calibrations such as those for high nickel stainless such as A286 and 904L .

SciAps recommends using at least 4 calibration points (iron blank can be one) and a linear fit. This prevents artifacts from incomplete sample prep from biasing the calibration. If an incorrectly prepped calibration sample is included, it will not lie on a straight line fit. In general the global carbon calibration has proven satisfactory for separations of L, straight, and H grades. In some cases for material with carbon content very close to 0.03%, operators utilize the type calibration option now available on the Z.

If it is important to analyze carbon chemistry to a very tight tolerance, we recommend adding a type calibration for a representative, certified material and then using the type calibration. This approach is common in OES usage and works equally well for LIBS.

When a test commences, the Z performs a pre-flush, a pre-burn, and a series of 3 second tests. After each test the running average is shown. The Z offers both automated and manual (i.e. operator specified) test rejection. The user may tap the screen to remove any test from the running average. The automated test rejection is currently configured to eliminate either the first 1-2 burns, or the highest and lowest values (hi/low rejection). In our experience, most operators performing in-field carbon analysis with OES prefer to make their own decisions on individual test quality.

Case Study: Separate 316 and 316L

Consider the important separation of 316 from 316L. The Z-200 C and C+ show multiple "burns" on the display, and a running average, just like most spark OES analyzers. The first table below (Table 2) shows five tests on a 316 and 316L stainless CRM, after the highest and lowest values have been automatically rejected. The results are generally in good agreement with the material assays. The deviation between the individual tests is about 0.006% (60 ppm). The 316L assay in this example is certified at 0.016 % carbon, barely above the limit of detection of the analyzer, which is about 0.015%. These two alloys were easily separated in less than a 20 second test time.

The global stainless/carbon calibration was used for these results. In practice, many operators employ a single point or type calibration approach with their OES devices for improved accuracy. This is acceptable practice since the operator knows what the material grade and specs are prior to testing. We have now added type calibration functionality to the Z software as well, for carbon analysis.

Table 3 shows results for a stainless 304. These were chosen to highlight the typical data rejection. In this case the operator shot the material 7 times, with all test results shown. The Z software, if using the default high/low rejection, will remove the two tests highlighted in red. The average in each case is shown at the bottom of the Table. Typically the average carbon result changes little with high/low rejection. In fact, in nearly all cases the first test is rejected as high in any case, indicating more pre-burn may have been needed.

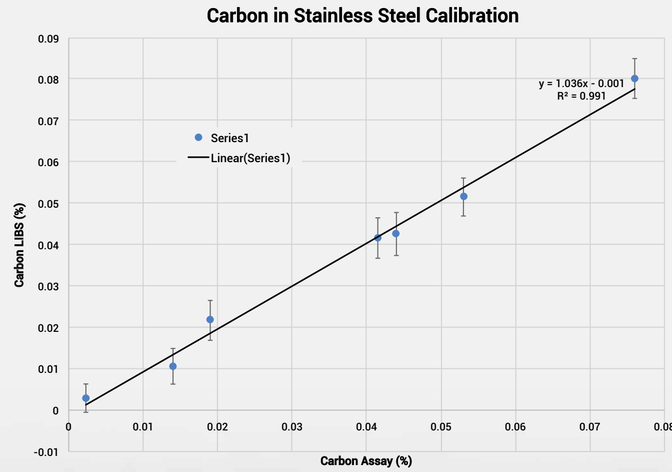

Fig 1. Carbon calibration curve for L and H grade stainless steels.

Carbon Test Results (%)	
316 Grade	**316L Grade**
0.050	0.015
0.052	0.028
0.057	0.022
0.041	0.016
0.052	0.011
Avg C %	
0.050	**0.018**
Assay	
0.049	**0.016**

Table 2 shows a typical result for 316 and 316L analysis, using the global carbon curve in stainless. stainless steels.

Table 3 shows a 304 stainless series of tests to highlight the automated data rejection.

Test #	Carbon (%)	Post Hi/Low Rejection
1377	0.070	-
1378	0.048	0.048
1379	0.033	-
1380	0.052	0.052
1381	0.044	0.044
1382	0.049	0.049
1383	0.045	0.045
Avg. C (%)	**0.049**	**0.048**
Assay (C%)	**0.051**	**0.051**

Iron Base Materials

Global Carbon Calibration, When to Use it:

The global iron base calibration curve is shown in Figure 2. The global curve spans a range of different carbon and low alloy steels including carbon steels 10XX, and 1117, low alloy steels (LAS) including 41XX, 4340, 4620, 4820, 8620 and several other steel grades, plus some Cr-Mo steels. The global curve is a great choice for separating carbon steels that differ by 0.1% C or more – 4130 from 4140 or 1010 from 1020. The curve spans multiple steel matrix types and eliminates the need for resorting to type calibrations. As with any global calibration, spanning multiple bases adds some bias to the calibration. Thus SciAps recommends using the global calibration for carbon separations of 0.1% or higher.

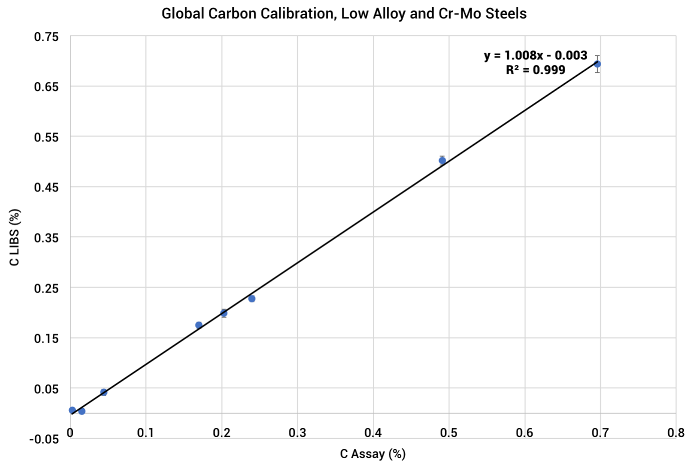

Fig 2.

Calibration to Carbon Steel Sub-types, When to Use it:

For more precise sorting of carbon steels – those that differ by 0.05% C or less – we recommend limiting the calibration curve and range to a family of alloys that encompass the steels of interest. For example to separate a series of carbon steels such as 1010, 1020 and 1030, modify the global calibration curve by enabling carbon steels in this concentration range. Results for the same global curve, limited to carbon steels between for blank and 0.5% is shown in Figure 3. As shown, with this more type-specific curve, the Z-200 will then yield reliable separation of these carbon steels.

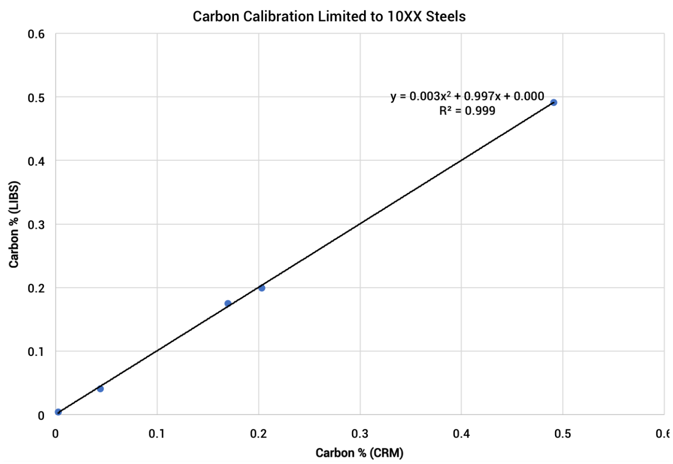

Fig 3.

Precision Data, Carbon Steels, Real-world Materials

As part of the field testing of this new carbon method, materials from several real-world applications were tested. Shown here are results from some A108 (0.161% C) refinery piping provided by a major refining company. These components were previously in-service components. They were prepped according to the grinding method described later, and analyzed with the same testing procedure. The global carbon steel calibration shown in Fig. 2 was utilized for these materials. The Z offers a way to measure BOTH the Mn and the C content, for a more confident analysis of these alloys.

The real-world carbon steel measurements performed with repeat tests and 3 runs over a 6 hour period. The runs began after warm-up, repeated about 3 hours later and repeated a final time about 6 hours later. Precision data is shown in Table 3 at for each run. These results were not based on type-calibration, and there were no offset or slope corrections made between runs. At a concentration of 0.16% C, the repeatability is better than +/- 0.01%, demonstrating that carbon steels that differ by 0.05% carbon or more are easily separated. There is a slight bias to the result, which can be managed by using a type calibration or a reduced set of steel materials for the calibration curve.

Table 4. Repeat data on an A108 carbon steel material provided by a major refinery.

Carbon Results on a 1016 over 8 Hours		
Run 1	Run 2	Run 3
0.150	0.162	0.162
0.151	0.161	0.164
0.151	0.160	0.155
0.144	0.151	0.155
0.148	0.135	0.146
Average %		
0.149	0.154	0.156
Assay %		
0.161	0.161	0.161

Method

The analysis method requires sample preparation with specific grinders and grinding pads, followed by testing with the Z-200. We utilize a handheld grinder operating > 5,000 rpm, with minimum 50 grit Al2O3 or ZrO ceramic.

Definitions: A "test" is a single test of the material with the Z LIBS analyzer. A "result" is a final answer that consists of typically three or more valid LIBS tests which are automatically averaged by the analyzer software. Each test takes 3 seconds, so a result is typically 9 - 15 seconds depending on the number of tests averaged.

Operators may run the Z-200 C+ in a manual mode or a selection of automated modes. Manual operation performs a pre-flush, preburn and then 5 consecutive 3s tests (default for stainless base) or 3 consecutive 3s tests (default for iron base). Each test is shown on the display, along with the running average. The user can tap on one or more tests to remove them from the averaging. The user may also pull the trigger to add additional tests. The user may run less than 5 tests, but a minimum of 3 tests are required for stainless and iron base.

A TEST is defined as a single analysis on the material, consisting of preburn and spectral data from 6 different raster locations. A test showing the six laser burns in the material is shown in Fig. 5.

A RESULT is defined as an average of 5 valid tests. A result shows the measured percent carbon and the measurement uncertainty.

There are two automated testing options: High/low rejection and rejection based on measurement precision. For high/low rejection the final result is the average of tests after the highest and lowest carbon values have been rejected. This mode requires a minimum of 5 tests. *Note: SciAps will incorporate additional rejection methods based on user input.*

For precision-based rejection the Z rasters the laser to six discrete positions during a test. Spectral intensity data is gathered for 0.5 seconds per position. The FPGA engine and Android processor analyzes the spectral data and compares carbon intensity ratios from the six locations. The Z rejects a test if the standard deviation in carbon intensity ratio exceeds a user-specified threshold. The software prompts the user for additional tests until the required 5 good tests (stainless) or 3 good tests (iron base) are achieved. For less experienced operators, especially regarding the rigorous sample preparation required for carbon testing, the automated rejection setting is a great option. Better sample prep means less tests rejected.

The precision-based rejection criteria in the SciAps Carbon Analyzer is a great tool to determine if materials are properly ground. Precision-based rejection takes advantage of the discrete nature of the laser pulse used with LIBS. The laser fires at multiple locations and yields intensity ratios at six different, discrete locations. Spark OES strikes the material with a wide diameter, random spark and yields an overall average without discrete position data. Poor precision from the consecutive LIBS tests almost always indicates improper sample grinding. The laser has likely struck a region with high carbon surface contamination that was not removed by grinding. If the resulting test is not rejected, then the overall result will be biased high. If zero or perhaps one test is rejected during a carbon measurement, then the sample was properly ground. Thus LIBS can be a great tool to teach proper sample prep, for less experienced operators. **Spark OES cannot offer this feature because the spark burn is on a single large location, rather than 6 discreet locations.**

Type Calibrations – Now Available!

Thanks to valuable input from our first dozen users we've added a type calibration or single point calibration option to the Z, in line with what spark OES offers. (and a free upgrade to existing users). As with OES, if the user wants to achieve very tight chemistry for a known material (i.e. 304L, or 316L, etc.) the user enters the chemistry for a CRM, tests the material several times, and then applies that as the calibration for PMI work on a load of the same material.

Summary

The SciAps Z-200 or Z-300 are handheld LIBS analyzers that now offer carbon concentration measurements in carbon steels and low-alloy steels. The method requires sample grinding using a specified handheld grinder, followed by a (typical) 15 sec test with the Z. The testing time includes pre-burn and purging time. Provided operators follow the procedures described, the Z will allow carbon steel grades that differ by 0.1% C or more to be reliably separated. The Z uses a data rejection algorithm to assure proper grinding, and argon purge to achieve the required precision. Consistently good sample prep and argon purge are critical for carbon analysis with HH LIBS.