

This article is a little dense with lots of information packed in tightly. I suppose I will need to rewrite it sometime to make it more understandable with in depth explanations. If you have a specific question about anything presented here, send me an email david@meltlab.com and I will be glad to answer your question.

First, some background: I was lab supervisor at ITT Grinnell, Shift Metallurgist in charge of the Spectrometer lab at Hayes Albion, and finally Quality Control Manager/Plant Metallurgist at Dana New Castle. Since then I have installed my aftermarket SpectrometerLab software systems on Jarrell Ashe, Baird, ARL, OBLF, Spectro and a few other brands. I have seen most of the problems with spectrometers, calibration, and standardization.

Definitions:

Standardization is the daily or more frequent correction of the Calibration curve that accounts for barometric pressure changes, and possibly other environmental changes. A good system will have minimized the environmental changes, but still can't cope with a warm front or a cold front moving in that changes the shape of the optical chamber. Do yourself a favor and mount a barometer near your spectrometer and teach the technician to read it. When it falls or rises sharply, restandardize. Other than that, try to keep the room temperature and humidity constant, keep the shape and the distance of the electrode point constant, keep your sample molds clean, and sample only when the iron has been over 1400 C or 2500 F to dissolve all the additions. Realize that running the spectrometer takes some talent. Samples need to be prepared and ground flat, need to be placed so that they cover the sample hole and don't bleed air with oxygen and water vapor into the spark chamber. Even though the chamber is pressurized, the turbulence of escaping gas around a sample disk will pull in unwanted air.

Calibration is the original shape of the curve as determined by the optical alignment, and the electrical amplification. Newer electronics are much better than what I originally learned on, but recalibration should be considered if the gain of the system has changed and caused a rotation of the curves. If you standardize the spectrometer, and the analysis in the parts of your curve away from the standards is off, a recalibration is indicated – the shape of your calibration curve has changed. Many new spectrometers are not made to be easy to recalibrate. I suppose you are supposed to throw them away and buy a new one. But a cheaper way would be to hire either the OEM or a good spectrometer service company to come in and recalibrate it. You will find that cheaper than a new spectrometer.

Certified Standards are what are sold, and are not always what you think they are. They are made in batches, and the certification is for the batch and not for the standard unless you are dealing with a certified ALCO aluminum standard. In that case each standard is certified. The certification for the other standards of the world should be viewed with a little doubt, and the best fit line of many standards should be used over just accepting a few points. Curves with multiple corrections for other elements are likewise suspect when only a few standards are used. For example, if you are using 5 standards and have 3 corrections for other elements, then you have only 2 degrees of freedom left (5-3). Many standards have had a mild heat treat to relieve stress and therefore have some graphite in them making them unuseable for carbon analysis. Others have a few elements that varied within the batch, and the block you received may be different than the certified value by 2 or 3 sigma. The standard 1 inch block like the MRDF standards was made in a mold of 495 pieces so 25 pieces would be outside of the +/- 2 sigma value. For this reason alone, multiple blocks should be used to build a calibration curve. Heavy elements standardize better than the light ones do.

Working Standards are sometimes purchased certified standards, purchased uncertified standards, or in-house secondary standards. Using certified standards is expensive. Be sure to stop using the standard when you reach the line on the side. The line is where the standard becomes unreliable due to shrinkage, and/or microsegregation or graphite. If you make your own iron standards, do the following: Find a thick copper plate to chill the samples. Make some rings with a 1 inch inside diameter out of ceramic or core material with a ¼ inch height. Obtain some tellurium to suppress graphite formation. You will need to make an initial trial run with a few rings. Place the tellurium in the bottom of a pouring spoon and pour from a second spoon into the pouring spoon. You do not want to overfill the spoon or you may lose too much tellurium. Allow a second or two for the tellurium to finish reacting, and then pour your rings. Squish each ring quickly on the top to remove excess metal, and help promote chill. On your first trial you are trying to determine the right amount of tellurium to add.





Too much tellurium or not enough waiting time will cause your standards to be full of gas holes. Note: a dirty surface on the copper plate may also generate gas holes. Each spoon of iron must be treated as a separate batch, so use a larger testbar spoon rather than the normal spectrometer sample spoon.

Now cut one of the standards from top to bottom and look for how far up from the copper plate you made a good standard. If you polish that cut face, you will be able to see where the well chilled good iron ends. Small tight crystals are to be preferred over large ones. The start of shrinkage or graphite will be the point where the standard has to be thrown away. If you can use half the height of the standard, you are doing well. Drill the top of one or two from each batch and analyze for carbon and sulfur. Then, on downtime or on a weekend, on a cleaned, profiled spectrometer, run each standard in rapid succession with 2 to 3 burns. Don't let the spectrometer have a chance to drift. Print out the results of each working standard and save the printout and the standard in separate envelopes. If the burns don't repeat well on any given working standard, you may have to discard that standard. When you put the working standard into use, edit your spectrometer settings and put in the printed results from that initial analysis plus the combustion carbon/sulfur, and you have your very own traceable working standard! Grind or cut one on the side to check for depth of chill, and mark with a line all standards for that height. The operator will see an increase in variability when that line is reached and should change standards at that point or slightly before.

Controlling the spectrometer is not an easy job. First you must ascertain that the burns reflect the sample. Generally, a repeatability target is set for each element and a sample is burned twice to check for that repeatability. Second you need to ascertain that the spectrometer is within tolerance of the standardization. Depending on the stability of the spectrometer, this should be checked by each operator at the start of his shift as the operator is responsible for the accuracy of his results. His skill is needed to cope with the problems of bad samples due to cracks, pinholes, and a lack of chill caused by hot or dirty sample molds. The point needs to be cleaned very often, and the spark chamber and the optic lens must also be periodically cleaned. If the spark hole is not properly covered or the grinding of the sample is not even, air (oxygen and water vapor) will get into the chamber and interfere with the lighter elements. Finally, if care is not taken in standardizing, the chemistry of different elements may move up or down by operator.

Once a week I would take a previous sample, remove the date and time from the sample and have each shift run and report the chemistry to me. The results told me who my best operators were and who might need further training. Another test that could only be done with my custom software was to note the variability of all the burns of a shift. I.e. record the difference between the two expected burns and take the standard deviation of those burns by element and plot a histogram by shift and by all shifts. Good operators and good samples produced a tight standard deviation. Over time, and increase in the deviation of an element on all shifts might indicate a problem with the element's electronics or the standard(s) used for that element. I also used a record of the amount of correction of each standardization combined with the reason for the standardization. The reasons were: 1) cleaned the machine, 2) routine standardization based on time, and 3) out of range chemistry causes a check on the standard and a standardization was performed. I would look at a graph of the corrections when there was no assignable cause, i.e. causes 2 and 3. Number 1 would be the only assignable cause. With one operator I found that he routinely jerked the silicon up and down 4 to 5 points on almost every standardization. For other operators, rarely ever moved more than 2 to 3 points. The operator was retrained and the problem got better even though he was still my worst operator.

Spectrometer limitations: The spectrometer works by breaking apart individual atoms from the metal and then working some quantum mechanical effects on the electrons to produce light characteristic of the element. I am not going to go into that here. What you need to know is that there are two blind spots that spectrometers have: 1) they don't see oxygen, and 2) they don't see molecules. So a spectrometer cannot tell you if the magnesium in your sample is oxidized or elemental. Oxidized magnesium is useless in producing ductile iron. You will note on your pallet of magferrosilicon that the percent of oxidized magnesium is reported, and should be very low, because you don't want to pay for stuff that you can't use. The spectrometer will report the total magnesium. Your effective magnesium is the total minus the mag-sulfides minus the mag-oxides. You can calculate the mag-sulfides from the sulfur, but not the mag-oxides. This is the reason that sometimes you get good nodularity with an 0.035% Mg, and at other times, you don't. The second limitation is the lack of understanding of the inoculation of the metal. With iron and with aluminum alloys, the state of the inoculant is very





important. In aluminum the TiB inoculates the aluminum dendrites, but the spectrometer only sees titanium and boron, not if they are still combined and effective. The same goes for strontium. Has it been neutralized by phosphorus from some A370 returns? Better get a phos channel to be sure. In iron, our inoculants decay much faster than aluminum. The alloys using FeSi break down and lose their effectiveness in minutes, not hours as in Aluminum. But the spectrometer cannot tell the difference between an inoculated iron and a dead iron. The spectrometer cannot tell you what kind of microstructure to expect, it can only tell you that the proper elements are there. And, with iron, you have the additional difficulties of unreliable carbon analysis, and lack of an oxygen measurement making the magnesium concentration less of an indicator of good castings.

One additional problem is that the spectrometer lab is typically a slow form of analysis. You have sample cooling time, sample preparation, sample transport, sample grinding, running the sample on the spectrometer and result reporting. If you can do that in less than 10 minutes you have one of the better labs. Most are at 15 to 20 minutes between pouring and reported chemistry. Thermal analysis chemistry (you knew I was going to say that) will report carbon and silicon in under 3 minutes from pouring the sample.

I am not advocating doing away with spectrometers. To make high quality constant castings, you do need to control your pearlite forming constituents' as well as the carbon and silicon. You will just need to add some additional testing.

Microstructure is a required one in today's world. The problem is it is what I call "post mortem analysis" – after the fact, and if the results are bad, the castings are scrap. Another post mortem test is ultrasonic velocity testing. This test is fast and made for processing large numbers of castings, but not quite as accurate as a microstructure check. The third test is a thermal analysis microstructure sample. This test generally takes 3 to 5 minutes and can test the molten iron as it is delivered to the molding line. While this kind of testing is still not as fast as could be desired, it does give the earliest warning of a problem and can be set up to give a warning in 2 minutes or less of a missed magnesium treatment. It will tell you the nodularity and nodule count information as well as solidification mode, ferrite, carbides and shrink.

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