

Improving the accuracy of Thermal Analysis  
By David Sparkman  
MeltLab Systems LLC  
April 2008

*Abstract: Thermal analysis is a fast and inexpensive way to see if a furnace of metal meets the basic criteria for pouring. Often melting is the bottleneck of a foundry and having a furnace of iron or aluminum or copper alloy on hold for the laboratory results can be costly. Some foundries have great success with thermal analysis results while others have problems with inaccuracy. This paper tries to cover all the sources of inconsistency and how to correct them so that foundries can get the most good out of these instruments.*

*Note: this is only a working paper and references have been left out.*

(blank page)

## Introduction

This paper will cover achieving consistency in electrical supply, metal melting, sampling and sampling supplies, electrical and chemical calibration, and instrumentation so as to achieve the most accurate and repeatable thermal analysis measurements.

Thermal analysis is a method of determining chemistry and microstructure in complex metals by measuring thermal arrests, and energy production during solidification, and sometimes energy production during solid state transformations. The temperatures of multiple arrests and the rate of change in temperature at various points is measured by means of an embedded thermal couple. The thermal couple produces a temperature dependent voltage which is converted to digital format and processed by a microprocessor or by a personal computer to produce the results.

In the production of irons, TA is commonly used to measure Carbon Equivant, Carbon and silicon. Less common uses include graphite morphology for gray, compacted and ductile irons, the degree of inoculation, the degree of chill, and the degree of pearlite/ferrite in final irons, and the effective magnesium in ductile and compacted graphitic irons. In white irons, where graphite production must be very tightly controlled, TA provides a comparison with production iron vs. 100% chilled iron.

In the production of aluminum alloys, TA is commonly used to measure the degree of inoculation and modification of hypoeutectic-silicon alloys (A319, A320, A355, A356 etc), and the degree of nucleation of A200 series and hypereutectic silicon alloys.

In the production of Copper alloys, TA is commonly used to measure the phosphorus levels for brazing alloys, and for high phosphorus copper alloys up to about 15%.

In steel production, TA is used to measure low carbon levels in low alloy steels, and to measure correct carbide levels in wear resistant alloys.

## Electrical Consistency

The signals used to make measurements, and to produce references are subject to variation due to electromagnetic interference and are best controlled through proper grounding, and shielding. One popular instrument gives its impedance at 10 mega ohms. Applying this value to the equation  $V=IR$  gives an amperage for the thermal couple in the range of  $10^{-6}$ . This is comparable to the energy level broadcast by an industrial walkie talkie.

An induction based furnace could affect the results simply by being on or off if the energy can get into the wire connecting the thermal couple with the instrument. Generally the thermal couple extension wire should be shielded, and, in extreme conditions, enclosed in conduit as well. Care should be taken to maximize the distance of the wire from induction furnaces, transformers and electrical busses. Do not run the thermal couple wire parallel to power cables or in conduits with high powerful cables.

If an extension wire needs to be run between two furnaces on a melt deck, try to use shielded wire and conduit when close to the furnace and when passing through the power control room. Cross any power buss at right angles to minimize electrical pickup, and run the conduit midway between the furnaces. Also avoid coiling the wire as this makes the wire more susceptible to electromagnetic pickup.

If the extension wire uses a foil shield, it will often come with a drain wire. This wire should be connected to a ground at only one end to avoid carrying current from the melt deck to the instrument. Ground the wire at the instrument end only. The wire itself should be what is called twisted pair. This twist again helps neutralize picking up electromagnetic radiation from the air.

### Electrical Grounding

The TA instrument is measuring 0.0 to 0.18 volts when using S or R type thermal couples and 0.0 to 0.55 volts when using K type thermal couples. The raw precision is generally listed at 0.1 degree C which can be improved through software filtering to about 0.05 degrees C. To achieve this degree, it is important to have a good ground for reference. Neutral lines typically have as much as ½ volt of induced energy in them. That is, the electrical noise in the lines can be equal to or greater than the signal we are trying to measure.

Long runs of thermal couple wire mean more susceptibility to picking up electromagnetic energy. The power pickup shoes of an overhead crane were arcing between rail segments in one foundry causing a pickup of energy equivalent to 10 degrees C of temperature. Running a shielded thermal couple wire solved the problem.

### Clean Instrument Electrical Power

The TA instrument should have the proper undamaged power it needs to function. The power supply must generate a clean 5 volt signal to power the Analog to Digital conversion process. For this, an iron core transformer is best. Other types of transformers are cheaper, but much more noise is generated by them. Spikes in the electrical supply will cause breakdowns in the transformer insulation, so use a surge protector before the transformer to prevent damage from strong surges. The iron core transformer will smooth out the smaller surges.

Second the rectifier circuits on the transformer filter out the AC components of the power. Check the DC outputs of the transformer for AC components. Standard “ripple” (ac component) is generally 0.01 volts or less. Higher results may be from a non-iron core transformer or from surge damage to the capacitors. It can also come from high frequency (1000 hertz +) furnaces. It might be useful to put a small capacitor across the DC power leads (0.01 to 0.05 microfarads) if this is suspected. Most DC transformers were not designed to filter such high frequencies.

### Metal Consistency

Thermal Analysis looks at the transitions between liquid and solid metal. To measure the effect of any element in the metal, that element must be dissolved in the liquid.

Undissolved crystals, while they may promote nucleation, can throw off the chemistry analysis. As a general rule, iron should be heated above 2550 F or 1400 C before it is sampled. This allows the silicon to go into solution. Once the iron has been heated above this temperature, it can be cooled down to lower temperatures and still successfully measured as all the silicon is now in solution.

Similar problems exist with Carbon and Silicon Carbide additions. Silicon Carbide dissolves over time and cannot be measured by TA until it is dissolved. One foundry was adding 4% silicon carbide to a cupola that was feeding into a 10 ton holding furnace. The cupola bed was low, and the holding furnace was almost empty when the TA and the chill wedges showed low silicon. The spectrometer reported the silicon as being within range. It was suspected that the silicon carbide had not finished dissolving, and when the castings turned out hard at shakeout, they were sent back to the cupola for remelting rather than try to machine them with undissolved silicon carbide in the iron.

Likewise Carbon floating on the surface of the furnace can create a carbon rich layer if the furnace is not powered on. Generally try to not sample through a carbon or slag layer. Clear a clean spot on the surface, and wash the sample spoon clean of any remains left over from previous samples.

### Sampler consistency

Some types of analysis depend on measuring the cooling rates of the sample. These rates and even the arrest points can be influenced by how full the sample cup is. Sample cups that are filled to less than 1 cm or 1/3 inch below the top are suspect. The thermal couple needs to be in the center of heat of the metal mass. This point is slightly above the geometric center of cup due to rapid cooling in the base of the cup. Manufacturers of tellurium cups used in the analysis of iron often have problems with excess gas evolution which spits the iron back out. Pour these cups by tapering off toward the last so that the cup remains full. As a note to manufacturers, there are ways to produce non-boiling tellurium cups.

Another problem with samplers is contamination of the cup with foundry dirt, graphite and other additives. It is preferred to store the cups upside down to prevent dirt from accumulating. This very fine material will quickly dissolve in the metal and can alter the analysis by 5 to 10 points of chemistry.

Samplers can also fail. This usually means that the thermal couple can melt, or come in contact with the metal. The K type of thermal couple is subject to melting when sampling molten iron. The TC melts at 2540 F or 1390 C. Since Iron is generally much hotter than that, we depend on a certain amount of temperature loss in transferring the sample, and in temperature loss to the cup before the thermal couple reaches its max. The twisted thermal couple has good mechanical bonding and will only fail if the ceramic tube cracks or the core wash over the TC is thin or missing, or the melting point is reached. The quartz tube style cup can fail if the quartz breaks, or if the wire softens enough. Due to the connection with the cup stand, the wire is in tension, and can pull apart if the joint

softens enough. The wire will pull away from one side of the cup about ½ centimeter. This will typically terminate the analysis.

If the molten metal comes in contact with the wire, a small amount of current will leak off through the turbulent air above the cup. This can be seen as a sudden drop in thermal couple temperature of 5 to 15 degrees C. This can give rise to an erroneous answer. This usually happens if the ceramic or quartz tube fails. This is typically later in the analysis and is small enough of a break that the molten iron cannot dissolve the thermal couple.

A final issue with cups is the variation in the thermal couples from lot to lot. The wire, which starts off as an ingot in a foundry, varies in chemistry. While the cup manufacturers do purchase special limits wire and should practice wire matching to minimize this error, mistakes have happened with at least one of the manufacturers where the wire differed from the previous shipment by 4 degrees C (two different foundries reported this error), the manufacture feigned ignorance.

One manufacturer reports the deviation from nominal as the cup bias value. The other major manufacturer only reports this value to selected customers. One degree C of error is about 0.01% Carbon and 0.08% Silicon when analyzing iron. Some TA instruments can input this bias number and correct for it. The correction is about 90% effective due to the non-linear aspect of the voltage versus temperature curve. But that can reduce this normal error of 1 degree C down to a 0.1 degree C error between manufacturing lots of cups. When the salesman tells his customer “We only use the best wire”, remember Regan’s words: “Trust but verify”.

### Calibration consistency

Many foundries make life hard for themselves by over calibration. Deming pointed out that this can be a major source of error, and TA proves the point. First the calibrator has an internal temperature sensor that corrects for differences between room temperature and the melting point of ice. This sensor is embedded inside of the instrument and can be fooled. If the calibrator was stored in an air conditioned (summer) or heated (winter) office, the cold junction sensor can be off by 10 to 15 degrees C.

Both the calibrator and the metal pins/rails of the cup stand need to be at room temperature to avoid errors. People who calibrate too often end up taking shortcuts and introduce errors into the calibration by not letting the calibrator and or stand heads come to room temperature: an operation that can take up to 30 minutes depending on the instrument. It is best if proper care is taken in the calibration, and then no further calibration is done until there is an assignable cause (damage or replacement of components) or the time period is expired for the calibration (usually 6 months).

The calibrator itself needs to be certified. The certification process itself can also lead to errors due to the lax standards of certifications. An instrument is considered certifiable if the instrument produces results that are within 1 degree C or 2 degrees F. For example, if the instrument has a nominal setting of 2250 F and is actually 2248 F, it is certified as 2250. If it was reading 2246 F and corrected to 2251 F it would also be certified as

calibrated. Some TA instruments have the ability to set the calibration temperature to actual instead of nominal.

### Laboratory Consistency

Another source of calibration is the laboratory chemistry. Spectrometers, carbon determinators, and outside labs do have errors, and trying get the TA equipment to agree with the lab is sometimes like trying to hit a moving target. Here are some suggestions to see how good your reference chemistry is.

The main source of error in carbon determinators is settling in the carbon standard. If the standard contains free graphite (dirties a white sheet of paper), then every time the technician sets the bottled standard down, he is segregating the standard, shaking the loose graphite to the bottom, and moving more low carbon steel to the top of the bottle. Always shake the bottle before using it. Most combustion carbon machines are rated at 1% of concentration for accuracy. That would mean that a 3.5% analysis would be plus or minus 0.035 % carbon. The manufacturers don't explain that result in statistical terms, but personal experience suggests that the "+/- 1% of range" applies to a 4 sigma deviation. Actual results depend on the state of the machine and the skill of the technician.

Using a Spectrometer for Carbon analysis is not a good idea if the carbon is 3% or higher. Spectrometers are notoriously inaccurate above that level as samples almost always have some amount of graphite in them. And even if the samples are perfectly chilled, the spectrometer standards are not. They often contain free graphite because the standards received a mild heat treatment to prevent them from cracking. This is an unfortunate but recommended NIST procedure in the making of standards. The NIST researcher who stated this practice said he found it caused less than 0.1% free graphite. The graphite is segregated and makes the carbon answer vary far too much.

Silicon consistency of a spectrometer can move around from day to day. Sometimes the standard has imperfections in it, sometimes the standardization was just poorly done, and sometimes the argon gas is contaminated. And some foundries mistakenly use silicon carbide sand paper to prepare their samples. The best way to check the performance of the spectrometer is to run historical checks that span days or even weeks. Take production samples from one week, two weeks and three weeks ago, and rerun them against their original values to get a feel of how consistent your spectrometer is. If the TA has a standard error against the spectrometer of 0.03% concentration, and the spectrometer has a standard error of 0.02% concentration, then one third of the variation in the TA instrument is due to the TA system, and two thirds is due to the spectrometer.

Outside labs vary in their carefulness and competence. The best way to judge their results is with either another lab and/or sending them the same sample twice spaced days or weeks apart. Remove or change the sample ID so that they don't know that this is a check sample. You may find out that you have a very good outside lab, or that you need to find another lab. Remember, the lab can change personnel which can change their reliability.

## Instrument calculation consistency

Thermal analysis is limited by some mathematical constraints called the degrees of freedom. Typically for example, in iron, we calculate chemistry from two data points and try to solve for Carbon and Silicon. Actually Carbon, Silicon, Phosphorus, Manganese and Chromium all affect the arrest points. To calculate silicon, it has to be assumed that phosphorus, manganese and chromium remain relatively consistent or that the change in those elements is insignificant. Manganese is the usual culprit when the silicon analysis varies. The handbook equation is  $C.E. = \text{Carbon} + \text{Silicon}/3 + \text{Phosphorus}/2 + \text{Manganese}/5 - \text{Chromium}/9$ . In actuality we generally find the silicon factor to vary between 2.5 and 3.3 depending on iron type. General practice is to determine the best silicon equation for each major metal type. A major metal type would be those that had significantly different levels of manganese, phosphorus, or chromium.

Carbon analysis agrees with combustion analysis to within the typical error of combustion analysis, so it is hard to tell which one is more correct.

Carbon Equivalent analysis is defined by the TA measurement. That is C.E. is determined by the Liquidus temperature. Some people confuse the issue by thinking that by using the spectrometer chemistry in a formula that they can calculate the C.E. and therefore what the Liquidus temperature should be. That is not so. The calculations using chemistry are approximant. The actual measurement of the Liquidus is exact. In the old days the Liquidus temperature was used to measure the fluidity of the metal (lower temperature implied more fluidity). This was an improvement on the fluidity spiral which could be affected by temperature or wetness of the mold.

## Instrument Detection Accuracy

Each different instrument manufacturer has a different way of determining arrests. Some are more accurate than others. Some have fewer susceptibilities to error. For example the older models available back in the 1970-1990's used a windowing technique to find arrests. These units declared an arrest when the rate of cooling fell below a given value. These were typically  $1/4^{\text{th}}$  degree C per second for liquidus, and  $1/10^{\text{th}}$  degree C per second for Eutectic (then mistakenly referred to as Solidus). This resulted in making the instrument sensitive to cooling rates. Using one vendor's cups on another vendor's instrument could result in a failed analysis. Having a fan or open door by a cup stand could also cause large sample to sample variations. Some cheap instruments today still have this problem.

In the 1990's instruments were introduced that used derivatives to find the strongest point in the arrest. This removed a lot of the variability due to partially filled cups, and air currents around cups. Still there are differences in the noise levels of the instruments. One manufacturer uses a single 24 bit analog to digital converter that is multiplexed. Others use separate a 12 or 16 bit analog to digital converter for each input. The 12 bit system has a built in precision of  $1/4^{\text{th}}$  degrees C. The 16 bit system has a built in precision of  $1/20^{\text{th}}$  degree C. To those numbers have to be added the electrical noise not canceled out by their smoothing algorithms. The 24 bit system would seem more accurate, but most of its added accuracy is nullified by the electrical noise of the system, the fact that stands

and wire runs cannot be individually calibrated, and that the system has only a primitive smoothing algorithm.

### Conclusion

Mathematically the standard error of a system is the square root of the sum of the squares of all the errors. It might be daunting to some to see all the sources of error possible. But with good engineering, a good instrument, and a good lab, it is possible for most foundries to benefit from the use of TA. In practice the amount of error varies from foundry to foundry. But generally a standard error of 0.03% carbon and 0.03% silicon can be obtained if these guidelines are followed. This compares with lab results of 0.035% for combustion carbon and 0.02% for spectrometer silicon.