Two-time Calibration at Both Ends for Sulfur Measurement by Using High Frequency Induction Infrared Absorption Method

Jianhuan Wei*
AECC Beijing Institute of Aeronautical Materials
Beijing Key Laboratory of Aeronautical Materials Testing and Evaluation
Aviation Key Laboratory of science and Technology on Materials Testing and Evaluation
*Corresponding author email: weijianhuan@sina.com

Abstract. High frequency induction heating infrared absorption method is a relative measurement method, and it requires calibrating the analyzer during the measurement process. Usually, one-time calibration on an analyzer is made for high sulfur value by using standard substances. The method proposed by this paper calibrates carbon-sulfur analyzers with a method of two-time calibration at both ends, which eliminates the impact of sulfur blank and thus improves the accuracy and precision of ultra-low sulfur measurement. The method extents the lower limit of measurement of sulfur in high temperature alloy, to 0.00005%, namely, 0.5ppm.

1. Introduction

High frequency induction heating infrared absorption method (hereinafter referred to as ”the Method”) is widely applied in analysis of sulfur contents in high temperature alloy, and a corresponding analysis method is established on the basis of high frequency infrared carbon/sulfur analyzers[1,2].

The Method is a relative analysis method, and it is necessary to make calibration on analyzers during analysis. Usually, only one time calibration on an analyzer is required by using standard substance.

High end sulfur value one time calibration is to use standard substances with the similar mark and sulfur content range with samples to calibrate analyzers. More than three times of analysis are required in choosing channels (methods), calibration coefficient is worked out, and then the verification is made by using standard substances. After confirmation, the analysis on samples is conducted [3].

If sulfur contents in the samples is less than 0.005% or close to the critical value of product standard, the blank value of agents and materials shall be analyzed[4].

There are two methods for measuring blank values, namely direct measurement method and indirect measurement method[5]. However, from a logical perspective, the sulfur blank value measured by direct measurement method is flawed. In practice, this method has to be used before better methods are available. Indirect measurement method measures the sulfur blank value by using measured sulfur value to subtract the standard sulfur value, but the result of this method is often negative, which indicates that this method is sometimes invalid. The reason for this lies in the fact that, the sulfur blank value is not at the same order of magnitudes with standard substance sulfur value, and using subtraction method causes a large error.

In conclusion, current calibration method and blank value measurement are two separate operation processes, without sufficiently considering the mutual effect of the two. It also does not distinguish the
differences between “blank value” and “blank effect value”, which leads to inaccurate measurement results. It is far from adequate for a high precision measurement.

Based on experiments [6], the paper has established a calibration method, which could improve the precision of measurement, and the key of the method is to conduct two calibrations on sulfur values at both high end and zero end, which is named as two-time calibration method at both ends.

2. Two-time Calibration Method at Both Ends [7]

After reducing and stabilizing blank values for a blank value source, the analyzer can be calibrated. The paper uses the carbon/sulfur analyzer (CS844ES) manufactured by LECO to conduct the analysis. The ultrapure complex flux is used, with its sulfur blank value of S<0.000 02%.

2.1. First Time Blank Value Calibration

Certain amount of ultrapure complex flux is taken and the blank value is measured for 3~5 times according to the instrumental analytical method and procedures. The value should be stable.

The blank calibration on the analyzer is conducted by choosing blank values. The results are saved.

**Table 1.** Data of the first time blank calibration

| Name                        | Sulfur content (%) | Sample weight (g) | Measured sulphur value (%) | Average value (%) | Standard deviation (%) | RSD (%) |
|-----------------------------|-------------------|-------------------|-----------------------------|-------------------|------------------------|--------|
| Measurement of blank value  | 0.000 000 00      | 1.0000            | 0.000 049 0                 | 0.000 040 0       | 0.000 007 7            | 19.2   |
|                             | 1.0000            | 0.000 043 6       |                             |                   |                        |        |
|                             | 1.0000            | 0.000 031 9       |                             |                   |                        |        |
|                             | 1.0000            | 0.000 035 6       |                             |                   |                        |        |

**Figure 1.** First time blank calibration curve and results

2.2. First Time Standard Sample Calibration

The analyzer is calibrated by choosing the materials with their marks same with or close to analytical samples, and their sulfur contents are slightly higher than the standard substance of samples. The paper uses AR-673[S=0.001 1±0.000 2%]: S=0.001 1±0.000 2% to conduct the analysis.

Sulfur content is measured for 3~5 times according to the instrumental analytical method and procedures. The value should be stable.

The standard sample calibration on the analyzer is made by choosing measurement values. After calibration, the displayed values shall be within the allowable value of standard substance. The results are saved.
Table 2. Data of the first time standard sample calibration

| Name                      | Sulfur content (%) | Sample weight (g) | Measured sulphur value (%) | Average value (%) | Standard deviation | RSD (%) |
|---------------------------|--------------------|-------------------|-----------------------------|-------------------|--------------------|--------|
| AR-673 measured value     | 0.001 ±0.0002      | 0.4979            | 0.001140                    | 0.001277          | 0.000100 5        | 8.2    |
|                           | 0.4898            | 0.4929            | 0.4941                      | 0.4890            | 0.4867            |        |
|                           | 0.4890            | 0.4867            |                              |                   |                    |        |
| First time standard sample calibration | 0.001 ±0.0002 | 0.4979            | 0.001022                    | 0.001100          | 0.000090 1        | 8.2    |
|                           | 0.4898            | 0.4929            | 0.4941                      | 0.4890            | 0.4867            |        |
|                           | 0.4890            | 0.4867            |                              |                   |                    |        |

Figure 2. AR-673 [S=0.001 1±0.000 2%] Oscillograph of standard substance release

2.3. Second Time Blank Value Calibration

Certain amount of ultrapure complex flux is taken and the blank value is measured for 3–5 times according to the instrumental analytical method and procedures. The value should be stable, and shall be less than 0.000 02%.

The blank calibration on the analyzer is conducted by choosing blank values. The results are saved.

Table 3. Data of the second time blank calibration

| Name                      | Sulfur content (%) | Sample weight (g) | Measured sulphur value (%) | Average value (%) | Standard deviation | RSD (%) |
|---------------------------|--------------------|-------------------|-----------------------------|-------------------|--------------------|--------|
| Measurement of blank value| 0.000 000 00       | 1.0000            | 0.00010 00                  | 0.000 009 46     | 0.000 003 3        | 35.1   |
|                           | 1.0000            | 0.00125           | -0.000 001 90               |                   |                    |        |
|                           | 1.0000            | 0.000 005 86      |                             |                   |                    |        |
| Second blank calibration  | 0.000 000 00       | 1.0000            | 0.00009 00                  | -0.000 000 26    | 0.000 008 1        | 30.8   |
|                           | 1.0000            | 0.000 03 56       | -0.000 008 16               |                   |                    |        |
|                           | 1.0000            | 0.000 004 41      |                             |                   |                    |        |

2.4. Second Time Standard Sample Calibration

The standard substance in the first standard sample calibration is used to measure the sulfur contents for 3–5 times according to the instrumental analytical method and procedures. The value should be stable.

The standard sample calibration on the analyzer is made by choosing measurement values. After calibration, the displayed values shall be within the allowable value of standard substance. The
results are saved.

**Table 4.** Data of the second time standard sample calibration

| Name                        | Sulfur content (%) | Sample weight (g) | Measured sulphur value (%) | Average value (%) | Standard deviation (%) | RSD (%) |
|-----------------------------|--------------------|-------------------|----------------------------|-------------------|------------------------|---------|
| AR-673 measured value       | 0.001 1 ±0.000 2   | 0.4979            | 0.001 011                  | 0.001 090         | 0.000 090 8           | 8.3     |
| First time standard sample  | 0.001 1 ±0.000 2   | 0.4979            | 0.001 022                  | 0.001 100         | 0.000 090 1           | 8.2     |

![Graph](image)

**Figure 3.** After two calibrations at both ends, the impact of blank values on working curve is minimized.

2.5. **Verification Measurement on Standard Samples**
The verification measurement on standard substance with sulfur contents close to samples is conducted, and the measurement results shall be within the range of admissible error.

**Table 5.** Data of verification measurement of standard samples

| Name   | Sulfur content (%) | Sample weight (%) | Measured sulphur value(%) | Average value (%) | Standard deviation (%) | RSD (%) |
|--------|--------------------|-------------------|----------------------------|-------------------|------------------------|---------|
| 502-704| 0.000 1±0.000 02   | 0.5015            | 0.000 132                  | 0.000 118         | 0.000 010 4           | 8.8     |

Table 5 shows that, by using AR-673[S=0.0011±0.0002%] calibrator CS844ES, and after two calibrations at both ends, the impact of blank values on working curve is minimized, and by using standard substance 502-704 to conduct verification measurement, good accuracy and precision is achieved.
2.6. Measurement on Blank Effect Value
Certain amount of ultrapure complex flux is taken and the blank effect value is measured for 3~5 times according to the instrumental analytical method and procedures. The value should be stable, and shall be less than 0.000 02%.

Table 6. Data of blank verification measurement

| Name                  | determined value of sulfur | Sample weight (g) | Measured sulphur value |
|-----------------------|----------------------------|-------------------|------------------------|
| Blank effect value    | 0.000 000 00               | 0.5000            | 0.000 000 30           |
|                       |                            | 0.5000            | -0.000 000 78          |
|                       |                            | 0.5000            | -0.000 015 26          |
|                       |                            | 0.5000            | -0.000 014 02          |

Table 6 shows that, all blank effect values measured from blank verification are less than 0.000 02%. Therefore, for sample measurement, as long as the measurement results are higher than 2~3 times of blank effect value (<0.000 02%), namely, >0.000 05%,0.5ppm, and even the lower limit of measurement extends downward to an order of magnitude, the results are still reliable.

3. Conclusion
After two calibrations at both ends, carbon/sulfur analyzers eliminate the blank effect, and its accuracy and precision on ultra-low sulfur measurement is improved, with its lower limit extending downward to an order of magnitude, to 0.000 05%, namely 0.5ppm.

4. References
[1] ASTM E1019 – 11 Standard Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel, Iron, Nickel, and Cobalt Alloys by Various Combustion and Fusion Techniques.
[2] GB/T 20123-2006/ISO 15350: 2000 Steel and iron-Determination of total carbon and sulfur content Infrared absorption method after combustion in an induction furnace (routine method).
[3] LIU Pan, TANG Wei, ZHANG Bin-bin, LI Zhi-ya, Application of High Frequency Induction Combustion-Infrared Absorption Spectroscopy for Analysis of Carbon or Sulfur in Metal Materials, Physical Testing and Chemical Analysis Part B: Chemical Analysis, 2016,52:109-118.
[4] HB 5220.6-2008 Methods for chemical analysis of superalloys --part 6: Determination of sulfur content by high frequency induction combustion -infrared absorption method.

[5] TANG Kuo hsiang, HE Hong-ling. Applied Technology with methods for Measuring Sulfur Blank Values by Using Infrared Absorption Method, Advanced materials Research[J], 2014, 977:141-145.

[6] Jianhuan Wei, and Huafeng Sun, and Shengjie Yang, the cycle measurement of sulfur blank value with the CS-444 infrared ray carbon sulfur analyzer, Advanced Materials Research, Vals. 399-401 (2012) pp. 2173-2176.

[7] China Patent A method on measuring ultra-low sulfur content in wrought superalloy, application number or patent number:201810319111.7, WEI Jianhuan, ZHANG Yong, YAN Jing.