Evaluation of Measurement Uncertainty of Oxygen in Titanium Alloys based on Monte Carlo Method

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Abstract. Uncertainty is a scientific representation of the quality level and dispersion of measured results. Considering the key issues of the application of Monte Carlo method (MCM) to evaluate the uncertainty of the single-point calibration linear measurement system, such as the MCM evaluation model and the introduction of the uncertainty from the apparatus calibration and repeated measurements, two correction factors were introduced to characterize the random effects of conditional variations and system fluctuations on the measurement repeatability of the certified reference material (CRM) for calibration and the tested sample, and a mathematical model for evaluating the uncertainty of single-point linear calibration measurement system based on MCM was proposed. Then the specific evaluation process and application of MCM was systematically explained based on a case study for determination of oxygen content in Ti-6Al-4V titanium alloy by inert gas fusion - infrared absorption method. Under the measurement condition that the CRM repeated 4 times and the Ti-6Al-4V sample repeated twice, the simulation result was $w_{\text{MCM}} = 0.178 \% \pm 0.009 \% (k=2)$, which was consistent with the result of $w_{\text{GUM}} = 0.178 \% \pm 0.009 \% (k=2)$, based on the traditional GUM method recommended by ISO/IEC Guide 98-3: 2008. The new method solved the application of MCM to evaluate the uncertainty of the single-point calibration linear measurement system. And it can be directly applied to the uncertainty evaluation of a single-point calibration linear measurement system. Further, it is expected that MCM will be developed and applied in other linear measurement system, which will promote the study and application of measurement uncertainty to open up new horizons.

1. Introduction
Titanium alloy is an important structural metal alloy material developed in the 1950s, with the advantages of high specific strength, excellent corrosion resistance and heat resistance. It has important applications in military and civilian fields such as aerospace, petrochemicals, automobiles, and medicine, which is known as the most promising metal material in the 21st century. Among them, Ti-6Al-4V is the earliest practical with the usage accounts about 80% of all titanium alloys.

Oxygen is the trace interstitial impurity element in titanium alloy, which should be strictly controlled. Under the premise of less than the upper control limit, the oxygen content also needs to maintain an appropriate range to improve the hardness and strength of the titanium alloys. Therefore, determination of the oxygen content in titanium alloys and evaluation of the dispersion of measured value accurately has important practical requirements and significance.
Uncertainty is a scientific representation of the quality level and dispersion of measured results. The evaluation methods are mainly based on ISO/IEC Guide 98-3: 2008 <Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM: 1995)> [1], ISO/IEC Guide 98-3: 2008/ Suppl.1: 2008 <Uncertainty of measurement — Supplement 1: Propagation of distributions using a Monte Carlo method (MCM)> [2], and the ‘Top-Down’ approach [3-4]. Now, GUM method has been widely used in the fields of chemical analysis and physical test [5-7]. But the application of MCM in chemical analysis is very rare, and limited to so-called ‘absolute methods’, such as gravimetry, electrolytic gravimetry, and Coulometric titration methods [8-9]. As the key issues, such as the MCM evaluation model and the introduction of the uncertainty from the apparatus calibration and repeated measurements, have not been solved, the application of MCM to evaluate the uncertainty of the "comparison method" measurement system needs further study.

The inert gas fusion - infrared absorption method is the routine method for determination of oxygen in metal alloy materials [10], which is adopted as the standard method for the determination of oxygen content in titanium alloys by International Organization for Standardization, American Society for Testing and Materials, Japanese Industrial Standards Committee, Standardization Administration of the People's Republic of China and other standardization organizations [11-14]. This method uses the CRM to calibrate the measurement system and realizes the traceability of the value based on the linear function relationship between the oxygen content of the tested sample and the signal response value, which belongs to a typical linear measurement system. Due to the lack and high cost of titanium alloy CRMs for gas analysis, labs often use a small number of alloy types and oxygen levels of CRMs for daily routine testing using single-point calibration, which is a typical single-point calibration linear measurement system.

In this work, a mathematical model for MCM evaluation of uncertainty of the single-point calibration linear measurement system was proposed and established, by introducing two random effect correction factors or random relative errors to characterize the effects of various conditional variations and system fluctuations on the measurement repeatability of CRM for calibration and the tested sample. A case study for determination of oxygen in titanium alloy by inert gas fusion- infrared absorption method was used to systematically explain the specific evaluation process and application of MCM. The evaluation result was \( w_{\text{MCM}} = 0.178\% \pm 0.009\% \) (\( k = 2 \)), consistent with the result of \( w_{\text{GUM}} = 0.178\% \pm 0.009\% \) (\( k = 2 \)), by traditional GUM method. This method can be directly applied to the uncertainty evaluation of a single-point calibration linear measurement system, including inert gas fusion- infrared absorption or thermal conductivity method for determination of oxygen, nitrogen and hydrogen, high frequency induction combustion infrared absorption method for carbon and sulfur, chromatographic analysis and titration analysis.

2. Materials and Methods

2.1. Apparatus and Materials

The following apparatus and materials were used: ONH - 2000 gas analyzer (ELTRA Corporation), electronic balance with the division value \( d = 0.1 \) mg. Titanium alloy CRM for calibration (501-320, LOT#0598-11, LECO Corporation) with the mass of 0.115 g \pm 0.001 g and oxygen content certified value of \( w(O) = 0.192 \% \pm 0.004 \% \) (\( k = 2 \)). Nickel basket flux, made of high-purity nickel, with the mass of 1 g and the oxygen less than 0.0010 \%.

2.2. Method and Process

The oxygen content in titanium alloys was determined by inert gas fusion - infrared absorption method with a single standard point calibration procedure, according to ISO 22963: 2008 <Titanium and titanium alloys — Determination of oxygen — Infrared method after fusion under inert gas> [11] and GB/T 4698.7-2011 <Methods for chemical analysis of titanium sponge, titanium and titanium alloys — Determination of oxygen and nitrogen content> [14]. The specific testing process was as follows:
Blank test: input the nominal mass of 50 mg, determine the blank value of the nickel basket and graphite crucible, and then subtract the system blank value by subtracting the signal response value.

Apparatus calibration: weigh 0.05 - 0.10 g specimen of titanium alloy CRM accurately, place it in a nickel basket, and measure the oxygen content. Then select repeated measurement results of the CRM, enter the certified value, and determine the calibration coefficient for single-point calibration.

Sample test: weigh 0.05 - 0.10 g test specimen of Ti-6Al-4V sample accurately, place it in a nickel basket, then determine the oxygen content with the result given in the form of mass percent.

2.3. Experimental Data
The raw data for determination of oxygen in blank, CRM and Ti-6Al-4V sample were listed in table 1. Meanwhile, the statistical values were given in table 2, such as the number of replicates (n), the mean of specimen mass, the signal and results of oxygen, the experimental standard deviations (s) of n replicates, and the relative standard deviation (RSD). Among them, the results of the blank and CRM in table 1 were recalculated based on the calibration coefficient after a single-point calibration, and the experimental standard deviations were calculated by range-method with the range coefficient of 1.13 (n = 2) and 2.06 (n = 4)\[15\].

| Samples       | Mass (mg) | Signal (V·s) | Results (%) |
|---------------|-----------|--------------|-------------|
| Blank         | 50.0      | 1.986, 1.797, 1.892, 1.949 | 0.00024, -0.00033, -0.00004, 0.00013 |
| CRM           | 52.8, 62.3, 65.941, 81.929, 79.483, 73.183 | 0.1828, 0.1936, 0.1956, 0.1950 |
| Ti-6Al-4V     | 57.0, 66.9 | 68.098, 81.856 | 0.1751, 0.1802 |

| Samples       | Mean of mass (mg) | Mean of signal (V·s) | Mean of results (%) | Range (%) | s (%) | RSD | RSD / \sqrt{n} |
|---------------|------------------|---------------------|---------------------|-----------|-------|-----|----------------|
| Blank         | 50.0             | 1.906               | 0.00000             | —         | —     | —   | —              |
| CRM           | 57.5             | 75.134              | 0.192               | 0.0128    | 0.0062 | 0.032 | 0.016         |
| Ti-6Al-4V     | 62.0             | 74.977              | 0.178               | 0.0051    | 0.0045 | 0.025 | 0.018         |

3. Results and Discussion
3.1. Measurement Model
A theoretical mathematical measurement model was given by ISO 22963-2008\[11\] and GB/T 4698.7-2011\[14\], as in equation (1).

\[
w = \frac{(A - A_0)}{m} \times f
\]

where:
\(A\) = signal response value of the specimen,
\(A_0\) = signal response value of the blank,
\(m\) = specimen mass,
\(f\) = calibration coefficient of the linear measurement system, and
\(w\) = mass percent fraction of oxygen in the sample.
Random effect, such as various conditional variations and system fluctuations, would introduce random errors. This meant that the practical measurement process didn't fully conform to the theoretical model as in equation (1), but obeyed a discrete distribution around the above model.

In order to reasonably characterize the random effects, a correction factor was introduced to modify the equation (1). Then the practical measurement model was obtained as in equation (2).

\[ w = \frac{(A - A_b)}{m} x f x e \]  \hspace{1cm} (2)

where:
\( e \) = random effect correction factor with the theoretical value of 1, a dimensionless quantity.

A CRM was used to determine the calibration coefficient of the single-point calibration linear measurement system. Then the relevant quantities of the CRM and the tested sample were substituted into the equation (2), and a new mathematical model was obtained as in equation (3), where the subscripts ‘a’ and ‘b’ refer to the CRM and Ti-6Al-4V sample.

\[ w_b = \frac{(A_b - A_0) x m_b x e_b x w_a}{(A_a - A_b) x m_a x e_a x w_a} \]  \hspace{1cm} (3)

where:
\( A_a \) = signal response value of the CRM specimen,
\( A_b \) = signal response value of the Ti-6Al-4V specimen,
\( A_0 \) = signal response value of the blank,
\( m_a \) = mass of CRM specimen,
\( m_b \) = mass of Ti-6Al-4V specimen,
\( w_a \) = mass percent fraction of oxygen in the CRM,
\( w_b \) = mass percent fraction of oxygen in the Ti-6Al-4V sample,
\( e_a \) = random effect correction factor of the measurement process of CRM, and
\( e_b \) = random effect correction factor of the measurement process of Ti-6Al-4V sample.

3.2. Probability Distribution
The uncertainty of the signal response value of the blank (\( A_0 \)) came from the repeated measurement differences by random effects, such as the non-uniformity of the mass and residual oxygen content in nickel basket flux, changes in environment, resolution of gas analyzer and others. This uncertainty component was combined with the uncertainty introduced by the signal response value of the CRM and the Ti-6Al-4V sample (\( A_a \), \( A_b \)), and finally included in the CRM and Ti-6Al-4V sample measurement repeatability uncertainty component.

In order to avoid repeated evaluations and simplify the calculation process, the mean of \( n \) replicates of \( A_0 \), \( A_a \), \( A_b \) were input in the form of a constant, instead, the probability distribution of random effect correction factor (\( e_a \), \( e_b \)) should be input to characterize the random effects on the blank, CRM and Ti-6Al-4V sample for random sampling, distribution propagation, and simulation calculation. \( e \) obeyed the normal distribution with the mean of 1, and the consistent estimator for its experimental standard deviation (\( s(e) \)) was RSD. According to the central limit theorem, the standard deviation of the mean \( (s^*) \) and the experimental standard deviation \( (s) \) had a relationship expressed in the equation (4).

\[ s^* = s / \sqrt{n} \]  \hspace{1cm} (4)

where:
\( s^* \) = the standard deviation of the mean,
\( s \) = the experimental standard deviation, and
\( n \) = the number of replicates.

According to table 2, the standard deviation of the mean of the random effect correction factor for CRM and the Ti-6Al-4V sample were calculated as \( s^*(e_a) = 0.016 \) and \( s^*(e_b) = 0.018 \). And the probability distribution of \( m_a \), \( m_b \) and \( w_a \) could be found from the certificate of balance and CRM. The probability distribution of each input quality of the measurement model was listed in table 3.
Table 3. Probability distribution of input quantities

| Input quantities | Distribution | Mean       | Standard deviation of mean ($s^*$) | Half-width |
|------------------|--------------|------------|------------------------------------|------------|
| $A_0$            | Constant     | 1.906 V·s  | —                                  | —          |
| $A_a$            | Constant     | 75.134 V·s | —                                  | —          |
| $A_b$            | Constant     | 74.977 V·s | —                                  | —          |
| $m_a$            | Uniform      | 57.5 mg    | 0.05 mg                            | —          |
| $m_b$            | Uniform      | 62.0 mg    | 0.05 mg                            | —          |
| $w_a$            | Normal       | 0.192 %    | 0.002 %                            | —          |
| $e_a$            | Normal       | 1          | 0.016                              | —          |
| $e_b$            | Normal       | 1          | 0.018                              | —          |

3.3. MCM simulation

MCM simulation was performed using Alchimia® 4.2 software. The measurement model according to equation (3) was input, and the input quantities shown in table 3 were import. Then, the number of simulations was set as $10^6$.

The simulation results were as follows: the mean and median of the determination results was 0.178 %, the standard deviation was 0.0047 %, and the confidence interval ($p = 95\%$) was [0.169 %, 0.187 %], which meant the expanded uncertainty was $U_{MCM} = 0.009 \%$ ($k = 2$). Meanwhile, the contribution rates of input quantities, such as $w_a$, $e_a$, and $e_b$, to the uncertainty were given with the percent of 15.1 %, 34.9 %, and 49.9 %, respectively.

3.4. GUM Method

The measurement uncertainty of Ti-6Al-4V titanium alloy by inert gas fusion-infrared absorption method was evaluated by the traditional GUM method based on ISO/IEC Guide 98-3: 2008 <Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM)>[1] and GB/T 28898-2012 <Evaluation of uncertainty in chemical composition analysis for metallurgical materials>[15]. The sources and components of measurement uncertainty based on GUM method were listed in table 4. And the relative combined standard uncertainty was calculated according to the equation (5).

Table 4. Sources and components of measurement uncertainty based on GUM method

| Sources                       | Probability distribution | Replicates | Uncertainty components |
|-------------------------------|--------------------------|------------|------------------------|
|                               | Type                     | Mean       | Standard deviation     | Half-width  | Component | $u$ | $u_{rel}(\%)$ |
| CRM’s certified value $w_{a1}$| Normal                   | 0.192 %    | 0.002 %                | —          | $u(w_a)$  | 0.002 % | 1.04 |
| CRM’s repeated test $w_{a2}$  | Normal                   | 0.192 %    | 0.0062 %               | —          | $u(s_a)$  | 0.0031 % | 1.61 |
| Ti-6Al-4V’s repeated test $w_b$| Normal                   | 0.178 %    | 0.0045 %               | —          | $u(s_b)$  | 0.0032 % | 1.89 |
| CRM’s weighting $m_a$         | Uniform                  | 57.5 mg    | —                      | 0.05 mg    | $u(m_a)$  | 0.03 mg  | 0.05 |
| Ti-6Al-4V’s weighting $m_b$   | Uniform                  | 62.0 mg    | —                      | 0.05 mg    | $u(m_b)$  | 0.03 mg  | 0.05 |
\[ u_{	ext{crel}} = \sqrt{[u_{\text{rel}}(w_{a1})]^2 + [u_{\text{rel}}(w_{a2})]^2 + [u_{\text{rel}}(w_b)]^2 + [u_{\text{rel}}(m_a)]^2 + [u_{\text{rel}}(m_b)]^2} \] (5)

where:

- \( u_{\text{crel}} \) = relative combined standard uncertainty,
- \( u_{\text{rel}}(w_{a1}) \) = component of \( u_{\text{rel}} \) contributed by CRM’s certified value,
- \( u_{\text{rel}}(w_{a2}) \) = component of \( u_{\text{rel}} \) contributed by CRM’s repeated test,
- \( u_{\text{rel}}(w_b) \) = component of \( u_{\text{rel}} \) contributed by Ti-6Al-4V’s repeated test,
- \( u_{\text{rel}}(m_a) \) = component of \( u_{\text{rel}} \) contributed by CRM’s weighting, and
- \( u_{\text{rel}}(m_b) \) = component of \( u_{\text{rel}} \) contributed by Ti-6Al-4V’s weighting.

Substituting the values into the equation (5), the relative combined standard uncertainty was found as \( u_{\text{crel}} = 2.63 \% \). The combined standard uncertainty was \( u_{\text{GUM}} = 0.0047 \% \), and the expanded uncertainty was \( U_{\text{GUM}} = 0.0093 \% \) \((k = 2)\). The measurement result was expressed as \( w_{\text{GUM}} = 0.178\% \pm 0.009 \% \) \((k = 2)\).

### 4. Conclusion

Two correction factors were introduced to characterize the random effects of conditional variations and system fluctuations on the measurement repeatability of the CRM for calibration and the tested Ti-6Al-4V sample. And a mathematical model for evaluating the uncertainty of single-point linear calibration measurement system based on Monte Carlo method (MCM) was proposed. The specific evaluation process and application of MCM was systematically explained based on a case study for determination of oxygen content in Ti-6Al-4V titanium alloy by inert gas fusion - infrared absorption method. Under the measurement condition that the CRM repeated 4 times and the Ti-6Al-4V sample repeated twice, the simulation result was \( w_{\text{MCM}} = 0.178\% \pm 0.009 \% \) \((k = 2)\), which was consistent with the result of \( w_{\text{GUM}} = 0.178\% \pm 0.009 \% \) \((k = 2)\), based on the traditional GUM method recommended by ISO/IEC Guide 98-3: 2008.

The key issues of the application of MCM to evaluate the uncertainty of the single-point calibration linear measurement system were solved, such as the MCM evaluation model and the introduction of the uncertainty from the apparatus calibration and repeated measurements. This method can be directly applied to the uncertainty evaluation of a single-point calibration linear measurement system, including inert gas fusion- infrared absorption or thermal conductivity method for determination of oxygen, nitrogen and hydrogen, high frequency induction combustion infrared absorption method for carbon and sulfur, chromatographic analysis and titration analysis. Further, it is expected that MCM will be developed and applied substantively in the linear measurement system, such as single-point calibration, two-point calibration, linear fitting multi-point calibration standard curve method and standard addition method, which will promote the study and application of measurement uncertainty to open up new horizons.

### References

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