EVALUATION OF THEUNCERTAINTY OF SILICON
DETERMINATION IN STEEL BY GRAVIMETRIC METHOD

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Abstract

Gravimetric method is widely used in chemical analysis. However, it’s difficult to evaluate the uncertainty of this method. Firstly, the standard deviation can be calculated by BESEL formula, but it can’t be used to represent the sub-uncertainty caused by random effect correctly. Secondly, while using the same balance, correlation can’t be ignored. Thirdly, when the linear and non-linear relationship is co-existed in the same mathematical model, it’s difficult to combine the sub-quantity rationally. Through choosing apt means, problems above can be solved successfully. As a typical case, the produced causes of the uncertainty in measurement of silicon in steel by gravimetric method are detailed discussed. By the meantime, the combined standard uncertainty for this example is also evaluated.

Key words

Uncertainty; steel; Silicon; gravimetric method

1 INTRODUCTION

In the chemical analysis of metallic material, gravimetric analysis method has been used widely. For some element, such as Si, Mo, Ni, Zr, W, quantitative gravimetric analysis are typical and traditional method. Balance is a fundamental instrument in the gravimetric method. Through the mathematical model, we can find that all the input quantities are related to the balance. And during the course of analysis, balance may be used for several times. In most cases, we recommend to use the same one balance, which could bring the minimum uncertainty. This conclusion can be testified. For example, when we make a moisture testing, we put sample on the balance, and we can obtain the sample mass
m₁, then we heat the sample to a constant weight and we weigh it again and obtain 
m₂, the loss quantities is \( \Delta m = m₁ - m₂ \), which is the moisture of sample. If we only 
considerate the uncertainty caused by the systematic effect, according to the “Guide 
to the Evaluation and Expression of uncertainty in Measurement” published in 1995,“
If some of the sub-quantity of uncertainty are significantly correlated, the correlations 
must be taken into account. There may be significant correlation between two input 
quantities if the same measuring instrument, physical measurement standard, or 
reference datum having a significant standard uncertainty is used in their 
determination.”

\[
u(\Delta m) = \sqrt{[u(m₁)]^2 + [u(m₂)]^2 - 2 \times u(m₁) \times u(m₂) \times r(m₁, m₂)}
\] (1)

If the balance is used to measure a mass of input quantity m₁, and the same balance 
is used to measure a similar mass of input quantity m₂. We consider that the input 
quantities could be significantly correlated, \( r(m₁, m₂) = 1 \), so

\[
u(\Delta m) = |u(m₁) - u(m₂)| = 0
\] (2)

From the Eq.1 and Eq.2 as above, we can find that during the course of analysis, 
using the same balance can minimize the uncertainty caused by systematic effect.

2 SAMPLE PREPARATION

Sample is decomposed with hydrochloric and nitric acids. The acid solution is heated 
and evaporated into dryness. Silica is separated as insoluble SiO\(_2\cdot\)xH\(_2\)O, filtered off. 
The filtrate is evaporated to dryness and ignited in a platinum crucible at 1050°C, 
weighed. The residue is treated with hydrofluoric and sulphuric acids, Silicon is 
volatilized as silicon tetra-fluoride, and the impurities are left as sulphates residue, the 
crucible is weighed. The loss in weight represents the amount of silica.

3 MODELLING THE MEASUREMENT

According to the gravimetric method, the result of silicon content in the sample can 
be calculated with Eq.3.

\[
w(\%) = 0.4674 \times \frac{[m₁ - m₂] - [m₄ - m₅]}{m₃} \times 100
\] (3)

0.4674:the conversion factor of SiO\(_2\) into Si
m₁: Mass of crucible and residue in sample before dealt with hydrofluoric acid, g 
m₂: Mass of crucible and residue in sample after dealt with hydrofluoric acid, g 
m₃: Mass of sample, g 
m₄: Mass of crucible and residue in blank before dealt with hydrofluoric acid, g 
m₅: Mass of crucible and residue in blank after dealt with hydrofluoric acid, g
As an example, we did the analysis according to ISO 439:1994 Steel and iron -- Determination of total silicon content -- Gravimetric method, the data we obtained are listed in table 1.

<table>
<thead>
<tr>
<th>m₁ (g)</th>
<th>m₂ (g)</th>
<th>m₃ (g)</th>
<th>m₄ (g)</th>
<th>m₅ (g)</th>
<th>Wₑₘₐₑ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.4380</td>
<td>24.3688</td>
<td>1.0005</td>
<td>26.0769</td>
<td>26.0767</td>
<td>0.0314</td>
</tr>
</tbody>
</table>

4 EVALUATION OF SUB-QUANLITY OF UNCERTAINTY

4.1 Sub-quantity of uncertainty caused by systematic effect - \( u(w₁) \)

In this model, we use the balance as the measure instrument. The sub-quantity of uncertainty caused by systematic effect decided by the balance resolution. According to the data provided by balance calibration certificate, the resolution of balance \( \delta_x \) is 0.0001g. Its unknown distribution is supposed to be a triangular distribution. So:

\[
\begin{align*}
    u(m₁) & = u(m₂) = u(m₃) = \frac{1}{2\sqrt{3}} \times \delta_x = 0.29 \times \delta_x = 0.000029 \text{ (g)} \quad (4)
\end{align*}
\]

We define \( \Delta m₁ = m₁ - m₂ \). Since the data \( m₁ \) and \( m₂ \) obtained from the same balance, we consider that they are significantly correlated. The correlation coefficient is 1.

\[
\begin{align*}
    u(\Delta m₁) & = \sqrt{\left(\frac{\Delta m₁}{m₁} \times u(m₁)\right)^2 + \left(\frac{\Delta m₁}{m₂} \times u(m₂)\right)^2 + 2 \times \frac{\Delta m₁}{m₁} \times \frac{\Delta m₁}{m₂} \times u(m₁) \times u(m₂) \times r(m₁,m₂)} \\
    & = \sqrt{u²(m₁) + u²(m₂) - 2 \times u(m₁) \times u(m₂)} = |u(m₁) - u(m₂)| = 0 \\
\end{align*}
\]

Assumed \( \Delta m₂ = m₄ - m₅ \), so: \( u(\Delta m₂) = 0 \)

Assumed \( \Delta m₃ = \Delta m₁ - \Delta m₂ \) so: \( u(\Delta m₃) = 0 \)

\[
\begin{align*}
    u(w₁) & = \sqrt{\left(\frac{w₁}{(\Delta m₃)} \times u(\Delta m₃)\right)^2 + \left(\frac{w₂}{m₃} \times u(m₃)\right)^2 + 2 \times \frac{w₁}{(\Delta m₃)} \times \frac{w₂}{m₃} \times u(\Delta m₃) \times u(m₃) \times r(\Delta m₃,m₃)} \\
    & = \frac{100 \times 0.4674 \times (\Delta m₁ - \Delta m₂)^2 \times u(m₃)}{m₃²} = \frac{100 \times 0.4674 \times [(m₁ - m₂) - (m₄ - m₅)] \times u(m₃)}{m₃²}
\end{align*}
\]

Calculated with Eq.6, \( u(w₁) = 0.0000935\% \)

4.2 \( u(w₂) \) ——sub-quantity of uncertainty caused by random effect

As known, sub-uncertainty caused by random effect is difficult to evaluate. The uncertainty for any measuring result consists of not only the random effect but also
the systematic effect. To valuate the random effect properly, the systematic effect should be subtracted. Moreover, statistic data are needed to determine the $u(w_2)$ properly. In this example, we analyse a sample twice simultaneously and compare the difference between these two runs. 14 pairs of results for different samples (see, table 2) are collected.

Table 2—statistical data of different samples

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>$\overline{\Delta}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_{1i}$</td>
<td>4.125</td>
<td>3.970</td>
<td>3.860</td>
<td>2.970</td>
<td>3.152</td>
<td>2.861</td>
<td>3.121</td>
<td></td>
</tr>
<tr>
<td>$x_{2i}$</td>
<td>4.110</td>
<td>3.941</td>
<td>3.885</td>
<td>2.954</td>
<td>3.167</td>
<td>2.882</td>
<td>3.164</td>
<td></td>
</tr>
<tr>
<td>$\Delta_i =</td>
<td>x_{1i} - x_{2i}</td>
<td>$</td>
<td>0.015</td>
<td>0.029</td>
<td>0.025</td>
<td>0.016</td>
<td>0.015</td>
<td>0.021</td>
</tr>
</tbody>
</table>

Since the two results, $x_{1i}$ and $x_{2i}$, for the same sample were obtained from the same instrument, we consider that the difference between them, $\Delta_i = |x_{1i} - x_{2i}|$, doesn't include the systematic effect. $u(w_2)$ can be calculated according to BESSEL Formula with Eq.7. The value of $S(\Delta)$ represents the uncertainty caused by random effect.

$$u(w_2) = S(x_i) = \frac{S(\Delta)}{\sqrt{2}} = \sqrt{\frac{1}{2} \sum_{i=1}^{14} \left(\Delta_i - \overline{\Delta}\right)^2} = 0.00725(\%) \quad (7)$$

4.3 Combination:

Since $w_1 \, \, w_2$ are not correlated input quantity so

$$u_c(w) = \sqrt{[u(w_1)]^2 + [u(w_2)]^2} = \sqrt{(0.0000935\%)^2 + (0.00725\%)^2} = 0.00725\% \quad (8)$$

According to JJF1059-1999, the expanded factor $k=2$ is adopted in most cases. So the expanded uncertainty, $U$, can be expressed in Eq.9:

$$U = k \times u_c(w) = 0.014(\%) \quad (9)$$

The result of Silicon content in this example by gravimetric method can be expressed as below:

$$w = w_{\text{mea.}} \pm U = 3.314 \pm 0.014(\%), k = 2 \quad (10)$$

Table 3 summarized the sub-quantity uncertainty for this model.
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Table 3—the overview of the uncertainty

<table>
<thead>
<tr>
<th>Sub-quantity</th>
<th>Introduced by the resource of</th>
<th>Sub-quantity</th>
<th>Introduced by the resource of</th>
</tr>
</thead>
<tbody>
<tr>
<td>$u(w_1)$</td>
<td>systematic effect</td>
<td>$u(m_1)$</td>
<td>the resolution of</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$u(m_2)$</td>
<td>the balance</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$u(m_3)$</td>
<td></td>
</tr>
<tr>
<td>$u(w_2)$</td>
<td>random effect</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5 CONCLUSION

Through choosing apt means, problems above can be solved successfully. As known, sub-uncertainty caused by random effect is difficult to evaluate. Analyse a sample twice simultaneously and value the difference between these two analysis results. Collect the differences of different sample and statistics according to the BESEL formula. Besides, through mathematical treatment, we simplify the mathematical model, that’s to say, in the final function, there’s only non-linear relationship included. As a typical case, the produced causes of the uncertainty in measurement of silicon in steel by gravimetric method are detailed discussed, the combined standard uncertainty is also evaluated.

REFERENCES