Taking degrees of freedom from uncertainty into minimum weight estimate for analytical balances

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Abstract. There is a great need to weigh very small mass samples in analytical balances due to cost reduction and sustainability requirements so weighing results should accomplish the accuracy requirements in selecting and quality checking tests. The minimum weight is an important balance performance requirement for small mass weighing and is defined as the load for which the relative expanded uncertainty is equal to the accuracy requirement. When “uncertainty” of uncertainty of repeatability is regarded in minimum weight determination, the lack of information about degrees of freedom can cause an underestimated value. Thus, here is shown a modified equation for minimum weight calculation which regards the uncertainty of repeatability uncertainty to take account of the degrees of freedom. Besides, it is developed a simple approximated equation for minimum weight calculation.

1. Introduction

Analytical electronic balances are widespread weighing instruments in fields of productive processes [1, 2]. Nowadays, there is a great need of weighing very small mass samples in analytical balances due to cost reduction and sustainability requirements [3] which impose stringent quality requirements to the process. Therefore, weighing results should accomplish the accuracy requirements stated according to the intended quality for the final processes results. The required weighing accuracies commonly are defined as a relative one specified as upper thresholds for relative expanded uncertainty, which relies on the balance properties such as repeatability, eccentricity, nonlinearity and sensitivity [4]. Thus, to achieve quality targets, also balance properties should be subject to performance requirements which should be assessed before selection of the weighing instrument and periodically checked when it is in use [5]. Measurement uncertainty evaluation before balance selection could be performed by assessing properties specification from manufacturer [6] and in use, should be performed taking account: calibration [7], testing of properties results [8] and others effects on weighing [9].

In small mass weighing, an important user’s performance requirement is the minimum weight defined as the load for which the relative expanded uncertainty is equal to the accuracy requirement [10]. In minimum weight evaluation the uncertainty dominant component is repeatability [11] so the expanded uncertainty is calculated by the multiplication of repeatability uncertainty and the coverage factor obtained by the effective degrees of freedom (repeatability degrees of freedom) from Student’s distribution [12]. By using this method to calculate minimum weight, one does not regard the measurement uncertainty as a measurement quantity with uncertainty and this assumption is mainly
important when repeatability uncertainty is derived from a few repetitions (i.e., few degrees of freedom) as in the case of degrees of freedom obtained from weighing instruments regulations or from performance checks.

This work proposes to complement the minimum weight calculation by taking account of the uncertainty of measurement by regarding that the measurement variance (square of uncertainty) is a Chi-squared distributed variable. This is a routine assumption when one supposes that the weighing reading obeys a Gaussian distribution [13].

Moreover, this study shows a modified equation to calculate minimum weight taking account uncertainty to repeatability uncertainty for degrees of freedom in the range from 1 to 1000. This equation is obtained by regarding coverage probabilities of 95.45% and 95% for, respectively, the reading and uncertainty and will be able to help users in tasks of selection and checking weighing instruments.

2. Uncertainty of uncertainty in minimum weight.

The minimum weight is defined as the load \( R_{\text{min}} \) for which the relative expanded uncertainty \( U(R_{\text{min}})/R_{\text{min}} \) is equal to the accuracy requirement \( Req \), equation (1).

\[
\frac{U(R_{\text{min}})}{R_{\text{min}}} = Req
\]  

(1)

The expanded uncertainty \( U(R_{\text{min}}) \) is defined as the multiplication of standard uncertainty \( u_c \) and the coverage factor \( k_{p,\text{eff}} \), regarding a coverage probability \( p \) and effective degrees of freedom \( \nu_{\text{eff}} \) (2).

\[
U(R_{\text{min}}) = k_{p,\text{eff}} \cdot u_c
\]  

(2)

The standard uncertainty may be written in linear form by the product of repeatability uncertainty \( S_{\text{rp}} \) and a multiplicative term \( \lambda \), which encompass the other uncertainty components (3). The underlying hypothesis is that the repeatability is non null.

\[
u_c = \lambda \cdot S_{\text{rp}}
\]  

(3)

For weighing uncertainties, degrees of freedom from repeatability \( \nu_{\text{rp}} \) are the main contribution for effective degrees of freedom \( \nu_{\text{eff}} \) [10], because the degrees of freedom of the systematic components are regarded infinite. So, the \( \nu_{\text{eff}} \) calculation by Welch-Satterthwaite formula [12] may be simplified (4).

\[
u_{\text{eff}} = \lambda \cdot \nu_{\text{rp}}
\]  

(4)

In small mass measurement the only two significative uncertainty components are repeatability and the balance resolution but repeatability uncertainty is the most meaningful [14]. Thus, in calculating the minimum weight, \( \lambda \) is very close to unit.

Thus, minimum weight \( R_{\text{min}} \) can be redefined from equation (1- 4) by (5).

\[
R_{\text{min}} = \frac{k_{p,\text{eff}} \cdot S_{\text{rp}}}{Req}
\]  

(5)

In a former method to calculate minimum weight, uncertainty of repeatability is regarded as a non measurement quantity (i.e. zero uncertainty variable) what implies \( S_{\text{rp}} \) is the true value for repeatability uncertainty. On the other hand, \( S_{\text{rp}} \) value is estimated by the weighing readings which are a measurement quantity, thus \( S_{\text{rp}} \) also should be regarded an uncertainty variable.
By the assumption that the weighing readings are variables from a normal probability distribution and $S_p$ is estimated by the sample standard deviation the repeatability variance is Chi-squared distributed with $v_p$ degrees of freedom. By this approach, the repeatability uncertainty is an estimate to weighing reading standard deviation $\sigma$, the true repeatability uncertainty value. Although the standard deviation of the weighing readings is not known, one can obtain its range of possible values from the Chi-squared confidence interval, calculated to some coverage probability $\alpha$ from the quantiles $Q$ [13], equation (6).

$$
\left( \frac{V_q}{Q(\frac{\alpha}{2},v_p)} \right)^{\frac{1}{2}} S_p \leq \sigma \leq \left( \frac{V_q}{Q(1-\frac{\alpha}{2},v_p)} \right)^{\frac{1}{2}} S_p
$$

In equation (6), the multiplicative terms for the 95% standard confidence interval approaches to 1 as $v_p$ increases. Thus, for few degrees of freedom the thresholds of the confidence interval deviate significantly from $S_p$. Regarding that the minimum weight is defined as the true value of repeatability uncertainty, it is necessary to include the upper threshold of the confidence interval in order to assure that the true repeatability uncertainty will be accounted for (7).

$$
R_{min} = k_{p,v_p} \left( \frac{V_q}{Q(1-\frac{\alpha}{2},v_p)} \right)^{\frac{1}{2}} S_p
$$

(7)

Usually, specifications of manufacturer include the repeatability uncertainty but no information about $v_p$ is provided. However, for countries where the weighing instruments are subject to type approval according to OIML, the manufacturer’s repeatability uncertainty is achieved by ten repetitions [15] implying $v_p$ value is nine. Thus, minimum weight can be calculated in selection of the balance for some weighing task. On routinely checking tests the value of degrees of freedom are not very different from this. Table 1 shows minimum weight values calculated for $v_p$ equals nine with and without uncertainty of uncertainty term and also it is calculated for infinite $v_p$. In this calculation the taking value for repeatability uncertainty was 0.03 mg a common value specified by manufacturers for balances with maximum capacity of 200 g and resolution 0.01 mg. Moreover, the accuracy requirement $Req$ value was taking 0.1% (“gold rule” [16]), the quantiles $Q$ and $k_{p,v_p}$ were calculated, respectively for Chi-square and Student’s distributions.

| Parameters | $S_p$ = 0.03 mg , $Req$ = 0.1% , $p$ = 95.45% , $\alpha$ = 95% |
|------------|---------------------------------------------------------------|
| $R_{min}$  | $R_{min}$  | $R_{min}$  |
| ($v_p$ = 9, $Q$ = 1.8 $k$ = 2.3) | ($v_p$ = 9, $k$ = 2.3) | ($v_p$ = $\infty$, $Q$ = 1 $k$ = 2) |
| 127        | 70           | 60           |

The minimum weight values show that to taking account uncertainty of uncertainty doubles the value in relation to the others. Indeed, the value of $R_{min}$ could be reduced if was known $v_p$ and $S_p$ from historical data [17], regarding there was not reproducibility problems [18]. These are the assumption when one use the uncertainty of repeatability from manufacturer’s manual, but the information about degrees of freedom is not provided. In checking tests, users could use theirs estimate repeatability uncertainty historical data to reduce minimum weight.
3. Minimum weight approximated equation

A five terms approximated equation has been developed (8) which allows calculating minimum weight directly from degrees of freedom $v_{rp}$, repeatability uncertainty $S_{rp}$ and accuracy requirement $Req$. This equation is valid for $v_{rp}$ range from 1 to 1000, coverage probabilities of 95.45% and 95% for respectively, the reading and uncertainty. The approximation has a maximum absolute relative error of 2%.

$$R_{m,n} = \left( A_0 + A_1 e^{-\frac{v_{rp}}{3}} + A_2 e^{-\frac{v_{rp}}{5}} + A_3 e^{-\frac{v_{rp}}{7}} + A_4 e^{-\frac{v_{rp}}{9}} \right) \frac{S_{rp}}{Req}$$ (8)

Table 2 shows the values and standard deviation for parameters of equation (8). The approximated equation may have utility when one does not wish to use formulas for calculating quantiles specifying additional terms of probability, for example, when one is not very familiar with uncertainty calculations. Thus this formula could help users in tasks of selection and checking weighing instruments.

| Parameter | Value  | Std. deviation |
|-----------|--------|----------------|
| $A_0$     | 2.1102 | 0.0008         |
| $A_1$     | 3.32   | 0.04           |
| $t_1$     | 11.2   | 0.1            |
| $A_2$     | 54.0   | 0.8            |
| $t_2$     | 1.46   | 0.01           |
| $A_3$     | 18237  | 146            |
| $t_3$     | 0.2640 | 0.0006         |
| $A_4$     | 0.519  | 0.006          |
| $t_4$     | 144    | 2              |

4. Conclusion

The minimum weight is an important performance requirement for measuring small mass sample which should be assessed in selection of analytical balances and in quality checking tests. By regarding uncertainty of repeatability uncertainty, the minimum weight dependence on degrees of freedom of repeatability become explicit and shows the importance of knowing the degrees of freedom for the assessments. In consequence, the lack of information about degrees of freedom of repeatability uncertainty can cause an underestimated minimum weight value in selection and checking tests on analytical balances, therefore the final process cost reduction and sustainability requirements may not be achieved.

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