TECHNICAL NOTE

The Paradox of Precision

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Abstract:

This paper is about a typical mistake in the calculation of standard deviation of measurements in cases in which there are no differences among repetitious replicates. Some students believe the standard deviation in those case is equal to zero. So, this mistake leaves to a paradox: worse balance should show better results (i.e. standard deviation equal to zero). The solution of this simple, but important situation is shown.

Keywords: standard deviation; global variance; precision of measurements; error propagation

1. Introduction

It is a well-established fact that the fewer the number of significant figures presented by an instrument, the lower the precision.

However, in laboratory replicated measurements sometimes student can get the same value in each repetition and then express the uncertainty (estimated standard deviation) as equal to zero. Student can often suppose that measurements were very precise and conclude that no errors occurred among the measurements.

It is important to demonstrated to the student that if this conclusion were correct, we will have a paradox: worse balance, with lower resolution should show a standard deviation of a set of measures equal to zero, and them, it will be better than more precise balance. It contradicts the first sentence.

2. Material and Methods

The hypothetical example used to illustrate the proposed paradox was a set of measurements of the mass of a solid was performed using three different balances with different resolutions (0.1 g, 0.01 g, and 0.001g). All calculations were done with Microsoft Excel

The error (ε) of each measurement (i) was done by Equation 1, where e is the half of balance resolution, and $rand$ is a random number which varies from 0 up to 1 with a square frequency distribution. It was obtained with the native function of Excel $rand(\ )$.

$$\varepsilon_i = rand_i * e_i \qquad (1)$$

By this way, each measurement (j) in the balance has two terms: the true value of mass ($m\mu$) and a random error (ε), Equation 2.

$$m_j = m_\mu + \varepsilon_j \qquad (2)$$

The crucible mass reading 'i' in each balance is the difference between two measurements: the effective value of crucible mass (with random error $rand_1$) and the null of scale (with $rand_2$). Thus, the Equation 3 was obtained for crucible mass.

In the end, the mass of crystal is the difference between the crucible with the crystal and the empty crucible.

The crucible mass was chosen freely around

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16 g. The true value of crystal mass has chosen with a variation in 3rd decimal digit. These values are presented in the Table 1.

$$crucible\ mass\ (i) \\ = m_{\mu,i} \\ + (rand_{1,i} + rand_{2,i}) \\ * e_i \quad (3)$$

The simulated reading values were obtained using the Equation 3 for empty and full crucible, for each resolution balance. The estimated standard deviation for crystal mass obtained in each kind of balance was calculated using Equation 4, where N is the total number of measurement. In this paper, N is equal to three.

Table 1. Chosen true values of mass for crystal and crucibles in each repetition.

Repetition	1	2	3
true crystal mass/g	1.1200	1.1210	1.1230
true crucible mass/g	15.9996	16.8340	15.4956

$$sd = \sqrt{\sum_{i=1}^{N} \frac{(m_i - \overline{m})^2}{N-1}} \quad (4)$$

3. Results and Discussion

The measurements of the mass of a non-hygroscopic crystal obtained by simulation of behavior of three different balances, each one with a different resolution are showed in Table 2.

Table 2. Hypothetical example of estimating the standard deviation of data obtained from balances with different resolutions.*

	Repetition	balance 1	balance 2	balance 3
Resolution /g	-	0.1	0.01	0.001
Crystal mass /g	1	1.1	1.12	1.122
	2	1.1	1.12	1.119
	3	1.1	1.12	1.118
Standard deviation /g	-	0.0	0.00	0.002

* data simulated with Equation 3 for empty and full crucible.

It is possible to observe the paradox in the Table 2. The results seem to indicate, erroneously, that lower resolution balances are more precise than balances with the highest resolution, once the first presented estimative of standard deviation equal to zero.

The situation described above is more common as the fewer the number of significant digits of the instrument (or the more reduced the instrument resolution). Thus, it would appear that as the worse the instrument resolution, more precise will be the result. Several papers discuss calculations of propagation of uncertainty, but few discuss this simple situation [1, 2].

The solution

A logical solution for this problem involves remembering that the measurement is expressed by Equation 2.

In all situations, the overall uncertainty ($\sigma_{overall}$) must include several contributions that are mutually independent [2]. For example, allowing adsorption of moisture is a source of uncertainty in the chemical procedure, but it does not depend on instrument uncertainty.

$$\sigma_{overall}^2 = \sigma_{procedure}^2 + \sigma_{instrument}^2 + \sigma_{others}^2 \quad (5)$$

Usually, the first term in Equation 5 is higher, thus explaining the exclusion of the other terms. However, to solve this paradox, the second term should be more important than the first, which is an exception to the previous sentence.

For simplicity, the estimated standard deviation (*sd*) were taken into account as a measure of uncertainty of the procedure. The

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uncertainty of a balance ($\sigma_{instrument}$) is usually considered equal to error *e*, half of resolution of instrument.

Comparing the results of Table 2 and Table 3, we can see that treating the uncertainty of the instrument as an overall uncertainty reveals that the expected, highest resolution balance displays the least uncertainty.

Obviously, similar arguments can be applied pedagogically to measuring burettes, volumes, absorbances, and so on.

Table 3. Calculation of global uncertainty of balances with different resolutions.

	Resolution /g	sd /g*	Uncertainty Instrument/g	Overall Uncertainty/g
Balance 1	0.1	0.0	0.05	0.1
Balance 2	0.01	0.00	0.005	0.01
Balance 3	0.001	0.002	0.0005	0.0021

* sd, estimative of standard deviation of replicates (N=3).

4. Conclusions

A usual paradox of precision found in laboratory class was shown. The understanding of importance of global variance on final results was shown as solution to this paradox.

References and Notes

[1] Gordon, R.; Pickering, M.; Bisson, D. *J. Chem. Ed.* **1984**, *61*, 780. [Crossref]

[2] Yates, P. C. *J. Chem. Ed.* **2001**, *78*, 770. [Crossref]

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