



Reporting Statistical Uncertainty of Certified Values for Reference Materials

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We here describe an approach used by a manufacturer of calibration standards and certified reference materials, CRMs (SPEX Certiprep, Metuchen, NJ), to standardize a way of reporting certified values and their associated uncertainties quoted on a CRM certificate of analysis. The method has evolved during many years in the authors' laboratories and is based on well-established principles discussed in a number of recognized statistical guides and publications (1–3), and reported in detail elsewhere (4).

Defining Measurement Uncertainty

To exemplify quantification of measurement uncertainty, we will examine a 1000-mg/L nickel ICP-MS certified reference standard determined by ethylenediaminetetraacetic acid (EDTA) titration. Normally we would report certified values by two independent methods, one wet and one instrumental; however, for brevity we will only examine the wet chemical determination here. From all the measurement uncertainties associated with the measurement of the reference standard, it was determined that the CRM had a certified value of 1001 mg/L \pm 4 mg/L. But what does an uncertainty of \pm 4 mg/L actually mean? Uncertainty is a parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand. From this we can conclude that uncertainty is a measure of the “goodness” of a result. There are three steps to defining this uncertainty.

Step one: Determine Type A and Type B uncertainties. Type A Standard Uncertainty is defined as the standard deviation of the mean of replicate measurements.

$$u_i = s/n^{1/2} \text{ where } s = \text{standard deviation and} \\ n = \text{number of replicates}$$

Type B Standard Uncertainty is based on judgment using all information available, including measurement data, experience, specifications, and calibration reports. This type is more complex.

- Convert to a standard uncertainty by dividing the listed uncertainty by the weight
- Weight the value based on the distribution ($u_i = \text{value}/\text{weight}$). The three common distributions used (5) are:
 - 1) Normal distribution: For a 95% level of confidence, convert to a standard uncertainty by using 1.96 as a multiplier;

e.g. uncertainty listed on a balance certificate.

- 2) Rectangular distribution: If the limits do not specify a level of confidence, use a multiplier of $3^{1/2}$; e.g. standard reference material (SRM) uncertainty.
- 3) Triangular distribution: For symmetric distribution use the multiplier $6^{1/2}$; e.g. uncertainty associated with volumetric glassware.

Step two: Combine Type A and Type B uncertainties (5):

- For only a sum or difference of quantities, where c is a constant and y is a function of the parameters p , q , and r , the combined standard uncertainty $u_c(y)$ is:

$$u_c(y) = c [u_c(p)^2 + u_c(q)^2 + u_c(r)^2]^{1/2}$$

- For only a product or quotient, the combined standard uncertainty $u_c(y)$ is:

Step three: Calculate the expanded uncertainty: $U = k u_c$, where u_c is the combined standard uncertainty from step two and $k = \text{cov-}$

$$u_c(y) = c \left(\frac{u_c(p)^2}{p^2} + \frac{u_c(q)^2}{q^2} + \frac{u_c(r)^2}{r^2} \right)^{1/2}$$

erage factor. U is the interval within which lies the value of the measurand (for example, true value $Y = y \pm U$).

The value of the coverage factor k depends on the desired level of confidence. A coverage factor of 2 ($U = 2u_c$) gives a level of confidence of approximately 95% ($k = 1.96$ at 95% confidence level).

Calculating Measurement Uncertainty

To show how this works, let's calculate the uncertainty for the wet assay determination of 1000-mg/L nickel solution by EDTA Titration. Here the EDTA was first standardized with NIST SRM Pb(NO₃)₂, using xylenol orange as the indicator. The concentration of nickel was then determined by titration with the standardized EDTA solution, using murexide as the indicator. Two steps are involved with this procedure:

1. Determine the molarity (concentration) of the EDTA solution using lead nitrate, NIST SRM #928.
2. Determine the concentration of nickel by titration against EDTA that was standardized against lead nitrate from step one. Equation used:

Table I. Total number of steps involved in calculating uncertainty of Ni by EDTA titration.

Task	Description	Value
1	Weight of Pb(NO ₃) ₂	270 mg
2	Purity of Pb(NO ₃) ₂	1
3	Molecular weight of Pb(NO ₃) ₂	331.2 g/mol
4	Volume of EDTA–Pb(NO ₃) ₂	32.38 mL
5	Atomic weight of Ni	58.6934 g/mol
6	Ni solution aliquot	50 mL
7	Volume of EDTA–Ni solution	33.8766 mL

$$C_{Ni} = \frac{\text{Weight of Pb(NO}_3)_2 \times \text{purity of Pb(NO}_3)_2 \times \text{volume of EDTA(Ni)} \times \text{atomic weight of Ni}}{\text{MW of Pb(NO}_3)_2 \times \text{volume of EDTA Pb(NO}_3)_2 \times \text{volume of Ni aliquot}}$$

Table I represents the analytical data generated from this method. Plugging in the data from Table I, the concentration (C_{Ni}) for this batch of nickel is:

$$C_{Ni} = \frac{270 \times 1 \times 33.8766 \times 58.6934}{331.2 \times 32.38 \times 50} = 1001.188 \text{ mg/L}$$

Let us calculate the uncertainties associated with this value.

Task 1: Uncertainty weighing lead nitrate: The electronic balance uncertainty was listed as ± 0.1 mg. The uncertainty at the 95% confidence level is $0.1/1.96 = 0.05102$ mg.

Five repeated weighings of the NIST weight gave no error; therefore, this uncertainty component can be considered negligible.

$$u(M_{Pb(NO_3)_2}) = [(0.0510204)^2 + (0)^2]^{1/2} = 0.05102 \text{ mg}$$

Task 2: Uncertainty of the purity of lead nitrate (5): The listed purity of Pb(NO₃)₂ is $100 \pm 0.03\%$ or 1.0 ± 0.0003 . Applying a rectangular distribution:

$$u\left(\text{Pb(NO}_3)_2\right) = \frac{0.03/100}{3^{1/2}} = \frac{0.0003}{1.732} = 0.0001732$$

Task 3: Uncertainty of the molecular weight of lead nitrate (5): From the latest IUPAC 1997 table, for each element, the standard uncertainty is determined by assuming a rectangular distribution and dividing these values by $3^{1/2}$. See Table II.

$$u(F_{Pb(NO_3)_2}) = \{(0.0577)^2 + (0.00004)^2 + (0.00052)^2\}^{1/2} = 0.0577 \text{ g/mol}$$

Task 4: Uncertainty in volume of EDTA titrant: The volumetric analysis uncertainty is a combination of the uncertainty of the titration (five replicates) plus the uncertainty in the internal volume of the burette. The uncertainty of the titration is represented by $s/n^{1/2} = 0.02916/5^{1/2} = 0.01304$. The internal volume uncertainty of the burette is derived from data on the certificate and the temperature difference. For a triangular distribution, the certificate uncertainty is $0.05/6^{1/2} = 0.0204$ mL and the uncertainty due to temperature is $32.38 \times 4 \times 2.1 \times 10^{-4}/3^{1/2} = 0.0157$ mL (temperature variation of ± 4 °C, the coefficient of volume expansion for water = 2.1×10^{-4} °C⁻¹). The combined uncertainty is represented by:

$$u(V_{\text{EDTA-1}}) = [(0.01304)^2 + (0.0204)^2 + (0.0157)^2]^{1/2} = 0.02887 \text{ mL}$$

Task 5: Uncertainty of the atomic weight of nickel: From the IUPAC table, the atomic weight of nickel uncertainty is 58.6934 ± 0.00018 . For a rectangular distribution, Type B:

$$u(F_{Ni}) = 0.00018/(3)^{1/2} = 0.0001039 \text{ g/mol}$$

Task 6: Volume uncertainties from pipetting a 50-mL aliquot: The pipette manufacturer stated the internal volume as $50 \text{ mL} \pm 0.05 \text{ mL}$. For a triangular distribution the standard uncertainty is $0.05/6^{1/2} + 0.02041$ mL. Uncertainty due to the room temperature being different from the calibrated temperature is $50 \times 4 \times 2.1 \times 10^{-4} = 0.02425$ mL (see Task 5). Combining:

$$u(V_{\text{Pipette}}) + (0.0204^2 + 0.02425^2)^{1/2} = 0.03170 \text{ mL}$$

Task 7: Uncertainty in titrated EDTA volume: The nickel volumetric analysis uncertainty is a combination of the uncertainties from the titration in replicates and the internal volume of the burette. As shown in task four, the uncertainty of the titration is represented by $s/n^{1/2} = 0.02517/3^{1/2} = 0.01453$. For in the internal volume uncertainty of the burette using a triangular distribution, the certificate uncertainty is $0.05/6^{1/2} = 0.0204$ mL and the uncertainty due to temperature is $33.88 \times 4 \times 2.1 \times 10^{-4}/3^{1/2} = 0.0164$ mL (see Task 5). The combined uncertainty is:

$$u(V_{\text{EDTA-2}}) = [(0.01453)^2 + (0.0204)^2 + (0.0164)^2]^{1/2} = 0.02996 \text{ mL}$$

We then calculate the total and the expanded uncertainty associated with the analysis of nickel by EDTA titration. The individual values from tasks 1–7 are summarized in Table III and calculated by:

$$u_c = C_{Ni} \sum^{1/2} (u_c/V)^2$$

Table II. Standard uncertainty of constituent elements of Pb(NO₃)₂ using 1997 IUPAC tables.

Element	Atomic weight	Quoted uncertainty	Total uncertainty	Standard uncertainty (Total/3 ^{1/2})
Pb	207.2	± 0.1	± 0.1	0.0577
N	14.00674	± 0.00007	± 0.00007	0.00004
O	15.9994	± 0.0003	O ₃ = 3 × 0.0003	0.00052

And applying the values from Table III, we obtain:

$$u_c = 1.4422 \text{ mg/L}$$

The expanded uncertainty $U(C_{\text{Ni}})$ for the EDTA titration is obtained by multiplying the standard combined uncertainty by the coverage factor, k , for a 95% confidence interval. Because the number of degrees of freedom for the EDTA titration method is less than six, one has to determine the value of the coverage factor from the “effective degrees of freedom,” a value that is approximated by combining the degrees of freedom of individual components making up the combined uncertainty. This is accomplished by using the Welch-Satterthwaite formula (5):

$$v_{\text{eff}} = u_c^4 / \sum \{V_i^4 u_i^4 / v_i\} = \text{Effective degrees of freedom} = 4.326 / 0.7217 = 6$$

Therefore, the coverage factor k for the effective degrees of freedom, $v_{\text{eff}} = 6$, from the student's t-distribution table is 2.45 for a confidence level of 95%, and the expanded uncertainty is:

$$U(C_{\text{Ni}}) = 2.45 \times 1.4422 = 3.533 \text{ mg/L}$$

And finally, the certified value for Nickel is:

$$1001 \pm 4 \text{ mg/L}$$

The individual uncertainty contributions in the volumetric analysis of Ni by titration with EDTA are represented in Figure 1.

Summary

This study has been the result of detailed research into developing a standard method for the reporting of certified values for CRMs by the authors and others at SPEX CertiPrep. It was undertaken

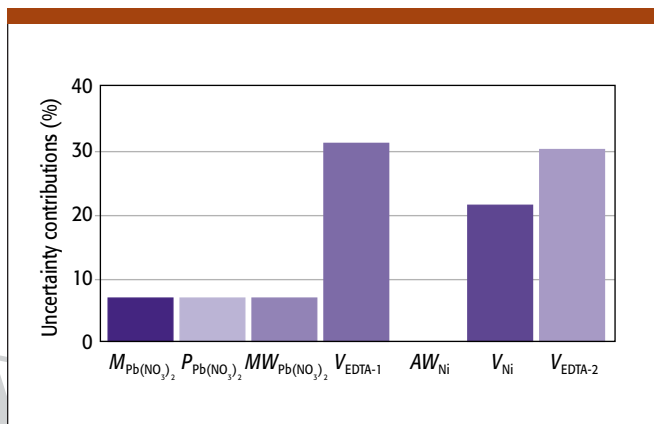


Figure 1. Uncertainty contributions from individual tasks in the volumetric analysis of nickel.

due to a lack of consistency in reporting both the stability and the standard error associated with elemental measurands on a CRM's certificate of analysis. All the measurement uncertainties must be quantified and correctly combined by proper statistical means to arrive at not only a certified value, but also to include the certified value's uncertainty.

References

1. ISO Guide 17025: Certification of Reference Materials, General and Statistical Principles (International Organization for Standardization/IEC, Geneva, Switzerland, 1999).
2. ASTM Guide D6362-98 (ASTM International, West Conshohocken, Pennsylvania, 2001).
3. ISO/REMCO N280 (International Organization for Standardization, Geneva, Switzerland).
4. N. Kocherlakota, R. Obenauf, and R. Thomas, "A Statistical Approach to Reporting Uncertainties on Certified Values of CRMs," *Spectroscopy* 17(9), 20 (2002).
5. S.L.R. Ellison, M. Rosslein, and A. Williams, *Eurachem/CITAC Guide, Second Edition* (Eurachem, 2000).

Table III. Uncertainties of each step of the volumetric analysis of Ni by EDTA titration.

Task	Description	Symbol	Value (v)	Combined uncertainty (u_c)	U_c/V ($\times 10^{-3}$)
1	Weight of Pb(NO ₃) ₂	$MPb(NO_3)_2$	270 mg	0.05102	0.1889
2	Purity of Pb(NO ₃) ₂	$PPb(NO_3)_2$	1	0.0001732	0.1732
3	Molecular weight of Pb(NO ₃) ₂	$MWPb(NO_3)_2$	331.2 g/mol	0.05774	0.1744
4	Volume of EDTA – Pb(NO ₃) ₂	$V_{\text{EDTA-1}}$	32.38 mL	0.02887	0.8915
5	Atomic weight of Ni	AW_{Ni}	58.6934 g/mol	0.0001039	0.00177
6	Ni solution aliquot	V_{Ni}	50 mL	0.03170	0.6339
7	Volume of EDTA – Ni solution	$V_{\text{EDTA-2}}$	33.88 mL	0.02996	0.8844

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