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White Paper

A Statistical Approach to Reporting Uncertainty on Certified Values of Chemical Reference Materials for Trace Metal Analysis

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Abstract

This article discusses an approach by a manufacturer of Calibration Standards and Certified Reference Materials to standardize the reporting of uncertainty associated with certified values quoted on a Certified Reference Material certificate of analysis. The method, based on well-established principles, relies on the authors' belief that to report accurate and reliable certified values, it is essential to determine the value in the final solution by two independent analytical methods - usually one instrumental technique such as inductively coupled plasma-optical emission spectrometry (ICP-OES) or inductively coupled plasma-mass spectrometry (ICP-MS), and one traditional wet chemical technique - both traceable to a standard reference material.

When you purchase a Certified Reference Material (CRM), you expect the certified values to be well defined and controlled; however, this is not always the case. If a number of different certificates of analysis (CoAs) are examined, often inconsistencies exist between the certified values' stated stability (change in value over time) and the uncertainty of its measurement. When you examine different certificates, it can be very confusing because many have their own unique way of stating measurement confidence limits. For example, it is not uncommon to see statements such as:

- Certified value . . . adjusted based on transpiration loss
- Standard concentration of . . .
- Formulated to the concentration of above ± . . . of reported value
- Guaranteed stable and accurate for . . .
- The uncertainty represents the standard deviation of a single measurement

What is the uncertainty associated with a certified value? A CoA doesn't have much value if the uncertainty of the measurement cannot be defined correctly and concisely. One needs to know what is really meant by measurement uncertainty. As a user of analytical instrumentation, it is critical to know the accuracy of the calibration standards you use, to report the confidence limits of your own data. To demonstrate the quality of a certified value (fitness for the purpose), a measure of the confidence must be given. One such measure is the measurement uncertainty.

This article describes an approach used by a manufacturer of Calibration Standards and 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 (1-4). This approach, which will be described in detail, relies on the authors' belief that to report accurate and reliable certified values, it is essential to determine the value in the final solution by two independent analytical methods - usually one instrumental technique like ICP-OES or ICP-MS, and one traditional wet chemical technique - both traceable to a standard reference material.

Table 1. Four Major Steps in the Analysis of Nickel Calibration Standard by ICP-OES.

Task	Procedure Description	Value
1	Sample Concentration Measurement	99.6533 mg/L
2	Sample Dilution	10
3	SRM Value/Dilution	100 mg/L
4	SRM Concentration Measurement	99.5611 mg/L

Table 2. Replicates, Mean and SD of Ni Sample Measurement by ICP-OES.

Measurement	Concentration (mg/L)
1	99.5785
2	99.6365
3	99.7869
4	99.5402
5	99.6477
6	99.8271
7	99.5903
8	99.5002
9	99.7726
Mean	99.6533
SD	0.1164

Defining Measurement Uncertainty

To exemplify how this statistical quantification of measurement uncertainty method works, a 1,000 mg/L nickel ICP-MS certified reference standard was determined by both ICP-OES and ethylenediaminetetraacetic acid (EDTA) titration. From all of the various measurement uncertainties associated with the measurement of the reference standard, it was determined that the CRM had a certified value of 1,001 mg/L ± 2 mg/L. But what does an uncertainty of ± 2 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 basically three steps to defining this uncertainty.

Step One: Determine Type A and Type B Uncertainties. The first step is to determine which types of uncertainty are appropriate for both the ICP-OES and titration methodologies.

Type A: Standard Uncertainty is defined as the standard deviation of the mean of replicate measurements and is represented by the equation:

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

Type B: Standard Uncertainty is based on scientific judgment using all the relevant information available, including previous measurement data, experience, manufacturer's specs, and data provided in calibration reports. This type is more complex to calculate but the following steps are generally used for determining Type B uncertainty:

- Convert the listed uncertainty to a standard uncertainty by dividing the listed uncertainty by the stated multiplier (weight) described in the next step

- Weight the specification value based on the assumed distribution (u_i = value/weight). The three common distributions used (5) are

  1) Normal distribution: Convert a listed uncertainty having a stated level of confidence of 95% to a standard uncertainty by using 1.96 as a multiplier; an example would be uncertainty listed on a balance certificate.

  2) Rectangular distribution: When a certificate or other specification gives limits without specifying a level of confidence, use a multiplier of $3^{1/2}$; an example is the uncertainty listed on a CRM or standard reference material (SRM).

  3) Triangular distribution: When the distribution is symmetric. Where values close to the target value are more likely than near the boundaries, use the multiplier $6^{1/2}$; an example would be the uncertainty associated with volumetric glassware.

Step Two: Combine Type A and Type B Uncertainties. For this step, we use two types of statistical models (5):

- For models involving only a sum or difference of quantities of the type $y = c(p + q + r)$, where c is a constant and the result y is a function of the parameters p, q, and r, then the combined standard uncertainty $u_c(y)$ is given by:

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

- For models involving only a product or quotient of the type $y = c(pqr)$ or $y = c(pq/r)$, the combined standard uncertainty $u_c(y)$ is given by:

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

Step Three: Calculate the expanded uncertainty. The expanded uncertainty (U) is represented by $U = ku_c$, where u_c is the combined standard uncertainty from step two and k = coverage factor. U defines 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 to be associated with the interval defined by $U = ku_c$. Typically, a coverage factor of 2 is used where the distributions concerned are normal. A coverage factor of 2 ($U = 2u_c$) gives an interval having a level of confidence of approximately 95% (k = 1.96 at 95% confidence level). However, it is recommended that the value of k be set equal to the two-tailed value of Student's t for the number of degrees of freedom when these are less than six. A coverage factor of 3 ($U = 3u_c$) defines an interval having a level of confidence greater than 99% (5).

Table 3. Uncertainty of Measuring Devices Used to Dilute the Sample.

Measuring Device and Volume (V)	Standard Uncertainty	Temperature Uncertainty (U [temp])	Volume Uncertainty (u_{vi})	Type	RSD of Uncertainty (u_{vi}/V)
Pipette (10 mL)	$0.02/6^{1/2} = 0.008165$	0.00485	$\{(0.008165^2 + 0.00485^2)\}^{1/2} = 0.009497$	B	$0.009497/10 = 0.0009497$
Volumetric Flask (100 mL)	$0.08/6^{1/2} = 0.03266$	0.0485	$\{(0.03266^2 + 0.0485^2)\}^{1/2} = 0.05847$	B	$0.05847/100 = 0.0005847$

Determination of Uncertainties Associated with a 1,000 mg/L Nickel CRM

To show how this works in practice, let's certify the 1,000 mg/L nickel solution by using two separate analytical methods to determine the nickel content - ICP-OES and titration with EDTA. This mirrors the methodology followed by the authors at SPEX CertiPrep; namely, certification by two independent methods, one spectroscopic and one traditional, wet chemical method.

The CRM was initially prepared by weighing 1.000 g of 99.9999% high purity Ni powder (balance was calibrated using NIST weights #32856 and 32867), dissolving in a few milliliters of concentrated nitric acid, and diluting to 1,000 mL with 2% nitric acid.

ICP-OES methodology. The analytical parameters and conditions used for the analysis will not be presented, except to say that the model chosen for quantitation was that of a traditional single-point calibration with the intercept passing through zero: $y=mx + c$, where y = analyte signal, x = analyte concentration, m = slope of calibration curve, and c = intercept (in this case $c = 0$) (6). A 10-fold dilution was made of the sample and compared against NIST SRM 3136, containing 10.00 mg/g Ni. Scandium was used as an internal standard.

So from this we can say the analyte concentration $x = y/m$.

$$\text{Analyte concentration} = \frac{\text{sample signal 3} \quad \text{SRM value 3} \quad \text{sample dilution}}{\text{SRM signal}}$$

Table 1 represents the analytical data generated from this method. (Where possible, four significant figures were used throughout all calculation, however, the final uncertainty value for each analytical method was rounded to three significant figures.)

If we insert the data into this formula, the concentration (C_{Ni}) for this particular batch of nickel is:

$$C_{Ni} = \frac{99.6533 \times 100 \times 10}{99.5611} = 1000.926 \text{ mg/L Ni}$$

Let us now go through the procedure of calculating the uncertainty associated with this value, based on the previous equations derived in steps 1-3. First of all, we have to calculate the uncertainty of each separate task outlined in Table 1 to get the uncertainty of the total analysis. By calculating the uncertainty of each one, adding them together, and then multiplying the combined uncertainty by the coverage factor for the appropriate confidence level, we will arrive at the standard uncertainty (6) for the Ni value on the certificate of analysis.

Task 1: Uncertainty of Sample Measurement by ICP-OES

For this analysis, the Ni sample was measured nine times (each measurement being five replicates) against a 100-fold dilution of the NIST SRM 3136. The individual, mean and standard deviation of the nine measurements are shown in Table 2.

This falls into a Type A standard uncertainty example, so we can then calculate the uncertainty of the measurement of the sample concentration (u_{sample}) from the following equation:

$$u_{sample} = s/n^{1/2}$$

$$u_{sample} = 0.1164/9^{1/2} = 0.03880 \text{ mg/L}$$

Task 2: Uncertainty of Sample Dilution

When samples are diluted using conventional techniques, three important criteria need to be considered. There are uncertainties associated with the pipetting, the volumetric flask, and the effect of temperature on the overall volume. Each of these has to be taken into consideration to determine the uncertainty involved with sample dilution. Table 3 shows how the uncertainty of each measuring device is calculated, taking into consideration the listed uncertainty of the device and variations in volume due to lack of temperature control. In this study, the listed uncertainty of a measuring device is taken from its certificate of calibration and the temperature uncertainty is based on a combination of knowing the coefficient of volume expansion for water and the difference between the room temperature during the experiment and the calibrated temperature of the measuring device. (For a temperature variation of ± 4 °C, the coefficient of volume expansion for water equals $4 \times 2.1 \times 10^{-4}$ °C^{-1}/mL. For a 10 mL pipette, the uncertainty due to temperature variation is $10 \times 4 \times 2.1 \times 10^{-4}/3^{1/2} = 0.0485$.)

We can then calculate the uncertainty of the dilution factor $f_{10} = V_{100}/V_{10}$, where V_{100} is the final volume and V_{10} is the initial volume - using the following equation (7):

$$\text{Uncertainty} \quad \frac{u(f_{10})}{10} = \left\{ \left(\frac{u(V_{100})}{100} \right)^2 + \left(\frac{u(V_{10})}{10} \right)^2 \right\}^{1/2}$$

$$\frac{u(f_{10})}{10} = \left[(0.0005847)^2 + (0.0009497)^2 \right]^{1/2}$$

$$u(f_{10}) = 0.001115 \times 10 = 0.01115$$

Table 4. Uncertainty Associated with Preparation of SRM Calibration Standard.

Measuring Device	Value	Standard Uncertainty	*U* (temp)	Combined Uncertainty (u_{vi})	Type	RSD of uncertainty (u_{vi}/V)
Balance (5 g)	5	0.0001/1.96 = 0.00005102	N/A	0.00005102	B	0.00005102/5 = 0.0000102
Volumetric Flask (500 mL)	500	$0.20/(6)^{1/2} = 0.08165$	0.2425	$(0.8165^2 + 0.2425^2)1/2$ = 0.2559	B	0.2559/500 = 0.0005117

Table 5. Combination of Uncertainties Associated with SRM Dilution and Concentration Value.

Description	Value	Standard Uncertainty	*U* (temp)	Combined Uncertainty	Type (U_{vi})	RSD of uncertainty (u_{vi}/V)
Dilution (100)	100	N/A	N/A	0.05118	B	0.05118/100 = 0.000518
Concentration of SRM (100 mg/L)	100	$0.3(3)^{1/2} = 0.1732$	N/A	N/A	B	0.1732/100 = 0.001732

Table 6. Replicates, Mean, and SD of Ni NIST SRM Measurement by ICP-OES.

Measurement	Concentration (mg/L)
1	99.5005
2	99.6409
3	99.6281
4	99.4802
5	99.6104
6	99.5661
7	99.4597
8	99.6021
9	99.5620
Mean	99.5611
SD	0.06660

Task 3: Uncertainty of SRM Value

To prepare the SRM used for calibration, 5.000 g of NIST SRM 3136 were weighed and diluted to 500 mL in a volumetric flask. The certified value for this SRM is 10.00 ± 0.03 mg/g Ni, so the final concentration of nickel in the calibration standard is 100 µg/mL Ni. There are two aspects to the uncertainty associated with this value - the balance used to weigh the SRM and the volumetric flask used for the dilution. By the same process we used to calculate the uncertainty of the sample dilution, we can measure the uncertainty associated with the weighing and dilution of the calibration standard. First we have to know the uncertainty associated with the balance and the volumetric flask. This is shown in Table 4.

The uncertainty of the dilution factor $f_{100} = V_{500}/V_5 = 100$ where V_{500} is the final volume and V_5 is the initial weight - is then calculated, using the following equation:

$$\text{Uncertainty} \quad \frac{u(f_{100})}{100} = \left\{ \left(\frac{u(V_{500})}{500} \right)^2 + \left(\frac{u(V_5)}{5} \right)^2 \right\}^{1/2}$$

$$\frac{u(f_{100})}{100} = \left[(0.0005117)^2 + (0.00001020)^2 \right]^{1/2}$$

$$\frac{u(f_{100})}{100} = \left[26.1941 \times 10^{-8} \right]^{1/2}$$

$$\frac{u(f_{100})}{100} = 5\ 0.000518$$

$$u(f_{100}) = 0.0005118 \times 100 = 0.0518$$

We can then combine the dilution step with the uncertainty of the actual SRM value as shown in Table 5. Therefore, using the same equation as in the previous task, the total uncertainty associated with the SRM value after dilution is:

$$U(\text{SRM})_{\text{value}} = [(0.001732)^2 + (0.000518)^2]^{1/2}$$

Task 4. Uncertainty Associated with SRM Measurement by ICP-OES

Table 6 shows the individual, mean and standard deviation values for nine measurements (each being five replicates) of the NIST SRM 3116 using a single-point calibration of the SRM diluted 100 times. Scandium was used as the internal standard.

Similar to the measurement of the sample signal by ICP-OES, this uncertainty falls into the Type A category, so we can then calculate the uncertainty of the measurement of the sample concentration (u_{SRM}) from the equation $u_{SRM} = s/n^{1/2}$:

$$u_{SRM} = 0.06660/9^{1/2} = 0.0222 \text{ mg/L}$$

Table 7. Summary of the Uncertainties Associated with Preparation and Measurement of Sample and SRM by ICP-OES.

Task	Description	Value (*V*)	*Uncertainty* (u_c)	u_c/V	$(u_c/V)^2$
1	Sample ICP-OES Measurement	99.6533 mg	0.0388	0.0003893	0.1522×10^{-6}
2	Sample Dilution	10	0.01115	0.001115	1.2438×10^{-6}
3	SRM Value/Dilution	100 mg	0.001806	0.00001806	3.2622×10^{-6}
4	SRM ICP-OES Measurement	99.5611 mg	0.0222	0.000223	0.04972×10^{-6}

We can now combine the individual uncertainty values derived from tasks 1-4 with the nickel concentration of 1000.93 mg/L by ICP-OES, to calculate the total and expanded uncertainties. The individual standard uncertainties are summarized in Table 7.

$$u_c = C_{Ni} [\Sigma (u_c/V)^2]^{1/2}$$

$$u_c = 1000.93 [(0.1522 + 1.2438 + 0.0003262 + 0.04972) \times 10^{-6}]^{1/2}$$

$$u_c = 1.2033 \text{ mg/L}$$

The expanded uncertainty $U(C_{Ni})$ is then obtained by multiplying the standard combined uncertainty by two, which is the coverage factor *k* for a 95% confidence interval.

$$U(C_{Ni}) = k \times u_c$$

$$U(C_{Ni}) = 2 \times 1.2033 = 2.4066$$

The ICP-OES certified value for Ni in this CRM is therefore:

$$1000.926 \text{ mg/L} \pm 2.407 \text{ mg/L}$$

Figure 1, therefore, shows the percentage of contributions from the individual tasks of the ICP-OES methodology outlined in Table 7.

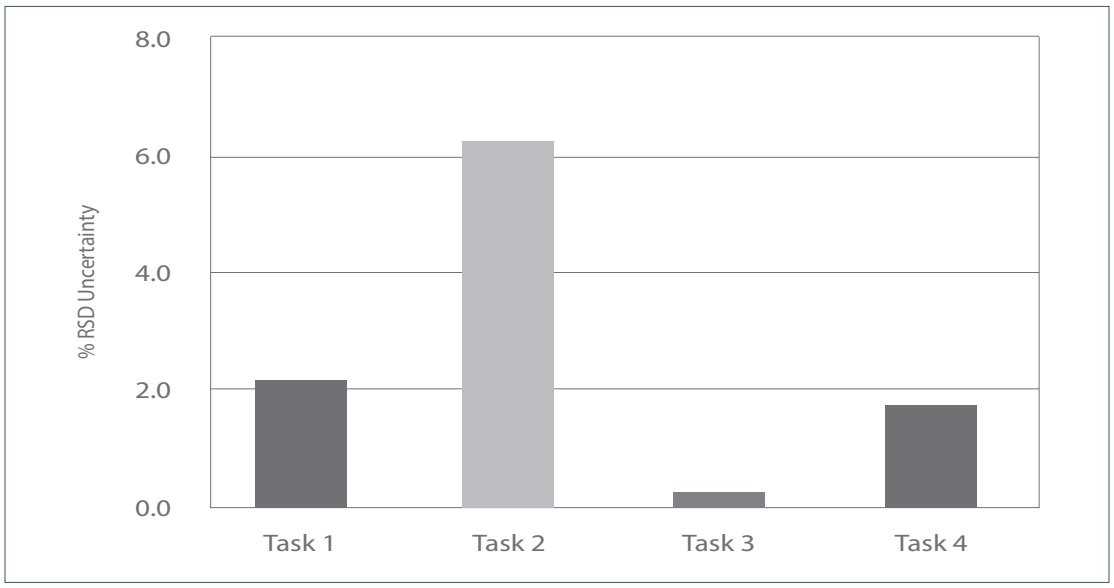

Figure 1. Uncertainty Contributions from Individual Tasks of the ICP-OES Analysis.

The next step is to use exactly the same procedure for the determination of nickel by EDTA titration. This uncertainty value is then combined with the ICP-OES determination uncertainty, so the value on the certificate of analysis is the mean standard measurement uncertainty of two separate analytical methods.

Calculation of Uncertainty for the Wet Assay Determination of 1,000 mg/L Nickel Solution by EDTA Titration

For this method of assay, the EDTA was first standardized with NIST SRM $Pb(NO_3)_2$ 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. Equations used:

$$\text{Molarity of EDTA } (M_{EDTA}) = \frac{\text{Weight of } Pb(NO_3)_2 \text{ x purity of } Pb(NO_3)_2}{\text{MW of } Pb(NO_3)_2 \text{ x volume of EDTA used}}$$

$$\text{Concentration of } Ni(C_{Ni}) = \frac{\text{Volume EDTA x molarity EDTA x atomic weight of Ni}}{\text{Volume of Ni aliquot}}$$

Combining 1 and 2 we get:

$$C_{Ni} = \frac{\text{Weight of } Pb(NO_3)_2 \text{ x purity of } Pb(NO_3)_2 \text{ x volume of EDTA(Ni) x atomic weight of Ni}}{\text{MW of } Pb(NO_3)_2 \text{ x volume of EDTA } Pb(NO_3)_2 \text{ x volume of Ni aliquot}}$$

Table 8 represents the analytical data generated from this method.

Table 8. 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

If we plug the data from Table 8 into equation 3, 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 now go through the procedure of calculating the uncertainties associated with this value, analogous to the approach previously discussed in the ICP-OES method.

Task 1: Uncertainty Associated with Weighing the Lead Nitrate. The uncertainty of the electronic balance was listed as ± 0.1 mg. Therefore, the uncertainty as a standard deviation at the 95% confidence level is represented by:

$$0.1/1.96 = 0.05102 \text{ mg}$$

Because repeated weighing (n = 5) of the 1,000 mg NIST weight gave no error, this uncertainty component can be considered negligible. Therefore:

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

Task 2: Uncertainty Associated with Purity of Lead Nitrate (5). The purity of $Pb(NO_3)_2$, as given in the supplier's certificate, is 100 ± 0.03%. The purity, $PPb(NO_3)_2$, can therefore be represented by 1.0 ± 0.0003. Applying a rectangular distribution, the standard uncertainty for the purity component is:

$$u\left(Pb(NO_3)_2 \right) = \frac{0.03/100}{3^{1/2}} = \frac{0.0003}{1.732} = 0.0001732$$

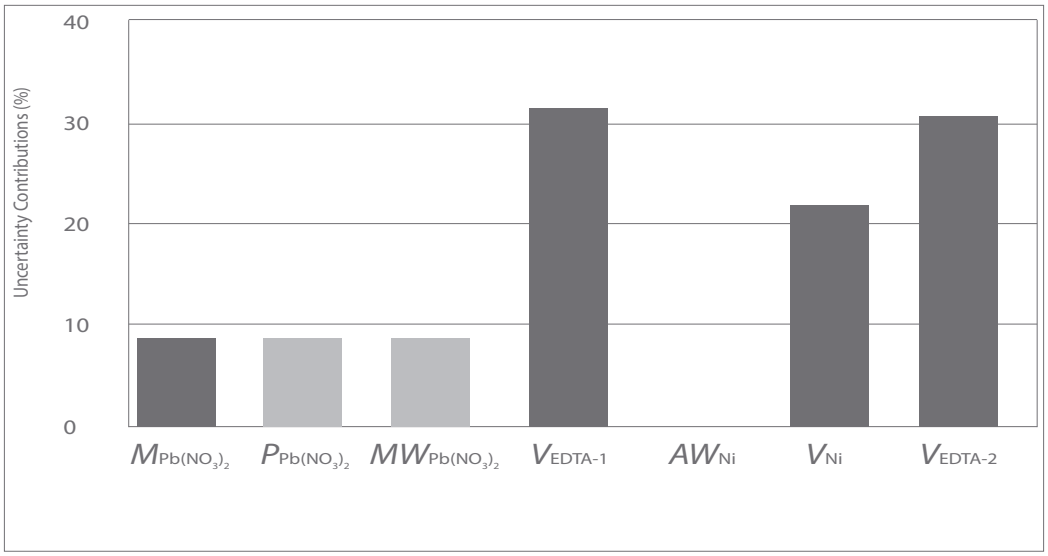

Figure 2. Uncertainty of Contributions from Individual Tasks in the Volumetric Analysis of Nickel.

Task 3. Uncertainties Associated with Molecular Weight of Lead Nitrate (5). The uncertainty in the molecular weight can be obtained by combining the uncertainties in the atomic weights of its constituent elements (from the latest IUPAC 1997 table). For each element, the standard uncertainty is determined by assuming the IUPAC-quoted uncertainty forming the bounds of a rectangular distribution. The corresponding standard uncertainty is therefore obtained by dividing these values by $3^{1/2}$. This is shown in Table 9.

Table 9. Standard Uncertainty of Constituent Elements of $Pb(NO_3)_2$ 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 x 0.0003	0.00052

$$u\,(F\mathrm{Pb(NO_3)_2}) = \{\,(0.0577)^2 + (0.00004)^2 + (0.00052)^2\,\}^{1/2}$$

$$u\,(F\mathrm{Pb(NO_3)_2}) = \{\,(0.0033) + (1.6 \times 10^{-9}) + (2.7 \times 10^{-7})\,\}^{1/2}$$

$$u\,(F\mathrm{Pb(NO_3)_2}) = 0.0577 \text{ g/mol}$$

Task 4: Uncertainty in Volume of EDTA Used in Lead Nitrate Titration. The EDTA titration was carried out five times. The replicates, mean and standard deviation of the values are shown in Table 10.

The uncertainty of this volumetric analysis 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 uncertainty in the internal volume of the burette if derived from data on the certificate and the temperature difference. If we apply a triangular distribution, the certificate uncertainty is 0.05/$6^{1/2}$ = 0.0204 mL and the uncertainty due to temperature is 32.38 x 4 x 2.1 x 10^{-4}/$3^{1/2}$ = 0.0157 mL. The combined uncertainty is represented by:

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

$$u(V_{EDTA\text{-}1}) = 0.02887 \text{ mL}$$

Table 10. Replicates, Mean and SD of $Pb(NO_3)_2$ Titration with EDTA.

Measurement	Volume EDTA (mL)
1	32.42
2	32.36
3	32.40
4	32.35
5	32.37
Mean	32.38
SD	0.02916

Task 5: Uncertainties Associated with the Atomic Weight of Nickel. From the IUPAC table, the listed uncertainty for the atomic weight of nickel is 58.6934 ± 0.00018. If we apply a rectangular distribution for a Type B error, we get:

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

Task 6: Volume Uncertainties Associated with Pipetting a 50 mL Aliquot of Sample. The stated internal volume of the pipette, as given by the manufacturer, is 50 mL ± 0.05 mL. Applying a triangular distribution for volumetric glassware, the standard uncertainty is $0.05/6^{1/2} = 0.02041$ mL. In addition, the uncertainty due to the room temperature being different from the calibrated temperature of the pipette is $50 \times 4 \times 2.1 \times 10^{-4} = 0.02425$ mL (based on a temperature variation of ± 4 °C and using the coefficient of volume expansion for water = 2.1×10^{-4} °C^{-1}). If we combine both uncertainties, the error associated with the 50 mL aliquot of Ni is:

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

Task 7: Uncertainty in Volume of EDTA Used in Nickel Titration. The EDTA titration was carried out in triplicate. The replicates, mean and standard deviation of the values are shown in Table 11.

Table 11. Replicates, Mean and SD of Ni Titration with EDTA.

Measurement	Volume EDTA (mL)
1	33.85
2	33.89
3	33.90
Mean	33.88
SD	0.02517

The uncertainty of the nickel volumetric analysis is a combination of the uncertainties of the titration in replicates, plus the uncertainty in the internal volume of the burette. Using exactly the same assumptions we used in task four, uncertainty of the titration is represented by $s/n^{1/2}$ = 0.02517/$3^{1/2}$ = 0.01453. The uncertainty in the internal volume of the burette is derived from data on the certificate and the temperature difference. If we apply a triangular distribution, the certificate uncertainty is 0.05/$6^{1/2}$ = 0.0204 mL and the uncertainty due to temperature is 33.88 x 4 x 2.1 x 10^{-4}/$3^{1/2}$ = 0.0164 mL. The combined uncertainty is represented by:

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

$$u(V_{EDTA\text{-}2}) = 0.02996 \text{ mL}$$

We can now calculate the total and the expanded certainty associated with the analysis of nickel by EDTA titration. The individual values from tasks 1-7 are summarized in Table 12.

Table 12. 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) x $(10)^{-3}$
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 - $Pb(NO_3)_2$	$V_{EDTA\text{-}1}$	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	$V_{EDTA\text{-}2}$	33.88 mL	0.02996	0.8844

First, the total uncertainty is calculated from the sum of the individual uncertainties using the following equation:

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

Applying the values from Table 12, we get

$$u_c = 1001.188$$

$$[(0.1889 \times 10^{-3})^2 + (0.1732 \times 10^{-3})^2 + (0.1744 \times 10^{-3})^2 + (0.8915 \times 10^{-3})^2 + (0.00177 \times 10^{-3})^2 + (0.6339 \times 10^{-3})^2 + (0.8844 \times 10^{-3})^2]^{1/2}$$

$$u_c = 1001.188\ (2.0750 \times 10^{-6})^{1/2}$$

$$u_c = 1001.188 \times 0.001441$$

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

The expanded uncertainty $U(C_{Ni})$ for the EDTA titration is then 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 (5,8).

$$v_{eff} = u_c^4/\Sigma\{V_i^4 u_i^4/v_i\}$$

v_{eff} = Effective degrees of freedom obtained by combining the degrees of freedom of individual components

u_c = Total combined uncertainty associated with EDTA titration of 1.4422 mg/L

V_i = Value of individual component or task

u_i = Individual combined uncertainty values for each task

v_i = Degrees of freedom associated with each individual step (n - 1)

Applying this equation to the data in Table 12, we get the results shown in Table 13.

$$v_{eff} = 4.326/0.7217 = 6$$

Table 13. Summary of Standard Uncertainty Components and their Degrees of Freedom.

Symbol	Value (V_i)	Combined Uncertainty (u_c)	$v_i = (n - 1)$	$v_i^4\, u_c^4/(n - 1)$	u_c^4
$MPb(NO_3)_2$	270 mg	0.05102	∞	0	_
$PPb(NO_3)_2$	1	0.0001732	∞	0	_
$MWPb(NO_3)_2$	331.2 g/mol	0.05774	∞	0	_
V_{EDTA-1}	32.38 mL	0.02887	4	0.1909	_
AW_{Ni}	58.6934 g/mol	0.0001039	∞	0	_
V_{Ni}	50 mL	0.03170	∞	0	_
V_{EDTA-2}	33.88 mL	0.02996	2	0.5308	_
Total				0.7217	$1.4422^4 = 4.326$

Note: For Type B uncertainties, when lower and upper limits are set in such a way that the probability of the quantity in question lying outside these limits is extremely small. In such cases, the degrees of freedom may be taken to be $\nu_i \rightarrow \infty$ (8).

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

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

The individual uncertainty contributions in the volumetric analysis of Ni by titration with EDTA are represented in Figure 2.

The final step is to determine whether it is valid to average both the ICP-OES and EDTA titration values for Ni. We can do this by comparing the "t-calculated" with "t-critical" as follows (5).

The standard deviations are pooled to give a combined standard deviation (s_c) and then used to calculate $t_{calculated}$ according to the following equations:

$$s_c = \{[(s_1)^2 \times v_1 + (s_2)^2 \times v_2]/v\}^{1/2}$$

$$t_{calculated} = (x1 - x2(/s_c(1/n_1 + 1/n_2)^{1/2}$$

for degrees of freedom $df = v = v_1 + v_2$

Where x_1 = wet assay mean, x_2 = ICP-OES mean, s_1 = standard deviation for wet assay values, s_2 = standard deviation for ICP-OES values, $v_1 = (n_1 - 1)$ where n_1 is the number of repetitions for wet assay determination, and $v_2 = (n_2 - 1)$ where n_2 is the number of repetitions for ICP-OES.

From the *National Institute of Standards and Technology Technical Note 1297* (8) and the *Guide to the Expression of Uncertainty in Measurement* (9): $t_{critical}$ for $v = v_1(\text{eff}) + v_2$ {(6-1) + (9-1) = 13 degrees of freedom} is 2.16 at the 95% confidence level, from the *t*-distribution table.

If we apply this to both methods, we can determine that $t_{calculated} = 0.496$, which is significantly lower than $t_{critical} = 2.16$, the accepted statistical validity boundary of averaging results from two different methods. This means that the difference between the two methods is insignificant. It is therefore valid to average both results and report the mean value for the nickel concentration. The final uncertainty value on the nickel CRM certificate of analysis is obtained by combining the two uncertainties in quadrature and dividing the result by 2, as shown here:

ICP-OES Determination = 1000.926 ± 2.407 mg/L

EDTA Titration Determination = 1001.188 ± 3.533 mg/L

$$u_c = \{(2.407)^2 + (3.533)^2\}^{1/2}/2 = 2.137$$

The certified value for Ni would therefore be = 1001 ± 2 mg/L

Summary

This study has been the result of detailed research into developing a standard method for the reporting of certified values on CRMs by the authors and others at SPEX CertiPrep. It was undertaken due to a lack of consistency in reporting both the stability and the standard error associated with elemental measurands on a CRMs certificate of analysis. The method outlined in this study relies on the authors' belief that to report accurate and reliable certified values, it is essential to determine the value in the final solution by two independent analytical methods - both traceable to a standard reference material. Furthermore, 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. The supporting data has shown that this approach has scientific merit.

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