Use and Handling of Uncertainties in Determining Metal Purity by Difference

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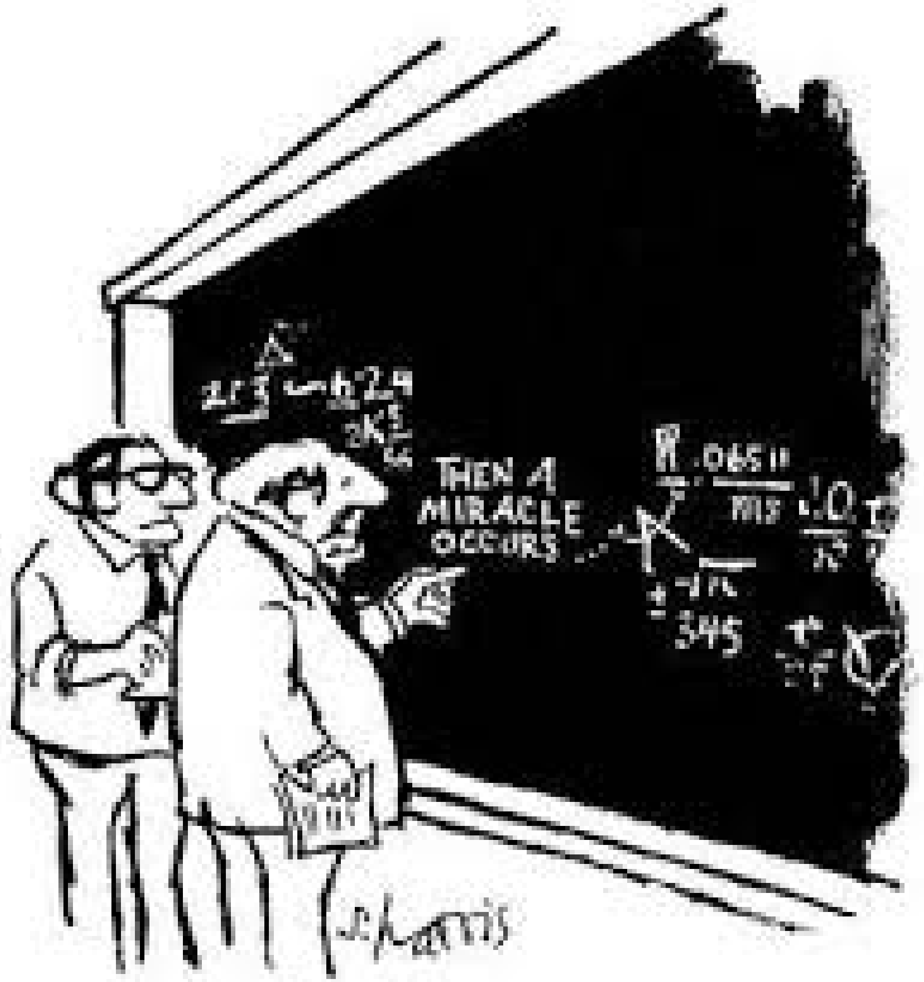


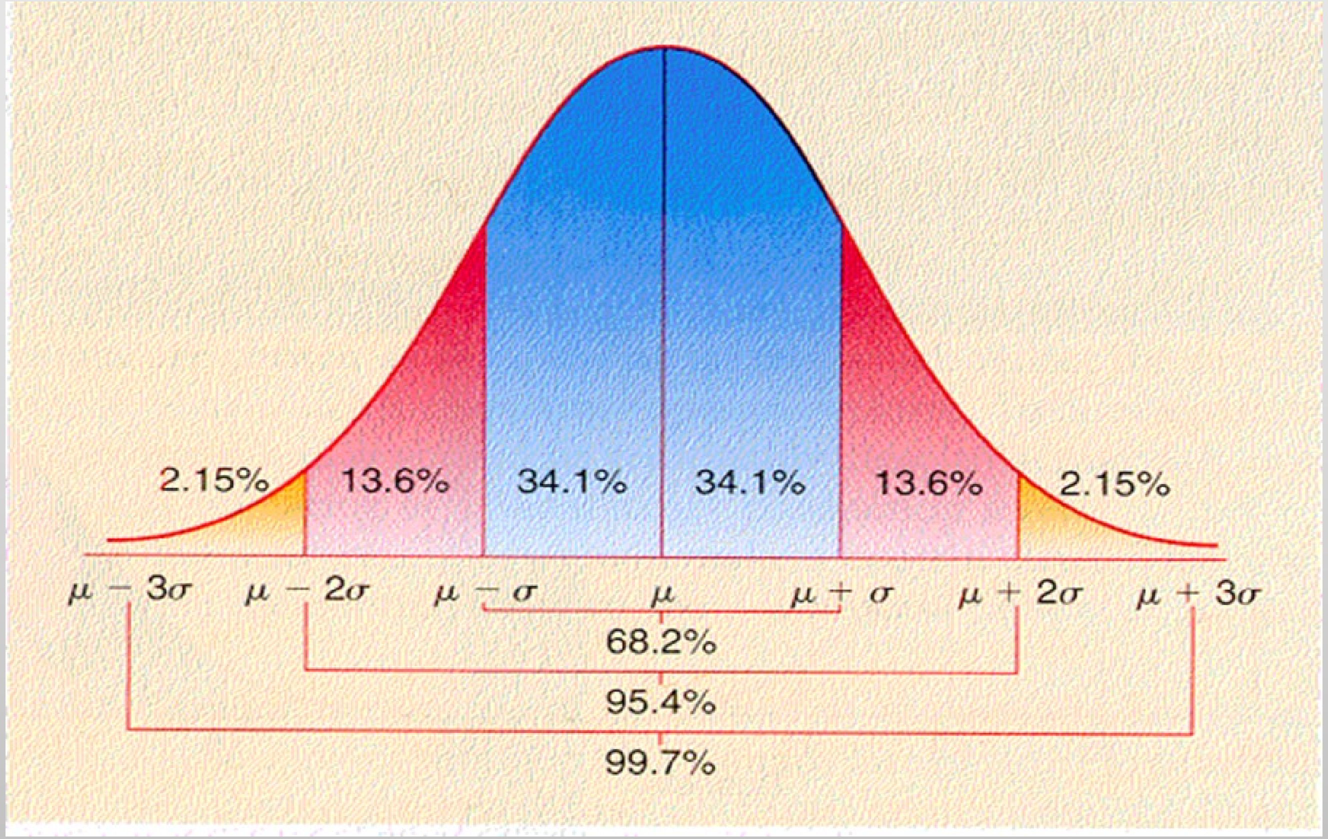
"I think you should be more explicit here in step two."

Metal Purity by Difference

- Determine the concentration of ‘x’ number of elements
- Possible Methods:
  - Solution ICP-OES
  - Spark OES
  - GD-MS
- Sum element concentrations and sum uncertainties
- Subtract the sum of element concentrations from 100% for purity

Uncertainty

A parameter associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand*



*EURACHEM/CITAC Guide Quantifying Uncertainty in Analytical Measurement, 3rd ed, 2012

Combining Uncertainties

- Uncertainty expressed as standard deviation
- Cannot directly add standard deviations
- Can combine variances = (Standard Deviation)^2
- Combine then take square root for combined uncertainty

$$Uncert = \sqrt{\Sigma(variances)} = \sqrt{\Sigma(std\_dev)^2}$$

Simple Example of Combining Uncertainties

Determination of Ag, Cu, Fe, Ni, Pd in Gold, n= 4 replicates

Element	Concentration, ppm	Std Dev, ppm	(Std Dev)^2, ppm^2
Ag	21.3	± 0.7	0.49
Cu	8.4	± 0.4	0.16
Fe	-0.1	± 0.2	0.04
Ni	0.6	± 0.1	0.01
Pd	5.6	± 0.3	0.09
Sum	**35.8**		**0.79**

$$Uncert = \sqrt{\Sigma(variances)} = \sqrt{\Sigma(std\_dev)^2} = \sqrt{0.79\,ppm^2} = 0.89\,ppm$$

$$Au\% = 100 - \left(\frac{35.8\,ppm}{10000\,ppm\%^{-1}}\right) = 99.99642\% \pm 0.00009\%$$

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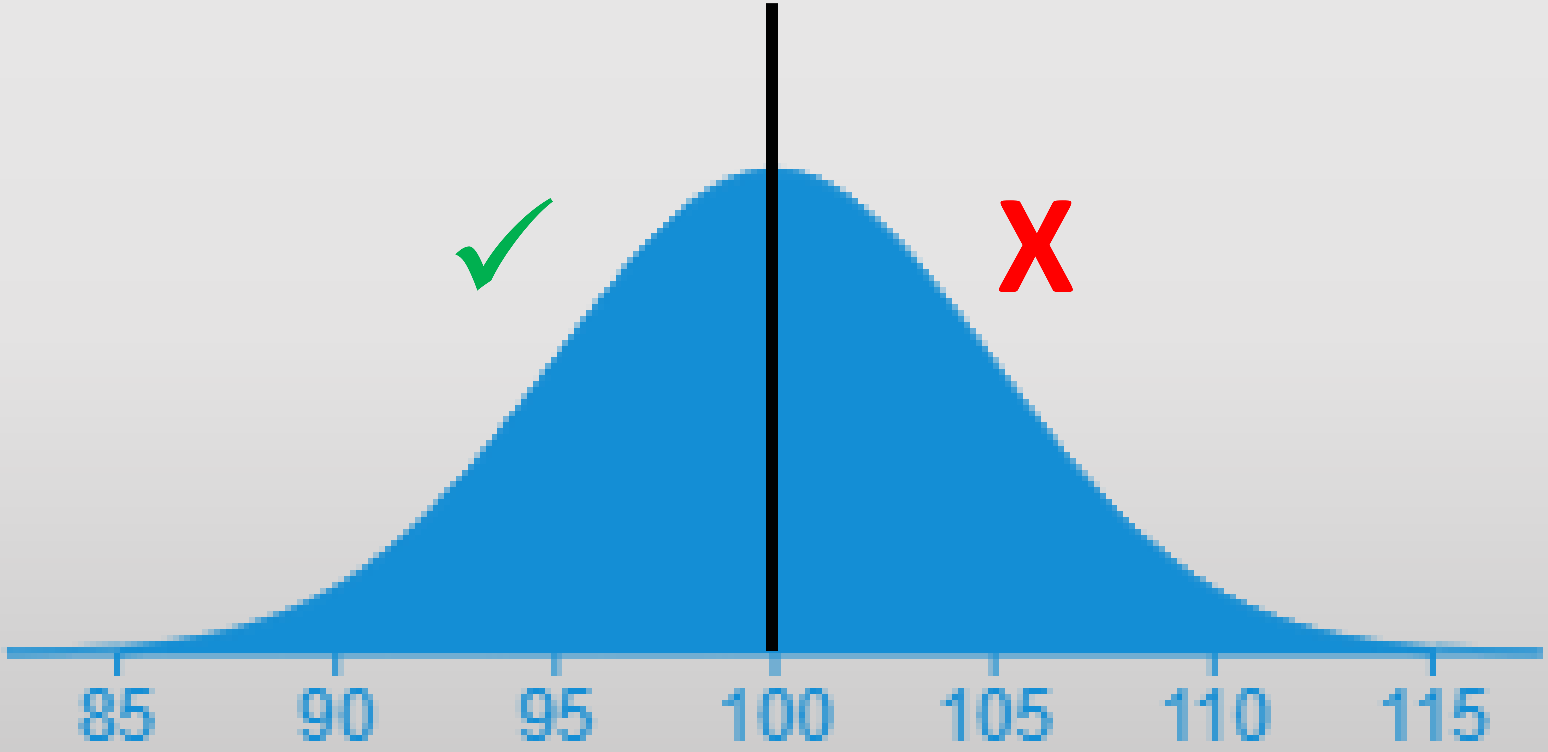
At 99.99% (100 ppm impurity elements)

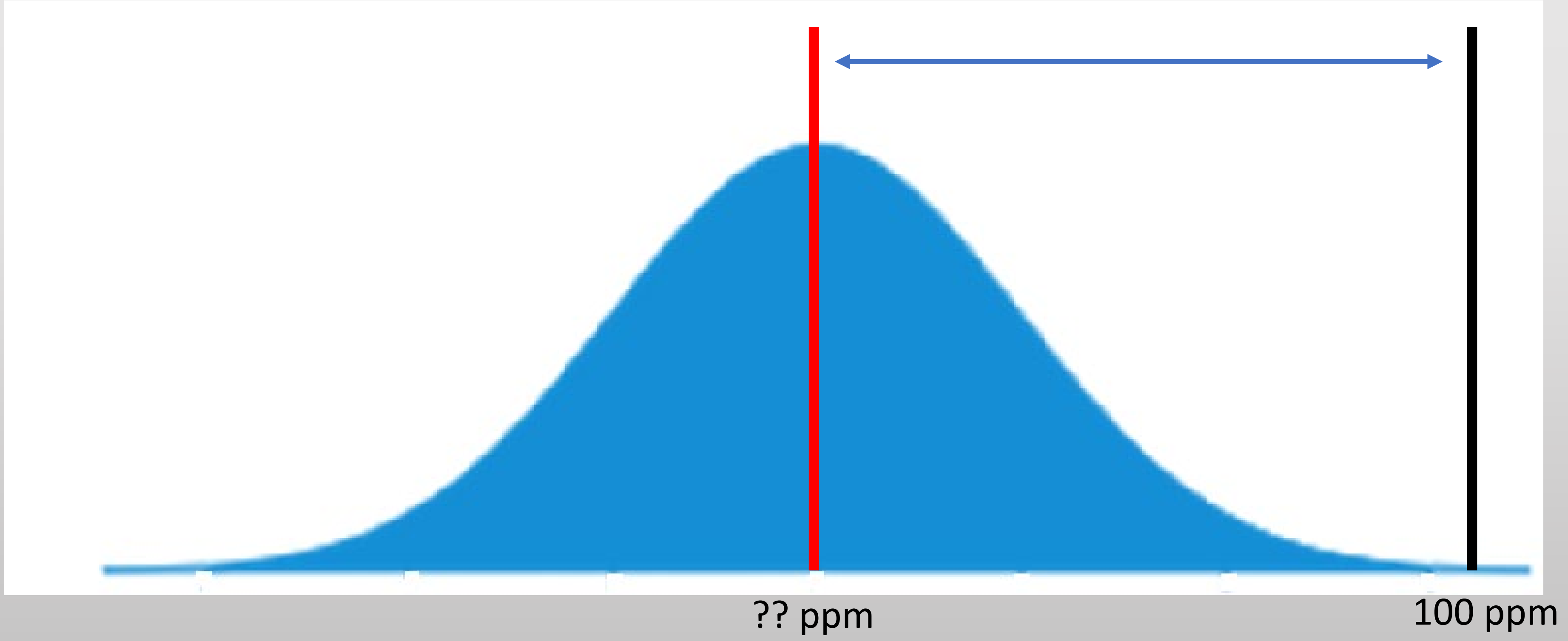
If assayed 50 times – 25 OK & 25 over limit



Sum of Determined Impurity Elements, ppm

Where to set an Internal Limit for Impurities?

Internal Limit Impurities



Information to Set Internal Limit for Impurities

- Sampling Uncertainty
  - Calculated from duplicate sample assays
- Measurement Uncertainty
- 99% Confidence Interval (CI)
  - 3(Combined Uncert) @ 99% CI
- Bias
  - Calculated from analysing Reference Materials
- Added Protection (extra buffer)

Sampling Uncertainty ($\mu_{sampling}$)
Difference between duplicate samples

- Take difference between sample duplicates (n>20)
- Calculate standard deviation of the differences (s_{Diff})

$$\mu_{Sampling} = \frac{s_{Diff}}{\sqrt{n}}$$

Example:
Calculating Sampling Uncertainty (34 replicates)

Sum of Impurities in Gold, ppm

Sample	Average Dip A n=2	Average Dip B n=2	Difference, ppm
101	82.0	85.0	-3.0
102	71.5	69.0	2.5
103	58.0	58.0	0.0
↓	↓	↓	↓
134	40.0	38.0	2.0

Standard Deviation of Difference = 1.4 ppm

$$\mu_{Sampling} = \frac{s_{Diff}}{\sqrt{n}} = \frac{1.4\,ppm}{\sqrt{34}} = 0.25\,ppm$$

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Overall Measurement Uncertainty (μ_M)

Use Au purity values & convert to ppm; Use QC standard

Combine

- Sampling uncertainty; $\mu_{Sampling}$
- Measurement uncertainty of a typical sample (n=4); μ_m
  - Sample homogeneity
- Short Term QC uncertainty – use QC data (n=6); μ_{STQC}
- Long Term QC uncertainty – use QC data (n >30); μ_{LTQC}

$$\mu_M = \sqrt{\mu_{Sampling}^2 + \mu_m^2 + \mu_{STQC}^2 - \mu_{LTQC}^2}$$

Bias and Safety Factor

- Bias
  - Estimation of Inaccuracy
  - Element Bias = Determined in Reference Material – Certificate Value
  - Sum Element Biases

- Safety Factor (Optional) extra “x” ppm
  - Coverage for:
    - Elements not determined – just in case
    - Comfort/Peace of Mind

Combining Factors
Example Calculation

Factor	Estimate, ppm	Coverage Factor = 3	Totals, ppm
Overall Measurement Uncertainty	3.5	10.5	10.5
Bias	2.0		2.0
Safety Factor	3.0		3.0
Combined Limit			**15.5**

Combined Factors estimate 15.5ppm → Maximum Limit for Impurities = 84.5 ppm

Combined Factors estimate 15.5ppm → Minimum Reporting Limit for Gold = 99.99155%

Concluding Remarks

- Suggested way to estimate minimum reporting limit for high purity Au
- Can use collected data to assess
  - Sampling Uncertainty
  - Overall Method Uncertainty
  - Bias
- Applicable to:
  - high purity Ag and other precious metals
  - 99.5% - 99.999%
- Not all uncertainties discussed
  - i.e., calibration uncertainty

Acknowledgements

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