Trace Element Analysis of Geological, Biological & Environmental Materials By Neutron Activation Analysis: An Exposure

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Session 3

- **Uncertainties in analytical measurements**
- **Sampling and Instrumental Neutron Activation Analysis sample preparation**
- **Hands on Experience with Sample Preparation in Laboratory.**

Uncertainties in analytical measurements

- Random and Systematic Errors
- Precision and Accuracy of an analytical measurement

Uncertainties in analytical measurements
- Random Errors

Random Error - Precision of an analysis:

Precision of an analytical measurement means – repeatability or reproducibility of the results of an experiment performed several times under the same conditions. The variation of random error in an analysis usually given by a normal distribution. Precision is measured by the standard deviation of replicate analysis.

Uncertainties in analytical measurements

- Random Errors– Precision – Standard Deviation …

- **The smaller the standard deviation, the more precise the analysis.**

Standard Deviation s

$$= \mathrm{SQRT}\left(\sum_{i=1}^{n} (X_i - \mu)^2 \,/\, (n-1) \right)$$

X_i = each individual reading in of n observations of the same variable.

μ = mean of the n observations.

Precision – Standard Deviation…

The standard deviation of replicate analysis of n readings

$$S = SQRT\left(\left(\sum_{i=1}^{n} (X_i - X_{Mean})^2 \right) / (n-1) \right)$$

Estimation of analytical precision:

In practical analytical terms, the most efficient method for estimating precision of an analytical method is to use replicate analyses of randomly selected samples. The median of % variation is considered as coefficient of variation.

Precision …

- A very simple example:

10 replicate measurements of Cr (μg/g) in a rock sample are :

247, 250, 249, 262, 245, 257, 246, 251,271, 248.

The mean Cr (μg/g) = 252.6

The standard deviation SD = 8.3

Precision expressed in percentage, relative to the mean = (8.3/252.6)*100= 3.3%

The Cr (μg/g) value in the rock sample = 253 ± 3%

Standard Deviation 1σ

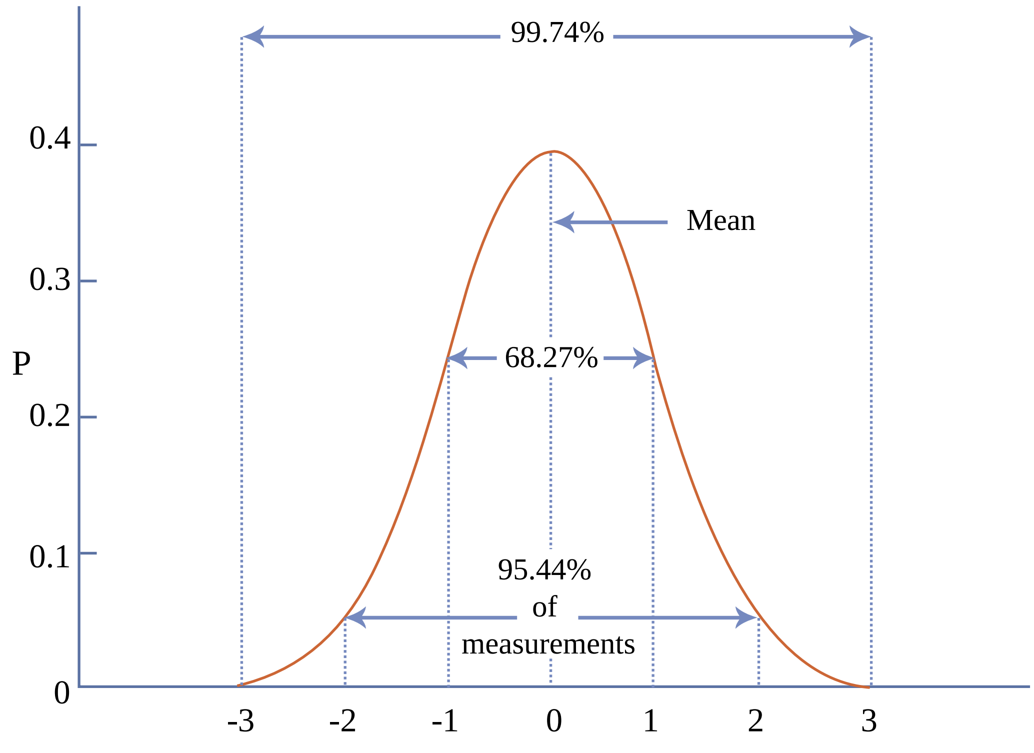
Probability vs. Individual Measurement in the Range of the Mean

- 68.27% of measurements lie within the range $\mu \pm 1\sigma$
- 95.44% of measurements lie within the range $\mu \pm 2\sigma$
- 99.74% of measurements lie within the range $\mu \pm 3\sigma$

or, conversely:

- 50% of measurements lie within the range $\mu \pm 0.676\sigma$
- 90% of measurements lie within the range $\mu \pm 1.645\sigma$
- 95% of measurements lie within the range $\mu \pm 1.960\sigma$
- 99% of measurements lie within the range $\mu \pm 2.576\sigma$
- 99.9% of measurements lie within the range $\mu \pm 3.290\sigma$

Shown pictorially on Gaussian distribution



The gaussian distribution function. The proportion of data lying within the range $\pm$ one sigma, $\pm$ 2 sigma and $\pm$ 3 sigma of the mean is indicated.

Accuracy of an analysis

Accuracy of an Analysis:

- **Accuracy of an analysis means – how close is the measured value to the true value.**
- **Accuracy is determined by measuring Certified reference materials (CRMs) or Standard Reference Materials (SRMs).**

Accuracy …

A very simple example:

6 replicate laboratory measurements of iron (μg/g) in samples of spinach standard are : 480, 510, 490, 470, 526, 473. The certified reference value of the standard is 550 $\pm$ 20 (μg/g).

The mean value of iron (μg/g) = 491.5

Precision = 4.5%

So, the observed value is 491 $\pm$ 22.

Accuracy = (mod(550 – 491))/ 550) *100 = 10.9%

So, even though precision may be good (4.5%), the accuracy may be poor (11%).

Accuracy …t - testing

The confidence level of accuracy is provided by t-value which measures the uncertainty on the mean value. If XM is the mean value and SD is standard deviation determined from n observations, and XR is the reference value, then t-statistic is tcalc = (XR – XM) / SD * sqrt(n). The comparison of calculated t value to the value under (n-1) degrees of freedom in the 't' Tables (Reference: J. C. Miller and J. N. Miller, Statistics for analytical chemistry, 3rd Edition, Chichester, EllisHorwood 1993) provides the level of confidence. Conversely, the required number, nr, of replicate analyses may be calculated to achieve the level of confidence.

nr = (t *SD/ (XR – XM))2 .

Systematic Errors in Neutron Activation Analysis…

Consider the activity equation

$A = N \sigma \phi [1 - \exp(-\lambda t_{irr})]$

where

N = number of atoms of the target isotope

$$= \frac{m}{W} \times \theta \times 6.023 \times 10^{23}$$

1) Anamalous isotopic abundances θ : Ar, B, Ba, Ce, Nd, …

2) Errors due to different fluxes ϕ in samples and standards or among samples

- **flux depression factor**
- **flux self absorption factor**
- **flux perturbation factor**

Systematic Errors …

3)Interfering nuclear reactions – same gamma-ray energy by different isotope

4) Enhancing nuclear reactions – same isotope by different nuclear reactions

$$^{59}Co(n,\gamma)^{60}Co \;\; ; \;\; ^{58}Ni(n,p)^{60}Co$$

Other Errors:

Failure to remove surface contaminants from the sample

In case of radiochemistry – incomplete exchange between carrier and trace element

Faulty preparation of comparator standards

Gross Errors

Minimum mass required for desired sampling precision

Grain Size of Rock vs. Minimum Sample Size for Homogeneous Representation

Grain size of rock (mm)	Minimum sample mass required (kg)
0-1	0.5
1-10	1.0
10-30	2.0
>30	5.0

For detailed information see reference: Ch. 2 Sampling and sample preparation: Theoretical approach to sampling, p14 By Michael H. Ramsey, Modern Analytical Geochemistry, Editor: Robin Gill, Addison Wesley Longman Ltd. 1997

Theoretical approach to sampling - How many samples are required?

For detailed information see reference:

Ch. 2 Sampling and sample preparation:
Theoretical approach to sampling, p16
By Michael H. Ramsey,
Modern Analytical Geochemistry,
Editor: Robin Gill
Addison Wesley Longman Ltd. 1997

Preparation of samples

- Samples and standards should be prepared with utmost importance, carrying out all procedures under controlled conditions and keeping track of the history.
- The procedures about sampling and sample preparation are well documented by authors like DeSoete, Gijbels and Hoste; and Ramsey.

Preparation of samples …

1. Chapter 7: Preparation of Samples and Standards (De Soete, Gijbels and Hoste, Neutron Activation Analysis)
2. Chapter 2: Sampling and sample preparation, Michael H Ramsey, Modern Analytical Geochemistry)

References

1. Modern Analytical Geochemistry,
   pp 1-28,
   Editor: Robin Gill
   Addison Wesley Longman Ltd. 1997

2. Handbook of Silicate Rock Analysis
   P. J. Potts
   Glasgow Blackie 1987

3. Neutron Activation Analysis,
   D. De Soete, R. Gijbels, J. Hoste
   Wiley –Interscience, New York

Session 3 End