

**A SUGGESTED METHOD FOR
CALCULATION OF
UNCERTAINTY
IN
ENVIRONMENTAL CHEMICAL
ANALYSIS**

by

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OBJECTIVE

*To provide insight
into UNCERTAINTY*

*...and to suggest a simple,
practical method for
calculation of uncertainty in
routine Environmental
Chemical Analysis*

AGENDA

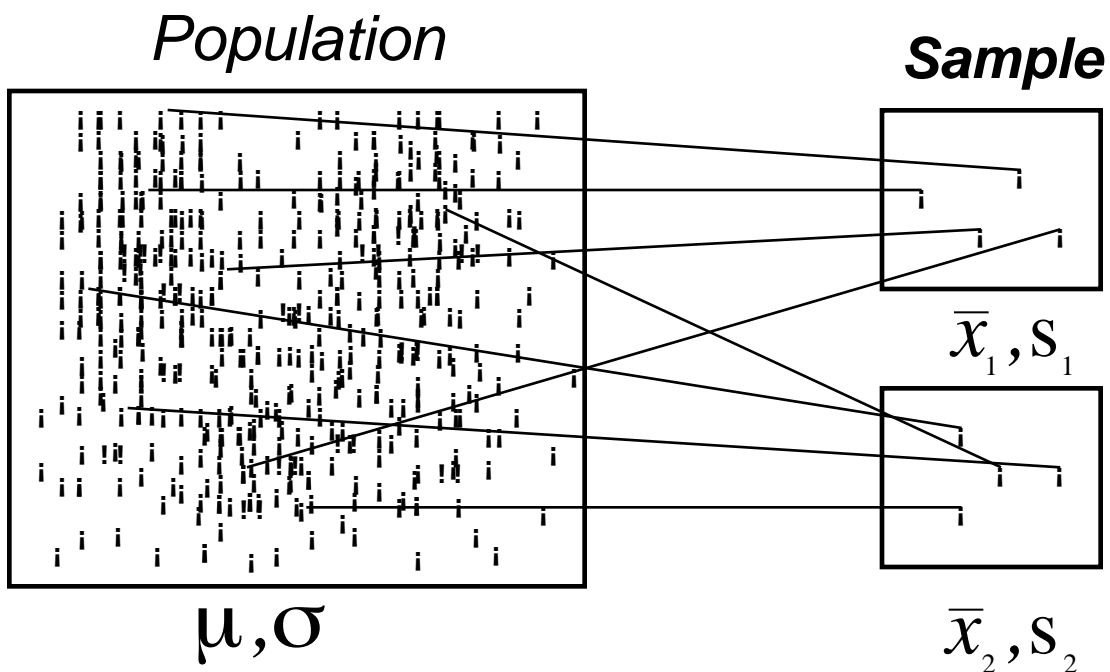
- Definition of Uncertainty
- Error and Uncertainty
- Components of Uncertainty
- Combined Uncertainty
- Standard Method Approach
- Sources of Uncertainty in Chemical Analysis
- Suggested solution and calculation

DEFINITION OF UNCERTAINTY

“Uncertainty is defined as a parameter associated with the result of a measurement that characterizes dispersion of the values that could reasonably be attributed to the true value.”

*ISO “Guide to The Expression of
Uncertainty in Measurement”*

STATISTICS CONCEPTS



Sample means is a normally distributed random variable.

Mean of sample means $\mu_{\bar{x}} = \mu$

STATISTICS CONCEPTS

Standard Deviation of sample means:

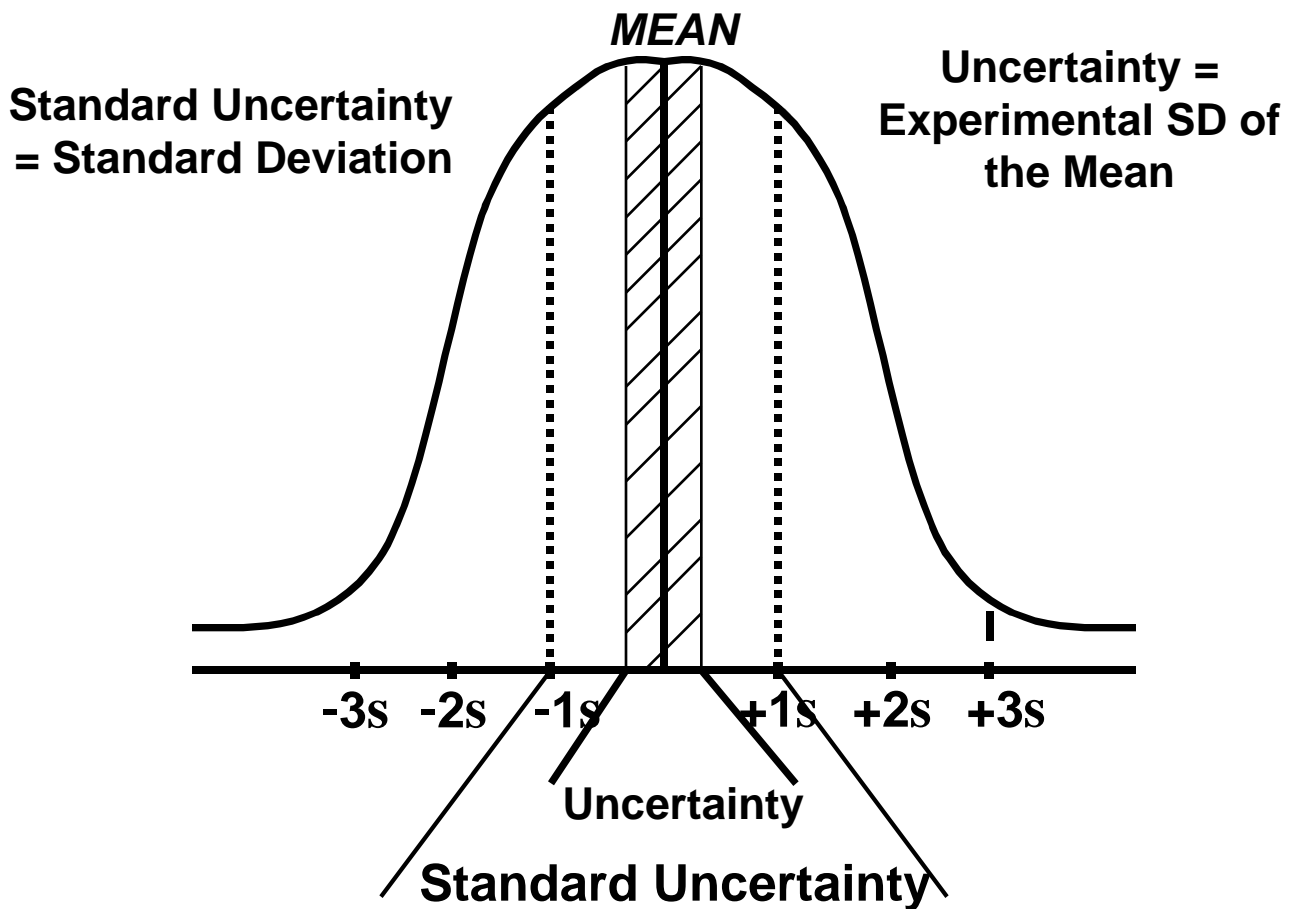
$$\sigma_{\bar{x}} = \frac{\sigma}{\sqrt{n}}$$

Experimental Standard Deviation of sample means:

$$s_{\bar{x}} = \frac{s}{\sqrt{n}}$$

UNCERTAINTY

Standard Normal Curve:



UNCERTAINTY AND ERROR

TRUE VALUE = MEASURED \pm ERROR

ERROR = RANDOM + SYSTEMATIC

Error contributes to but is different from Uncertainty.

COMPONENTS OF UNCERTAINTY

Contributing factors

$$y = f(x_1, x_2, \dots, x_n)$$

Combined Uncertainty

$$U_{C(y)} = \sqrt{U_{x_1}^2 + U_{x_2}^2 + \dots + U_{x_n}^2}$$

COMBINED UNCERTAINTY

In physical parameters
– **direct calculation**

$$V = L/T$$

$$U_V = \sqrt{U_L^2 + U_T^2}$$

TOTAL UNCERTAINTY (STANDARD METHOD)

- random uncertainty S_x
- systematic uncertainty B

$$U_x = \sqrt{S_x^2 + B^2}$$

Reference: US EPA 1980

UNCERTAINTY IN ANALYTICAL CHEMISTRY

- **Many random and systematic errors**
- **The components not fully known**
- **No mathematical model for components that are known**

SOURCES OF UNCERTAINTY IN ANALYTICAL CHEMISTRY

- **Non-representative sampling & sub-sampling**
- **Inadequate knowledge of the effect of environmental conditions on measurement**
- **Imperfect measurement of environmental conditions**
- **Personal bias in reading analogue signals**
- **Operator skill, knowledge, experience**

SOURCES OF UNCERTAINTY IN ANALYTICAL CHEMISTRY

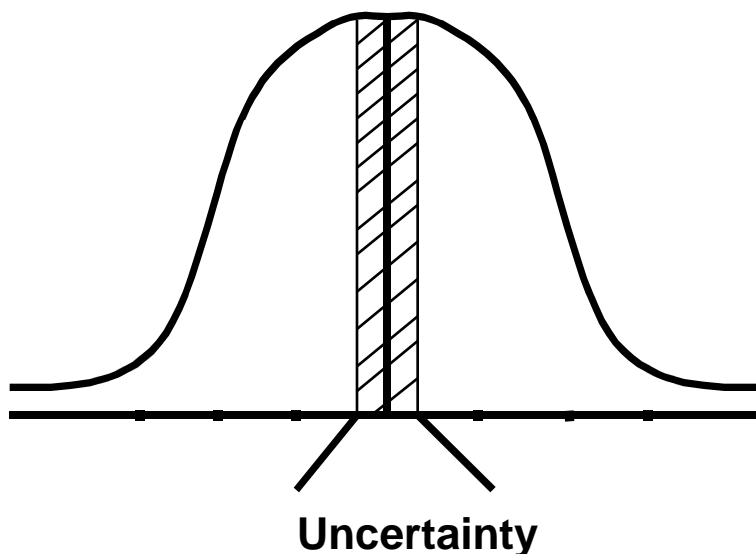
- **Inexact values of calibration standards and reference materials**
- **Approximation and assumptions incorporated in methods**
- **Random variation in repeated measurement under apparently identical conditions**
- **Systematic error in sample preparation**

SOURCES OF UNCERTAINTY IN ANALYTICAL CHEMISTRY

- **Bias in analytical methods**
- **Impurities in consumable materials (water, reagents)**
- **Bias in measuring devices (weight, volumes)**
- **Bias in instruments (calibration)**
- **Interferences (chemical, physical, spectral)**

UNCERTAINTY QUESTION IN ANALYTICAL CHEMISTRY

What is the Uncertainty in a single routine analysis in a band of infinite number of results?



SUGGESTED SOLUTION

**Using the latest matrix spike recoveries
having a combined components of:**

- **Accuracy**
- **Precision**
- **Interferences**
- **Environmental effects**
- **Method bias**

(continued)

SUGGESTED SOLUTION

- **Operator bias**
- **Sampling bias**
- **Sample preparation bias**
- **Reagent bias**
- **Measuring device bias**
- **Calibration standard bias**
- **Instrument bias**

UNCERTAINTY CALCULATION

...For a single analytical result:

- **Choose about 20 recent spike recoveries using the same matrix as the sample (RATIO)**
- **Calculate the Standard Deviation for them (RATIO)**

UNCERTAINTY CALCULATION

- Calculate uncertainty of recoveries equal to the Standard Deviation of the Mean (RATIO):

$$S_{\bar{x}} = \frac{S}{\sqrt{n}}$$

UNCERTAINTY CALCULATION

- **The Uncertainty of a result (Concentration) =
Result (concentration) X
Uncertainty of Spikes (RATIO)**
- **REPORT:
Result ± Uncertainty**

SUMMARY

- ❖ **Definition of Uncertainty**
- ❖ **Error and Uncertainty**
- ❖ **Components of Uncertainty**
- ❖ **Combined Uncertainty**
- ❖ **Standard Method Approach**
- ❖ **Sources of Uncertainty in Chemical Analysis**
- ❖ **Suggested solution and calculation**

CONCLUSION

Using the historical data of matrix spike recoveries of a parameter analyzed under routine conditions in a laboratory, is a simple, practical, and realistic approach to calculate the uncertainty of an environmental chemical analysis.

**UNCERTAINTY IN
ENVIRONMENTAL CHEMICAL ANALYSIS**

Thank you!

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