Chapter 2
Basic statistical concept of measurement uncertainty

Understand the terms related to "Uncertainty"

- Consider expression like:

  "100.0 ml ± 0.15 ml with 95% confidence"

- The ± 0.15 ml is the ***uncertainty (U)*** *of the supposed 100.0 ml volume of the volumetric flask measured.*
- *This uncertainty (sometimes also known as* ***expanded uncertainty****) is actually estimated by having multiplied a* ***coverage factor k*** *with a* ***standard uncertainty (u)****, expressed as standard deviation. i.e.* $U = k * u$
- The coverage factor k can be 2 or 3 for 95% or 99% confidence level, respectively
- ***Relative standard uncertainty*** = relative standard deviation or coefficient of variation CV, $s / \bar{x}$

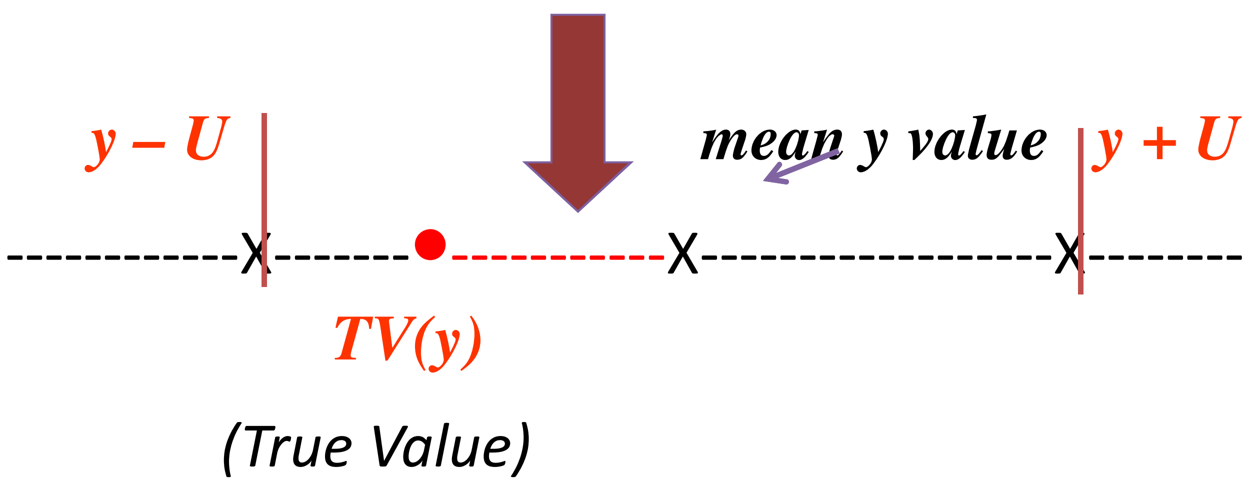
Important Note

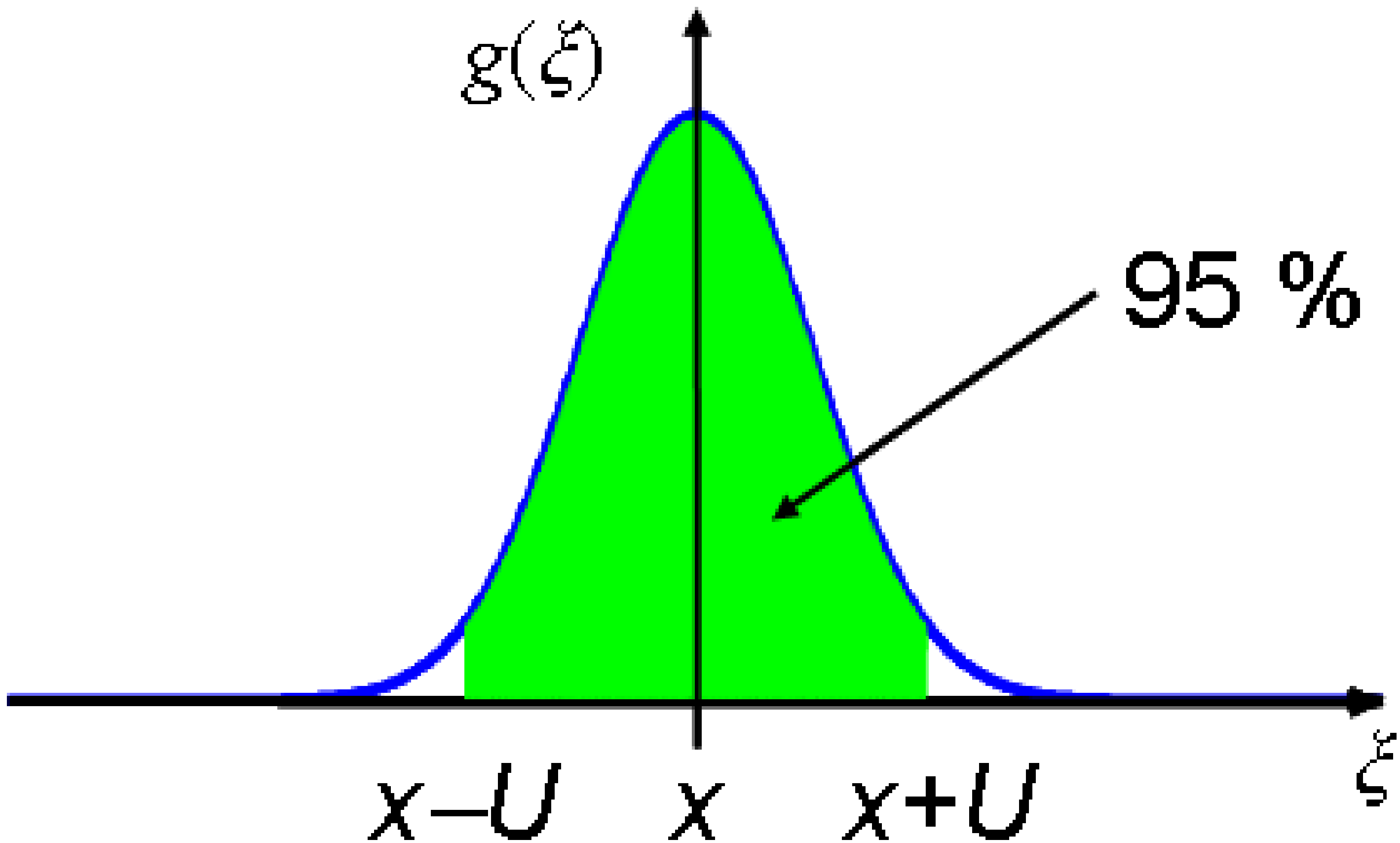
"Standard uncertainty is expressed as standard deviation"

Understand the terms related to "Uncertainty"

- ***uncertainty range*** : $y - U \ldots\ldots y + U$ ***with*** **95% confidence interval**

- $Error = y - TV(y)$





$g(\xi)$
95 %
$x-U$
x
$x+U$
ξ

Propagation Law of Standard Deviations

- A test procedure, y involves many steps and each step can have a standard uncertainty, expressed as standard deviation, say x_i, then :

  $y = f\,[x_1, x_2, x_3, \ldots, x_n]$

- The combined or total uncertainty of ***independent*** components is:

$$s(y)^2 = \sum_{i=1}^{n}\left[\frac{\partial f}{\partial x_i}\right]^2 s(x_i)^2$$

- $s(y)^2 = \sum\{[\partial f/\partial x_1]^2 s(x_1)^2 + [\partial f/\partial x_2]^2 s(x_2)^2 + [\partial f/\partial x_3]^2 s(x_3)^2 + \ldots.\}$

Propagation Law of Standard Deviations

- If the components of uncertainty or errors are **NOT** independent, there is an extra **covariance** factor to be considered:

$$s^2(y) = \sum \left(\frac{\partial f}{\partial x_i} \right)^2 s(x_i)^2 + \sum \frac{\partial f}{\partial x_i} \frac{\partial f}{\partial x_j} Cov\left(x_i, x_j\right)$$

Sensitive coefficient i

Example of calculation

- Let y (with uncertainty u_y)has the following relationship with c, v and w which have standard uncertainty of $u(c)$, $u(v)$ and $u(w)$, respectively:

$$y = \frac{c \times v \times 1000}{w}$$

- Differentiation of y with respect to c, v and w give:

$$\frac{dy}{dc} = \frac{v \times 1000}{w} \qquad \frac{dy}{dv} = \frac{c \times 1000}{w} \qquad \frac{dy}{dw} = -\frac{c \times v \times 1000}{w^2}$$

Example of calculation

- Given c = 0.45*mg/L*, v = 10*ml*, w = 1.5682*g*, and std uncertainty $u(c)$ = 0.05*mg/L*, $u(v)$ = 0.08*ml*, $u(w)$ = 0.002*g* , then

$$y = \frac{c \times v \times 1000}{w} = \frac{0.45 \times 10 \times 1000}{1.5682} = 2{,}870 \mu g / L$$

- Individual sensitive coefficient is :

$$c_c = \frac{dy}{dc} = \frac{10 \times 1000}{1.5682} = 6376.74 \qquad c_v = \frac{dy}{dv} = \frac{0.45 \times 1000}{1.5682} = 286.95$$

$$c_w = \frac{dy}{dw} = -\frac{0.45 \times 10 \times 1000}{1.5682^2} = -1829.83$$

Example of calculation

- Hence, the combined standard uncertainty of y, u_y is calculated as follows:
- $u_y^2 = \{c_c^2 u(c)^2 + c_v^2 u(v)^2 + c_w^2 u(w)^2\}$

  $= \{6376.74^2 x 0.05^2 + 286.95^2 x 0.08^2 + (-1829.83)^2 x 0.002^2\} = 102197$
- $u_y = 320 \mu g/L$

Alternative approach

- Some may find the above calculus calculation messy. However, it can be simplified as below:
- Let y has a relationship with A, B and C with a constant m as follows:

$$y = m\frac{AB}{C}$$

- By differentiation, we get:

$$u_y^{\,2} = \left(m\frac{B}{C}\right)^2 u_A^{\,2} + \left(m\frac{A}{C}\right)^2 u_B^{\,2} + \left(-m\frac{AB}{C^2}\right)^2 u_C^{\,2}$$

Alternative approach

- By dividing the above equation on both sides with $\left(m\dfrac{AB}{C}\right)^2$
- we get : $\left(\dfrac{u_y}{y}\right)^2 = \left(\dfrac{u_A}{A}\right)^2 + \left(\dfrac{u_B}{B}\right)^2 + \left(\dfrac{u_C}{C}\right)^2$
- where u's are the standard uncertainties of y, A, B and C, respectively.
- Note that each of the above component is in fact their own coefficient of variation (CV).

Propagation Law of Standard Deviation simplified

- **Linear Combination of standard deviations**
- $y = K(a + b - c)$ with std deviations s_a, s_b, s_c and K is a constant factor (or a fixed value such as 100),
- then,
- the combined standard deviation s_y is
- $s_y = K * \sqrt{(s_a^2 + s_b^2 + s_c^2)}$
- **Note** : components a, b and c must be of same unit and involve in addition / subtraction

Example of Linear Combination of standard deviations

- Combined uncertainty, $U =$
- $\sqrt{(0.0015)^2 + (0.0015)^2}$
- $= 0.0021$ *gm*

	Weight, gm	Uncertainty, gm
Wt of crucible + sample	45.3426	0.0015
Wt of crucible	40.2325	0.0015
Wt of sample	5.1101	?

Propagation Law of Random Errors

- **Multiplicative Combination**
- $y = K(a * b) / c$ with std deviations s_a, s_b, s_c and K is a constant factor,
- Then,
- the combined standard deviation s_y is
- $s_y / y = \sqrt{[(s_a / a)^2 + (s_b / b)^2 + (s_c / c)^2]}$
- Why is there no K in the above equation?

Worked Example

- $y = (A * B) / C$

	Value, V	Uncertainty U
A	22.5 mg/L	0.2 mg/L
B	250 ml	1.2 ml
C	100 gm	0.8 gm
y	56.25 mg/kg	?

- $U_y / y = \sqrt{(u_a/A)^2 + (u_b/B)^2 + (u_c/C)^2}$
- *Answer :* $U_y = 0.725$ *mg/kg*