Propagation of random errors

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Linear combination

Propagation of the error in the linear combination of independent measurements

2.11.1 Linear combinations

In this case the final value, y, is calculated from a linear combination of measured quantities a, b, c, etc., by:

$$y = k + k_a a + k_b b + k_c c + \cdots \tag{2.10}$$

where k, k_a, k_b, k_c, etc., are constants. Variance (defined as the square of the standard deviation) has the important property that the variance of a sum or difference of independent quantities is equal to the sum of their variances. It can be shown that if σ_a, σ_b, σ_c, etc., are the standard deviations of a, b, c, etc., then the standard deviation of y, σ_y, is given by:

$$\sigma_y = \sqrt{(k_a\sigma_a)^2 + (k_b\sigma_b)^2 + (k_c\sigma_c)^2 + \cdots} \tag{2.11}$$

Illustration in **R**

Illustration using random samples generated by **R**:

```
#generating data
#initial reading
x=rnorm(100,3.51,0.02)
#final reading
y=rnorm(100,15.67,0.02)
#volume used
z=y-x

mean(x)
mean(y)
mean(z)
sd(x)
sd(y)
sd(z)
sqrt(var(x)+var(y))
```

Multiplicative expressions

Multiplicative expressions

The following is true only approximately. Still measurements are assumed to be independent.

2.11.2 Multiplicative expressions

If y is calculated from an expression of the type:

$$y = kab/cd \tag{2.12}$$

(where a, b, c and d are independent measured quantities and k is a constant) then there is a relationship between the squares of the *relative* standard deviations:

$$\frac{\sigma_y}{\cancel{y}\,\mu_y} = \sqrt{\left(\frac{\sigma_a}{\cancel{a}\,\mu_a}\right)^2 + \left(\frac{\sigma_b}{\cancel{b}\,\mu_b}\right)^2 + \left(\frac{\sigma_c}{\cancel{c}\,\mu_c}\right)^2 + \left(\frac{\sigma_d}{\cancel{d}\,\mu_d}\right)^2} \tag{2.13}$$

Example

Example 2.11.2

The quantum yield of fluorescence, ϕ, is calculated from the expression:

$$\phi = I_f/(kclI_0\varepsilon)$$

where the quantities involved are defined below, with an estimate of th relative standard deviations in brackets:

I_0 = incident light intensity (0.5%)
I_f = fluorescence intensity (2%)
ε = molar absorptivity (1%)
c = concentration (0.2%)
l = path-length (0.2%)
k is an instrument constant.

From equation (2.13), the relative standard deviation of ϕ is given by:

$$\mathrm{RSD} = \sqrt{2^2 + 0.2^2 + 0.2^2 + 0.5^2 + 1^2} = 2.3\%$$

Illustration in **R**

Illustration using random samples generated by **R**:

```
#generating data
#incident light intensity
I0=rnorm(100,10,0.005*10)
#fluorescence intensity
If=rnorm(100,15,0.02*15)
#molar absorptivity
e=rnorm(100,5,0.01*5)
#concentration
c=rnorm(100,2,0.002*2)
#path-length
l=rnorm(100,11,0.002*11)

#Computing quantum yield of fluorescence

phi=If/(c*l*I0*e)

sd(x)/mean(phi)
```

Propagation of systematic errors

2.12.1 Linear combinations

If y is calculated from measured quantities by use of equation (2.10), and the systematic errors in a, b, c, etc., are Δa, Δb, Δc, etc., then the systematic error in y, Δy, is calculated from:

$$\Delta y = k_a \Delta a + k_b \Delta b + k_c \Delta c + \cdots \tag{2.17}$$

Remember that the systematic errors are either positive or negative and that these signs must be included in the calculation of Δy.

The total systematic error can sometimes be zero. Suppose, for example, a balance with a systematic error of –0.01 g is used for the weighings involved in making a standard solution. Since the weight of the solute used is found from the difference between two weighings, the systematic errors cancel out. It should be pointed out that this applies only to an electronic balance with a single internal reference weight. Carefully considered procedures, such as this, can often minimize the systematic errors, as described in Chapter 1.

2.12.2 Multiplicative expressions

If y is calculated from the measured quantities by use of equation (2.12) then *relative* systematic errors are used:

$$(\Delta y/y) = (\Delta a/a) + (\Delta b/b) + (\Delta c/c) + (\Delta d/d) \tag{2.18}$$

When a quantity is raised to some power, then equation (2.15) is used with the modulus sign omitted and the standard deviations replaced by systematic errors.