Estimation of measurement uncertainty in chemical analysis (analytical chemistry)

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2013

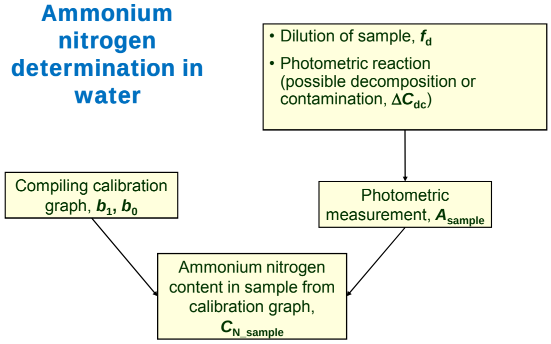
Measurement uncertainty by the modeling approach:

Determination of NH_4^+ in water

- A dye (photometric complex) is formed quantitatively from NH_4^+ and its absorbance is measured at 640-660 nm by a photometer
- The concentration of ammonium nitrogen is found from calibration graph

Procedure

Ammonium nitrogen determination in water



Step 1 – defining the measurand

Measurand = The quantity intended to be measured

Our measurand:
Concentration of NH_4^+ expressed as ammonium concentration $\boldsymbol{C_{N\_sample}}$ mg/l in the water sample

Step 2 – Model

Model is the equation which enables calculating the measurand (**output quantity *Y***) value from the values of directly measured quantities (**input quantities X_1 .. X_n**) :

$$Y = f(X_1, X_2, ..., X_n)$$

Step 2 – Model

- Model:

$$C_{N\_sample} = \frac{(A_{sample} - b_0)}{b_1} \times f_d + \Delta C_{dc}$$

- A_{sample} – absorbance of the dye solution obtained from the sample
- b_1 and b_0 – slope and intercept of the calibration graph
- f_d – dilution factor
- ΔC_{dc} – component taking into account uncertainty originating from possible decomposition or contamination

Step 3 – Uncertainty sources

- **All possible uncertainty sources need to be considered**
  - **The important ones need to be accounted for**
  - **This can be done individually or by grouping**
- For this the source has to be linked with some input quantity in the model
- If an important uncertainty source exists that cannot be linked with any input quantity then the model has to be modified

7

Step 3 – Uncertainty sources

– **Sampling**
- Sample non-representativeness

The result is expressed for sample, sampling is not included

– **Sample preparation**
- Inhomogeneity
- Separation of analyte incomplete
- Analyte adsorbs

The sample is homogenous, the analyte is not separated and does not adsorb

- Analyte or photometric complex decomposes
- Analyte volatilizes
- Incomplete reaction
- Contamination

Analyte or the photometric complex can decompose or get contaminated: ΔC_{dc}

8

Step 3 – Uncertainty sources

– Preparation and dilution of solutions

f_d accounts for this

– Weighing

Is included in b_1 and b_0 uncertainty

– Calibration of instrument
- Standard substance purity
- Solution preparation

b_1 and b_0 uncertainty

– Measurement of sample
- Interferences
- Repeatability of reading
- Drift of reading

A_{sample} accounts for these

- Memory effects

Absent in our example

9

Step 3 – Uncertainty sources

- Interferences
- Repeatability and drift of photometer

- Contamination
- Decomposition
- Volatilization

$$C_{N\_sample} = \frac{(A_{sample} - b_0)}{b_1} \times f_d + \Delta C_{dc}$$

- Standard substance purity
- Preparation of solutions
- Repeatability and drift of photometer

- Preparation of solutions

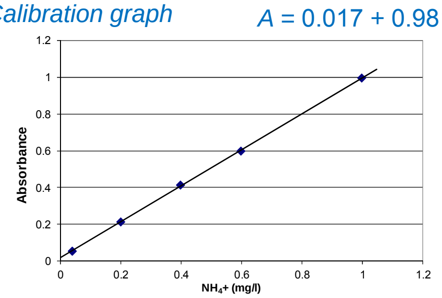
10

Step 4 – Finding values of input quantities

$A = b_0 + b_1 \times C$

Calibration graph

$A = 0.017 + 0.981 \times C$



11

Step 4 – Finding values of input quantities

Quantity	Value	Unit
A_{sample}	0.1860	AU*
b_0	0.0171	AU*
b_1	0.9808	AU×l/mg
f_d	1.2500	–
ΔC_{dc}	0.0000	mg/l

* Absorbance in fact does not have a unit, AU is used for clarity

12

Step 5 – Standard uncertainties of the input quantities: A_{sample}

- Absorbance of the sample solution A_{sample}:

u (A_{sample}, rep) =	0.0010	AU
u (A_{sample}, drift) =	0.0012	AU
u (A_{sample}, chem) =	0.0030	AU

$$u(A_{\text{sample}}) = \sqrt{u(A_{\text{sample}},\text{rep})^2 + u(A_{\text{sample}},\text{drift})^2 + u(A_{\text{sample}},\text{chem})^2} = 0.0034\,\text{AU}$$

13

Step 5 – Standard uncertainties of the input quantities: b_0 and b_1

- Standard deviations of b_0 and b_1 as found from regression statistics are used as standard uncertainty estimates

$u(b_0)$ = 0.0025 AU

$u(b_1)$ = 0.0046 AU×l/mg

- This is an approximation!

14

Step 5 – Standard uncertainties of the input quantities: f_d

- The standard uncertainty of dilution factor is estimated here as 0.5% of the dilution factor value
- This is a safe estimate if volumetric operations are performed correctly

$u(f_d)$ = 1.25 / 200 = 0.0063

15

Step 5 – Standard uncertainties of the input quantities: ΔC_{dc}

- The *possible* contribution of decomposition or contamination at this concentration level is estimated from the experience of the laboratory as follows:

$u(\Delta C_{dc})$ = 0.004 mg/l

16

Step 5 – Standard uncertainties of the input quantities: summary

- **The uncertainties of the input quantities have to be used as standard uncertainties (*u*)**

Quantity	Value	*u*	Unit
A_{sample}	0.1860	0.0034	AU
b_0	0.0171	0.0025	AU
b_1	0.9808	0.0046	AU×l/mg
f_d	1.2500	0.0063	–
ΔC_{dc}	0.0000	0.0040	mg/l

17

Step 6 – Calculating the measurand value

$$C_{\text{N\_sample}} = \frac{(A_{\text{sample}} - b_0)}{b_1} \times f_{\text{d}} + \Delta C_{\text{dc}}$$

$$C_{\text{N\_sample}} = \frac{(0.1860 - 0.0171)}{0.9808} \times 1.25 + 0$$

C_{N_sample} = 0.215 mg/l

18

Step 7 – Finding combined standard uncertainty (1)

- In the case on non-correlating input quantities:

$$u_c(y)=\sqrt{\left[\frac{\partial Y}{\partial X_1}u(x_1)\right]^2+\left[\frac{\partial Y}{\partial X_2}u(x_2)\right]^2+\ldots..+\left[\frac{\partial Y}{\partial X_n}u(x_n)\right]^2}$$

$u_c(y)$ = combined standard uncertainty of the output quantity
$u(x_i)$ = standard uncertainties of the input quantities

19

Step 7 – Finding combined standard uncertainty (2)

$$u_c(C_{\text{N\_sample}})=\sqrt{\left(\frac{\partial C_{\text{N\_sample}}}{\partial A_{\text{sample}}}u(A_{\text{sample}})\right)^2+\left(\frac{\partial C_{\text{N\_sample}}}{\partial b_0}u(b_0)\right)^2+\left(\frac{\partial C_{\text{N\_sample}}}{\partial b_1}u(b_1)\right)^2+\left(\frac{\partial C_{\text{N\_sample}}}{\partial f_d}u(f_d)\right)^2+\left(\frac{\partial C_{\text{N\_sample}}}{\partial \Delta C_{dc}}u(\Delta C_{dc})\right)^2}$$

20

Step 7 – Finding combined standard uncertainty (3)

$$u_c(C_{\text{N\_sample}})=\sqrt{(0.00429)^2+(-0.00324)^2+(-0.0010)^2+(0.00108)^2+(0.00400)^2}$$

$u_c(C_{\text{N\_sample}})$ = 0.00686 mg/l

21

Step 8 – Finding expanded uncertainty

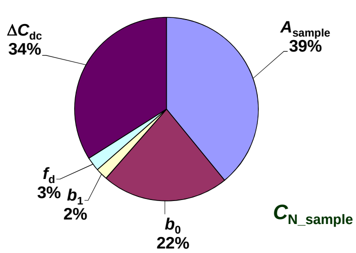
- Expanded uncertainty ***U*** is found by multiplying $\boldsymbol{u_c}$ with coverage factor ***k***
  - Very often k = 2, which in the case of normal distribution corresponds to ca 95% probability

U = 0.00686 x 2 = 0.014 mg/l

Result: **$C_{\text{N\_sample}}$ = (0.215 ± 0.014) mg/l**
k = 2

22

Step 9 – Contributions of uncertainty sources



The most important uncertainty sources:

- Interference
- Contamination
- Instability of the dye

$C_{\text{N\_sample}}$ = (0.215 ± 0.014) mg/l
k = 2, norm.

$$C_{\text{N\_sample}}=\frac{(A_{\text{sample}}-b_0)}{b_1}\times f_d+\Delta C_{dc}$$

23

Step 9 – Contributions of uncertainty sources

- Uncertainty contributions (indexes) are found as follows:

$$Index(x_1)=\frac{\left[\frac{\partial Y}{\partial X_1}u(x_1)\right]^2}{\left[\frac{\partial Y}{\partial X_1}u(x_1)\right]^2+\left[\frac{\partial Y}{\partial X_2}u(x_2)\right]^2+\ldots..+\left[\frac{\partial Y}{\partial X_n}u(x_n)\right]^2}$$

24