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Evaluation of the Uncertainty of Measurement

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EVALUATION OF THE UNCERTAINTY OF MEASUREMENT

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For Determination of Total Phosphorus in Water by Means of Merck 1.14848

Valcan Angela

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Keywords : uncertainty, water, total phosphorus, budget, laboratory.

I. Principle

Phosphate ions in solution acidified with sulfuric acid reacts with molybdate ions to form molybdophosphoric acid is reduced by ascorbic acid phosphomolybdic blue (PMB) which is determined photometrically at 690 nm.

II. Definitions

a) Uncertainty of Measurement

Parameter, associated with a test result which characterizes the dispersion of values that could reasonably be attributed to the measurement.

b) Uncertainty Budget

A table which centralizes the size to which uncertainty is associated, the value / estimate size, standard uncertainty, probability distributions, coefficient sensitivity, contributing to uncertainty / relative standard uncertainty (ratio of standard uncertainty and sensitivity coefficient)

c) Assessment of type A (uncertainty)

Method for analyzing the uncertainty by the statistical analysis of the sequence of observations.

d) Assessment of type B (uncertainty)

Method of evaluating the uncertainty by means other than statistical analysis of the sequence of observations.

e) Standard Uncertainty

Uncertainty about the outcome of a measurement expressed as standard deviation.

f) Combined standard uncertainty, u_c

Standard uncertainty of the result of a measurement when that result is obtained based on the values of different sizes, equal to the positive square root of a sum of terms, those terms being the variances or covariances of those sizes, weighted in accordance with variation of the measurement for varying respective sizes.

g) Expanded Uncertainty, U

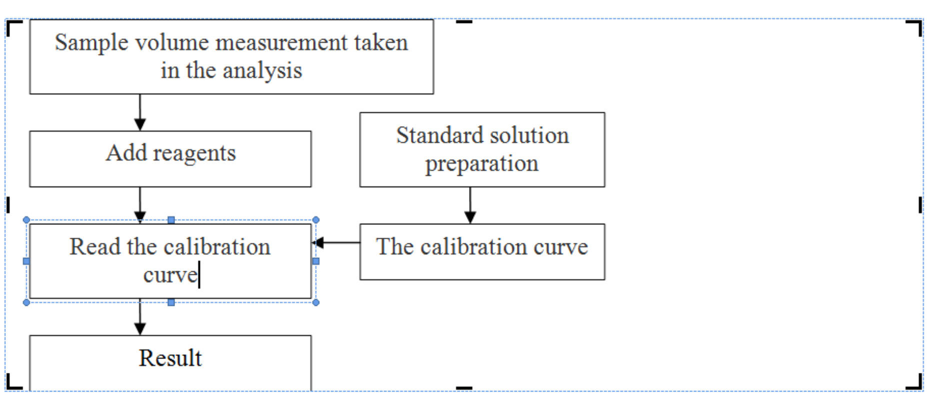
Quantity defining an interval around a measurement result, the range is expected to be within a fraction of the distribution of high values that can reasonably be attributed to the measurement.

h) Coverage Factor, K

Numerical coefficient used as a multiplier of the combined standard uncertainty to obtain the expanded uncertainty.

$U=2\cdot u_c$, k=2 defines a confidence interval of approximately 95%.

III. Step of the Determination of Phosphorus



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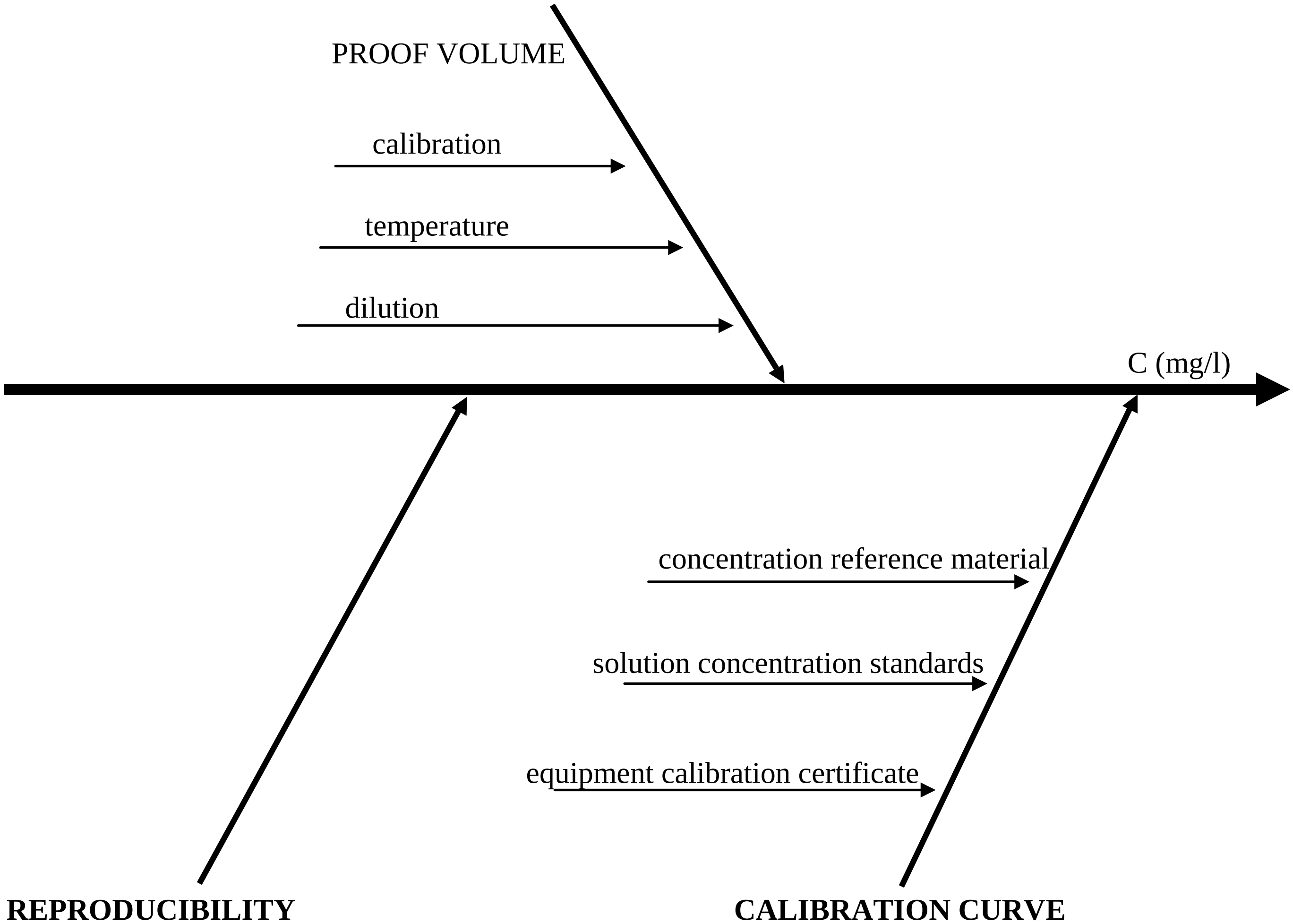
IV. Identify Sources of Uncertainty

To identify sources of uncertainty:

- all the sources of uncertainty affecting the value of measurement are listed;
- sources of uncertainty that have been found unimportant, will be deleted;
- the diagram cause and effect is constructed (diagram Ishikawa).

CAUSE-AND-EFFECT DIAGRAM



WITHIN-LABORATORY

Sources of uncertainty within-laboratory analyzes concerned the diagram – effect (of all sizes that affect the result). Also included are important sources of type A and B.

V. Quantification of Uncertainties

Uncertainties are evaluated by the method of type A and type B.

a) Sample volume (dilution)

Measure the sample volume using a 5 ml pipette, class A, with a tolerance of ± 0,03.

i. *Glass calibration*

a- measurement tolerance;

$$u_{etal.} = \frac{a}{\sqrt{6}} = \frac{0{,}03}{\sqrt{6}} = 0{,}0122 ml$$

ii. *Repeatability*

10 are measurements of volume are made, then the average is calculated, and then the standard deviation, which is

$u_{repet.} = 0{,}029$ ml

iii. *Temperature*

$$u_{temp.} = \frac{V \cdot \Delta T \cdot \alpha}{\sqrt{3}} = \frac{5 \cdot 4 \cdot 2{,}1 \cdot 10^{-4}}{\sqrt{3}} = 0{,}0024 ml$$

Where: V-volume

ΔT-temperature interval

α-thermal expansion coefficient for water: $2{,}1 \cdot 10^{-4}$ K^{-1}

$$u_v = \sqrt{u_{etal.}^2 + u_{repet.}^2 + u_{temp.}^2} = 0{,}0316ml$$

Calculation of the relative uncertainty ($u_{\text{proof vol.}}$):

$$u_{\text{proof vol}} = \frac{0{,}0316ml}{5ml} = 0{,}0063$$

b) The calibration curve

Uncertainty of the calibration is obtained by composing the uncertainty of the measuring equipment (spectrophotometer), the reference material, the preparation of working standard solutions and standard deviation S_{X0} calculated according to the standard method ISO 8466-1/1999.

i. *Equipment calibration certificate*

Certificate of calibration of the spectrophotometer no. 05.01-056/2011:

Expanded uncertainty: U = 0,012 for k = 2 and P = 95% at 690 nm

Uncertainty consists: $u_c = \frac{U}{k} = \frac{0{,}012}{2} = 0{,}006$

Relative uncertainty ($u_{\text{calibration certificat}}$):

$$u_{calib.certif.} = 0{,}006$$

ii. *The calibration curve no. 8/2013 was evaluated according to ISO 8466.*

We chose to work from 0,05 to 3,65 mg/l PO_4-P wastewater, 10 points were selected for different levels, balanced on the chosen work.

The first and last points of concentration were made for 10 determinations, accounting for 10 values of pads for each point. Values were plotted according to the strength pads. The method proved linear chosen field by performing verification tests: homogeneous dispersion and linearity.

a. *Solutions for calibration curve preparation*

Out of the reference material Merck KH_2PO_4 in H_2O, 999 ± 2 mg/l standard solution I was prepared and work of 10 mg/l and standard working solution II 1 mg/l.

i. Reference material

$$u_{MR.} = \frac{a}{\sqrt{3}} = \frac{2}{\sqrt{3}} = 1{,}1547mg/l$$

Calculation of the relative uncertainty ($u_{\text{conc.MR}}$):

$$u_{conc.MR} = \frac{1{,}1547mg/l}{999mg/l} = 0{,}0012$$

ii. Standard solution I of concentration 10 mgP/l:

Take 7, 68 ml of Merck standard solution with a burette of 10 ml and placed in a 250 ml volumetric flask and dilute to the mark with distilled water.

a. *burette 10 ml (class A, 0,02 ml mark, tolerance ± 0,02 ml)*

1. *Glass calibration*

$$u_{etal.} = \frac{a}{\sqrt{6}} = \frac{0{,}02}{\sqrt{6}} = 0{,}0082ml$$

2. *Repeatability are 10 measurements of volume averaging, standard deviation which is*

$u_{repet.}$=0,005 ml

3. *Temperature*

$$u_{temp.} = \frac{V \cdot \Delta T \cdot \alpha}{\sqrt{3}} = \frac{7{,}68 \cdot 4 \cdot 2{,}1 \cdot 10^{-4}}{\sqrt{3}} = 0{,}0037ml$$

$$u_{burette} = \sqrt{u_{etal.}^2 + u_{repet.}^2 + u_{temp.}^2} = 0{,}0103ml$$

Calculation of the relative uncertainty (u_{burette}):

$$u_{V_{burette}} = \frac{0{,}0103ml}{7{,}68ml} = 0{,}0013$$

b. *250 ml volumetric flask (class A tolerance of ± 0.15 ml)*

1. *Glass calibration*

$$u_{etal.} = \frac{a}{\sqrt{6}} = \frac{0{,}15}{\sqrt{6}} = 0{,}0612ml$$

2. *Repeatability are 10 measurements of volume averaging, standard deviation which is*

$u_{repet.}$=0,092 ml

3. *Temperature*

$$u_{temp.} = \frac{V \cdot \Delta T \cdot \alpha}{\sqrt{3}} = \frac{250 \cdot 4 \cdot 2{,}1 \cdot 10^{-4}}{\sqrt{3}} = 0{,}1212ml$$

$$u_{balloon\,250} = \sqrt{u_{etal.}^2 + u_{repet.}^2 + u_{temp.}^2} = 0{,}164ml$$

Calculation of the relative uncertainty ($u_{\text{balloon 250}}$):

$$u_{V_{balloon\,250}} = \frac{0{,}164ml}{250ml} = 0{,}00066$$

Calculation of the relative uncertainty ($u_{\text{sol.et.I}}$):

$$u_{V_{sol.et.I}} = \sqrt{u_{MR}^2 + u_{V_{burrete.}}^2 + u_{V_{balloon.}}^2} = 0{,}0019$$

iii. Standard solution II of concentration 1 mgP/l:

10 ml of standard working solution I is taken with a 10 ml burette (Class A, 0,02 ml mark, tolerance ±

0,02 ml) and it is placed in a flask of 100 ml and then make up to volume with distilled water.

a. burette 10 ml (Class A, 0,02 ml mark, tolerance ± 0,02 ml)

1. Glass calibration

$$u_{etal.} = \frac{a}{\sqrt{6}} = \frac{0{,}02}{\sqrt{6}} = 0{,}0082ml$$

2. *Repeatability* - 10 volume measurements are made, their average and the standard deviation which is

$u_{repet.}$=0,005 ml

3. Temperature

$$u_{temp.} = \frac{V \cdot \Delta T \cdot \alpha}{\sqrt{3}} = \frac{10 \cdot 4 \cdot 2{,}1 \cdot 10^{-4}}{\sqrt{3}} = 0{,}0485ml$$

$$u_{burette} = \sqrt{u_{etal.}^2 + u_{repet.}^2 + u_{temp.}^2} = 0{,}01073ml$$

Calculation of the relative uncertainty ($u_{burette}$):

$$u_{V_{burette}} = \frac{0{,}01073ml}{10ml} = 0{,}001073$$

b. 100 ml volumetric flask (class A tolerance of ± 0.01 ml)

1. Glass calibration

$$u_{etal.} = \frac{a}{\sqrt{6}} = \frac{0{,}01}{\sqrt{6}} = 0{,}0041ml$$

2. *Repeatability* – 10 volume measurements are made, then their average and the standard deviation which is

$u_{repet.}$=0,090 ml

3. Temperature

$$u_{temp.} = \frac{V \cdot \Delta T \cdot \alpha}{\sqrt{3}} = \frac{100 \cdot 4 \cdot 2{,}1 \cdot 10^{-4}}{\sqrt{3}} = 0{,}0485ml$$

Calculation of the relative uncertainty ($u_{balon\ 100}$):

$$u_{V_{balloon100}} = \frac{0{,}1023ml}{100ml} = 0{,}001023$$

Calculation of the relative uncertainty ($u_{sol.et.II}$):

$$u_{V_{sol.et.II}} = \sqrt{u_{sol.et.I}^2 + u_{V_{burette.}}^2 + u_{V_{balloon.}}^2} = 0{,}00240$$

b. *Following the evaluation of the calibration no.8/2013, the ISO 8466 standards were obtained:*

- standard deviation of the method S_{x0}=0,0185 mg/l.
- average concentrations of standard solutions of curve x_0 =1,85 mg/l

Calculation of the relative uncertainty (u_{Sx0}):

$$u_{S_{x0}} = \frac{0{,}0185mg/l}{1{,}85mg/l} = 0{,}010$$

$$u_{\text{reading the curve}} = \sqrt{u_{certif.etal.}^2 + u_{Sx0}^2 + u_{sol.et.I}^2 + u_{sol.et.II}^2} = 0{,}0120$$

c) Within-laboratory reproducibility

Concentrations were taken from the control chart (98 values determined in the period 3 January 2012-31 March 2013) and were calculated:

i. *Arithmetic mean: ratio of sum of x_i and their number, n.*

$$\bar{x} = \frac{\sum x_i}{n} = 1{,}496mg/l \text{ , n=98}$$

ii. *standard deviation S:*

$$S = \sqrt{\frac{\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2}{n-1}} = 0{,}0137mg/l$$

Where:

xi- outcome measurement (values corresponding to n measurements)

$\bar{x}$ – arithmetic mean of n data

n-1: degrees of freedom

i – number of measurements (43)

iii. *Relative standard deviation: n values measured for the calculation equation is:*

$$RSD = \frac{S}{\bar{x}} = \frac{0{,}0137}{1{,}496} = 0{,}0091$$

Standard uncertainty evaluated as type method can be:

u_{xi}= RSD= 0,0091

d) Bias

Analyzing samples of known concentration (reference material) and comparing the measured value with the real one.

$$u_{bias} = \frac{\left|x_{ref} - \bar{x}\right|}{x_{ref}} = \frac{1{,}500 - 1{,}496}{1{,}500} = 0{,}0026$$

VI. UNCERTAINTY BUDGET

	Method of evaluation	Value (x) UM	Standard uncertainty u(x)	Relative standard uncertainty u(x)/x
Proof volume	Type B (glassware)	5 ml	0,0316 ml	0,0063
The calibration curve				
a. certificate calibration equipment	Type B			0,006
b. standard working solution I	Type A			0,0019
c. standard working solution II	Type A			0,0024
d. evaluation of the calibration curve	Type A	1,85 mg/l	0,0185	0,010
Within-laboratory reproducibility	Type A	1,496 mg/l	0,0137	0,0091
Bias	Type A	1,5 mg/l		0,0026

COMPOSITE UNCERTAINTY OF THE PROCEDURE IS:

$$u_c = \sqrt{u^2_{\text{proof vol.}} + u^2_{\text{reading the curve}} + u^2_{x_i} + u^2_{bias}} = 0{,}0166$$

THE EXPANDED UNCERTAINTY is calculated from the combined standard uncertainty multiplied by a coverage coefficient, k.

$$U = k \cdot u_c$$

choice of k is based on a level of confidence required.

Expanded uncertainty at confidence level 95%, k=2 is U=0,033; 3, 31%.

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