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Aspects Concerning the Estimation of Uncertainty of Measurement Issues for Determination of Sulphate in Waste Waters Through Spectrophotometric Method

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Summary

This paper aims to present a model of estimation of the uncertainty for the determination of sulphate in wastewater made in a test laboratory accredited by RENAR. One of the fundamental requirements placed before testing laboratories ISO 17025 standard is the estimation and reporting of budget uncertainty and traceability to international standards. Knowing the measurement uncertainty of test results is a fundamental importance for all laboratories and institutions using these results for comparative purposes. Measurement uncertainty is a parameter associated with the outcome of a measurement, which characterizes the scattering of which could reasonably be attributed to the measure. It is important to take into account not only one measurement, but the overall result of the measurement. In this case the uncertainty of measurement takes into account all components of the test. Test results must represent the best approximation to the true value.

Keywords: estimation of uncertainty; determination; spectrophotometric method.

Introduction

Estimating measurement uncertainty allows comparison of results generated by several laboratories, or a laboratory with specific data.

When the estimated uncertainty of test results must be taken into account all uncertainty components which are important in a given situation using appropriate analytical methods.

Laboratories should evaluate measurement uncertainty according to field of activity, type of testing or regulatory practices and requirements of customers.

Testing laboratories shall have and shall apply procedures foe estimating uncertainty. In certain cases the nature of the test method may preclude rigorous, metrological and statistically valid, calculation of uncertainty of measurement. In these cases the laboratory shall at least attempt to identify all the components and make a reasonable estimation, and shall ensure that the form of reporting of the result does not give a wrong impression of the uncertainty

MATERIALS AND METHODS

DEFINING THE MEASURAND, MEASUREMENT AND ANALYSIS PROCESS TO DETERMINE THE MATHEMATICAL MODEL

Defining the measurand and the measurement

The concentration of sulphate, expressed in mg/L

The mathematical model applied, resulting in the measurement model

conc SO_4 [mg/L] = _____ [mg/L] SO_4 (on the display of the spectrophotometer)

Measurement uncertainty budget

The sulphate concentration in analyzed water samples volume depends on the following factors:

- average measurement results due to varying individual observations
- spectrophotometer's precision (EMI 1)
- standard solution concentration / concentration of used reagent
- volume of standard solution
- accuracy of 100 mL flask (Vflask)
- temperature (Vst * f (temp))

Figure 1. The equipment used for the measurements (DR 2800 Spectrophotometer)

Estimation of standard uncertainty

We will determine the standard uncertainty associated with each source of uncertainty identified by assessment: Type A: - statistical evaluation, Type B - non-statistical evaluation

***) The standard uncertainty associated with the spectrophotometer, type rating B rectangular distribution**

u(EMI 1) = a /SQRT (3)

a - photometric accuracy = 0.04

u (EMI 1) = 0.023

****) Average standard measurement uncertainty (of the results), Type A: - statistical evaluation**

No. of the measurements: n(X1, X2, X3, ...Xi, Xn)

The arithmetic mean of the "n" results: Xmed = n(X1, X2, X3, ...Xi, Xn)/Xn

Standard deviation: $s = \sqrt{\frac{\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2}{n-1}}$

Table I. Experimental results

Nr.	Reference value [mg/l]	Determined value [mg/L]	X_i - M_{med}	$(X_i-X_{med})^2$
1	700	697	2.666	7.111
2	700	704	4.333	18.777
3	700	698	1.666	2.777

The arithmetic mean of results = 699.7

Number of measurements = 3

Standard deviation = 3.78

Standard uncertainty u(Xmed) = 2.18

*****) The standard uncertainty associated to the calibrated flask (V_{flask})**

The calibrated flask volume has two influences:

Uncertainty of calibrated flask volume of 100 mL (B rating, triangular distribution)

The manufacturer indicates "a" ± ml volume measured at 20 °C

calibrated flask 100 = 0.1 mL

u(Vflask) = a /SQRT (6)

Uncertainty u(Vflask) =0.04

Temperature, type rating B rectangular distribution

In the laboratory, temperature variation is ± 2 °C

Standard uncertainty, assuming that the temperature variation is rectangular distribution is:

$$\text{u(Vflask, f(t))} = \frac{V \cdot \Delta T \cdot 2{,}1 \cdot 10^{-4}}{\sqrt{3}}$$

V – volume of calibrated flask, mL = 100

ΔT-temperature (temperature at which the determination was made and the calibration temperature = 4)

Vol. expansion coefficient of water = $21*10^{-4}$

Uncertainty of temperature variation u(f(t))= 0.048

Uncertainty associated to the volume of solution:

$$u(V_{flask}) = \sqrt{u(V_{flask})^2 + u(V_{flask} * f_{temp})^2}$$

u(Vflask, f(t)) = 0.06

******) The standard uncertainty associated to dosage pipette type B evaluation, triangular distribution**

Pipette volume = 2 mL
u(Vpipette) = a /SQRT (6)
a - pipette = 0.01
Uncertainty associated with the pipette:
u(Vpipette) = 0.004 mL

*******) Relative uncertainty associated to the test cuvettes used at measurements**

$u_{TC\ rel}$ = 6.5 %; u(TC) =0.065 mg/L

********) Relative uncertainty associated to the standard solution**
u st.sol =0.002 mg/L

COMPOSED UNCERTAINTY ESTIMATION

We will calculate the uncertainty related compounds identified and evaluated sources of uncertainty

$$\frac{u_c\left(C_{SO_4^{2-}}\right)}{C_{SO_4^{2-}}}=\sqrt{\left[\frac{u(C_{St.Sol})}{C_{St.Sol}}\right]^2+\left[\frac{u(C_{CT})}{C_{CT}}\right]^2+\left[\frac{u(V_{pipette})}{V_{pipette}}\right]^2+\left[\frac{u(V_{flask})}{V_{flask}}\right]^2+\left[\frac{u(V_T)}{V_{T)}}\right]^2+u(EMI)^2+u(\bar{x})^2}$$

$$u_c\left(C_{SO_4^{2-}}\right)=\bar{C}_{SO_4^{2-}}\cdot\sqrt{\left[\frac{u(C_{St.Sol})}{C_{St.Sol}}\right]^2+\left[\frac{u(C_{CT})}{C_{CT}}\right]^2+\left[\frac{u(V_{pipette})}{V_{pipette}}\right]^2+\left[\frac{u(V_{flask})}{V_{flask}}\right]^2+\left[\frac{u(V_T)}{V_{T)}}\right]^2+u(EMI)^2+u(\bar{x})^2}$$

DETERMINATION AND EXPRESSION OF THE OVERALL UNCERTAINTY OF THE FINAL RESULT

U_e=k*u_c=0,4317 (k=2 for a confidence level of 95%)
The expression of the final result

$$\bar{C}_{SO_4} = 699.7 \pm 43.17 \text{ mg/L}$$

The uncertainty stated is the expanded uncertainty obtained by multiplying the standard uncertainty with a coefficient of expansion composite k = 2 which corresponds to about a range of 95% confidence level.

CONCLUSIONS

The test were made with the DR 2800 spectrophotometer and sulphate cuvette tests in range 150.0 – 900.0 mg/L and reference certified material (sulphate standard solution) traceable to NIST.

Molecular spectrometric method for determining sulphate in industrial wastewater is linear and accurately.

A basic requirement of the expression of uncertainty in measurement is the use of a model for the evaluation of uncertainty. The model should include all quantities that can contribute significantly to the uncertainty associated with the test result.

The uncertainty in measurement is based on sound theory and provides a consistent and transferable evaluation of measurement uncertainty and supports metrological traceability.

In the followings I present several advantages linked with the evaluation of measurement uncertainty in testing:

- measurement uncertainty assists in a quantitative manner in important issues such as risk control and the credibility of test results;
- the evaluation of measurement uncertainty provides starting points for optimizing the test procedures through a better understanding of the test process;
- calibration costs can be reduced if it can be shown from the evaluation that particular influence quantities do not substantially contribute to the uncertainty.

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