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Uncertainty in spectrophotometric analysis—“Error propagation break up”, a novel statistical method for uncertainty management

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ABSTRACT

In this work, is given the Combined Standard Uncertainty (CSU) calculation procedure, which can be applied in spectrophotometric measurements. For the assessment of the computations, different approaches are discussed, such as the contribution to the Combined Standard Uncertainty of the reproducibility, the repeatability, the total bias, the calibration curve, and the type of the measurand. Results of inter-laboratory measurements confirmed the assumptions. For the minimization of the errors propagation a controlled experimental procedure was applied by this laboratory, called “errors propagation break-up” (ERBs). The uncertainty of sample concentration from a reference curve dominates the Combined Standard Uncertainty. The contribution of the method and the laboratory bias (total bias) to the CSU is insignificant under controlled conditions of a measurement. This work develops a simple methodology that can be utilized to evaluate the uncertainty and errors control on routine methods used both by academic researchers or the industrial sector.

1. Introduction

The result of a measurement is only an estimation of the measurand value. The measured value (μ) is accepted only when it is accompanied by a quantitative statement of its uncertainty (U) and is expressed as ($\mu \pm U$).

The Uncertainty (U) is a parameter related to the results of a measurement and indicates the distribution of the values attributed to measured quantity. It is the combination of the uncertainties which are due to random phenomena (type A estimation) and systematic phenomena (type B estimation) and is used by the term Combined Standard Uncertainty (CSU). For the uncertainty estimation the steps involved are: (a) the measurand specification, (b) the uncertainty sources identification, (c) the uncertainty components quantification, and (d) the CSU calculation.

Managing uncertainty is a basic effort in analytical chemistry laboratories. Since the quality of a measurement is expressed as its uncertainty, calculating the uncertainty is a prerequisite for a testing laboratory to gain accreditation. An analytical chemistry research laboratory shall apply procedures for estimating uncertainty of its measurements. Uncertainty components identification and reasonable estimation are necessary for a rigorous and statistically valid calculation of the measurement uncertainty [1]. However, a lot of analysts and laboratories do not know how to quantify neither the sources of uncertainty nor Combined Standard Uncertainty. What seems to be missing from the literature are simple ways for quantifying the uncertainty components and the Combined Standard Uncertainty.

In this study a simple methodology for the quantification of uncertainty components, the calculation of Combined Standard Uncertainty for spectrophotometric measurements and CSU management by applying a controlled experimental procedure, is presented.

2. Material and methods

2.1. General

The Combined Standard Uncertainty (CSU) is calculated according to the error propagation law [2]. The methodology suggested by literature [3,4] was used to construct a computation procedure of the CSU for spectrophotometric measurement. To achieve that, all the uncertainty sources were listed and was shown how they relate to each other and was indicated their influence on the uncertainty of the result. This helps to avoid double counting of sources (Table 1). Not all the components have a significant contribution to the CSU, in practice only a small number is taken into account. The uncertainties for each of the chosen components were expressed separately by a relevant equation. All these individual uncertainty equations were used in the final CSU mathematical expression.

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Table 1
Uncertainty components in spectrophotometric measurements.

Uncertainty components	Uncertainty error sources	Data sources
1. Sample volume	Filling Temperature Tolerance Reading	Glassware calibration certificate Measurements Literature data
2. Sample concentration	Calibration curve	Measurements
3. Apparatus (spectrophotometer UV–vis)	Apparatus technical data (included in sample concentration uncertainty from calibration curve)	Spectrophotometer calibration certificate
4. Random phenomena (type A uncertainty)	Repeatability Reproducibility	Measurements
5. Weighing	Balance technical data (included in standard solution preparation uncertainty)	Balance calibration certificate
6. Standard Solutions preparation	Weigh, dilutions (included in sample concentration uncertainty from calibration curve, in type A uncertainty and in bias)	Measurements
7. Reagents purity	included in standard solution preparation uncertainty	Reagent certificates of analysis
8. Method and laboratory total bias	Standard solutions	Certificates of analysis Measurements

This mathematical expression was applied in nitrites and nitrates spectrophotometer measurements used in water analysis.

The experimental measurements contributed decisively:

- in the confirmation of the uncertainty components choice;
- in the verification of mathematical expressions; and
- in improving the way of the CSU management.

The CSU management, proposed in this study, is aiming to error propagation break-up, to rapid error identification, to simplifying the CSU calculation and to application of a stable inter-laboratory quality control system (QC).

The algorithm for the evaluations of the Combined Standard Uncertainty by the errors propagation break-up method has been implemented in an user friendly excel file which is available from our laboratory.

2.2. Identification of uncertainty components in spectrophotometric measurements

The Combined Standard Uncertainty components of the spectrophotometric measurement are presented in Table 1.

Because of the in-house or field sampling do not form part of the specified procedure; the components of uncertainty related to the sampling procedure are not included in this calculation procedure.

2.3. Calculation of uncertainty components

The measurement procedure is considered as a series of discrete operations. Each of them may be assessed separately to obtain estimates of uncertainty associated with it.

So, as is described below, the separate uncertainties for individual or groups of components were estimated and expressed as standard uncertainty that contributed to the CSU calculation.

The apparatus (spectrophotometer) uncertainty and the weighing uncertainty are included (Table 1) in the concentration uncertainty from the calibration curve and in the standard solution preparation uncertainty, respectively, and will not be taken account at the CSU estimation.

In the following is presented the calculation of the components uncertainties.

2.3.1. Sample volume uncertainty

The volume of the solution contained in the volumetric flask is subjected to three major sources of uncertainty [5]:

a. the volumetric glassware uncertainty (tolerance);
b. the repeatability (glassware filling uncertainty, u_R); and
c. the uncertainty caused by the volume difference between the glassware calibration temperature (20 °C) and the solution temperature, $u(t) = \Delta V/\sqrt{3}$.

By a, b, c, the combined volume uncertainty, $u(v)$, is calculated in Eq. (1):

$$u(v) = \sqrt{\left(\frac{\text{tol}}{\sqrt{3}}\right)^2 + [u(R)]^2 + \left(\frac{\Delta V}{\sqrt{3}}\right)^2} \tag{1}$$

However, the glassware filling uncertainty [6] is included in the measurement of the repeatability or/and the reproducibility, as well as at the standard solution preparation uncertainty and it will not be taken account at the volume uncertainty estimation. So the final relation is expressed in Eq. (2):

$$u(v) = \sqrt{\left(\frac{\text{tol}}{\sqrt{3}}\right)^2 + \left(\frac{\Delta V}{\sqrt{3}}\right)^2} \tag{2}$$

2.3.2. Uncertainty of sample concentration

The sample concentration uncertainty in spectrophotometric measurements is expressed as concentration uncertainty from the calibration curve and is given in Eq. (3) [2]. A short description of the different calculation steps is given:

$$u(c_0)\frac{S}{B_1} \times \sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(c_0 - \bar{c})^2}{S_{XX}}} \tag{3}$$

$$\text{where} : S = \sqrt{\frac{\sum_{j=1}^{n}[A_j - (B_0 + B_1 \cdot c_j)]^2}{n-2}} \tag{4}$$

S_{XX} is calculated from Eq. (5):

$$S_{XX} = \sqrt{\sum_{j=1}^{n}(c_j - \bar{c})^2} \tag{5}$$

The term $B_0 + B_1 \cdot c_j$ expresses the absorption value (A) deriving from the regression line equation having as c_i the concentration of a known standard solution.

A_j: jth measurement of the absorbance of the ith calibration standard
i: index for the number of calibration standards
j: index for the number of measurement replicates for each calibration standard
B_1: slope
p: number of measurements to determine the concentration of unknown sample, c_0
n: number of solution standard measurements for the calibration curve preparation (i, j)
c_0: unknown sample concentration
B_0: intercept
$\bar{c}$: mean value of the calibration standards concentration (for n measurements)

Table 2
Concentration of standards used for constructing the calibration curve.

Parameter	1st standard conc.	2nd standard conc.	3rd standard conc.	4th standard conc.	5th standard conc.	6th standard conc.
Nitrite ($mgNO_2{}^- L^{-1}$)	0.0	0.0328	0.06569	0.16423	0.32846	0.49269
Nitrate ($mgNO_3{}^- L^{-1}$)	0.0	0.88543	1.7709	4.4272	8.8543	13.2814

S: The residual standard deviation or standard deviation about the regression line, which expresses the distribution of the measurements around the regression line and contributes to the calculation of random errors. It measures the standard deviation between the differences of the experimental and theoretical values.

2.3.3. *Type A uncertainty*

The estimation of type A uncertainty [4] was performed under repeatability and reproducibility conditions, as following:

(a) Calculation under repeatability conditions from n determinations of the measurand in the same day. The relative standard deviation (RSDr) was considered as the typical statistical uncertainty of type A.
(b) Calculation under inter-laboratory reproducibility conditions, by n determinations of the measurand at m different days. The type A uncertainty was expressed as the relative standard deviation of the total average value.

The use of one of the above type A uncertainty expressions did not cause any important differentiation to the total uncertainty calculation, as was confirmed by the relevant intra- and inter-laboratory measurements (Section 3).

2.3.4. *Standard solutions preparation uncertainty*

The preparation uncertainty of standard solutions is calculated separately and depends on the weigh, the dissolution and the reagents' purity.

In the standard solutions preparation uncertainty participates:

a. the reagent purity uncertainty, $u(P) = (1 - P)/\sqrt{3}$;
b. the mass uncertainty, $u(m) = \sqrt{2(u_{m,\text{gross}})^2}$; and
c. the volume uncertainty, Eq. (2).

By a, b, c, the standard solutions preparation uncertainty, $u(c)$, is calculated in Eq. (6):

$$u(c) = c\sqrt{\left(\frac{u(P)}{P}\right)^2 + \left(\frac{u(m)}{m}\right)^2 + \left(\frac{u(V)}{V}\right)^2} \quad (6)$$

When dilution from a stock solution is needed, Eq. (6) is transformed to Eq. (7):

$$u(c)_{\text{final}} = c_{\text{final}}\sqrt{\left(\frac{u(V_{\text{final}})}{V_{\text{final}}}\right)^2 + \left(\frac{u(c_{\text{initial}})}{c_{\text{initial}}}\right)^2 + \left(\frac{u(V_{\text{initial}})}{V_{\text{initial}}}\right)^2} \quad (7)$$

Table 3
Comparison of sample concentration uncertainty to the correlation coefficient of different calibration curves for the parameter of $NO_2{}^-$ at 16.425 $\mu g\,L^{-1}$ concentration.

Calibration curve	Correlation coefficient	Sample concentration uncertainty at 16.425 $\mu g\,L^{-1}$ $NO_2{}^-$
1	0.996	$\pm 21.19\ \mu g\,L^{-1}$
2	0.999611	$\pm 12.46\ \mu g\,L^{-1}$
3	0.999717	$\pm 2.89\ \mu g\,L^{-1}$
4	0.9998	$\pm 2.125\ \mu g\,L^{-1}$
5	0.999883	$\pm 1.74\ \mu g\,L^{-1}$
6	0.9999	$\pm 1.525\ \mu g\,L^{-1}$

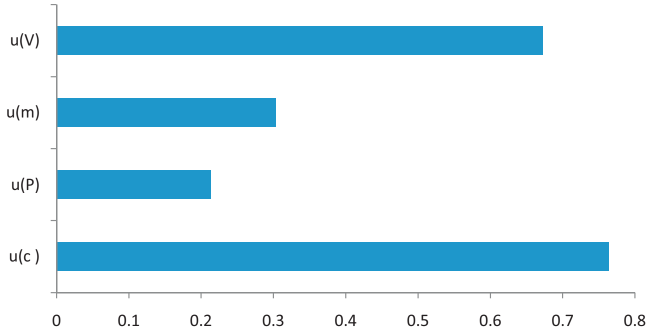

Fig. 1. Contribution of the mass weigh $u(m)$, solution volume $u(v)$ and reagents' purity $u(p)$, at the standard solution preparation uncertainty, $u(c)$, of 1232 $NaNO_2$ mg L^{-1}(stock solution concentration).

The volume uncertainty has the major contribution in the standard solution preparation uncertainty as is shown in Fig. 1.

Because this uncertainty is included in the uncertainty of concentration from the calibration curve as well as in the repeatability/reproducibility, it is not taken into account in calculating Combined Standard Uncertainty (CSU). Nevertheless, the presentation of this uncertainty calculation was necessary, since the standard solution preparation is a discrete operation in the application of a controlled measurement procedure and therefore, in the uncertainty management.

2.3.5. *Method and laboratory total bias*

Method and laboratory total bias [7] is estimated by the analysis of the Certificated Reference Material (CRM) under repeatability conditions. It is the combination of the standard deviation of the mean for n determinations and of the CRM true standard uncertainty value given in its certificate of analysis (at level of confidence 95%). The total bias [8] is expressed in Eq. (8):

$$u_{\text{bias}} = \sqrt{u_{\text{CRM}}^2 + \frac{S_r^2}{n}} \quad (8)$$

where $u_{\text{CRM}} = \alpha/2$ (α = certificate value); S_r, standard deviation.

Under controlled conditions of the method application procedure, the total bias is insignificant compared to the combined uncertainty and it can be neglected in the total uncertainty calculation. It was confirmed by repeated inter-laboratory measurements (Table 4).

2.4. *Combined Standard Uncertainty calculation*

Taking into account the uncertainty components mentioned, the Combined Standard Uncertainty of a spectrophotometric concentration measurement, is expressed by Eq. (9).

The contribution of the sensitivity coefficient has been included at the component uncertainties estimation and was considered equal to one [9].

$$u(c) = c \times \sqrt{\left(\frac{u(\text{bias})}{c_0}\right)^2 + \left(\frac{u(m)}{m}\right)^2 + \left(\frac{u(V_{\text{sample}})}{V_{\text{sample}}}\right)^2 + (\text{RSDr})^2 + \left(\frac{u(c_0)}{c_0}\right)^2} \quad (9)$$

Table 4
Contribution of repeatability, reproducibility and total bias to the CSU for nitrite spectrophotometric concentration determination (St.Method 4500-NO_2^- B).

Spectrophotometer[a] HITACHI UV–vis 2001	Calibration curve: 1/19-02-06 $y = 0.000905797C - 0.0027953$ Correlation coef. 0.9999		Calibration curve: 2/7-03-08 $y = 0.000884173C + 0.00064633$ Correlation coef. 0.99999		Calibration curve: 3/23-011-09 $y = 0.00093457943C - 0.00062336$ Correlation coef. 0.9999	
	Measured concentration 65.23 μg L^{-1} True value: 65.69 ± 0.8 μg L^{-1}	Measured concentration 166.40 μg L^{-1} True value: 164.23 ± 1.6 μg L^{-1}	Measured concentration 65.37 μg L^{-1} True value: 65.48 ± 0.8 μg L^{-1}	Measured concentration 327.42 μg L^{-1} True value: 327.40 ± 3 μg L^{-1}	Measured concentration 65.55 μg L^{-1} True value: 65.69 ± 0.8 μg L^{-1}	Measured concentration 168.29 μg L^{-1} True value: 164.23 ± 1.6 μg L^{-1}
Combined Standard Uncertainty (calculated by using repeatability as type A unc.)	1.505	1.48	3.944	4.029	1.211	1.250
%Deviation (in comparison to the measured concentration)	2.3%	0.9%	6.033%	1.23%	1.85%	0.74%
Combined Standard Uncertainty (calculated by using reproducibility as type A unc.)	1.536		3.945		1.328	1.193
%Deviation (in comparison to the measured concentration)	2.35%		6.036%		1.82%	0.71%
Combined Standard Uncertainty with bias (calculated by using repeatability as type A unc.)	1.567		3.969		1.289	1.540
%Deviation (in comparison to the measured concentration)	2.40%		6.073%		1.97%	0.915%
Sample Concentration Uncertainty from the calibration curve	1.494	1.46	3.938	4.010	1.194	1.170

[a] For the Perkin Elmer spectrophotometer: with curve equation $y = 0.000884215C + 0.001287$, and correlation coef. 0.999971, for measured concentration 65.85 μL^{-1} and true value 65.48 ± 0.8 μL^{-1}, the CSU of the measurement was similar to the Uncertainty of Sample Concentration Uncertainty from the calibration curve and they were 1.14 μL^{-1} or 1.73% and 1.113 μL^{-1} relatively.

Table 5
Contribution of repeatability and reproducibility and total bias to the CSU for the nitrate spectrophotometric concentration determination (St.Method 4500-NO_3^- B).

Spectrophotometer HITACHI UV–vis 2001	Calibration curve: 1/06-02-06 $y = 0.054914881C + 0.00274574409$ Correlation coef. 0.9999		Calibration curve: 2/10-03-08 $y = 0.059136605C + 0.0019515$ Correlation coef. 0.99999		Calibration curve: 3/24-03-09 $y = 0.056116722C + 0.004657687$ Correlation coef. 1	
	Measured concentration: 8.80 mg L^{-1} True value: 8.854 ± 0.037 mg L^{-1}	Measured concentration: 13.12 mg L^{-1} True value: 13.280 ± 0.056 mg L^{-1}	Measured concentration: 8.90 mg L^{-1} True value: 8.854 ± 0.037 mg L^{-1}	Measured concentration: 13.81 mg L^{-1} True value: 13.280 ± 0.056 mg L^{-1}	Measured concentration: 8.37 mg L^{-1} True value: 8.854 ± 0.037 mg L^{-1}	Measured concentration: 12.73 mg L^{-1} True value: 13.281 ± 0.056 mg L^{-1}
Combined Standard Uncertainty (calculated by using repeatability as type A unc.)	0.0444	0.0463	0.0311	0.0313	0.0478	0.0511
%Deviation (in comparison to the measured concentration)	0.50	0.35	0.35	0.24	0.57	0.38
Combined Standard Uncertainty (calculated by using reproducibility as type A unc.)	0.0463		0.0420		0.0507	0.0467
%Deviation (in comparison to the measured concentration)	0.53		0.47		0.60	0.56
Combined Standard Uncertainty with bias (calculated by using repeatability as type A unc.)	0.0563		0.0385		0.0632	0.0582
%Deviation (in comparison to the measured concentration)	0.64		0.433		0.64	0.46
Sample Concentration Uncertainty from the Calibration Curve	0.0420	0.0421	0.0272	0.0284	0.0461	0.0500

Table 6
Contribution of the Repeatability and reproducibility and total bias to the CSU at the Spectrophotometric estimation of nitrate (St.Method 4500-NO_3^- B).

Spectrophotometer Perkin Elmer Lamda 40	Calibration curve 1/06-02-06 $y = 0.05746736x + 0.003986$ Correlation coef. 0.999963		Calibration curve 3/24-03-08 $y = 0.05671215x \pm 0.006356$ Correlation coef. 0.999905		Calibration curve 4/10-03-09 $y = 0.05951166x + 0.003829$ Correlation coef. 0.999968	
	Measured concentration: 8.858 mg L^{-1} True value: 8.854 ± 0.038 mg L^{-1}	Measured concentration: 13.48 mg L^{-1} True value: 13.281 ± 0.057 mg L^{-1}	Measured concentration: 8.60 mg L^{-1} True value: 8.854 ± 0.037 mg L^{-1}	Measured concentration: 12.730 mg L^{-1} True value: 13.281 ± 0.056 mg L^{-1}	Measured concentration: 8.850 mg L^{-1} True value: 8.854 ± 0.037 mg L^{-1}	Measured concentration: 13.335 mg L^{-1} True value: 13.281 ± 0.056 mg L^{-1}
Combined Standard Uncertainty (calculated by using repeatability as type A unc.)	0.0508	0.0505	0.0706	0.0737	0.0410	0.0435
%Deviation (in comparison to the measured concentration)	0.57	0.37	0.82	0.54	0.46	0.33
Combined Standard Uncertainty (calculated by using reproducibility as type A unc.)	0.0511					
%Deviation (in comparison to the measured concentration)	0.57					
Combined Standard Uncertainty with bias (calculated by using repeatability as type A unc.)	0.0580		0.0744		0.0453	
%Deviation (in comparison to the measured concentration)	0.65		0.86		0.51	
Sample Concentration Uncertainty from the calibration curve	0.0459	0.0477	0.0687	0.0716	0.0400	0.0415

where $u(v)$, volume uncertainty; RSDr, type A uncertainty (expressed by the repeatability or the reproducibility); $u(c_0)$, sample measurement concentration uncertainty from calibration curve; $u(m)$, sample weighing uncertainty (for solid samples, Section 2.3.5); and $u(\text{bias})$, method and laboratory total bias.

If the contribution of the method and laboratory total bias uncertainty is insignificant, is not taken into account in the Combined Standard Uncertainty calculation [6], as it is explained in Section 3, and Eq. (9) is reformed to Eq. (10):

$$u(c) = c \times \sqrt{\left(\frac{u(V_{\text{sample}})}{V_{\text{sample}}}\right)^2 + (\text{RSDr})^2 + \left(\frac{u(c_0)}{c_0}\right)^2} \tag{10}$$

The expanded uncertainty, for a coverage factor k, is evaluated from the relation: $U = k \cdot U(c)$. For an approximate level of confidence of 95%, $k = 2$ and $U = 2 \times u(c)$.

3. Results and discussion

The above procedure of Combined Standard Uncertainty (CSU) calculation was applied, in the framework of our research, in nitrites and nitrates spectrophotometer measurements used in water analysis.

For the determination of nitrite the St.Method 4500-NO_2^- B[1] is used. This is spectrophotometric method and the ion is determined through the formation of reddish purple azo dye produced by using certain reagents. The method is suitable for concentrations of 16.423 μg L^{-1} to 3285 μg L^{-1} NO_2^- and has very little interference [10].

For the determination of nitrate the St.Method 4500-NO_3^- B[1] is used. This method is suitable for concentrations of 0 mg L^{-1} to 48.717 mg L^{-1} NO_3^-. It is a simple spectrophotometric method, suitable for waters with low organic matter, and the measurement of UV absorption at 220 nm enables the rapid determination of the ion.

For the measurements, certified Hittachi UV–vis 2001 and Perkin Elmer Lamda 40 spectrophotometers as well as certified balance and glasswear were used.

The following experimental procedure was applied:

- Preparation of six calibration standard solutions with the use of high purity reagents and calculation of their concentration uncertainty (Section 2.3.4). The concentrations of the solutions are given in Table 2.
- Construction of spectrophotometer calibration curve for each parameter.
- Calculation of sample concentration uncertainty (calibration curve concentration uncertainty). Three different concentrations of nitrites and nitrates standard solutions were used as samples (Tables 4–6). The average of three measurements for each concentration was used in this uncertainty calculation.
- Calculation of type A uncertainty from repeatability and reproducibility at three selected concentrations [11].
- Method and laboratory bias calculation (Section 2.3.5).
- CSU calculation with repeatability and reproducibility separately.
- CSU calculation with bias and repeatability.

For achieving the CSU management, a number of calibration curves were constructed and the variation of the

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[1] Standard Method for Water & Wastewater Analysis, 21st Edition 2005.

sample concentration uncertainty in comparison to the correlation coefficient (R^2) of each curve was studied. This is presented in Table 3 for the low detection limit of the nitrite determination method.

The use of a curve with correlation coefficient 0.9999 had the more acceptable uncertainty. Calibration curves with correlation coefficient <0.9998 were rejected, because of the increased sample concentration uncertainty especially at low concentrations (Table 3).

The preparation of the standard solutions had significant contribution in the construction of the calibration curves and consequently in the estimation of sample concentration uncertainty obtained from them (Fig. 1).

Therefore, considering a measurement procedure as a series of discrete operations each of which may be assessed separately and in the frame of applying a controlled experimental procedure, this laboratory calculated separately the concentration uncertainties of the standard solutions as is described in Section 2.3.4. Only standard solutions with uncertainty ≤1–2% were used for the construction of the calibration curves and for the internal quality control applied. The use of such standard solutions contributed in reducing the type A uncertainty of this study in which standard solutions were used as samples.

This procedure was called “errors propagation break-up (ERBs)” by this laboratory. Control charts for the internal quality control were used.

This laboratory examined also comparatively the contribution of the repeatability and reproducibility at the CSU, using data of measurements for the two parameters at the existing two different spectrophotometers and at different reference curves for a period of 3 years. By the application of the ERB method, the use of either the repeatability or the reproducibility in the total uncertainty calculation, did not altered significantly the results and for this reason the repeatability was preferred to use in the calculations of the total uncertainty (Tables 4–6).

The CSU for the same parameter and the same concentration at the two spectrophotometers did not either differed significantly (Tables 4–6). The differences were due to the technical characteristics of the two instruments and to the calibration curve, with the precondition that the uncertainty of the standard solutions was controlled and the calibration curve used had correlation coefficient at least 0.9999.

The calculation of the method and the laboratory total bias showed that its contribution to the total measurement uncertainty was less than 0.2%. In Tables 4 and 5 the calculation of the total uncertainty with and without the total bias is shown.

From Tables 4–6 results that the CSU is dominated by the sample concentration uncertainty of the calibration curve even for different concentrations [12].

The results of the inter-laboratory measurements confirmed the assumptions and verified the calculations of the Combined Standard Uncertainty (for 95% confidence level).

4. Conclusions

A method of achieving error propagation break up (ERB) was invented and applied in the present work simplifying the CSU calculation and the application of a stable inter-laboratory quality control system (QC). This major aim of the CSU management for chemical analysis laboratories was achieved only by taking few simple precautions: The use of standard solutions with uncertainties ≤1–2% on the reference curve construction and in the internal quality control bringing about error reduction/control. By the application of the ERB, the repeatability could be used in the calculations of the total uncertainty (Table 2).

In addition, the following measurement improvements were made by present work.

The uncertainty of sample concentration from a reference curve contributes mostly to the Combined Standard Uncertainty. The use of calibration curves with correlation coefficient values ca. 0.9999 is preferable for spectophotometric methods and such calibration curves can be achieved by the ERB application. Also the CSU of measurement referring to the same parameter and the same concentration does not vary considerably when using different calibration curves with a correlation factor of 0.9999. The contribution of the method and the laboratory bias (total bias) to the CSU of measurement is insignificant under controlled conditions of a measurement.

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