Uncertainty of measurement in spectrometric analysis: A case study

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ABSTRACT

The methods of spectrometric analysis belong to a group of measurement methods that are used for their simplicity, speed of analysis, and large selectivity to solve various problems of analytes. Accuracy and reliability of any chemical analysis largely depend on the way the analyzed sample is prepared.

The objective of this work is to evaluate the uncertainty and metrological reliability of material concentration measurement considering sample preparation and chemical–physical transformation of spectrometric analysis.

Metrological properties of spectrophotometric method have been evaluated experimentally and influence of analysis conditions on the measurement result was described.

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1. Introduction

Spectrometric analysis is a widely used measurement method for qualitative and quantitative analysis.

Qualitative evaluation of spectrometric analysis result comprises influence of all possible sources and factors, including sample preparation technique, measurement principle, analyte concentration, matrix properties, etc. The measurement uncertainty depends upon all mentioned parameters [1].

Technical specifications of measuring device play important role in any measurement. Quite often producers as well as users are proud of high accuracy of their measuring instruments. However, while evaluating the results of spectrometric analysis, sample preparation procedures are considered insufficient. It takes place in spite of the fact that the newest, fast, automated, needed the minimum amount of sample and chemical reagents technology, and measuring equipment providing high repeatability are applied for analysis.

Uncertainty evaluation is not a simple task because of the peculiarities of chemical measurements. The chemical parameter always is transformed into physical parameter and only then this value is measured. Different sample procedures are carried out and they can influence measurement result by chemical–physical transformation. The sample is prepared mechanically and chemically during sample preparation process. Mostly these procedures are not assessed in practice.

Numerous authors have published on the topic of uncertainty evaluation of chemical measurements results. Also some guides are published on uncertainty estimation [2,3]. The material reported in journal articles is rather general because of every chemical measurement is exclusively specific. So uncertainty cannot be excluded from the working practices. It is very important to evaluate all possible parameters that have influence on uncertainty and all of them have to be taken into account.

This paper discusses qualitative evaluation of chemical–physical transformation and its impact on uncertainty of measurement results in spectrometric analysis.

The measurement of the concentration of iron in a water sample using spectrophotometric method was chosen to show experimentally the influence of chemical–physical transformation conditions on the measurement uncertainty.

The physical basis of spectrophotometric measurements is well known [4]. Uncertainty sources for measuring instrument (repeatability of spectrophotometer reading,

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spectrophotometer drift, stray light, etc.) are known as well [5–7]. "Classical" uncertainty sources (weighing, volumetric operations, etc.) are estimated enough [7–9]. Measurement uncertainty associated with linear least squares calibration is estimated [2,7–9]. However, in evaluation of uncertainty of measurement results in routine laboratory attention that is paid to chemical–physical transformation conditions (sample pH, content of chemical reagent, exposure time of prepared sample, etc.) are insufficient.

2. Peculiarities of chemical measurements

Chemical analysis differs from other measurements. There is no way to measure the "true value" of anything. The best we can do in a chemical analysis is to apply carefully a technique that experience tells us is reliable. If the results of measuring the same quantity by different methods agree with each other, then we become confident that the results are near the "true" value. But sample preparation procedures always contribute their own input to measurement result.

Three main stages that have to be evaluated are required for chemical analysis:

1. Transformation of chemical parameter into physical parameter (all sample preparation procedures, auxiliary reactions, etc.).
2. Measurement of transformed parameter.
3. Evaluation of the result including uncertainty.

2.1. Chemical–physical transformation in spectrometric analysis

Spectrometric analysis involves series of methods. Parameters that have impact on the uncertainty of measurement result for various spectrometric methods are different because measured parameter differs as well. External conditions and error of measuring device have impact on every analysis. But it is not as strong as chemical–physical transformation.

Chemical–physical transformation stage comprises all mechanical and chemical sample preparation procedures. During the transformation sample is prepared in such a way that it should be a possibility to measure physical parameter that is directly related with analyte concentration.

All methods of chemical instrumental analysis are based upon receiving of analytical signal and measuring its intensity, i.e. upon chemical and physical characteristics of any material [10]. Fig. 1 illustrates procedures which have influence to uncertainty of measured concentration of analyte.

Sample preparation procedures comprise all treatments or procedures from sample collection (place the sample is collected, expected concentration of analyte), storing (temperature, time-span till analysis), transportation conditions (vessels, duration, temperature, etc.), sample preparation for analysis (all mechanical treatments applied to the sample in order to convert it to a laboratory sample form) to
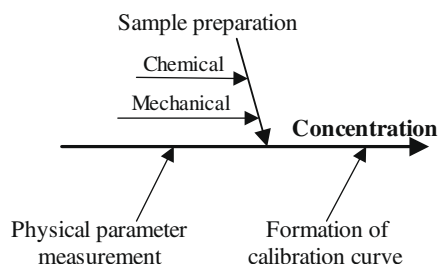

Fig. 1. Diagram of procedures affecting the result.

measurement procedures when the final expression of the analysis is obtained by measuring a certain physical parameter. A series of preparation procedures must be performed before measuring the concentration of analyte. Amount and complexity of operations depend upon the chosen method and aim of analysis [11].

Sample preparation is still one of the most time-consuming, labor-intensive, and error-prone steps in the analysis cycle [12]. The selection of a sample preparation method is dependent upon several factors such as:

1. The analyte(s).
2. The analyte concentration level(s).
3. The sample matrix.
4. The instrumental measurement technique.
5. The required sample size.

Selected method will require specific sample preparation equipment and reagents.

So, to solve a particular task an appropriate method of spectrometric analysis, where the quantity of analyte is determined by measurement of various material parameters, such as absorption, emission, mass-to-charge ratio, etc., is used [4].

2.1.1. Mechanical sample preparation

Any treatments or procedures applied to the sample in order to convert it in to a form suitable for the chosen analytical method are attributed to sample preparation [13]. Different methods require of conformable sample preparation but there can be find common aims and preparation procedures for some spectrometric analysis methods (atomic absorption and atomic emission spectroscopy, spectrophotometry, infrared spectroscopy). At first analyte has to be converted into a physical/chemical form compatible with chosen method of analysis (most analytical methods do not work well for solid or inhomogeneous samples) also sample for analysis must be as pure as possible (remove the maximum amount of extraneous material from the sample so that it would not interfere with subsequent measurement of the analyte of interest). Table 1 shows mechanical sample preparation procedures for different aggregative states for different spectrometric analysis methods.

2.1.2. Chemical sample preparation

The uncertainty of the chemical sample preparation is the component of the combined uncertainty of the result.

Table 1
Mechanical sample preparation procedures for different aggregation states in spectrometric analysis.

Method of analysis	Solid sample preparation for analysis	Liquid sample preparation for analysis	Gaseous sample preparation for analysis
Atomic emission spectroscopy	Heating, dissolution, impurity separation, evaporation	Preconcentration or dilution, impurities separation	Impurities separation, drying
Atomic absorption spectroscopy	Drying, homogenization, impurities separation, milling, sieving, extraction, filtration, atomization	Impurities separation, filtration, preconcentration or dilution, atomization	–
Spectrophotometry	Extraction, drying, preconcentration, sorption, precipitation, impurities separation, filtration, dissolution	Preconcentration or dilution, impurities separation	–
IR spectrometry	Milling, dissolution, suspension, pressing	Dehydration	Filtration
Mass spectroscopy	Milling, evaporation	Direct testing	Direct testing

Unfortunately this uncertainty is mostly forgotten or ignored and this then leads to an optimistic underestimation of the uncertainty of the resulting measurement. It is the purpose of modern uncertainty evaluation that the uncertainty associated with the chemical preparation of the sample be a part of the uncertainty budget of the final result.

The influence of chemical sample preparation and external factors that can affect the result of spectrometric analysis on measurement of analyte concentration is presented in Table 2. Also there is given physical parameter, which has to be measured in different methods. Data in Table 2 show that temperature of test sample is the most important factor for evaluation of results of above listed analysis methods. Significance of other components depends upon specific measurement method.

3. Uncertainty sources of spectrophotometric analysis

By force of spectrometric analysis simplicity, speed of analysis, and large selectivity, these methods are used to solve many problems of different analytes. Advanced equipment appears to be simple, but the relation between concentration of analyte in material and the signal that has been registered is rather complicated. For this reason the research of metrological characteristics becomes more complicated. In addition, an analyte signal usually depends not only on analyte concentration, but on the concentration of all other materials, material structure, sample form, environmental conditions. Furthermore, using any measurement instrument, accuracy and reliability of chemical analysis depend largely on the way the analyzed sample is prepared, because preparation mechanism is specific in chemical measurements.

For the evaluation of measurement result it is necessary to analyze all possible factors [14] that could influence the result.

Method of spectrophotometric analysis is commonly used group of measurement methods in laboratories of chemical analysis. However, metrological assessment of photometric measurement results is insufficient.

A diagram for evaluation of uncertainty for results obtained from the spectrophotometric analysis is provided in Fig. 2.

It shows that the tested object and the measuring instrument cannot be separated during the evaluation process.

According to the diagram, in order to evaluate a measurement result thoroughly, all the factors that can influence the measurement results have to be analyzed.

These factors are: technical characteristics of measuring instrument, measurement conditions, measurement matrix, sample preparation procedures, the interaction of a test item and measuring instrument, restrictions of the measurement method used, reading uncertainty, and data processing. Only after the close analysis of the above-mentioned factors and the evaluation of additional conditions of a certain case, the uncertainty as accurate estimate of the measurement result can be properly provided.

4. Methods and results

4.1. Elaboration of method and identification of uncertainty sources

The measurement of the concentration of iron in a water sample was chosen for the analysis of spectrophotometric method.

The measurement of iron content by spectrophotometric method was carried out using a calibration curve.

The absorbance of standard solutions $c_1 - c_n$ was measured and the values $A_1 - A_n$ were obtained. In this case the concentration is calculated from the data obtained by the evaluation of regression equation parameters of a calibration curve and is given by following formula:

$$A_i = c_i \cdot B_1 + B_0 \tag{1}$$

where c_i is content of analyte in the sample, calculated from a calibration curve, mg/l; A_i, measured absorption of the test sample; B_1, slope of the calibration curve; and B_0 is intercept of the calibration curve.

The slope of the linear least squares calibration curve B_1 and intercept of the prepared calibration curve B_0 are calculated from the following equations:
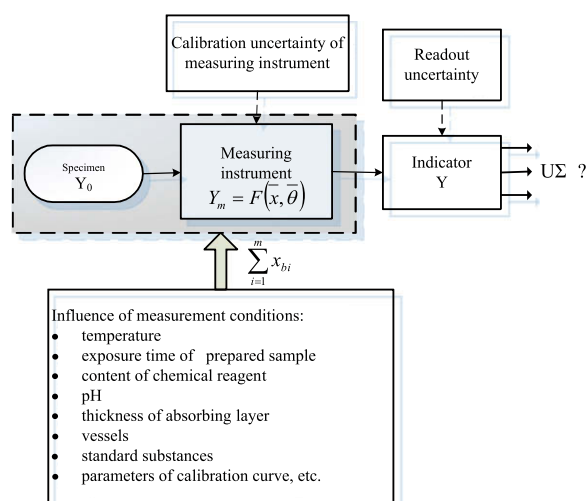
$$B_1 = \frac{\sum_{i=1}^{n} c_i A_i - n\bar{c}\bar{A}}{\sum_{i=1}^{n} c_i^2 - n\bar{c}^2} \tag{2}$$

$$B_0 = \frac{\bar{A}\sum_i \bar{c}_i^2 - \bar{c}\sum_{i=1}^{n} c_i A_i}{\sum_{i=1}^{n} c_i^2 - n\bar{c}^2} \tag{3}$$

Table 2
Impact of chemical sample preparation and external factors on results of spectrometric analysis.

Methods of spectrometric analysis	Physical parameter corresponding chemical value (concentration)	Uncertainty sources										
		Sample pH	Impact of impurities	Reaction between sample and reagents	Separation of analyte from sample matrix	Amount of chemical reagent	Volume of prepared sample	Dilution	Temperature of test sample	Stability of test sample	Retention time of prepared sample	Pressure
Atomic absorption spectroscopy	Absorption		+	+	+	+	+	+	+		+	
Atomic emission spectroscopy	Emission		+		+	+	+	+	+	+		+[a]
Spectrophotometry	Absorption	+	+	+		+	+	+	+	+	+	
IR spectroscopy	Absorption	+	+	+		+	+	+	+	+	+	
Mass spectroscopy	Mass-to-charge ratio								+			+

[a] Only for gases.

Fig. 2. Diagram for evaluation of uncertainty of spectrophotometric analysis results.

where c_i is the concentration of the ith iron standard solution; A_i, the absorbance of the ith standard solution $(A_1, \ldots, A_i, \ldots, A_n)$; and n is the number of points in the line.

In order to ensure the comparability among the research results, two methods of measurement of iron concentration in water have been chosen:

1. ISO 6332:1988 Water quality – Determination of iron – Spectrometric method using 1,10-phenanthroline (hereinafter method A) [15].
2. Measurement method of iron content using sulfosalicylic acid (hereinafter method B).

A range of determination of the concentration of iron was 0.10–2.00 mg/l. This range covers the area of both chosen methods.

The procedure of measurement of analyte by spectrophotometric method according to the chosen methods consists of some stages:

- sample preparation for measurement,
- measurement of absorption,
- formation of calibration curve,
- evaluation of the result.

These procedures are shown in Fig. 3.

It is very important to evaluate all possible factors that can affect the result solving the question of measurements reliability. For this reason detailed analysis of both chosen methods of measurement of iron concentration in water is accomplished and shown in Fig. 4. There are shown possible factors of chemical–physical transformation in different measurement stages for methods A and B respectively in the right and left sides of Fig. 4.

Analysis of measurement procedure showed that expression (1) of concentration of analyte is not sufficient. In order to evaluate the influence of all the stages of the measurement procedure, the mathematical model for calculation of iron quantity in the water sample has to be supplemented with new correction coefficients:

$$c = c_0 \cdot d \cdot f_r \cdot f_T \cdot f_{pH} \cdot f_t \cdot f_\phi \cdot f_b \cdot f_V \qquad (4)$$

where c is concentration of iron in a test sample, mg/l; c_0, content of iron in a sample calculated from calibration curve, mg/l; d, dilution factor; f_r, correction factor related to the content of chemical reagent; f_T, temperature correction factor; f_{pH}, correction factor related to the solution pH; f_t, correction factor related to the exposure time of prepared solution; f_ϕ, correction factor related to the impurities in the solution; f_b, correction factor related to the thickness of absorption layer; and f_V is correction factor related to the volume of vessels.

In the case of measurement according to this mathematical model, the sources of uncertainty and their influence on the measurement results are given in Fig. 5.

Comparative cycle of measurements was performed in order to evaluate variation of analysis conditions. Analysis in both cases was carried out changing temperature of test sample, exposure time of prepared sample, content of chemical reagent, thickness of absorption layer, pH value of prepared solution, or by adding additional substances as impurities into specimen. The matrix of measurement procedure used for experiments is displayed in Table 3.

Parameters given in Table 3: block letters show the normal value of appropriate parameter and the lower letters
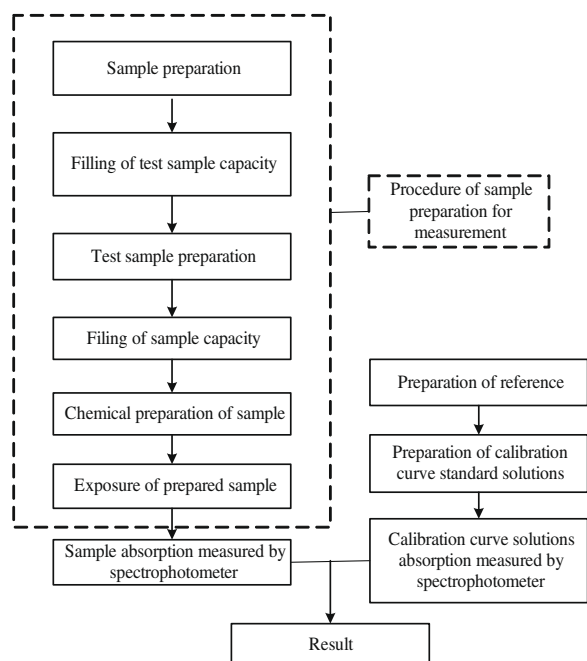
Fig. 3. Procedure for measurement of iron concentration by spectrophotometric method.

show the values that are lower or higher than the normal value.

C/c is the temperature of test solution,
D/d is the exposure time of a prepared sample,
E/e is the amount of a chemical reagent,
F/f is the thickness of an absorption layer,
G/g is the pH value in a test solution,
H/h is the impurities in a test sample.

Limits of experimental conditions of possible variants for iron concentration measurement procedure are shown in Table 4.

Performed experimental researches demonstrated that the deviations of temperature had the most significant influence on the results of both methods in the range of small concentrations (up to 0.5 mg/l). However, deviations of temperature are significant in the range of concentrations over 0.5 mg/l as well, as deviations in particular points can reach up to 20% of the nominal value. Referring to the calculations of experimental results it can be concluded that both methods require including uncertainty component associated with temperature when calculating expanded uncertainty in the range of concentration up to 1 mg/l with test temperature of $20 \pm 3\,°C$.

Deviations in the amount of chemical reagents from the normal value are important for the results of both methods, particularly in the concentration over 1 mg/l, where the deviations of result gain up to 40% of the nominal value. In the range of smaller concentrations, deviations reach up to 10% from the nominal value. Analysis of measurement results showed that the influence of component

associated with chemical reagent differs with the different concentration of a test analyte.

The permissible deviation of thickness of the absorbing layer is (from -0.05 to $+0.05$) and this influence would be not significant for both used methods. More considerable deviations of the absorbing layer make an influence on measurement results over full range of concentrations. Particularly large deviations of results are met in the range of small concentrations.

Deviations of the sample pH from the normal value influences the measurement results of both methods in full range of concentrations. Increased or decreased pH value determinate more intense deviations of the results.

Deviations from the specified conditions do not influence measurement results if measurements are carried out using the method B and exposure time of prepared sample is kept $(-1; +2)$ min. The deviations of exposure time of prepared sample have a significant influence on results of method A in the range of concentration from 1 mg/l up to 2 mg/l, when the exposure time for prepared sample is less than required according to the methodic.

If a solution contains impurities, they reduce the accuracy and reliability of measurement results. Experiments proved that the influence of impurities decreases if the concentration of test material increases. When measuring iron concentration in polluted samples or the ones of unknown composition, it is necessary to include the component of sample pollution in the calculations of combined relative standard uncertainty.

4.2. Evaluation of combined uncertainty and uncertainty components

The uncertainty of measurement of iron content in water sample is calculated by combining all standard uncertainties of input values $c_0, f_r, f_T, f_{pH}, f_t, f_\phi, f_b, f_V$. Uncertainties have been combined using the errors propagation rule [2,3].

Relation between the measurement result and input parameters is expressed by the following model:

$$c = f(x_1, x_2, \ldots \ldots, x_i \ldots \ldots x_N) \qquad (5)$$

where $x_1, \ldots, x_i, \ldots, x_n$ expresses input parameters $(c_0, f_r, f_T, f_{pH}, f_t, f_\phi, f_b, f_V)$.

An uncertainty component due to the calibration curve $u(C_{cal})$ comprises three constituents that depend on the parameters of regression equation, the characteristics of measuring instrument and the concentration of calibration curve standard solutions. The uncertainty of the calibration curve $u(C_{cal})$ is calculated as:

$$u(C_{cal}) = \sqrt{u(C_{cal}, reg)^2 + u(C_{cal}, inst)^2 + u(C_{cal}, st)^2} \qquad (6)$$

where $u(C_{cal}, reg)$ is the standard uncertainty of regression equation for calibration curve; $u(C_{cal}, inst)$, the standard uncertainty of measuring instrument characteristics; and $u(C_{cal}, st)$ is the uncertainty of concentration of standard solutions.

The standard uncertainty of regression equation for calibration curve $u(C_{cal}, reg)$ is calculated by the least squares method:
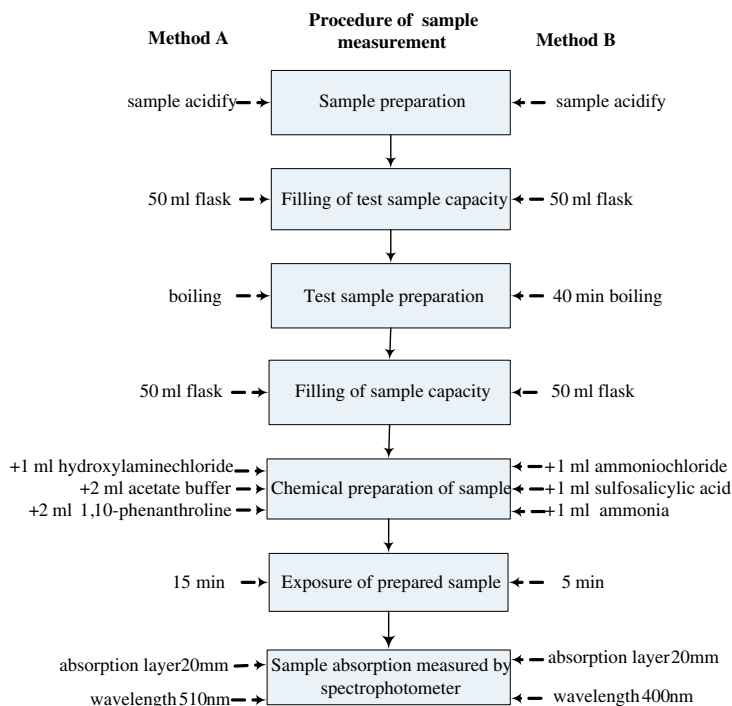
Fig. 4. Procedure for measurement of iron concentration by methods A and B.

$$u(C_{\mathrm{cal}}, \mathrm{reg}) = \frac{s}{B_1} \sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(c_0 - \bar{c})^2}{S}} \qquad (7)$$

$$s = \frac{\sum_{j=1}^{n} \left[A_j - (B_0 + B_1 \cdot c_j) \right]^2}{n-2} \qquad (8)$$

$$S = \sum_{j=1}^{n} (c_j - \bar{c})^2 \qquad (9)$$

where B_1 is a slope of the calibration curve; p, the number of measurements to determine c_0; n, the number of measurements for calibration; c_0, determined concentration of iron; $\bar{c}$, the mean value of different calibration standards; i, the index of number of calibration standards; j, the index of number of measurements to obtain the calibration curve; and s is the residual standard deviation.

The standard uncertainty for characteristics of measuring instrument is:

$$u(C_{\mathrm{cal}}, \mathrm{inst}) = \frac{\Delta_{\mathrm{instr}}}{3} \qquad (10)$$

where Δ_{instr} is the accuracy of spectrophotometer.

The concentration of reference solution and volume of standard solutions influences the uncertainty of standard solutions concentration $u(C_{\mathrm{cal}}, \mathrm{st})$.

The uncertainty of reference solution concentration is stated as uncertainty of the purity of reference material $u(P)$, weighing uncertainty of reference material $u(m)$ and uncertainty of the volumetric flask of reference solution $u(V_{\mathrm{fl}}, \mathrm{ref})$. The uncertainty of the reference solution concentration $u(c_{\mathrm{ref}})$ is calculated as:

$$u(c_{\mathrm{ref}}) = \sqrt{u(m)^2 + u(P)^2 + u(V_{\mathrm{fl}}, \mathrm{ref})^2} \qquad (11)$$

The uncertainty of the weight $u(m)$ is stated as uncertainty of repeatability $u(m, \mathrm{rep})$, calibration uncertainty of the weight $u(m, \mathrm{cal})$ and uncertainty caused by rounding of the digital reading $u(m, \mathrm{roun})$ The equation for the uncertainty of the weight is as follows:

$$u(m) = \sqrt{u(m, \mathrm{rep})^2 + u(m, \mathrm{roun})^2 + u(m, \mathrm{cal})^2} \qquad (12)$$

The uncertainty associated with the purity of the reagent is calculated from the producer's specifications. The purity of iron is given in the certificate and the value is divided by $\sqrt{3}$ to obtain the standard uncertainty (a rectangular distribution is assumed).

The uncertainty of the volumetric flasks is stated as the uncertainty of filling the flask to the mark $u(V_{\mathrm{fl}}, \mathrm{fill})$, calibration uncertainty of the flask volume $u(V_{\mathrm{fl}}, \mathrm{cal})$, and uncertainty of the volume caused by the temperature difference. The uncertainty of the volume of a flask is:

$$u(V_{\mathrm{fl}}) = \sqrt{u(V_{\mathrm{fl}}, \mathrm{cal})^2 + u(V_{\mathrm{fl}}, \mathrm{fill})^2 + u(V_{\mathrm{fl}}, \mathrm{temp})^2} \qquad (13)$$

$$u(V_{\mathrm{fl}}, \mathrm{temp}) = \frac{V_{\mathrm{fl}} \cdot \Delta t \cdot \gamma}{\sqrt{3}} \qquad (14)$$

where V_{fl} is volume of flask; Δt, the temperature difference between the value used for the calibration of the flask and the temperature of the medium used in the laboratory; and γ is thermal expansion coefficient of water.

The uncertainty of the volume of pipette is stated as the repeatability of the volume delivered by the pipette, calibration uncertainty of the pipettes $u(V_{\mathrm{p}}, \mathrm{cal})$, and uncertainty of the volume caused by the temperature difference between the value used for the calibration of
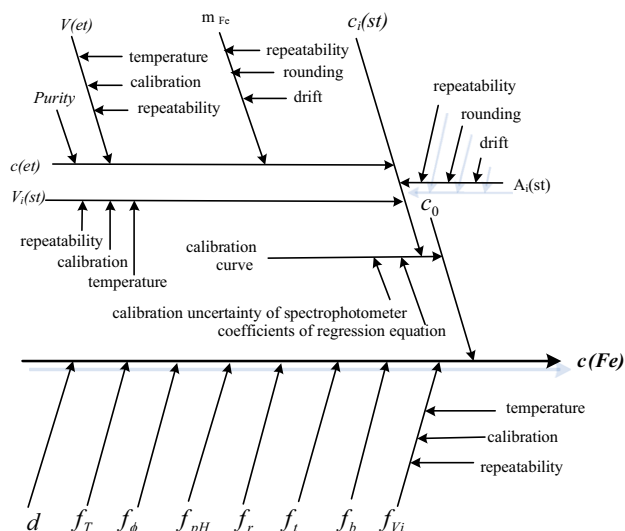
Fig. 5. Diagram of factors affecting the result.

Table 3
Matrix of experiments for iron concentration measurement procedure.

Parameter	Possible variants					
	J	K	L	M	N	O
C/c	c	C	C	C	C	C
D/d	D	d	D	D	D	D
E/e	E	E	e	E	E	E
F/f	F	F	F	f	F	F
G/g	G	G	G	G	g	G
H/h	H	H	H	H	H	h

the flask and the temperature of the medium used in the laboratory $u(V_p, \text{temp})$. The uncertainty of the pipette is:

$$u(V_p) = \sqrt{u(V_p, \text{cal})^2 + u(V_p, \text{rep})^2 + u(V_p, \text{temp})^2} \quad (15)$$

The components of evaluated uncertainty according to the experiments are the following:

- the component evaluating the amount of chemical reagent;
- the component of the temperature of the test solution;
- the pH component of the test solution;
- the component associated with the exposure time of prepared solution;
- the component of the impurities in the test solution;
- the component of the thickness of absorbing layer.

The standard uncertainties $u(f_i)$ of the above-mentioned components are calculated from experimental curves of each uncertainty component and taking into account possible real conditions of the analysis.

$$u(f_i) = \frac{a_{i+} - a_{i-}}{\sqrt{12}} \quad (16)$$

where a_{i+} and a_{i-} are the lowest and the highest values of each component in chosen range.

Table 4
Limits of experimental conditions.

Measurement condition	Method	Experimental conditions		
		Low limit	Normal conditions	High limit
Temperature (°C)	A	10	20	30
	B	10	20	30
Exposure time of a prepared sample (min)	A	5	15	20
	B	3	5	10
Amount of chemical reagent (ml)	A	1	2	4
	B	0.5	1	2.5
Absorption layer (mm)	A	5	20	30
	B	5	20	30
pH	A	1	4.5	9
	B	4	⩾9	10
Impurities: Fe:Zn Fe:Cu Fe:Co	A and B	–	–	1:10

The combined standard uncertainty of the measured analyte in full range of measured concentrations is calculated as:

$$u(c_{Fe})^2 = \sum_{i=1}^{N} \left(\frac{\partial c_{Fe}}{\partial x_i}\right)^2 \cdot u(x_i)^2 \quad (17)$$

where $u(x_i)$ are standard uncertainties of input parameters, $(\partial c_{Fe}/\partial x_i)$ are coefficients of sensitivity.

The expanded uncertainty of iron measurement $U(c)$ is obtained by multiplying the combined uncertainty by a coverage factor $k = 2$. A level of confidence is 95%.

5. Discussion of results

In carrying out measurements by method A different influence of uncertainty components to expanded uncertainty has been determined for the following concentration
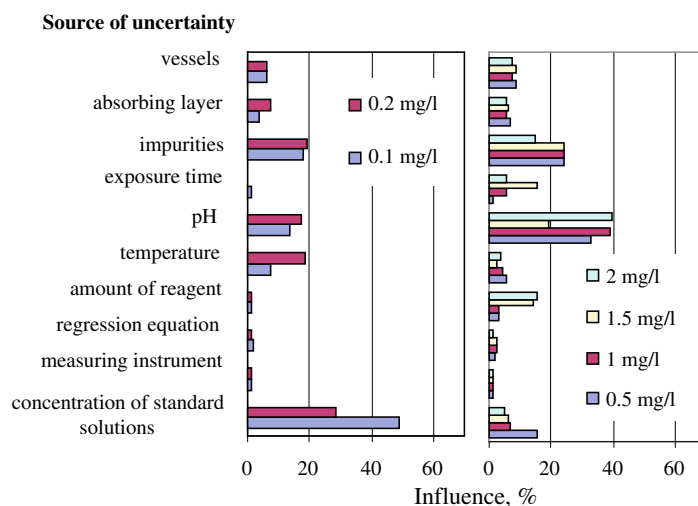
Source of uncertainty

Fig. 6. The influence of uncertainty components on expanded uncertainty in the measurement of iron concentration using method A.

ranges: up to 0.2 mg/l and from 0.2 mg/l to 2 mg/l. This influence is illustrated in Fig. 6.

Relative combined standard uncertainty is up to 0.12 in the range of small concentrations up to 0.2 mg/l and up to 0.07 in the range of concentrations from 0.2 mg/l up to 2 mg/l. The analysis of uncertainty components has shown that in the range of small concentrations the components depending on the temperature, the pH of test solution, the sample matrix, and the calibration curve have the most significant influence on the measurement uncertainty.

In the range of concentrations over 0.2 mg/l the components of the amount of chemical reagent, the pH of test solution, the sample matrix, and the concentration of standard solutions of calibration curve have a dominant influence on the measurement uncertainty of analyte.

In carrying out measurements at specified conditions of analysis using method B, the influence of uncertainty com-ponents on expanded uncertainty has been determined in the range of concentrations up to 0.5 mg/l and from 0.5 mg/l to 2 mg/l. This influence is shown in Fig. 7.

Relative combined standard uncertainty is up to 0.17 in the range of concentrations up to 0.5 mg/l and up to 0.07 in the range of concentrations from 0.5 mg/l up to 2 mg/l.

Research results on uncertainty components demon-strate that the component of solution exposure time has not any significant influence on measurement results in full range of tested concentrations. Predominant components are different in particular concentration. In the range of small concentrations, components of the calibration curve and the matrix of a tested sample have the most significant influence on the measurement uncertainty of analyte. In the range of concentrations over 0.5 mg/l, the biggest uncer-tainty components are due to the amount of chemical reagent, the pH of test solution, and the sample matrix.
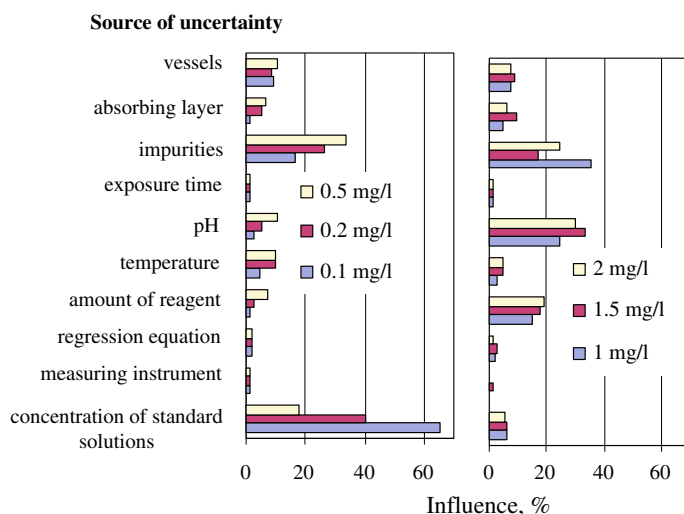
Source of uncertainty

Fig. 7. The influence of uncertainty components on expanded uncertainty in measurement of iron concentration by method B.

Histograms in Figs. 6 and 7 confirm the statement that characteristics of measuring instrument are not sufficient to evaluate analyte measurement uncertainty. Therefore it is very important to ensure the conditions of sample preparation and measurement process, and it is necessary to take into account correction factors in the measurement model of analyte.

6. Conclusion

It is necessary to evaluate parameters that appear in three main phases: physical–chemical transformation, measurement and estimation of the result to make the final chemical measurement model.

The influence of separate sample preparation procedures and quality of their performance has direct impact on uncertainty of spectrometric analysis results. Most of the hints are not new. They should already be considered in standard procedures in well-organized professional laboratories. It is a new challenge to put them in the context of measurement uncertainty, which arises from chemical and mechanical sample preparation. The knowledge of measurement uncertainty is an additional value to any analytical result.

The analysis of measurement of iron content in water by spectrophotometric method was performed and showed that uncertainty was basically formed by the first chemical analysis phases (measurement conditions, the standard solutions, and the parameters of calibration curve). Therefore, the total measurement uncertainty of material concentration is insignificantly sensitive to the parameters of the used measuring instrument.

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