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Theoretical and experimental examination of recovery in the context of trueness of analytical results

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ABSTRACT

In the report of the International Union of Pure and Applied Chemistry (IUPAC) estimation of analyte recovery (RV) is recommended as one of the ways for assessment of trueness of analytical results. RV is usually estimated with the use of samples spiked with known amount of analyte. However, neither the IUPAC guidelines, nor the available literature take into consideration various effects of different nature that may occur along the sample preparation steps prior and during measurements. Hence, in this work the attempt was made to classify these effects and to evaluate their influence on the analyte recovery. For this purpose a mathematical model has been developed, enabling to judge usefulness of the recovery test in objective estimation of trueness, and the results predicted by the model were checked experimentally. Trueness was estimated on the basis of analytical results obtained by both interpolative and extrapolative ways. The experiments were performed with the use of a dedicated flow injection system coupled to UV/VIS spectrometer and covered determination of chromium(III) as chromium(III) nitrate at a wavelength of 590 nm.

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1. Introduction

According to the terminology proposed in ISO 3534-1 [1] trueness is "the closeness of agreement between the expectation of a test result or a measurement result and a true value". Trueness accounts for accuracy of analytical results, along with precision (random component) [1–3]. Assessment of trueness can be performed with the use of certified reference materials (CRMs), reference methods, inter-laboratory analyses and spiked samples. With regard to CRMs and spiked samples, recovery of an analyte must be calculated [4,5]. The International Union of Pure and Applied Chemistry (IUPAC) has compiled guidelines for the use of recovery information in analytical measurement [6,7].

Applying reference materials to the assessment of trueness is the best measure since they have the highest level of traceability. This approach is based on determination of concentration of an analyte in a CRM with the use of an appropriate analytical procedure. Recovery of the analyte (RV) is the ratio of concentration of the analyte found to that declared to be present in a CRM. However, this approach is restricted due to many limitations: analytical method used for estimation of RV must be unbiased, the range of appropriate reference materials available is limited, the matrix mismatch between the sample and the most appropriate reference material available is usually present and the cost of such material is high [6].

It is because of these limitations that trueness can be assessed by the recovery information from surrogates. In this approach, a sample is spiked with an analyte in a well-defined concentration, which is regarded as a surrogate analyte for the native analyte. Measurements are performed for the sample before and after spiking and the recovery is calculated as a ratio of the difference of the concentrations found to the concentration of the analyte spiked.

There are two distinct contexts of the term "recovery", which must be clearly distinguished in order to avoid any confusion over the use of recovery information. IUPAC recommends applying the terms "recovery" or "recovery factor" to the yield of an analyte in a preconcentration or extraction step of an analytical procedure. If the ratio of an observed value, obtained from the procedure via a calibration graph, divided by a reference value is considered, the term "apparent recovery" should be used [7]. For simplification, the term "recovery" instead of "apparent recovery" is used in this work. For the same reason the term "recovery test" not "surrogate recovery test" is employed, as the version with a sample spiked with an analyte is exclusively exploited.

In the previous papers we proved experimentally by the determination of selenium in biological samples with the use of atomic fluorescence spectrometry with hydride generation that the recovery test could fail as a tool serving for evaluation of the analytical results (and consequently – for evaluation of an analytical method) in terms of trueness when a sample analyzed is prepared to measurements in accordance to a laboratory operation (e.g. digestion) or when it contains interferents [8,9]. The same problem was discussed in the case of bioanalytical methods utilizing liquid

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chromatography with mass spectrometric detection for the determination of drugs and metabolites [10–12]. Several experimental approaches for studying, identifying and eliminating interferences were described. In particular, Matuszewski et al. [10] presented a procedure for quantitative assessment of matrix effects at individual steps of the analytical procedure. Moreover, he described experiments for the determination of "true" recovery of analytes using HPLC–MS/MS and noticed that "the matrix effect may also affect the reliability of determination of recovery values in conventional bioanalytical methods". Veuthey et al. [12] presented an exhaustive classification of matrix effects occurring when a sample preparation step is performed prior to LC–MS analyses and applied recovery in order to recognize the matric effect typology.

In this work the attempt has been made to study the relation between recovery and trueness more thoroughly without focusing on a specific sample preparation process and analytical method applied. For this purpose a mathematical model has been developed, including the contribution of different effects, which may potentially occur during sample preparation and measurements. The relationship between recovery and trueness predicted by the model was verified experimentally. Trueness was estimated on the basis of analytical results obtained by both interpolative and extrapolative ways. The experiments were performed with the use of a dedicated flow injection system.

2. Background

The principle of the recovery test is shown in Fig. 1. The preliminary step is preparation of the calibration graph (a) on the basis of several standard solutions. Usually pure analyte is used for this purpose, allowing a linear graph to be constructed with the intercept equal to zero:

$$R = Ac \pm \varepsilon \tag{1}$$

where R stands for an analytical signal, A for a slope, c for an analyte concentration and ε represents random error following a normal distribution $N(0, \sigma)$. Then, a sample with native analyte of concentration c_s is spiked with surrogate analyte of concentration c_{st}, both portions of the sample (non-spiked and spiked) are treated in accordance with a required preparative operation and they are exposed to measurements. The signals obtained (R_s and R_{s+st}) are referred to the calibration graph enabling to find two corresponding values of analyte concentration (c_s and c_{s+st}) in an interpolative way:

$$\hat{c}_s = \frac{R_s + \varepsilon}{A} \tag{2}$$

$$\hat{c}_{s+st} = \frac{R_{s+st} + \varepsilon}{A} \tag{3}$$

The recovery, RV, is calculated from the formula:

$$\mathrm{RV}\ (\%) = \frac{\hat{c}_{s+st} - \hat{c}_s}{c_{st}} \times 100 \tag{4}$$

Every preparative operation carries the risk of occurrence of various effects, which can be, in general, divided into two main categories:

- the preparative effect, revealing as a systematic loss of the analyte from the sample or as uncontrolled addition of the analyte to the sample as a contaminant and/or
- the interference effect, i.e. a change in the analytical signal as a result of an action of a substance other than the analyte, present in the original sample or added to the sample in the course of the analytical procedure.

Both effects may act on both the native and surrogate analyte separately or jointly changing their signals by different means. In particular, both of them can reveal as additive or multiplicative effect when the signals are changed to the same extent or proportionally to the analyte concentration, respectively. If effects of both characters are taken into consideration, dependence (1) takes the following form:

$$R = A(1 + P_1)[1 + Q_1(c_m)](c + P_2) + AQ_2(c_m) + Q_3 + \varepsilon \tag{5}$$

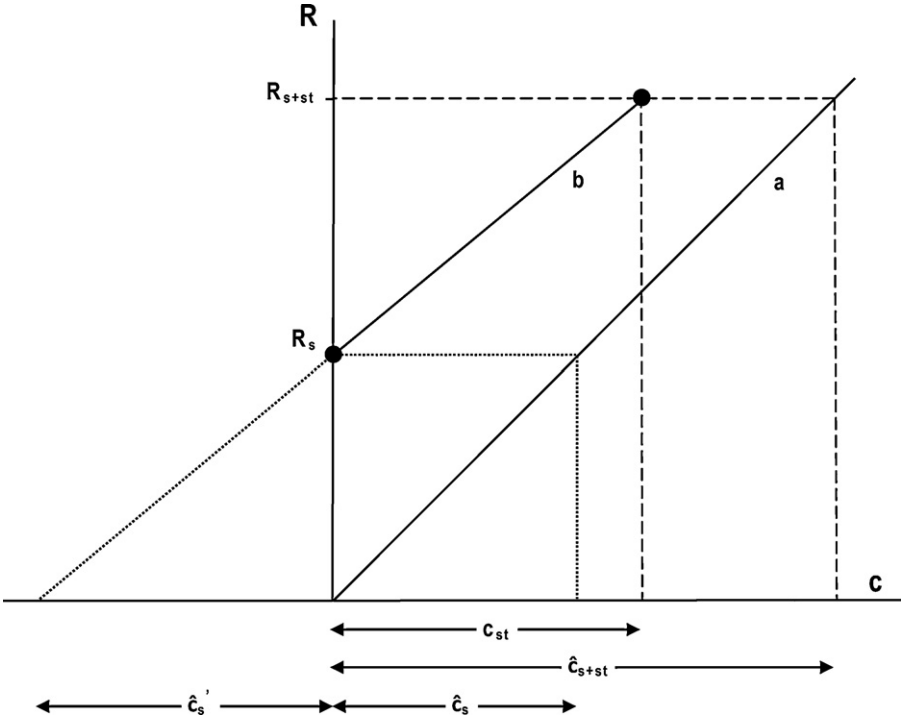

Fig. 1. The results possible to obtain in the recovery test: analyte concentrations, $\hat{c}_s$ and $\hat{c}_{s+st}$, found in the interpolative way (on the basis of graph a) in a sample before and after spiking with the analyte in concentration c_{st}, respectively, and the analyte concentration, $\hat{c}_s$', found in the extrapolative way (on the basis of graph b).

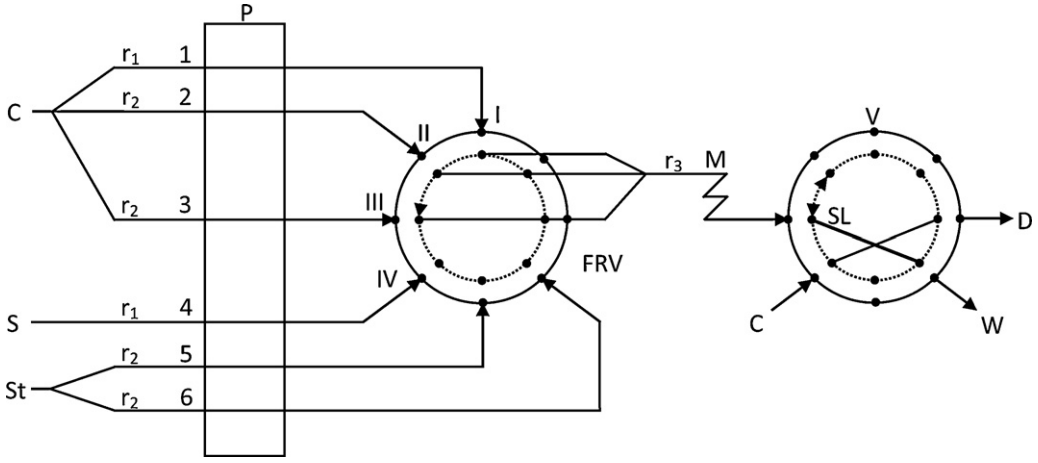

Fig. 2. Scheme of the flow-injection system used: P – peristaltic pump, FRV – fully rotary valve, M – mixing coil, V – two-positional injection valve, SL – sample loop, C – carrier, S – sample, St – standard solution, W – waste, D – detector, 1–6 – pump tubes, r_1–r_3 – flow rates, I–IV – working positions of FRV.

where c_m is the total concentration of interferents in a sample, P_1 and P_2 describe preparative effect of multiplicative and additive character, respectively, Q_1 corresponds to multiplicative interference effect, and Q_2 and Q_3 stand for the factors expressing additive interference effect dependent on and independent of the concentration of interferents, respectively.

Thus, the analytical signals R_s and R_{s+st} measured for the sample containing native analyte (c_s) only and additionally the surrogate analyte (c_{st}), are given by

$$R_s = A(1+P_1)[1+Q_1(c_m)](c_s+P_2)+AQ_2(c_m)+Q_3+\varepsilon \quad (6)$$

$$R_{s+st} = A(1+P_1)[1+Q_1(c_m)](c_s+c_{st}+P_2)+AQ_2(c_m)+Q_3+\varepsilon \quad (7)$$

When Eqs. (6) and (7) are substituted to Eqs. (2) and (3), respectively, the concentrations $\hat{c}_s$ and $\hat{c}_{s+st}$ found in interpolative way are as follows:

$$\hat{c}_s = \frac{A(1+P_1)[1+Q_1(c_m)](c_s+P_2)+AQ_2(c_m)+Q_3}{A} \quad (8)$$

$$\hat{c}_{s+st} = \frac{A(1+P_1)[1+Q_1(c_m)](c_s+c_{st}+P_2)+AQ_2(c_m)+Q_3}{A} \quad (9)$$

and Eq. (4) expressing the recovery values RV takes the following form:

$$\mathrm{RV}\ (\%) = (1+P_1)[1+Q_1(c_m)]\times 100 \quad (10)$$

In order to calculate trueness of the analytical result, $\hat{c}_s$, relative error, RE, is commonly used:

$$\mathrm{RE}\ (\%) = \frac{\hat{c}_s - c_s}{c_s}\times 100 \quad (11)$$

Taking Eq. (8) into account, RE values can be calculated from

$$\mathrm{RE}\,(\%) = \left\{\frac{A(1+P_1)[1+Q_1(c_m)](c_s+P_2)+AQ_2(c_m)+Q_3}{Ac_s}-1\right\}\times 100 \quad (12)$$

Another possibility of estimating analyte concentration is to use the extrapolative way exploiting the measured data obtained for non-spiked and spiked samples in accordance with the standard addition method (SAM). Namely, both signals (R_s and R_{s+st}) can be used for construction of the calibration graph as presented in Fig. 1 (line b) and then the analyte concentration may be calculated according to the formula:

$$\hat{c}'_s = \frac{R_s+\varepsilon}{A(1+P_1)[1+Q_1(c_m)]} \quad (13)$$

where the expression $A(1+P)[1+Q_1(c_m)]$ is – consistently with Eq. (5) – the slope of line b. Based on the formula analogous to Eq. (11):

$$\mathrm{RE'}\,(\%) = \frac{\hat{c}'_s - c_s}{c_s}\times 100 \quad (14)$$

the relative error of the analytical result estimated in such way is given by

$$\mathrm{RE'}\,(\%) = \left\{\frac{A(1+P_1)[1+Q_1(c_m)](c_s+P_2)+AQ_2(c_m)+Q_3}{A(1+P_1)[1+Q_1(c_m)]\,c_s}-1\right\}\times 100 \quad (15)$$

When multiplicative and additive effects occur together, their sequence must be carefully considered and included in Eqs. (12) and (15). If the additive effect influences the analyte before the multiplicative effect, Eqs. (12) and (15) can be used directly. However, when the multiplicative effect (P_1) is considered in the first instance, P_1 does not influence the additive effect (P_2). In this case Eqs. (12) and (15) take the following forms, respectively:

$$\mathrm{RE}\ (\%) = \left\{\frac{A(1+P_1)[1+Q_1(c_m)](c_s)+A[1+Q_1(c_m)]P_2+AQ_2(c_m)+Q_3}{Ac_s}-1\right\}\times 100 \quad (16)$$

$$\mathrm{RE'}\,(\%) = \left\{\frac{A(1+P_1)[1+Q_1(c_m)](c_s)+A[1+Q_1(c_m)]P_2+AQ_2(c_m)+Q_3}{A(1+P_1)[1+Q_1(c_m)]\,c_s}-1\right\}\times 100 \quad (17)$$

3. Experimental

Stock standard solution of 1000 mmol L^{-1} Cr was prepared by dissolving $Cr(NO_3)_3{\cdot}9H_2O$, p.a. (POCh, Gliwice, Poland). Working standard solutions were prepared by diluting the stock solution with deionized water obtained from HLP5sp system (Hydrolab, Poland).

The flow injection system, presented in Fig. 2, was designed to perform the examinations. It consisted of a peristaltic pump Minipuls 3 (Gilson, France), fully rotary eight-port valve (operated via software created in our laboratory), and two-positional eight-port valve (PerkinElmer, USA) equipped with 1855 μL loop volume and Tygon® pump tubes of 0.76 or 1.52 mm i.d. (Cole-Palmer, USA)

Table 1
Comparison of theoretical and experimental values of recoveries (RV) and relative errors of analytical results obtained in interpolative (RE) and extrapolative (RE') ways in the presence of preparative (P_1, P_2) and interference (Q_1, Q_2) effects of multiplicative and additive characters simulated by adequate analyte concentrations established in the sample and standard solutions introduced to the flow injection system (see Fig. 2).

Effect/effects combined	Analyte concentration [mmol L^{-1}]		RV [%]		RE [%]		RE' [%]	
	Sample	Standard	Theoret.	Experim.	Theoret.	Experim.	Theoret.	Experim.
No effect	20.0	60.0	100	99.4	0	−0.8	0	−2.1
P_2 or Q_2	28.0	60.0	100	100.8	+40	+41.5	+40	+41.1
$P_2 + Q_2$	36.0	60.0	100	99.7	+80	+79.8	+80	+79.7
P_1 (−20%)	16.0	48.0	80	80.7	−20	−19.9	0	+0.6
P_1 (−60%)	8.0	24.0	40	40.8	−60	−57.6	0	+7.4
Q_1	30.0	90.0	150	148.8	+50	+53.6	0	−1.8
P_1 (−20%) + Q_1	24.0	72.0	120	122.0	+20	+19.9	0	+0.4
P_1 (−60%) + Q_1	12.0	36.0	60	62.0	−40	−40.6	0	−1.8
P_1 (−20%) + P_2	24.0	48.0	80	80.4	+20	+19.3	+50	+48.4
P_1 (−40%) + P_2	20.0	36.0	60	59.8	0	+1.4	+67	+65.0
P_1 (−60%) + P_2	16.0	24.0	40	40.5	−20	−21.8	+100	+92.9
$P_2 + P_1$ (−20%)	22.4	48.0	80	79.8	+12	+12.6	+40	+43.2
$P_2 + P_1$ (−60%)	11.2	24.0	40	40.3	−44	−44.9	+40	+40.3
$P_2 + Q_1$	42.0	90.0	150	155.5	+110	+107.8	+40	+33.0
$Q_1 + Q_2$	38.0	90.0	150	149.4	+90	+89.5	+27	+26.7

were exploited. The manifold was coupled to UV/VIS spectrophotometer Cintra 101 (GBC, Australia). Absorbance was measured at 590 nm.

The sample (S), standard (St) and carrier (C) solutions were delivered to the fully rotary valve (FRV) through tubes 1–6 as presented in Fig. 2. FRV was operated in four positions (I–IV) changed by counter-clockwise gradual rotation of the FRV moving part of 45°. In each position three streams of solutions, one propelled with flow rate r_1 and the other two propelled with flow rate r_2, were selected from six streams introduced to FRV and were merged with each other with the total flow rate of $r_3 = r_1 + 2r_2$. Since $r_1 = 3r_2$, in each step of the procedure the sample and the standard solutions were diluted in a constant degrees of 3/5 and 1/5, respectively. Then, they were mixed in the mixing coil, injected to the carrier stream by two-positional injection valve (V) and subjected to measurements in the detector.

In the step of calibration graph preparation a set of standards solutions were directed to FRV in position II through tube 4, allowing each standard to be merged and mixed with two streams of the carrier solution. For the purpose of recovery examination tube 4 was filled with a sample (as seen in Fig. 2) and the position of FRV was changed from position I to IV, hence the following solutions were prepared: C + C + C (in position I), C + C + S (II), C + S + St (III) and S + St + St (IV).

4. Results

Experimental work was performed with the aid of synthetic solutions of chromium(III) nitrate playing the role of both the sample and standard solutions. Calibration graph was prepared with the use of 20, 60 and 120 mmol L^{-1} Cr solutions. Analyte concentration in the original sample (considered as not influenced by preparative and interference effects) introduced into the flow injection system (through tube 4, Fig. 2) was equal to 20 mmol L^{-1} (c_s). A sample could be merged with one or two streams of the standard solution (flowing through tubes 5 and 6) containing the analyte in concentration 60 mmol L^{-1}.

The following effects were considered throughout experiments:

- −20, −40 and −60% for multiplicative preparative effect (P_1),
- +40% for additive preparative effect (P_2),
- +50% for multiplicative interference effect (Q_1) and
- +40% for additive interference effect (Q_2).

The values of effects were chosen on the basis of analytical practice. Negative preparative effect of multiplicative nature can occur as a result of operations, such as digestion or extraction. Positive additive preparative effect may appear when a sample is treated with a reagent containing some amount of the analyte. Positive interference effects of multiplicative and additive characters are caused quite often by the sample matrix components during analysis by methods, such as atomic absorption spectrometry and UV/VIS spectrophotometry, respectively. Not only single but also combined (double) effects were taken into account, assuming that in the latter case the interference effect follows the preparative one.

Both the preparative and interference effects were simulated by preparation of sample and standard solutions containing native and added analyte in decreased or increased analyte concentrations in comparison to the initial ones (20 and 60 mmol L^{-1}) adequately to the kind and value of a given effect/effects. For instance, when multiplicative effect of −20% was considered, the analyte concentrations in solutions were decreased to 16 and 48 mmol L^{-1}, while in case of additive effect of 40% the concentrations were increased to 28 and 60 mmol L^{-1}, respectively. The analyte concentrations in the sample and standard solutions composing all the samples analysed are given in Table 1.

Theoretical values of recovery, RV, were calculated from Eq. (10), while the relative errors, RE and RE', related to interpolative and extrapolative analytical results were estimated theoretically according to Eqs. (12) and (15) or Eqs. (16) and (17), respectively, depending on what the sequence of multiplicative and additive effects was considered. For multiplicative and additive preparative effects, e.g. −20% and +40%, $P_1 = -0.2$ and $P_2 = 8.0$ mmol L^{-1} values were considered, nevertheless for multiplicative and additive interference effects of +50% and +40%, $Q_1 = +0.5$ and $Q_2 = 8.0$ mmol L^{-1} values were taken into account. Additive interference effect independent of concentration of interferents was not taken into consideration (i.e. it was assumed that $Q_3 = 0$).

Two calibration graphs (a and b in Fig. 1) were constructed by fitting linear function to the experimental points with the use of the least squares method and analyte concentrations in the samples were estimated in both interpolative ($\hat{c}_s$, $\hat{c}_{s+st}$) and extrapolative ($\hat{c}_s$') way. Since two values of $\hat{c}_{s+st}$ could be found for each sample (as in the flow system the analyte was added to each sample twice), two experimental values of RV were calculated from Eq. (4) and the mean value was assumed as the final one. Experimental values of RE and RE' were calculated from Eqs. (11) and (14), respectively.

Theoretical and experimental values of RV, RE and RE' are compared in Table 1. It can be seen that, in general, they are very similar

to each other in case of all the samples examined. It means that the mathematical model (5) expressing the impact of different effects, which may occur during sample preparation and measurements, on the relationship between the analytical signal and the analyte concentration is correct and, consistently, all following equations (e.g. for RV, RE and RE') have been derived properly.

The results shown in Table 1, provided by the theoretical and experimental equations for RV, RE and RE', reveal that

- Additive preparative effect (P_2) influences recovery (RV) and relative errors (RE, RE') to the same extent as additive interference effect (Q_2) does. When single additive effect (P_2 or Q_2) or a combination of additive effects ($P_2 + Q_2$) occurs, then RV equals 100% (neglecting random errors), while the RE and RE' values are the same and different from 0% of the value, which is equal to either single or total effect occurring.
- Multiplicative preparative effect (P_1) influences recovery (RV) and relative errors (RE, RE') to the same extent as multiplicative interference effect (Q_1) does. When multiplicative effects occur as single (P_1 or Q_1) or combined effects ($P_1 + Q_1$), they influence both RV and RE to the same extent, which is equal to the level of these effects (e.g. if $P_1 = -20\%$ then RV = 80% and RE = −20%). In the case of both single and combined multiplicative effects RE' is always equal to 0%.
- When multiplicative and additive effects occur together (e.g. $P_1 + P_2$, $P_2 + P_1$, $P_2 + Q_1$, $Q_1 + Q_2$), RV is influenced only by multiplicative effects, but RE and RE' – by both multiplicative and additive effects. It means that in such cases RV and RE are changed to different extent. In particular, if multiplicative and additive effects are of the same value but of different course of action (e.g. negative and positive), then RV $\neq$ 100% (because of contribution of the multiplicative effect) but RE = 0% (because of compensation of both effects).
- When multiplicative and additive effects occur together but in different sequence, RV values remain the same, while RE and RE' values are different. In particular, if the additive effect precedes the multiplicative one, RE' is strictly dependent on contribution of the additive effect, but if both effects occur in the opposite sequence, RE' depends additionally on the value of the multiplicative effect.

5. Conclusions

To perform the experiments presented in this paper a dedicated flow injection system has been designed. It enabled to save time and laboratory efforts and to prepare the samples examined with very good accuracy. The system has been adapted to examination of samples of low analyte concentration, since a sample was introduced to the system three times faster than the standard solutions were and thanks to that it could be three times less diluted. Besides, the system enabled to prepare a sample with two additions of an analyte (unlike the conventional one addition), providing more experimental data than the conventional recovery test and giving an opportunity to estimate both the recovery values and the extrapolative analytical results with improved reliability. As a consequence, the experimental data obtained could be definitely consistent with theoretical results and confirm the correctness and usefulness of the mathematical model developed. The system designed may be additionally equipped with optional modules serving for preparation of a sample prior to measurements and in such form it will be used for recovery examinations in future.

The obtained theoretical and experimental results have proved that the recovery test can evaluate properly the trueness of analytical results only in two cases: (a) when no effect occurs in the course of the sample preparation and measurement or (b) when the only occurring effect is of multiplicative (preparative, interference or combined) character. In the latter case the recovery value is admittedly different from 100% and the relative error of the interpolative analytical result is different from 0%, however both differences are consistent with each other (e.g. when RV = 80%, then RE = −20%) and connected in accordance with well-defined relationship: RE = RV − 100%.

Additive effects cannot be detected with the use of the recovery test at all. It means that RV has to be expected to be 100% even when, for instance, the native analyte would be lost in the same amount from the sample before and after dosing it with surrogate analyte. In such situation the relative error would be estimated as 0% despite the facts. The recovery test fails also in cases very probable in analytical practice, when additive effect is combined with the multiplicative one. Then, as revealed, there is a risk to estimate the recovery as different than 100%, while the analyte can still be determined with very good trueness (RE ≈ 0%).

An assumption was made that analytical results may be estimated not only interpolatively but also extrapolatively. As expected, the extrapolative way enabled to compensate the multiplicative effects providing accurate analytical result (and allowing to assume that RE' ≈ 0). However, when the combinations of multiplicative and additive effects ($P_1 + P_2$ or $Q_1 + Q_2$) are taken into consideration, the extrapolative approach is not able to totally compensate the multiplicative effects (P_1 or Q_1) and RE' differs from 0. In this case, such an approach seems to be aimless. Nevertheless, comparison between the interpolative and extrapolative results as well as recovery value enables to recognize whether the combinations ($P_1 + P_2$ or $Q_1 + Q_2$) are present during an analytical procedure or not.

In the century of accreditation, certification and validation in chemical laboratories, recovery tends to be overused by practitioners and is very often uncritically exploited in order to assess trueness of analytical results directly. However, considering the number and complexity of the effects accompanying the analytical procedure, trueness of analytical results should not be – contrary to the IUPAC recommendations – controlled by the recovery test but some other approaches should rather be applied for this purpose (in particular, reference methods and/or inter-laboratory analyses).

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