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Human errors and measurement uncertainty in chemical analysis

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Abstract

Evaluating the residual risk of human errors in chemical analysis, remaining after the error reduction by a laboratory quality system, and quantifying the consequences of this risk for the quality of chemical analytical results are discussed based on expert judgments and Monte Carlo simulations. A procedure for evaluation of the contribution of the residual risk to the measurement uncertainty budget is proposed. Examples are provided using earlier published sets of expert judgments on human errors in pH measurement of groundwater, elemental analysis of geological samples by inductively coupled plasma mass spectrometry, and multi-residue analysis of pesticides in fruits and vegetables. The human error contribution to the measurement uncertainty budget in the examples was not negligible, yet also not dominant. This was assessed as a good risk management result.

Keywords: chemical analysis, human error, expert judgment, measurement uncertainty, quality risk management

1. Introduction

1.1. Measurement error and human error

The international vocabulary of metrology [1] defines measurement error as a difference between measured and reference quantity values, and stipulates that measurement errors should not be confused with mistakes. Since a mistake is a kind of human error, the meaning of this stipulation is the distinction of measurement error from human error.

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3 Human error in a chemical analytical (testing) laboratory is any action or lack thereof
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5 that leads to exceeding the tolerances of the conditions required for the normative work
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7 of the analytical measuring system with which the human interacts [2]. Such tolerances
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9 (interval of temperature values for a sample decomposition, pH values for an analyte
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11 extraction, etc.) are formulated in standard operation procedures of the analysis based
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13 on results of the analytical method validation study.
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16 Just as 20-30 years ago managers of chemical analytical laboratories were afraid that
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18 evaluating and reporting measurement uncertainty [3-5] could compromise the
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20 laboratory reputation, today any discussion of human errors in a laboratory is sensitive
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22 also. One can even find an opinion that human errors in an analytical laboratory “are not
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24 interesting for science and have no influence on uncertainty” [6]. However, there are a
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26 number of factors effecting chemical analytical (measurement/test) results to various
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28 degrees and human errors are a part of them. Gross errors are easily identifiable, and
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30 corresponding results can be separated from the data set. At the same time, small human
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32 errors are in principle not distinguishable from other components of measurement
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34 uncertainty. Therefore, an uncertainty budget is not complete when consequences of
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36 possible human errors of a sampling inspector and/or an analyst/operator are not taken
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38 into account as a contribution to the budget [2, 7-9]. Moreover, consideration of human
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40 errors is required now by national and international documents for correct evaluation of
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42 quality of chemical analytical results in medicine, food and drug analysis and other
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44 fields [10-14].
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52 *1.2. Background*

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3 Risk of human error can be defined as a combination of the likelihood (probability) of
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5 occurrence of the error in a chemical analysis and the severity of that error for the
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7 quality of the analytical results [15]. A particular kind of human error and a certain step
8
9 of the analysis at which this error may happen, are considered as the error scenario.
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11 Evaluation of likelihood and severity of an error scenario is possible on the basis of
12
13 expert judgments [16]. An expert in the analytical method can judge the likelihood of
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15 error scenarios $i = 1, 2, \dots, I$ by the following scale: likelihood of an unfeasible scenario
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17 – as $p_i = 0$, weak likelihood - as $p_i = 1$, medium – as $p_i = 3$, and strong (maximal)
18
19 likelihood – as $p_i = 9$. A discussion of this scale is available in ref. [16]. Other scales
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21 can also be used depending on the tasks. The normalized and averaged value of the
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23 expert judgments $P^* = (100\%/9) \sum_{i=1}^I p_i / I$ is a kind of “intuitive” or “subjective”
24
25 (mean) error probability [4]. The similarly calculated severity score
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27 $L^* = (100\%/9) \sum_{i=1}^I l_i / I$, where l_i is the expert judgment on the severity of error
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29 scenario i , given again on the scale (0, 1, 3, 9), reflects the (mean) loss of quality of the
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31 analytical results caused by human errors.
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36 Protection of the quality of analytical results by managing potential risks and
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38 mitigation of their severity is an important task for the quality system of any laboratory
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40 [17]. A laboratory quality system should answer this requirement using components $j =$
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42 $1, 2, \dots, J$, such as validation of the analytical method, training the staff, quality control,
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44 supervision, etc. Evaluation of possible reduction r_{ij} of likelihood and severity of human
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46 error scenario i as a result of error blocking by quality system component j is made by
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48 the same expert(s) using the same scale (0, 1, 3, 9). Notice that blocking human error
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50 according to scenario i by quality system component j can be more effective in the
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52 presence of another component j' ($j' \neq j$) because of their synergy $\Delta_{jj'}^{(i)}$, which is equal to
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54 0 when the synergy is absent, and equal to 1 when it exists. For example, training ($j = 2$)
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3 is more effective against any error scenario i when the analytical method is validated
4 already and a corresponding standard operation procedure is formulated ($j' = 1$). Thus,
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7 $\Delta_{21}^{(i)} = 1$. The average synergy factor for quality system component j is $s_{ij} = 1 +$
8 $\sum_{j' \neq j}^J \Delta_{jj'}^{(i)} / (J - 1)$, $1 \leq s_{ij} \leq 2$. Therefore, reduction of the likelihood and severity of
9
10 error scenario i by quality system component j (i.e., the risk reduction [15]) is given by
11
12 $\tilde{r}_{ij} = r_{ij}s_{ij}$. In general, there is an $I \times J$ interrelationship matrix of \tilde{r}_{ij} values.
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14 Effectiveness score $Eff^* = (100\%/9) \sum_{j=1}^J \sum_{i=1}^I p_i l_i \tilde{r}_{ij} / \sum_{j=1}^J \sum_{i=1}^I p_i l_i s_{ij}$ of the quality
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16 system, as a whole, against human errors was formulated in [16] in comparison to an
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18 ideal quality system with the maximal $r_{ij} = 9$ for all i and j .
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25 The influence of the variability of expert judgments on the score values was studied
26 using Monte Carlo simulations of the judgments performed by an R code [18]. The
27 simulations were based on modeling the expert behavior by means of different
28 probability mass functions (pmfs) of the expert judgments, i.e., the expert choices on the
29 scale (0, 1, 3, 9). In particular, reasonably doubting expert judgments were modelled
30 using a pmf of a chosen value equal to 0.70 and a pmf of close values on the scale in
31 total equal to 0.30. For example, a judgment equal to 3 from the scale, made by a
32 reasonably doubting expert, was modelled by a pmf equal to 0.70 at 3, and 0.15 at both
33 1 and 9 - the closest to 3 values on the scale. It was shown that robustness of the
34 discussed scores is satisfactory for the quality risk management and improvement of the
35 laboratory quality system against human errors.
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49 The technique for quantification of human errors in a chemical analytical laboratory
50 was successfully applied for pH measurement of groundwater [16], elemental analysis
51 of geological samples by inductively coupled plasma mass spectrometry (ICP-MS) [18],
52 and multi-residue analysis of pesticides in fruits and vegetables [19].
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1.3. Aim

The subject of the present paper is evaluating residual risk of human error in chemical analysis (remaining after the error reduction by the laboratory quality system [15]) and quantifying its consequences for quality of analytical results. A procedure for evaluation of the contribution of the residual risk to the measurement uncertainty budget is proposed.

2. Residual risk of human errors and its consequences

2.1. Quantification

A value of risk reduction \tilde{r}_{ij} can be normalized by dividing its multipliers r_{ij} and s_{ij} by their maximal values, 9 and 2, respectively. Averaging the normalized risk reduction values for the interrelationship matrix (over all the error scenarios and quality system components) leads to score r^* characterizing the (mean) risk reduction by the laboratory quality system, expressed in %:

$$r^* = (100 \% / 18IJ) \sum_{j=1}^J \sum_{i=1}^I \tilde{r}_{ij} . \quad (1)$$

Then, a score of residual risk of human errors, which are not prevented/blocked or reduced/mitigated by the quality system, is

$$R^* = 100 \% - r^* . \quad (2)$$

The percentage (%) of the quality of analytical results which may be lost due to residual risk of human errors is

$$f_{\text{HE}} = (P^*/100\%) (L^*/100\%) R^* . \quad (3)$$

When a laboratory quality system is able to prevent or block human errors completely, one has $R^* = 0\%$ and $f_{\text{HE}} = 0$: there is no loss of quality, the quality system is ideal and its effectiveness score is $Eff^* = 100\%$. If a quality system is not effective at all (or absent), $Eff^* = 0\%$ since $\tilde{r}_{ij} = 0$ for all i and j . Then $R^* = 100\%$ and $f_{\text{HE}} = (P^*/100\%) L^*$. The extreme case of a complete loss of quality is theoretically possible when, in absence of a quality system ($R^* = 100\%$), scores P^* and L^* reach also 100%, i.e., human errors are inevitable and destructive. Thus, $f_{\text{HE}} = 100\%$ as well.

2.2. Distribution of possible loss of quality

Distributions of f_{HE} values were studied with Monte Carlo simulations for the model of reasonably doubting expert judgments, analogous to that presented in work [18]. The three sets of expert judgments on human errors in different analytical methods published in papers [16,-18-19] were used here as examples. The values of scores P^* , L^* and R^* , as well as the results of f_{HE} calculations and simulations on a base of 100000 Monte Carlo trials, are presented in Table 1. The f_{HE} values calculated directly by formula (3) are close for the three examples. These values can be interpreted as obtained from completely confident expert judgments. A Dirac delta function is applied for modelling pmf of such a judgment: pmf of an expert choice on the scale (0, 1, 3, 9) by this model

Table 1

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3 is 1.00, being 0.00 in total at the rest part of this scale. The mean and median f_{HE} values
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5 obviously coincide in such a case, the standard deviation (STD) of the simulated values
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7 being zero. For all examples, the mean of the simulated f_{HE} values for the model of
8
9 Fig. 1 reasonably doubting expert judgments is a little larger than the f_{HE} calculated directly
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11 (not more than for one STD of the simulated values). In other words, the estimated
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13 possible loss of quality due to residual risk of human errors is larger when an expert
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15 doubt is taken into account. A similar effect was noted in paper [18] concerning scores
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17 of likelihood, severity and quality system effectiveness: less confident expert judgments
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19 lead to less optimistic score values. Histograms of f_{HE} simulated values are shown in
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21 Fig. 1a for pH measurement of groundwater, in Fig. 1b – for elemental analysis of
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23 geological samples with ICP-MS, and in Fig. 1c – for pesticide residue analysis in fruits
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25 and vegetables. These histograms are practically symmetric, their mean and median
26
27 values differing insignificantly. Relative standard deviation values (STD/mean) are in
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29 the range 0.12 - 0.15, i.e., smaller than 0.4. The same is true if one compares the
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31 maximal difference between the f_{HE} calculated directly by formula (3) and the mean of
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33 the simulated values with their common average. In Table 1 it is the case of ICP-MS,
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35 where $f_{HE} = 8.1\%$ by formula (3), while the simulated mean f_{HE} is 9.5 %, and their
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37 average is $(8.1\% + 9.5\%)/2 = 8.8\%$. Since $(9.5 - 8.1)/8.8 = 0.15 < 0.4$, one can
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39 conclude that the f_{HE} estimates are robust enough to variability of corresponding expert
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41 judgments [18].
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3. Contribution of human errors to measurement uncertainty budget

3.1. Evaluation

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3 Considering the combined uncertainty u_c , evaluated according to guides [3, 4], as a
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5 quality parameter of an analytical result, one can say that quality Q is better, when u_c is
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7 smaller, i.e., $Q = 1/u_c$. This is the simplest model $Q(u_c)$ and its simplicity is the main
8
9 model advantage. More complicated models could be also investigated and applied in
10
11 specific cases.
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14 Possible loss of quality because of residual risk of human errors is $Q f_{HE}/100$ % (an
15
16 absolute value). Therefore, the resulting quality according to the proposed model is
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$$20 \quad Q_{res} = Q - Q f_{HE}/100 \% = (1/u_c)(1 - f_{HE}/100 \%). \quad (4)$$

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23 Since $Q_{res} = 1/u_{cHE}$, where u_{cHE} is the combined uncertainty including the human error
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25 contribution, from formula (4) one has
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$$32 \quad u_{cHE} = u_c / (1 - f_{HE}/100 \%). \quad (5)$$

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35 In the view of guide [4, pp. 24-25] concerning uncertainty evaluation based on
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37 judgment “as for standard deviations derived by other methods”, the contribution of the
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39 uncertainty u_{HE} caused by residual risk of human errors into the uncertainty budget can
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41 be approximated by
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$$45 \quad u_{cHE} = (u_{HE}^2 + u_c^2)^{1/2}. \quad (6)$$

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48 Thus, it follows from formulas (5) and (6) that
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$$54 \quad u_{HE} = u_c [(1 - f_{HE}/100 \%)^{-2} - 1]^{1/2}. \quad (7)$$

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3 When $f_{\text{HE}} = 0 \%$, the uncertainty contribution due to human errors $u_{\text{HE}} = 0$ and $u_{\text{CHE}} = u_c$.

4
5 When f_{HE} increases in the range $0 \% < f_{\text{HE}} < 100 \%$, values of u_{HE} increase also as shown

6
7 Fig. 2

8 In Fig. 2. In particular, u_{HE} achieves $1/3u_c$ at $f_{\text{HE}} = 5 \%$ and begins to be a significant
9 component of the uncertainty budget by formula (6). At $f_{\text{HE}} = 68 \%$, value $u_{\text{HE}} = 3u_c$
10 dominates already in the budget: this point is indicated by dotted lines in Fig. 2. When
11 f_{HE} exceeds 68% , u_{HE} increases with f_{HE} dramatically. In the theoretical case of
12 $f_{\text{HE}} = 100 \%$ formulas (5) and (7) tend to infinity. However, such a contribution of
13 human error to uncertainty is not realistic, inasmuch as the error becomes apparent: it
14 will be identified and treated.
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23 It is known that the largest contribution/component of a combined uncertainty needs
24 to be investigated more thoroughly [4, p. 49]. Such a contribution may be overestimated
25 and, hence, simply improved after investigation, or be a subject of a corrective action
26 requiring an investment. Identified human errors can usually be reduced [20]. Thus, a
27 good risk management result is when human errors are treated enough by the quality
28 system to avoid their dominance in the measurement uncertainty budget.
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38 3.2. Examples

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43 The combined standard uncertainty u_c presented in Table 1 is evaluated, respectively, for
44 test item preparation for proficiency testing of pH measurement of groundwater [21]
45 (pH units), for determination of 10 ng g^{-1} of ^{60}Ni in aqueous samples by ICP-MS [22],
46 and for multi-residue analysis of pesticides in fruits and vegetables (averaged for all
47 analytes and expressed in % of an analytical result) [23]. Results of calculations of
48 human error contributions to the measurement uncertainty budget are also presented in
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56 Table 1.
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3 The f_{HE} values obtained directly by formula (3) were used for calculation of u_{HE} and
4 u_{CHE} by formulas (6) and (7). At the same time, the mean of the simulated f_{HE} values
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6
7 allow to examine which uncertainty contribution u_{HE} can be obtained if another expert
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10 will participate in the elicitation process (with different knowledge and experience and,
11
12 as a result, with different confidence of judgments). For example, using the mean f_{HE}
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14 obtained from judgments of a reasonably doubting expert in ICP-MS leads to
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16 $u_{\text{HE}} = 0.35 \text{ ng g}^{-1}$ and $u_{\text{CHE}} = 0.83 \text{ ng g}^{-1}$, which are very close to the u_{HE} and u_{CHE} values in
17
18 Table 1.
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21 From Table 1, one can understand also that the human error contributions to the
22
23 measurement uncertainty budget in the examples were not negligible. However, it is
24
25 important that these contributions were not dominant and could not influence seriously
26
27 the combined uncertainty. This is a good risk management result.
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30 31 32 *3.3. Specificity* 33 34 35

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37 In general, the residual risk of human errors and the corresponding contribution to
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39 measurement uncertainty may be different in different laboratories active in the same
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41 field and using the same analytical method. On the other hand, it is impossible to expect
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43 an equal risk of human errors in chemical analysis by different analytical methods even
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45 in the same laboratory.
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48 Changes in the laboratory environment, as well as in any quality system component
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50 and staff require re-evaluation of the quality of analytical results which may be lost due
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52 to residual risk of human errors f_{HE} and corresponding combined uncertainty u_{CHE} . The
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54 re-evaluation result may indicate either f_{HE} increase (e.g., due to retirement of an
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56 experienced supervisor and/or manager) or its decrease (e.g., due to acquisition of a new
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3 more accurate and more automated analytical instrument and/or a laboratory
4 information management system - LIMS) as shown schematically in Fig. 3. The current
5 f_{HE} value is demonstrated here by straight line 1 as a result of balance between human
6 error scenarios $i = 1, 2, \dots, I$ and quality system components $j = 1, 2, \dots, J$ blocking the
7 errors and mitigating their severity. The increased and decreased f_{HE} values are
8 demonstrated by straight lines 2 and 3, respectively. The f_{HE} change will not appear
9 immediately, a certain time t is necessary for that, as a rule. This process is indicated by
10 smooth dotted lines connecting the straight lines. Consequently, the combined
11 uncertainty values u_{CHE} will also change according to formulas (6) and (7).
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25 **4. Conclusion**

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29 In spite of the delicacy of the topic of human errors in chemical analytical laboratories
30 and a certain misunderstanding of its importance for metrology, this topic should be
31 discussed without any fear of compromising a laboratory's reputation, just as
32 measurement uncertainty is discussed. Nowadays, there are no databases of human
33 errors in different chemical analytical methods. However, experts in these methods have
34 accumulated the necessary information. Their knowledge and experience may be
35 quantified using an appropriate scale of expert judgments. Evaluating the residual risk
36 of human errors in chemical analysis, remaining after the error reduction by a laboratory
37 quality system, and quantifying the consequences of this risk for quality of analytical
38 results are possible on the basis of relevant expert judgments. We hope that the
39 procedure proposed in the present paper for evaluation of the contribution to the
40 uncertainty budget due to residual risk of human errors will be helpful for a more
41 complete vision and evaluation of measurement uncertainty in chemical analysis.
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Figure captions

Fig. 1. Histograms of simulated values $f_{HE}/\%$ of possible quality loss due to residual risk of human errors for a) pH measurement of groundwater, b) ICP-MS elemental analysis of geological samples, and c) pesticide residue analysis in fruits and vegetables.

Fig. 2. Ratio u_{HE}/u_c of the uncertainty contribution due to residual risk of human errors to the combined uncertainty in dependence on the quality loss $f_{HE}/\%$. The case $u_{HE} = 3u_c$ is indicated by the dotted lines.

Fig. 3. A scheme of possible changes of the quality lost due to residual risk of human errors $f_{HE}/\%$ vs time t/day . The current f_{HE} value is shown by straight line 1 as a result of the balance between human error scenarios $i = 1, 2, \dots, I$ and quality system components $j = 1, 2, \dots, J$ blocking the errors and mitigating their severity. The increased and decreased f_{HE} values are demonstrated by straight lines 2 and 3, respectively. The process of f_{HE} changing is indicated by smooth dotted lines connecting the straight lines.

Table 1. Evaluation of quality loss due to residual risk of human errors and corresponding contribution to the uncertainty budget

Analytical method	P^* %	L^* %	R^* %	f_{HE} %	MC simulation of $f_{HE}/\%$			u_c	u_{HE}	u_{CHE}
					Mean	Median	STD			
pH metry of groundwater	26	67	62	10.8	11.2	11.1	1.6	0.10	0.05	0.11
ICP-MS of geo-samples	22	56	65	8.1	9.5	9.4	1.4	0.75 ng g ⁻¹	0.32 ng g ⁻¹	0.82 ng g ⁻¹
Pesticide residues in fruits	19	84	63	9.9	10.4	10.4	1.3	20 %	10 %	22 %

Note: STD is the standard deviation of the simulated values from their mean.

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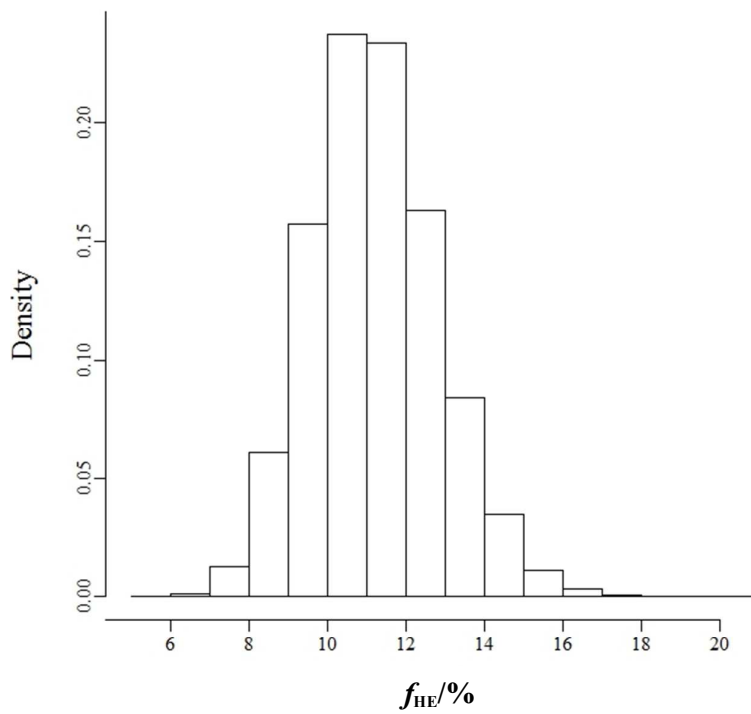


Fig. 1a

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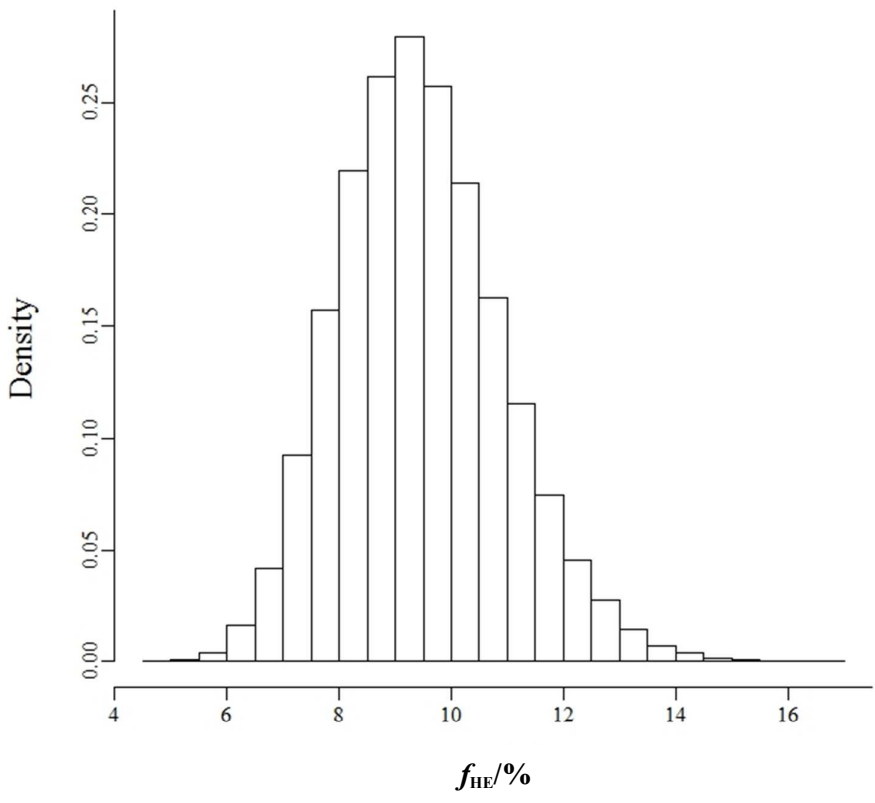


Fig. 1b

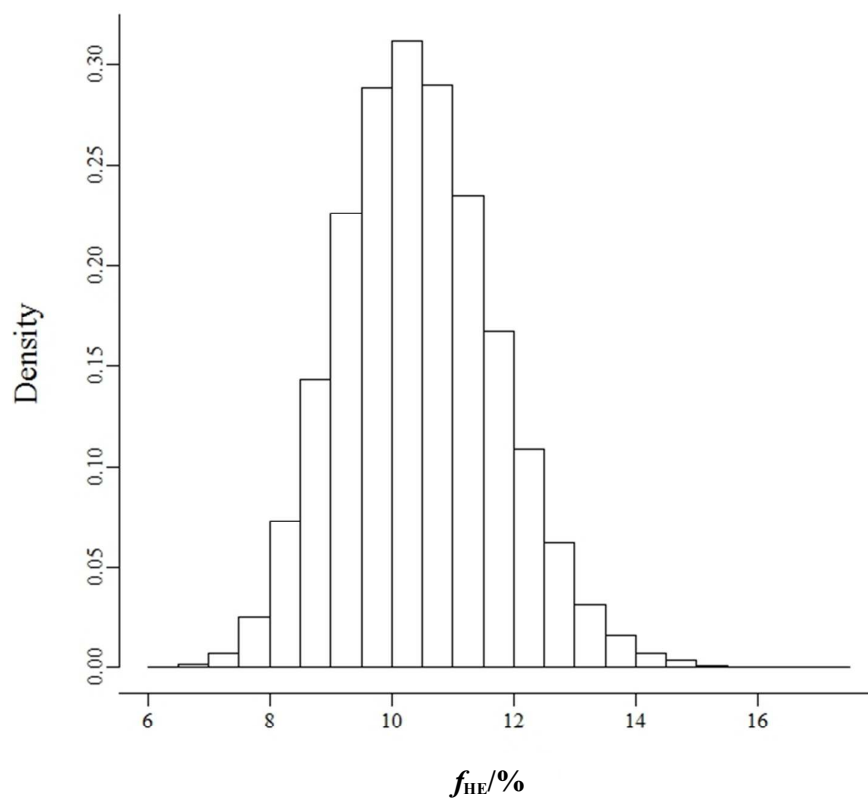


Fig. 1c

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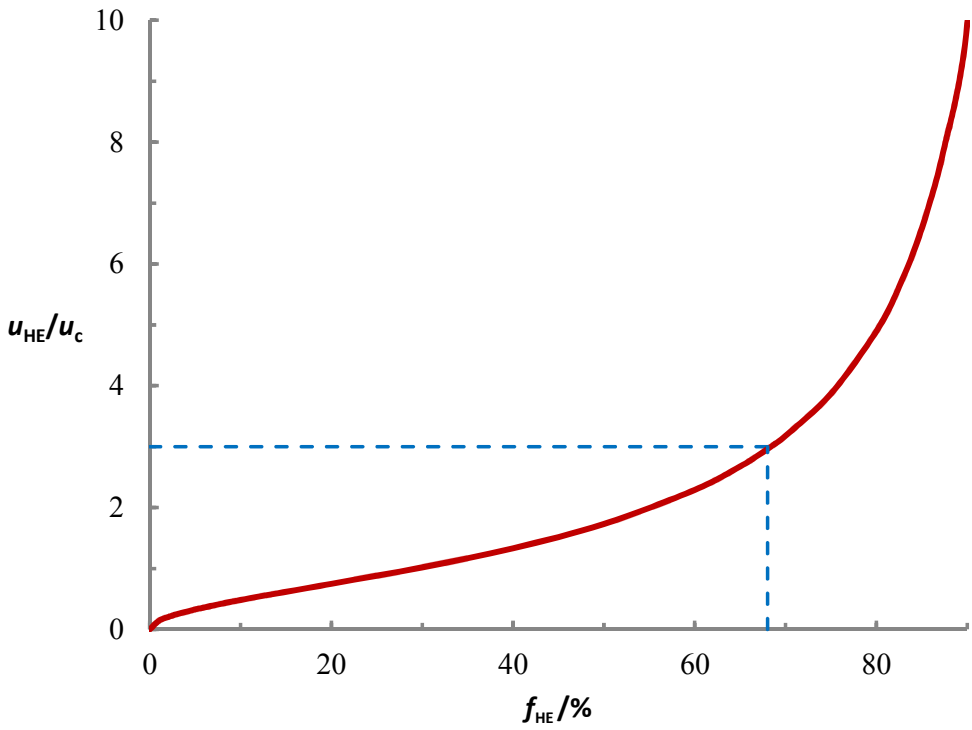


Fig. 2

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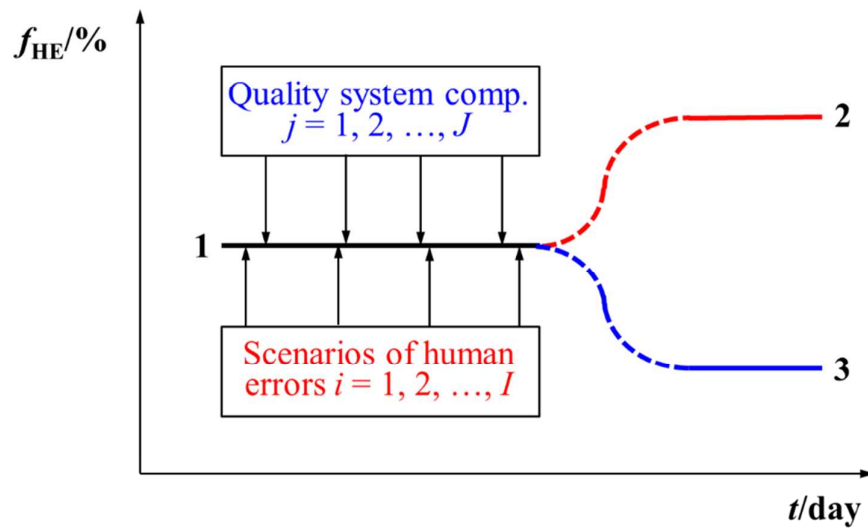


Fig. 3