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Original Research

Assessment of Human Errors in the Determination of the Concentration of Water Pollutants

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Abstract

Despite the achievements in the field of instrumental methods of pollutant analysis, human error (HE) is still a significant issue affecting the quality of data obtained during environmental analysis and should be taken into account for quality risk management in the laboratory and field. Numerous scenarios that depend on the performance shaping factor (PSF) can lead to HE in the chemical analysis of environmental pollutants. Considering this, we applied, for the first time, the Success likelihood index method (SLIM) for the identification and quantification of HE in the analysis of polluting substances. As a case study, a spectrophotometric determination of ammonia concentration in water was examined. By applying SLIM, the impact of PSFs, such as procedure, experience, training, time, communication, and teamwork, on the occurrence of HE for specific activities was assessed by experts. It is estimated that "taking an unrepresentative sample" is the error with the highest probability of occurrence. The obtained results indicate that experience and training, followed by procedures and time, are PSFs that contribute to the greatest extent to the reduction of errors during the analysis of polluting substances. Considering the above-mentioned, the appropriate corrective measures that would lead to a reduction of HE in the analysis of pollutants are proposed.

Keywords: human error, Success likelihood index method (SLIM), human error probability (HEP), spectrophotometry, pollutants

Introduction

Despite the achievements that have been made in the field of the development of analytical instruments and instrumental methods of environmental analysis, as well as detailed procedures for their implementation, human error is still a significant issue affecting the quality of data obtained during environmental analysis and should be taken into account for quality risk management in the laboratory and the field. Human error frequently arises from a complex interplay of events, making it challenging to provide a comprehensive definition. Kanky summarized key definitions, highlighting a shared trait among them [1]. She suggested that despite the variety of definitions, they all converge on the idea that human error refers to an action resulting in adverse outcomes or the failure to achieve the intended goal [1].

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Errors committed by individuals, i.e., operators, are often a direct consequence of their performance, actions, or personal characteristics. The performances of the operator, in our case analyst, depend on many factors called performance shaping factors (PSFs). PSFs are variables that influence human behavior and performance in a human reliability analysis (HRA) [2]. As human error is one of the manifestations of human behavior, PSFs are also considered possible causes of errors. PSFs that are generally adopted in HRA methods include experience, complexity, stress, adequacy of procedure, workload (time pressure), training (practice), teamwork (team structure and cooperation), communication (written or oral), etc. [2, 3].

One of the most flexible and commonly used HRA techniques for estimating the human error probability (HEP) under the combined effect of a set of PSFs is the Success likelihood index method (SLIM) [4]. This method was developed for measuring the HEP that occurs during the execution of a particular task based on the evaluation of the PSFs by experts [5]. In SLIM, the group of experts is asked to consider the human errors that are possible for the analyzed activities and to decide to what extent the PSF affects the occurrence of errors for specific activities. Although SLIM has been applied for the assessment and prediction of human error in various fields, such as the railway driving process [6, 7], maritime transportation [8], oil spill response [9], offshore evacuation [10], energy (electric power) supply sector [11], coal mining [12], nuclear safety [13], the quantification of medication error probability [14], etc., the literature survey revealed no data concerning the application of SLIM in chemical and environmental analysis. In addition, there is scarce data on the analysis of human error in chemistry in general and the analysis of chemical parameters of environmental quality, although human errors in an analytical laboratory may lead to test results of questionable reliability [15]. Hellieret and co-workers performed a hierarchical task analysis as a methodological framework for looking at the process of analytical measurement in chemistry, followed by an account of the potential errors that can occur, and gave a series of recommendations on how to reduce error at each stage of analytical measurement [16]. Ellison and Hardcastle reported the causes of error in analytical chemistry after conducting a web-based survey of respondent-identified causes of unacceptable results in several, predominantly environment and food analysis, proficiency testing schemes [17]. Various error scenarios in stable isotope analysis were identified, and their preventability by quality assurance processes was discussed by Hawke et al. [18].

An expert judgment was applied for the quantification of human errors in chemical and environmental analysis on several previous occasions. For example, the house-of-security technique was used for the quantification of human errors in the pH measurement of groundwater [19] and the multi-residue analysis of pesticides in fruits and vegetables [20], while the Monte Carlo simulation of expert judgments on human errors in elemental analysis of geological samples by inductively coupled plasma mass spectrometry (ICP–MS) was applied for the determination of distributions of the error quantification scores, i.e., scores of likelihood and severity and scores of the effectiveness of a laboratory quality system in the prevention of the errors [21]. Kuselman and co-workers gave a review of human errors in a chemical analytical laboratory using a Swiss cheese model for the characterization of the interaction of errors with a laboratory quality system [22]. The classification, modeling, and quantification of human errors in routine chemical analysis are described by Kuselman and Pennecchi [15].

Considering the above-mentioned, the goal of this paper is to identify and quantify activities that are potentially susceptible to human errors in the spectrophotometric determination of the concentration of pollutants in water using the Success probability index method (SLIM). As a specific case, the scenario of UV-Vis spectrophotometric determination of ammonia concentration in water was used. Since the SLIM has never before been applied for human error assessment in environmental analysis, this paper bridges the gap between chemical analysis of environmental pollutants and human error assessment methods to offer solutions for the reduction of human error in environmental analysis.

Experimental

A Brief Description of the Experiment

After sampling water in the field, the determination of the concentration of ammonia in the water samples is carried out in the laboratory [23]. The sample is collected in a clean sampling bottle made of chemically inert plastic and preserved by the addition of concentrated H_2SO_4 so that the pH of the sample is less than 2. The bottle is closed, and the sample is kept in a cool (4ºC) and dark place during transportation and storage. A sample preserved in this way can be analyzed within 24 hours after sampling.

Since the solution of ammonia in water is without a clour, spectrophotometric determination of the concentration of ammonia in water is performed after the addition of Nessler's reagent at a wavelength of 425 nm. Nessler's reagent is an alkaline solution of potassium tetraiodomercurate (II) ($K_2[HgI_4]$) that, in the presence of ammonium ions, forms a dark yellow complex compound. The intensity of the color of this compound depends on the concentration of ammonia in the sample.

First, a series of standard solutions of ammonia is made by diluting the basic solution of ammonium chloride (NH_4Cl). Then, Nessler's reagent is added to each standard solution, and after 10 to 15 minutes, the absorbance of the yellow solutions is read according

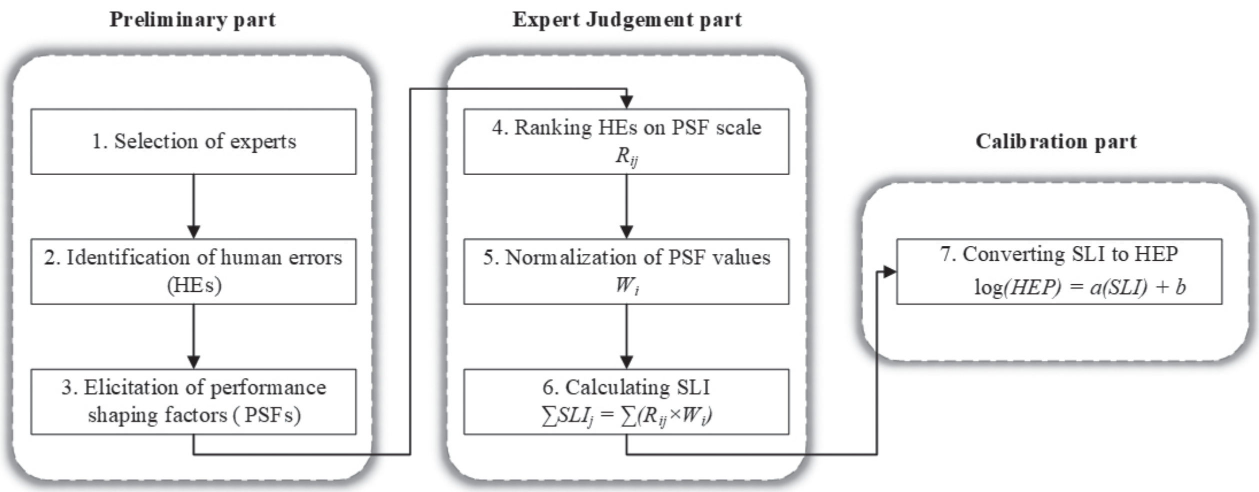

Fig. 1. Procedural steps in SLIM.

to the blank (deionized water) at 425 nm, and a calibration curve, absorbance *vs.* the concentration of ammonium ions, is drawn. The same procedure is repeated with the water sample, after which the ammonium ion concentration is read either from the curve or the equation.

Description of the SLIM Procedure

Assessment of human errors in the spectrophotometric determination of polluting substances, specifically ammonia in water, was performed using the SLIM procedure [11, 24] (Fig 1).

Selection of Experts

For the current investigation, 10 experts from the Department of Chemistry, Faculty of Sciences and Mathematics, University of Niš (Serbia), with professional experience in spectrophotometric analysis of a minimum of 10 years, were selected.

Human Error Identification

The research coordinator identified various scenarios that may lead to human error in each step of the spectrophotometric determination of ammonium in water (water sampling and sample preparation, preparation of standard solutions, analysis, and evaluation of the results). Some of the potential errors are listed below:

I Sampling and sample preparation:
– Taking an unrepresentative sample
– Sampling an insufficient amount of sample
– Changes during transport and storage
– Mislabeling of sample
– Inadequate sample preparation

II Standard solution preparation:
– An inadequate substance for preparing a standard solution (e.g., NH_4OH)
– Weighting an incorrect quantity of NH_4Cl on the scale
– A volumetric flask loading error
– Pipetting errors when diluting
– Mislabeling of standard solutions
– Miscalculation of the concentration of a series of standard solutions

III Analysis:
– Wrong choice of blank
– Measuring errors when pipetting the sample, solutions, and reagents
– Interference from the other substances present in the sample
– An unequal reaction time between standard solutions and the sample
– Recording the absorbance at the wrong wavelength
– An insufficiently clean cuvette
– An insufficiently filled cuvette
– The concentration of ammonia in the tested sample is not within the calibration range
– Poor recording of results

IV Evaluation of the results:
– Wrong construction of the calibration curve
– Wrong reading of the concentration of ammonia in the sample from the calibration curve
– Rounding error

After defining the possible scenarios, the research coordinator and the team selected 10 errors (tasks) for analysis and quantification using SLIM (Table 1).

Elicitation of Typical PSFs

For the current research, six typical PFSs were selected:
1. training (practice),
2. procedures (type/procedure quality),
3. time (time pressure),
4. teamwork (team structure and cooperation),
5. communication (written or oral),
6. experience (state of current experience or skills).

Table 1. Ten errors chosen for the assessment of human errors in the spectrophotometric determination of the concentration of pollutants by SLIM.

Error N°	Error
1.	Taking an unrepresentative sample
2.	Transport and storage changes
3.	Mislabeling the sample
4.	Weighting an incorrect quantity of NH_4Cl on the scale
5.	A volumetric flask loading error
6.	Pipetting error when diluting
7.	Miscalculation of the concentration of standard solutions
8.	Interference from the other substances present in the sample
9.	An unequal reaction time of standard solutions and the sample
10.	Wrong reading of the NH_3 concentration in the sample from the calibration curve

Experts estimated the influence of each PFS on the 10 selected errors on a scale from 1 to 9, where 1 represented the smallest and 9 represented the greatest influence.

Results and Discussion

Since human error is still a significant issue affecting the quality of data obtained during environmental analysis, herein, for the first time, we applied the Success likelihood index method (SLIM) for the identification and quantification of human errors in the analysis of polluting substances, taking a UV-Vis spectrophotometric determination of ammonia concentration in water as a case study. After identifying possible human errors in the experiment in question and defining PSFs by a research coordinator, a group of experts evaluated the influence of each PSF on 10 selected errors (Table 1). The average values of the expert judgment on the influence of each PFS on the specific error are given in Table 2. If the experts considered each PSF equally important for the analyzed situation, the rankings could be summed up together to conclude which error is the most common one. Since this is not the case, PSF significance is determined by normalizing the PSF values (Table 2).

Table 2. The estimated and normalized PSF values.

Error N°	R_{ij}^{*}						Σ
	Training	Procedures	Time	Teamwork	Communication	Experience	
1.	7	8	4	3	4	7	**33**
2.	5	7	3	4	5	6	**30**
3.	5	4	6	5	7	5	**32**
4.	7	3	5	2	3	7	**27**
5.	9	3	6	2	2	8	**30**
6.	8	3	5	2	2	8	**28**
7.	7	5	4	2	3	8	**29**
8.	6	7	6	4	3	7	**33**
9.	5	8	4	4	4	6	**31**
10.	7	4	4	3	4	8	**30**
ΣPSF	**66**	**52**	**47**	**31**	**37**	**70**	**303**
W_i^{**}	**0.22**	**0.17**	**0.16**	**0.10**	**0.12**	**0.23**	**1**

$^{*}R_{ij}$ rating of task on the given PSF (1 represents the smallest, while 9 represents the highest influence of PSF on a specific task); $^{**}W_i$ normalized importance weighting for the given PSF

Success likelihood index (*SLI*) is then calculated by multiplying the rating of task *j* on the given PSF (R_{ij}) with normalized importance weighting for the given PSF (W_i):

$$SLI = R_{ij} \times W_i$$

while the total *SLI* for the given task *j* (∑*SLI*) could be calculated using the expression:

$$\sum SLI = SUM(R_{ij} \times W_i), \text{ for } i=1,...i=x$$

where *x* is the number of PSFs considered.

Calculated *SLI* values are given in Table 3. SLI is an indication of the relative probability of different errors and shows the order of probabilities. Taking the unrepresentative sample is the task with the highest ∑*SLI* value (5.93), indicating that this is the most frequent error, while one could say that weighting an incorrect quantity of NH_4Cl on the scale is the rarest error (the task with the lowest ∑*SLI* value of 5.02).

However, *SLI* still does not determine the absolute probability of the occurrence of a specific human error. This probability is defined by another factor called human error probability (*HEP*). To transform *SLI* into *HEP*, it is necessary to establish their logarithmic relationship using the following expression:

$$\log(HEP) = a(SLI) + b$$

where *a* and *b* are constants that can be derived either by a computer system or by solving simultaneous equations, as long as at least two calibration probabilities have been assessed within each task subset. For the research problem in question, the values of -0.93 and 2.56 were taken for coefficients *a* and *b*, respectively [24]. *HEP* values are given in Table 3 and Fig. 2.

Fig. 2 shows that during the spectrophotometric determination of ammonia in water, human errors with the highest probability of occurrence are "Taking an unrepresentative sample" (*HEP* = 1.12×10^{-3}), "An unequal reaction time of standard solutions and the sample" (*HEP* = 1.35×10^{-3}), and "A volumetric flask loading error" (*HEP* = 1.70×10^{-3}), followed by "Wrong reading of the concentration of ammonia in the sample from the calibration curve" and "Miscalculation of the concentration of a series of standard solutions" with *HEP* values of *ca*. 3×10^{-3}. The same probabilities of occurrence (*HEP* = 3.80×10^{-3}) have "Pipetting errors when diluting" and "Interference from the other substances present in the sample". Three errors with the lowest probability of occurrence value are "Mislabeling of sample", "Changes during transport and storage " and "Weighing an incorrect quantity of NH_4Cl on the scale", with HEP values of 5.01×10^{-3}, 5.89×10^{-3}, and 7.76×10^{-3}, respectively.

Numerous scenarios can lead to human error in the chemical analysis of environmental pollutants that depend on the PSFs. Based on the results and normalized PSF values (Table 2), it can be concluded that "experience" and "training" are the two most important performance-shaping factors that contribute to error reduction, followed by "procedures" and "time". "Communication" and "teamwork" are estimated as the least contributing PSFs to the occurrence of human error in the experiment in question (Fig. 3).

Experience affects the precision and safe execution of work tasks, *i.e.,* experimenting, but on the other hand, psychophysical abilities related to the time and speed of the analyst's reaction decline with age. In addition, training is one of the mechanisms for improving work experience, knowledge, and skills. This gradation of PSFs (Fig. 3) is in general agreement with literature data related to the analysis of human error not only in the chemical laboratory but also in general.

Table 3. Success likelihood index (*SLI*) and human error probability (*HEP*).

Error Nº	*PSF*						∑*SLI*	*HEP*
	Experience	Training	Procedures	Time	Communication	Teamwork		
1.	1.61	1.54	1.36	0.64	0.48	0.30	5.93	0.00112
2.	1.38	1.1	1.19	0.48	0.6	0.40	5.15	0.00589
3.	1.15	1.1	0.68	0.96	0.84	0.50	5.23	0.00501
4.	1.61	1.54	0.51	0.8	0.36	0.20	5.02	0.00776
5.	1.84	1.98	0.51	0.96	0.24	0.20	5.73	0.00170
6.	1.84	1.76	0.51	0.8	0.24	0.20	5.35	0.00380
7.	1.84	1.54	0.85	0.64	0.36	0.20	5.43	0.00324
8.	1.61	1.32	1.19	0.96	0.36	0.40	5.84	0.00135
9.	1.38	1.1	1.36	0.64	0.48	0.40	5.36	0.0038
10.	1.84	1.54	0.68	0.64	0.48	0.30	5.48	0.00288

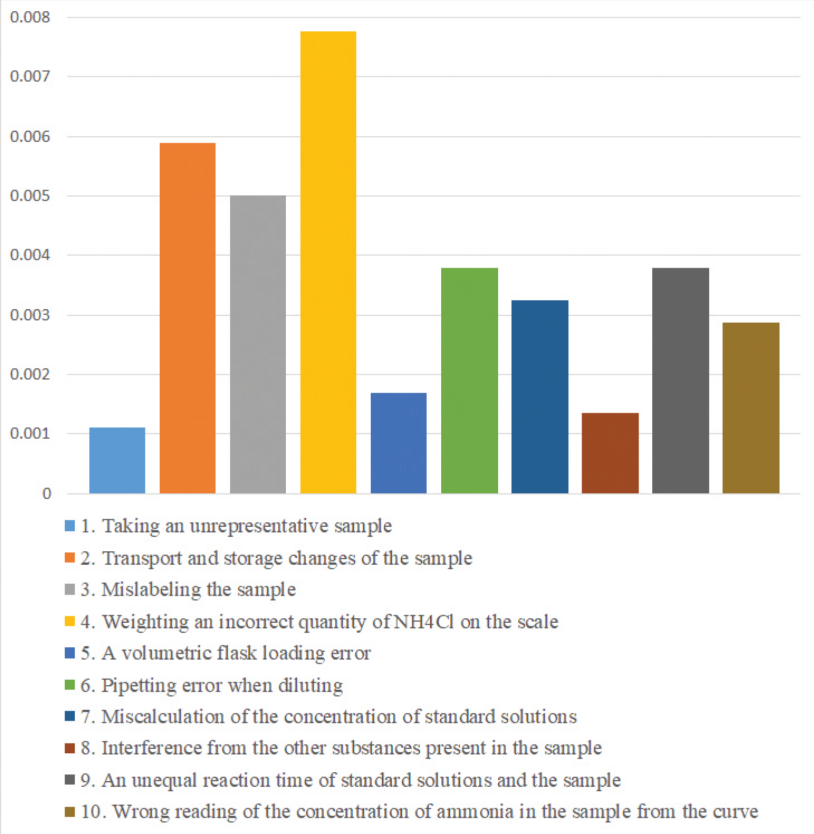

Fig. 2. HEP values for specific tasks in spectrophotometric determination of ammonia in water.

In a study conducted by Ellison and Hardcastle (2012), respondents who participated in an online survey on errors in analytical chemistry, primarily the analysis of environmental and food samples, named lack of training and experience as the most significant cause of errors [17]. According to Kuselman and co-workers, training is the most important component of the quality system for measuring the pH of groundwater [19] and determining pesticide residues in fruits and vegetables [20]. The next most important PSF is the procedure, which indicates that the type/quality of the procedure and good knowledge of the procedures are important factors in shaping operator performance, which agrees with the previously published observation that deficiencies in even basic laboratory procedures can be a serious problem [17].

Although the spectrophotometric determination of pollutants (ammonia) in water can be considered a routine experiment, among the analyzed PSFs, time is ranked as the fourth most important factor. This agrees with the results of the human error test during the analysis of stable isotopes, according to which pressure, i.e., workload, is the most significant cause of human error among the ecologists who submit the sample for analysis and analysts who analyze the sample in the laboratory [18]. Communication and teamwork occupy the last two places in the PSF gradation (Fig. 3), implicating that team structure, socializing with people from the same workgroup, good interpersonal relations, cooperation, and help when performing work tasks can lead to the reduction of errors.

Considering the aforementioned, the most common cause of human errors is insufficient knowledge about how exactly the work operations should be performed. Thus, it can be concluded that additional training of analysts, the implementation of new and more detailed procedures, and better time (workload) management could be useful corrective measures that would lead to a reduction of human error in the analysis of polluting

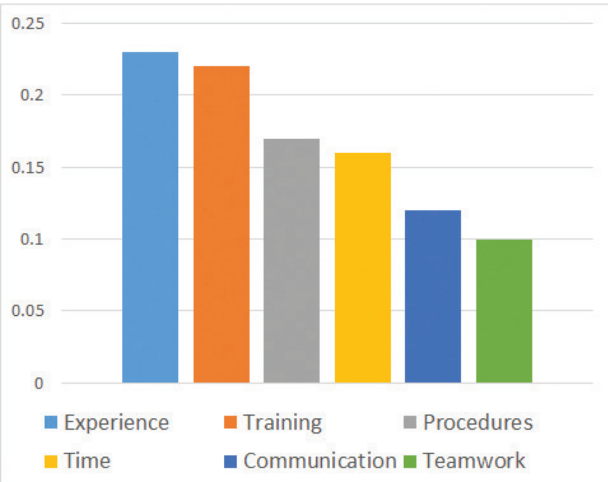

Fig. 3. Normalized PSF values.

substances. However, it should be noted that this cannot be generalized, and corrective measures must be adapted to each specific scenario (error) individually.

Conclusions

Although human error is part of everyday laboratory practice, there is only scarce data on the quantification of the human error probability in environmental analytical chemistry. This study aimed to point out the importance of considering human error in quantitative risk assessment in environmental pollutant analysis. Herein, for the first time, the Success likelihood index method (SLIM) was applied for the identification and quantification of human errors during the analysis of environmental pollutants, whereas a UV-Vis spectrophotometric determination of ammonia concentration in water was examined as a case study. By applying SLIM, the influence of performance shaping factors (PSFs), such as procedure, experience, training, time, communication, and teamwork, on the occurrence of errors for specific tasks was assessed by experts. The obtained results indicated that experience and training, followed by procedures, are the factors that contribute to the greatest extent to the reduction of errors during the analysis. Considering this, corrective activities such as additional training of analysts, the implementation of new and more detailed procedures, and better time (workload) management could be proposed.

Thus, SLIM not only represents a good framework for the analysis and identification of human errors in pollutant and chemical analysis in general but can also be a useful tool for defining corrective measures and reducing human errors in these areas. This method can be the basis for future research that would contain the analysis of various human errors during the implementation of not only routine but also complex experiments under similar conditions in similar work environments, which would broaden the picture of the causes of errors. The importance of this research lies in the fact that the analysis of human error not only identifies human errors and considers the human role in the occurrence of a risk, but it also gives us a possibility for preliminary identification of error reduction measures.

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Conflict of Interest

The authors declare no conflict of interest.

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