The state of the art of the impact of sampling uncertainty on measurement uncertainty

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Abstract: The measurement uncertainty is a parameter that marks the reliability and can be divided into two large groups: sampling and analytical variations. Analytical uncertainty is a controlled process, performed in the laboratory. The same does not occur with the sampling uncertainty, which, because it faces several obstacles and there is no clarity on how to perform the procedures, has been neglected, although it is admittedly indispensable to the measurement process. This paper aims at describing the state of the art of sampling uncertainty and at assessing its relevance to measurement uncertainty.

Keywords: sampling, sampling uncertainty, measurement uncertainty

1. INTRODUCTION

Lately, estimating the measurement uncertainty with higher reliability has been a goal, in order to guarantee a measurement process with quality. The measurement process starts with the selection of the sample, so the measurement uncertainty is constituted by the association of the uncertainty from both the sampling and the analytical processes.

The whole process involving sampling and its uncertainty has been neglected by analytical chemists and metrologists due to the lack of knowledge regarding the impact on the quality of the result [1-2]. Thus, everything that involves the control and supervision of this step, and which allows assessing the associated uncertainty, is rarely considered, even with ISO / IEC 17025 stating that sampling is an element of paramount importance for total measurement uncertainty [4].

The difficulties found in the sampling process usually mean that only the analytical uncertainty process is computed for the measurement uncertainty. This approach can offset the value of the uncertainty informed from its real value, since it underestimates the measurement uncertainty by disregarding the sampling uncertainty. This in turn leads to decisions based on quality control and assurance that not always are the most reliable. It is imperative that there are methodologies which are capable of estimating the measurement uncertainty taking into account each part of the measurement process and all associated uncertainties [5].

Thus, this article aims at presenting the state of the art of sampling uncertainty with regard to measurement uncertainty, examples that proves the need to consider both sampling uncertainty

and analytical uncertainty in the process of measurement uncertainty and pointing out the possible gaps to be filled.

2. MEASUREMENT UNCERTAINTY

Measurement uncertainty is a "non-negative parameter that characterizes the dispersion of values assigned to a measurand, based on the information used." For this, it is necessary to know the sampling target with its location in space and time [5,6].

The simplest way to categorize the various sources that can influence the uncertainty is to separate them into two groups: sampling uncertainty and analytical uncertainty.

Although they have the same purpose with well-defined roles, the estimates of each uncertainty group are independent. Thus, the sampling manager should be able to reliably define the sampling uncertainty and the analyst process manager must be able to define the analytical uncertainty, composing the total measurement uncertainty [5].

The standard measurement uncertainty, u, can be estimated by [8]

$$u = S_{med} = \sqrt{S_{sample}^2 + S_{anal}^2} \qquad (1)$$

where S_{med} is the estimate of the measurement uncertainty; S_{sample}^2 is the estimate of the variance of the sampling and S_{anal}^2 is the estimate of the analytical variance.

The standard JCGM 100:2008 [6] cites two approaches, empirical (top-down) and modeling (bottom-up), to quantify the sources of uncertainty. Oliveira and Aguiar [9] present three more, namely Barwick and Ellison, study of variability and fuzzy arithmetic, among others.

The measurement uncertainty value cannot be expressed in a more reliable way if the characteristic part of the sampling uncertainty is missing, in other words, considering only the analytical uncertainty, regardless of the procedure used by the laboratory. However, since the sampling uncertainty is not recognized, it is performed carelessly by inexperienced professionals, although this uncertainty may significantly interfere with the final result [7].

For the analytical chemist with poor knowledge about quality management systems, the uncertainty of interest is the one coming only from the analytical process; however, for the end user and the customer, the uncertainty of interest is the one compounded by all the uncertainties in the measurement process [1,7].

3. STATE OF THE ART

The demand for studies involving sampling uncertainty is not yet expressive, since conducting research in the area is time and cost consuming. The literature reports the importance of the uncertainty evaluation regarding the sampling process, however, not showing how significant it may be.

The works carried out in the sampling sector are recent and did not delve into this issue. It has been convenient to consider the sampling target only as a representative sample of the population, and don't describe or express the representativeness of the sample and how relevant it is. Thompson goes so far as to use the expression "awakening the sleeping dogs of sampling" [10] to describe how difficult it is to consider this process since there are no clear guidelines and professionals interested in developing research.

From 2001 to 2004, the National Environmental Protection Agency of Italy (ANPA) funded a project to assess practically the uncertainty of sampling [4].

In 2005, the sampling workshop was initiated at the request of the Nordic Innovation Center aimed at highlighting and emphasizing the importance of adequate sampling for environmental or chemical purposes, promoting actions to improve sample reliability, among other actions [7].

In 2007, a seminar about sampling uncertainty in Denmark was held to disseminate a manual on sampling and uncertainty assessment. A set of techniques and tools available for the calculation and control of uncertainty related to sampling was presented [5].

To further justify this relevant subject, two examples have been drawn from the Eurachem and are discussed in [8], both from the food sector.

In the first example, the ion nitrate measurement process in greenhouse grown lettuce is discussed. In this study, a "bay" of up to 20,000 heads of lettuce was used to estimate the ion nitrate concentrations. Considering each "bay" as a sampling target, 10 heads of lettuce were removed from each "bay" for sample. With an empirical approach (top-down) and duplicate method, the calculations were made from robust ANOVA. So, this study presented 22.6 % as contributions from the sampling and 6.3 % from the analytical process, in a combined measurement uncertainty of 28.9 %, being the sampling a dominant factor, responsible for 78.2 % of the measurement variance.

In the second example, evaluation of Vitamin A concentration in baby porridge, with fruits and ground cereals, it has been estimated the measurement uncertainty and the contributions of sampling and analysis. For the sampling target, 10 different batches of porridge were determined, each batch being 1,092 kg and, as a sample, a batch of approximately 400 g powder. Two samples were taken per batch and two portions of approximately 40-50 g were sampled from each sample. With an empirical approach (top-down) and duplicate method, by means of one way ANOVA, and with 95 % confidence level, the expanded uncertainty related to the sampling is of 10 %, while for the analytical step is of 17 % [8].

It was observed that the first example presented a sampling uncertainty more representative than the analytical uncertainty and the second one showed an analytical uncertainty more representative than a sampling uncertainty, being the latter still relevant. Thus, it is not possible to predict which uncertainty step will have the greater representativeness, so it is essential the calculation of measurement uncertainty considering both steps.

4. BREAKING PARADIGMS

In some areas, sampling uncertainty is more representative than analytical uncertainty, in special when it involves raw materials (natural or industrial) that are being tested [10].

In the scientific community, it is still common practice to ignore sampling since there is no clear description of how to measure its uncertainty, only the measurement uncertainty from the post-entry process of the material in the laboratory. [4]

There are procedures called "best practices" or "suitable for the purpose", which are intended to describe and facilitate the process; however, these are trivial, not having the depth required in practice for the attainment of uncertainty.

There is no detailed description of how to perform a sampling procedure, that is technically complicated when not instructed, and whose validation is much less developed than that of the analysis. That is, there are few regulations that require sampling to be accredited, both in Brazil and abroad and the assumptions for quality assurance when required, are derisory [5].

Developing surveys or adding reliability to the entire measurement process from planning,

sampling to completion of the analytical process requires investment. However, by reducing uncertainty, with the possibility of controlling the quality of the process, it could generate much greater benefits [1,10]. Thompson shows industrial cases where investment in the sampling process generated a substantial net gain due to the importance given to sampling errors. Therefore, knowing and defining well each contribution of uncertainty leads to quality control and its efficiency can be guaranteed.

5. CONCLUSION

It is necessary to develop research and projects that aim at estimating the uncertainties, focusing to the process of the sampling uncertainty with regard to measurement uncertainty.

When one knows all the phases that compose the uncertainty, one can control and evaluate where, in what particularity of the process it is more profitable to invest for profit-seeking. Management process becomes more tangible.

However, there is a need for investment from interested organizations involved in the process, breaking paradigms for metrologists and analytical chemists, in order to leave their comfort zone and deepen in this area.

As future work, other real examples related to effluent, food, oil and ore industries are being studied to establish patterns of the impact of sampling uncertainty on measurement uncertainty for each matrix and specific analytes.

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