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Practical and valid guidelines for realistic estimation of measurement uncertainty in multi-residue analysis of pesticides

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ABSTRACT

To assist the understanding and adoption of measurement uncertainty principles in chemical tests, during the last decade, a number of specific guidelines have been published by EURACHEM/CITAC, EUROLAB, NORDTEST and others international bodies. All these guidelines agree that, in certain cases, the nature of the test method may preclude rigorous, metrologically and statistically valid, calculation of uncertainty of measurement, multi-residue analysis of pesticides being, without any doubt, one of these cases. In 2006, the Codex Alimentarius Commission established its guidelines on estimation of uncertainty of results for the determination of pesticide residues, which only include "empirical, practical or top-down" approaches based on whole-method performance investigations or scientific judgments from previous experience. The aim of this publication is to make a simple and comparative critical review of the most relevant international guidelines published on measurement uncertainty in both chemical analysis and pesticide residues analysis, extracting from them those proposals and practical conclusions that can be applied in a pesticide residue laboratory with full warranty and validity.

1. Introduction

The International Organization for Standardization (ISO), in 2007, defined measurement uncertainty as *a non-negative parameter characterizing the dispersion of quantity values being attributed to a measurand, based on the information used* (International Organization for Standardization-ISO, 2007), but measurement uncertainty principles were first established in 1993 by the "BIPM-IEC-IFCC-ISO-IUPAC-OIML Guide to the Expression of Uncertainty in Measurement (GUM)", whose last revision is referenced as ISO Guide 98-3 (International Organization for Standardization-ISO, 2008). Today, most of the laboratories reporting results of chemical tests have accepted that measurement uncertainty is a "positive" parameter associated with the test result, which must be neither too low nor too high, but realistic and reliable for the intended purpose. Likewise, today it is worldwide accepted that uncertainty should always be reported because it accounts for the quality of the result, being necessary for comparisons between laboratories and compliance decisions. However, the application of measurement uncertainty principles in the area of pesticide residues analysis is not yet well established and harmonized, and is still a subject for active discussions between analysts, managers, regulators or laboratory clients.

To assist the understanding and adoption of measurement uncertainty principles in chemical tests, during the last decade, a number of specific guidelines have been published by EURACHEM/CITAC (EURACHEM, 2012), EUROLAB (EUROLAB, 2002; 2006; 2007), NORDTEST (NORDTEST, 2003) and other international bodies. All these guidelines agree that, in addition to the "modeling, theoretical or bottom-up" approach, the GUM also includes the possibility of using, in certain cases, "empirical, practical or top-down" approaches, which may be based on whole-method performance investigations or scientific judgments from previous experience. These approaches are accepted, in certain cases, by the accreditation standard ISO/IEC 17025: 2005 (International Organization for Standardization-ISO, 2005), but just for testing laboratories. Specifically, the technical requirement 5.4.6 of ISO/IEC 17025: 2005, entitled "Estimation of uncertainty of measurement", states: … *Testing laboratories shall have and shall apply procedures for estimating uncertainty of measurement. In certain cases the nature of the test method may preclude rigorous, metrologically and statistically valid, calculation of uncertainty of measurement* … Without any

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doubt, multi-residue analysis of pesticides is one of these cases.

For many years, measurement uncertainty in pesticide residue analysis has also been a discussion topic in the Codex Committee on Pesticide Residues (CCPR). In 2006, the Codex Alimentarius Commission (CAC) established its guidelines CAC/GL 59-2006 on estimation of uncertainty of results for the determination of pesticide residues (Codex Alimentarius Commission, 2006; 2011), which only include “empirical, practical or top-down” approaches.

The main objective of this publication is to make a simple, comparative and critical review of the most relevant international guidelines published on measurement uncertainty in both chemical analysis and pesticide residue analysis, extracting from them those proposals and practical conclusions that can be applied in a pesticide residue laboratory with full warranty and validity.

2. Measurement uncertainty and confidence in a test result

According to the GUM definition, Measurement Uncertainty is *a parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand*. This parameter may be either a standard deviation (combined standard uncertainty “u_c”) or the width of a confidence interval (expanded uncertainty “U”). The relationship between standard uncertainty and expanded uncertainty, when the dispersion of the measured values is characterized by a normal distribution, is shown in Fig. 1. The coverage factor “k” depends on the type of distribution and the level of confidence, but it is usual to assume, by default, a normal distribution with a value of “k = 2” for a confidence level of 95%. Fig. 1 refers to the measurement of a pesticide residue, and it is assumed that measurement of the identical sample (different test portions) is repeated several times in one, or more, laboratories at different occasions, with different analysts, chemicals, standards or instruments. As a consequence, different results are obtained, which are often normally distributed around the mean (true?) value. In this example, a standard deviation of 0.15 mg/kg was observed for the mean value of 0.85 mg/kg, the standard uncertainty being equal to the standard deviation.

Fig. 1 also visualizes an example of the three different ways of reporting a result for a pesticide residue: 1) just the value, 2) the value with the estimated precision, and 3) the value with the estimated uncertainty. When just the value of the result is reported (0.85 mg/kg in this example), due to the rounding factor, what is being reported is that the result could be between 0.845 mg/kg and 0.854 mg/kg, and as can be seen in Fig. 1, the confidence level for this result would be 2.5% approximately (percentage of the normal distribution total area defined by this concentration interval). In the event that the result would include the estimated precision (for example, ± 0.10 mg/kg), the concentration range defined by the reported result would be 0.75–0.95 mg/kg, and the corresponding level of confidence would not exceed 50%. However, when the “measurement uncertainty” parameter is included in the reported result, the concentration range encompassing the result is defined by the degree of confidence that has been previously set for it (in this example, 95%). Undoubtedly, this is the key idea, and the most valuable aspect, of the parameter “measurement uncertainty”. That is to say, the quality of the result, when it is reported with its uncertainty, is much higher because it presents a previously fixed high level of confidence. But this will have reduced, or potentially no value, if the estimated uncertainty is not realistic.

In the example of Fig. 1, the standard uncertainty is ± 0.15 mg/kg and, consequently, the expanded uncertainty value is ± 0.30 mg/kg (k = 2; 95%) and the relative expanded uncertainty value (expanded uncertainty × 100/measured value) is 35% approximately. These uncertainty values are quite realistic considering the characteristics of multi-residue methods for pesticide analysis. Certainly, we should not have much confidence in a laboratory reporting a pesticide residue result of 0.85 ± 0.01 mg/kg. This laboratory could argue that it is using a very precise methodology, and that it has followed a comprehensive procedure for calculating measurement uncertainty based on the GUM mathematical model. However, proficiency test results have shown that laboratories producing permanently results with such low uncertainty do not exist (Medina-Pastor, Rodriguez-Torreblanca, Andersson, & Fernandez-Alba, 2010; Valverde, Fernández-Alba, Ferrer, & Aguilera, 2016).

3. “Bottom-up” and Top-down” approaches for evaluation of uncertainty in analytical measurement

The Guide to the Expression of Uncertainty in Measurement

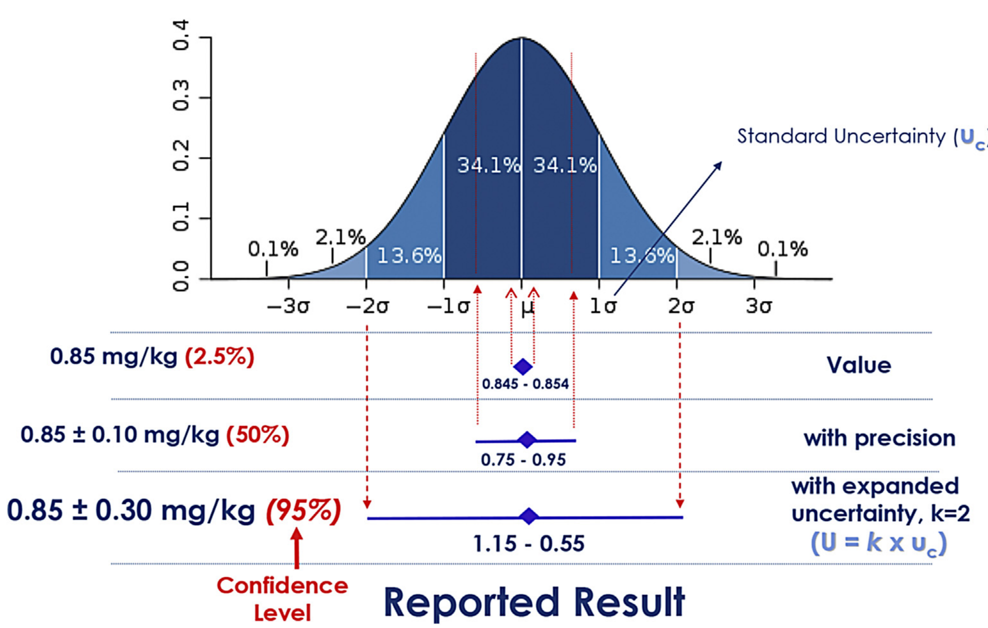

Fig. 1. Confidence in a result of 0.85 mg/kg, which was measured with a precision of ± 0.10 mg/kg and reported with/without uncertainty.