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Uncertainty evaluation for the quantification of low masses of benzo[a]pyrene: Comparison between the Law of Propagation of Uncertainty and the Monte Carlo method

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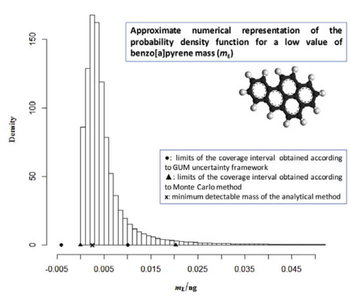
HIGHLIGHTS

- Comparison between the uncertainty evaluation carried out according to the GUM uncertainty framework and the Monte Carlo (MC) method starting from real data sets obtained from the quantification of the mass of benzo[a]pyrene (BaP).
- The two approaches for the uncertainty evaluation provide different results for BaP masses in samples containing different masses of the analyte, MC method giving larger coverage intervals.
- In cases of analyte masses close to zero, the GUM uncertainty framework leads to a coverage interval stretching into a region of negative unfeasible values for the measurand.
- Application of MC simulation to the propagation of probability distributions particularly fits the cases of measurement results of intrinsically positive quantities close to zero.
- MC simulation can be configured in a way that only positive values are generated thus obtaining a coverage interval for the measurand that is always reliable.

GRAPHICAL ABSTRACT



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A R T I C L E I N F O

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A B S T R A C T

A proper evaluation of the uncertainty associated to the quantification of micropollutants in the environment, like Polycyclic Aromatic Hydrocarbons (PAHs), is crucial for the reliability of the measurement results. The present work describes a comparison between the uncertainty evaluation carried out according to the GUM uncertainty framework and the Monte Carlo (MC) method. This comparison was carried out starting from real data sets obtained from the quantification of benzo[a]pyrene (BaP), spiked on filters commonly used for airborne particulate matter sampling. BaP was chosen as target analyte as it is listed in the current European legislation as marker of the carcinogenic risk for the whole class of PAHs.

MC method, being useful for nonlinear models and when the resulting output distribution for the measurand is non-symmetric, can particularly fit the cases in which the results of intrinsically positive quantities are very small and the lower limit of a desired coverage interval, obtained according to the GUM uncertainty framework, can be dramatically close to zero, if not even negative.

In the case under study, it was observed that the two approaches for the uncertainty evaluation provide different results for BaP masses in samples containing different masses of the analyte, MC method giving larger coverage intervals. In addition, in cases of analyte masses close to zero, the GUM uncertainty framework would give even negative lower limit of uncertainty coverage interval for the measurand, an unphysical result which is avoided when using MC method. MC simulations, indeed, can be configured in a way that only positive values are generated thus obtaining a coverage interval for the measurand that is always positive.

1. Introduction

The quantification of low masses of Polycyclic Aromatic Hydrocarbons (PAHs) is an important issue as they are ubiquitous toxic contaminants which can be present in all the environmental compartments [1] even at trace levels. PAHs with five or more aromatic rings, among which the compounds having major toxicological relevance, are mainly absorbed onto fine and ultrafine particulate matter [2]. The most studied PAH is benzo[a]pyrene (BaP) which is classified as carcinogenic agent by the International Agency for Research on Cancer [3] and thus listed in the current European legislation as marker of the carcinogenic risk for the whole class of PAHs [4].

There are many difficulties in establishing a realistic uncertainty budget associated with measurement results for the quantification of chemical pollutants in environmental samples, among which the definition of the measurand and of a proper model equation, the small amount of different compounds to be determined and quantified, the effect of the matrix, the identification and quantification of the various uncertainty sources. In this framework, the evaluation of the uncertainty associated with the quantification of micropollutants like PAHs in the environment plays an important role to give reliability to the estimate obtained for the measurand. Examples of uncertainty evaluation for organic micropollutants can be found in literature [5–9] and the main approach adopted is the GUM uncertainty framework, as summarized in [10, G.6.6]. The approach proposed in the GUM relies on the Law of Propagation of Uncertainty (LPU), which requires the linearization of the measurement model. Monte Carlo (MC) method [11], instead, is based on the propagation of the whole probability distribution of the input quantities, thus providing a numerical approximation to the distribution to be associated to the measurand which is consistent with the measurement model and with the distributions assigned to the input quantities. In general, MC method fits better than the GUM approach to nonlinear models, it does not require any linear approximation of the model nor the determination of the effective degrees of freedom for calculating the expanded uncertainty to be associated to the measurand. In case of an asymmetric output density function, for example, MC method automatically provides a realistic coverage interval, contrary to the approach prescribed within the GUM which resorts to the approximation of the output density function with a Student (symmetric) one. Therefore, MC method particularly fits the cases of results of chemical measurements dealing with intrinsically positive quantities having values close to zero. However, there are only few examples of its implementation in chemical measurements, mainly focused on case studies derived from literature [12–14]. The application of MC method to chemical measurements is also reported in Ref. [15], but the example given in the Guide does not concern models with correlated input quantities.

The present work aims at comparing the results obtained by application of the GUM uncertainty framework and the MC method to real data sets derived from the quantification of the mass of BaP spiked on filters commonly used for airborne particulate matter sampling. The development of a method to quantify BaP in ambient air is beyond the scope of the paper as it was addressed in Ref. [16]. The main outcome of the present work is that the application of the GUM uncertainty framework may lead to poorly reliable coverage intervals when the resulting output distribution for the measurand is non-symmetric. In the considered cases, the results of masses of BaP are very small and the lower limit of the uncertainty coverage interval can be dramatically close to zero, even negative for simulated results. This situation was faced by applying MC method.

2. Experimental

2.1. Materials and methods

A glass fiber filter (*Pall & Whatman*) having diameter of 47 mm, a type of filter commonly used for the sampling of airborne particulate matter, was spiked with the Certified Reference Material