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CONTENT

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MONTE CARLO SIMULATION AS AN ALTERNATIVE APPROACH FOR ESTIMATION OF UNCERTAINTY MEASUREMENT OF 2,4-DIMETHYLPHENOL

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ABSTRACT
The estimation of uncertainty measurement using different approaches is increasingly applied to assess the reliability of results generated by applied analytical methods. This paper presents the Monte Carlo simulation model (MCS) for calculating the uncertainty of the measurement associated with the result of the analysis. The results of MCS were compared with the commonly used a standard method (GUM). The calculations of the measurement uncertainty were demonstrated in the case of the determination of 2,4-dimethylphenol by gas chromatography in concrete samples.

INTRODUCTION
The estimation of measurement uncertainty is an important aspect in evaluating measurement results. The International Standardization Organization (ISO) was published the Guide to Expression of Uncertainty in Measurement (GUM) in 1993 [1].

This approach to estimating measurement uncertainty is based on theoretical principles but exhibit some important limitations that are mainly derived from the use of the law of uncertainty propagation and from the application of the central limit theorem. To avoid these limitations, the joint committee for guides in Metrology (JCGM) presents a methodology that uses Monte Carlo method (MCS) for propagation of distributions, which is described in JCGM 101 [2, 3]. Monte Carlo approach for evaluation of uncertainty is a reliable tool when GUM framework is not adequate [3]. In analytical chemistry, uncertainty estimation is crucial, since it determines

conformance or non-conformance with a referent level, thus affecting risk management directly related to human health.

2,4-dimethylphenol (DMP) is used in the manufacture of commercial products for industry and agriculture. The presence of DMP in manufacture of numerous products, shows the potential for water, soil, air or building materials contamination [4]. DMP is termed as "toxic" in all regulatory resources listed by the EPA. It is estimated that the total annual discharge of DMP is around 72640 kg per year of which about 95% is slated for onsite disposals (air, water, land, underground injection, surface water discharge) [5]. In our previous research, we validated gas chromatography-mass spectrometry (GC-MS) method for the analysis of phenol compound in solid-solid concrete [6]. In the present work the uncertainty estimation for DMP in a concrete sample, using the Monte-Carlo simulated method, is studied. The results are compared to the ones obtained using the GUM method.

EXPERIMENTAL

Uncertainty estimation

Input data for calculating measurement uncertainty were taken from our previously presented validation study [6].

C++ programming language was used for estimation of measurement uncertainty by Monte-Carlo simulated method.

RESULTS AND DISCUSSION

Information about uncertainty is summarized in Table 1. The results obtained by processing the set of available information by GUM uncertainty approach and corresponding statistical parameters obtained by Monte Carlo simulation for the DMP are presented in Table 2.

Table 1. Uncertainty sources and associated distributions with their respective parameters for the estimation of uncertainty for the 2,4-dimethylphenol compound

Uncertainty source	Distribution	Parameters of a distribution
Volume (V)	Normal	Mean: 75 ml; SD: 2.55 ml
Mass (m)	Normal	Mean: 10 g; SD: 0.22g
Recovery (R)	Student's t Location-Scale	Mean: 33.71%; SD: 3.47 %; DF: 3
The peak area (y)	Student's t Location-Scale	Mean: 73259; SD: 4000; DF: 3
Slope (a)	Student's t Location-Scale	Mean: -10495; SD: 7726; DF: 3
Intercept (b)	Student's t Location-Scale	Mean: 50044/mg; SD: 15007l/mg; DF: 3
Purity of standard	Uniform	Min: -0.0193 mg/kg; Max: 0.0193 mg/kg

*SD – Standard Deviation; DF – Degrees of Freedom

Table 2: Results obtained using the GUM and Monte Carlo uncertainty approach for uncertainty estimation for the 2,4-dimethylphenol compound

Parameter (GUM)	Value	Parameter (MC)	Value
Mean	3.72 mg/kg	Median	3.72 mg/kg
Combined standard uncertainty	0.58 mg/kg	*Low endpoint for 95%	1.99 mg/kg
Expanded uncertainty for 95%	1.30 mg/kg	*High endpoint for 95%	5.83 mg/kg

*The values represent the limits of the shortest-length 95 % confidence intervals

Deviation of PDF (probability density function) of the output estimated by Monte Carlo simulation from distribution assigned to measurand through GUM analysis is shown in Figure 1. It can be seen that these two ways of expressing measurement results are in disagreement.

Since these disagreements came from the assumptions and approximation included in GUM Uncertainty Framework, for analysis of this kind of uncertainty the Monte Carlo method described in JCGM 101:2008 is proposed.

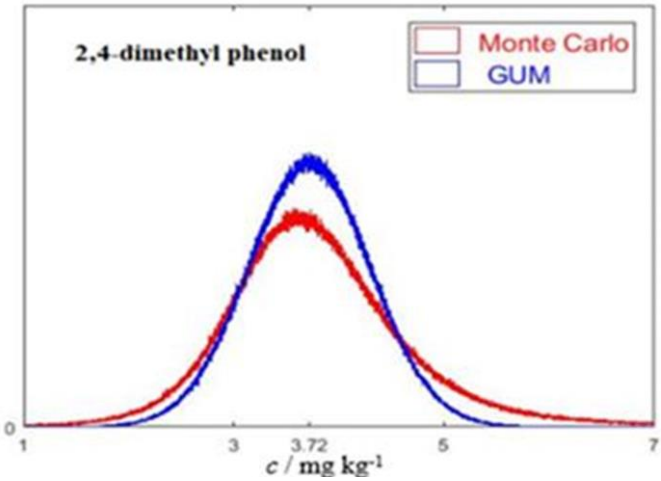

Figure 1. Comparison of PDFs obtained with GUM and Monte Carlo method for the 2,4-dimethylphenol compound

CONCLUSION

Two alternative approaches approved nowadays for estimation of combined measurement uncertainty in case of DMP were evaluated and demonstrated in the presented study. It has been shown that there is disagreement in the estimation of combined uncertainty of measurement using GUM recommendations and Monte-Carlo simulated method.

Monte Carlo method for uncertainty estimation should be encouraged, since the MCS does not require the evaluation of partial derivatives as the GUM method.

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