



Measurement Uncertainty of a Matrix Solid Phase Dispersion Analysis Method of Endocrine Disruptors in Different Food Commodities

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Abstract

In this work, a fully nested experimental design was applied to study the measurement uncertainty arising from trueness as well as to examine the usability of an optimized Matrix Solid Phase Dispersion (MSPD) method for the analysis of two potential Endocrine Disruptors (linuron and diuron) and their common metabolites in diverse food commodities. The recovery was estimated in three food commodities of different nature. For each matrix, the analysis was carried out on three concentration levels and samples in triplicates. Generally, the matrices tested seemed to cause a negligible variation in the measured recovery values than the different concentration levels for all target analytes with the exception of linuron.

Introduction

The phenylurea herbicides linuron and diuron, which are believed to damage health by interfering with the way hormones work, have been included in the Endocrine Disrupting Chemicals (EDCs) lists by the European Commission and identified as potential and suspected endocrine disruptors, respectively. Their common metabolites include 1-(3,4-dichlorophenyl)-3-methylurea (DCPMU), 1-(3,4-dichlorophenyl) urea (DCPU) and 3, 4-dichloroaniline (3, 4-DCA). This globally increased concern towards EDCs induced a necessity to develop highly sensitive and multiresidue analytical methods for the simultaneous determination of the parent compounds and their metabolites in several food commodities consumed by humans.

Moreover, analytical results must be both reliable and comparable because they are often used as a piece of valuable information for a certain aim. Nested experimental designs can be used to evaluate the method's performance criteria involving proportional bias and measurement uncertainty, which is an essential part of quantitative results. In the above-mentioned framework, Matrix Solid-Phase Dispersion (MSPD), a relatively recent extraction and clean up technique was used for the determination of the target analytes in diverse food commodities [1] and in this work, the application of a fully nested design is explored for the assessment of the method's measurement uncertainty arising from trueness. A high-performance liquid chromatography system coupled to UV-diode array detector (HPLC/UV-DAD) was used for the target analytes quantification.

Materials & Methods

HPLC-grade solvents, were purchased from Merck (Darmstadt, Germany). Analytical grade standards of diuron and linuron were obtained from Riedel-de-Häen, (Seelze-Hannover, Germany) while metabolites were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Stock solutions of each analyte were prepared at 2000 µg/ml in acetonitrile. Florisil (60–100 mesh) was obtained from Sigma-Aldrich (Milwaukee, WI, USA). Membrane filters Supor-200 (25mm, 0.2 µm) obtained from Pall Corp. (MI, USA) were used as column frits to retain the column packing. Polypropylene solid-phase extraction syringe barrels were obtained from International Sorbent Technology (Mid Glamorgan, UK). HPLC-UV/DAD analysis conditions and MSPD method were performed as already described [1].

Results

Checking the trueness of an analytical procedure involves estimating its bias. One of the two types of bias that may be present is the proportional bias which is expressed as recovery. The variability of recovery can mainly depend on the concentration, type of matrix and within-day variation of the method. The ISO guidelines require that the factor most affected by systematic effects should be arranged in the highest ranks of the hierarchy [2]. In our study, contrary to other literature [3], matrices tested are placed in the highest ranks while concentrations and replicates follow due to the quite different and complex nature of the food samples used, which make them a factor most influenced by systematic effects. The recovery was estimated in three food commodities of different nature (wheat flours, potatoes and apples). For each matrix, the analysis was carried out on three concentration levels, that is, 0.05, 0.1 and 0.5 mg/Kg and samples in triplicates. This resulted in 27 different analyses for each of the five target analytes. In this fully nested experimental set-up all factors are implicitly assumed to be random. The overall recoveries, that is, those determined by the nested experiments were in the range of 79.7 to 94.3 %, except 3,4-DCA for which a lower overall recovery of 57.0 % was observed. Table 1 shows the variances, that is, mean squares of factors and uncertainties of the HPLC-UV/DAD quantitative results of the two EDCs in spiked food matrices. Generally, the matrices tested seem to cause a negligible variation in the measured recovery values than the different concentration levels for all target analytes with the exception of linuron for which the exact opposite behaviour was observed. Fig. 1 shows the percent variability attributable to matrices, concentrations and replicates of each of the five analytes as indicated by the variance component estimates.

Table 1; Mean squares (MS), degrees of freedom (df) and components of uncertainty for diuron and linuron

Source	df	diuron	linuron
		MS	
Matrices	2	0.03721	0.10801
Concentration (matrices)	6	0.09193	0.00878
Replicates	18	0.02223	0.02244
Uncertainty			
$u(\Delta R_M)^2$		-0.006080	0.011025
$u(\Delta R_C)^2$		0.023231	-0.004552
$u(\Delta R_r)^2$		0.022232	0.022441
$u(\bar{R}_m)^2$		0.003405	0.000325
$u(R)$		0.163205	0.106539

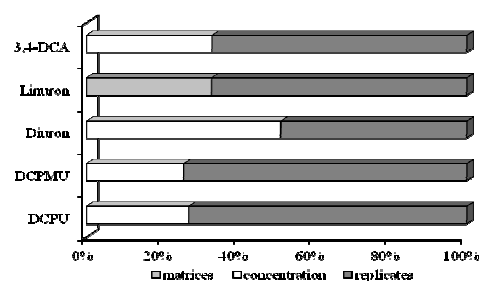


Fig. 1; Relative variance components (in percent).

Conclusions

A fully-nested experimental design was applied for the determination of the overall recoveries and a practical estimation of the measurement uncertainty of the method derived from uncertainty associated to matrix and concentration level effects was attempted. Clearly, the nature of food commodities to be analyzed affects the recoveries of linuron while concentration levels contribute to method uncertainty in all other cases. The methodology presented fulfilled analytical validation criteria.

References

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