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Characterization of recovery profiles using gas chromatography-triple quadrupole mass spectrometry for the determination of pesticide residues in meat samples

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Abstract

The assessment of the recovery factor with the analyte concentration in meat samples has been studied for the determination of organochlorine and organophosphorus pesticides in meat by gas chromatography-triple quadrupole mass spectrometry (GC–MS/MS). For that purpose, recent IUPAC recommendations, which distinguishes between two terms, recovery factor and apparent recovery, have been followed. Besides, the systematic error due to the matrix effect has been evaluated by a new term recently proposed, calibration recovery. Recovery profiles were obtained analyzing spiked blank matrix, where the analytes were added before and after the extraction procedure. In a first step, the quantification of the compounds was carried out using a solvent calibration curve. The systematic errors due to the matrix effect during the quantification step and the error due to the sample treatment have been evaluated. Both apparent and calibration recovery components depend on the actual analyte concentration in the sample while the recovery factor remains constant except for analyte concentration close to quantification limit. In addition, the concentration limits, from which an acceptable recovery value (70–110%) can be obtained, are given. If spiked samples are quantified by matrix-matched calibration, the matrix effect is minimized and the calibration recovery component is 100%, and apparent recovery only depends on the recovery factor. The obtained values indicate recovery factor does not depend on the analyte concentration, except for those values closed to quantification limit.

Keywords: Pesticide residues; Meat analysis; GC–MS/MS; Recovery components; Recovery profiles

1. Introduction

Gas chromatography (GC)-triple quadrupole mass spectrometry (MS/MS) detection is considered a powerful technique for the quantitative determination of trace and ultra trace levels of contaminants in complex matrices. In this sense, it has been used for the determination of pesticide residues in matrices such as vegetables, honey, beer, baby food [1–4] and meat [5,6]. However, the analysis of pesticides in fatty matrices such as meat, involve a very complex sample treatment, including gel permeation chromatography (GPC) or other techniques [7]. Thus, during the validation of these methodologies, sensitivity and precision can be achieved with GC–MS/MS. However, accuracy, which is an essential component of the validation of chromatographic methods [8], is usually characterized by recovery, and it can seriously be affected by sample treatment and quantification procedure.

Different approaches have been proposed for the estimation of recovery [9–11]. Thus, recovery studies can be carried out using certified reference materials, and if they are not available, a matrix blank can be spiked with a known concentration of analyte, and recovery can be determined [12]. However, recovery is not easy to be evaluated, since it depends on the matrix, sample processing procedure, analyte properties [13] and analyte concentration [14]. Most of the published papers only study recovery at one or two concentration levels, which are only representative of the tested concentrations, and the recovery values could not be used for other concentrations. That

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is why, recovery studies should cover the whole concentration range of the method [15], and should include one analyte concentration close to the quantification limit.

Recovery can be defined as "the proportion of the amount of analyte present in or added to the analytical portion of the test material which is extracted and presented for measurement" [16], and it is an estimation of the systematic error of the whole analytical process. However, the presence of systematic errors can be due to two different sources, chemical operations during the sample treatment and measurement step, which can be affected by the matrix effect. In this sense, IUPAC distinguishes between two different terms [17]: "recovery or recovery factor, R", used to indicate the yield of an analyte in a preconcentration or extraction stage, and "apparent recovery, R^*", understood as the observed value derived from an analytical procedure by means of a calibration graph divided by the reference value. "Apparent recovery" includes the overall systematic error of the analytical procedure, whereas "recovery factor" only studies the yield in the sample treatment process. That is why, a new term, named "calibration recovery, R^c", was recently introduced to evaluate the influence of the quantification step on the "apparent recovery" [18], which can be expressed as:

$$R^* = R \times R^c \quad (1)$$

The corresponding values of the different components of recovery can be evaluated by different additions of analyte before (pre-addition) and after (post-addition) the sample treatment step, from the equations:

$$R^* = \frac{C_{\text{measured}}}{C_{\text{pre-addition}}} \quad (2)$$

$$R^c = \frac{C_{\text{measured}}}{C_{\text{post-addition}}} \quad (3)$$

where C_{measured} is the corresponding experimentally measured concentration, quantified from a solvent calibration curve, $C_{\text{pre-addition}}$ is the added concentration before the sample treatment, and $C_{\text{post-addition}}$ is the added concentration after the sample treatment.

Thus, for each tested analyte concentration value, the addition before treatment gives information about the overall systematic error and R^* can be estimated by applying Eq. (2), whereas the addition after sample treatment is just related to the quantification step error, and R^c can be evaluated (Eq. (3)). Finally, R can be obtained by applying Eq. (1).

In addition, apparent recovery profiles can be achieved when different concentration levels are assayed, and information of the overall error, related to both sample treatment and quantification step over the working range of the analytical method, can be obtained during the recovery study. Besides, R^* profile can be fitted to Eq. (4) [18],

$$R^* = \Delta p + \Delta c \frac{1}{C_{\text{pre-addition}}} \quad (4)$$

where Δp and Δc are the proportional and constant analytical process bias, respectively.

The proportional and constant bias can be estimated fitting the experimental values of R^* to Eq. (4). Thus, if Δc is equal to zero, $R^* = \Delta p$ and the recovery will be independent of the added concentration. However, if Δc is different from zero, Δp is an estimation of R^* at high concentration levels.

When this methodology is used, it is possible to determine the analyte concentration interval for which recovery value is within the range indicated in accepted guidelines or regulations [8,19], to get results that are fit for purpose.

The aim of this paper is to obtain the recovery profiles during the determination of organophosphorus and organochlorine pesticides (thionazin, isofenphos, famfur, p,p′-DDT, mirex, γ-lindane) in meat by GC–MS/MS. The method was based on the extraction of homogenized meat mixed with sodium sulphate and ethyl acetate in polytron, followed by a clean-up step by GPC before the chromatographic determination [7]. The dependence of the recovery factor with analyte concentration was checked. If R depends on the analyte concentration, the concentration range within the recovery is constant, will be fixed, and therefore, the recovery factor could be used in that range during routine analysis to correct systematic errors. Finally, the influence of the matrix and the sample treatment has been evaluated during the recovery study, considering the possibility of minimizing the systematic errors associated with both factors.

2. Experimental

2.1. Chemicals and reagents

Isofenphos (purity 99.1%) and famfur (purity 98.3%) were purchased from Riedel-de-Haën (Seelze-Hannover, Germany); mirex (purity 98.5%), p,p′-DDT (purity 98.7%) and the internal standard, caffeine (purity 99.0%) were from Dr. Ehrenstorfer GmbH (Augsburg, Germany); thionazin (purity 99.9%) was purchased from Supelco (Bellefonte, PA, USA) and γ-lindane (purity 99.5%) was from ChemService (West Chester, PA, USA). Stock standard solutions of individual compounds (with concentrations between 250 and 375 μg/mL) were prepared by exact weighing of powder and dissolution in 100 mL of acetone from Panreac (Barcelona, Spain), and were stored in a freezer (−30 °C). A multianalyte working standard solution (2 μg/mL concentration of each compound) was prepared by appropriate dilutions of the stock solutions with acetone and stored under refrigeration (4 °C).

Pesticide-quality solvents (ethyl acetate and cyclohexane) were purchased from Scharlau (Barcelona, Spain) and anhydrous sodium sulphate (instrumental analysis quality) was from Panreac.

2.2. Apparatus

The ProStar GPC system used was from Varian (Valnut Creek, CA, USA), consisted of a 410 autosampler with a 24 vials (10 mL) tray, a 230 solvent delivery module, a 325 UV–vis detector with dual wavelength operation, a 704 fraction collector and two on-line Envirogel GPC clean-up columns from Waters