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Short communication

Identification of transformation products of pesticides and veterinary drugs in food and related matrices: Use of retrospective analysis

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ABSTRACT

Retrospective analysis has been applied in different samples, including honey, meat, feed and nutraceutical products from ginkgo biloba, soya, royal jelly and green tea, with the aim of searching transformation products of pesticides and veterinary drugs, which were not included in an initial analysis. Generic extraction and analytical procedures based on high resolution mass spectrometry (Exactive-Orbitrap analyser was used) have been applied. All obtained data have been reprocessed and some compounds as anhydroerythromycin in honey and 3,5,6-trichloro-2-pyridinol in feed have been detected, demonstrating the applicability and the utility of the procedure. Advantages and disadvantages of retrospective approach have been highlighted.

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1. Introduction

Agrochemicals (including pesticides) and veterinary drugs are used to increase the quantity and quality of food needed to sustain the human population [1]. These compounds and their transformation products (TPs) can affect human health due to their toxicity or carcinogenicity, and their presence in food and feed is a cause of concern to consumers, food producers, academics and government agencies [2]. Maximum residue limits (MRLs) have been established to ensure food safety, and in most cases, the MRL definition is established for the sum of the parent compound and its relevant TPs because, sometimes, the parent compound has disappeared, but TPs are still detectable [3]. TPs are those chemicals that may occur in food due to unintended chemical reactions, industrial and/or other processes [4]. Many of them are usually included in target lists, but lots of them are not, because the lack of standards, ignorance, etc.

Liquid chromatography coupled to high resolution mass spectrometry (LC–HRMS) plays here an important role [3,5,6], allowing the detection and identification of target and non-target (retrospective analysis) compounds at low concentration levels in complex sample matrices with high mass accuracy. Retrospective analysis is gaining interest and involves the selection of compounds to be investigated in samples after MS acquisition. This approach could be considered as a 'post-target' analysis [7–9], being very efficient for wide-scope screening of a large number of compounds. For that purpose, the development and application of generic extraction procedures is necessary. To successfully apply this approach, the MS analyser (ion trap, IT or time of flight, TOF) has to work on full spectrum acquisition mode [10]. Orbitrap is considered as a powerful tool due to its high resolving power for qualitative and quantitative residue analysis in food and feed matrices [11–13].

The aim of this study is the application and evaluation of retrospective analysis to find TPs in positive samples, including new matrices as nutraceutical products, where pesticide residues and/or veterinary drugs have been detected, highlighting some of the shortcomings of this approach.

2. Materials and methods

2.1. Chemicals and apparatus

Analytical standards were purchased from Sigma–Aldrich (Madrid, Spain), Riedel-de-Haën (Seelze, Germany), Fluka (Steinheim, Germany) and Dr. Ehrenstorfer GmbH (Ausburg, Germany). Individual stock standard solutions (100–450 mg L^{-1}) were prepared in methanol, acetone or acetonitrile, and they were stored

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at 5 °C or −18 °C. LC-MS grade methanol, acetonitrile and acetone were obtained from Fluka. Formic acid (purity > 98%) and ammonium formate (purity > 99%) were obtained from Panreac (Barcelona, Spain). LC-MS water was provided by Scharlau (Barcelona, Spain). For accurate mass calibration, a mixture of caffeine, Met-Arg-Phe-Ala acetate salt (MRFA) and Ultramark 1600 (Proteo Mass LTQ/FT-Hybrid ESI positive mode calibration mix) and a mixture of acetic acid, sodium dodecyl sulphate, taurocholic acid sodium salt hydrate and ultramark 1621 (fluorinated phosphazines) (ProteoMass LTQ/FT-Hybrid ESI negative mode calibration mix) from Thermo Fisher Scientific (Rockford, IL, USA) were used in the Orbitrap analyser. For the extraction procedure, a rotary agitator from Heidolph (Schwabach, Germany) and an analytical AB204-S balance (Mettler Toledo, Greinfesee, Switzerland) were used. Centrifugations were performed in a Consul 21 high-volume centrifuge from Olto Alresa (Madrid, Spain).

2.2. UHPLC-Orbitrap-MS analysis

The separation of the analytes was carried out using a Transcend 600 LC (Thermo Scientific Transcend™, Thermo Fisher Scientific, San Jose, CA, USA) equipped with an analytical column Hypersil GOLD aQ C18 column (100 mm × 2.1 mm, 1.7 μm particle size) from Thermo. The mobile phase consisted of 0.1% (v/v) formic acid and ammonium formate 4 mM in water (eluent A) and 0.1% (v/v) formic acid and ammonium formate 4 mM in methanol (eluent B). The analysis started with 95% of eluent A. After 1 min, this percentage was linearly decreased up to 0% in 7.0 min. This composition was held during 4.0 min and increased again up to 95% in 0.5 min, followed by a re-equilibration time of 1.5 min (total running time = 14.0 min). The flow rate was 0.3 mL min^{-1} and the column temperature was set at 30 °C. Aliquots of 10 μL of the sample extract were injected into the chromatographic system.

The UHPLC system was coupled to a single stage Orbitrap mass spectrometer (Exactive™, Thermo Fisher Scientific, Bremen, Germany) operating with a heated electrospray interface (HESI-II, Thermo Fisher Scientific, San Jose, CA, USA), in positive (ESI+) and negative ionization mode (ESI−) using the parameters developed previously [11]. The mass spectra were acquired using four alternating acquisition functions: (1) full MS, ESI+ without fragmentation (the higher collisional dissociation (HCD) collision cell was switched off), mass resolving power = 25,000 FWHM; scan time = 0.25 s; (2) All ions fragmentation (AIF), ESI+ with fragmentation (HCD on, collision energy = 30 eV), mass resolving power = 10,000 FWHM; scan time = 0.10 s; (3) full MS, ESI- using the settings explained for (1); and (4) AIF, ESI- using the settings explained for (2). Mass range in the full scan experiments was set at *m/z* 70–1000. All the analyses were performed without lock mass. Mass accuracy was carefully monitored as follows: checked daily with the calibration mix solution (see Section 2.1); evaluated (once a week) and calibrated when necessary (every 2 weeks at least). Data were acquired using matrix-matched external calibration mode and they were processed using Xcalibur™ version 2.2.1 (Thermo Fisher Scientific, Les Ulis, France) with Qual and Quanbrowser. Genesis peak detection was applied. ToxID™ 2.1.1 (automated compound screening software, Thermo Scientific) was used for screening and LCQuan™ 2.6 software (Thermo Scientific) was used for quantification during method validation and sample analysis.

2.3. Sample preparation

A total of 31 samples belonging to different matrices (honey, meat, feed, ginkgo, soya, green tea and royal jelly) were used. All of them were previously extracted applying generic procedures based on “dilute and shoot” [14] or QuEChERS [15] and they have been analysed by liquid chromatography coupled to Exactive-Orbitrap. Later, a retrospective analysis was applied to these samples with the aim of identifying TPs which were not included in the initial analysis, testing the applicability and utility of this approach.

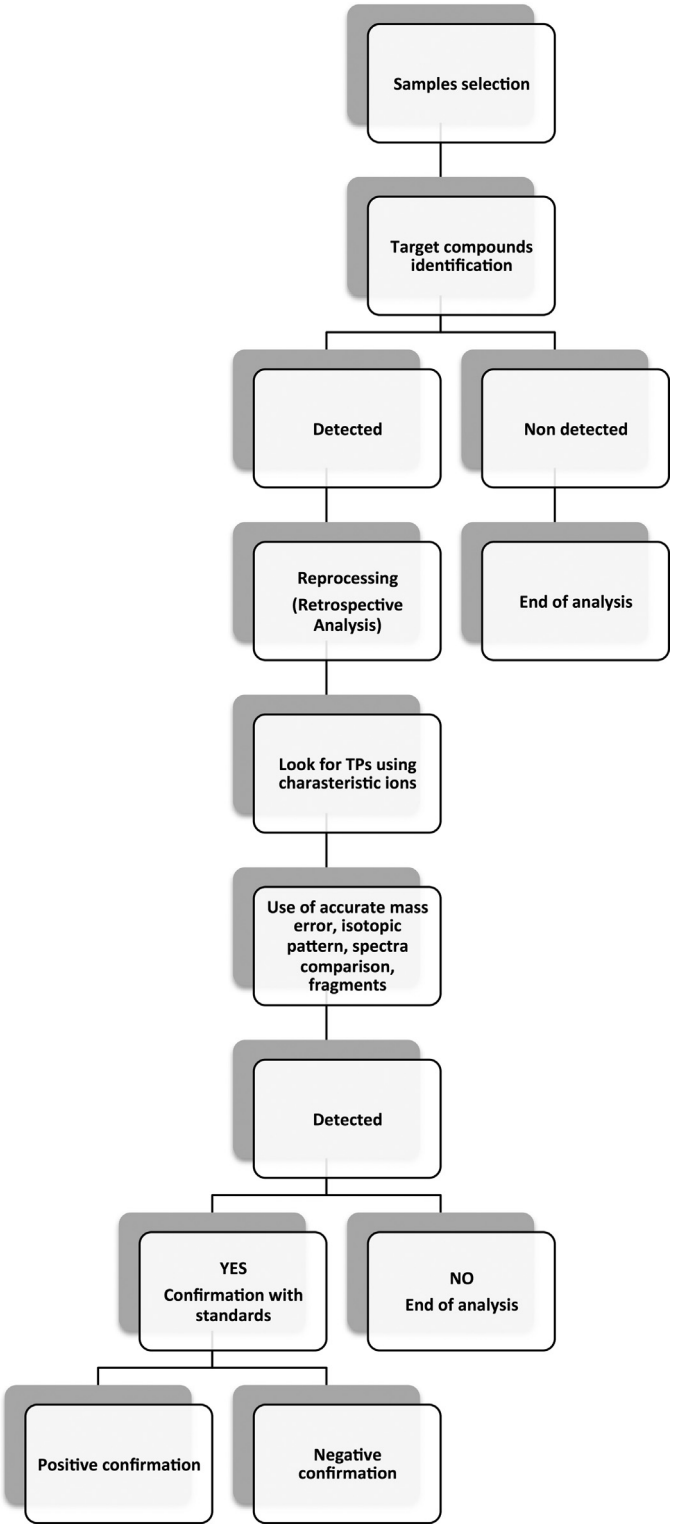

Fig. 1. Workflow used for retrospective analysis.

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