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Simultaneous determination of 19 triazine pesticides and degradation products in processed cereal samples from Chinese total diet study by isotope dilution–high performance liquid chromatography–linear ion trap mass spectrometry

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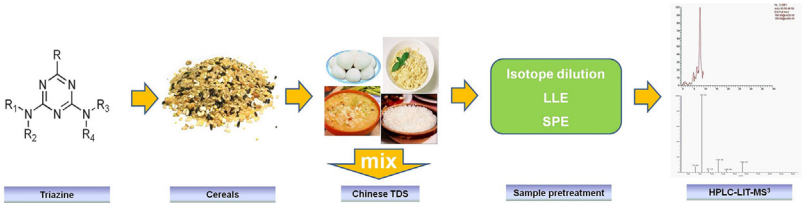
HIGHLIGHTS

- 19 triazines were determined in cereal samples from Chinese TDS for the first time.
- Isotope dilution technique and HPLC–LIT-MS^3 method are both applied in this study.
- CCαs and CCβs are much lower in this work than those of the previous publications.

GRAPHICAL ABSTRACT



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ABSTRACT

A selective and sensitive isotope dilution–high performance liquid chromatography–linear ion trap mass spectrometry (Isotope Dilution–HPLC–LIT-MS^3) method was developed for the simultaneous determination of 19 triazine pesticides and their degradation products in processed cereal samples from Chinese total diet study (TDS). The method integrated the addition of isotope internal standards, liquid–liquid extraction (LLE), clean-up with MCX solid-phase extraction (SPE) cartridges and HPLC–LIT-MS^3 analysis with selected reaction monitoring (SRM) mode. Matrix-matched calibration curves showed good linearity ($R^2 \geq 0.9940$) verified by applying the Mandel's fitting test ($p > 0.087$) performed at the 95% confidence level. Decision limits (CCαs) and detection capabilities (CCβs) of the 19 triazine pesticides and their degradation products fell in the ranges of 0.0020–0.4200 μg kg^{-1} and 0.0024–0.4500 μg kg^{-1}, respectively. Recoveries ranged from 70.1% to 112.8%, with the relative standard deviations (RSDs) ranging from 1.5% to 13.5%. Furthermore, the proposed method was applied to analyzing the proposed cereal samples from the fourth Chinese TDS. Eleven triazines were detected in six cereal samples with the concentrations ranging from 0.013 to 0.987 μg kg^{-1}. This method can also be used for the further determination of the triazines in other food group composites, and ultimately served as a methodological foundation for assessing the triazines in the average Chinese diet in the general population.

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1. Introduction

Triazine pesticides have been widely used to control annual and perennial grass in various crops since 50 years ago. They play a crucial role in cereal cultivation, such as maize and rice. However, the excessive use can cause a potential hazard for human beings, because such residues in plant-derived foodstuffs can induce

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cancers, birth defects and interruption of hormone functions [1,2]. With the development of toxicological studies on triazine pesticides, more and more researches focused on their safe-use aspects. In 2006, ametryn, atrazine, cyanazine, cyromazine, dipropetryn, hexazinone, metamitron, methoprotryne, metribuzin, prometryn, simazine, simetryn, terbumeton, terbuthylazine and terbutryn, the most widely used triazines, have been listed in the national and European Union (EU) coordinated monitoring program for the routine monitoring and consumer risk assessment [3]. In addition, EU added atrazine and simazine to the List 2 of the *Dangerous Substance Directive* (76/464/EEC) [4] and proclaimed maximum residue limits (MRLs) for atrazine, simazine, metamitron and metribuzin in maize (0.1 mg kg^{-1} for each component). However, more triazines such as cyanazine, propazine, terbutryn and their degradation products (atrazine-2-hydroxy, atrazine-desethyl and atrazine-desisopropyl) were also recommended to be added to the List 2 [5]. Furthermore, atrazine, hexazinone, metribuzin, simazine and terbumeton have been listed as Potential Environmental Endocrine Disruptors by the United States (U.S.) Environmental Protection Agency (USEPA) in 2012 [6]. The U.S. Food and Drug Administration (USFDA) also defined MRLs as 0.1–0.25 mg kg^{-1} for simazine, atrazine, ametryn, prometryn, propazine, terbutryn, terbuthylazine, and dipropetryn in maize. In China, simeton was listed in the Chinese national standard [7] for routine monitoring and the MRLs of atrazine, cyanazine and metribuzin were all defined as 0.05 mg kg^{-1} in maize.

Many studies have reported various analytical methods for the determination of triazine herbicides in water, soil [8–10] and raw foodstuffs which have not been processed, such as fruit, vegetable and cereals [11–15]. These methods included gas chromatography (GC) [16,17], gas chromatography mass spectrometry (GC–MS) [18,19], high-performance liquid chromatography (HPLC) with diode array detection [20,21] and high-performance liquid chromatography tandem mass spectrometry (HPLC–MS/MS) [22,23]. Although a few methods had been reported to determine triazine residues in cereals [12–15], all of above-mentioned methods have one or more points of the following drawbacks: (1) tested samples collected in these studies only limited to raw foodstuffs; (2) only parts of the triazine pesticides of interest were investigated; (3) isotope dilution method was not applied to the quantitative analysis so that the analysis in complex matrixes suffered difficulties and (4) LC–MS^3 has not been used for qualitation and quantification yet. The 19 compounds determined in this work not only cover all the set maximum residue limits (MRLs) for triazine pesticides by China, EU and U.S., but also include some potential analytes of interest such as atrazine-2-hydroxy, atrazine-desethyl, atrazine-desisopropyl, hexazinone, methoprotryne, simeton and terbumeton [3,6,7]. In the present work, the cereal samples were selected from the Chinese TDS, which was recommended by the World Health Organization (WHO) to estimate dietary intake of contaminants and to monitor the safety and quality of the food supply [24]. Cooking oil and condiments were used during the preparation and cooking of the TDS samples, therefore, compared with the raw products, the properties of the cereal samples determined in this study were more complex which needed an advanced method for the analysis. Toward this end, MS^3 and isotope dilution technique were applied in our study. Compared with MS^2, MS^3 could further reduce the background signal and achieve lower detection limits [25]. Meanwhile, mass spectrometric detection enabled the integration of isotope dilution technique, which could overcome problems with quantification caused by the matrix effects and achieve high accuracy and precision with trace levels.

Thus, it can be concluded that the proposed method is highly selective and sensitive for the analysis of triazine pesticides and their degradation products residues in processed cereal samples from Chinese TDS at trace levels. To the best of our knowledge, this is the first report for the simultaneous analysis of 19 triazine pesticides and their degradation products in processed cereal samples from Chinese TDS by HPLC–LIT-MS^3. The developed method can be also applied to investigating the levels of triazines in other group composites and to assess the general population's dietary exposure to triazines.

2. Materials and methods

2.1. Chemicals and reagents

19 triazine pesticides and degradation products standards (ametryn, atrazine, atrazine-2-hydroxy, atrazine-desethyl, atrazine-desisopropyl, cyanazine, cyromazine, dipropetryn, hexazinone, metamitron, methoprotryne, metribuzin, prometryn, simazine, simeton, simetryn, terbumeton, terbuthylazine and terbutryn) (>96.5% purity) and 11 internal standard (IS) solutions (atrazine-d_5, atrazine-2-hydroxy-d_5, atrazine-desethyl-d_7, atrazine-desisopropyl-d_5, cyanazine-d_5, cyromazine-d_4, hexazinone-d_6, prometryn-d_6, simazine-d_5, terbuthylazine-d_5 and terbutryn-d_5) (100 mg L^{-1}) were all obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The chemical structures of the 19 triazines were shown in Supplemental Fig. S1.

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.aca.2013.04.027.

Methanol, acetonitrile and petroleum ether (HPLC grade) were obtained from Fisher (Fair Lawn, USA). Ammonium formate, ammonium acetate, formic acid and acetone were purchased from Tedia (Fairfield, USA). The ultra-pure water used throughout this study was deionized and purified to 18.3 MΩ by a water purification system from Millipore (Barnstead, USA). Petroleum ether saturated with acetonitrile was prepared by adding 150 mL acetonitrile to 800 mL petroleum ether. Acetonitrile saturated with petroleum ether was prepared by adding 150 mL petroleum ether to 800 mL acetonitrile. OASIS MCX SPE columns (300 mg, 6 mL) were purchased from Waters (Milford, USA). Alumina-N SPE (2 g, 6 mL) and Florisil SPE (2 g, 12 mL) columns were obtained from Supelco (Bellefonte, USA).

2.2. Preparation of standards

1000 mg L^{-1} individual stock solutions of 19 triazine pesticides and degradation products were prepared in methanol and stored at −18 °C. A mixed IS working solution (1 mg L^{-1} for 11 internal standards) was prepared by diluting each IS solution to 100 mL with acetonitrile.

Mixed stock solution of 19 compounds (50 mg L^{-1} for atrazine-desisopropyl, simazine, cyanazine and cyromazine, 10 mg L^{-1} for atrazine, atrazine-desethyl, metamitron, ametryn and metribuzin, 5 mg L^{-1} for atrazine-2-hydroxy, terbuthylazine, hexazinone, simeton and simetryn, 1 mg L^{-1} for prometryn, terbumeton, dipropetryn and methoprotryne and 0.5 mg L^{-1} for terbutryn) was prepared by transferring appropriate volumes of the individual stock solutions into a 100 mL volumetric flask and fixed to 100 mL with acetonitrile.

2.3. Sample collection and preparation

The processed cereal samples were collected from 12 provinces in China for the fourth Chinese TDS. The 12 provinces included Fujian, Guangxi, Hebei, Heilongjiang, Henan, Hubei, Jiangxi, Liaoning, Ningxia, Shanghai, Shaanxi and Sichuan. Overall, the design and collection of the fourth Chinese TDS were similar to the previous publication [26].

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