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Simple, cost-effective and sensitive liquid chromatography diode array detector method for simultaneous determination of eight sulfonylurea herbicides in soya milk samples☆

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ABSTRACT

In this study authors propose a simple, cost-effective and sensitive liquid chromatography diode array detector (HPLC-DAD) method for the simultaneous determination of eight sulfonylurea herbicides (oxasulfuron, metsulfuron-methyl, triasulfuron, rimsulfuron, chlorsulfuron, mesosulfuron-methyl, amidosulfuron and bensulfuron-methyl) in soya milk samples. QuEChERS-based extraction procedure presents good performance for all of the analytes with recoveries in the range of 61–108% and relative standard deviations (RSD%) less than 15%. No significant matrix effect was observed thanks to application of effective zirconium-dioxide based sorbent (Z-Sep). Method LOQs for all investigated analytes were set at satisfactory low value of 10 ng mL^{-1} of food product. The procedure was evaluated in terms of natural samples analysis. Chlorsulfuron was determined at concentration of 14.2 ng mL^{-1} of soya milk product, which was qualitatively confirmed via LC coupled with tandem mass spectrometry (LC–MS/MS). The most important steps of procedure optimization are presented.

1. Introduction

Soybean is one of the most valuable legume species due to high content of protein and other beneficial nutrients. In 2014–2015, soybeans were planted on about 118.39 million hectares worldwide with production of 319.72 million metric tons [1]. In 2015, 83% of the soybean planted globally were genetically modified (GM) [2], whereas glyphosate-tolerant GM soy is the number one GM crop plant. Besides Roundup Ready® soybean, Sulfonylurea Ready (SR) varieties, with increased tolerance to the sulfonylurea herbicides (SUs), are popularly cultivated. SR soybean technology enhances a soybean plant's natural tolerance to the sulfonylurea family of acetolactate synthase (ALS) inhibitor herbicides [3]. SUs, because of their low application rates (10–40 g ha^{-1}), low mammalian toxicity, and high herbicidal activity have become very popular worldwide [4]. Sulfonylureas are based on a general structure where R_1 moiety can be either aliphatic, aromatic, or heterocyclic group connected by the sulfonylurea bridge to the R_2 moiety which is a substituted triazine or pyrimidine system [4].

SUs are moderately polar and weakly acidic compounds with pKa values generally ranging from 3 to 5.2. Therefore, liquid chromatography (LC) is preferred in monitoring of these herbicides. Most of the known applications concerns analysis of sulfonylurea herbicides in water [5–16] and soil [8,15–19] samples. Outside of these types of samples, analytical methods for SUs determinations were developed in different crops and food products, like rice [18,20], soybean [18,21,22], corn [18,22], wheat [22], cereals [23] and milk [24]. Detection methods in LC based procedures rely mostly on triple quadrupole-tandem mass spectrometry (QqQ-MS/MS) operating in the multiple reaction monitoring (MRM) mode, which enables accurate identification and quantification of targeted analytes [25]. These instrumentation is still fairly expensive and not always available in all environmental laboratories [24]. For that reason, sufficiently selective and sensitive analytical procedures involving low-cost instrumentation, such as HPLC–DAD, might be of high demand for pesticide residue analysis [24]. Stoev and Stoyanov concluded that the reliability of identification of an analyte by DAD is comparable to the reliability of identification by low resolution MS–MS [26,27]. DAD might be useful in the analysis of samples with complicated matrices by obtaining UV spectra and evaluating the purity of the peaks on the chromatograms indicating spectra homogeneity and insignificant influence of co-extracted

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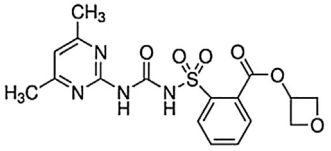
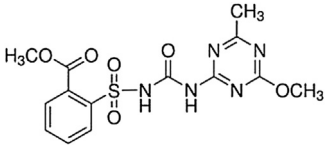
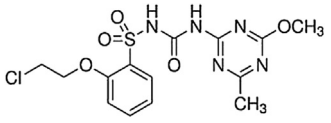
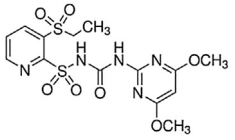
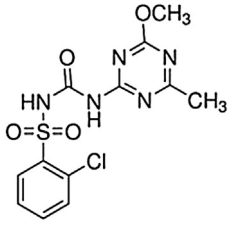
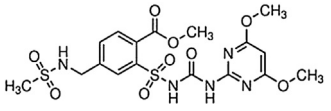
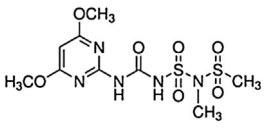
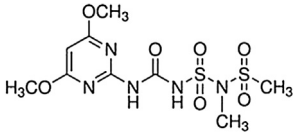
compounds [28]. However, it does not change the fact that a critical aspect of pesticide residue analysis is the extract purification process, which is required to isolate the residues from matrix components and reduce matrix effect [29]. HPLC–DAD may be utilized for residue analysis in case when matrix effect is negligible [30].

Up to date, solid-phase extraction (SPE) was the most often applied as efficient extraction and purification technique for SUs analysis [5–14,19,21]. Ghobadi et al. adopted ultrasound-assisted surfactant-enhanced emulsification microextraction (UASEME) for SUs determination in water and soil samples [15]. Wu et al. combined dispersive solid-phase extraction (d-SPE) with dispersive liquid–liquid microextraction (DLLME) [17]. Pareja et al. evaluated various QuEChERS based methods for the analysis of herbicides and other commonly used pesticides in polished rice [20]. Important advantage of the QuEChERS technique is its rapid character and high sample throughput, as well as, the possibility of introducing modifications based on the application of different solvents, salts, buffers and sorbents [31]. Therefore, QuEChERS methodology might be implemented in the analysis of broad spectrum of analytes and matrices.

In this study, authors proposed a rapid, efficient, and reliable method for extraction of selected SUs from soya milk samples, based on modified QuEChERS procedure. To the best of authors knowledge, there are no literature reports on analytical procedures for SUs analysis in soya milk. Earlier report, proposed by Hernández-Borges et al., provide a method for triazolopyrimidine sulfoanilide herbicides analysis in soya milk samples. In this case, authors developed analytical procedure based on SPE and capillary electrophoresis – mass spectrometry (CE-MS) [32].

Table 1
Structures and physicochemical properties of the studied sulfonylurea herbicides.[a]

No.	Sulfonylurea herbicide	Structure	Octanol–water partition coefficient at pH 7, 20 °C (log P)	Dissociation constant (pKa) at 25 °C
1	Oxasulfuron		−0.81	5.1 Note: Weak acid
2	Metsulfuron-methyl		−1.87	3.75 Note: Weak acid
3	Triasulfruon		−0.59	4.64 Note: Weak acid
4	Rimsulfuron		−1.46	4 Note: Weak acid
5	Chlorsulfuron		−0.99	3.4 Note: Weak acid
6	Mesosulfuron-methyl		−0.48	4.35
7	Amidosulfuron		−1.56	3.58 Note: Weak acid
8	Bensulfuron-methyl		0.79	5.2 Note: Weak acid

[a] All physicochemical data were provided from Pesticide Properties Database [33]. Only pKa value for mesosulfuron-methyl was provided from PubChem database [34].