

Development of a Method for the Simultaneous Determination of Six Sulfonylurea Herbicides in Wheat, Rice, and Corn by Liquid Chromatography–Tandem Mass Spectrometry

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S Supporting Information

ABSTRACT: A sensitive and reliable method was developed and validated for trace determination of sulfonylurea herbicides residues in cereals (wheat, rice, and corn) by liquid chromatography–tandem mass spectrometry. The selected analytes were ethoxysulfuron, ethametsulfuron-methyl, bensulfuron-methyl, chlorimuron-ethyl, pyrazosulfuron-ethyl, and cyclosulfamuron. In this work, the extraction procedure was performed by using a mixture solvent of phosphate buffer (pH 9.5)/acetonitrile (8:2, v/v) as the extraction solvent and then was cleaned up by using Spe-ed C18/18% SPE cartridges, providing good recoveries for all of the tested analytes and with no matrix effects affecting method accuracy. The limits of detection for the studied analytes in cereal samples were between 0.043 and 0.23 $\mu\text{g kg}^{-1}$, and the limits of quantification were between 0.14 and 0.77 $\mu\text{g kg}^{-1}$, lower in all cases than the maximum residue limits permitted by the European Union for this kind of food. The developed methodology has demonstrated its suitability for the monitoring of these residues in cereal samples with high sensitivity, precision, and satisfactory recoveries.

KEYWORDS: Sulfonylurea herbicides, residue, cereals, LC-MS/MS

INTRODUCTION

Sulfonylurea is an herbicide with high efficiency and low application rates in field crops ($2\text{--}60\text{ g ha}^{-1}$)¹ and has been largely employed for the control of grassy and broad-leaf weeds in cereals, pasture plantation crops, and noncrop situations.^{2–4} However, most of sulfonylurea herbicides (SUHs) have a long residual effect, which is regarded as a potential risk, especially for crops, aquatic plants, and microorganisms.^{5–8} With the increase of the application scope of SUHs, the concern for the effects of SUHs in the environment and human health has increased. Some countries and organizations successively regulate SUHs maximum residue limits (MRLs) in crops. For example, the European Union has laid down MRLs of 0.01–0.1 mg kg^{-1} for SUHs in cereals, such as 0.05 mg kg^{-1} for imazosulfuron and 0.1 mg kg^{-1} for chlorsulfuron; the United States regulated the MRLs at 0.05 mg kg^{-1} for SUH residues in rice from February 2007. Coming with it is the requirement of the simultaneous quantitative determination of a few dozen SUHs residues in diverse biological matrices. Although in the past 20 years SUH residual analytical methods have been developed, high-performance liquid chromatography (HPLC) with an UV or diode array or MS detection system^{9–19} was the most common approach because of the polar characteristic, low volatility, and thermal instability of SUHs. Capillary electrophoresis,^{20–25} bioassays,^{26–28} and enzyme-linked immunosorbent assay²⁹ methods have also been tried. In the above studies, the studied matrices were mainly environmental media, such as soil^{10,14,16,18,25,28} and water,^{11,14,19,21,23} but there were very few reports on the analysis of cereals.¹³ Detection methods were dominated by single residue analysis, and the detection limit was at the mg kg^{-1} level. Because of their low application rates and thermal instability, the determination of SUH residues continues to present an analytical challenge, which also promotes the development of pretreatment of sample and new

detection technology. Zhou et al.³⁰ applied a carbon nanotubes packed cartridge for preconcentration nicosulfuron, thifensulfuron-methyl, and metsulfuron-methyl in water samples and obtained satisfactory results. Wang et al.³¹ reported that ionic liquid-functionalized silica was prepared as a sorbent to extract 12 SUHs in water and soil samples and showed higher selectivity than C_{18} . In recent years, because of their comprehensive approach, multiresidue analytical methods^{32–34} allow determination of a large number of trace pesticides in a single analysis and have become preferred tools for simultaneous quantification of pesticide residues up to a low $\mu\text{g kg}^{-1}$ level, in which liquid chromatography–tandem mass spectrometry (LC-MS/MS) is applied to reduce interference from coextractives in the complex sediment matrix while achieving good sensitivity at low $\mu\text{g kg}^{-1}$. Degenhardt et al.³⁵ reported an analytical method for the extraction and the determination of seven SUHs (thifensulfuron-methyl, tribenuron-methyl, ethametsulfuron-methyl, metsulfuron-methyl, rimsulfuron, nicosulfuron, and sulfosulfuron) in wetland sediment by LC-MS/MS. However, up to date, no multiresidue LC-MS/MS method has been published for simultaneous determination of pyrazosulfuron-ethyl, ethametsulfuron-methyl, chlorimuron-ethyl, bensulfuron-methyl, ethoxysulfuron, and cyclosulfamuron in wheat, rice, and corn. The purpose of the present work was to develop a rapid, selective, sensitive, and reliable method for the simultaneous determination of the selected six SUHs from cereals (wheat, rice, and corn) using LC-MS/MS.

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MATERIALS AND METHODS

Chemicals and Standard Solutions. Methanol and acetonitrile (HPLC grade) were purchased from Fisher Chemicals (Fair Lawn, NJ). Pesticide quality formic acid was purchased from Tianjin Yongda Technology Co., Ltd., and other reagents used were of analytical grade and purchased from Beijing Chemical Reagents Company (Beijing, China). The water used to prepare the solutions was purified with a Milli-Q system (Millipore, United States).

Phosphate-buffered solution (PBS), 0.1 mol L⁻¹ dipotassium hydrogen phosphate solution, was adjusted to pH 9.5 with 0.1 mol L⁻¹ sodium hydroxide. Certified analytical standards of pyrazosulfuron-ethyl (99%), ethametsulfuron-methyl (98%), chlorimuron-ethyl (96%), bensulfuron-methyl (97%), ethoxysulfuron (97%), and cyclosulfamuron (95%) were supplied by Pesticide Analysis Laboratory, China Agricultural University (Beijing, China). Structures of the selected SUHs are shown in Figure 1.

Stock standard solutions containing 1000 mg L⁻¹ of each compound were prepared by dissolving accurately weighed amounts in acetonitrile and stored in darkness at -18 °C. A standard multicomponent solution was prepared by diluting each primary standard solution with acetonitrile and stored in darkness at 4 °C. Working standard solutions were obtained at various concentrations by dilution of the standard multicomponent solution in acetonitrile. The sorbent used for solid-phase extraction (SPE) was Spe-ed C18/18% (500 mg, 6 mL), from Applied Separation Inc. (United States).

Sample Preparation and Matrix Spiking. The cereal samples (wheat, rice, and corn) were ground to a fine powder (High-Speed Universal Disintegrator, FW-80, Tianjin Taisite Instrument Co., Ltd.)

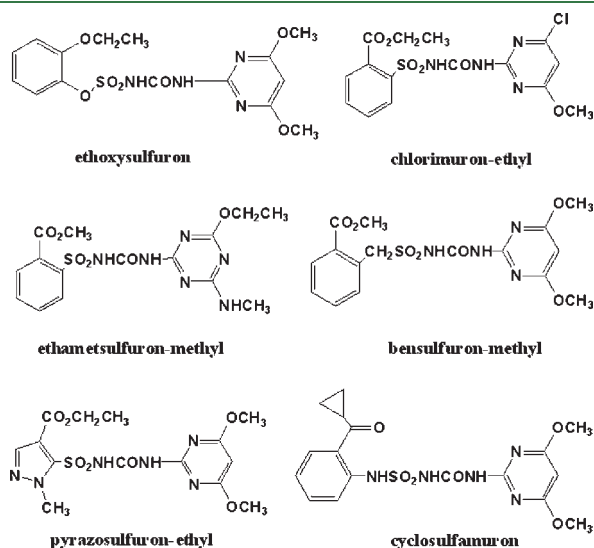


Figure 1. Structures of the selected six SUHs.

and stored in darkness at 4 °C until analysis. Samples for recovery studies were spiked with a corresponding volume of the working solution and left for 30 min before beginning the extraction.

The sample (5.00 g) was extracted with a 10.0 mL aliquot of PBS/ acetonitrile (8:2, v/v) in an ultrasonic bath for 1 min and then in an oscillator for 40 min. The extract was placed into a 50 mL Teflon centrifuge tube and centrifuged for 5 min at 8000 rpm. The above extraction was repeated three times, and the upper layers were merged and transferred to a 50 mL beaker. Phosphoric acid (85%) was dropped into the beaker to regulate solution the pH value to 2.5 ± 0.1.

SPE was carried out on Spe-ed C18/18% cartridges preconditioned with 5 mL of acetonitrile soaking for 30 min, and a 5 mL aliquot of PBS/ acetonitrile (8:2, v/v) (the pH value of this mixture was adjusted to 2.5 beforehand) prewashing at the rate of 1 mL min⁻¹. The cereal extracts were loaded through the cartridge at the rate of 1 mL min⁻¹ until draining, and the eluate was abandoned. The cartridges were vacuumized for 10 min and washed with a 3 mL aliquot of PBS/acetonitrile (1:9, v/v), and the eluate was collected and brought to dryness under nitrogen-blow. The dry residue was dissolved in acetonitrile to the 1 mL mark, and 10 μL was injected into the LC system for analysis. Matrix-matched standards were prepared by the addition of multicomponent working solution to the eluate from the SPE prior to dilution to the final volume.

Instrumental and Chromatographic Conditions. Chromatographic separation was carried out on an Agilent HPLC 1200 system (Agilent, United States) using an Agilent Zorbax SB-C18 column (4.6 mm × 150 mm, 3.5 μm). The mobile phases, A and B, were aqueous 0.1% formic acid and acetonitrile, respectively. The gradient program was as follows: from 80 to 4% A in 14 min, from 4 to 80% A in 2 min. The total running time was 16 min and a 10 min for re-equilibration after each analysis. The column oven was 30 °C, the flow rate was constant, 0.6 mL min⁻¹ during the whole process, and 5 μL of sample was injected in every case.

Mass spectrometry was carried out on an Agilent 6410 Mass Spectrometer Triple Quad detector (Agilent) using the multiple reaction monitoring (MRM) mode and positive ESI mode. Its parameters were as follows: gas temperature, 300 °C; gas flow, 6 L min⁻¹; nebulizer gas, 40 psi; and capillary voltage, 4000 V. Nitrogen served as the nebulizer and collision gas. Precursor ions and their products ions used for quantification and confirmation purposes and the operating parameters as well as declustering potential and collision energy are summarized in Table 1. Figure 2 shows the MRM chromatogram of six SUHs at the 0.01 mg kg⁻¹ concentration level. Agilent Mass Hunter Data Acquisition, Qualitative Analysis and Quantitative Analysis software was used for method development and data acquisition.

RESULTS AND DISCUSSION

Extraction Procedure Optimization. The selection of an optimal extraction solvent is one of the most important factors in

Table 1. LC-MS/MS Analysis Conditions for the Selected Six SUHs

analyte	MW	cone voltage (V)	MRM transitions, <i>m/z</i> (collision energy, eV)		
			identification	quantification	retention time (min)
ethoxysulfuron	398.4	140	399.2 > 218.0 (20)	399.2 > 260.8 (10)	9.95
ethametsulfuron-methyl	410.4	140	411.2 > 168.0 (30)	411.2 > 196.0 (15)	7.23
bensulfuron-methyl	410.4	140	411.2 > 182.0 (20)	411.2 > 149.0 (20)	8.31
chlorimuron-ethyl	414.8	140	415.2 > 121.0 (45)	415.2 > 185.8 (15)	9.89
pyrazosulfuron-ethyl	414.4	140	415.3 > 139.0 (50)	415.3 > 182.0 (20)	9.47
cyclosulfamuron	421.4	120	422.2 > 260.0 (15)	422.2 > 217.8 (30)	10.82

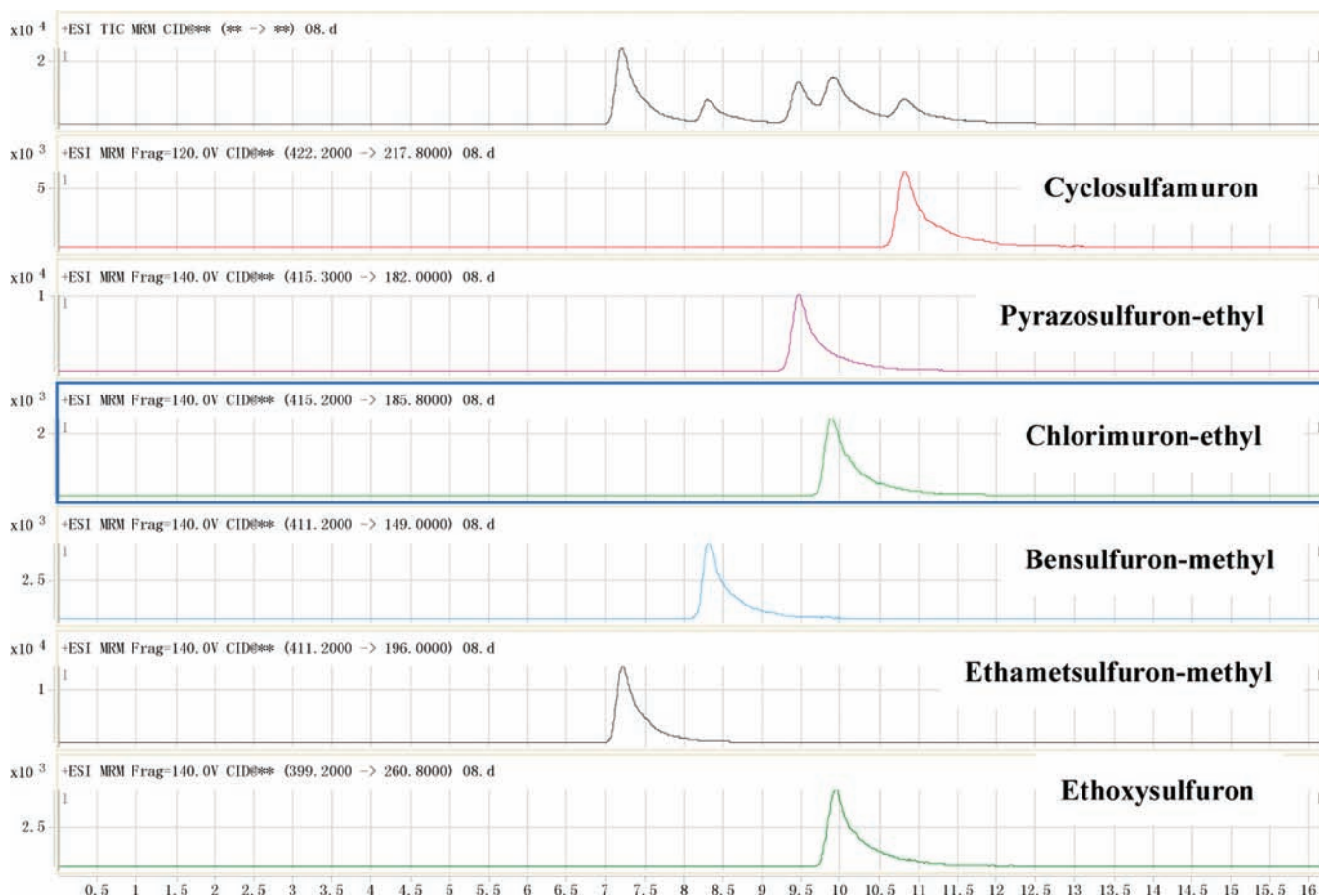


Figure 2. MRM chromatogram of the spiked rice sample at 0.01 mg kg^{-1} .

determining the effect of extraction. Some extraction methods were reported in literatures that SUHs were extracted from soil with the mixtures of acidic (or basic) solvent and acetonitrile (or methanol). The reason for applying acidic or basic solvent in extraction process is that SUH, weak acidic compound, can be ionized in it. The ionization extent of SUH is affected by its pK_a and pH value of the extraction solvent, which determines the extraction efficiency. In this study, to study the extraction efficiency of extraction solvent, different pH values (such as pH 5.0, 7.0 and 9.5) of PBS (8 mL) were mixed with acetonitrile (2 mL) and tested. We observed that the average recoveries of wheat sample fortified at 0.1 mg kg^{-1} ranged from 33 to 57% at pH 5.0 of PBS, from 42 to 76% at pH 7.0, and from 79 to 100% at pH 9.5. Therefore, the extraction solvent of PBS (9.5)/acetonitrile (8:2, v/v) was adopted. For the cleanup, the pH value of the obtained extract should be adjusted to 2.5. Under this acidic condition, the SUH is in molecular form, which is easily combined with the adsorbent of SPE and consequently retained in SPE column, and then eluted by acetonitrile/PBS (9:1, v/v). The obtained results indicated that the recoveries of the adjusted extract were higher than that of unadjusted extract.

Method Validation. To validate the method for each matrix, recoveries, repeatability, and limits of detection (LOD) and quantification (LOQ) were determined. The linearity of the calibration curves was studied by using pesticide standard solutions at five concentrations ranging between 0.01 and 0.5 mg L^{-1} . The response function is found to be linear with a coefficient of determination (R^2) higher than 0.99 in the tested range for the

six SUHs. The matrix effect (ME) of the present method was investigated by comparing standards in solvent with matrix-matched standards. The matrix-matched standard calibration was performed for the six SUHs in wheat, rice, and corn at the same concentrations with solvent standards of 0.005 , 0.01 , 0.1 , 0.2 , and 0.5 mg L^{-1} . Curves display good linearity with R^2 higher than 0.98. Table 2 summarizes the analytical results obtained for each pesticide in solvent and in matrix, including slope, R^2 , and ME values calibrated by using slope ratio method in three matrices. The ME values of six SUHs in three matrices are between 0.896 and 1.285, and the standard deviations are less than 10%, which indicates that the matrix effect is negligible in determining the target compounds.

Precision and accuracy data were obtained for all of the pesticides spiked at concentrations of 0.01 , 0.02 , and 0.1 mg kg^{-1} in wheat, rice, and corn samples. Accuracy was evaluated in terms of recovery, and the satisfactory recoveries were from 68.1 to 115.4%. In this study, the samples were extracted following the above-described pretreatment and cleanup steps, and three replicates were prepared at each concentration level, and each one was injected in duplicate. The obtained values of the recovery study for each compound are shown in Table 3.

The validation procedure of the method precision included intralaboratory and interlaboratory studies. In intralaboratory studies, the precision of the method was determined by intraday and interday studies on rice samples fortified at 0.1 mg kg^{-1} , expressed by the relative standard deviation (% RSD). Intraday precision (% RSD) was lower than 20%. The interday precision

Table 2. Linear Regression Data for Matrix-Matched Calibration Standards and Solvent (Chromatographic Mobile Phase) Calibration Standards

analyte	slope	r^2	matrix effect (ME) ^a
ethoxysulfuron	solvent 341406	0.9994	
	wheat matrix 305859	0.9987	0.896
	rice matrix 313578	0.9834	0.918
	corn matrix 341492	0.9993	1.000
ethametsulfuron-methyl	solvent 542183	0.9999	
	wheat matrix 562565	0.9996	1.038
	rice matrix 561266	0.9994	1.035
	corn matrix 570405	0.9992	1.052
bensulfuron-methyl	solvent 256823	0.9991	
	wheat matrix 268908	0.9996	1.047
	rice matrix 269334	0.9992	1.049
	corn matrix 290063	0.9989	1.129
chlorimuron-ethyl	solvent 128521	0.9999	
	wheat matrix 132215	0.9996	1.029
	rice matrix 132558	0.9996	1.031
	corn matrix 145780	0.9994	1.134
pyrazosulfuron-ethyl	solvent 190785	0.9988	
	wheat matrix 220912	0.9986	1.158
	rice matrix 218142	0.9995	1.143
	corn matrix 245113	0.9957	1.285
cyclosulfamuron	solvent 170918	0.9970	
	wheat matrix 174579	0.9959	1.021
	rice matrix 175511	0.9993	1.027
	corn matrix 200478	0.9824	1.172

^a Slope matrix/slope solvent.

(%, RSD) was determined by analyzing the same spiked samples on five different days at 0.1 mg L⁻¹, and RSDs were lower than 20%. In interlaboratory studies, the repeatability and reproducibility of the method were determined by comparison tests between four laboratories and expressed by the RSD. These data were obtained from the statistic analysis of a set of results for cereal samples fortified with analytes at 0.01 and 0.1 mg kg⁻¹ level (each level five replicate). The calculated repeatability and reproducibility at each level are shown in Table S1 in the Supporting Information. It indicates that repeatability RSD and reproducibility RSD of the method ranged from 4.8 to 15.2% and 5.8 to 12.6%, respectively, and meet measurement requirements.

The analytical method detection limit (LOD) was calculated for a signal-to-noise ratio of 3 (S/N = 3). Method quantification limits (LOQ), corresponding to the concentrations giving the value of ratio S/N = 10, were also calculated. Estimated values of LODs were in the range from 0.05 to 0.19 $\mu\text{g kg}^{-1}$, whereas LOQ values were in the range from 0.14 to 0.77 $\mu\text{g kg}^{-1}$. The results are summarized in Table 4.

In conclusion, a method for simultaneous determination of six SUHs in cereals was developed and validated. Residual SUHs were extracted from cereals with alkaline PBS, adjusted to acidity, and cleaned up by C₁₈ SPE. Determination and quantitation of analytes were performed by LC-MS/MS. Simple and efficient pretreatment, rapid cleanup and separation, and reliable detection technology are suitable for the concentration and determination of trace SUHs in agricultural products.

Table 3. Average Recoveries (%) and Relative Standard Deviations (RSD, %) from Three Representative Commodities (Wheat, Rice, and Corn) Fortified at 0.01, 0.02, and 0.1 mg kg⁻¹ Levels

analyte	average recoveries % (RSD, %)						average recoveries % (RSD, %)	
	0.01 mg kg ⁻¹			0.02 mg kg ⁻¹			0.1 mg kg ⁻¹	
	wheat	rice	corn	wheat	rice	corn	intraday precision (n = 7)	interday precision (n = 5)
ethoxysulfuron	113.9 (5.5)	109.1 (3.4)	107.3 (6.3)	100.1 (12.7)	100.1 (2.0)	99.4 (12.8)	81.7 (1.4)	98.7 (2.4)
ethametsulfuron-methyl	101.8 (16.3)	101.1 (6.6)	73.0 (12.9)	80.1 (9.5)	89.2 (4.2)	84.9 (8.1)	85.0 (1.7)	74.5 (2.6)
bensulfuron-methyl	110.2 (19.4)	103.1 (5.9)	104.1 (12.2)	80.1 (8.7)	88.3 (12.6)	69.1 (7.8)	91.0 (2.5)	82.1 (3.3)
chlorimuron-ethyl	115.4 (5.6)	96.3 (6.1)	102.2 (5.3)	76.6 (9.3)	94.1 (9.4)	74.9 (4.5)	86.3 (1.6)	80.2 (2.3)
pyrazosulfuron-ethyl	114.6 (14.9)	97.4 (5.1)	110.2 (4.9)	75.5 (7.8)	97.7 (11.5)	79.0 (10.5)	91.7 (1.4)	82.6 (1.7)
cyclosulfamuron	111.2 (9.6)	93.8 (6.1)	116.6 (8.4)	81.2 (10.3)	95.8 (4.2)	87.2 (11.2)	80.7 (2.0)	70.0 (1.3)

Table 4. LODs and LOQs of Selected Six SUHs in Cereals

analyte	LOD ($\mu\text{g kg}^{-1}$)			LOQ ($\mu\text{g kg}^{-1}$)		
	wheat	rice	corn	wheat	rice	corn
ethoxysulfuron	0.069	0.043	0.072	0.23	0.14	0.24
ethametsulfuron-methyl	0.050	0.11	0.053	0.17	0.37	0.18
bensulfuron-methyl	0.14	0.12	0.19	0.47	0.40	0.63
chlorimuron-ethyl	0.071	0.060	0.058	0.24	0.20	0.19
pyrazosulfuron-ethyl	0.12	0.056	0.097	0.40	0.19	0.32
cyclosulfamuron	0.11	0.097	0.23	0.37	0.32	0.77

■ ASSOCIATED CONTENT

S Supporting Information. Table of statistical data from test results between four laboratories. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ ABBREVIATIONS USED

SUH, sulfonylurea herbicide; LC-MS/MS, liquid chromatography–tandem mass spectrometry; RSD, percent relative standard deviation; SPE, solid-phase extraction; LOD, limit of detection; LOQ, limit of quantification

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