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Study on herbicide residues in soybean processing based on UPLC-MS/MS detection

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Abstract

Soybean meal is an important component of poultry and fish feed formulations. Soybean cultivation and use date back to China's agrarian era. Its usage for human consumption is mentioned in Chinese medicinal collections reaching back 6,000 years. For generations, soybean has meant oil, bread, cheese, milk, and meat to the people of Indonesia, the Philippines, Manchuria, Korea, Japan, and China. Soybeans are an oilseed crop that provides food for wildlife, birds, and humans. Acetochlor and clomazone are two insecticides that are commonly employed to safeguard soybeans from weeds and are both highly problematic. The goal of this research was to see the effect of acetochlor and clomazone on soybean food safety. Employing UPLC-MS/MS (ultra-performance liquid chromatography coupled with tandem mass spectrometer), acetochlor and clomazone concentrations in mature straw, mature soybean, green straw, and green soybean were measured. The RSDs (relative standard deviations) range from 2-11%, the compound recoveries varied from 86-110% at various concentration levels. 0.01 mg kg^{-1} was the quantitation limit for each herbicide matrix. When taken at the prescribed dose, clomazone and acetochlor residues in soybeans were all less than 0.01 mg.kg^{-1} at harvest. Soybean is an oilseed crop and significant edible, as well as a valuable source of human nourishment.

Keywords: soybean; residue analytical method; acetochlor; food safety; clomazone.

Practical Application: Soybean has great prospects, primarily as a high-protein feed in animal husbandry. Therefore, analysis of residual herbicide concentrations in soybean processing products is an important practical task. In the context of soybean farming, this research will assist farmers in using acetochlor and clomazone safely and correctly, as well as give a means for regulatory agencies to monitor herbicide administration.

1 Introduction

Soybean is the most significant seed legume on the planet, providing approximately 48.2-60% of worldwide edible oil and two-thirds of global protein concentrate for animal nutrition (Barman et al., 2018; Cabanillas et al., 2018; Khan et al., 2020; Marinkovic et al., 2018; Satriawan et al., 2021; Sverguzova et al., 2021; Vozhehova et al., 2018). Soybean by-products, such as straw and shell, provide significant nutritional value to some animals and poultry (Colletti et al., 2020; Jiang et al., 2021; Rudraraju et al., 2020). Alternatively, weeds would contend with soybeans for nutrients throughout the growing season, lowering soybean quality and production. In 1994, acetochlor (Figure 1a) was employed to manage weeds on corn, while clomazone (Figure 1b) was used to manage grasses and broadleaf weeds (Bellaloui et al., 2020; Djanta et al., 2020; Shea et al., 2020).

The two herbicides are commonly utilized in soybean because of their strong weed control characteristics. They do, nevertheless, pose a threat to the ecosystem and wildlife (Ferebee, 2019; Hussan et al., 2020; Norsworthy et al., 2019; Song et al., 2020). In a study, clomazone and its leftovers were proven to be embryotoxic (Silva et al., 2021). Following exposure to varying concentrations of clomazone and the production of its emulsifiable concentrate (EC), the researchers also discovered underdeveloped embryos (Liu et al., 2021; Sheng et al., 2020). A liquid formulation including technical material, one or more organic water-insoluble solvents, and an emulsifier is known as an emulsifiable concentration. ECs are one of the most widely used pest control formulations in the world (Stevanovic et al., 2017). Clomazone may affect N_2-cycling, increase fungal abundance, and reduce the bacterial number (Du et al., 2018). Acetochlor is classed as a non-target microorganism because of its high leaching capability and widespread usage (da Conceição Marinho et al., 2020; Mohanty & Jena, 2019). It is regarded as an environmental hazard in water and soil (Hao et al., 2018; Li et al., 2018; Zhang et al., 2021). Acetochlor has also been proven to be harmful to the liver and kidneys of rats, as well as altering urine metabolomics (Li et al., 2016; Mahmood et al., 2021; Song et al., 2019). As a result, acetochlor and clomazone residues in soybeans need to be determined.

The concentrations of acetochlor and clomazone in various matrices have been measured using a variety of analytical techniques. High-performance liquid chromatography (HPLC) with ultraviolet (UV) or diode array detector (DAD) has been used to identify

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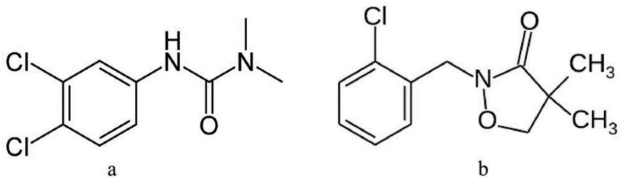

Figure 1. Molecular geometry of acetochlor (a) and clomazone (b).

Table 1. Temperature and precipitation averages in the course of the experiment.

Mean Precipitation Levels (mm)	Mean Temperature (°C)
160-420	7-29
650-1100	16-35
350-750	15-34
79-193	10-30
300-500	11-31
180-200	10-29

clomazone residues in rice-field water, river water, soil, and soybean (Farajzadeh et al., 2014; Hu et al., 2011; Liao et al., 2014; Pang & Hu, 2020; Sondhia, 2019; Zanella et al., 2002). Liquid chromatography-mass spectrometry (LC-MS) is a robust analytical method for separating, identifying, and quantifying new and recognized chemicals, as well as elucidating their chemical and structure characteristics. LC-MS was used to determine the presence of clomazone residues in bovine milk (Shinde et al., 2021; Tian, 2011). Acetochlor has been detected in human blood, soybean, maize, and soil using gas chromatography (GC), and acetochlor has been determined in plasma and food using GC-MS, and in human urine using HPLC-MS (Huff & Foster, 2011; Ward et al., 2006; Yu et al., 2018). Acetochlor and clomazone have been detected simultaneously in dry animal feed, cereals, vegetable oils, and soybeans using GC-MS (European Food Safety Authority, 2013; He et al., 2017; Walorczyk & Drożdżyński, 2012). Furthermore, for oilseed samples, LC-MS/MS has been employed (Ozkan, 2015). Previous procedures were proven to be time-consuming and necessitated the use of numerous organic solvents.

The UPLC-MS/MS method is a fantastic way to analyze herbicide residues in less solvent and time (Guo et al., 2019; Kovalczuk et al., 2008; Ly et al., 2020; Tong et al., 2016; Xiong et al., 2014). This investigation's purpose was to come up with a convenient way to measure acetochlor and clomazone residues in soybeans. In the context of soybean farming, this research will assist farmers in using acetochlor and clomazone safely and correctly, as well as give a means for regulatory agencies to monitor herbicide administration.

2 Materials and methods

Beijing Qincheng Yixin Technology Development Co., Ltd. supplied analytical standards for acetochlor (purity, 99.4%) and clomazone (purity, 97.6%). For herbicide residue analysis, Beihua Fine Chemical Co., Ltd. supplied graphitized carbon black (GCB), magnesium sulfate anhydrous ($MgSO_4$), commonly called anhydrous Epsom salt, and sodium chloride (NaCl). Honeywell International provided us with formic and acetonitrile acid. Harbin Fuli Biochemical Technology Development Co., Ltd. offered acetochlor and clomazone 51% EC. The Milli-Q system provided ultrapure water. Heilongjiang, Hunan, Guizhou, Inner Mongolia, Liaoning, and Jilin were among the provinces where field experiments were undertaken in 2018. They each have their own climatic zone. For the course of the experiment, average precipitation levels and temperature means were accordingly shown in Table 1.

The research followed the regulations of the Russian ministry of agriculture for herbicide residue experiments. Each location had an untreated control plot and an experimental plot, including a 100 m^2 area, separated by irrigation channels. Every plot had two samples, each weighing at least 1 kg and including plant components from at least 12 different plants. The samples were transported to the testing lab right away and kept at 20 °C until they were needed. The materials were homogenized using an Ultra homogenizer, and a 50 mL polypropylene centrifuge tube was loaded with 10 g of homogenized aliquots.

The samples were given 10 mL of acetonitrile after 7.5 mL of water. Before being poured to 4 g $MgSO_4$ and 2 g NaCl and vortexed for one minute, the samples were strenuously shaken for five minutes. Then, the mixes were centrifuged at 4000 rpm/min for five minutes to separate the components. Place 1.5 mL of the top layer in a 2 mL centrifuge vial holding 150 mg $MgSO_4$, 20 mg GCB, and 50 mg PSA. After a minute of vortexing, the samples were centrifuged at 4000 rpm/min for five minutes. After that, a 0.22 m nylon syringe filter was used for chromatography injection to filter the top layer before it was moved to an auto-sampler vial. A C_{18} column of Waters ACQUITY UPLC BEH (bridged ethylene hybrid) was used to separate acetochlor and clomazone via chromatography. At a flow rate of 0.3 mL/min, the mobile phases were pumped and were made up of solvent A (0.1% formic acid in water) and solvent B (acetonitrile). Then, 3 µL was injected. The sample manager's temperature was maintained at 5 °C, while to reduce viscosity, the column has remained at 40 °C.

In less than two minutes, the chemicals were eluted. An electrospray ionization (ESI) source coupled with a triple quadrupole mass spectrometer was used to identify acetochlor and clomazone targets. In the T-wave cell with a pressure of 2×10^{-3} mbar, the collision gas and the nebulizer gas were 99.99% argon and 99.95% nitrogen, respectively. Positive ion mode of MS/MS detection was used, and the target chemicals' monitoring conditions were optimized. The desolvation and source temperature were maintained at 350 °C and 120 °C, respectively, while 3.0 kV was used as the capillary voltage. The desolvation and cone gas flow rate was set at 600 and 50 liters per hour, respectively. With a dwell period of 50 milliseconds, multi-reaction monitoring (MRM) was employed to identify all chemicals. Each target compound's MS and ESI parameters were optimized separately, as shown in Table 2. Quantitative data from samples and calibration standards were processed using the Masslynx NT v4.1 (Waters) software (Katoch et al., 2012; Yang et al., 2012; Zhao et al., 2018).

Acetochlor and clomazone standard stock solutions (100 mg/L) were made in acetonitrile. To make serial dilution standard curves

(0.01, 0.05, 0.1, 0.5, 1 mg/L), the stock solutions were needed. Blank sample extracts at the aforementioned concentrations were used to generate matrix-matched standard solutions. All specimens were kept at 4 °C in the dark in a refrigerator for 6 months, and the quality of the standard functioning solutions did not deteriorate.

3 Results and discussion

Direct infusion of the standard solution (100 mg/L) was used in flow injection analysis studies to optimize MS/MS parameters of the chemicals. The MS parameter was optimized using both negative and positive ionization techniques, with the positive mode detecting the two chemicals more sensitively. Table 2 shows the collision voltages, cone voltages, precursor ions, and molecular weights. The blank sample had no interference (Figure 2a), and with a total analysis time of five minutes for each injection, the acetochlor and clomazone analysis durations were less than two minutes. As a result, detection reliability is increased, and the organic solvent is required less. As shown in Figure 2b, Acetochlor and clomazone had retention times of 1.79 and 1.58 minutes, respectively.

Acetonitrile was utilized to extract target chemicals from matrixes, according to an extraction approach for herbicide residue in matrices, known as the QuEChERS method (Anastassiades et al., 2003). The technique was verified using the limit of quantifications (LOQs) and linearity (Kumar et al., 2014; Tandon & Singh, 2012). The presence of interfering species in the vicinity of the analyte's retention period was confirmed by analyzing blank samples from the matrix. Varied matrices at five concentrations were available, ranging from 0.01 to 1 mg $L^{-1,}$ and the standard solution's linear regression analysis was used to investigate the linearity of the method. When the correlation coefficients (R^2) of clomazone and acetochlor were higher than 0.999, satisfactory linearities were achieved. All matrices had a LOQ of 0.01 mg kg^{-1} for these two herbicides. The samples were spiked at three levels to assess the method's sensitivity and accuracy. In China, acetochlor and clomazone have maximum residual limits (MRLs) of 0.1 and 0.05 mg kg^{-1}, respectively. The spiking levels were established at 0.01, 0.1, and 1 mg kg^{-1} based on the MRLs. RSD was used to assess the method's accuracy (Table 3). The approach was found to be appropriate to assess the amounts

Table 2. Analytes investigated in ESI mode have different UPLC-MS/MS and experimental conditions.

Compound	Collision voltage/V	Diagnostic ion transition	Cone voltage (V)	Quantification ions(m/z)	Molecular weight	t_R (min)	Molecular formula
Acetochlor	19 10	270.47→224.5	20 20	270.47→148.18	269.8 269.8	1.54	$C_{14}H_{20}ClNO_2$
Clomazone	26 15	240.44→89.00	26 26	240.44→124.98	396.7 396.7	1.54	$C_{12}H_{14}ClNO_2$

Table 3. RSD (%) and recovery (%) for target chemicals at three spiked levels from various matrices.

Matrix	RSD	Clomazone Recovery	RSD	Acetochlor Recovery	spiked level (μgkg^{-1})
	4	98	2	93	0.01
Soybean straw	4	106	3	87	0.1
	5	91	3	93	1
	5	102	6	95	0.01
Dry soybean	4	94	5	86	0.1
	6	106	6	106	1
	11	109	8	110	0.01
Green soybean	6	89	6	89	0.1
	4	97	6	92	1

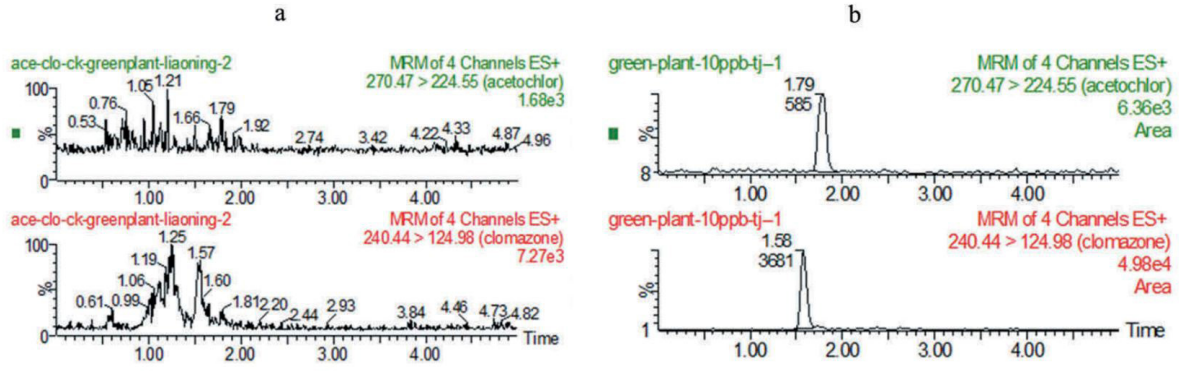

Figure 2. Acetochlor and clomazone chromatograms of the blank green straw sample (a), green straw peaked at 10^{-2} mg kg^{-1} (b).

Table 4. Clomazone and acetochlor residues in mature straw samples, mature soybean, green straw, and green soybean.

Compounds	Location	Mature straw	Mature soybean	Green Straw	Green soybean
Clomazone	Jilin		<0.01		
	Liaoning				
	Neimenggu				
	Guizhuo				
	Hunan				
	Heilongjiang				
Acetochlor	Jilin		<0.01		
	Liaoning				
	Neimenggu				
	Guizhuo				
	Hunan				
	Heilongjiang				

of residues of acetochlor and clomazone in soybeans such as straw, dried soybean, and green soybean.

Samples were obtained from the crop fields after the soybean was sprayed with the formula at a single dosage. In all matrices, less than 0.01 mg kg^{-1} residues of acetochlor and clomazone were seen (Table 4). According to the MRLs for acetochlor and clomazone in China, soybean residues at the end of the process were found to be harmless for humans. This research demonstrated that herbicides might be used safely on soybeans at the approved dosage by farm owners.

4 Conclusion

A precise and efficient residue analytical technique for determining acetochlor and clomazone residues in soybean was devised in this research. UPLC-MS/MS was employed in conjunction with the QuEChERS sample preparation protocols. The strategy used in this research is straightforward, quick, and credible. The RSDs ranged from 2 to 11% for all matrices, while the recoveries ranged from 86 to 110%. The LOQ concentration (10^{-2} μg/mg) was higher than all acetochlor and clomazone residues. As required by the worldwide community, the accuracy and linearity were adequate. Therefore, the analytical approach proposed in this study can assist in the appropriate and safe usage of acetochlor and clomazone in soybeans.

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