

One-Step QuEChERS-Based Approach to Extraction and Cleanup in Multiresidue Analysis of Sulfonylurea Herbicides in Cereals by Liquid Chromatography–Tandem Mass Spectrometry

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Abstract A one-step quick, easy, cheap, effective, rugged, and safe (QuEChERS)-based approach to extraction and cleanup in multiresidue pesticide analysis is presented for the first time. The experiment was designed to detect 23 sulfonylurea herbicides in a complex cereal matrix. The challenge was to choose the optimal conditions of one-step extraction and cleanup. Chitin, diatomaceous earth, and octadecyl were investigated as cleanup sorbents. Chitin, citrate buffer, and 1 % formic acid in acetonitrile yielded the best results. The effectiveness of sulfonylureas extraction was evaluated at three different spiking levels (0.005, 0.05, and 0.5 mg kg⁻¹) in wheat, rye, and oat using liquid chromatography–tandem mass spectrometry. The one-step QuEChERS provided recoveries in the 70–120 % range for 23 sulfonylureas in all cereal matrices. Matrix effects were evaluated and were not significant for all herbicides, showing suppression or enhancement (between -19 and 13 %). Precision, calculated as relative standard deviation (RSD), was below 20 %. A linear dependence was observed in the range of 0.005–2.0 mg kg⁻¹, and the correlation coefficient was $R^2 > 0.999$. Expanded measurement uncertainty was estimated to be between 9 and 24 %, on average. The validated method was employed in analysis of 89 real grain samples.

Keywords One-step QuEChERS · Sulfonylurea herbicides · Cereal · LC–MS/MS

Introduction

Cereal crops cover more than 65 % of world agricultural production. The intensive use of agrochemicals, especially herbicides, in cereal production is an important method of increasing yield (Łozowicka et al. 2012a, 2014). Sulfonylureas are one of the most popular groups (Hang et al. 2012), used as selective pre- and post-emergence herbicides for control of most broad-leaved weeds and annual grasses. Sulfonylureas represent a homogeneous group of the general formula R1-NH-O=C-NH-SO₂-R2(-R3), where R3 ortho substitution on the ring is often a key to dramatic changes in plant selectivity between different sulfonylureas (Fig. 1). The mode of action is inhibition of acetolactate synthase, a key enzyme in the branched amino acid (i.e., valine, leucine, and isoleucine) biosynthesis pathway (Panten et al. 1996).

As use of sulfonylurea herbicides in cereals increases, the problem of the effects of residues on human health and the environment is increasingly being discussed. The consequences are stricter maximum residue levels (MRLs) for some herbicides in certain crops (e.g., amidosulfuron in wheat from 0.5 to 0.01 mg kg⁻¹). To ensure the quality and safety of cereals, highly sensitive and selective analytical methods must be used. Detection of sulfuroneureas at very low concentrations in a matrix with high content of fatty acids, lipids, proteins, and polysaccharides is a big challenge. These co-extracts can interfere with chromatographic analysis (Łozowicka et al. 2012a, 2014; Walorczyk and Drożdżyński 2012). Several analytical procedures have been developed for determination of sulfonylurea residues in cereals, mainly based on enzyme-linked immunosorbent assays (Degelmann et al. 2006), capillary electrophoresis with ultraviolet-diode array detection (Springer and Lista 2010), and high-performance liquid chromatography with diode array

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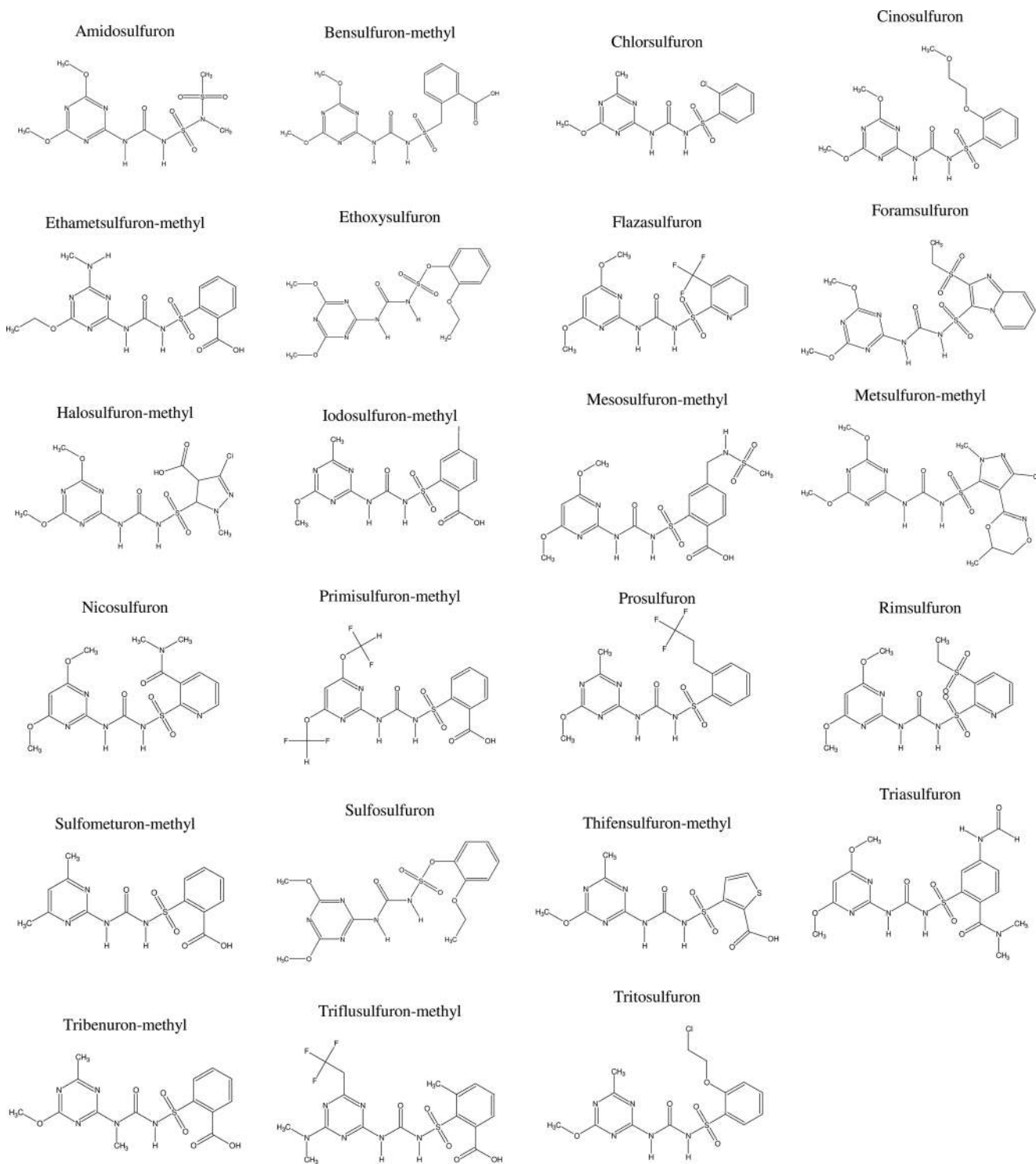


Fig. 1 Structures of sulfonylurea herbicides

detection (Chao et al. 2002; Zhou et al. 2006; Gallitzendorfer et al. 2011). Although various gas chromatography (GC) and GC–mass spectrometry (MS) methods have been developed, they require chemical derivatization of polar sulfonylureas due to their low volatility. Excessive matrix interference and exhaustive

cleanup make this method unpopular (Klaffenbach et al. 1993; Gerecke et al. 2001). Liquid chromatography (LC), or ultra-LC coupled with MS, is a more suitable and conventional method, and many papers describe the application of these techniques in sulfonylurea analysis (She et al. 2010; Perreau et al. 2007; Fenoll et al. 2012).

Several techniques of sample preparation, enrichment, and purification, up to isolation of sulfonylureas have been described. Many of them are based on solid-phase extraction (SPE) (Carabias-Martinez et al. 2004; Seccia et al. 2011), dispersive solid-phase extraction (DSPE) combined with dispersive liquid–liquid microextraction (DLLME) (Wu et al. 2009), molecularly imprinted SPE (She et al. 2010), or matrix soil-phase dispersion (MSPD) (Liang et al. 2014; Łozowicka et al. 2009). Most published methods involve liquid–soil extraction (LLE) (Liu et al. 2010; Noche et al. 2011) or salting-out liquid–liquid extraction (SALLE) (Nanita and Padivitage 2013).

In recent years, the very promising quick, easy, cheap, effective, rugged, and safe (QuEChERS) method has been commonly used to prepare different matrices for pesticide analysis. The main advantages of this methodology are speed, simplicity, and good recoveries for pesticides having different physicochemical properties at low concentrations in complex matrices, besides the significant volume reduction of organic solvents (Oshita and Jardim 2014). Several modifications of the original method (Anastassiades et al. 2003) are present in the literature, intended to adjust the method to a specific application. One modification can be the choice of dispersive sorbent type(s), which depends on the analyte's properties and on the nature of co-extracts from the matrix. Primary and secondary amine (PSA), graphitized carbon black (GCB), or their combinations are commonly used sorbents (Lehotay et al. 2010; Mantzos et al. 2013; Tomasini et al. 2012; Walorczyk et al. 2015a). PSA retains many polar compounds, including sugars, organic acids, and fatty acids, and GCB removes pigments but adsorbs compounds with planar functionality (Walorczyk et al. 2015b). Non-polar sorbents such as octadecyl (C18) and octyl (C8) remove non-polar co-extractives (Walorczyk 2014). The wide spectrum of phospholipids, carboxylic acids, and proteins is adsorbed by zirconium dioxide: Z-Sep and Z-Sep+ (Rajski et al. 2013). Some research evaluated the use of other types of sorbents, including alumina (Koesukwiwat et al. 2008) or Florisil (Patil et al. 2009), graphene (Guan et al. 2014), CarbonX (non-friable GCB) (Han et al. 2014), and ChloroFiltr (Walorczyk et al. 2015b). Arias et al. (2014) proposed the use of chitin and diatomaceous earth as environmentally friendly natural sorbents in wastewater samples. There have been a few reports in scientific literature for determining individual or selected sulfonylurea herbicides in plant material by means of QuEChERS methods (Wu et al. 2012; Min et al. 2012). However, there is lack of data about analysis of sulfonylureas in grain matrices involving QuEChERS sample preparation.

The greatest interest and objective of this work was to apply the QuEChERS method and evaluate a quick one-step

extraction–cleanup procedure for the determination of a wide range covering 23 sulfonylureas in grain samples followed by liquid chromatography–tandem quadrupole mass spectrometry (LC–MS/MS).

Materials and Methods

Materials and Reagents

Pesticide standards were purchased from Dr. Ehrenstorfer Laboratory (Augsburg, Germany). The purities of the standard pesticides ranged from 98.5 to 99.8 %. The internal standard, isoproturon- d_6 , was obtained from Sigma-Aldrich (Steinheim, Germany).

Formic acid, acetic acid, ammonium formate, and ammonium acetate were purchased from Merck (Darmstadt, Germany). HPLC and LC–MS grade acetonitrile and methanol were purchased from POCh (Gliwice, Poland). LC grade water (18 M Ω cm) was obtained from a MilliQ water purification system (Millipore Ltd., Bedford, MA, USA). Magnesium sulfate, sodium chloride, sodium citrate dibasic sesquihydrate, and sodium citrate tribasic dehydrate were purchased from Agilent Technologies (Santa Clara, USA). C18 (40 μ m) was obtained from J.T. Baker (Deventer, Holland). Chitin from shrimp shells (0.28–0.46 mm) and diatomaceous earth (8–23 μ m) were purchased from Sigma-Aldrich (Steinheim, Germany).

Preparation of Standards

Stock solutions of pesticides (around 1000 μ g mL $^{-1}$) were prepared separately by dissolving an accurately weighed amount of each reference standard in acetone. The combined working standard solutions were generated by serial dilution of the stock solutions with the same solvent. The working standard solutions were used for preparation of matrix-matched standards within the concentration range of 0.005–2.0 μ g mL $^{-1}$ and for spiking samples in validation studies. The internal standard (IS), isoproturon- d_6 solution, was prepared as described above. All stock, working standard solutions, and IS were stored in a freezer at about -20 °C until analysis.

Sample Preparation

QuEChERS—Original

Five grams of sample was weighed into a 50-mL disposable polypropylene centrifuge tube, and 5 mL of water was added. Next, 100 μ L 5 μ g mL $^{-1}$ internal standard solution (isoproturon- d_6) was added, followed by 10 mL of acetonitrile. The tubes were immediately shaken for 1 min. Then, 4 g

anhydrous magnesium sulfate and 1 g sodium chloride were added. The tubes were immediately shaken for 5 min and then centrifuged for 5 min at 4500 rpm. One milliliter of extract was filtered through a 0.2- μm hydrophilic PTFE filter, transferred into the autosampler vial, and analyzed via LC–MS/MS.

QuEChERS—Citrate

Five grams of sample was weighed into a 50-mL disposable polypropylene centrifuge tube, and 5 mL of water was added. Next, 100 μL 5 $\mu\text{g mL}^{-1}$ internal standard solution (isoproturon- d_6) was added, followed by 10 mL of acetonitrile or 10 mL 1 % formic acid in acetonitrile (citrate acidic method). The tubes were immediately shaken for 1 min. Then, 4 g anhydrous magnesium sulfate, 1 g sodium chloride, 1 g trisodium citrate dihydrate, and 0.5 g disodium hydrogen citrate sesquihydrate were added. The tubes were immediately shaken for 5 min and then centrifuged for 5 min at 4500 rpm. One milliliter of the extract was filtered through a 0.2- μm hydrophilic PTFE filter, transferred into the autosampler vial, and analyzed via LC–MS/MS.

QuEChERS—One-Step

Five grams of sample was weighed into a 50-mL disposable polypropylene centrifuge tube, and 5 mL of water was added.

Next, 100 μL 5 $\mu\text{g mL}^{-1}$ internal standard solution (isoproturon- d_6) was added, followed by 10 mL 1 % formic acid in acetonitrile. The tubes were immediately shaken for 1 min. Then, 4 g anhydrous magnesium sulfate, 1 g sodium chloride, 1 g trisodium citrate dihydrate, and 0.5 g disodium hydrogen citrate sesquihydrate, as well as 200 mg of C18 or 1 g of diatomaceous earth or 1 g of chitin, were added. The tubes were immediately shaken for 5 min and then centrifuged for 5 min at 4500 rpm. One milliliter of the extract was filtered through a 0.2- μm hydrophilic PTFE filter, transferred into the autosampler vial, and analyzed via LC–MS/MS.

LC–MS/MS Conditions

An Eksigent Ultra LC-100 (Eksigent Technologies, Dublin, CA, USA) liquid chromatography system was operated at a flow rate of 0.35 mL min^{-1} without split using a SunFire C18 2.5 μm , 2.1 \times 75 mm (Waters) analytical column, maintained at 40 $^\circ\text{C}$ during the experiments. The volume injected into the LC–MS/MS system was 10 μL . The binary mobile phase consisted of water with 0.5 % formic acid, 2 mM ammonium formate (phase A), and methanol with 0.5 % formic acid and 2 mM ammonium formate (phase B).

The gradient elution, starting at 95 % A and 5 % B, was held for 1.5 min, rising linearly to 10 % A and 90 % B in 2.5 min, and was held for 2.5 min. After ramping, the mobile

Table 1 LC–MS/MS optimized parameters for sulfonylureas

Active substance	Retention time (min)	Quantification				Confirmation				EP (V)	MRM ratio (RSD) (%)
		MRM transition m/z	DP (V)	CE (V)	CXP (V)	MRM transition m/z	DP (V)	CE (V)	CXP (V)		
Amidosulfuron	6.25	370 > 261	25	19	14	370 > 218	25	33	12	10	22 (8)
Bensulfuron-methyl	7.0	411 > 149	101	27	8	411 > 118.9	101	57	12	10	52 (12)
Chlorsulfuron	6.15	358 > 167	25	23	10	358 > 141.1	25	23	6	10	14 (10)
Cinosulfuron	5.5	414 > 183	76	23	10	414 > 157	38	24	10	10	57 (9)
Ethametsulfuron-methyl	6.15	411.2 > 196.1	46	15	10	411.2 > 168.1	46	30	10	10	33 (12)
Ethoxysulfuron	7.9	399 > 261	56	25	14	399 > 218	56	35	14	10	27 (12)
Flazasulfuron	7.1	408 > 182	66	25	10	408 > 139	26	44	14	10	37 (13)
Foramsulfuron	6.05	453 > 182.2	71	35	12	453 > 272	76	21	16	10	12 (8)
Halosulfuron-methyl	8.25	435 > 182	61	31	10	435 > 83.1	61	79	4	10	35 (12)
Iodosulfuron-methyl	7.15	507.9 > 167	71	25	10	507.9 > 141	71	40	8	10	23 (14)
Mesosulfuron-methyl	6.4	504 > 182	101	29	10	504 > 83	101	81	10	10	39 (17)
Metsulfuron-methyl	5.8	382 > 167	61	21	10	382 > 198.9	61	29	12	10	52 (16)
Nicosulfuron	5.7	411.1 > 182	86	27	10	411.1 > 213	86	23	12	10	41 (10)
Primisulfuron-methyl	8.05	469 > 254	76	29	14	469 > 199	76	31	10	10	17 (21)
Prosulfuron	7.6	420 > 141	76	25	8	420 > 167	76	25	10	10	24 (14)
Rimsulfuron	6.1	432 > 182	76	29	10	432 > 325	76	21	18	10	23 (16)
Sulfometuron-methyl	5.75	365 > 150	66	23	8	365 > 107	66	59	12	10	14 (17)
Sulfosulfuron	7.3	471 > 211	76	19	12	471 > 261	76	23	12	10	8 (8)
Thifensulfuron-methyl	5.65	388 > 167	61	21	8	388 > 204.9	61	35	12	10	49 (12)
Triasulfuron	5.65	402 > 167.1	81	23	10	402 > 141	81	27	8	10	17 (10)
Tribenuron-methyl	6.45	396 > 155	76	19	8	396 > 181	76	27	10	10	12 (9)
Triflusulfuron-methyl	7.7	493 > 264	76	29	14	493 > 96	34	45	12	10	81 (8)
Tritosulfuron	7.9	446 > 195	36	18	10	446 > 145	36	34	10	10	7 (16)
Isoproturon d_6 (IS)	6.3	213.1 > 78.3	66	10	21	213.1 > 171.2	66	10	21	10	32 (7)

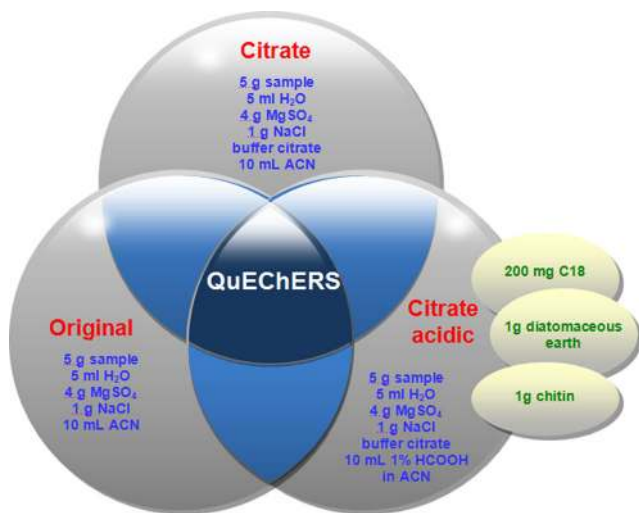


Fig. 2 Scheme of QuEChERS sample preparation with and without cleanup

phase composition was returned to its initial condition in 1 min, and this was held for 4 min for re-equilibration.

The MS/MS 6500 QTRAP System (AB Sciex Instruments, Foster City, CA), equipped with an electrospray ionization source (ESI), was used for mass spectrometric analysis. The capillary voltage was maintained at 5000 V for positive ion mode and the temperature of the turbo heaters was set to 450 °C. Nitrogen was used as the nebulizer gas (GS1), auxiliary gas (GS2), and curtain gas (CUR), at a pressure of 55, 45, and 35 psi, respectively. Nitrogen was also used as the nebulizer and collision gas. Compounds were optimized by

injecting individual standard solutions directly into the source (flow injection analysis methods—FIA). All pesticides were detected in multiple reaction monitoring mode (MRM). The precursor ion and two product ions were determined for each pesticide, one product ion for quantification and one for qualification. The MRM transitions for the pesticides are given in Table 1.

Validation Study

The developed method was subjected to a validation study using wheat, rye, and oat samples (previously checked to be free of the target pesticides) in order to determine linearity, recovery, precision, limit of quantification (LOQ), matrix effects (ME), and uncertainty (U).

The linearity of the method was determined by analysis of a series of standard samples with five different concentrations 0.005–2.0 µg mL⁻¹ in pure solvent and in matrix extracts of wheat, rye, and oat on three consecutive days. In accordance with EU SANCO/12571/2013 guidelines, the level of quantification (LOQ) was defined as the lowest spiking level validated with satisfactory values of recovery (70–120 %) and RSD (≤20 %) (SANCO 2014). Limits of detection (LOD) were calculated using a signal-to-noise ratio equal to 3.

In the recovery experiments, pesticide-free wheat, rye, and oat samples were spiked after homogenization with the appropriate volumes of representative standards of pesticides at three different levels: 0.005, 0.05, and 0.5 mg kg⁻¹. The mixture was left standing for 1 h to allow for equilibration and then processed according to the procedure described above.

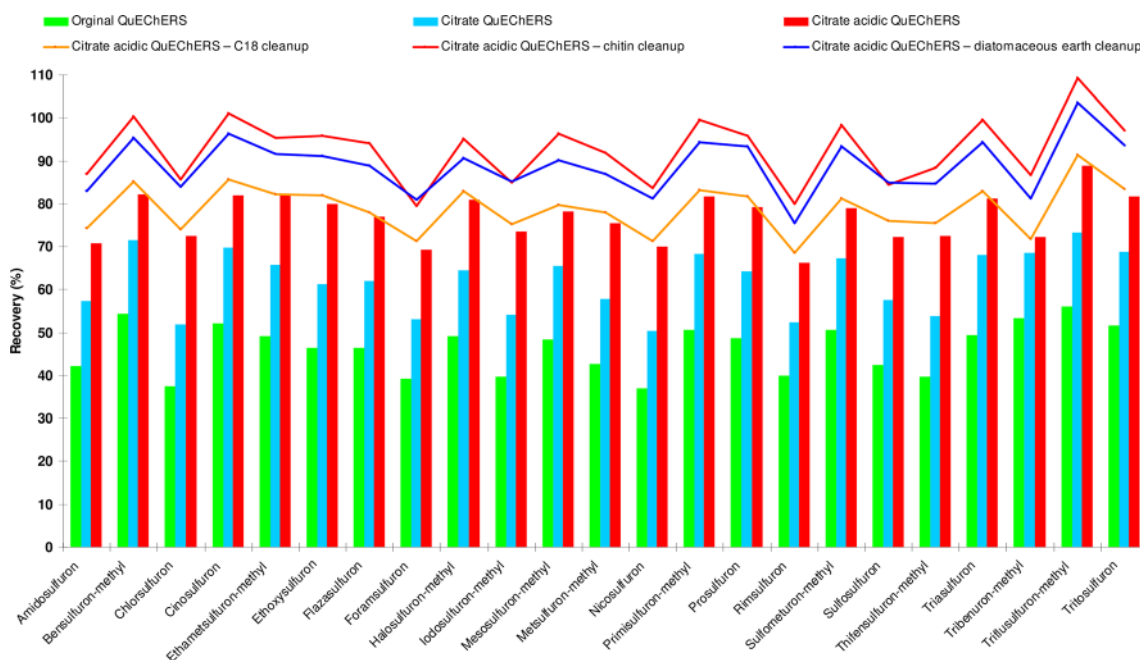


Fig. 3 Recovery of 23 sulfonyleureas employing different QuEChERS procedures (wheat at 0.05 mg kg⁻¹ fortification level)

Five replicate samples were analyzed for each fortification level. Precision was expressed in terms of relative standard deviation (RSD%) and calculated for each spiking level. The results of the recovery study were assessed for compliance with European Union guidelines SANCO/12571/2013, according to which recovery should fall within the range of 70–120 %, with the associated RSD less than or equal to 20 % (SANCO 2014).

To evaluate the percentage of matrix effects (%ME) for each analyte, the slopes of obtained calibration curves were used, at the same concentration levels, which were determined by comparing solvent and matrix-matched calibration curves in terms of slope ratios: $\%ME = (\text{slope}_{\text{matrix}}/\text{slope}_{\text{solvent}} - 1) \times 100$. Negative values of matrix effects signify suppression of the signal, and positive values signify enhancement (Anagnostopoulos et al. 2012).

Uncertainty of measurement was estimated based on the data obtained in the validation study. Relative expanded uncertainty was calculated by using coverage factor $k = 2$ at the confidence level of 95 % (Walorczyk 2014).

Results and Discussion

In our work, we investigated the possibility of using alternative sorbents such as chitin and diatomaceous earth as cleanup sorbents. Liquid chromatography–tandem quadrupole mass spectrometry (LC–MS/MS) was used for the final determination, in order to achieve improved selectivity and high accuracy. Validation parameters—recovery, precision, linearity, matrix effects, and measurement uncertainty—were evaluated. In order to prove the suitability of the validated method, real samples were applied to analysis.

Optimization of LC–MS/MS Condition

The procedure of identifying 23 sulfonyleurea herbicides in cereals was carried out using retention time and two ion transitions. Selection and optimization of the precursor ion and product ions were carried out for each tested analyte by direct injection of standards prepared in water:methanol (50:50) at a flow rate of $20 \mu\text{L min}^{-1}$. Optimal values of MS/MS parameters were selected and applied to obtain the best multi-reaction monitoring (MRM) transition with the highest intensities. The two most intensive transitions of precursor-product ions were chosen for each compound, with the more intensive transition being used for quantification and the other for confirmation. The results of optimization of mass spectrometric conditions for sulfonyleurea showed that abundances of all analytes were halved in the negative ionizing mode compared to positive mode. Optimization of voltage, temperature, pressure of nebulizer gas, auxiliary gas, and curtain gas was performed for the compound with the weakest signal

Fig. 4 Matrix effect of sulfonyleureas in the QuEChERS method (wheat at 0.05 mg kg^{-1} fortification level): **a** citrate acidic without cleanup, **b** citrate acidic with C18, **c** citrate acidic with diatomaceous earth, and **d** citrate acidic with chitin

(primisulfuron-methyl) by injecting standard solution directly into the source (flow injection analysis method—FIA). Optimized MRM transition parameters—declustering potential (DP), collision energy (CE), entrance potential (EP) and collision cell exit potential (CXP) for each compound, attained in positive ion mode—are presented in Table 1.

Different eluents and modifiers have been tested in this study for LC separation. Water, acetonitrile, and methanol were tested to achieve peaks with good resolution as well as to minimize background noise. The optimized gradient made it possible to obtain the best signal-to-noise ratio, sensitivity, and retention time. Methanol and acetonitrile, as mobile phase components, gave good retention of tested compounds in the LC column. Therefore, methanol, the less costly solvent, was chosen for further study. To ensure the highest resolution for all analytes, the gradient slope and the methanol/water ratio were optimized as described in the “LC–MS/MS Conditions” section. All analyzed herbicides are weak acids ($\text{p}K_{\text{a}}$ value in the approximate range of 3 to 5) because they contain a functional sulfonic group. This affects the behavior compounds in the column and the pH of the mobile phase, which plays an important role in retaining herbicides. The acidic mobile phase yielded better retention and chromatographic separation, and the additions of formic and acetic acid, ammonium formate, and acetate to the water–methanol mobile phase were investigated. The use of formic acid was crucial for separation of tested compounds and retention time. However, the addition of ammonium formate to formic acid led to a greater intensity of peaks. The addition of buffer also assisted ionization in ESI analysis mode. Finally, LC separation was achieved by means of a mixture of water:methanol and 2 mM ammonium formate and 0.5 % formic acid, as the mobile phase in gradient elution.

Extraction and Cleanup Method Selection

Many modifications of the QuEChERS method have been proposed in recent years. Applications of different extraction solvents, additions of buffers, optimization of the amount of solvents and salt or sample weight have been published (Wu et al. 2009; Oshita and Jardim 2014; Walorczyk et al. 2015b; Walorczyk 2014; Arias et al. 2014; Min et al. 2012; Anagnostopoulos et al. 2012). The effective cleanup step in complex matrices reduces co-extracted interferences, and many studies considered the use of different d-SPE sorbents (Oshita and Jardim 2014; Walorczyk 2014; Kwon et al. 2012; Lehotay 2011; Łozowicka et al. 2012b; He et al. 2015). This procedure leads to extension of the time of analysis and to

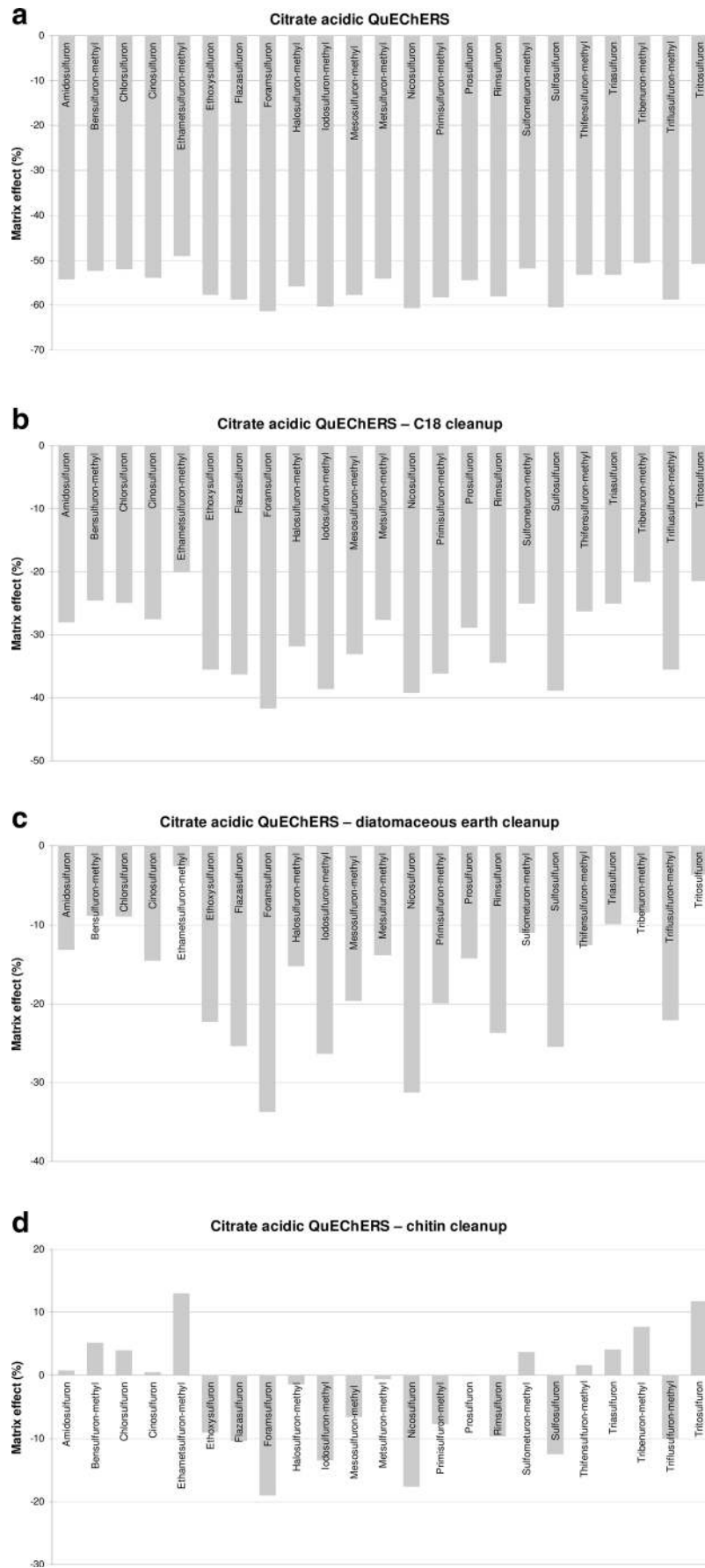


Table 2 Recovery (*R*), relative standard deviation (RSD, *n* = 5), and matrix effect (ME)

Pesticide	Original QuEChERS			Citrate QuEChERS			Citrate acidic QuEChERS			Citrate acidic QuEChERS—C18 cleanup			Citrate acidic QuEChERS—chitin cleanup			Citrate acidic QuEChERS—diatomaceous earth cleanup		
	<i>R</i> (%)	RSD (%)	ME (%)	<i>R</i> (%)	RSD (%)	ME (%)	<i>R</i> (%)	RSD (%)	ME (%)	<i>R</i> (%)	RSD (%)	ME (%)	<i>R</i> (%)	RSD (%)	ME (%)	<i>R</i> (%)	RSD (%)	ME (%)
Amidosulfuron	42	22	-67	57	14	-63	71	11	-54	74	15	-28	87	9	1	83	11	-13
Bensulfuron-methyl	54	15	-66	72	15	-62	82	9	-52	85	12	-25	100	8	5	95	10	-9
Chlorsulfuron	37	14	-66	52	14	-62	73	10	-52	74	14	-25	86	5	4	84	12	-9
Cinosulfuron	52	17	-65	70	9	-61	82	15	-54	86	12	-28	101	6	1	96	8	-15
Ethametsulfuron-methyl	49	14	-66	66	8	-61	82	14	-49	82	14	-20	95	7	13	92	9	-3
Ethoxysulfuron	47	11	-67	61	11	-63	80	12	-58	82	9	-36	96	6	-9	91	7	-22
Flazasulfuron	46	9	-67	62	14	-63	77	14	-59	78	8	-36	94	8	-10	89	6	-25
Foramsulfuron	39	14	-68	53	16	-65	69	10	-61	71	11	-42	80	6	-19	81	10	-34
Halosulfuron-methyl	49	15	-67	65	17	-62	81	9	-56	83	14	-32	95	8	-1	91	12	-15
Iodosulfuron-methyl	40	10	-68	54	15	-65	74	8	-60	75	15	-39	85	9	-13	85	9	-26
Mesosulfuron-methyl	48	9	-67	66	14	-64	78	11	-58	80	8	-33	96	8	-7	90	8	-20
Metsulfuron-methyl	43	7	-66	58	11	-62	76	9	-54	78	7	-28	92	10	-1	87	14	-14
Nicosulfuron	37	10	-67	50	9	-63	70	7	-61	71	8	-39	84	7	-18	81	7	-31
Primisulfuron-methyl	51	9	-67	68	8	-64	82	11	-58	83	9	-36	99	5	-8	94	6	-20
Prosulfuron	49	14	-66	64	14	-62	79	9	-54	82	7	-29	96	9	0	93	9	-14
Rimsulfuron	40	12	-67	52	11	-64	66	4	-58	68	8	-34	80	7	-10	75	10	-24
Sulfometuron-methyl	51	7	-67	67	10	-62	79	8	-52	81	5	-25	98	8	4	93	9	-11
Sulfosulfuron	42	16	-68	58	9	-65	72	11	-60	76	7	-39	84	5	-13	85	8	-26
Thifensulfuron-methyl	40	14	-65	54	12	-61	73	15	-53	75	9	-26	88	8	2	85	11	-13
Triasulfuron	50	11	-66	68	9	-62	81	14	-53	83	11	-25	99	3	4	94	8	-10
Tribenuron-methyl	53	10	-65	69	15	-60	72	12	-51	72	12	-22	87	7	8	81	6	-8
Triflusulfuron-methyl	56	9	-67	73	17	-64	89	10	-59	91	14	-36	109	8	-10	104	7	-22
Tritosulfuron	52	13	-66	69	12	-61	82	14	-51	83	9	-22	97	7	12	94	7	-4

use of additional materials, which increases the cost, and most importantly, carries the risk of losing the analyte and introducing additional sources of error.

Thus, the main goal of this novel study is to reduce the complicated, laborious, and time-consuming extraction and cleanup step, which required a high amount of solvents and incurred greater costs in the QuEChERS procedure for complex matrices. Our proposal was to incorporate the extraction–cleanup step into the one-step QuEChERS method for determination of 23 sulfonylureas in grain samples with high protein content. Preliminary studies were performed to assess the effectiveness of extraction of the target pesticides from the grain sample at 0.05 mg kg⁻¹ spiking level in three variants of the QuEChERS method (Fig. 2). In the first experiment, the extraction conditions were based on an original QuEChERS procedure (Anastassiades et al. 2003). Sodium chloride, magnesium sulfate, and acetonitrile were added to the homogenized sample for extraction. Relatively weak recovery values (between 37 and 56 %) were obtained, proving that this method was not very effective for acid compounds (Fig. 3). To improve phase separation, an extraction-partitioning step was conducted by the addition of magnesium sulfate, sodium chloride,

and buffer citrate (Lehotay et al. 2010). The citrate buffer salts gave recovery values higher by 12–18 % (Fig. 3) but still did not meet the criteria specified in the European Union SANCO/12571/2013 guidelines (SANCO 2014). The next tested modification was the addition of formic acid to acetonitrile. Satisfactory recoveries within the range of 70–89 %, with RSD less than 15 %, were obtained for all of the tested sulfonylureas (Fig. 3). Foramsulfuron (69 %) and rimsulfuron (66 %) showed recovery values outside the range of 70–120 %.

The second criterion, matrix effect (ME), was used in the method of estimation because strong interactions of sulfonylureas with the wheat matrix were observed (Fig. 4a). ME were outside the acceptable range of -20–20 %, with values below -49 %, for all investigated herbicides (Table 2). It could be seen that the procedure without a cleanup step was inherently associated with co-extracts. Thus, purification of extract was needed to minimize the matrix effect.

PSA, GCB, and C18 are the sorbents most commonly used to remove co-extracts from grain (Walorczyk et al. 2015b; Anagnostopoulos et al. 2012; He et al. 2015). Because of the weak acidic nature of the studied sulfonylureas, which can be adsorbed by PSA or GCB, we considered using synthetic

octadecyl, natural chitin, and diatomaceous earth as cleanup sorbents in the one-step extraction–cleanup strategy. Chitin is a polymer extracted from crab and shrimp shells, consisting of 2-acetamido-2-deoxy- β -D-glucose with a $\beta(1 \rightarrow 4)$ linkage. Diatomaceous earth is a naturally occurring, soft, siliceous sedimentary rock containing 80 to 90 % silica, with 2 to 4 % alumina, and 0.5 to 2 % iron oxide. These adsorbents have attracted much interest because of their biodegradability and biocompatibility. Our last experiment was based using a mixture of salts and buffers as previously described with the addition of 200 mg octadecyl or chitin or diatomaceous earth (1 g). The effectiveness of the three sorbents was compared. Synthetic C18 showed recovery between 65 and 89 % for all herbicides and a significant reduction of matrix effects (about 20–30 %), but was below -20 % (Fig. 4b). As presented in Fig. 4c, when natural diatomaceous earth was used, 15 of the target pesticides fell within the acceptable ME range (-20 – 20 %). Furthermore, 10–15 % greater recoveries were obtained for all analytes in contrast to the citrate procedure without cleanup (Fig. 3). Excellent results have been achieved using natural chitin. All sulfonylureas exhibited satisfactory ME

between -19 and 13 % (Fig. 4d). This sorbent also provided the best recovery values within the 80–109 % range (Fig. 3). The presence of specific functional groups such as carbonyl, amide, and enolic ether on a sorbent's surface successfully reduced co-extracts from cereal matrices. Total ion chromatograms of matrix-matched standard with and without cleanup using chitin are compared in Fig. 5. As can be seen, this sorbent reduced the background and level of co-extracted interferences and yielded satisfactory and stable recoveries as well as low matrix effect of the analyzed compounds.

Validation Study

A series of validation experiments, covering linearity, recovery, precision, limit of detection (LOD), limit of quantification (LOQ), and uncertainty (U), was performed to validate the one-step extraction–cleanup method under optimized conditions using wheat, rye, and oat samples (previously checked to be free of the target pesticides).

Linearity of calibration curves was studied by LC–MS/MS analysis of six calibration solutions at pesticide concentrations of

Fig. 5 Overlay of total ion chromatograms of matrix-matched standard (wheat at 0.05 mg kg^{-1} fortification level): without cleanup (*red line*) and with chitin cleanup (*blue line*)

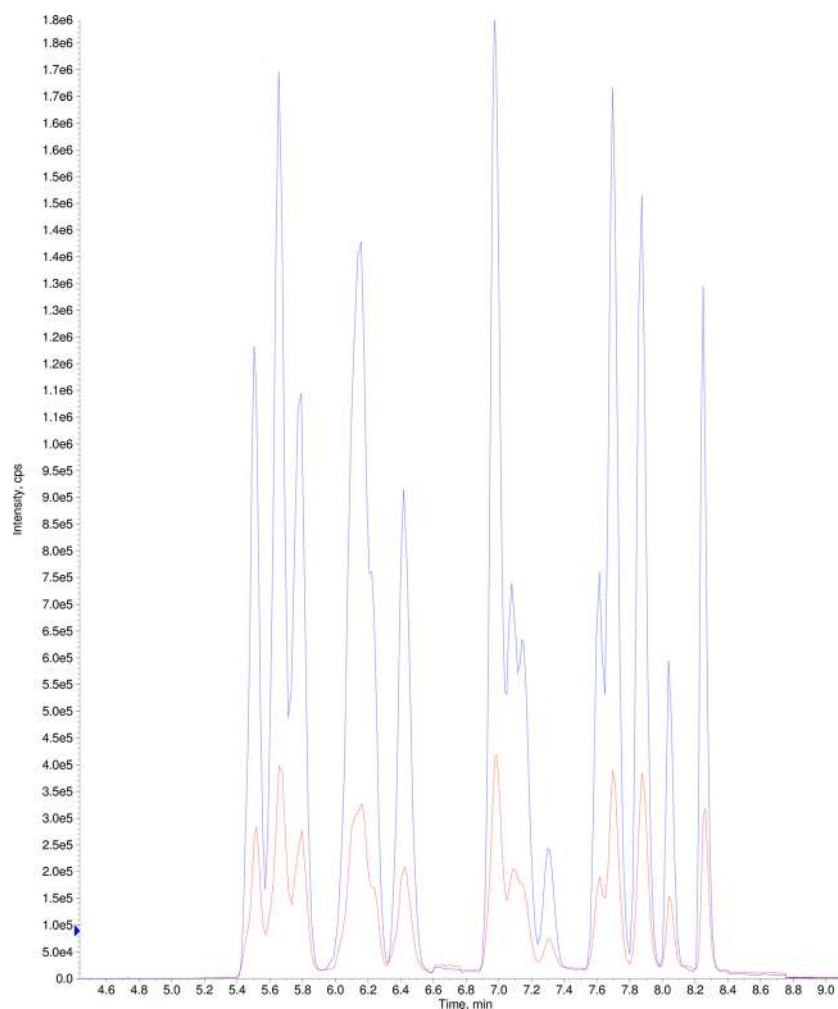
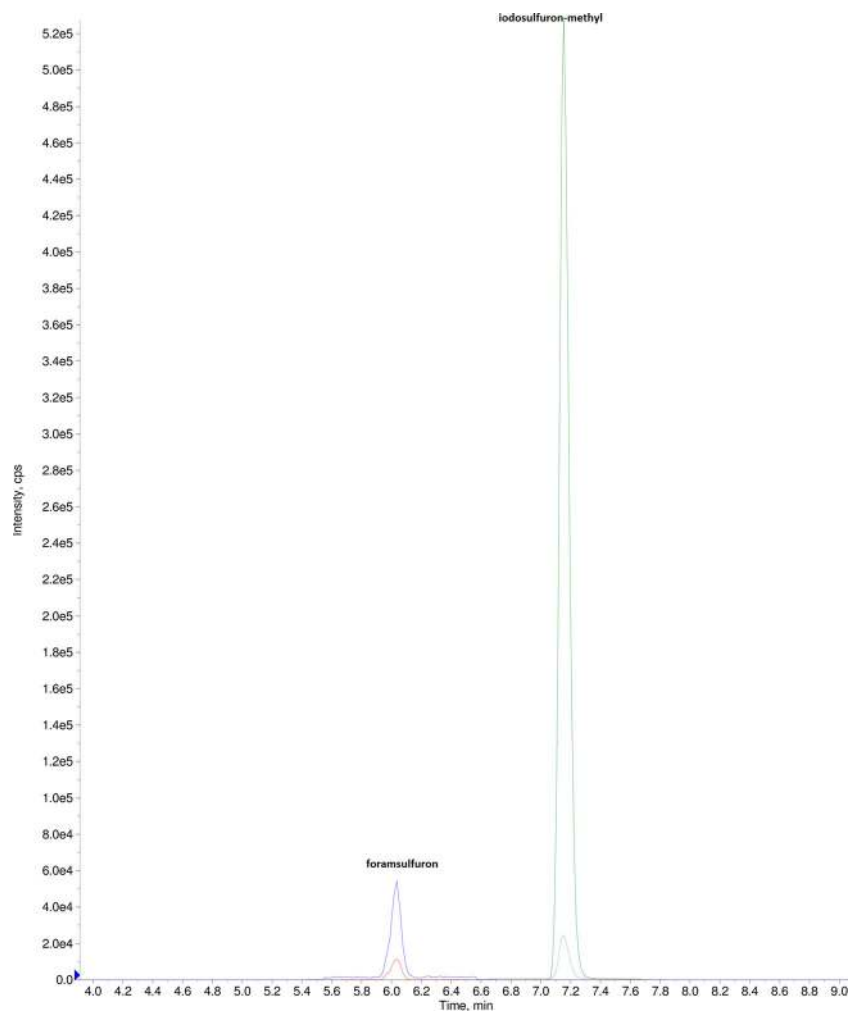


Table 3 Average recoveries, RSDs and expanded uncertainties U, % (k = 2, confidence level 95 %) of 23 sulfonylurea herbicides in wheat, rye and oat

Pesticide	LOD (mg/kg)	LOQ (mg/kg)	Wheat			Rye			Oat								
			Recovery (RSD, n = 5) (%)			Recovery (RSD, n = 5) (%)			Recovery (RSD, n = 5) (%)								
			0.005 (mg/kg)	0.05 (mg/kg)	0.5 (mg/kg)	U (%)	R ²	U (%)	R ²	U (%)	R ²	U (%)					
Amidosulfuron	0.001	0.005	84 (7)	87 (9)	88 (7)	0.99999	12	94 (10)	96 (8)	111 (7)	0.99998	13	76 (8)	74 (9)	78 (6)	0.99997	17
Bensulfuron-methyl	0.001	0.005	96 (6)	100 (8)	102 (8)	0.99997	15	106 (14)	108 (6)	105 (5)	0.99998	17	87 (9)	92 (8)	89 (5)	0.99996	20
Chlorsulfuron	0.002	0.005	86 (7)	86 (5)	91 (7)	0.99998	14	95 (15)	99 (7)	102 (4)	0.99998	16	76 (7)	78 (6)	81 (7)	0.99998	19
Cinosulfuron	0.002	0.005	98 (8)	101 (6)	98 (5)	0.99996	19	107 (17)	105 (8)	98 (6)	0.99996	17	88 (10)	92 (8)	93 (4)	0.99993	18
Ethamsulfuron-methyl	0.002	0.005	94 (5)	95 (7)	97 (8)	0.99998	9	103 (16)	101 (5)	97 (7)	0.99999	15	84 (12)	86 (5)	88 (5)	0.99998	16
Ethoxysulfuron	0.001	0.005	91 (7)	96 (6)	92 (6)	0.99994	12	102 (9)	98 (9)	95 (2)	0.99990	17	84 (8)	91 (7)	94 (6)	0.99978	21
Flazasulfuron	0.001	0.005	85 (6)	94 (8)	94 (4)	0.99997	15	100 (8)	97 (8)	93 (8)	0.99999	16	80 (9)	86 (6)	87 (7)	0.99999	18
Foramsulfuron	0.001	0.005	74 (9)	80 (6)	84 (7)	0.99967	14	92 (10)	95 (8)	97 (4)	0.99984	17	73 (7)	70 (9)	72 (5)	0.99985	14
Halosulfuron-methyl	0.002	0.005	89 (10)	95 (8)	91 (8)	0.99989	17	102 (12)	101 (7)	99 (2)	0.99985	16	85 (12)	89 (8)	93 (9)	0.99974	23
Iodosulfuron-methyl	0.002	0.005	79 (8)	85 (9)	88 (8)	0.99992	12	96 (9)	97 (5)	94 (4)	0.99995	9	77 (11)	83 (4)	87 (4)	0.99997	17
Mesosulfuron-methyl	0.0005	0.005	84 (6)	96 (7)	98 (8)	0.99990	10	101 (14)	99 (9)	97 (3)	0.99991	10	82 (8)	85 (8)	91 (5)	0.99993	13
Metsulfuron-methyl	0.001	0.005	86 (7)	92 (10)	95 (6)	0.99997	15	98 (16)	95 (8)	94 (5)	0.99999	12	80 (5)	87 (9)	88 (8)	0.99996	18
Nicosulfuron	0.001	0.005	86 (5)	84 (7)	87 (7)	0.99990	20	92 (20)	93 (6)	96 (6)	0.99996	17	73 (7)	79 (8)	83 (5)	0.99994	17
Primisulfuron-methyl	0.0005	0.005	94 (15)	99 (5)	105 (5)	0.99996	18	105 (8)	100 (7)	103 (5)	0.99988	13	85 (6)	91 (7)	94 (4)	0.99982	22
Prosulfuron	0.002	0.005	89 (15)	96 (9)	101 (8)	0.99997	17	104 (14)	98 (6)	97 (3)	0.99996	14	84 (9)	94 (5)	94 (5)	0.99989	24
Rimsulfuron	0.002	0.005	82 (11)	80 (7)	78 (8)	0.99994	13	86 (12)	91 (9)	94 (4)	0.99999	16	68 (8)	75 (7)	83 (6)	0.99999	18
Sulfometuron-methyl	0.001	0.005	93 (12)	98 (8)	101 (6)	0.99998	15	104 (14)	97 (8)	94 (7)	0.99994	10	83 (10)	84 (5)	89 (7)	0.99996	18
Sulfosulfuron	0.002	0.005	82 (14)	84 (5)	87 (4)	0.99990	15	96 (8)	94 (8)	96 (8)	0.99991	11	78 (8)	85 (8)	88 (5)	0.99988	14
Thifensulfuron-methyl	0.001	0.005	81 (15)	88 (8)	94 (7)	0.99988	17	96 (7)	97 (4)	102 (5)	0.99999	13	77 (12)	91 (8)	94 (4)	0.99998	16
Triasulfuron	0.002	0.005	97 (10)	99 (3)	104 (8)	0.99998	13	105 (9)	109 (7)	112 (7)	0.99999	17	85 (15)	88 (9)	83 (3)	0.99998	13
Tribenuron-methyl	0.001	0.005	84 (11)	87 (7)	93 (9)	0.99985	17	92 (10)	97 (10)	103 (4)	0.99982	14	74 (10)	81 (6)	84 (5)	0.99989	18
Triflusulfuron-methyl	0.0005	0.005	121 (9)	109 (8)	107 (7)	0.99987	12	115 (8)	112 (6)	108 (6)	0.99986	13	93 (14)	95 (7)	101 (3)	0.99985	20
Tritosulfuron	0.002	0.005	103 (14)	97 (7)	99 (5)	0.99983	17	105 (9)	104 (5)	109 (4)	0.99992	17	85 (11)	91 (4)	92 (7)	0.99988	17

Fig. 6 Chromatogram of real wheat sample containing foramsulfuron and iodosulfuron-methyl (0.005 and 0.02 mg kg^{-1} , respectively)



0.005 , 0.01 , 0.05 , 0.1 , 0.5 , and 2.0 $\mu\text{g mL}^{-1}$ ($n = 3$) in grain extracts. These concentrations corresponded to pesticide concentrations in real samples within the range of 0.005 – 2.0 mg kg^{-1} . Linear regression data is listed in Table 3. As shown in Table 3, satisfactory correlation coefficients were obtained for the 23 sulfonylureas, ranging from 0.99967 to 0.99999 .

Recoveries were determined in five replicates at three spiking levels: 0.005 , 0.05 , and 0.5 mg kg^{-1} . Results were assessed for compliance with the European Union SANCO/12571/2013 guidelines, according to which average recovery should be within the range of 70 – 120 % with $\text{RSD} \leq 20$ % (SANCO 2014). As can be seen in Table 3, all compounds presented satisfactory recoveries from wheat, rye, and oat within the range between 73 and 115 %. Only triflurosulfuron-methyl in wheat, at the lowest concentration level (0.005 mg kg^{-1}), showed recovery values insignificantly outside the acceptance range— 121 %. All pesticides gave RSD lower than 20 %. RSD generally did not exceed 10 % at fortification levels of 0.05 and 0.5 mg kg^{-1} . This value exceeded 10 % only at the 0.005 mg kg^{-1} level.

LOD values of individual pesticides were calculated based on the noise level in chromatograms at S/N of $3:1$, which have been presented in Table 3. These values were within the range of 0.0005 – 0.002 mg kg^{-1} . The limit of quantification (LOQ) was set at the lowest spiking concentration. Twenty six herbicides were validated with satisfactory recovery and precision parameters at this level. All pesticides yielded RSD lower than 20 % and signal-to-noise ratio >10 allowing for practical quantification. For all analytes, the level of 0.005 mg kg^{-1} was accepted as the practical LOQ.

The data derived from the validation study was used to estimate the measurement uncertainty (U) associated with the analytical results. Expanded measurement uncertainties were estimated employing a “top-down” empirical model (Medina-Pastor et al. 2011) to be between 9 and 20 % for wheat, 9 and 17 % for rye, and 13 and 24 % for oat (coverage factor $k = 2$, confidence level 95 %). Precision was identified as the main contributor to uncertainty. The uncertainty associated with recovery, calculated according to rectangular distribution, was also included in the uncertainty budget to avoid underestimation of

the total uncertainty. The results are presented in Table 3, which clearly demonstrates the suitability of the proposed method.

Real Samples

The quick, validated one-step QuEChERS extraction–cleanup method was employed in analysis of 89 real grain samples (barley, 5; oats, 5; rye, 7; triticale, 16; wheat, 56). Seven samples were positive, and four were found among 23 herbicides. Detected residues did not exceed the MRLs (maximum residue levels) specified in the European Union Regulation no. 396/2005 in any sample. The pesticides detected in cereal samples were chlorsulfuron (two samples; 0.005 and 0.02 mg kg⁻¹; MRL = 0.05 mg kg⁻¹), foramsulfuron (two samples; 0.005 and 0.02 mg kg⁻¹; MRL = 0.05 mg kg⁻¹), iodosulfuron-methyl (two samples; 0.02 and 0.03 mg kg⁻¹; MRL = 0.05 mg kg⁻¹), and tribenuron-methyl (two samples; 0.01 and 0.05 mg kg⁻¹; MRL = 0.1 mg kg⁻¹). In one sample, two herbicides, foramsulfuron and iodosulfuron-methyl (0.005 and 0.02 mg kg⁻¹, respectively), were detected (Fig. 6).

Conclusions

The first innovative approach of one-step QuEChERS extraction and cleanup was developed for analysis of 23 sulfonylureas in cereals. Among synthetic and natural cleanup sorbents, polysaccharide chitin was the best. It must be highlighted that, in the present study, integration of extraction and cleanup into the one-step method yielded short and convenient sample preparation of complex matrices. In our optimized method, mean recovery values were within the range of 70–120 % regardless of cereal species. Repeatability of the method, expressed as the relative standard deviation, was generally lower than 20 %. Low limits of quantification and detection were readily achieved using this method and allowed analysis of real samples.

The presented procedure is efficient, cost-effective, time-saving, and environment-friendly. Due to the wide use of herbicides in agriculture, our rapid method is very important in analysis, as a promising alternative to the traditional two-step QuEChERS method.

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Compliance with Ethical Standards

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Conflict of Interest Piotr Kaczyński declares that he has no conflict of interest. Bożena Łozowicka declares that she has no conflict of interest.

Ethical Approval This article does not contain any studies with human participants or animals performed by any of the authors.

Informed Consent Not applicable.

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