EURL for Cereals and Feeding stuff

National Food Institute

Technical University of Denmark

Screening Validation Report S11

Validation of a target screening method for pesticide residues in cereals using LC-Q-ToF-MS

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Contents

1. Introduction

This report describes the screening validation method of pesticide residues. The method was validated for 125 analytes in cereals at the three screening detection limits (SDLs) of 0.005, 0.01 and 0.02 mg/kg. The method validated in this report is based on the QuEChERS extraction procedure for dry matrices (<30% water content) according to the document EN 15662:2008[1]. The SDL of the qualitative screening method is the lowest level at which an analyte has been detected in at least 95% of the samples [(2)].

2. Principle of analysis

2.1 Validation design

Samples of wheat, rye, oat, barley, and rice were spiked at three different concentration levels of 0.005, 0.01, and 0.02 mg/kg. Five replicates were prepared with each of the matrices and at each of the concentration levels. Thus, 25 cereal samples were spiked at each level, and in total the number of injections was 125. Matrix matched calibration was prepared using rye at the 5 concentration levels of 0.1, 0.033, 0.01, 0.0033, and 0.001 mg/kg.

2.2 Extraction method

The samples were extracted using the citrate buffered QuEChERS (EN 15662) (CEN 2008) method without cleanup. Five g of sample were weighed. Procedural standard (dichlorvos-d6) was added to all samples before extraction. Then 10 mL of cold water was added, followed by 10 mL of acetonitrile. To aid the extraction, a ceramic homogenizer was used. The tubes were shaken for 1 min by hand. Next, 4.0 g of magnesium sulphate, 1.0 g of sodium chloride, 1.0 g of sodium citrate dehydrate, and 0.5 g of sodium citrate sesquihydrate were added. After 1 min of shaking by hand followed by centrifugation for 10 min at 4500 rpm, 8 mL of the supernatant was transferred to a clean tube and stored at – 80°C for 1 h. The extracts were then thawed, and

while they were still very cold, they were centrifuged at 4500 rpm for 5 min. Thereafter, 200 µL were diluted 1:1 with acetonitrile and filtered. Internal standard was added to the vials prior to injection. Different cereal samples were spiked at 0.005, 0.01 and 0.02 mg/kg with a mixture of pesticide standards and extracted by QuEChERS method.

2.3 Instrumentation

LC conditions

The analysis was performed on an Ultimate 3000RS UHPLC focused from Thermo Fisher Scientific. The mobile phases used were A (water + 0.1% formic acid + 5 mM ammoniac) and B (methanol). The column used was an InfinityLab Poroshell 120 SB-C18, 2.1 x 100 mm, 2.7 µm, narrow bore LC column. The injection volume was set to 2µL. Table 1 shows the elution gradient on LC. The total runtime was 20 min.

Table 1: LC eluent gradient:

Retention time (min)	Flow (mL/min)	% A	% B
0	0.2	90	10
0.5	0.2	90	10
3		55	45
14	0.4	5	95
16	0.4	5	95
16.1	0.4	90	10
19	0.2	90	10
20	0.2	90	10

QToF conditions

The analysis was performed on a maXis II^{TM} ToF from Bruker using Full scan mode ranging from 30-1000 m/z with bbCID. The bbCID is a data acquisition process where both TOF MS full scan data and MS/MS fragments are continuously generated in two independent, rapidly alternating data channels, without either precursor ion or threshold selection. In the first channel, low collision energy is applied. Precursor ions are not isolated or fragmented and full scan TOF MS spectra is produced. In the second channel, bbCID is applied with high collision energy. All ions are fragmented in the collision cell resulting in bbCID MS/MS spectra. The ion source was ESI and it runned in positive mode.

Chromeleon Xpress was used for LC initialization. Hystar version 3.2.44.0 from Bruker Daltonics was used for data acquisition. OTOF control software 3.4 (Compass for otoSeries 1.7) was used for MS tuning and optimization. Bruker Target Analysis for Screening and Quantitation (TASQ) client 2.1 was used for data processing. A database consisting of 942 compounds was used. For each analyte, information on corresponding formula, mass (Da), cas number and retention time were included in the database. The principal ion corresponding to the protonated ion generated

from the FullScan and the corresponding isotopes, and ions generated from the bbCID are introduced in the database. Each analyte has at least one ion from the FullScan or bbCID. In total, each analyte has a minimum of two fragments ions. Table 2 shows the database display of the studied compounds.

Table 2: Retention time, and the exact masses of principal ions, isotopic ions, and fragment ions for each compound.

Compound	CAS	RT (min)	Mass (Da)	Ion formula	m/z	Spectrum type
Alachlor	15972-60-8	9.91	238.0993	$C_{13}H_{17}ClNO^{1+}$		
				$C_{13}H_{17}ClNO^{1+}$	238.0993	FullScan
				$C_{13}H_{17}ClNO^{1+}$	240.0967	FullScan
				$C_{11}H_{16}N^{1+}$	162.1277	bbCID
				$C_{10}H_{13}N^{1+}$	147.1043	bbCID
				$C_{9}H_{10}N^{1+}$	132.0808	bbCID
Alanycarb	83130-01-2	10.62	238.0896	$C_{12}H_{16}NO_2S^{1+}$		
				$C_{12}H_{16}NO_2S^{1+}$	238.0896	FullScan
				$C_{7}H_{8}NS^{1+}$	138.0372	bbCID
				$C_{7}H_{7}^{1+}$	91.0542	bbCID
Allethrin	584-79-2	12.22	302.1882	$C_{19}H_{26}O_3$		
				$C_{19}H_{27}O_3^{1+}$	303.1955	FullScan
				$C_{9}H_{11}O^{1+}$	135.0804	bbCID
				$C_{9}H_{15}^{1+}$	123.1168	bbCID
				$C_{8}H_{11}^{1+}$	107.0855	bbCID
Ametryn	834-12-8	7.64	227.1205	$C_{9}H_{17}N_5S$		
				$C_{9}H_{18}N_5S^{1+}$	228.1277	FullScan
				$C_{6}H_{12}N_5S^{1+}$	186.0808	bbCID
				$C_{6}H_{6}NO^{1+}$	108.0444	bbCID
				$C_{6}H_{6}N^{1+}$	92.0495	bbCID
Asulam	3337-71-1	3.54	230.0361	$C_{8}H_{10}N_2O_4S$		
				$C_{8}H_{11}N_2O_4S^{1+}$	231.0434	FullScan
				$C_{6}H_{6}NO^{1+}$	108.0444	bbCID
				$C_{6}H_{6}N^{1+}$	92.0495	bbCID
Bensulfuron-methyl	83055-99-6	8.49	410.0896	$C_{16}H_{18}N_4O_7S$		
				$C_{16}H_{19}N_4O_7S^{1+}$	411.0969	FullScan
				$C_{9}H_{9}O_2^{1+}$	149.0597	bbCID
				$C_{7}H_{8}N_3O_3^{1+}$	182.056	bbCID
Bifenazate	149877-41-8	9.48	198.0913	$C_{13}H_{12}NO^{1+}$		
				$C_{13}H_{12}NO^{1+}$	198.0913	FullScan
				$C_{17}H_{21}N_2O_3^{1+}$	301.1547	FullScan
				$C_{12}H_{12}N^{1+}$	170.0964	bbCID
Bioresmethrin	28434-01-7	13.55	338.1882	$C_{22}H_{26}O_3$		
				$C_{22}H_{27}O_3^{1+}$	339.1955	FullScan
				$C_{12}H_{11}O^{1+}$	171.0804	bbCID

Compound	CAS	RT (min)	Mass (Da)	Ion formula	m/z	Spectrum type
				$C_{10}H_8^{1+}$	128.0621	bbCID
Bixafen	581809-46-3	10.25	413.031	$C_{18}H_{12}Cl_2F_3N_3O$		
				$C_{18}H_{13}Cl_2F_3N_3O^{1+}$	414.0382	FullScan
				$C_{18}H_{13}Cl_2F_3N_3O^{1+}$	416.0356	FullScan
Bromacil	314-40-9	6.52	260.016	$C_9H_{13}BrN_2O_2$		
				$C_9H_{14}BrN_2O_2^{1+}$	261.0233	FullScan
				$C_9H_{14}BrN_2O_2^{1+}$	263.0213	FullScan
				$C_5H_6BrN_2O_2^{1+}$	204.9607	FullScan
Butocarboxim	34681-10-2	5.69	75.0263	$C_3H_7S^{1+}$		
				$C_3H_7S^{1+}$	75.0263	FullScan
				$C_3H_7S^{1+}$	75.0263	FullScan
Butocarboxim-sulfoxide	34681-24-8	3.5	132.0478	$C_5H_{10}NOS^{1+}$		
				$C_5H_{10}NOS^{1+}$	132.0478	FullScan
				$C_3H_7S^{1+}$	75.0263	bbCID
				$C_3H_8NS^{1+}$	90.0372	bbCID
Butralin	33629-47-9	12.72	295.1532	$C_{14}H_{21}N_3O_4$		
				$C_{14}H_{22}N_3O_4^{1+}$	296.1605	FullScan
				$C_{10}H_{14}N_3O_4^{1+}$	240.0979	bbCID
				$C_{10}H_{12}N_3O_3^{1+}$	222.0873	bbCID
Buturon	3766-60-7	7.77	236.0716	$C_{12}H_{13}ClN_2O$		
				$C_{12}H_{14}ClN_2O^{1+}$	237.0789	FullScan
				$C_{12}H_{14}ClN_2O^{1+}$	239.0763	FullScan
				$C_5H_{10}N^{1+}$	84.0808	bbCID
Carfentrazone-ethyl	128639-02-1	10.33	429.0703	$C_{15}H_{18}Cl_2F_3N_4O_3^{1+}$		
				$C_{15}H_{18}Cl_2F_3N_4O_3^{1+}$	429.0703	FullScan
				$C_{15}H_{15}Cl_2F_3N_3O_3^{1+}$	412.0437	FullScan
				$C_{13}H_8Cl_2F_2N_3O_2^{1+}$	345.9956	bbCID
Chlorbromuron	13360-45-7	8.85	291.9614	$C_9H_{10}BrClN_2O_2$		
				$C_9H_{11}BrClN_2O_2^{1+}$	294.9665	FullScan
				$C_9H_{11}BrClN_2O_2^{1+}$	292.9687	FullScan
				$C_6H_4BrClN^{1+}$	203.921	bbCID
Chlorbufam	1967-16-4	8.67	172.016	$C_7H_7ClNO_2^{1+}$		
				$C_7H_7ClNO_2^{1+}$	172.016	FullScan
				$C_7H_7ClNO_2^{1+}$	174.0132	FullScan
				$C_{11}H_{11}ClNO_2^{1+}$	224.0473	FullScan
Chlorfluazuron	71422-67-8	13.09	538.963	$C_{20}H_9Cl_3F_5N_3O_3$		
				$C_{20}H_{10}Cl_3F_5N_3O_3^{1+}$	539.9702	FullScan
				$C_{20}H_{10}Cl_3F_5N_3O_3^{1+}$	541.9676	FullScan
				$C_{13}H_5Cl_3F_3N_2O_2^{1+}$	382.9363	bbCID
Chlorotoluron	15545-48-9	7.42	212.0716	$C_{10}H_{13}ClN_2O$		
				$C_{10}H_{14}ClN_2O^{1+}$	213.0789	FullScan

Compound	CAS	RT (min)	Mass (Da)	Ion formula	m/z	Spectrum type
				$C_{10}H_{14}ClN_2O^{1+}$	215.0762	FullScan
				$C_3H_6NO^{1+}$	72.0444	bbCID
Chlorsulfuron	64902-72-3	7.06	357.0299	$C_{12}H_{12}ClN_5O_4S$		
				$C_{12}H_{13}ClN_5O_4S^{1+}$	358.0371	FullScan
				$C_{12}H_{13}ClN_5O_4S^{1+}$	360.0344	FullScan
				$C_5H_9N_4O^{1+}$	141.0771	bbCID
Chromafenozide	143807-66-3	9.75	175.0754	$C_{11}H_{11}O_2^{1+}$		
				$C_{11}H_{11}O_2^{1+}$	175.0754	FullScan
				$C_{11}H_{11}O_2^{1+}$	175.0754	FullScan
Clodinafop-propargyl	105512-06-9	10.29	349.0517	$C_{17}H_{13}ClFNO_4$		
				$C_{17}H_{14}ClFNO_4^{1+}$	350.059	FullScan
				$C_{13}H_{10}ClFNO_2^{1+}$	266.0379	bbCID
				$C_7H_7^{1+}$	91.0542	bbCID
Coumaphos	56-72-4	10.77	362.0145	$C_{14}H_{16}ClO_5PS$		
				$C_{14}H_{17}ClO_5PS^{1+}$	363.0217	FullScan
				$C_{14}H_{17}ClO_5PS^{1+}$	365.0191	FullScan
				$C_{10}H_8ClO_2S^{1+}$	226.9928	bbCID
Crufomate	299-86-5	10.22	291.0791	$C_{12}H_{19}ClNO_3P$		
				$C_{12}H_{20}ClNO_3P^{1+}$	292.0864	FullScan
				$C_{12}H_{20}ClNO_3P^{1+}$	294.0838	FullScan
				$C_8H_{12}ClNO_3P^{1+}$	236.0238	bbCID
Cyanazine	21725-46-2	6.13	240.089	$C_9H_{13}ClN_6$		
				$C_9H_{14}ClN_6^{1+}$	241.0963	FullScan
				$C_9H_{14}ClN_6^{1+}$	243.0935	FullScan
				$C_8H_{13}ClN_5^{1+}$	214.0854	bbCID
Cyanophos	13067-93-1	7.77	303.0483	$C_{15}H_{14}NO_2PS$		
				$C_{15}H_{15}NO_2PS^{1+}$	304.0556	FullScan
				$C_6H_6OPS^{1+}$	156.9871	bbCID
Cyclanilide	113136-77-9	9.78	272.9959	$C_{11}H_9Cl_2NO_3$		
				$C_{11}H_{10}Cl_2NO_3^{1+}$	274.0032	FullScan
				$C_{11}H_{10}Cl_2NO_3^{1+}$	276.0004	FullScan
					161.9871	bbCID
Cyflufenamid	180409-60-3	10.86	412.121	$C_{20}H_{17}F_5N_2O_2$		
				$C_{20}H_{18}F_5N_2O_2^{1+}$	413.1283	FullScan
					223.0286	bbCID
					241.0391	bbCID
Cymoxanil	57966-95-7	5.22	128.0455	$C_4H_6N_3O_2^{1+}$		
				$C_4H_6N_3O_2^{1+}$	128.0455	FullScan
				$C_4H_3N_2O_2^{1+}$	111.0189	bbCID
Cyprazin	22936-86-3	7.64	227.0938	$C_9H_{14}ClN_5$		
				$C_9H_{15}ClN_5^{1+}$	228.101	FullScan

Compound	CAS	RT (min)	Mass (Da)	Ion formula	m/z	Spectrum type
				$C_6H_9ClN_5^{1+}$	186.0541	bbCID
				$C_5H_6N_3^{1+}$	108.0556	bbCID
DEET	134-62-3	7.82	191.131	$C_{12}H_{17}NO$		
				$C_{12}H_{18}NO^{1+}$	192.1383	FullScan
				$C_8H_7O^{1+}$	119.0491	bbCID
Demeton-S	126-75-0	8.45	89.0419	$C_4H_9S^{1+}$		
				$C_4H_9S^{1+}$	89.0419	FullScan
				$C_4H_9S^{1+}$	89.0419	FullScan
Demeton-S	126-75-0	8.45	89.0419	$C_4H_9S^{1+}$		
				$C_4H_9S^{1+}$	89.0419	FullScan
				$C_4H_9S^{1+}$	89.0419	bbCID
Desmetryn	1014-69-3	6.61	213.1048	$C_8H_{15}N_5S$		
				$C_8H_{16}N_5S^{1+}$	214.1121	FullScan
				$C_3H_4N_3^{1+}$	82.04	bbCID
				$C_5H_{10}N_5S^{1+}$	172.0651	bbCID
Dichlofenthion	97-17-6	12.1	313.97	$C_{10}H_{13}Cl_2O_3PS$		
				$C_{10}H_{14}Cl_2O_3PS^{1+}$	314.9773	FullScan
				$C_{10}H_{14}Cl_2O_3PS^{1+}$	316.9744	FullScan
				$C_6H_6Cl_2O_3PS^{1+}$	258.9147	bbCID
Difenoxuron	14214-32-5	7.97	286.1317	$C_{16}H_{18}N_2O_3$		
				$C_{16}H_{19}N_2O_3^{1+}$	287.139	FullScan
				$C_7H_7O_2^{1+}$	123.0441	bbCID
Dimefuron	34205-21-5	8.44	338.1146	$C_{15}H_{19}ClN_4O_3$		
				$C_{15}H_{20}ClN_4O_3^{1+}$	339.1218	FullScan
				$C_{15}H_{20}ClN_4O_3^{1+}$	341.1194	FullScan
				$C_3H_6NO^{1+}$	72.0444	bbCID
Dimethachlor	50563-36-5	8.13	255.1026	$C_{13}H_{18}ClNO_2$		
				$C_{13}H_{19}ClNO_2^{1+}$	256.1099	FullScan
				$C_{13}H_{19}ClNO_2^{1+}$	258.1073	FullScan
				$C_{12}H_{15}ClNO^{1+}$	224.0837	FullScan
Dimethirimol	5221-53-4	5.52	209.1528	$C_{11}H_{19}N_3O$		
			M+nH	$C_{11}H_{20}N_3O^{1+}$	210.1601	FullScan
			71.06	$C_3H_7N_2^{1+}$	71.0604	bbCID
			140.107	$C_8H_{14}NO^{1+}$	140.107	bbCID
Dinotefuran	165252-70-0	3.67	202.1066	$C_7H_{14}N_4O_3$		
				$C_7H_{15}N_4O_3^{1+}$	203.1139	FullScan
				$C_3H_9N_3^{1+}$	87.0791	bbCID
				$C_2H_7N_3^{1+}$	73.0634	bbCID
Dioxacarb	6988-21-2	4.92	223.0845	$C_{11}H_{13}NO_4$		
				$C_{11}H_{14}NO_4^{1+}$	224.0917	FullScan
				$C_9H_{11}O_3^{1+}$	167.0703	FullScan

Compound	CAS	RT (min)	Mass (Da)	Ion formula	m/z	Spectrum type
				$C_7H_7O_2^{1+}$	123.0441	bbCID
Dodine	10/3/2439	10.83	228.2434	$C_{13}H_{30}N_3^{1+}$		
				$C_{13}H_{30}N_3^{1+}$	228.2434	FullScan
				$C_3H_8O^{1+}$	60.057	bbCID
Edifenphos	17109-49-8	10.56	310.0251	$C_{14}H_{15}O_2PS_2$		
				$C_{14}H_{16}O_2PS_2^{1+}$	311.0324	FullScan
				$C_6H_5S^{1+}$	109.0106	bbCID
				$C_6H_7S^{1+}$	111.0263	bbCID
EPTC	759-94-4	10.15	189.1187	$C_9H_{19}NOS$		
				$C_9H_{20}NOS^{1+}$	190.126	FullScan
				$C_9H_{20}NOS^{1+}$	191.1289	FullScan
Esprocarb	85785-20-2	11.93	265.15	$C_{15}H_{23}NOS$		
				$C_{15}H_{24}NOS^{1+}$	266.1573	FullScan
				$C_7H_7^{1+}$	91.0542	bbCID
Ethiofencarb-sulfone	53380-23-7	4.54	257.0722	$C_{11}H_{15}NO_4S$		
				$C_{11}H_{16}NO_4S^{1+}$	258.0795	FullScan
				$C_9H_{13}O_3S^{1+}$	201.058	FullScan
Ethiofencarb-sulfoxide	53380-22-6	4.63	241.0773	$C_{11}H_{15}NO_3S$		
				$C_{11}H_{16}NO_3S^{1+}$	242.0845	FullScan
				$C_9H_{13}O_2S^{1+}$	185.0631	FullScan
				$C_7H_7O^{1+}$	107.0491	bbCID
Ethirimol	23947-60-6	5.52	209.1528	$C_{11}H_{19}N_3O$		
				$C_{11}H_{20}N_3O^{1+}$	210.1601	FullScan
				$C_8H_{14}NO^{1+}$	140.107	bbCID
				$C_5H_8NO^{1+}$	98.06	bbCID
Ethoprophos	13194-48-4	9.83	242.0564	$C_8H_{19}O_2PS_2$		
				$C_8H_{20}O_2PS_2^{1+}$	243.0637	FullScan
				$H_2O_2PS^{1+}$	96.9508	bbCID
				$H_4O_2PS_2^{1+}$	130.9385	bbCID
Etofenprox	80844-07-1	14	394.2377	$C_{25}H_{32}NO_3^{1+}$		
				$C_{25}H_{32}NO_3^{1+}$	394.2377	FullScan
				$C_{25}H_{27}O_2^{1+}$	359.2006	FullScan
				$C_{12}H_{17}O^{1+}$	177.1274	bbCID
Etoxazole	153233-91-1	12.77	359.1697	$C_{21}H_{23}F_2NO_2$		
				$C_{21}H_{24}F_2NO_2^{1+}$	360.177	FullScan
					141.0145	bbCID
Fenchlorphos	299-84-3	11.95	319.8997	$C_8H_8Cl_3O_3PS$		
				$C_8H_9Cl_3O_3PS^{1+}$	322.9041	FullScan
				$C_8H_9Cl_3O_3PS^{1+}$	320.907	FullScan
Fenothiocarb	62850-32-2	10.2	253.1137	$C_{13}H_{19}NO_2S$		
				$C_{13}H_{20}NO_2S^{1+}$	254.1209	FullScan

Compound	CAS	RT (min)	Mass (Da)	Ion formula	m/z	Spectrum type
				$C_3H_6NO^{1+}$	72.0444	bbCID
Fenoxaprop-ethyl	66441-23-4	11.73	361.0717	$C_{18}H_{16}ClNO_5$		
				$C_{18}H_{17}ClNO_5^{1+}$	362.079	FullScan
				$C_{18}H_{17}ClNO_5^{1+}$	364.0768	FullScan
				$C_{15}H_{11}ClNO_3^{1+}$	288.0422	bbCID
Fenpiclonil	74738-17-3	8.4	235.9908	$C_{11}H_6Cl_2N_2$		
				$C_{11}H_7Cl_2N_2^{1+}$	236.9981	FullScan
				$C_{11}H_7Cl_2N_2^{1+}$	238.9952	FullScan
				$C_{11}H_7ClN_2^{1+}$	202.0292	bbCID
Fenuron	101-42-8	4.86	164.095	$C_9H_{12}N_2O$		
				$C_9H_{13}N_2O^{1+}$	165.1022	FullScan
				$C_3H_6NO^{1+}$	72.0444	bbCID
Fipronil-sulfide	120067-83-6	10.36	419.9438	$C_{12}H_4Cl_2F_6N_4S$		
				$C_{12}H_5Cl_2F_6N_4S^{1+}$	420.9511	FullScan
				$C_{12}H_5Cl_2F_6N_4S^{1+}$	422.9482	FullScan
Flamprop-isopropyl	52756-22-6	10.6	363.1037	$C_{19}H_{19}ClFNO_3$		
				$C_{19}H_{20}ClFNO_3^{1+}$	364.111	FullScan
				$C_{19}H_{20}ClFNO_3^{1+}$	366.1088	FullScan
				$C_7H_5O^{1+}$	105.0335	bbCID
Flonicamid	158062-67-0	4.12	229.0463	$C_9H_6F_3N_3O$		
				$C_9H_7F_3N_3O^{1+}$	230.0536	FullScan
				$C_6H_5F_3N^{1+}$	148.0369	bbCID
				$C_8H_6F_3N_2O^{1+}$	203.0427	bbCID
Fluacrypyrim	229977-93-9	11.27	205.0859	$C_{12}H_{13}O_3^{1+}$		
				$C_{12}H_{13}O_3^{1+}$	205.0859	FullScan
				$C_{10}H_9O^{1+}$	145.0648	FullScan
Flumetsulam	98967-40-9	4.77	325.0445	$C_{12}H_9F_2N_5O_2S$		
				$C_{12}H_{10}F_2N_5O_2S^{1+}$	326.0518	FullScan
				$C_6H_5F_2N^{1+}$	129.0385	bbCID
Flumioxazin	103361-09-7	8.38	354.1016	$C_{19}H_{15}FN_2O_4$		
				$C_{19}H_{16}FN_2O_4^{1+}$	355.1089	FullScan
				$C_{18}H_{16}FN_2O_3^{1+}$	327.1139	bbCID
Fluometuron	2164-17-2	7.22	232.0823	$C_{10}H_{11}F_3N_2O$		
				$C_{10}H_{12}F_3N_2O^{1+}$	233.0896	FullScan
				$C_3H_6NO^{1+}$	72.0444	bbCID
Foramsulfuron	173159-57-4	7.18	452.1114	$C_{17}H_{20}N_6O_7S$		
				$C_{17}H_{21}N_6O_7S^{1+}$	453.1187	FullScan
				$C_{17}H_{20}N_6NaO_7S^{1+}$	475.1006	FullScan
				$C_7H_8N_3O_3^{1+}$	182.056	bbCID
Forchlorfenuron	68157-60-8	8.01	247.0512	$C_{12}H_{10}ClN_3O$		
				$C_{12}H_{11}ClN_3O^{1+}$	248.0585	FullScan

Compound	CAS	RT (min)	Mass (Da)	Ion formula	m/z	Spectrum type
				$C_{12}H_{11}ClN_3O^{1+}$	250.0559	FullScan
				$C_5H_6ClN_2^{1+}$	129.0214	bbCID
Furalaxyl	57646-30-7	8.72	301.1314	$C_{17}H_{19}NO_4$		
				$C_{17}H_{20}NO_4^{1+}$	302.1387	FullScan
				$C_{16}H_{16}NO_3^{1+}$	270.1125	FullScan
				$C_5H_3O_2^{1+}$	95.0128	bbCID
Furathiocarb	65907-30-4	11.97	382.1562	$C_{18}H_{26}N_2O_5S$		
				$C_{18}H_{27}N_2O_5S^{1+}$	383.1635	FullScan
				$C_{10}H_{11}O_2S^{1+}$	195.0474	bbCID
Furilazole	121776-33-8	7.31	219.9927	$C_8H_8Cl_2NO_2^{1+}$		
				$C_8H_8Cl_2NO_2^{1+}$	219.9927	FullScan
				$C_5H_8N^{1+}$	82.0651	bbCID
Hexaflumuron	86479-06-3	11.52	482.9708	$C_{16}H_8Cl_2F_6N_2NaO_3^{1+}$		
				$C_{16}H_8Cl_2F_6N_2NaO_3^{1+}$	482.9708	FullScan
				$C_{16}H_8Cl_2F_6N_2NaO_3^{1+}$	484.9682	FullScan
Imazamox	114311-32-9	5.28	305.1376	$C_{15}H_{19}N_3O_4$		
				$C_{15}H_{20}N_3O_4^{1+}$	306.1448	FullScan
				$C_5H_{12}N^{1+}$	86.0964	bbCID
				$C_9H_9N_2O_3^{1+}$	193.0608	bbCID
				$C_{14}H_{17}N_2O_3^{1+}$	261.1234	bbCID
Imazapyr	81334-34-1	4.73	261.1113	$C_{13}H_{15}N_3O_3$		
				$C_{13}H_{16}N_3O_3^{1+}$	262.1186	FullScan
				$C_7H_5N_2O_2^{1+}$	149.0346	bbCID
				$C_{12}H_{13}N_2O_2^{1+}$	217.0972	bbCID
Imazaquin	81335-37-7	6.78	311.127	$C_{17}H_{17}N_3O_3$		
				$C_{17}H_{18}N_3O_3^{1+}$	312.1343	FullScan
				$C_{11}H_7N_2O_2^{1+}$	199.0502	bbCID
				$C_{16}H_{15}N_2O_2^{1+}$	267.1128	bbCID
Isopropalin	33820-53-0	13.04	309.1689	$C_{15}H_{23}N_3O_4$		
				$C_{15}H_{24}N_3O_4^{1+}$	310.1761	FullScan
				$C_9H_{12}N_3O_4^{1+}$	226.0822	bbCID
				$C_9H_{10}N_3O_3^{1+}$	208.0717	bbCID
Isoxaben	82558-50-7	9.12	332.1736	$C_{18}H_{24}N_2O_4$		
				$C_{18}H_{25}N_2O_4^{1+}$	333.1809	FullScan
				$C_9H_9O_3^{1+}$	165.0546	bbCID
Isoxathion	18854-01-8	10.86	313.0538	$C_{13}H_{16}NO_4PS$		
				$C_{13}H_{17}NO_4PS^{1+}$	314.061	FullScan
				$H_3O_3PS^{1+}$	113.9535	bbCID
				$C_7H_5O^{1+}$	105.0335	bbCID
Lenacil	8/1/2164	7.83	234.1368	$C_{13}H_{18}N_2O_2$		
				$C_{13}H_{19}N_2O_2^{1+}$	235.1441	FullScan

Compound	CAS	RT (min)	Mass (Da)	Ion formula	m/z	Spectrum type
				$C_7H_9N_2O_2^{1+}$	153.0659	bbCID
				$C_7H_9N_2O_2^{1+}$		FullScan
Leptophos	21609-90-5	13.43	409.87	$C_{13}H_{10}BrCl_2O_2PS$		
				$C_{13}H_{11}BrCl_2O_2PS^{1+}$	412.8748	FullScan
				$C_{13}H_{11}BrCl_2O_2PS^{1+}$	410.8772	FullScan
				$C_7H_8OPS^{1+}$	171.0028	bbCID
Mefenacet	73250-68-7	9.49	298.0776	$C_{16}H_{14}N_2O_2S$		
				$C_{16}H_{15}N_2O_2S^{1+}$	299.0849	FullScan
				$C_9H_{10}NO^{1+}$	148.0757	bbCID
				$C_8H_{10}N^{1+}$	120.0808	bbCID
Mepronil	55814-41-0	9.22	269.1416	$C_{17}H_{19}NO_2$		
				$C_{17}H_{20}NO_2^{1+}$	270.1489	FullScan
				$C_8H_7O^{1+}$	119.0491	bbCID
Metamitron	41394-05-2	4.95	202.0855	$C_{10}H_{10}N_4O$		
				$C_{10}H_{11}N_4O^{1+}$	203.0927	FullScan
				$C_9H_{11}N_4^{1+}$	175.0978	bbCID
Methoprene	40596-69-8	12.88	279.2319	$C_{18}H_{31}O_2^{1+}$		
				$C_{18}H_{31}O_2^{1+}$	279.2319	FullScan
				$C_{10}H_{15}^{1+}$	135.1168	bbCID
Metolachlor	51218-45-2	9.94	283.1339	$C_{15}H_{22}ClNO_2$		
				$C_{15}H_{23}ClNO_2^{1+}$	284.1412	FullScan
				$C_{14}H_{19}ClNO^{1+}$	252.115	bbCID
				$C_{12}H_{18}N^{1+}$	176.1434	bbCID
Metosulam	139528-85-1	6.84	417.0065	$C_{14}H_{13}Cl_2N_5O_4S$		
				$C_{14}H_{14}Cl_2N_5O_4S^{1+}$	418.0138	FullScan
				$C_{14}H_{14}Cl_2N_5O_4S^{1+}$	420.011	FullScan
				$C_7H_7Cl_2N^{1+}$	174.995	bbCID
Metoxuron	19937-59-8	5.75	228.0666	$C_{10}H_{13}ClN_2O_2$		
				$C_{10}H_{14}ClN_2O_2^{1+}$	229.0738	FullScan
				$C_{10}H_{14}ClN_2O_2^{1+}$	231.0711	FullScan
				$C_3H_6NO^{1+}$	72.0444	bbCID
Monuron	150-68-5	6.3	198.056	$C_9H_{11}ClN_2O$		
				$C_9H_{12}ClN_2O^{1+}$	199.0633	FullScan
				$C_9H_{12}ClN_2O^{1+}$	201.0605	FullScan
				$C_3H_6NO^{1+}$	72.0444	bbCID
Naled	300-76-5	8.02	377.7826	$C_4H_7Br_2Cl_2O_4P$		
				$C_4H_8Br_2Cl_2O_4P^{1+}$	380.7876	FullScan
				$C_4H_8Br_2Cl_2O_4P^{1+}$	382.7853	FullScan
				$C_2H_8O_4P^{1+}$	127.0155	bbCID
Neburon	555-37-3	10.26	274.064	$C_{12}H_{16}Cl_2N_2O$		
				$C_{12}H_{17}Cl_2N_2O^{1+}$	275.0712	FullScan

Compound	CAS	RT (min)	Mass (Da)	Ion formula	m/z	Spectrum type
				$C_{12}H_{17}Cl_2N_2O^{1+}$	277.0684	FullScan
				$C_5H_{14}N^{1+}$	88.1121	bbCID
Nitenpyram	150824-47-8	3.88	270.0884	$C_{11}H_{15}ClN_4O_2$		
				$C_{11}H_{16}ClN_4O_2^{1+}$	271.0956	FullScan
				$C_{11}H_{16}ClN_4O_2^{1+}$	273.093	FullScan
				$C_6H_5ClN^{1+}$	126.0105	bbCID
Novaluron	116714-46-6	11.65	515.0015	$C_{17}H_9ClF_8N_2NaO_4^{1+}$		
				$C_{17}H_9ClF_8N_2NaO_4^{1+}$	515.0015	FullScan
				$C_{17}H_9ClF_8N_2NaO_4^{1+}$	516.9992	FullScan
				$C_7H_6F_2NO^{1+}$	158.0412	bbCID
Orbencarb	34622-58-7	10.95	257.0641	$C_{12}H_{16}ClNOS$		
				$C_{12}H_{17}ClNOS^{1+}$	258.0714	FullScan
				$C_{12}H_{17}ClNOS^{1+}$	260.0686	FullScan
				$C_7H_6Cl^{1+}$	125.0153	bbCID
Oxadiargyl	39807-15-3	10.84	358.072	$C_{15}H_{18}Cl_2N_3O_3^{1+}$		
				$C_{15}H_{18}Cl_2N_3O_3^{1+}$	358.072	FullScan
				$C_{15}H_{18}Cl_2N_3O_3^{1+}$	360.0693	FullScan
Oxadiazon	19666-30-9	12.1	344.0694	$C_{15}H_{18}Cl_2N_2O_3$		
				$C_{15}H_{19}Cl_2N_2O_3^{1+}$	345.0767	FullScan
				$C_{15}H_{19}Cl_2N_2O_3^{1+}$	347.074	FullScan
Paraoxon-methyl	950-35-6	5.94	247.0246	$C_8H_{10}NO_6P$		
				$C_8H_{11}NO_6P^{1+}$	248.0319	FullScan
				$C_8H_{11}O_4P^{1+}$	202.0389	bbCID
Pebulate	1114-71-2	11.1	203.1344	$C_{10}H_{21}NOS$		
				$C_{10}H_{22}NOS^{1+}$	204.1417	FullScan
				$C_3H_6NO^{1+}$	72.0444	bbCID
Penoxsulam	219714-96-2	7.14	483.0636	$C_{16}H_{14}F_5N_5O_5S$		
				$C_{16}H_{15}F_5N_5O_5S^{1+}$	484.0709	FullScan
				$C_7H_9N_5O_2^{1+}$	195.0751	bbCID
Promecarb	2631-37-0	9.02	207.1259	$C_{12}H_{17}NO_2$		
				$C_{12}H_{18}NO_2^{1+}$	208.1332	FullScan
				$C_7H_9O^{1+}$	109.0648	bbCID
				$C_{10}H_{15}O^{1+}$	151.1117	FullScan
Prometon	1610-18-0	6.98	225.159	$C_{10}H_{19}N_5O$		
				$C_{10}H_{20}N_5O^{1+}$	226.1662	FullScan
				$C_4H_8N_5O^{1+}$	142.0723	bbCID
				$C_7H_{14}N_5O^{1+}$	184.1193	bbCID
Propazine	139-40-2	8.63	229.1094	$C_9H_{16}ClN_5$		
				$C_9H_{17}ClN_5^{1+}$	230.1167	FullScan
				$C_9H_{17}ClN_5^{1+}$	232.1139	FullScan
				$C_3H_5ClN_5^{1+}$	146.0228	bbCID

Compound	CAS	RT (min)	Mass (Da)	Ion formula	m/z	Spectrum type
				$C_6H_{11}ClN_5^{1+}$	188.0697	bbCID
Propetamphos	31218-83-4	9.34	156.0243	$C_3H_{11}NO_2PS^{1+}$		
				$C_3H_{11}NO_2PS^{1+}$	156.0243	FullScan
				$C_3H_9NOPS^{1+}$	138.0137	bbCID
				CH_5NOPS^{1+}	109.9824	bbCID
Propetamphos	31218-83-4	9.34	156.0243	$C_3H_{11}NO_2PS^{1+}$		
				$C_3H_{11}NO_2PS^{1+}$	156.0243	FullScan
				$C_3H_9NOPS^{1+}$	138.0137	bbCID
				CH_5NOPS^{1+}	109.9824	bbCID
				$C_3H_{11}NO_2PS^{1+}$	156.0243	bbCID
Propoxycarbazone	145026-81-9	6.5	398.0896	$C_{15}H_{18}N_4O_7S$		
				$C_{15}H_{19}N_4O_7S^{1+}$	399.0969	FullScan
				$C_3H_6N_3O_2^{1+}$	116.0455	bbCID
				$C_8H_7O_4S^{1+}$	199.006	bbCID
				$C_6H_{12}N_3O_2^{1+}$	158.0924	bbCID
Pyraflufen-ethyl	129630-19-9	10.57	412.0204	$C_{15}H_{13}Cl_2F_3N_2O_4$		
				$C_{15}H_{14}Cl_2F_3N_2O_4^{1+}$	413.0277	FullScan
				$C_{15}H_{14}Cl_2F_3N_2O_4^{1+}$	415.0251	FullScan
				$C_{12}H_8Cl_2F_3N_2O_2^{1+}$	338.9909	bbCID
Pyributicarb	88678-67-5	12.23	330.1402	$C_{18}H_{22}N_2O_2S$		
				$C_{18}H_{23}N_2O_2S^{1+}$	331.1475	FullScan
				$C_8H_9N_2OS^{1+}$	181.043	bbCID
				$C_6H_6NO^{1+}$	108.0444	bbCID
Pyrifenox	88283-41-4	9.46	294.0327	$C_{14}H_{12}Cl_2N_2O$		
				$C_{14}H_{13}Cl_2N_2O^{1+}$	295.0399	FullScan
				$C_{14}H_{13}Cl_2N_2O^{1+}$	297.0372	FullScan
				$C_6H_7N^{1+}$	93.0573	bbCID
Pyrimidifen	105779-78-0	12.14	377.187	$C_{20}H_{28}ClN_3O_2$		
				$C_{20}H_{29}ClN_3O_2^{1+}$	378.1943	FullScan
				$C_{20}H_{29}ClN_3O_2^{1+}$	380.1921	FullScan
				$C_8H_{11}ClN_3^{1+}$	184.0636	bbCID
Pyroquilon	57369-32-1	6.67	173.0841	$C_{11}H_{11}NO$		
				$C_{11}H_{12}NO^{1+}$	174.0913	bbCID
				$C_8H_7N^{1+}$	117.0573	bbCID
				$C_9H_{10}N^{1+}$	132.0808	bbCID
Quinclorac	84087-01-4	5.81	240.9697	$C_{10}H_5Cl_2NO_2$		
				$C_{10}H_6Cl_2NO_2^{1+}$	241.977	FullScan
				$C_{10}H_6Cl_2NO_2^{1+}$	243.9742	FullScan
				$C_{10}H_4Cl_2NO^{1+}$	223.9664	bbCID
Quinoxyfen	124495-18-7	12.4	306.9967	$C_{15}H_8Cl_2FNO$		
				$C_{15}H_9Cl_2FNO^{1+}$	308.004	FullScan

Compound	CAS	RT (min)	Mass (Da)	Ion formula	m/z	Spectrum type
				$C_{15}H_9Cl_2FNO^{1+}$	310.0012	FullScan
				$C_{15}H_9Cl_2FNO^{1+}$	308.004	bbCID
Rotenone	83-79-4	10.2	394.1416	$C_{23}H_{22}O_6$		
				$C_{23}H_{23}O_6^{1+}$	395.1489	FullScan
				$C_{14}H_{13}O_2^{1+}$	213.091	bbCID
				$C_{11}H_{12}O_3^{1+}$	192.0781	bbCID
Sebuthylazine	7286-69-3	8.87	229.1094	$C_9H_{16}ClN_5$		
				$C_9H_{17}ClN_5^{1+}$	230.1167	FullScan
				$C_9H_{17}ClN_5^{1+}$	232.1139	FullScan
				$C_5H_9ClN_5^{1+}$	174.0541	bbCID
Simetryn	1014-70-6	6.57	213.1048	$C_8H_{15}N_5S$		
				$C_8H_{16}N_5S^{1+}$	214.1121	FullScan
				$C_4H_6N_3^{1+}$	96.0556	bbCID
				$C_2H_2N_3^{1+}$	68.0243	bbCID
Sulfometuron-methyl	74222-97-2	6.69	364.0841	$C_{15}H_{16}N_4O_5S$		
				$C_{15}H_{17}N_4O_5S^{1+}$	365.0914	FullScan
				$C_7H_8N_3O^{1+}$	150.0662	bbCID
Sulprofos	35400-43-2	12.41	322.0285	$C_{12}H_{19}O_2PS_3$		
				$C_{12}H_{20}O_2PS_3^{1+}$	323.0358	FullScan
				$C_7H_8O_2PS_2^{1+}$	218.9698	bbCID
				$C_7H_7OS^{1+}$	139.0212	bbCID
Tebuthiuron	34014-18-1	6.81	228.1045	$C_9H_{16}N_4OS$		
				$C_9H_{17}N_4OS^{1+}$	229.1118	FullScan
				$C_9H_{17}N_4OS^{1+}$	230.1142	FullScan
Temephos	3383-96-8	12.16	465.9897	$C_{16}H_{20}O_6P_2S_3$		
				$C_{16}H_{21}O_6P_2S_3^{1+}$	466.997	FullScan
				$C_{15}H_{17}O_6P_2S_2^{1+}$	418.9936	bbCID
				$C_2H_6O_2PS^{1+}$	124.9821	bbCID
Terbacil	5902-51-2	6.75	161.0112	$C_5H_6ClN_2O_2^{1+}$		
				$C_5H_6ClN_2O_2^{1+}$	161.0112	FullScan
				$C_5H_3ClNO_2^{1+}$	143.9847	bbCID
				$C_3H_3ClN^{1+}$	87.9949	bbCID
Terbumeton	33693-04-8	7.12	225.159	$C_{10}H_{19}N_5O$		
				$C_{10}H_{20}N_5O^{1+}$	226.1662	FullScan
				$C_6H_{12}N_5O^{1+}$	170.1036	bbCID
				$C_4H_8N_3O^{1+}$	114.0662	bbCID
Terbuthylazine	5915-41-3	8.87	229.1094	$C_9H_{16}ClN_5$		
				$C_9H_{17}ClN_5^{1+}$	230.1167	FullScan
				$C_9H_{17}ClN_5^{1+}$	232.1139	FullScan
				$C_5H_9ClN_5^{1+}$	174.0541	bbCID
Tetramethrin	7696-12-0	11.98	331.1784	$C_{19}H_{25}NO_4$		

Compound	CAS	RT (min)	Mass (Da)	Ion formula	m/z	Spectrum type
				$C_{19}H_{26}NO_4^{1+}$	332.1856	FullScan
				$C_{19}H_{26}NO_4^{1+}$	333.1889	FullScan
Thidiazuron	51707-55-2	6.65	220.0419	$C_9H_8N_4OS$		
				$C_9H_9N_4OS^{1+}$	221.0492	FullScan
				$C_2H_4N_3S^{1+}$	102.012	bbCID
Thiobencarb	28249-77-6	10.95	257.0641	$C_{12}H_{16}ClNOS$		
				$C_{12}H_{17}ClNOS^{1+}$	258.0714	FullScan
				$C_{12}H_{17}ClNOS^{1+}$	260.0686	FullScan
				$C_7H_6Cl^{1+}$	125.0153	bbCID
Tribenuron-methyl	101200-48-0	7.75	395.09	$C_{15}H_{17}N_5O_6S$		
				$C_{15}H_{18}N_5O_6S^{1+}$	396.0972	FullScan
				0	181.072	bbCID
				$C_6H_{11}N_4O^{1+}$	155.0927	bbCID
Trifloxysulfuron	145099-21-4	7.69	437.0617	$C_{14}H_{14}F_3N_5O_6S$		
				$C_{14}H_{15}F_3N_5O_6S^{1+}$	438.069	FullScan
				$C_7H_8N_3O_3^{1+}$	182.056	bbCID
Triflumizole	68694-11-1	11.51	345.0856	$C_{15}H_{15}ClF_3N_3O$		
				$C_{15}H_{16}ClF_3N_3O^{1+}$	346.0929	FullScan
				$C_{12}H_{12}ClF_3NO^{1+}$	278.0554	FullScan
				$C_4H_9O^{1+}$	73.0648	bbCID
Triforine	26644-46-2	8.27	387.9106	$C_9H_{12}Cl_6N_3O^{1+}$		
				$C_9H_{12}Cl_6N_3O^{1+}$	389.9077	FullScan
				$C_{10}H_{14}Cl_6N_4NaO_2^{1+}$	454.914	FullScan
				$C_9H_{12}Cl_6N_3O^{1+}$	387.9106	bbCID
Trinexapac-ethyl	95266-40-3	7.99	252.0998	$C_{13}H_{16}O_5$		
				$C_{13}H_{17}O_5^{1+}$	253.1071	FullScan
				$C_{13}H_{17}O_5^{1+}$	254.1105	FullScan
Warfarin	81-81-2	9.18	308.1049	$C_{19}H_{16}O_4$		
				$C_{19}H_{17}O_4^{1+}$	309.1121	FullScan
				$C_{16}H_{11}O_3^{1+}$	251.0703	bbCID

2. Results

Data were processed using the TASQ software. For each analyte (including its qualifiers) an individual score is displayed and summarized as MRSQ score. The capital letters stand for mass accuracy (M), retention time (R), isotope pattern fit (mSigma value; S), and qualifier ions (presence and ion ratio quality; Q). MRSQ are used to assign a rating and color to each of the mentioned parameters.

The retention time accuracy is measured by the difference between the expected and measured retention time. ΔRt was checked for all compounds at all levels. The mass accuracy is measured by the difference between the calculated and measured m/z value (in mDa or ppm). Δm/z of ±5 ppm were accepted. The isotopic peak pattern fit (mSigma value) is a quality factor obtained from the difference between the theoretical and measured isotopic patterns. Height/area values are indicators of real chromatographic peaks. Additionally, the presence or not of qualifiers with ion ratio values are also displayed. Figure 1 shows the Δm/z of the principal ion for each analyte detected in the cereal samples spiked at 0.005 mg/kg. In the case were Δm/z of the principal ion was slightly higher than 5, the mass accuracy of other detected ions was checked. Figure 2 shows the ΔRt which was between ±0.5 min for all successfully validated analytes.

An SDL of 0.005 mg/kg was achieved for 75 compounds. An SDL of 0.01 mg/kg was obtained for 12 compounds, and an SDL of 0.02 mg/kg was obtained for other 12 compounds. A total of 27 compounds were not successfully validated at any of the spiked levels. Table 3 shows the SDL of the successfully validated compounds. Table 4 shows the list of compounds not successfully validated.

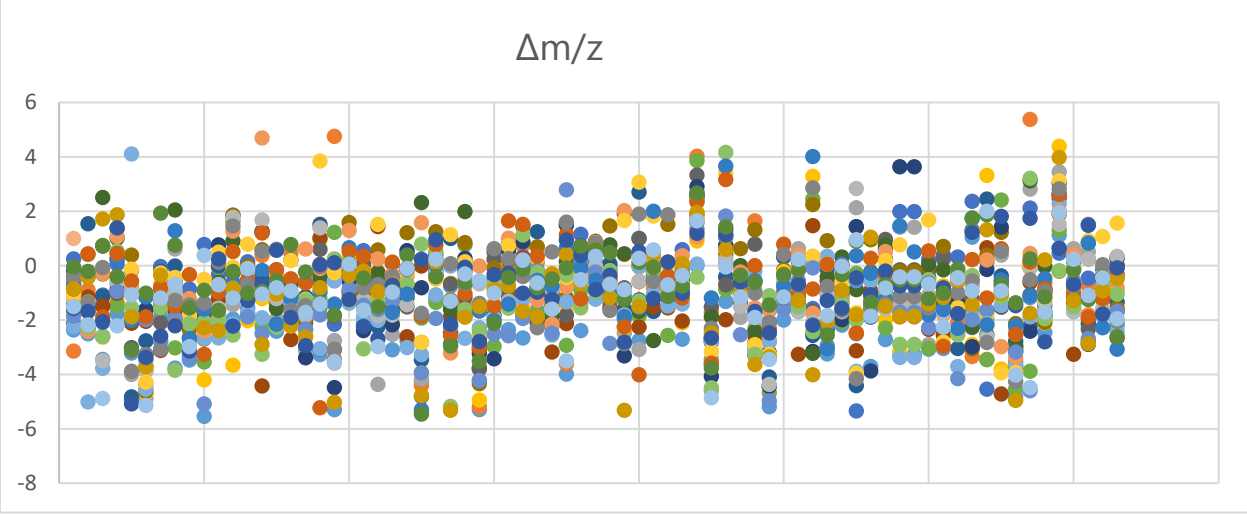

Figure 1: Δm/z of the principal ion for the 72 analysed detected in the 25 cereal samples spiked at 0.005 mg/kg. Only Δm/z of less than ± 5ppm were accepted.

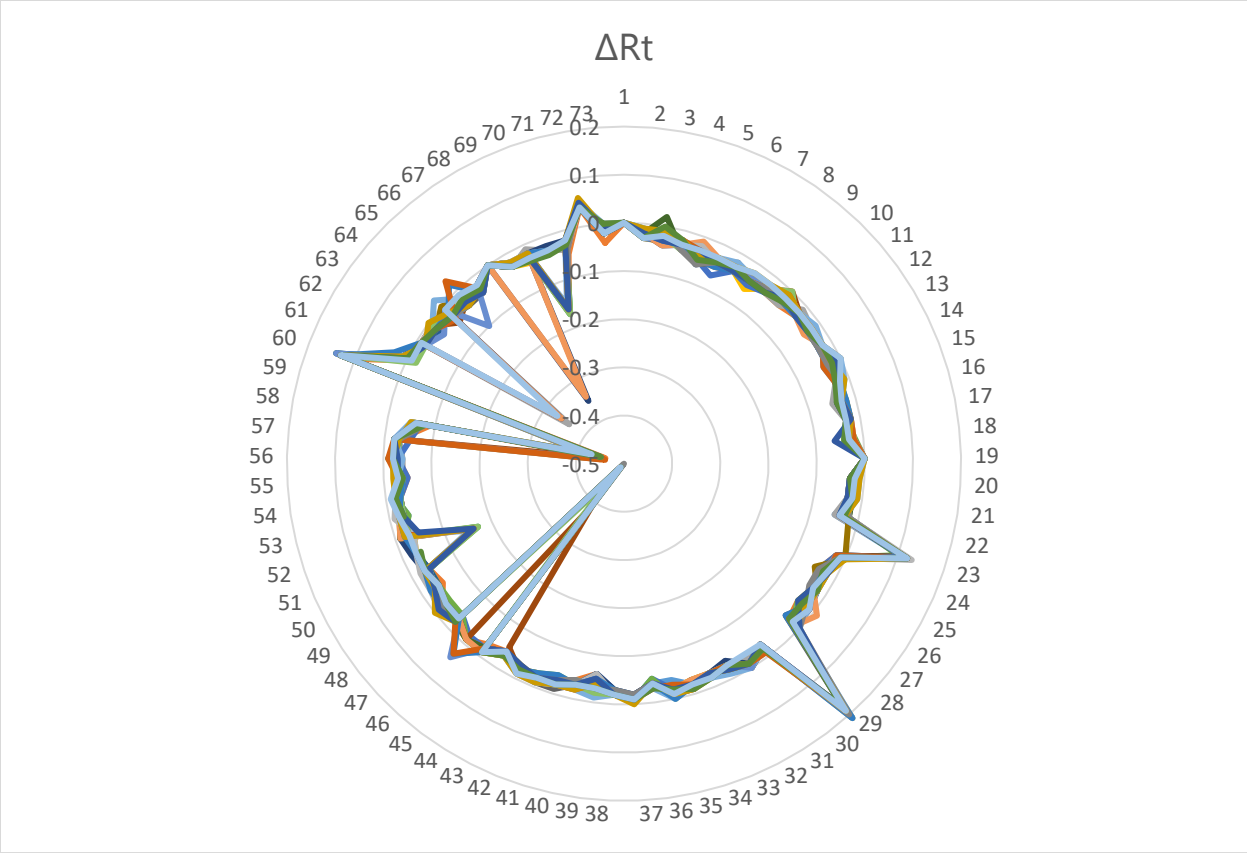

Figure 2: ΔRt of the 72 analysed detected in the 25 cereal samples spiked at 0.005 mg/kg.

Table 3: SDL of the studied compounds

Compounds	SDL mg/kg)
Alachlor	0.005
Ametryn	0.005
Bensulfuron-methyl	0.005
Bifenazate	0.005
Bioresmethrin	0.005
Bixafen	0.01
Bromacil	0.005
Butocarboxim	0.01
Butralin	0.02
Buturon	0.005
Carfentrazone-ethyl	0.005
Chlorbromuron	0.005
Chlorotoluron	0.005
Chlorsulfuron	0.02
Chromafenozide	0.005
Clodinafop-propargyl	0.005

Coumaphos	0.005
Crufomate	0.005
Cyanazine	0.005
Cyanophos	0.02
Cyflufenamid	0.005
Cymoxanil	0.02
Cyprazin	0.005
DEET	0.005
Demeton-S	0.005
Desmetryn	0.005
Dichlofenthion	0.02
Difenoxuron	0.005
Dimefuron	0.005
Dimethachlor	0.005
Dimethirimol	0.02
Dioxacarb	0.02
Dodine	0.005
Edifenphos	0.005
EPTC	0.005
Esprocarb	0.005
Ethiofencarb-sulfone	0.005
Ethiofencarb-sulfoxide	0.005
Ethirimol	0.005
Ethoprophos	0.005
Etoxazole	0.005
Fenothiocarb	0.005
Fenoxaprop-ethyl	0.005
Fenpiclonil	0.01
Fipronil-sulfide	0.02
Flamprop-isopropyl	0.005
Flonicamid	0.005
Fluacrypyrim	0.02
Fluometuron	0.005
Forchlorfenuron	0.01
Furalaxyl	0.005
Furathiocarb	0.005
Furilazole	0.005
Isopropalin	0.005
Isoxaben	0.005
Isoxathion	0.005
Lenacil	0.02
Mefenacet	0.005
Mepronil	0.005
Metamitron	0.005
Methoprene	0.005

Metolachlor	0.005
Metoxuron	0.005
Monuron	0.005
Neburon	0.005
Nitenpyram	0.02
Novaluron	0.02
Orbencarb	0.005
Oxadiargyl	0.005
Oxadiazon	0.005
Paraoxon-methyl	0.005
Pebulate	0.005
Penoxsulam	0.01
Promecarb	0.005
Prometon	0.01
Propazine	0.005
Pyraflufen-ethyl	0.005
Pyributicarb	0.005
Pyrifenox	0.005
Pyrimidifen	0.005
Pyroquilon	0.01
Quinoxyfen	0.005
Rotenone	0.005
Sebuthylazine	0.005
Simetryn	0.01
Sulfometuron-methyl	0.005
Sulprofos	0.005
Tebuthiuron	0.005
Temephos	0.01
Terbacil	0.01
Terbumeton	0.005
Terbuthylazine	0.005
Tetramethrin	0.005
Thidiazuron	0.01
Thiobencarb	0.005
Tribenuron-methyl	0.005
Trifloxysulfuron	0.01
Triflumizole	0.005
Warfarin	0.005

Table 4: List of compounds not successfully validated

Compounds	**SDL mg/kg)**

Alachlor	0.005
Ametryn	0.005
Bensulfuron-methyl	0.005
Bifenazate	0.005
Bioresmethrin	0.005
Bixafen	0.01
Bromacil	0.005
Butocarboxim	0.01
Butralin	0.02
Buturon	0.005
Carfentrazone-ethyl	0.005
Chlorbromuron	0.005
Chlorotoluron	0.005
Chlorsulfuron	0.02
Chromafenozide	0.005
Clodinafop-propargyl	0.005
Coumaphos	0.005
Crufomate	0.005
Cyanazine	0.005
Cyanophos	0.02
Cyflufenamid	0.005
Cymoxanil	0.02
Cyprazin	0.005
DEET	0.005
Demeton-S	0.005
Desmetryn	0.005
Dichlofenthion	0.02
Difenoxuron	0.005
Dimefuron	0.005
Dimethachlor	0.005
Dimethirimol	0.02
Dioxacarb	0.02
Dodine	0.005
Edifenphos	0.005
EPTC	0.005
Esprocarb	0.005
Ethiofencarb-sulfone	0.005
Ethiofencarb-sulfoxide	0.005
Ethirimol	0.005
Ethoprophos	0.005
Etoxazole	0.005
Fenothiocarb	0.005
Fenoxaprop-ethyl	0.005
Fenpiclonil	0.01
Fipronil-sulfide	0.02

Flamprop-isopropyl	0.005
Flonicamid	0.005
Fluacrypyrim	0.02
Fluometuron	0.005
Forchlorfenuron	0.01
Furalaxyl	0.005
Furathiocarb	0.005
Furilazole	0.005
Isopropalin	0.005
Isoxaben	0.005
Isoxathion	0.005
Lenacil	0.02
Mefenacet	0.005
Mepronil	0.005
Metamitron	0.005
Methoprene	0.005
Metolachlor	0.005
Metoxuron	0.005
Monuron	0.005
Neburon	0.005
Nitenpyram	0.02
Novaluron	0.02
Orbencarb	0.005
Oxadiargyl	0.005
Oxadiazon	0.005
Paraoxon-methyl	0.005
Pebulate	0.005
Penoxsulam	0.01
Promecarb	0.005
Prometon	0.01
Propazine	0.005
Pyraflufen-ethyl	0.005
Pyributicarb	0.005
Pyrifenox	0.005
Pyrimidifen	0.005
Pyroquilon	0.01
Quinoxyfen	0.005
Rotenone	0.005
Sebuthylazine	0.005
Simetryn	0.01
Sulfometuron-methyl	0.005
Sulprofos	0.005
Tebuthiuron	0.005
Temephos	0.01
Terbacil	0.01

Terbumeton	0.005
Terbuthylazine	0.005
Tetramethrin	0.005
Thidiazuron	0.01
Thiobencarb	0.005
Tribenuron-methyl	0.005
Trifloxysulfuron	0.01
Triflumizole	0.005
Warfarin	0.005

Alanycarb	Foramsulfuron
Allethrin	Hexaflumuron
Asulam	Imazamox
Butocarboxim_sulfoxid	Imazapyr
Chlorbufam	Imazaquin
Chlorfluazuron	Leptophos
Cyclanilide	Metosulam
Dinotefuran	Naled
Etofenprox	Propetamphos
Fenchlorphos	Propoxycarbazone
Fenuron	Quinclorac
Flumetsulam	Triforine
Flumioxazin	Trinexapac-ethyl

5 References

1. *EN 15662:2008. Foods of plant origin - Determination of pesticide residues using GC-MS and/or LC-MS/MS following acetonitrile extraction/partitioning and clean-up by dispersive SPE - QuEChERS-method*
2. *Method Validation and Quality Control Procedures for Pesticide Residue Analysis in Food and Feed, Document No. SANTE/11312/2021.*