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Screening of Over 600 Pesticides, Veterinary Drugs, Food-Packaging Contaminants, Mycotoxins, and Other Chemicals in Food by Ultra-High Performance Liquid Chromatography Quadrupole Time-of-Flight Mass Spectrometry (UHPLC-QTOFMS)

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Abstract In this article, an accurate mass multiresidue screening method has been developed for the determination of over 630 multiclass food contaminants in different matrices using ultra-high performance liquid chromatography/(quadrupole)-time-of-flight mass spectrometry. The compounds included in the study were 426 pesticides, 117 veterinary drugs, 42 food-packaging contaminants, 21 mycotoxins, 10 perfluorinated compounds, 9 nitrosamines, and 5 sweeteners. The separation was carried out by liquid chromatography using a C_{18} column (50 mm × 2.1 mm, 1.8 μm particle size). The identification of the targeted species was accomplished using accurate masses of the targeted ions (protonated or deprotonated molecule) along with retention time data and characteristic fragment ion for reliable identification, using specific software for automated data mining and exploitation. The performance of the screening method was validated in terms of linearity, matrix effect, and limits of quantification for three representative food matrices (tomato, orange, and baby food) using a generic sample treatment based on liquid partitioning with acetonitrile (QuEChERS). The overall method performance was satisfactory with limits of quantification lower than 10 μg kg^{-1} for the 44 % of studied compounds. In some cases (ca. 10–15 % of the pesticides depending on the matrix tested, maximum residue levels were not fulfilled). In orange, 15 % of the compounds displayed LOQs above the maximum residue levels (MRLs) set for the studied pesticides, which can be partially attributed to matrix effects. Moderate signal suppression was observed in the three matrices tested in most cases, being orange the matrix which produced the highest matrix effect and baby food the lowest one.

Keywords Screening method · Organic contaminants · Matrix effect · Liquid chromatography-mass spectrometry · Foodstuffs

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Abbreviations

CCL-3	Contaminant candidate lists
CID	Collision-induced dissociation
GC-MS/MS	Gas chromatography/tandem mass spectrometry
HRMS	High-resolution mass spectrometry
LC-MS/MS	

	Liquid chromatography/tandem mass spectrometry
MeOH	Methanol
QC	Quality control
QuEChERS	Quick, easy, cheap, effective, rugged, and safe

Introduction

Food quality and safety have become of increasing concern for consumers, governments, and producers in such globalized market, where commodities are produced and distributed throughout the world (Malik et al. 2010; Di Stefano et al. 2012). Food chemical contaminants have been defined as "any chemical not intentionally added to food but present from many potential sources," including residues from the application of pesticides and veterinary medicines, those entering the food chain from the environment, and those formed during the processing of food, natural toxins, accidental contamination, or adulteration (Hird et al. 2014).

To protect the health of consumers, stringent regulations enforced with diligent monitoring of foods have been recently established. The need of methods covering multiclass contaminants such as pesticides, veterinary drugs, and mycotoxins is illustrated by selected recent examples in the literature (Zhan et al. 2012; Mol et al. 2008; Garrido Frenich et al. 2014; Ferrer-Amate et al. 2010; Pérez-Ortega et al. 2012; Gómez-Pérez et al. 2015). For instance, derivate food products such as baby food combine different matrices: cereal-based food, meat-based food, powdered milk-based infant formulae, and fruit- and vegetable-based food (European commission 2006a). Consequently, they should be tested keeping in mind the potential simultaneous presence of both pesticides and veterinary drugs. Other contaminants such as parabens, human pharmaceuticals and antibiotics, and veterinary drugs have been recently reported in processed food (Fussell et al. 2014) due to contamination either during farming/crop production—as the use of reclaimed water is becoming more common (Matamoros et al. 2012)—or in the food-producing scenarios. Furthermore, contaminants can also enter the food chain through adulteration of food (international contamination, e.g., melamine in milk formulae) (Langman 2009). To cope with these outstanding numbers of contaminants/commodity combinations, laboratories must use multiresidue strategies.

The monitoring of residues from either pesticides or other contaminants in products of both plant and animal origin is of great interest for the protection of human health. It is currently addressed by means of a plethora of regulations worldwide (EPA 2016; European Commission 2005; US Department of Agriculture 2014; European Commission 2010; US Food Drug Administration 2011; European Commission 2006b; Canadian Food Inspection Agency 2016; European Commission 2016; Health Canada 2014; National Standard GB-2763 2014; Codex Alimentarius 2016). Laboratories monitoring these chemicals must have cost-effective, rapid, and comprehensive methods for detecting their presence. Current food safety methods are aimed at the simultaneous determination of several families of contaminants and/or residues. These methods increase sample throughput and the capabilities of routine laboratories (Malik et al. 2010; Di Stefano et al. 2012; Hird et al. 2014; Picó et al. 2015).

The standard method for determining pesticides, veterinary drugs, and other relevant contaminants, namely multiresidue method, is a targeted approach based on multiple reaction monitoring (MRM) acquisition, using liquid chromatography/tandem mass spectrometry (LC-MS/MS) or/and gas chromatography/tandem mass spectrometry (GC-MS/MS) (Gilbert-López et al. 2010). However, the main flaw of the approach is the previous knowledge required to set up the acquisition method (retention time and optimized MS/MS transitions for each analyte sought). Consequently, LC-MS/MS multiresidue methods are blind to compounds not defined in the MRM method, so that none or scarce information on possible non-target or unknown pesticides or their degradation products are available when using these techniques. Multiresidue methods also require dedicated validation and quality control (QC) (due to the large number of species). In quantitative multiresidue methods, valuable time and effort are wasted in generating ongoing QC data for many compounds that are not frequently detected. Therefore, screening methods skipping such reference materials and all ongoing QC measurements associated are desirable.

Liquid chromatography combined with high-resolution mass spectrometry (LC-HRMS) has shown to be an effective approach to screen food samples for the presence of high number of analytes. In contrast to low-resolution MS/MS acquisition, LC full-scan HRMS enables a fully untargeted measurement with the ability to retrospectively detect additional compounds in the raw data, which were not anticipated to be of interest at the time of sample analysis (Gómez-Ramos et al. 2013; Mezcua et al. 2009; Polgar et al. 2012; Díaz et al. 2011; Pérez-Ortega et al. 2016). Although the interrogation of the data is performed against the list of compounds included in the database or library, retrospective evaluation is always possible as data for all compounds that have given sufficient detector response is acquired (Gómez-Ramos et al. 2013; Mezcua et al. 2009; Polgar et al. 2012; Díaz et al. 2011).

The development of accurate mass LC-HRMS screening methods has been addressed by different authors, using either time-of-flight (Mezcua et al. 2009; Polgar et al. 2012; Díaz et al. 2011; García-López et al. 2014; Lacina et al. 2010; Wang et al. 2014) or Orbitrap mass spectrometers (Gómez-Pérez et al. 2015; Alder et al. 2011). These methodologies include typically between 200 and 450 pesticides, although there are also a few examples covering other contaminants such as veterinary drugs (Masía et al. 2016, Picó et al. 2015, Romero-González et al. 2011). Hybrid mass spectrometers performing

MS/MS acquisition of product ions at high resolution provide additional structural information for identification purposes, enabling the discrimination among isobaric or isomeric species and the discovering of metabolites or degradation pathways. In this article, an accurate mass multiresidue screening method using ultra-high performance liquid chromatography quadrupole time-of-flight mass spectrometry (UHPLC-Q-TOFMS) has been developed and its performance evaluated for over 600 multiclass food contaminants (pesticides, veterinary drugs, mycotoxins, nitrosamines, perfluorinated compounds, sweeteners, and food-packaging contaminants) in food, using tomato, orange, and baby food as model matrices.

Experimental Section

Chemicals and Reagents Pesticides, veterinary drugs, food-packaging contaminants, perfluorinated compounds, mycotoxins, nitrosamines, and sweeteners of analytical grade standards were purchased from Fluka (Pestanal quality) (Madrid, Spain), Sigma-Aldrich (Madrid, Spain), or Dr. Ehrenstorfer (Augsburg, Germany). Individual stock solutions (ca. 500 mg L^{-1} each) were prepared in different solvents depending on compound solubility and stability (acetonitrile, methanol (MeOH), and/or water in basic or acidic media) and were stored at −20 °C. Working solutions containing ca. 30 compounds each were prepared by appropriate dilution of the stock solutions with MeOH at 10 mg L^{-1}. HPLC-grade acetonitrile and MeOH were obtained from Merck (Darmstadt, Germany). Formic acid was obtained from Fluka (Buchs, Switzerland). Primary-secondary amine (PSA) Bond Elut was obtained from Varian, Inc. (Palo Alto, CA, USA). Acetic acid was from Panreac (Barcelona, Spain). Anhydrous magnesium sulfate anhydrous ($MgSO_4$) and sodium acetate ($NaCOOCH_3$) were from Sigma-Aldrich (Madrid, Spain). A Milli-Q-Plus ultrapure water system from Millipore (Milford, MA, USA) was used throughout the study to obtain the HPLC-grade water used during the analyses.

Selection of the Studied Compounds The 630 compounds included in the screening method were carefully selected considering different lists established by official bodies from the European Union and the USA, previous relevant literature, and thus their potential presence in different types of foodstuffs and water. Up to 426 pesticides, 117 veterinary drugs and pharmaceuticals, 42 food-packaging contaminants, 10 perfluorinated compounds, 21 mycotoxins, 9 nitrosamines, and 5 sweeteners were included. From the 426 pesticides included, most of them are covered in Annex 1 of Directive 396/2005 for several commodities (European Commission 2005). A significant number (over 130 species), of priority pesticides (according to Annex I of Commission Implementing Regulation 788/2012 due to their usage and frequency of detection), were also included in the targeted list (Gallart-Ayala et al. 2013). Most of the selected food-packaging contaminants and perfluorinated compounds are regulated by different documents (European Commission 2012; Gallart-Ayala et al. 2013; European Commission 2011; FDA 2016; European Commission 2006b; EPA 2009, 2015; European Commission 2015). With regards to the veterinary drugs and pharmaceuticals, most of the selected substances are US FDA-approved veterinary drugs for animal use (FDA 2016) or authorized products in the European Union. It should be noted that some of the species are included in Table 1 as pesticides, although they can be also classified as veterinary drugs such as albendazole, fenbendazole, fenthion, ivermectin, lufenuron, spinosad, sulfaquinoxaline, thiabendazole, and trichlorfon, all of them included in US FDA-approved list for animal use. Along with the veterinary drugs, other human pharmaceuticals were included due to their ubiquitous presence in the environment. Besides, all the main mycotoxins including those regulated in Commission Regulation EC 1881/2006 (European Commission 2006b) are among those 21 substances selected. The nine nitrosamines selected are included in US EPA final Drinking Water Contaminant Candidate lists (CCL-3) (EPA 2009, 2015). Finally, all the sweeteners included are SANTE-authorized food additives (European Commission 2015).

Sample Treatment Different baby food samples from different local markets containing meat and vegetables were pooled and used as model matrix, along with tomato and orange. Extraction was accomplished using QuEChERS approach (Lehotay 2011). A representative 10-g portion of homogenized sample was weighed in a 50-mL plastic centrifuge tube and mixed with 10 mL of 0.1 % acetic acid in acetonitrile, being the tube vigorously shaken for 1 min. Then, 1 g of $NaCOOCH_3$ and 4 g of $MgSO_4$ anhydrous were added, and the tube was shaken again to prevent coagulation of $MgSO_4$. The extract was centrifuged (1464 rcf) for 3 min. A 5-mL aliquot of supernatant (acetonitrile phase) was taken with a pipette and transferred to a 15-mL centrifuge tube containing 250 mg of PSA and 750 mg of $MgSO_4$ anhydrous that was energetically shaken for 20 s. The extract was centrifuged again (1464 rcf) for 3 min. Three milliliters of supernatant were taken and evaporated to near dryness and reconstituted to 3 mL of 20 % MeOH. Prior UHPLC-MS analysis, the extract was filtered through a 0.45-μm PTFE filter and transferred into a vial. These extracts were used for method performance evaluation by appropriate spiking with the compound mixtures.

Ultra-High Performance Liquid Chromatography-Electrospray-Quadrupole-Time-of-Flight Mass Spectrometry The separation and identification of the analytical standards were carried out using a reversed phase C_{18} column (50 mm × 2.1 mm and 1.8 μm particle size, Zorbax Rapid Resolution High Definition (RRHD) Eclipse-Plus C_{18}) by means of an Agilent UHPLC system (Agilent 1260,

Table 1 Accurate mass database of the studied pesticides, veterinary drugs, food-packaging contaminants, mycotoxins, perfluorinated compounds, nitrosamines, and sweeteners, including elemental composition, retention time (t_R), theoretical and experimental *m/z* values, and error (ppm) for the main ion of each compound in baby food extracts (50 μg kg^{-1})

Compound	Elemental composition (M)	t_R (min)	Ion	Theoretical *m/z*	Experimental *m/z*	Error (ppm)
Pesticides						
1-Naphtalene-acetamide	$C_{12}H_{11}NO$	4.28	$C_{11}H_9^+$	141.0699	141.0698	-0.71
1-Naphtyl-methylcarbamate	$C_{12}H_{15}NO_3$	4.83	$C_{10}H_{13}O_2^+$	165.0910	165.0912	1.21
2,4-Dichlorophenoxy acetic acid	$C_8H_6Cl_2O_3$	5.10	$[M-H]^-$	218.9621	218.9621	0.00
2,4-Dinitrophenol	$C_6H_4N_2O_5$	4.58	$[M-H]^-$	183.0047	183.0049	1.09
3,3-Dichlorobenzidine	$C_{12}H_{10}Cl_2N_2$	5.61	$[M+H]^+$	253.0294	253.0291	-1.19
3,5-Dichloroaniline	$C_6H_3NH_2Cl_2$	5.52	$[M+H]^+$	161.9872	161.9871	-0.62
4-Chloro-2-methylphenol	$C_7H_6N_2O_5$	5.10	$[M-H]^-$	141.0113	141.0114	0.71
4-Chloro-*o*-tolyoxyacetic acid	$C_9H_9ClO_3$	5.11	$C_7H_6ClO^-$	141.0113	141.0131	-2.84
Acephate	$C_4H_{10}NO_3PS$	0.81	$C_2H_9O_3PS^+$	142.9926	142.9927	0.70
Acetamiprid	$C_{10}H_{11}ClN_4$	3.96	$[M+H]^+$	223.0745	223.0745	0.00
Acibenzolar-*S*-methyl	$C_8H_6N_2OS_2$	5.69	$[M+H]^+$	210.9994	210.9994	0.00
Aclonifen	$C_{12}H_9ClN_2O_3$	6.31	$[M+H]^+$	265.0374	265.0378	1.51
Alachlor	$C_{14}H_{20}ClNO_2$	6.14	$C_{11}H_{16}N^+$	162.1277	162.1276	-0.62
Albendazole	$C_{12}H_{15}N_3O_2S$	4.42	$[M+H]^+$	266.0958	266.0959	0.38
Aldicarb	$C_7H_{14}N_2O_2S$	4.30	$[M+H]^+$	213.0668	213.0667	-0.47
Aldicarb sulfone	$C_7H_{14}N_2O_4S$	2.71	$C_4H_8NO^+$	86.0600	86.0603	3.49
Aldicarb sulfoxide	$C_7H_{14}N_2O_3S$	1.61	$C_4H_9S^+$	89.0419	89.0422	3.37
Allethrin isomer 1	$C_{19}H_{26}O_3$	7.11	$C_9H_{11}O^+$	135.0804	135.0803	-0.74
Allethrin isomer 2	$C_{19}H_{26}O_3$	7.07	$C_9H_{11}O^+$	135.0804	135.0807	2.22
Ametryne	$C_9H_{17}N_5S$	4.35	$[M+H]^+$	228.1278	228.1278	0.00
Aminocarb	$C_{11}H_{16}N_2O_2$	0.96	$[M+H]^+$	209.1285	209.1287	1.01
Amitraz	$C_{19}H_{23}N_3$	7.10	$[M+H]^+$	294.1965	294.1970	1.70
Amitrol	$C_2H_4N_4$	0.27	$[M+H]^+$	85.0509	85.0509	0.00
Ampa	CH_6NO_3P	0.34	$[M-H]^-$	110.0013	110.0015	1.82
Anilazine	$C_9H_5Cl_3N_4$	5.82	$[M-H]^-$	272.9507	272.9509	0.73
Anilofos	$C_{13}H_{19}ClNO_3PS_2$	6.46	$[M+H]^+$	368.0305	368.0308	0.82
Asulam	$C_8H_{10}N_2O_4S$	2.23	$C_6H_6NO_2S^+$	156.0114	156.0115	0.64
Atrazine	$C_8H_{14}ClN_5$	4.95	$[M+H]^+$	216.1011	216.1010	-0.46
Atrazine desethyl	$C_6H_{10}ClN_5$	3.73	$[M+H]^+$	188.0697	188.0699	1.06
Atrazine desisopropyl	$C_5H_8ClN_5$	3.08	$[M+H]^+$	174.0541	174.0542	0.57
Azaconazole	$C_{12}H_{11}Cl_2N_3O_2$	5.04	$[M+H]^+$	300.0301	300.0298	-1.00
Azamethiphos	$C_9H_{10}ClN_2O_5PS$	4.63	$[M+H]^+$	324.9809	324.9807	-0.62
Azinphos ethyl	$C_{12}H_{16}N_3O_3PS_2$	6.20	$[M+Na]^+$	368.0263	368.0261	-0.54
Azinphos methyl	$C_{10}H_{12}N_3O_3PS$	5.65	$C_8H_6NO^+$	132.0444	132.0441	-1.51
Azobenzene	$C_{12}H_{10}N_2$	5.55	$[M+H]^+$	183.0917	183.0916	-0.55
Azocyclotin	$C_{20}H_{35}N_3Sn$	6.73	$[M-C_2H_2N_3]^+$	369.1604	369.1598	-1.63
Azoxystrobin	$C_{22}H_{17}N_3O_5$	5.78	$[M+H]^+$	404.1241	404.1245	0.99
Barban	$C_{11}H_9Cl_2NO_2$	6.04	$C_{10}H_9ClN^+$	178.0418	178.0420	1.12
Benalaxyl	$C_{20}H_{23}NO_3$	6.35	$[M+H]^+$	326.1751	326.1752	0.31
Bendiocarb	$C_{11}H_{13}NO_4$	4.80	$C_9H_{11}O_3^+$	167.0703	167.0705	1.20
Benfluralin	$C_{13}H_{16}F_3N_3O_4$	7.29	$[M+H]^+$	336.1166	336.1173	2.08
Benfuracarb	$C_{20}H_{30}N_2O_5S$	7.05	$[M+H]^+$	411.1948	411.1947	-0.24
Bensulfuron methyl	$C_{16}H_{18}N_4O_7S$	5.37	$[M+H]^+$	411.0969	411.0968	-0.24
Bensulide	$C_{14}H_{24}NO_4PS_3$	6.49	$C_8H_{13}NO_4PS_3^+$	313.9739	313.9740	0.32
Bentazone	$C_{10}H_{12}N_2O_3S$	4.97	$[M-H]^-$	239.0496	239.0495	-0.42
Benzidine	$C_{12}H_{12}N_2$	0.43	$[M+H]^+$	185.1073	185.1070	-1.62

Table 1 (continued)

Compound	Elemental composition (M)	t_R (min)	Ion	Theoretical *m/z*	Experimental *m/z*	Error (ppm)
Bifenazate	$C_{17}H_{20}N_2O_3$	5.99	$C_{13}H_{12}NO^+$	198.0913	198.0913	0.00
Bifenox	$C_{14}H_9Cl_2NO_5$	6.74	$C_{13}H_6Cl_2NO_4^+$	309.9668	309.9668	0.00
Bitertanol	$C_{20}H_{23}N_3O_2$	5.99	$C_{18}H_{21}O_2^+$	269.1536	269.1536	0.00
Boscalid	$C_{18}H_{12}Cl_2N_2O$	5.85	$[M+H]^+$	343.0399	343.0397	-0.58
Brodifacoum isomer 1	$C_{31}H_{23}BrO_3$	7.54	$[M-H]^-$	521.0758	521.0760	0.38
Brodifacoum isomer 2	$C_{31}H_{23}BrO_3$	7.67	$[M-H]^-$	521.0758	521.0760	0.38
Bromacil	$C_9H_{13}BrN_2O_2$	4.42	$C_5H_6BrN_2O_2^+$	204.9607	204.9610	1.46
Bromadiolone isomer 1	$C_{30}H_{23}BrO_4$	6.76	$[M-H]^-$	525.0707	525.0723	3.04
Bromadiolone isomer 2	$C_{30}H_{23}BrO_4$	6.82	$[M-H]^-$	525.0707	525.0721	2.67
Bromophos methyl	$C_8H_8BrCl_2O_3PS$	7.12	$[M+H]^+$	364.8565	364.8574	2.47
Bromoxynil	$C_7H_3ONBr_2$	5.07	$[M-H]^-$	273.8509	273.8512	1.10
Bromuconazole isomer 1	$C_{13}H_{12}BrCl_2N_3O$	5.66	$[M+H]^+$	375.9614	375.9612	-0.53
Bromuconazole isomer 2	$C_{13}H_{12}BrCl_2N_3O$	5.84	$[M+H]^+$	375.9614	375.9611	-0.80
Bupirimate	$C_{13}H_{24}N_4O_3S$	5.30	$[M+H]^+$	317.1642	317.1646	1.26
Buprofezin	$C_{16}H_{23}N_3OS$	6.08	$[M+H]^+$	306.1635	306.1632	-0.98
Butachlor	$C_{17}H_{26}ClNO_2$	7.18	$[M+H]^+$	312.1725	312.1729	1.28
Butocarboxim	$C_7H_{14}N_2O_2S$	4.17	$[M+Na]^+$	213.0668	213.0668	0.00
Butoxycarboxim	$C_7H_{14}N_2O_4S$	2.56	$[M+Na]^+$	245.0564	245.0569	2.56
Butralin	$C_{14}H_{21}N_3O_4$	7.37	$C_{10}H_{14}N_3O_4^+$	240.0979	240.0980	0.42
Buturon	$C_{12}H_{13}ClN_2O$	5.42	$[M+H]^+$	237.0789	237.0782	-0.84
Cadusafos	$C_{10}H_{23}O_2PS_2$	6.48	$C_2H_8O_2PS_2^+$	158.9698	158.9696	-1.26
Carbaryl	$C_{12}H_{11}NO_2$	4.95	$C_{10}H_9O^+$	145.0648	145.0648	0.00
Carbendazim	$C_9H_9N_3O_2$	2.24	$[M+H]^+$	192.0768	192.0768	0.00
Carbofuran	$C_{12}H_{15}NO_3$	4.81	$[M+H]^+$	222.1125	222.1124	-0.45
Carbofuran 3-hydroxy	$C_{12}H_{15}NO_4$	3.75	$C_{10}H_{11}O_2^+$	163.0754	163.0755	0.61
Carbosulfan	$C_{20}H_{32}N_2O_3S$	8.11	$[M+H]^+$	381.2206	381.2200	-1.57
Carboxine	$C_{12}H_{13}NO_2S$	5.05	$[M+H]^+$	236.0740	236.0744	1.69
Carfentazone ethyl	$C_{15}H_{14}Cl_2F_3N_3O_3$	6.35	$[M+H]^+$	412.0437	412.0439	0.49
Chlorbromuron	$C_9H_{10}BrClN_2O_2$	5.74	$[M+H]^+$	292.9687	292.9688	0.34
Chlordimeform	$C_{10}H_{13}ClN_2$	3.35	$[M+H]^+$	197.0840	197.0841	0.51
Chlorfenvinfos	$C_{12}H_{14}Cl_3O_4P$	6.21	$[M+H]^+$	358.9768	358.9769	0.28
Chlorfluazuron	$C_{20}H_9Cl_3F_5N_3O_3$	7.33	$[M+H]^+$	539.9702	539.9703	0.19
Chloridazon	$C_{10}H_8ClN_3O$	3.78	$[M+H]^+$	222.0429	222.0428	-0.45
Chlormequat chloride	$C_5H_{13}NCl^+$	0.28	$[M]^+$	122.0370	122.0370	4.22
Chloropropham	$C_{10}H_{12}ClNO_2$	5.93	$C_7H_7ClNO_2^+$	172.0160	172.0158	-1.16
Chlorotoluron	$C_{10}H_{13}ClN_2O$	4.89	$[M+H]^+$	213.0789	213.0787	-0.94
Chloroxuron	$C_{15}H_{15}ClN_2O_2$	5.67	$[M+H]^+$	291.0895	291.0898	1.03
Chlorpyrifos	$C_9H_{11}Cl_3NO_3PS$	7.22	$[M+H]^+$	349.9336	349.9345	2.57
Chlorpyrifos methyl	$C_7H_7Cl_3NO_3PS$	6.71	$[M+H]^+$	321.9023	321.9029	1.86
Chlorsulfuron	$C_{12}H_{12}ClN_5O_4S$	4.92	$[M+H]^+$	358.0371	358.0373	0.56
Cinosulfuron	$C_{15}H_{19}N_5O_7S$	4.79	$[M+H]^+$	414.1078	414.1085	1.69
Clethodim isomer E	$C_{17}H_{26}ClNO_3S$	7.02	$[M+H]^+$	360.1395	360.1401	1.67
Clethodim isomer Z	$C_{17}H_{26}ClNO_3S$	5.70	$[M+H]^+$	360.1395	360.1402	1.04
Clethodim sulfoxide	$C_{17}H_{26}ClNO_4S$	5.03	$[M+H]^+$	376.1344	376.1343	-0.27
Clethodim imine	$C_{14}H_{23}NO_2S$	5.01	$[M+H]^+$	270.1522	270.1512	-3.70
Clodinafop-propargyl	$C_{17}H_{13}ClFNO_4$	6.46	$[M+H]^+$	350.0590	350.0574	-4.57
Clofentezine	$C_{14}H_8Cl_2N_4$	6.60	$C_7H_5ClN^+$	138.0105	138.0104	-0.72
Clomazone	$C_{12}H_{14}ClNO_2$	5.39	$[M+H]^+$	240.0786	240.0788	0.83
Clopyralid	$C_6H_3Cl_2NO_2$	1.18	$C_5H_2Cl_2N^+$	145.9559	145.9555	-2.74

Table 1 (continued)

Compound	Elemental composition (M)	t_R (min)	Ion	Theoretical *m/z*	Experimental *m/z*	Error (ppm)
Clothianidin	$C_6H_8ClN_5O_2S$	3.72	$C_6H_9N_4S^+$	169.0541	169.0542	-0.59
Coumaphos	$C_{14}H_{16}ClO_5PS$	6.60	$[M+H]^+$	363.0217	363.0219	0.55
Cyanazine	$C_9H_{13}ClN_6$	4.61	$[M+H]^+$	241.0963	241.0966	1.24
Cyazofamid	$C_{13}H_{13}ClN_4O_2S$	6.35	$C_2H_6NO_2S^+$	108.0114	108.0115	0.96
Cycloate	$C_{11}H_{21}NOS$	6.71	$[M+H]^+$	216.1417	216.1417	0.00
Cycloheximid	$C_{15}H_{23}NO_4$	4.22	$[M+H]^+$	282.1700	282.1701	0.35
Cycloxydim	$C_{17}H_{27}NO_3S$	6.87	$[M+H]^+$	326.1784	326.1785	0.31
Cymoxanil	$C_7H_{10}N_4O_3$	1.63	$[M+H]^+$	199.0826	199.0823	-1.51
Cyphenothrin	$C_{24}H_{25}NO_3$	7.76	$[M+Na]^+$	398.1727	398.1724	-0.75
Cyproconazole	$C_{15}H_{18}ClN_3O$	5.54	$[M+H]^+$	292.1211	292.1210	-0.34
Cyprodinil	$C_{14}H_{15}N_3$	5.18	$[M+H]^+$	226.1339	226.1336	-1.33
Cyromazine	$C_6H_{10}N_6$	0.46	$[M+H]^+$	167.1040	167.1041	0.60
Daminozide	$C_6H_{12}O_3N_2$	0.40	$C_6H_{11}O_2N_2^+$	143.0815	143.0818	2.10
Dazomet	$C_5H_{10}N_2S_2$	2.51	$C_3H_6NS_2^+$	119.9936	119.9937	0.87
DEET	$C_{12}H_{17}NO$	5.01	$[M+H]^+$	192.1383	192.1381	-1.04
Demeton-*S*-methyl	$C_6H_{15}O_3PS_2$	4.59	$[M+Na]^+$	253.0092	253.0099	2.77
Desethyl terbuthylazine	$C_7H_{12}ClN_5$	4.58	$C_3H_5ClN_5^+$	146.0227	146.0223	-2.74
Desmedipham	$C_{16}H_{16}N_2O_4$	5.65	$C_9H_{12}NO_3^+$	182.0812	182.0816	2.20
Desmetryn	$C_8H_{15}N_5S$	3.99	$[M+H]^+$	214.1121	214.1119	-0.93
Diafenthiuron	$C_{23}H_{32}N_2OS$	7.54	$[M+H]^+$	385.2308	385.2309	0.26
Diazinon	$C_{12}H_{21}N_2O_3PS$	6.57	$[M+H]^+$	305.1083	305.1084	0.33
Dibrom	$C_4H_7Br_2Cl_2O_4P$	5.31	$C_2H_8O_4P^+$	127.0155	127.0148	-5.51
Dicamba	$C_8Cl_2H_6O_3$	4.49	$C_7H_6Cl_2O^-$	174.9723	174.9730	4.00
Dichlofenthion	$C_{10}H_{13}Cl_2O_3PS$	7.20	$C_6H_6Cl_2O_3PS^+$	258.9147	258.9154	2.70
Dichlofluanid	$C_9H_{11}Cl_2FN_2O_2S_2$	6.34	$C_7H_5Cl_2FNS^+$	223.9498	223.9499	0.45
Dichlorprop	$C_9H_8Cl_2O_3$	5.42	$C_6H_3Cl_2O^-$	160.9566	160.9567	0.62
Dichlorvos	$C_4H_7Cl_2O_4P$	4.56	$[M+H]^+$	220.9532	220.9531	-0.45
Dicloran	$C_6H_4N_2O_2Cl_2$	5.40	$[M-H]^-$	204.9577	204.9585	3.90
Dicrotophos	$C_8H_{16}NO_5P$	3.39	$C_6H_{10}NO^+$	112.0757	112.0757	0.00
Diethanolamine	$C_4H_{11}NO_2$	0.27	$C_4H_{10}NO^+$	88.0757	106.0864	0.94
Diethofencarb	$C_{14}H_{21}NO_4$	5.65	$C_{11}H_{16}NO_4^+$	226.1074	226.1074	0.00
Difenacoum isomer 1	$C_{31}H_{24}O_3$	7.15	$[M+H]^+$	445.1798	445.1798	0.00
Difenacoum isomer 2	$C_{31}H_{24}O_3$	7.29	$[M+H]^+$	445.1798	445.1796	-0.45
Difenoconazole	$C_{19}H_{17}Cl_2N_3O_3$	6.32	$[M+H]^+$	406.0720	406.0722	0.49
Difenoxuron	$C_{16}H_{18}N_2O_3$	5.14	$[M+H]^+$	287.1390	287.1389	-0.35
Difenzoquat	$C_{17}H_{17}N_2$	4.11	$[M]^+$	249.1392	249.1390	-0.80
Diflubenzuron	$C_{14}H_9ClF_2N_2O_2$	6.00	$[M-H]^-$	309.0248	309.0252	1.29
Diflufenican	$C_{19}H_{11}F_5N_2O_2$	6.74	$[M+H]^+$	395.0813	395.0811	-0.51
Dimethametryn	$C_{11}H_{21}N_5S$	5.06	$[M+H]^+$	256.1590	256.1595	1.95
Dimethenamid	$C_{12}H_{18}ClNO_2S$	5.67	$C_{11}H_{15}ClNOS^+$	244.0557	244.0560	1.23
Dimethoate	$C_5H_{12}NO_3PS_2$	3.85	$C_2H_6O_2PS^+$	124.9821	124.9819	-1.60
Dimethomorph isomer 1	$C_{21}H_{22}ClNO_4$	5.37	$[M+H]^+$	388.1310	388.1313	0.77
Dimethomorph isomer 2	$C_{21}H_{22}ClNO_4$	5.45	$[M+H]^+$	388.1310	388.1311	0.26
Diniconazole	$C_{15}H_{17}Cl_2N_3O$	6.12	$[M+H]^+$	326.0821	326.0823	0.61
Diphenylamine	$C_{12}H_{11}N$	6.09	$[M+H]^+$	170.0964	170.0965	0.59
Diquat dibromide	$C_{12}H_{12}Br_2N_2$	0.26	$[M-Br_2-H]^+$	183.0917	183.0916	-0.55
Diuron	$C_9H_{10}Cl_2N_2O$	5.08	$[M+H]^+$	233.0243	233.0245	0.86
DMST	$C_9H_{14}N_2O_2S$	5.03	$C_7H_9N^+$	106.0651	106.0650	-0.94
DNOC	$C_7H_6N_2O_5$	5.31	$[M-H]^-$	197.0204	197.0203	0.00

Table 1 (continued)

Compound	Elemental composition (M)	t_R (min)	Ion	Theoretical *m/z*	Experimental *m/z*	Error (ppm)
Edifenphos	$C_{14}H_{15}O_2PS_2$	6.21	$[M+H]^+$	311.0324	311.0325	0.32
Emamectin isomer 1	$C_{49}H_{75}NO_{13}$	5.74	$[M+H]^+$	886.5311	886.5342	0.32
Emamectin isomer 2	$C_{49}H_{75}NO_{13}$	5.81	$[M+H]^+$	886.5311	886.5343	0.33
Endosulfan sulfate	$C_9H_6Cl_6O_4S$	6.65	$[M-H]^-$	418.8045	418.8066	5.01
EPN	$C_{14}H_{14}NO_4PS$	6.82	$[M+H]^+$	324.0454	324.0458	1.23
Epoxiconazole	$C_{17}H_{13}ClFN_3O$	5.79	$[M+H]^+$	330.0804	330.0801	-0.91
EPTC	$C_9H_{19}NOS$	6.26	$[M+H]^+$	190.1260	190.1260	0.00
Etaconazol	$C_{14}H_{15}Cl_2N_3O_2$	5.74	$[M+H]^+$	328.0614	328.0614	0.00
Ethephon	$C_2H_6ClO_3P$	1.40	$[M-H]^-$	142.9670	142.9672	0.41
Ethidimuron	$C_7H_{12}N_4O_3S_2$	3.80	$C_5H_{10}N_3O_2S_2^+$	208.0209	208.0210	0.48
Ethiofencarb	$C_{11}H_{15}NO_2S$	5.06	$C_7H_7O^+$	107.0491	107.0494	2.80
Ethiofencarb sulfone	$C_{11}H_{15}NO_4S$	3.71	$C_7H_7O^+$	107.0491	107.0492	0.93
Ethiofencarb sulfoxide	$C_{11}H_{15}NO_3S$	3.48	$C_7H_7O^+$	107.0491	107.0493	1.81
Ethion	$C_9H_{22}O_4P_2S_4$	7.26	$C_5H_{12}O_2PS_2^+$	199.0011	199.0015	2.01
Ethiprole	$C_{13}H_9Cl_2F_3N_4OS$	5.57	$[M+H]^+$	396.9899	396.9901	0.50
Ethofumesate	$C_{13}H_{18}O_5S$	5.97	$C_{11}H_{12}O_4S^+$	241.0529	241.0525	-1.66
Ethoprophos	$C_8H_{19}O_2PS_2$	5.83	$[M+Na]^+$	243.0637	243.0637	0.00
Ethoxyquin	$C_{14}H_{19}NO$	4.62	$[M+H]^+$	218.1539	218.1541	0.92
Ethylenthiourea	$C_3H_6N_2S$	0.41	$[M+H]^+$	103.0324	103.0329	4.85
Etofenprox	$C_{25}H_{28}O_3$	7.96	$[M+NH_4]^+$	394.2377	394.2372	-1.27
Etoxazole	$C_{21}H_{23}F_2NO_2$	7.34	$[M+H]^+$	360.1770	360.1767	-0.83
Etrimphos	$C_{10}H_{17}N_2O_4PS$	6.52	$[M+H]^+$	293.0719	293.0715	-1.36
Famoxadone	$C_{22}H_{18}N_2O_4$	6.51	$C_{21}H_{19}N_2O_2^+$	331.1441	331.1438	-2.72
Famphur	$C_{10}H_{16}NO_5PS_2$	5.64	$[M+H]^+$	326.0280	326.0278	-0.61
Fenamidone	$C_{17}H_{17}N_3OS$	5.79	$[M+H]^+$	312.1165	312.1165	0.00
Fenamiphos	$C_{13}H_{22}NO_3PS$	5.70	$[M+H]^+$	304.1131	304.1129	-0.66
Fenamiphos sulfone	$C_{13}H_{22}NO_5PS$	4.73	$[M+H]^+$	336.1029	336.1029	0.00
Fenamiphos sulfoxide	$C_{13}H_{22}NO_4PS$	4.31	$[M+H]^+$	320.1080	320.1078	-0.62
Fenarimol	$C_{17}H_{12}Cl_2N_2O$	5.66	$[M+H]^+$	331.0399	331.0402	0.91
Fenazaquin	$C_{20}H_{22}N_2O$	7.14	$[M+H]^+$	307.1805	307.1807	0.65
Fenbendazole	$C_{15}H_{13}N_3O_2S$	4.94	$[M+H]^+$	300.0801	300.0803	0.67
Fenhexamid	$C_{14}H_{17}Cl_2NO_2$	5.84	$[M+H]^+$	302.0709	302.0705	-1.32
Fenitrothion	$C_9H_{12}NO_5PS$	6.10	$[M+H]^+$	278.0247	278.0246	-0.36
Fenobucarb	$C_{12}H_{17}NO_2$	5.55	$C_6H_7O^+$	95.0491	95.0491	0.00
Fenoxaprop-*P*-ethyl	$C_{18}H_{16}ClNO_5$	6.83	$[M+H]^+$	362.0790	362.0790	0.00
Fenoxycarb	$C_{17}H_{19}NO_4$	6.10	$[M+H]^+$	302.1387	302.1389	0.66
Fenpiclonil	$C_{11}H_6Cl_2N_2$	5.55	$[M+H]^+$	236.9981	236.9982	0.42
Fenpropathrin	$C_{22}H_{23}NO_3$	7.56	$C_8H_{13}O^+$	125.0960	125.0954	-4.80
Fenpropidine	$C_{19}H_{31}N$	4.88	$[M+H]^+$	274.2529	274.2533	1.46
Fenpropimorph	$C_{20}H_{33}NO$	4.91	$[M+H]^+$	304.2635	304.2639	1.31
Fenpyroximate	$C_{24}H_{27}N_3O_4$	7.31	$[M+H]^+$	422.2074	422.2084	2.37
Fensulfothion	$C_{11}H_{17}O_4PS_2$	5.18	$[M+H]^+$	309.0379	309.0378	-0.32
Fenthion	$C_{10}H_{15}O_3PS_2$	6.48	$[M+H]^+$	279.0273	279.0274	0.36
Fentin chloride	$C_{18}H_{15}SnCl$	4.69	$[M-Cl]^+$	351.0196	351.0192	-1.14
Fenuron	$C_9H_{12}N_2O$	3.63	$[M+H]^+$	165.1022	165.1022	0.00
Fipronil	$C_{12}H_4Cl_2F_6N_4OS$	6.33	$[M+H]^+$	436.9460	436.9459	-0.23
Fluazifop	$C_{15}H_{12}F_3NO_4$	5.61	$[M+H]^+$	328.0791	328.0791	0.00
Fluazifop-butyl	$C_{19}H_{20}F_3NO_4$	7.17	$[M+H]^+$	384.1417	384.1414	-0.78
Fluazinam	$C_{13}H_4Cl_2F_6N_4O_4$	7.04	$[M+H]^+$	464.9587	464.9584	-0.65

Table 1 (continued)

Compound	Elemental composition (M)	t_R (min)	Ion	Theoretical *m/z*	Experimental *m/z*	Error (ppm)
Fluchloralin	$C_{12}H_{13}ClF_3N_3O_4$	6.91	$[M+H]^+$	356.0619	356.0620	0.28
Flucythrinate	$C_{26}H_{23}F_2NO_4$	7.45	$[M+NH_4]^+$	469.1933	469.1931	-0.43
Fludioxonil	$C_{12}H_6F_2N_2O_2$	5.66	$[M-H]^-$	247.0325	247.0337	4.85
Flufenacet	$C_{14}H_{13}F_4N_3O_2S$	6.15	$C_{11}H_{13}FNO^+$	194.0976	194.0971	-1.03
Flufenoxuron	$C_{21}H_{11}ClF_6N_2O_3$	7.17	$[M+H]^+$	489.0435	489.0434	-0.20
Fluomethuron	$C_{10}H_{11}F_3N_2O$	4.96	$[M+H]^+$	233.0896	233.0897	0.43
Fluquinconazole	$C_{16}H_8Cl_2FN_5O$	5.89	$[M+H]^+$	376.0163	376.0168	1.33
Fluroxypyr	$C_7H_5Cl_2FN_2O_3$	4.54	$C_5Cl_2H_2FN_2O^-$	194.9534	194.9534	0.00
Flusilazole	$C_{16}H_{15}F_2N_3Si$	5.93	$[M+H]^+$	316.1076	316.1076	0.00
Flutolanil	$C_{17}H_{16}F_3NO_2$	6.09	$[M+H]^+$	324.1206	324.1208	0.62
Flutriafol	$C_{16}H_{13}F_2N_3O$	4.96	$[M+H]^+$	302.1099	302.1098	-0.33
Fomesafen	$C_{15}H_{10}ClF_3N_2O_6S$	6.00	$[M+NH_4]^+$	456.0238	456.0233	-1.10
Fonofos	$C_{10}H_{15}OPS_2$	6.58	$C_2H_6OPS^+$	108.9871	108.9870	3.67
Foramsulfuron	$C_{17}H_{20}N_6O_7S$	4.57	$[M+H]^+$	453.1187	453.1184	-0.66
Forchlorfenuron	$C_{12}H_{10}ClN_3O$	4.98	$[M+H]^+$	248.0585	248.0580	-2.02
Formetanate	$C_{11}H_{15}N_3O_2$	1.16	$[M+H]^+$	222.1237	222.1235	-0.90
Fosetyl	$C_2H_7O_3P$	0.36	$H_4PO_3^+$	82.9893	82.9899	7.23
Fosthiazate	$C_9H_{18}NO_3PS_2$	4.98	$C_5H_{11}NO_3PS_2^+$	227.9912	227.9917	2.19
Fuberidazol	$C_{11}H_8N_2O$	3.14	$[M+H]^+$	185.0709	185.0709	0.00
Furalaxyl	$C_{17}H_{19}NO_4$	5.59	$[M+H]^+$	302.1387	302.1394	2.32
Furathiocarb	$C_{18}H_{26}N_2O_5S$	7.07	$[M+H]^+$	383.1635	383.1635	0.00
Furmecyclox	$C_{14}H_{21}NO_3$	6.21	$[M+H]^+$	252.1594	252.1591	-1.19
Gibberellic acid	$C_{19}H_{22}O_6$	3.70	$[M-H]^-$	345.1344	345.1353	2.61
Glufosinate ammonium	$C_5H_{12}NO_4P$	0.32	$[M-H]^-$	180.0431	180.0435	2.22
Glufosinate-*N*-acetyl	$C_7H_{14}NO_5P$	0.41	$[M-H]^-$	222.0537	222.0539	0.90
Glyphosate	$C_3H_8NO_5P$	0.33	$[M-H]^-$	168.0067	168.0072	2.98
Griseofulvin	$C_{17}H_{17}ClO_6$	5.15	$[M+H]^+$	353.0786	353.0784	-0.57
Haloxyfop	$C_{15}H_{11}ClF_3NO_4$	6.04	$[M+H]^+$	362.0401	362.0400	-0.28
Hexaflumuron	$C_{16}H_8Cl_2F_6N_2O_3$	6.63	$[M+H]^+$	460.9889	460.9885	-0.87
Hexazinone	$C_{12}H_{20}N_4O_2$	4.32	$[M+H]^+$	253.1659	253.1661	0.79
Hexythiazox	$C_{17}H_{21}ClN_2O_2S$	7.24	$[M+H]^+$	353.1085	353.1086	0.28
Hydramethylnon	$C_{25}H_{24}F_6N_4$	6.02	$[M+H]^+$	495.1978	495.1975	-0.61
Imazalil	$C_{14}H_{14}Cl_2N_2O$	4.52	$[M+H]^+$	297.0556	297.0556	0.00
Imazalil metabolite	$C_9H_{10}Cl_2N_2O$	3.69	$[M+H]^+$	257.0243	257.0243	0.00
Imazamethabenz-methyl	$C_{16}H_{20}N_2O_3$	4.11	$[M+H]^+$	289.1547	289.1547	0.00
Imazamox	$C_{15}H_{19}N_3O_4$	3.82	$[M+H]^+$	306.1448	306.1450	0.65
Imazapyr	$C_{13}H_{15}N_3O_3$	3.41	$[M+H]^+$	262.1186	262.1187	0.38
Imazaquin	$C_{17}H_{17}N_3O_3$	4.56	$[M+H]^+$	312.1343	312.1342	-0.32
Imidacloprid	$C_9H_{10}ClN_5O_2$	3.81	$[M+H]^+$	256.0596	256.0594	-0.78
Indoxacarb	$C_{22}H_{17}ClF_3N_3O_7$	6.79	$[M+H]^+$	528.0780	528.0790	1.89
Ioxynil	$C_7H_3I_2NO$	5.41	$[M-H]^-$	369.8231	369.8228	-0.81
Iprodione	$C_{13}H_{13}N_3Cl_2O_3$	6.60	$[M+H]^+$	330.0407	330.0409	0.61
Iprovalicarb	$C_{18}H_{28}N_2O_3$	5.68	$C_9H_{11}^+$	119.0855	119.0855	0.00
Isazophos	$C_9H_{17}ClN_3O_3PS$	6.27	$[M+H]^+$	314.0490	314.0488	-0.64
Isocarbophos	$C_{11}H_{16}NO_4PS$	5.54	$C_8H_8O_4PS^+$	230.9875	230.9883	3.46
Isofenphos	$C_{15}H_{24}NO_4PS$	6.84	$[M+H]^+$	346.1236	346.1245	2.60
Isoprocarb	$C_{11}H_{15}NO_2$	5.18	$C_6H_7O^+$	95.0491	95.0488	-3.16
Isoprothiolane	$C_{12}H_{18}O_4S_2$	6.09	$C_6H_5O_3S_2^+$	188.9675	188.9677	1.06
Isoproturon	$C_{12}H_{18}N_2O$	5.04	$[M+H]^+$	207.1492	207.1495	1.45

Table 1 (continued)

Compound	Elemental composition (M)	t_R (min)	Ion	Theoretical *m/z*	Experimental *m/z*	Error (ppm)
Isoxaben	$C_{18}H_{24}N_2O_4$	5.96	$[M+H]^+$	333.1809	333.1798	-3.30
Isoxaflutole	$C_{15}H_{12}F_3NO_4S$	5.78	$[M+H]^+$	360.0512	360.0516	1.11
Ivermectin	$C_{48}H_{72}O_{14}$	7.58	$[M+Na]^+$	895.4814	895.4811	-0.34
Karbutilate	$C_{14}H_{21}N_3O_3$	4.70	$[M+H]^+$	280.1656	280.1655	-0.36
Kresoxim methyl	$C_{18}H_{19}NO_4$	6.33	$C_{17}H_{16}NO_3^+$	282.1125	282.1116	-3.19
Lactofen	$C_{19}H_{15}ClF_3NO_7$	7.16	$[M+Na]^+$	484.0381	484.0386	1.03
Lenacil	$C_{13}H_{18}N_2O_2$	4.64	$C_7H_9N_2O_2^+$	153.0659	153.0662	1.96
Linuron	$C_9H_{10}Cl_2N_2O_2$	5.64	$[M+H]^+$	249.0192	249.0195	1.20
Lufenuron	$C_{17}H_8Cl_2F_8N_2O_3$	7.00	$[M+H]^+$	510.9857	510.9870	2.54
Malaoxon	$C_{10}H_{19}O_7PS$	4.76	$C_4H_3O_3^+$	99.0077	99.0080	3.03
Malathion	$C_{10}H_{19}O_6PS_2$	6.07	$[M+H]^+$	331.0433	331.0435	0.60
Maleic hydrazine	$C_4H_4N_2O_2$	0.41	$[M+H]^+$	113.0346	113.0348	1.77
Mecarbam	$C_{10}H_{20}NO_5PS_2$	6.29	$C_6H_{14}O_3PS_2^+$	226.9961	226.9961	0.00
Mecoprop	$C_{10}H_{11}ClO_3$	5.41	$C_7H_6ClO^-$	141.0113	141.0109	-2.84
Mefenacet	$C_{16}H_{14}N_2O_2S$	5.82	$C_9H_{10}NO^+$	148.0757	148.0757	0.00
Mepanipyrim	$C_{14}H_{13}N_3$	5.91	$[M+H]^+$	224.1182	224.1183	0.45
Mephosfolam	$C_8H_{16}NO_3PS_2$	4.42	$[M+H]^+$	270.0382	270.0385	1.11
Mepiquat chloride	$C_7H_{16}N^+$	0.40	$[M]^+$	114.1283	114.1283	0.00
Mepronil	$C_{17}H_{19}NO_2$	6.03	$[M+H]^+$	270.1489	270.1492	1.11
Mesotrione	$C_{14}H_{13}NO_7S$	4.79	$[M+H]^+$	340.0485	340.0484	-0.29
Metaflumizone	$C_{24}H_{16}F_6N_4O_2$	6.99	$[M+H]^+$	507.1250	507.1252	0.39
Metalaxyl	$C_{15}H_{21}NO_4$	5.07	$[M+H]^+$	280.1543	280.1541	-0.71
Metamitron	$C_{10}H_{10}N_4O$	3.61	$[M+H]^+$	203.0927	203.0925	-0.98
Metazachlor	$C_{14}H_{16}ClN_3O$	5.30	$C_9H_{12}N^+$	134.0964	134.0958	-4.47
Methabenzthiazuron	$C_{10}H_{11}N_3OS$	4.81	$C_8H_9N_2S^+$	165.0481	165.0482	0.61
Methacrifos	$C_7H_{13}O_5PS$	5.64	$C_6H_{10}O_4PS^+$	209.0032	209.0031	-0.48
Methamidophos	$C_2H_8NO_2PS$	0.55	$CH_5NO_2P^+$	94.0052	94.0054	2.13
Methidathion	$C_6H_{11}N_2O_4PS_3$	5.63	$C_3H_5N_2O^+$	85.0396	85.0403	5.88
Methiocarb	$C_{11}H_{15}NO_2S$	5.56	$C_9H_{12}OS^+$	169.0682	169.0678	-2.37
Methiocarb sulfoxide	$C_{11}H_{15}NO_3S$	3.64	$C_9H_{13}O_2S^+$	185.0631	185.0630	-0.54
Methomyl	$C_5H_{10}N_2O_2S$	2.86	$C_3H_4NS^+$	88.0215	88.0217	2.27
Methoprotryne	$C_{11}H_{21}N_5OS$	4.38	$[M+H]^+$	272.1540	272.1538	-0.73
Methoxyfenozide	$C_{22}H_{28}N_2O_3$	5.98	$C_{18}H_{21}N_2O_3^+$	149.0597	149.0596	-0.67
Metobromuron	$C_9H_{11}BrN_2O_2$	5.22	$[M+H]^+$	259.0077	259.0080	1.16
Metolachlor	$C_{15}H_{22}ClNO_2$	6.08	$[M+H]^+$	284.1412	284.1415	1.06
Metolcarb	$C_9H_{11}NO_2$	4.57	$C_7H_9O^+$	109.0648	109.0649	0.92
Metoxuron	$C_{10}H_{13}ClN_2O_2$	4.33	$[M+H]^+$	229.0738	229.0739	0.44
Metribuzin	$C_8H_{14}N_4OS$	4.62	$[M+H]^+$	215.0961	215.0963	0.93
Metsulfuron methyl	$C_{14}H_{15}N_5O_6S$	4.80	$[M+H]^+$	382.0816	382.0816	0.00
Mevinphos	$C_7H_{13}O_6P$	4.06	$C_2H_8O_4P^+$	127.0155	127.0153	-1.57
Molinate	$C_9H_{17}NOS$	5.77	$[M+H]^+$	188.1104	188.1106	1.06
Monocrotophos	$C_7H_{14}NO_5P$	3.18	$C_2H_7O_4P^+$	127.0155	127.0156	0.79
Monolinuron	$C_9H_{11}ClN_2O_2$	5.10	$[M+H]^+$	215.0582	215.0577	-2.32
Monuron	$C_9H_{11}ClON_2$	4.48	$[M+H]^+$	199.0633	199.0632	-0.50
Morpholin	C_4H_9NO	0.27	$[M+H]^+$	88.0757	88.0762	5.68
Myclobutanil	$C_{15}H_{17}ClN_4$	5.73	$[M+H]^+$	289.1215	289.1212	-1.04
Naptalam	$C_{18}H_{13}NO_3$	4.75	$C_{10}H_{10}N^+$	144.0808	144.0812	1.71
Neburon	$C_{12}H_{16}Cl_2N_2O$	6.18	$[M+H]^+$	275.0715	275.0711	-1.45
Nereistoxin	$C_5S_2NH_{11}$	0.49	$C_3H_5S_2^+$	104.9827	104.9830	2.86

Table 1 (continued)

Compound	Elemental composition (M)	t_R (min)	Ion	Theoretical *m/z*	Experimental *m/z*	Error (ppm)
Nitenpyram	$C_{11}H_{15}ClN_4O_2$	2.95	$[M+H]^+$	271.0956	271.0961	1.84
N,*N*-Diethyl-2-naphtoloxypropamide	$C_{17}H_{21}O_2N$	5.91	$[M+H]^+$	272.1645	272.1646	0.37
Norflurazone	$C_{12}H_9ClF_3N_3O$	5.20	$[M+H]^+$	304.0459	304.0457	-0.66
Novaluron	$C_{17}H_9ClF_8N_2O_4$	6.81	$[M-H]^-$	491.0050	491.0061	2.24
Nuarimol	$C_{17}H_{12}ClFN_2O$	5.32	$[M+H]^+$	315.0695	315.0692	-0.95
Ofurace	$C_{14}H_{16}ClNO_3$	5.10	$[M+H]^+$	282.0891	282.0890	-0.35
Omethoate	$C_5H_{12}NO_4PS$	1.10	$C_2H_6O_2PS^+$	124.9821	124.9822	0.80
Orbencarb	$C_{12}H_{16}ClNOS$	6.56	$C_7H_6Cl^+$	125.0153	125.0154	0.80
Oryzalin	$C_{12}H_{18}N_4O_6S$	6.10	$[M+H]^+$	345.0874	345.0882	2.32
Oxadiazon	$C_{15}H_{18}Cl_2N_2O_3$	7.21	$[M+H]^+$	345.0757	345.0772	4.35
Oxadixyl	$C_{14}H_{18}N_2O_4$	4.55	$C_{12}H_{15}N_2O_2^+$	219.1128	219.1131	1.37
Oxamyl	$C_7H_{13}N_3O_3S$	2.82	$C_3H_6NO^+$	72.0444	72.0447	4.16
Oxfendazole	$C_{15}H_{13}N_3O_3S$	3.97	$[M+H]^+$	316.0751	316.0751	0.00
Oxyfluorfen	$C_{15}H_{11}ClF_3NO_4$	7.07	$[M+H]^+$	362.0401	362.0398	-0.83
Paclobutrazol	$C_{15}H_{20}ClN_3O$	5.46	$[M+H]^+$	294.1368	294.1370	0.68
Paraoxon methyl	$C_8H_{10}NO_6P$	4.60	$[M+H]^+$	248.0319	248.0315	-1.61
Paraquat dichloride	$C_{12}H_{14}Cl_2N_2$	0.27	$[M-Cl_2-H]^+$	185.1073	185.1069	-2.16
Parathion	$C_{10}H_{14}NO_5PS$	6.45	$C_6H_7NO_5PS^+$	235.9777	235.9780	1.27
Parathion-methyl	$C_8H_{10}NO_5PS$	5.88	$[M+H]^+$	264.0090	264.0092	0.76
Pebulate	$C_{10}H_{21}NOS$	6.69	$[M+H]^+$	204.1417	204.1417	0.00
Penconazole	$C_{13}H_{15}Cl_2N_3$	5.97	$[M+H]^+$	284.0716	284.0716	0.00
Pencycuron	$C_{19}H_{21}ClN_2O$	6.65	$[M+H]^+$	329.1415	329.1415	0.00
Pendimethalin	$C_{13}H_{19}N_3O_4$	7.23	$C_8H_{10}N_3O_4^+$	212.0666	212.0667	0.47
Phenmedipham	$C_{16}H_{16}N_2O_4$	5.61	$C_8H_{10}NO_3^+$	168.0655	168.0661	3.57
Phenothrin	$C_{23}H_{26}O_3$	7.96	$[M+H]^+$	351.1955	351.1956	0.28
Phenthoate	$C_{12}H_{17}O_4PS_2$	6.51	$C_{10}H_{11}O_2^+$	163.0754	163.0758	2.45
Phosalone	$C_{12}H_{15}ClNO_4PS_2$	6.73	$C_8H_5ClNO_2^+$	182.0003	182.0005	1.10
Phosmet	$C_{11}H_{12}NO_4PS_2$	4.30	$C_9H_6NO_2^+$	160.0393	160.0394	0.62
Phosphamidon	$C_{10}H_{19}ClNO_5P$	4.36	$[M+H]^+$	300.0762	300.0762	0.00
Phosphonic acid	H_3O_3P	0.50	$[M-H]^-$	80.9747	80.9750	3.70
Picloram	$C_6H_3Cl_3N_2O_2$	3.25	$[M+H]^+$	240.9333	240.9334	2.49
Picolinafen	$C_{19}H_{12}F_4N_2O_2$	6.96	$[M+H]^+$	377.0908	377.0910	0.53
Piperonyl butoxide	$C_{19}H_{30}O_5$	7.03	$C_{11}H_{13}O_2^+$	177.0910	177.0913	1.69
Piperophos	$C_{14}H_{28}NO_3PS_2$	6.76	$[M+H]^+$	354.1321	354.1324	0.85
Pirimicarb	$C_{11}H_{18}N_4O_2$	3.51	$[M+H]^+$	239.1503	239.1503	0.00
Pirimiphos methyl	$C_{11}H_{20}N_3O_3PS$	6.41	$[M+H]^+$	306.1036	306.1034	-0.65
Pretilachlor isomer 1	$C_{17}H_{26}ClNO_2$	6.81	$[M+H]^+$	312.1725	312.1723	-0.64
Pretilachlor isomer 2	$C_{17}H_{26}ClNO_2$	6.73	$[M+H]^+$	312.1725	312.1723	-0.64
Prochloraz	$C_{15}H_{16}Cl_3N_3O_2$	5.40	$C_{12}H_{13}Cl_3NO_2^+$	308.0006	308.0008	0.65
Procymidone	$C_{13}H_{11}Cl_2NO_2$	6.09	$[M+H]^+$	284.0240	284.0242	0.70
Profenofos	$C_{11}H_{15}BrClO_3PS$	6.79	$[M+H]^+$	372.9424	372.9424	0.00
Prohexadione	$C_{10}H_{12}O_5$	4.09	$[M-H]^-$	211.0612	211.0613	0.47
Promecarb	$C_{12}H_{17}NO_2$	5.69	$C_{10}H_{15}O^+$	151.1117	151.1118	0.66
Prometon	$C_{10}H_{19}N_5O$	4.05	$[M+H]^+$	226.1662	226.1659	-1.33
Prometryn	$C_{10}H_{19}N_5S$	4.76	$[M+H]^+$	242.1434	242.1437	1.24
Propachlor	$C_{11}H_{14}ClNO$	5.27	$[M+H]^+$	212.0837	212.0836	-0.47
Propamocarb	$C_9H_{20}N_2O_2$	1.14	$[M+H]^+$	189.1598	189.1599	0.53
Propanil	$C_9H_9Cl_2NO$	5.47	$[M+H]^+$	218.0134	218.0132	-0.92
Propaquizafop	$C_{22}H_{22}ClN_3O_5$	6.93	$[M+H]^+$	444.1321	444.1321	0.00

Table 1 (continued)

Compound	Elemental composition (M)	t_R (min)	Ion	Theoretical *m/z*	Experimental *m/z*	Error (ppm)
Propargite	$C_{19}H_{26}O_4S$	7.40	$[M+Na]^+$	373.1444	373.1446	0.54
Propazine	$C_9H_{16}ClN_5$	5.41	$[M+H]^+$	230.1167	230.1169	0.87
Propetamphos	$C_{10}H_{20}NO_4PS$	6.16	$C_3H_{11}NO_2PS^+$	156.0243	156.0245	1.28
Propham	$C_{10}H_{13}NO_2$	5.30	$C_7H_8NO_2^+$	138.0550	138.0560	7.24
Propiconazole	$C_{15}H_{17}Cl_2N_3O_2$	6.13	$[M+H]^+$	342.0771	342.0771	0.00
Propisochlor	$C_{15}H_{22}ClNO_2$	6.40	$C_{10}H_{15}N^+$	148.1121	148.1122	0.68
Propoxur	$C_{11}H_{15}NO_3$	4.75	$[M+H]^+$	232.0944	232.0944	0.00
Propylene thiourea	$C_4H_8N_2S$	0.53	$[M+H]^+$	117.0481	117.0481	0.00
Propyzamid	$C_{12}H_{11}Cl_2NO$	5.89	$C_7H_6Cl_2NO^+$	189.9821	189.9824	1.58
Proquinazid	$C_{14}H_{17}IN_2O_2$	7.51	$[M+H]^+$	373.0407	373.0405	-0.54
Prosulfocarb	$C_{14}H_{21}NOS$	6.91	$[M+H]^+$	252.1417	252.1418	0.40
Prosulfuron	$C_{15}H_{16}F_3N_5O_4S$	5.64	$[M+H]^+$	420.0948	420.0946	-0.48
Pymetrozin	$C_{10}H_{11}N_5O$	0.70	$[M+H]^+$	218.1036	218.1036	0.00
Pyracarbolid	$C_{13}H_{15}NO_2$	4.89	$[M+H]^+$	218.1176	218.1176	0.00
Pyraclostrobin	$C_{19}H_{18}ClN_3O_4$	6.60	$[M+H]^+$	388.1059	388.1056	-0.77
Pyranocoumarin	$C_{20}H_{18}O_4$	6.47	$[M+H]^+$	323.1278	323.1277	-0.31
Pyrazophos	$C_{14}H_{20}N_3O_5PS$	6.51	$[M + H]^+$	374.0934	374.0935	0.27
Pyridaben	$C_{19}H_{25}ClN_2OS$	7.61	$[M+H]^+$	365.1449	365.1451	0.55
Pyridaphenthion	$C_{14}H_{17}N_2O_4PS$	5.86	$[M+H]^+$	341.0719	341.0719	0.00
Pyrifenox isomer 1	$C_{14}H_{12}Cl_2N_2O$	4.57	$[M+H]^+$	295.0399	295.0390	-3.05
Pyrifenox isomer 2	$C_{14}H_{12}Cl_2N_2O$	4.65	$[M+H]^+$	295.0399	295.0397	-0.68
Pyrimethanil	$C_{12}H_{13}N_3$	4.54	$[M+H]^+$	200.1182	200.1179	-1.50
Pyriproxifen	$C_{20}H_{19}NO_3$	7.10	$[M+H]^+$	322.1438	322.1440	0.62
Pyroquilon	$C_{11}H_{11}NO$	4.28	$[M+H]^+$	174.0913	174.0912	-0.57
Quinalphos	$C_{12}H_{15}N_2O_3PS$	6.35	$[M+H]^+$	299.0614	299.0615	0.33
Quinmerac	$C_{11}H_8ClNO_2$	3.67	$C_{11}H_7ClNO^+$	204.0211	204.0212	0.44
Quinoclamine	$C_{10}H_6ClNO_2$	4.59	$[M+H]^+$	208.0160	208.0159	-0.48
Quinoxyfen	$C_{15}H_8Cl_2FNO$	6.75	$[M+H]^+$	308.0040	308.0043	0.97
Quizalofop-*P*-ethyl	$C_{19}H_{17}ClN_2O_4$	6.85	$[M+H]^+$	373.0950	373.0949	-0.27
Resmethrin (R^+S isomers)	$C_{22}H_{26}O_3$	7.73	$[M+H]^+$	339.1955	339.1948	-2.06
Rimsulfuron	$C_{14}H_{17}N_5O_7S_2$	4.96	$[M+H]^+$	432.0642	432.0631	-2.55
Rotenone	$C_{23}H_{22}O_6$	6.15	$[M+H]^+$	395.1489	395.1487	-0.51
Secbumeton	$C_{10}H_{19}N_5O$	4.05	$[M+H]^+$	226.1662	226.1663	0.44
Sethoxydim	$C_{17}H_{29}NO_3S$	7.13	$[M+H]^+$	328.1941	328.1942	0.30
Siduron	$C_{14}H_{20}N_2O$	5.51	$[M+H]^+$	233.1648	233.1648	0.00
Simazine	$C_7H_{12}ClN_5$	4.44	$[M+H]^+$	202.0854	202.0856	0.99
Spinosyn A	$C_{41}H_{65}NO_{10}$	5.37	$[M+H]^+$	732.4681	732.4677	-0.55
Spinosyn D	$C_{42}H_{67}NO_{10}$	5.54	$[M+H]^+$	746.4838	746.4832	-0.80
Spiromesifen	$C_{23}H_{30}O_4$	7.62	$C_{17}H_{22}O_3^+$	273.1485	273.1490	-1.83
Spirotetramat	$C_{21}H_{27}NO_5$	5.60	$[M+H]^+$	374.1962	374.1961	-0.27
Spiroxamine	$C_{18}H_{35}NO_2$	4.91	$[M+H]^+$	298.2741	298.2740	-0.34
Sulcotrione	$C_{14}H_{13}ClO_5S$	4.86	$[M+H]^+$	329.0245	329.0245	0.00
Sulfometuron methyl	$C_{15}H_{16}N_4O_5S$	4.87	$[M+H]^+$	365.0914	365.0913	-0.27
Sulfotep	$C_8H_{20}O_5P_2S_2$	6.65	$[M+H]^+$	323.0300	323.0299	-0.31
Sulprofos	$C_{12}H_{19}O_2PS_3$	7.31	$[M+H]^+$	323.0358	323.0358	0.00
Tebuconazole	$C_{16}H_{22}ClN_3O$	5.86	$[M+H]^+$	308.1524	308.1522	-0.65
Tebufenpyrad	$C_{18}H_{24}ClN_3O$	6.85	$[M+H]^+$	334.1681	334.1683	0.60
Tebutam	$C_{15}H_{23}NO$	6.05	$[M+H]^+$	234.1852	234.1854	0.85
Tebuthiuron	$C_9H_{16}N_4OS$	4.27	$[M+H]^+$	229.1118	229.1120	0.87

Table 1 (continued)

Compound	Elemental composition (M)	t_R (min)	Ion	Theoretical *m/z*	Experimental *m/z*	Error (ppm)
Teflubenzuron	$C_{14}H_6Cl_2F_4N_2O_2$	6.68	$[M-H]^-$	378.9670	378.9673	0.79
Tembotrione	$C_{17}H_{16}ClF_3O_6S$	5.76	$C_{15}H_{14}ClO_5S^+$	341.0245	341.0250	1.47
Temephos	$C_{16}H_{20}O_6P_2S_3$	7.18	$[M+H]^+$	466.9970	466.9971	0.21
Tepraloxydim isomer 1	$C_{17}H_{24}ClNO_4$	5.84	$[M+H]^+$	342.1467	342.1467	0.00
Tepraloxydim isomer 2	$C_{17}H_{24}ClNO_4$	4.65	$[M+H]^+$	342.1467	342.1462	-1.46
Terbacil	$C_9H_{13}ClN_2O_2$	4.50	$[M-H]^-$	215.0593	215.0585	-3.72
Terbufos	$C_9H_{21}O_2PS_3$	7.13	$C_4H_{13}O_2PS_2^+$	187.0011	187.0017	3.21
Terbumeton	$C_{10}H_{19}N_5O$	4.10	$[M+H]^+$	226.1662	226.1662	0.00
Terbuthylazine	$C_9H_{16}ClN_5$	5.54	$[M+H]^+$	230.1167	230.1171	1.30
Terbutryn	$C_{10}H_{19}N_5S$	4.79	$[M+H]^+$	242.1434	242.1435	0.41
Tetrachovinphos	$C_{10}H_9Cl_4O_4P$	6.08	$C_8H_3Cl_4^+$	127.0155	127.0154	-0.79
Thiabendazole	$C_{10}H_7N_3S$	2.98	$[M+H]^+$	202.0433	202.0437	1.98
Thiacloprid	$C_{10}H_9ClN_4S$	4.30	$[M+H]^+$	253.0309	253.0309	0.00
Thiamethoxam	$C_8H_{10}ClN_5O_3S$	3.43	$C_8H_{11}N_4OS^+$	211.0648	211.0647	-1.03
Thidiazuron	$C_9H_8N_4OS$	4.50	$[M+H]^+$	221.0492	221.0488	-1.81
Thifensulfuron methyl	$C_{12}H_{13}N_5O_6S_2$	4.68	$[M+H]^+$	388.0380	388.0375	-1.29
Thiocyclam	$C_5H_{11}NS_3$	0.78	$C_5H_5S_3^+$	136.9548	136.9551	2.19
Thiodicarb	$C_{10}H_{18}N_4O_4S_3$	4.77	$[M+Na]^+$	377.0382	377.0379	-0.80
Thiofanox	$C_9H_{18}N_2O_2S$	4.99	$[M+Na]^+$	241.0981	241.0983	0.83
Thiophanate methyl	$C_{12}H_{14}N_4O_4S_2$	4.72	$[M+H]^+$	343.0529	343.0528	-0.29
Tolclofos methyl	$C_9H_{11}Cl_2O_3PS$	6.67	$[M+H]^+$	300.9616	300.9615	-0.33
Tralkoxidym	$C_{20}H_{27}NO_3$	7.24	$[M+H]^+$	330.2064	330.2064	0.00
Transfluthrin	$C_{15}H_{12}Cl_2F_4O_2$	7.36	$C_7H_3F_4^+$	163.0165	163.0166	0.61
Triadimefon	$C_{14}H_{16}ClN_3O_2$	5.80	$[M+H]^+$	294.1004	294.1007	1.02
Triadimenol isomer 1	$C_{14}H_{18}ClN_3O_2$	5.43	$C_2H_4N_3^+$	70.0399	70.0400	1.43
Triadimenol isomer 2	$C_{14}H_{18}ClN_3O_2$	5.53	$C_2H_4N_3^+$	70.0399	70.0400	1.43
Triallat	$C_{10}H_{16}Cl_3NOS$	7.41	$[M+H]^+$	304.0091	304.0092	0.33
Triasulfuron	$C_{14}H_{16}ClN_5O_5S$	4.91	$[M+H]^+$	402.0633	402.0630	-0.75
Triazophos	$C_{12}H_{16}N_3O_3PS$	6.11	$[M+H]^+$	314.0723	314.0726	0.96
Triazoxide	$C_{10}H_6ClN_5O$	4.14	$[M+H]^+$	248.0334	248.0333	-0.40
Trichlorfon	$C_4H_8Cl_3O_4P$	3.52	$[M+H]^+$	256.9299	256.9302	1.17
Tridemorph	$C_{19}H_{39}NO$	5.44	$[M+H]^+$	298.3105	298.3105	0.00
Trietazine	$C_9H_{16}ClN_5$	5.95	$[M+H]^+$	230.1167	230.1170	1.30
Triethanolamine	$C_6H_{15}NO_3$	0.28	$[M+H]^+$	150.1125	150.1120	-3.33
Trifloxystrobin	$C_{20}H_{19}F_3N_2O_4$	6.81	$[M+H]^+$	409.1370	409.1368	-0.49
Trifloxysulfuron	$C_{14}H_{13}F_3N_5O_6S$	5.12	$[M+H]^+$	438.0690	438.0685	-1.14
Triflumizole	$C_{15}H_{15}ClF_3N_3O$	5.88	$C_{12}H_{12}ClF_3NO^+$	278.0554	278.0555	0.36
Triflumuron	$C_{15}H_{10}ClF_3N_2O_3$	6.38	$[M-H]^-$	357.0259	357.0265	1.68
Trifluralin	$C_{13}H_{16}F_3N_3O_4$	7.27	$[M+H]^+$	336.1166	336.1176	2.98
Triforine	$C_{10}H_{14}Cl_6N_4O_2$	5.16	$C_9H_{12}Cl_6N_3O^+$	387.9106	387.9102	-1.03
Trimethylsulfonium	C_3H_8S	0.26	$[M+H]^+$	77.0425	77.0423	-2.60
Trinexapac-ethyl	$C_{13}H_{16}O_5$	5.35	$[M+H]^+$	253.1071	253.1072	0.40
Triticonazole	$C_{17}H_{20}ClN_3O$	5.53	$[M+H]^+$	318.1368	318.1366	-0.63
Vamidothion	$C_8H_{18}NO_4PS_2$	3.65	$C_6H_{12}NOS^+$	146.0634	146.0637	2.05
Vinclozolin	$C_{12}H_9Cl_2NO_3$	6.27	$C_{11}H_{10}Cl_2NO^+$	242.0134	242.0128	-2.48
Zoxamide	$C_{14}H_{16}Cl_3NO_2$	6.51	$[M+H]^+$	336.0319	336.0316	-0.89
Veterinary drugs						
Albendazole sulfone	$C_{12}H_{15}N_3O_4S$	3.97	$[M+H]^+$	298.0856	298.0863	2.95
Albendazole sulfoxide	$C_{12}H_{15}N_3O_3S$	3.51	$[M+H]^+$	282.0907	282.0911	1.42

Table 1 (continued)

Compound	Elemental composition (M)	t_R (min)	Ion	Theoretical *m/z*	Experimental *m/z*	Error (ppm)
Amoxicillin	$C_{16}H_{19}N_3O_5S$	0.93	$C_{16}H_{17}N_2O_5S^+$	349.0853	349.0857	1.15
Ampicillin	$C_{16}H_{19}N_3O_4S$	3.17	$[M+H]^+$	350.1169	350.1164	-1.43
Antimycin A	$C_{28}H_{40}N_2O_9$	7.59	$[M+H]^+$	549.2807	549.2804	-0.55
Benzothiazole	C_7H_5NS	4.35	$[M+H]^+$	136.0215	136.0213	-1.47
Benzydamine	$C_{19}H_{23}N_3O$	4.47	$[M+H]^+$	310.1914	310.1914	0.00
Caffeine	$C_8H_{10}N_4O_2$	3.04	$[M+H]^+$	195.0877	195.0875	-1.03
Carbadox	$C_{11}H_{10}N_4O_4$	3.40	$[M+H]^+$	263.0775	263.0775	0.00
Carbamazepine	$C_{15}H_{12}N_2O$	4.65	$[M+H]^+$	237.1022	237.1020	-0.84
Chloramphenicol	$C_{11}H_{12}O_5N_2Cl_2$	4.14	$[M-H]^-$	321.0051	321.0052	0.31
Chlortetracycline iso. 1	$C_{22}H_{23}ClN_2O_8$	3.62	$[M+H]^+$	479.1216	479.1210	-1.25
Chlortetracycline iso. 2	$C_{22}H_{23}ClN_2O_8$	3.87	$[M+H]^+$	479.1216	479.1206	-2.09
Ciprofloxacin	$C_{17}H_{18}FN_3O_3$	3.46	$[M+H]^+$	332.1405	332.1401	-1.20
Clarithromycin	$C_{38}H_{69}NO_{13}$	4.67	$[M+H]^+$	748.4842	748.4823	-2.54
Clenbuterol	$C_{12}H_{18}Cl_2N_2O$	3.61	$[M+H]^+$	277.0869	277.0870	0.36
Clofibric acid	$C_{10}H_{11}O_3Cl$	5.24	$C_6H_4ClO^-$	126.9951	126.9951	0.00
Cloxacillin	$C_{19}H_{18}ClN_3O_5S$	5.17	$[M+CH_4OH]^+$	468.0991	468.0995	0.85
Cotinine	$C_{10}H_{12}N_2O$	0.41	$[M+H]^+$	177.1022	177.1022	0.00
Danofloxacin	$C_{19}H_{20}FN_3O_3$	3.48	$[M+H]^+$	358.1561	358.1563	0.56
Demeclocycline isomer 1	$C_{21}H_{21}ClN_2O_8$	3.46	$[M+H]^+$	465.1059	46.1041	-3.87
Demeclocycline isomer 2	$C_{21}H_{21}ClN_2O_8$	3.64	$[M+H]^+$	465.1059	465.1069	2.15
Diclofenac	$C_{14}H_{11}Cl_2NO_2$	5.89	$C_{13}H_8Cl_2N^-$	250.0196	250.0210	5.60
Dicloxacillin isomer 1	$C_{19}H_{17}N_3Cl_2O_5S$	5.34	$[M+CH_4OH]^+$	502.0601	502.0606	1.00
Dicloxacillin isomer 2	$C_{19}H_{17}N_3Cl_2O_5S$	5.45	$[M+CH_4OH]^+$	502.0601	502.0609	1.59
Difloxacin	$C_{21}H_{19}F_2N_3O_3$	3.72	$[M+H]^+$	400.1467	400.1466	-0.25
Digoxin	$C_{41}H_{64}O_{14}$	4.45	$C_{35}H_{55}O_{11}^+$	651.3739	651.3733	-0.92
Dimetridazole	$C_5H_7N_3O_2$	1.29	$[M+H]^+$	142.0611	142.0611	0.00
Diphenhydramine	$C_{17}H_{21}NO$	4.30	$C_{13}H_{11}^+$	167.0855	167.0856	0.60
Doramectin	$C_{50}H_{74}O_{14}$	7.99	$C_{21}H_{31}O_3^+$	331.2268	331.2272	1.21
Doxicycline	$C_{22}H_{24}N_2O_8$	3.98	$[M+H]^+$	445.1605	445.1608	0.67
Enoxacin	$C_{15}H_{17}FN_4O_3$	3.33	$[M+H]^+$	321.1357	321.1357	0.00
Enrofloxacin	$C_{19}H_{22}FN_3O_3$	3.54	$[M+H]^+$	360.1718	360.1720	0.56
Eprinomectin B_{1a}	$C_{50}H_{75}NO_{14}$	7.14	$[M+Na]^+$	936.5080	936.5093	1.39
Eprinomectin B_{1b}	$C_{49}H_{73}NO_{14}$	7.14	$[M+Na]^+$	922.4923	922.4902	-2.28
Erythromycin	$C_{37}H_{67}NO_{13}$	4.32	$[M+H]^+$	734.4685	734.4671	-1.91
Estrone	$C_{18}H_{22}O_2$	5.47	$[M+H]^+$	271.1693	271.1693	0.00
Febantel 1	$C_{16}H_{18}N_4O_2S$	4.16	$[M+H]^+$	331.1223	331.1231	2.72
Febantel 2	$C_{18}H_{20}N_4O_4S$	4.29	$[M+H]^+$	389.1278	389.1271	-1.80
Fleroxacin	$C_{17}H_{18}F_3N_3O_3$	3.31	$[M+H]^+$	370.1373	370.1378	0.14
Flufenamic acid	$C_{14}H_{10}F_3NO_2$	6.22	$C_{14}H_9F_3NO^+$	264.0631	264.0628	-1.14
Flumequine	$C_{14}H_{12}FNO_3$	4.75	$[M+H]^+$	262.0874	262.0871	-1.14
Fluoxetine	$C_{17}H_{18}F_3NO$	4.75	$[M+H]^+$	310.1413	310.1416	0.97
Furosemide	$C_{12}H_{11}ClN_2O_2S$	4.70	$[M-H]^-$	329.0040	329.0033	-2.13
Gemfibrozil	$C_{15}H_{22}O_3$	6.33	$C_7H_{13}O_2^+$	129.0910	129.0912	1.55
Hydrochlorothiazide	$C_7H_8ClN_3O_4S_2$	2.64	$[M-H]^-$	295.9572	295.9568	-1.69
Hydroflumethiazide	$C_8H_8F_3N_3O_4S_2$	3.58	$C_8H_6F_3N_2O_4S_2^+$	314.9716	314.9720	1.27
Ibuprofen	$C_{13}H_{18}O_2$	5.97	$C_{12}H_{17}^+$	161.1325	161.1325	0.00
Indomethacine	$C_{19}H_{16}ClNO_4$	5.90	$[M+H]^+$	358.0841	358.0838	-0.84
Irgasan	$C_{12}H_7Cl_3O_2$	6.69	$C_6H_3Cl_2O^+$	160.9555	160.9559	2.49
Josamycin	$C_{42}H_{69}NO_{15}$	4.93	$[M+H]^+$	828.4740	828.4739	-0.12

Table 1 (continued)

Compound	Elemental composition (M)	t_R (min)	Ion	Theoretical *m/z*	Experimental *m/z*	Error (ppm)
Ketoprofen	$C_{16}H_{14}O_3$	5.24	$[M+H]^+$	255.1016	255.1008	-3.14
Leucomalachite green	$C_{23}H_{26}N_2$	4.88	$[M+H]^+$	331.2169	331.2171	0.60
Levamisole	$C_{11}H_{12}N_2S$	1.98	$[M+H]^+$	205.0794	205.0790	-1.95
Lincomycin	$C_{18}H_{34}N_2O_6S$	2.94	$[M+H]^+$	407.2210	407.2206	-0.98
Lomefloxacin	$C_{17}H_{19}F_2N_3O_3$	3.47	$[M+H]^+$	352.1467	352.1462	-1.42
Malachite green	$C_{23}H_{24}N_2$	5.06	$[M+H]^+$	329.2012	329.2013	0.30
Marbofloxacin	$C_{17}H_{19}FN_4O_4$	3.30	$[M+H]^+$	363.1463	363.1466	0.83
Mebendazole	$C_{16}H_{13}N_3O_3$	4.42	$[M+H]^+$	296.1030	296.1025	-1.69
Meclofenamic acid	$C_{14}H_{11}Cl_2NO_2$	6.26	$C_{14}H_{10}Cl_2NO^+$	278.0134	278.0138	1.44
Mefenamic acid	$C_{15}H_{15}NO_2$	6.25	$C_{15}H_{14}NO^+$	224.1070	224.1071	0.45
Menadione	$C_{11}H_{10}O_5S$	3.16	$[M-H]^-$	253.0171	253.0171	0.00
Metformin	$C_4H_{11}N_5$	0.27	$[M+H]^+$	130.1087	130.1086	-0.77
Metronidazole	$C_6H_9N_3O_3$	1.06	$C_4H_6N_3O_2^+$	128.0456	128.0455	-0.08
Miconazole	$C_{18}H_{14}Cl_4N_2O$	5.35	$[M+H]^+$	414.9933	414.9934	0.24
Minocycline	$C_{23}H_{27}N_3O_7$	3.06	$[M+H]^+$	458.1922	458.1921	-0.22
Monensin	$C_{36}H_{62}O_{11}$	8.94	$[M+Na]^+$	693.4184	693.4207	3.46
Naproxen	$C_{14}H_{14}O_3$	5.27	$C_{13}H_{13}O^+$	185.0961	185.0960	-0.54
Natamycin	$C_{33}H_{47}NO_{13}$	4.37	$[M+H]^+$	666.3120	666.3115	-0.75
Nicotine	$C_{10}H_{14}N_2$	0.40	$[M+H]^+$	163.1230	163.1231	0.61
Nifuroxazide	$C_{12}H_9N_3O_5$	4.20	$[M+H]^+$	276.0615	276.0623	2.90
Norfloxacin	$C_{16}H_{18}FN_3O_3$	3.38	$[M+H]^+$	320.1405	320.1406	0.31
Orbifloxacin	$C_{19}H_{20}F_3N_3O3$	3.58	$[M+H]^+$	396.1530	396.1532	0.50
Oxacillin isomer 1	$C_{19}H_{19}N_3O_5S$	4.96	$[M+CH_4OH]^+$	434.1380	434.1383	0.69
Oxacillin isomer 2	$C_{19}H_{19}N_3O_5S$	5.04	$[M+CH_4OH]^+$	434.1380	434.1379	-0.23
Oxolinic Acid	$C_{13}H_{11}NO_5$	4.19	$[M+H]^+$	262.0710	262.0713	1.14
Oxybendazole	$C_{12}H_{15}N_3O_3$	3.99	$[M+H]^+$	250.1186	250.1186	0.00
Oxytetracycline	$C_{22}H_{24}N_2O_9$	3.36	$[M+H]^+$	461.1555	461.1559	0.87
Penicillin G isomer 1	$C_{16}H_{18}N_2O_4S$	4.50	$[M+H]^+$	335.1060	335.1060	0.00
Penicillin G isomer 2	$C_{16}H_{18}N_2O_4S$	4.56	$[M+H]^+$	335.1060	335.1061	0.30
Penicillin V Isomer 1	$C_{17}H_{22}N_2O_6S$	4.73	$[M+CH_4OH]^+$	383.1271	383.1277	1.57
Penicillin V isomer 2	$C_{16}H_{18}N_2O_5S$	4.87	$[M+CH_4OH]^+$	383.1271	383.1271	0.00
Pentylenetetrazole	$C_6H_{10}N_4$	2.43	$[M+H]^+$	139.0978	139.0976	-0.14
Phenylbutazone	$C_{19}H_{20}N_2O_2$	6.12	$[M+H]^+$	309.1598	309.1595	-0.97
Pravastatin	$C_{23}H_{36}O_7$	4.54	$[M-H]^-$	423.2388	423.2399	2.60
Prednisolone	$C_{21}H_{28}O_5$	4.36	$[M+H]^+$	361.2010	361.1996	-3.88
Promethazine	$C_{17}H_{20}N_2S$	4.45	$[M+H]^+$	285.1420	285.1420	0.00
Propanolol	$C_{16}H_{21}O_2N$	4.15	$[M+H]^+$	260.1645	260.1647	0.77
Ranitidine	$C_{13}H_{22}N_4O_3S$	1.44	$[M+H]^+$	315.1485	315.1485	0.00
Robenidine	$C_{18}H_{23}NO_3$	3.43	$[M+H]^+$	302.1751	302.1748	-0.99
Ronidazole	$C_6H_8N_4O_4$	1.55	$C_5H_6N_3O_2^+$	140.0455	140.0454	-0.71
Roxithromycin	$C_{41}H_{76}N_2O_{15}$	4.74	$[M+H]^+$	837.5318	837.5299	-2.27
Salbutamol	$C_{13}H_{21}NO_3$	1.01	$[M+H]^+$	240.1594	240.1596	0.83
Sarafloxacin	$C_{20}H_{17}F_2N_3O_3$	3.69	$[M+H]^+$	386.1311	386.1306	-1.29
Spiramycin	$C_{43}H_{74}N_2O_{14}$	3.79	$[M+H]^+$	843.5213	843.5215	0.24
Streptomycin	$C_{21}H_{39}N_7O_{12}$	0.24	$C_8H_{19}N_6O_4^+$	263.1462	263.1466	1.52
Sulfabenzamide	$C_{13}H_{12}N_2O_3S$	4.30	$C_6H_6NO_2S^+$	156.0114	156.0108	-3.85
Sulfacetamide	$C_8H_{10}N_2O_3S$	1.33	$C_6H_6NO_2S^+$	156.0114	156.0114	0.00
Sulfachloropyridazine	$C_{10}H_9ClN_4O_2S$	3.80	$[M+H]^+$	285.0208	285.0210	0.07
Sulfadiazine	$C_{10}H_{10}N_4O_2S$	1.63	$[M+H]^+$	251.0597	251.0597	0.00

Table 1 (continued)

Compound	Elemental composition (M)	t_R (min)	Ion	Theoretical *m/z*	Experimental *m/z*	Error (ppm)
Sulfadimethoxyn	$C_{12}H_{14}N_4O_4S$	4.39	$[M+H]^+$	311.0809	311.0805	-0.13
Sulfadoxine	$C_{12}H_{14}N_4O_4S$	3.94	$[M+H]^+$	311.0809	311.0812	0.96
Sulfaguanidine	$C_7H_{10}N_4O_2S$	0.47	$[M+H]^+$	215.0597	215.0596	-0.46
Sulfamerazine	$C_{11}H_{12}N_4O_2S$	2.90	$[M+H]^+$	265.0754	265.0754	0.00
Sulfameter	$C_{11}H_{12}N_4O_3S$	3.51	$[M+H]^+$	281.0703	281.0701	-0.71
Sulfamethazine	$C_{12}H_{14}N_4O_2S$	3.32	$[M+H]^+$	279.0910	279.0911	0.36
Sulfamethizole	$C_9H_{10}N_4O_2S_2$	3.49	$[M+H]^+$	271.0318	271.0318	0.00
Sulfamethoxazole	$C_{10}H_{11}N_3O_3S$	3.97	$[M+H]^+$	254.0594	254.0594	0.00
Sulfamethoxypyridazine	$C_{11}H_{12}N_4O_3S$	3.53	$[M+H]^+$	281.0703	281.0703	0.00
Sulfamonomethoxine	$C_{11}H_{12}N_4O_3S$	3.74	$[M+H]^+$	281.0703	281.0703	0.00
Sulfanilamide	$C_6H_8N_2O_2S$	0.54	$[M+H]^+$	173.0379	173.0380	0.58
Sulfapyridine	$C_{11}H_{11}N_3O_2S$	2.68	$[M+H]^+$	250.0645	250.0646	0.40
Sulfaquinoxaline	$C_{14}H_{12}N_4O_2S$	4.38	$[M+H]^+$	301.0754	301.0752	-0.66
Sulfathiazole	$C_9H_9N_3O_2S_2$	2.51	$[M+H]^+$	256.0209	256.0210	0.39
Sulfisoxazol	$C_{11}H_{13}N_3O_3S$	4.14	$[M+H]^+$	268.0750	268.0750	0.00
Sulindac	$C_{20}H_{17}FO_3S$	4.93	$[M+H]^+$	357.0955	357.0957	0.00
Tetracycline	$C_{22}H_{24}N_2O_8$	3.46	$[M+H]^+$	445.1605	445.1601	-0.90
Theobromine	$C_7H_8N_4O_2$	1.08	$[M+H]^+$	181.0720	181.0719	-0.55
Theophylline	$C_7H_8N_4O_2$	1.87	$[M+H]^+$	181.0720	181.0721	0.55
Thiamphenicol	$C_{12}H_{15}Cl_2NO_5S$	3.32	$[M-H]^-$	353.9975	353.9964	-3.11
Tilmicosin	$C_{46}H_{80}N_2O_{13}$	4.02	$[M+2H]^{2+}$	435.2903	435.2901	-0.46
Tolfenamic acid	$C_{14}H_{12}ClNO_2$	6.39	$[M+H]^+$	262.0629	262.0633	1.53
Tolmetin	$C_{15}H_{15}NO_3$	5.13	$[M+H]^+$	258.1125	258.1121	-1.55
Triclocarban	$C_{13}H_9Cl_3ON_2$	6.63	$[M+H]^+$	314.9853	314.9850	-0.95
Trimethoprim	$C_{14}H_{18}N_4O_3$	3.22	$[M+H]^+$	291.1452	291.1451	-0.34
Tylosin	$C_{46}H_{77}NO_{17}$	4.43	$[M+H]^+$	916.5264	916.5257	-0.76
ß-Estradiol	$C_{18}H_{24}O_2$	5.16	$C_{18}H_{23}O^+$	255.1743	255.1748	1.96
Food-packaging contaminants						
1,3-Phenylenediamine	$C_6H_8N_2$	0.29	$[M+H]^+$	109.0760	109.0757	-2.75
2-EHDP	$C_{20}H_{27}O_4P$	7.55	$C_{12}H_{12}O_4P^+$	251.0468	251.0476	3.19
2-Methoxy-5-methylalanine	$C_8H_{11}ON$	1.70	$[M+H]^+$	138.0913	138.0912	-0.72
2,4-Diaminoanisole	$C_7H_{10}N_2O$	0.41	$[M+H]^+$	139.0866	139.0867	0.72
2,4-Diaminotoluene	$C_7H_{10}N_2$	0.40	$[M+H]^+$	123.0917	123.0920	2.44
2,4-Dimethylaniline	$C_8H_{11}N$	1.72	$[M+H]^+$	122.0964	122.0963	-0.82
2,4,5-Trimethylaniline	$C_9H_{13}N$	3.27	$[M+H]^+$	136.1121	136.1120	-2.18
2,6-Diaminotoluene	$C_7H_{10}N_2$	0.40	$[M+H]^+$	123.0917	123.0915	0.81
4-Aminobiphenyl	$C_{12}H_{11}N$	4.16	$[M+H]^+$	170.0964	170.0962	-1.18
4-Chloroaniline	C_6H_6ClN	1.60	$[M+H]^+$	128.0262	128.0261	-0.78
4-Hexylresorcinol	$C_{12}H_{18}O_2$	5.77	$[M+H]^+$	195.1380	195.1395	7.69
Aniline	$C_6H_5NH_2$	0.44	$[M+H]^+$	94.0651	94.0655	4.25
Benzyl butyl phthalate	$C_{19}H_{20}O_4$	6.88	$C_7H_7^+$	91.0542	91.0547	5.49
Bisphenol A	$C_{15}H_{16}O_2$	5.10	$[M-H]^-$	227.1078	227.1079	0.44
BA(2,3-DHP)GE	$C_{21}H_{26}O_5$	5.25	$[M+NH_4]^+$	376.2118	376.2119	0.27
BA(3Cl,2HP)(2,3DHP)E	$C_{21}H_{27}ClO_5$	5.22	$[M+COOH]^-$	439.1529	439.1529	0.00
BA(3Cl2HP)GE isomer 1	$C_{21}H_{25}ClO_4$	6.22	$[M+NH_4]^+$	394.1780	394.1774	-1.52
BA(3Cl2HP)GE isomer 2	$C_{21}H_{25}ClO_4$	6.41	$[M+NH_4]^+$	394.1780	394.1785	1.27
BAB(2,3DHP)E	$C_{21}H_{28}O_6$	4.44	$C_{12}H_{17}O_3^+$	209.1172	209.1171	-0.48
Bisphenol A diglycidyl ether	$C_{21}H_{24}O_4$	6.31	$[M+NH_4]^+$	358.2013	358.2011	-0.56
Butyl *p*-hydroxybenzoate	$C_{11}H_{14}O_3$	5.45	$[M-H]^-$	193.0870	193.0868	-1.04

Table 1 (continued)

Compound	Elemental composition (M)	t_R (min)	Ion	Theoretical *m/z*	Experimental *m/z*	Error (ppm)
Di (2-ethylhexyl)adipate (DEHA)	$C_{22}H_{42}O_4$	8.77	$[M+Na]^+$	393.2975	393.2980	1.27
Dibutyl sebacate	$C_{18}H_{34}O_4$	7.95	$[M+H]^+$	315.2530	315.2536	1.90
Dicyclohexyl phthalate	$C_{20}H_{26}O_4$	7.64	$C_8H_5O_3^+$	149.0233	149.0230	0.67
Diethyl phthalate	$C_{12}H_{14}O_4$	5.50	$C_8H_5O_3^+$	149.0233	149.0240	4.70
Diisodecyl phthalate	$C_{28}H_{46}O_4$	9.65	$[M+H]^+$	447.3469	447.3479	2.24
Diisononyl phthalate	$C_{26}H_{42}O_4$	8.96	$[M+H]^+$	419.3156	419.3156	0.00
Dimethyl phthalate	$C_{10}H_{10}O_4$	4.71	$C_9H_7O_3^+$	163.0390	163.0391	0.61
Di-*N*-butyl phthalate	$C_{16}H_{22}O_4$	6.97	$C_8H_5O_3^+$	149.0233	149.2040	4.70
Di-*N*-octyl phthalate iso. 1	$C_{24}H_{38}O_4$	8.88	$[M+H]^+$	391.2843	391.2843	0.00
Di-*N*-octyl phthalate iso. 2	$C_{24}H_{38}O_4$	8.94	$[M+H]^+$	391.2843	391.2847	1.02
Dipropyl phthalate	$C_{14}H_{18}O_4$	6.29	$C_8H_5O_3^+$	149.0233	149.0236	2.01
Ethyl 4-hydroxybenzoate	$C_9H_{10}O_3$	4.58	$[M-H]^-$	165.0557	165.0556	-0.61
Melamine	$C_3H_6N_6$	0.26	$[M+H]^+$	127.0727	127.0733	4.72
Methyl paraben	$C_8H_8O_3$	4.08	$[M-H]^-$	151.0401	151.0413	7.94
N,*N*-diethylhydroxylamine	$C_4H_{11}NO$	0.41	$[M+H]^+$	90.0913	90.0912	-1.11
Nordihydroguaiaretic acid	$C_{18}H_{22}O_4$	5.17	$[M-H]^-$	301.1445	301.1462	5.65
o-Anisidine	C_7H_9ON	0.65	$C_6H_7NO^+$	109.0522	109.0525	2.75
o-Toluidine	C_7H_9N	0.79	$[M+H]^+$	108.0808	108.0811	2.78
Propyl 4-hydroxybenzoate	$C_{10}H_{12}O_3$	5.06	$[M-H]^-$	179.0714	179.0710	-2.23
Tributyl *o*-acetylcitrate	$C_{20}H_{34}O_8$	7.38	$[M+H]^+$	403.2326	403.2333	1.79
Tributyl phosphate	$C_{12}H_{27}PO_4$	6.43	$H_4PO_4^+$	98.9842	98.9847	5.05
Triethyl phosphate	$C_6H_{15}O_4P$	4.03	$H_4PO_4^+$	98.9842	98.9847	5.05
Tris(chloropropyl)phosphate (TCPP)	$C_9H_{18}Cl_3O_4P$	5.65	$C_4H_9Cl_2O_3^+$	174.9923	174.9922	-0.57
Mycotoxins						
3-Acetyldeoxynivalenol	$C_{17}H_{22}O_7$	3.84	$[M+H]^+$	339.1438	339.1447	2.65
Aflatoxin B_1	$C_{17}H_{12}O_6$	4.66	$[M+H]^+$	313.0707	313.0704	-0.96
Aflatoxin B_2	$C_{17}H_{14}O_6$	4.49	$[M+H]^+$	315.0863	315.0861	-0.63
Aflatoxin G_1	$C_{17}H_{12}O_7$	4.51	$[M+H]^+$	329.0656	329.0656	0.00
Aflatoxin G_2	$C_{17}H_{14}O_7$	4.32	$[M+H]^+$	331.0812	331.0813	0.30
Aflatoxin M_1	$C_{17}H_{12}O_7$	4.18	$[M+H]^+$	329.0656	329.0657	0.30
Alfa zearalenol	$C_{18}H_{24}O_5$	5.22	$C_{18}H_{23}O_4^+$	303.1591	303.1593	0.66
Citrinin	$C_{13}H_{14}O_5$	5.03	$[M+H]^+$	251.0914	251.0915	0.40
Cyclopiazonic acid	$C_{20}H_{20}N_2O_3$	6.11	$[M+H]^+$	337.1547	337.1549	0.59
Deoxynivalenol	$C_{15}H_{20}O_6$	2.37	$[M+H]^+$	297.1333	297.1340	2.36
Diacetoxyscirpenol	$C_{19}H_{26}O_7$	4.56	$[M+Na]^+$	389.1571	389.1571	0.00
Ergocornine isomer 1	$C_{31}H_{39}N_5O_5$	4.30	$[M+H]^+$	562.3024	562.3016	-1.42
Ergocornine isomer 2	$C_{31}H_{39}N_5O_5$	4.40	$[M+H]^+$	562.3024	562.3017	-1.24
Fumonisin B_1	$C_{34}H_{59}NO_{15}$	4.41	$[M+H]^+$	722.3957	722.3934	-3.18
Fumonisin B_2	$C_{34}H_{59}NO_{14}$	4.78	$[M+H]^+$	706.4008	706.3995	-1.84
Gliotoxin	$C_{13}H_{14}N_2O_4S_2$	4.45	$C_{13}H_{15}N_2O_4^+$	263.1026	263.1030	1.52
HT-2 toxin	$C_{22}H_{32}O_8$	4.77	$[M+H]^+$	425.2170	425.2169	-0.24
Ochratoxin A	$C_{20}H_{18}ClNO_6$	5.63	$[M+H]^+$	404.0895	404.0890	-1.24
Patulin	$C_7H_6O_4$	1.09	$[M+H]^+$	155.0339	155.0341	1.29
Sterigmatocystin	$C_{18}H_{12}O_6$	5.81	$[M+H]^+$	325.0707	325.0704	-0.92
T2-toxin	$C_{24}H_{34}O_9$	5.40	$[M+Na]^+$	489.2095	489.2096	0.20
Zearalenone	$C_{18}H_{22}O_5$	5.66	$[M+H]^+$	319.1540	319.1539	-0.31
Perfluorinated compounds						
C_3 pentafluoropropionic acid	$C_3F_5HO_2$	0.81	$C_2F_5^-$	118.9926	118.9927	0.84
C_4 perfluorobutyric acid	$C_4F_7HO_2$	2.96	$C_3F_7^-$	168.9894	168.9898	2.37

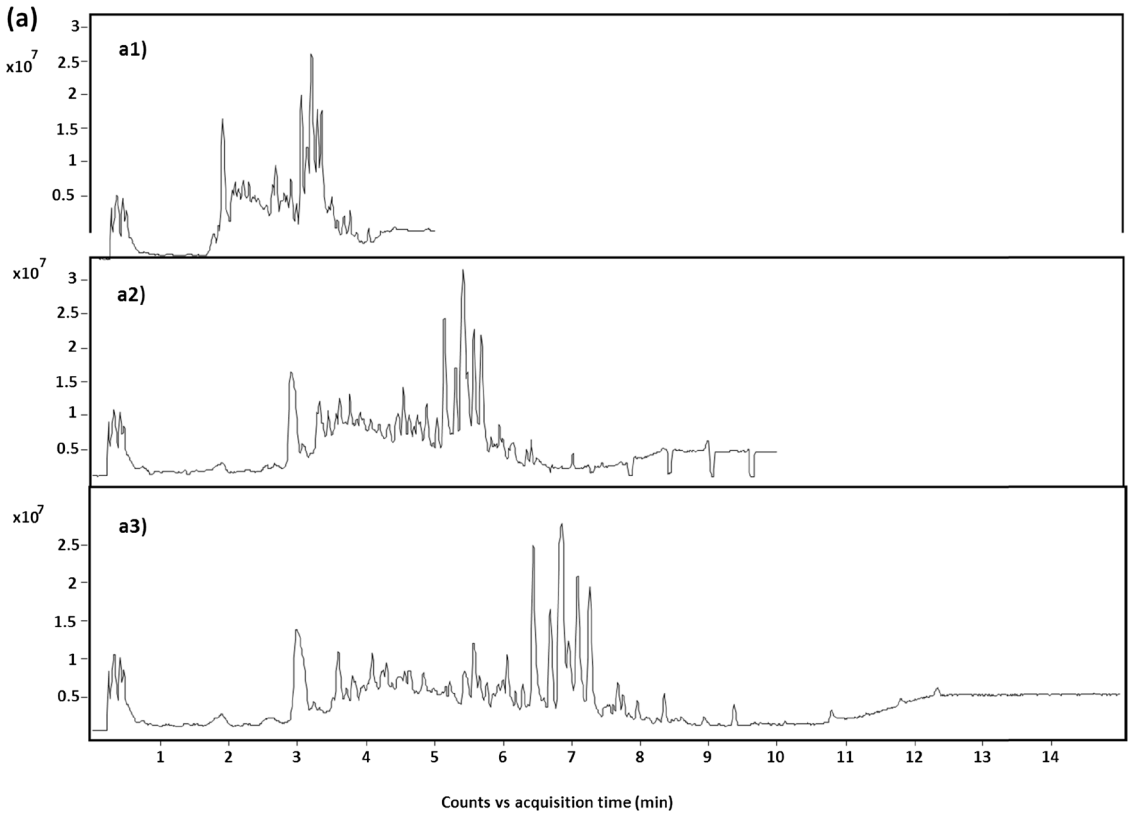
Table 1 (continued)

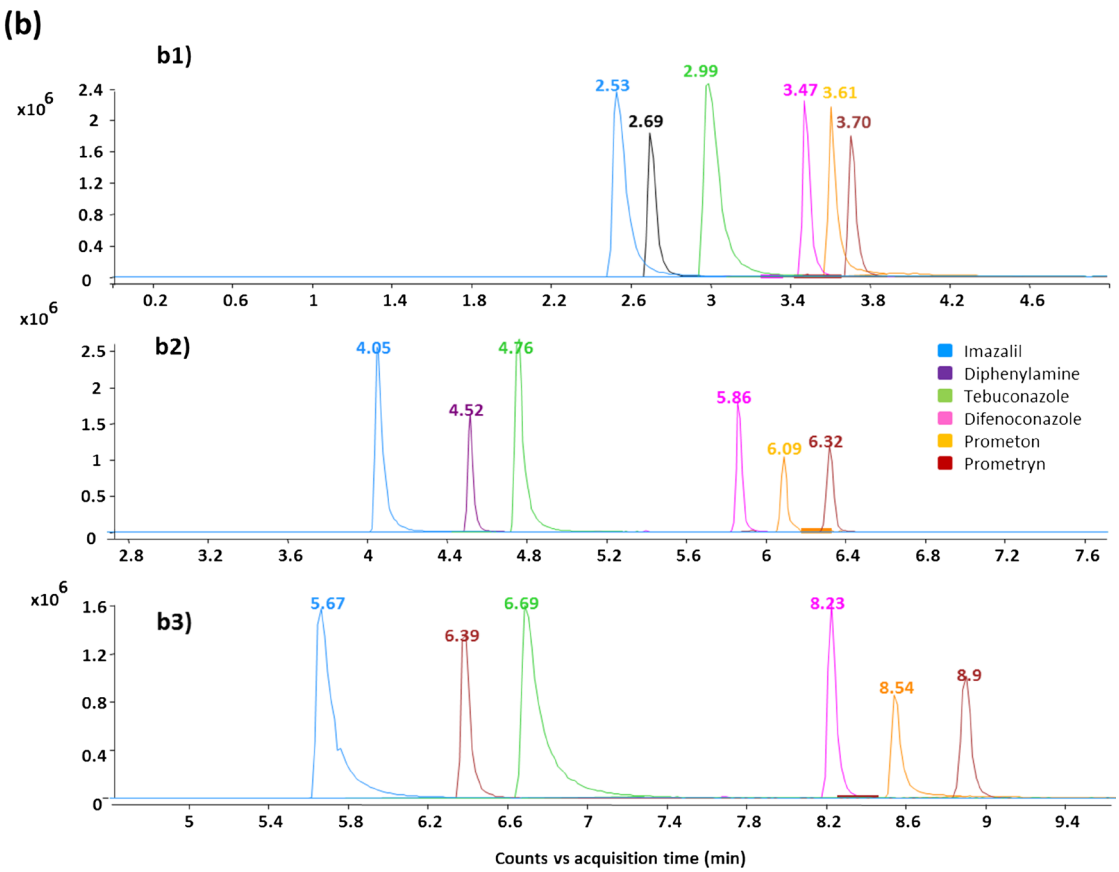
Compound	Elemental composition (M)	t_R (min)	Ion	Theoretical *m/z*	Experimental *m/z*	Error (ppm)
C_5 perfluoropentanoic acid	$C_5HO_2F_9$	4.09	$C_4F_9^-$	218.9862	218.9867	2.28
C_7 perfluoroheptanoic acid	$C_7HO_2F_{13}$	5.05	$C_6F_{13}^-$	318.9798	318.9814	5.02
C_8 perfluorooctanoic acid	$C_8F_{15}O_2H$	5.47	$C_7F_{15}^-$	368.9766	368.9781	4.07
C_9 perfluorononanoic acid	$C_9F_{17}O_2H$	5.89	$C_8F_{17}^-$	418.9734	418.9755	5.01
C_{10} perfluorodecanoic acid	$C_{10}F_{19}O_2H$	6.33	$C_9F_{19}^-$	468.9702	468.9714	2.56
C_{11} perfluoroundecanoic acid	$C_{11}F_{21}O_2H$	6.81	$C_{10}F_{21}^-$	518.9670	518.9682	2.31
C_{12} perfluorododecanoic acid	$C_{12}F_{23}O_2H$	7.35	$C_{11}F_{23}^-$	568.9638	568.9629	-1.58
Heptadecafluorooctane sulfonic acid	$C_8HSO_3F_{17}$	6.66	$[M-H]^-$	498.9302	498.9327	5.01
Nitrosamines						
N-nitrosodiethylamine	$C_4H_{10}N_2O$	2.24	$[M+H]^+$	103.0866	103.0862	3.88
N-nitrosodimethylamine	$C_2N_2H_6O$	0.51	$[M+H]^+$	75.0553	75.0556	4.00
N-nitrosodi-*n*-dibutylamine	$C_8H_{18}N_2O$	5.75	$[M+H]^+$	159.1492	159.1494	1.26
N-nitrosodi-*n*-dipropylamine	$C_6H_{14}N_2O$	4.62	$[M+H]^+$	131.1174	131.1177	-1.53
N-nitrosomethylethylamine	$C_3H_8N_2O$	0.89	$[M+H]^+$	89.0709	89.0715	6.74
N-nitrosomorpholine	$C_4H_8N_2O_2$	0.75	$[M+H]^+$	117.0659	117.0660	0.85
N-nitroso-*n*-diphenylamine	$C_{12}H_{10}N_2O$	5.94	$C_9H_{11}N^+$	169.0886	169.0885	-0.94
N-nitrosopiperidine	$C_5H_{10}N_2O$	2.96	$[M+H]^+$	115.0866	115.0866	0.00
N-nitrosopyrrolidine	$C_4H_8N_2O$	0.96	$[M+H]^+$	101.0709	101.0710	0.99
Sweeteners						
Aspartame	$C_{14}H_{18}N_2O_5$	3.38	$[M-H]^-$	293.1143	293.1152	3.07
Acesulfame	$C_4H_5NO_4S$	0.63	$[M-H]^-$	161.9867	161.9871	2.47
Saccharin	$C_7H_5NO_3S$	1.25	$[M-H]^-$	181.9917	181.9921	2.20
Sucralose	$C_{12}H_{19}Cl_3O_8$	3.40	$[M-H]^-$	395.0073	395.0091	4.56
Cyclamate	$C_6H_{12}NO_3S$	1.45	$[M-H]^-$	178.0538	178.0538	0.00

2-EHDP 2-ethylhexyl diphenyl phosphate, *BA(2,3-DHP)GE* bisphenol A (2,3-dihydroxypropyl) glycidyl ether, *BA(3Cl,2HP)(2,3DHP)E* bisphenol A (3-chloro-2-hydroxypropyl) (2,3-dihydroxypropyl) ether, *BA(3Cl,2HP)GE* bisphenol A (3-chloro,2-hydroxypropyl) glycidyl ether, *BAB (2,3DHP)E* bisphenol A bis(2,3-dihydroxypropyl) ether

Agilent Technologies, Santa Clara, CA, USA), consisting of a vacuum degasser, an autosampler, and a binary pump. Mobile phases A and B were water and acetonitrile, respectively, both with 0.1 % formic acid. The flow rate used was 0.5 mL min^{-1}. The chromatographic method held the initial mobile phase composition (5 % B) constant for 2 min, followed by a linear gradient to 100 % B at 8 min and held constant for a 2 min at 100 % B. Twenty microliters of extract was injected in each study. A 5-min post-time was used for each analysis.

The UHPLC system was connected to a quadrupole-time-of-flight mass spectrometer Agilent Q-TOF 6530 (Agilent Technologies, Santa Clara, CA, USA) equipped with an electrospray interface operated in either positive or negative ionization mode, using the following operation parameters: capillary voltage, 4000 V; nebulizer pressure, 40 psig; drying gas, 9 L min^{-1}; gas temperature, 325 °C; and fragmentor voltage, 90 V. LC-MS accurate mass spectra were recorded across the range *m/z* 50–1000. Two different experiments were conducted, full-scan acquisition and *all-ion mode* MS/MS, in order to perform CID experiments in a dedicated collision cell with no precursor ion isolation along with high-resolution full-scan acquisition. *All-ion mode* full-scan acquisition was used at two different collision energy conditions (0 (full scan with no fragmentation) and 20 V), using 400 ms for each experiment (1.25 spectra/acquisition points per second). Accurate mass measurements of each peak from the total ion chromatograms were obtained by means of an automated calibrant delivery system using a dual-nebulizer electrospray source that introduces the flow from the outlet of the chromatograph together with a low flow of a calibrating solution (calibrant solution A, Agilent Technologies), which contains the internal reference masses (purine ($C_5H_4N_4$ at *m/z* 121.050873 and HP-0921 [hexakis-(1H,1H,3H-tetrafluoropentoxy)-phosphazene] ($C_{18}H_{18}O_6N_3P_3F_{24}$) at *m/z* 922.009798). All data was recorded with Agilent MassHunter Data Acquisition software (version B.04.00) and processed with Agilent MassHunter Qualitative Analysis software (version B.04.00), which included both *Molecular Feature Extractor* and *Find by Formula* applications used.


(a)
a1)
a2)
a3)
x10^7
Counts vs acquisition time (min)


(b)
b1)
b2)
b3)
x10^6
2.53
2.69
2.99
3.47
3.61
3.70
4.05
4.52
4.76
5.86
6.09
6.32
5.67
6.39
6.69
8.23
8.54
8.9
Imazalil
Diphenylamine
Tebuconazole
Difenoconazole
Prometon
Prometryn
Counts vs acquisition time (min)

◀ **Fig. 1** **a** Total ion chromatograms (TICs) of a pesticide mixture (100 μg kg^{-1}) in orange using elution gradients A (*a1*), B (*a2*), and C (*a3*). **b** Extracted ion chromatograms (EICs) of some database compounds (imazalil, diphenylamine, tebuconazole, difenoconazole, prometon, and prometryn (100 μg L^{-1}) in orange with elution gradients A (*b1*), B (*b2*), and C (*b3*)

Development of an Accurate Mass Database of 630 Multiclass Food Contaminant Pollutants Mixtures containing ca. 30–50 compounds, at individual concentrations of 200 μg L^{-1} each, were injected in the UHPLC-QTOFMS system to collect retention time (t_R) data and the accurate masses of target ions together with the elemental composition. For confirmatory purposes, the mass spectra acquired using all-ion mode acquisition were carefully investigated to identify characteristic fragment ions. In some cases, individual standards of target compounds were required for further confirmation of diagnostic fragment ions. For the screening method step, an Excel spreadsheet was constructed containing for each analyte the compound name, molecular formula, theoretical exact mass, fragment ions, and retention time. This file was converted into csv format for use by the Agilent MassHunter Data Acquisition software (version B.04.00). When a sample run is completed and the corresponding raw data acquired, its components are automatically matched against the csv file (Find by formula application) by the MassHunter software taking into account a defined tolerance for mass and retention time deviations (t_R ± 0.25 min and ion exact mass ± 10 ppm), and a report is generated with the compounds tentatively found in the analyzed sample data file.

Results and Discussion

Screening Method Development and General Acquisition Method Considerations

Selection of UHPLC Gradient Before developing the screening method, different elution gradients were assayed using matrix-matched standards in representative matrices (such as tomato and orange) in order to obtain appropriate separation of analytes and matrix components within the shortest time period while displaying relatively low or moderate signal suppression effects. Three methods (A, B, and C) were assayed by varying the total gradient time, using the same flow rate (0.5 mL min^{-1}) and mobile phases (total time of 5, 10, and 15 min, respectively). Mobile phases were 0.1 % HCOOH in water (A) and 0.1 % HCOOH in acetonitrile (B). The details of the different gradient elution programs are shown in Table S1 (Electronic Supplementary Material (ESM)). An example on the analysis of a mixture of selected pesticides in orange and some representative extracted ion chromatograms (EICs) (100 μg kg^{-1}) are shown in Fig. 1. To develop the screening method, different criteria were employed to select the most appropriate elution gradient. The comparison of the total ion chromatograms (TICs) revealed that the matrix components and analytes were not separated properly with the shortest method. The number of coelutions and thus the possibility of interferences and quantitation issues due to matrix effects would be clearly increased under these conditions (method A). It must be taken into account the large number of components from a matrix (typically with 5000–10,000 (Gómez-Ramos et al. 2013; Gómez-Ramos et al. 2016) at relevant concentrations which must be separated. For this reason, the shortest method (method A) was discarded. Given the differences of run time, it would be expected that coelutions with method B were more frequent than with method C. This fact was further examined using matrix effects.

Matrix effects were evaluated using 15 representative analytes (including pesticides, veterinary drugs, and mycotoxins) in tomato and orange matrices with the two remaining methods (B and C). Matrix effects were calculated as follows: [(calibration curve slope in matrix / calibration curve slope in solvent) − 1] × 100. Positive values indicate signal enhancement while negative signal involves values suppression—the more common phenomenon. Depending on this percentage, matrix effect was classified in different categories, according to previous literature (Ferrer-Amate et al. 2010; González-Antuña et al. 2013). A percentage between −20 and 20 % was considered as mild matrix effect, as the slope ratios matrix/solvent would be approaching the unit. A medium matrix effect occurred when this percentage was from −50 to −20 % or from +20 to +50 %. Strong matrix effect would be produced when this percentage was below −50 % or above +50 %.

As shown in Fig. 2a, all the selected compounds showed signal suppression in tomato with both elution gradients B and C, with the exception of aflatoxin B_1, thiabendazole, and azoxystrobin. The extent of matrix effects was not significantly different between the two gradients (B and C). In the case of orange (Fig. 2b), all tested compounds showed signal suppression with both elution gradients assayed, although, in general, the matrix effects are slightly less intense in the case of the longer method. This is consistent with the fact that there is more time to separate species, thus minimizing the potential coelutions and the associated ionization competition and subsequent matrix suppression. As the main objective was to develop a screening method which separate and identify the most number of compounds in a single run in the shortest time possible, elution gradient B was selected.

Identification of the Targeted Species by UHPLC-Q-TOFMS A generic full-scan acquisition method with default source parameters was used for the mass spectrometric detection of the studied species. Default values were set for drying

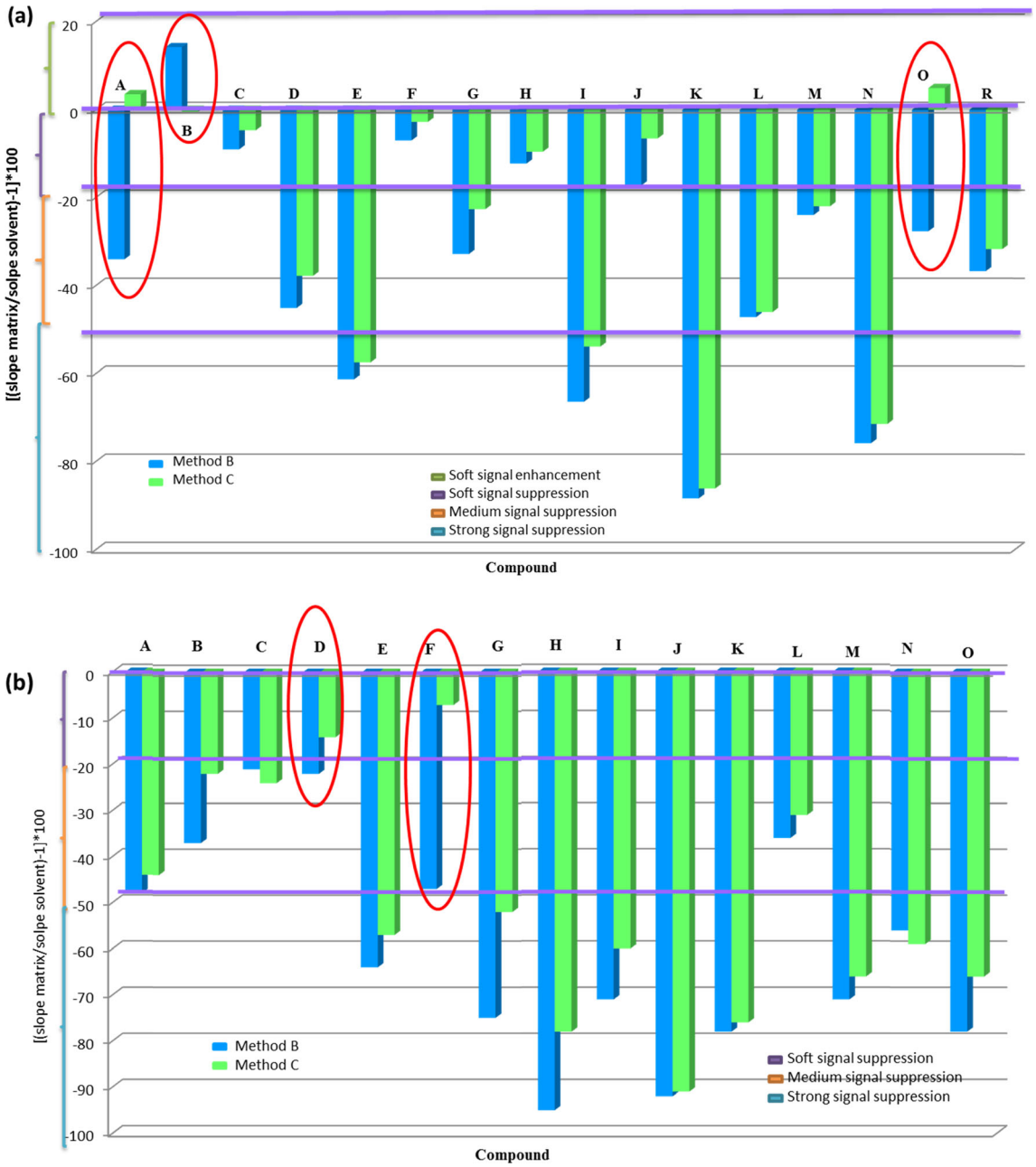


Fig. 2 **a** Percentages of signal suppression or enhancement for selected compounds in tomato (*A* aflatoxin B_1; *B* azoxystrobin; *C* buprofezin; *D* carbendazim; *E* cyromazine; *F* DEET; *G* diuron; *H* imazalil; *I* imidacloprid; *J* prochloraz; *K* sarafloxacin; *L* sulfamethoxazole; *M* tebuconazole; *N* tetracycline; *O* thiabendazole; *R* thiacloprid). **b** Percentages of signal suppression or enhancement for selected compounds in orange (*A* aflatoxin B_1; *B* azoxystrobin; *C* buprofezin; *D* carbendazim; *E* cyromazine; *F* DEET; *G* diuron; *H* imidacloprid; *I* prochloraz; *J* sarafloxacin; *K* sulfamethoxazole; *L* tebuconazole; *M* tetracycline; *N* thiabendazole; *O* thiacloprid)

and nebulizer flow rates and pressures and drying gas temperatures considering the LC flow rate and mobile phase composition.

The identification of the target species was carried out using retention time values and accurate mass measurements of the (de)protonated molecules in most cases. Exceptionally, either sodium or ammonium adducts were identified as the most abundant ion for a few compounds (4 %). In general, 90 % of compounds were detected in positive ion mode whereas only 10 % of targeted compounds were identified in negative ionization mode. Additionally, for ca. 20 % of the species, it was found that fragments generated—from in-source CID during ion transportation—were more abundant than the corresponding (de)protonated molecules. The detailed information including detected ion, elemental composition, retention time, theoretical *m/z* (exact mass), and experimental measured accurate masses with the relative mass error (expressed in ppm) are shown in Table 1, where compounds

are grouped according to their class (pesticides, veterinary drugs, mycotoxins, perfluorinated compounds, food-packaging contaminants, nitrosamines, and sweeteners). For confirmation of the species, acquisition with the UHPLC-Q-TOFMS instrument was undertaken in the "all-ion mode" acquisition mode. This consists on the use of CID fragmentation in a collision cell without previous precursor isolation, so that all ions entering the mass spectrometer are subjected to thorough fragmentation, thus avoiding restrictions on the number of coeluting compounds subjected to MS/MS and also previous information required information to conduct the MS/MS experiments such as retention time windows or precursor ion masses. The acquisition method proposed consisted on two full-scan experiments with the collision cell different collision energies: 0 V (no fragmentation) and 20 V (fragmentation), using an acquisition time of 400 ms for each experiment. With such experiments, at least two ions were obtained for identification/purposes in most cases with the exception of few low molecular weight molecules, difficult to fragment.

Study of Searching Parameters for Automated Screening

A snapshot of the software application used (*Find by Formula tool*, Agilent MassHunter Qualitative Analysis (version B.04.00)) is shown in Fig. 3 along with the main information included in the database. The main search parameters (accurate mass tolerance and retention time (t_R) window) affecting the performance of the automated search using *Find by Formula* tool were carefully examined. Different experiments were assayed varying t_R windows (±0.05, ±0.1, ±0.25,

Elemental Composition	RT	Mass (M)	Compound	Comments
C25H24F6N4	6.02	494.1905	Hydramethylnon	pesticide
C14H14Cl2N2O	4.52	296.0483	Imazalil	pesticide
C9H10Cl2N2O	3.69	256.017	Imazalil Metabolite	pesticide
C16H20N2O3	4.11	288.1474	Imazamethabenz-Methyl	pesticide
C15H19N3O4	3.82	305.1376	Imazamox	pesticide
C13H15N3O3	3.41	261.1113	Imazapyr	pesticide
C17H17N3O3	4.56	311.127	Imazaquin	pesticide
C9H10ClN5O2	3.81	255.0523	Imidacloprid	pesticide
C22H17ClF3N3O7	6.79	527.0707	Indoxacarb	pesticide
C7H3I2NO	5.41	370.8304	Ioxinil	pesticide
C13H13N3Cl2O3	6.6	329.0334	Iprodione	pesticide
C9H10	5.68	118.0783	Iprovalicarb F1	pesticide
C9H17N3O3PS	6.27	313.0417	Isazophos	pesticide
C15H24NO4PS	5.54	229.9803	Isocarbophos F1	pesticide
C15H23NO4	6.84	344.1085	Isofenphos f1	pesticide
C6H6O	5.18	94.0419	Isoprocarb F1	pesticide
C6H4O3S2	6.09	187.9602	Isoprothiolane F1	pesticide
C12H18N2O	5.04	206.1419	Isoproturon	pesticide

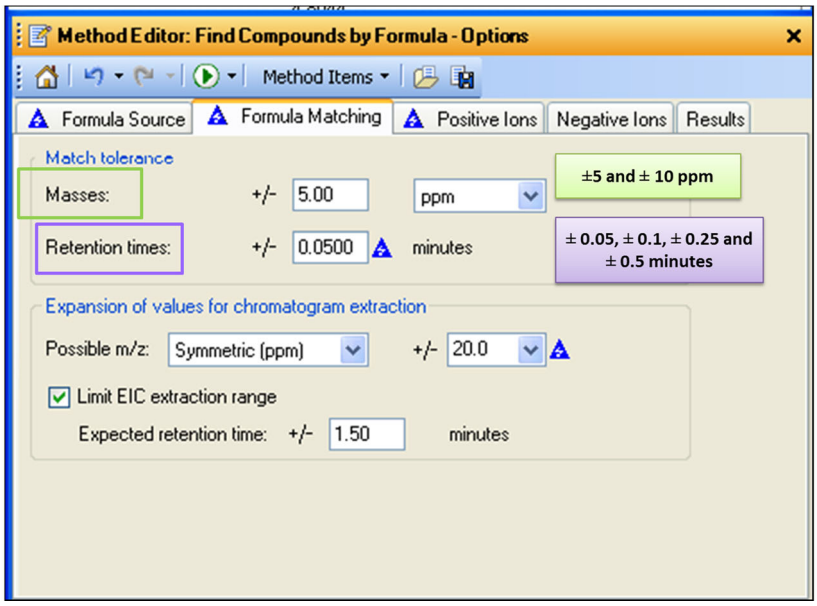


Fig. 3 **a** Csv file with relevant information (elemental composition, retention time, exact mass, compound name for the main ion of each compound) for the automatic search of compounds with Agilent MassHunter Qualitative Analysis software. **b** Selection of mass error tolerance and retention time window for the automatic search using the specific software

±0.5 min) with two fixed accurate mass tolerances (±5 or ±10 ppm). Default settings of peak filtering were used to remove background and mobile phase ion contribution. In these experiments, the database (630 compounds) was applied to 16 synthetic mixtures of pesticides (100 μg L^{-1}) with 30 compounds each. The number of false positives and negatives, average score (%), and success rate (%) were evaluated for each mixture. The term false positive meant that a compound was reported, but it was not present in the actual sample. On the other hand, a compound which was present in the synthetic mixture but not reported by the software after the automated search was a false negative.

In most cases, false negatives were due to two main reasons: (i) detector saturation occurring with high sensitive compounds or compounds at high concentrations and (ii) low sensitivity compounds with very low response factors—those which do not really perform properly mainly because of poor electrospray ionization. In the first scenario, spectra obtained displayed low score values due to accurate mass drifting with saturated detector and also due to the spectra collected which was not statistically representative of the sample. In the latter case, the concentration tested (100 μg L^{-1}) was not high enough to detect the compounds, and thus, they were reported as false negatives.

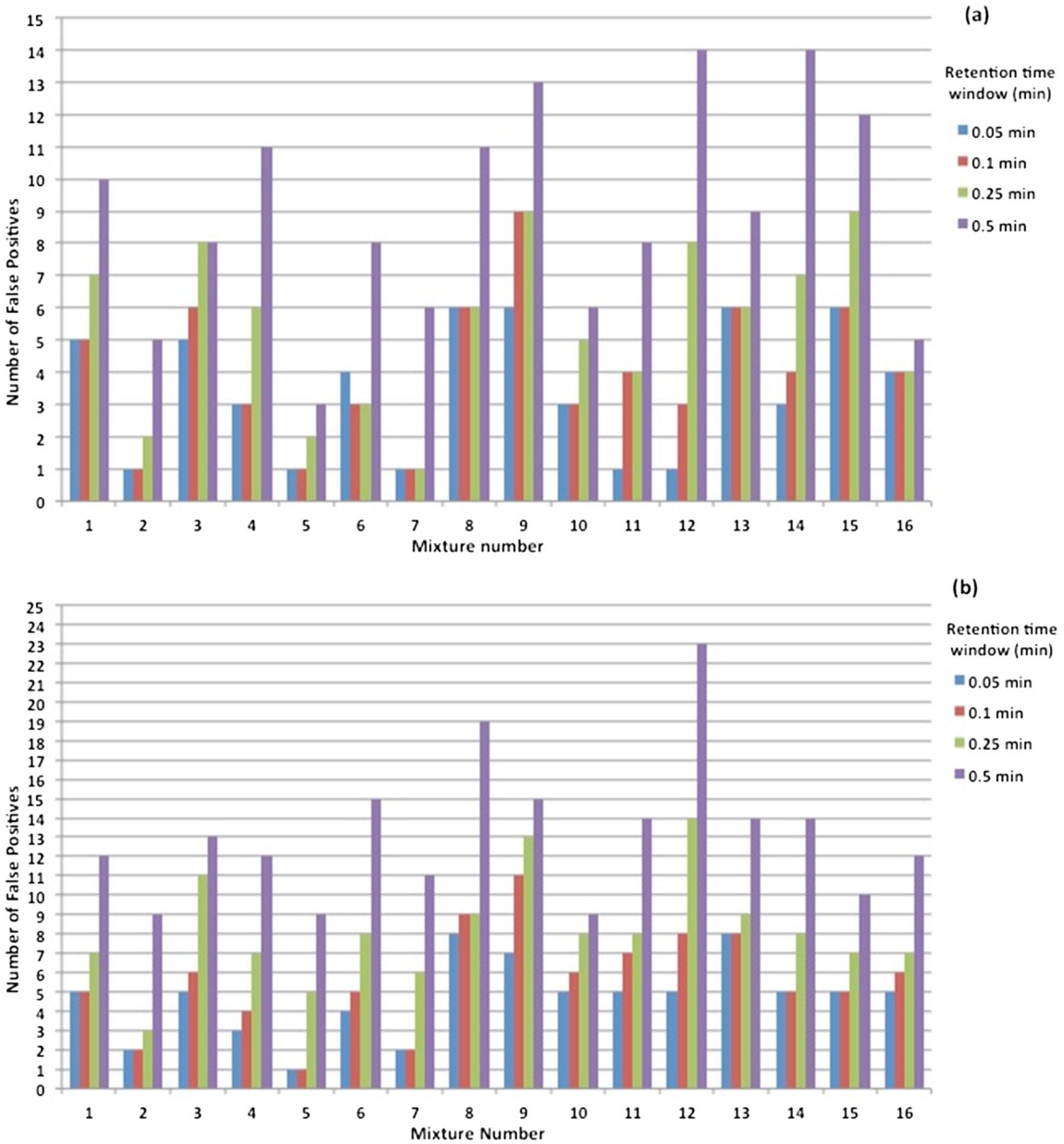


Fig. 4 **a** Number of false positives reported by the software when retention time windows varied from ±0.05 to ±0.5 min, using ±5 ppm as mass error tolerance. **b** Number of false positives reported by the software when retention time windows varied from ±0.05 to ±0.5 min, using ±10 ppm as mass error tolerance

Subtle differences were found in terms of the number of false negatives, average score, and success rate for each mixture using the experiments at different retention time and mass bias. In contrast, significant differences were found in the number of false positives, when different retention time windows were employed with ±5 and ±10 ppm as mass error tolerance. The results in terms of false positive rates obtained for each of the synthetic mixture tested (using ±5 and ±10 ppm as mass error tolerance) are shown in Fig. 4. The results are expressed in number of false positives (out of 630) related to the number of compounds expected (30 in each experiment).

The data collected concluded that wider retention time windows yielded a higher value of false positives. The highest number of compounds was reported when ±0.5 min was used and the lowest with ±0.05 min. Those results did not depend heavily on the mass error tolerance employed. In this sense, it should be kept in mind that complex food extracts may shift the retention times so that these results may be affected, particularly in the case of early eluting compounds (more affected by matrix, pH, and/or composition). For this reason, the narrowest retention time tolerance (± 0.05 min) was discarded. On the other hand, the results obtained using ±0.1 and ±0.25 min tolerances were relatively similar with minor differences in the number of false positives. Both tolerances could be adopted for the final method, although, in order to prevent false negatives due to retention time shifts particularly for polar compounds, and also due to relatively high mass errors obtained for small molecules with *m/z* lower than 150, ±0.25 min and ±10 ppm were finally selected as the most appropriate retention time window and mass error tolerance for screening step. Eventually, a final additional step would involve confirmation of the findings and accurate mass measurements of ions and fragments for each tentative compound detected, which would be within the widely accepted standard 5-ppm relative mass error threshold (or 1 mDa for molecules below 200 Da) (European Commission 2015)).

Analytical Performance Three representative food matrices (tomato, orange, and baby food) were employed to evaluate the performance of the proposed screening method in terms of linearity, matrix effects, and limits of quantification (LOQs). In order to avoid coelutions between analytes that could shift the actual performance in terms of matrix effects, mixtures containing ca. 30 compounds (each) were used to prepare the calibration curves in the concentration range from 1 to 1000 μg kg^{-1} (1, 10, 50, 100, 200, 500, and 1000) in solvent standards (20 % methanol), tomato, orange, and baby food extracts. LOQs were estimated as the minimum concentration of analyte corresponding to a signal-to-noise ratio (*S/N*) = 10:1. This was experimentally calculated from the injection of matrix-matched standards at low concentration levels, using the more abundant ion for each extracted ion chromatograms with narrow mass windows (±10 ppm relative mass error). In the case of pesticides, sample extracts were prepared by spiking samples before sample extraction step so that recovery percentages were considered. Results obtained for pesticides are detailed in Table S-2 (ESM), along with the maximum residue level (MRLs) established for the pesticide/commodity combinations tested. The data for the rest of classes studied is included in Table S-3 (ESM). They are also summarized in Fig. 5, and the overall data of LOQs for each individual group of compounds is included as Supplementary material (Figs. S1–S2). Most of pesticides and veterinary drugs showed limits of quantification from 1 to 10 μg kg^{-1} in tomato, orange, and baby food. The percentage of those compounds with LOQs < 1 μg kg^{-1} was higher in baby food and tomato than in orange. On the other hand, 65 % of food-packaging contaminants displayed LOQs <10 μg kg^{-1} in baby food. In tomato and orange, most of those compounds exhibited LOQs from 10 to 100 μg kg^{-1}. For the rest of compound classes tested (food-packaging contaminants, mycotoxins, and perfluorinated compounds), the highest percentage of compounds with LOQs > 10 μg kg^{-1} was obtained in orange extracts. This can be attributed to the complexity of the orange matrix (and the extent of matrix effects therein) compared to both tomato and baby food matrices, as clearly illustrated in Fig. 6. Examples of compounds detected in incurred food samples are shown in Fig. 7, where the extracted ion chromatograms and mass spectra of tebuconazole and imazalil detected in peach jam and oranges, respectively, are shown.

In the case of the pesticides, the LOQs obtained were contrasted with the MRLs for the pesticide/commodity combinations available. Considering the default MRLs for

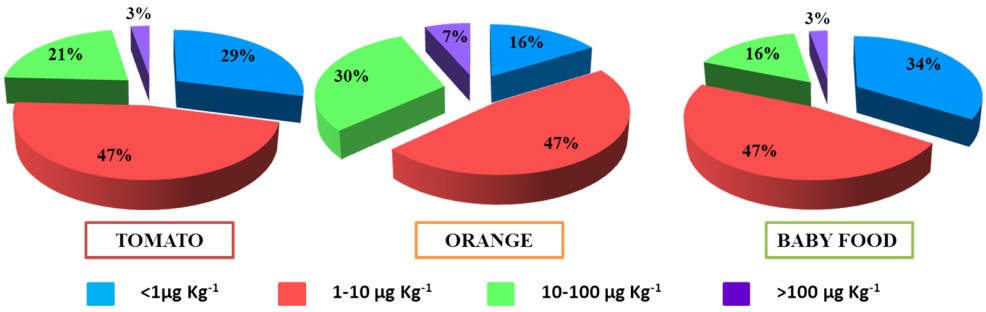


Fig. 5 Percentage of database compounds classified according to their LOQs in tomato, orange, and baby food

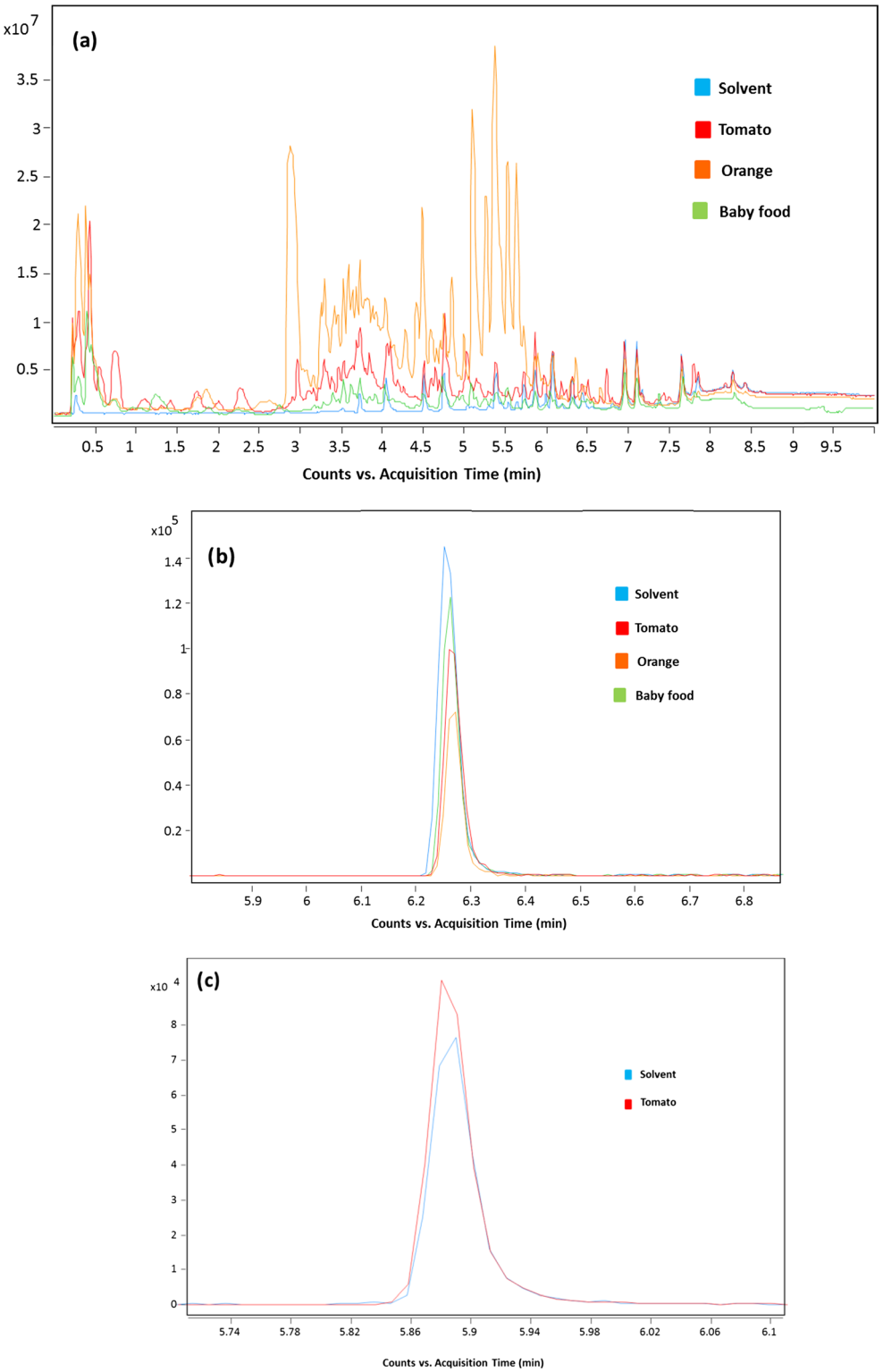


Fig. 6 **a** Overlapped total ion chromatograms (TICs) of a pesticide mixture (100 μg L^{-1}) in solvent, tomato, orange, and baby food. **b** Overlapped extracted ion chromatograms (EICs) of metribuzin (100 μg kg^{-1}) in solvent, tomato, orange, and baby food. **c** Overlapped extracted ion chromatograms (EICs) of fluquinconazole (200 μg kg^{-1}) in solvent and tomato

pesticides in baby food set at 10 μg kg^{-1}, over 90 % of the compounds fulfilled this threshold, being 56 above the value set, either because they were not recovered (e.g., highly polar compounds requiring dedicated sample treatment) or because of lower response factors. In the latter case, the compounds are low sensitive due to poor ionization with electrospray. As has been reported by other authors, there is always a percentage in the range of 10 %, which does not yield good response factors due to its features not compatible to electrospray (Alder et al. 2011; García-López et al. 2014), even despite using state-of-

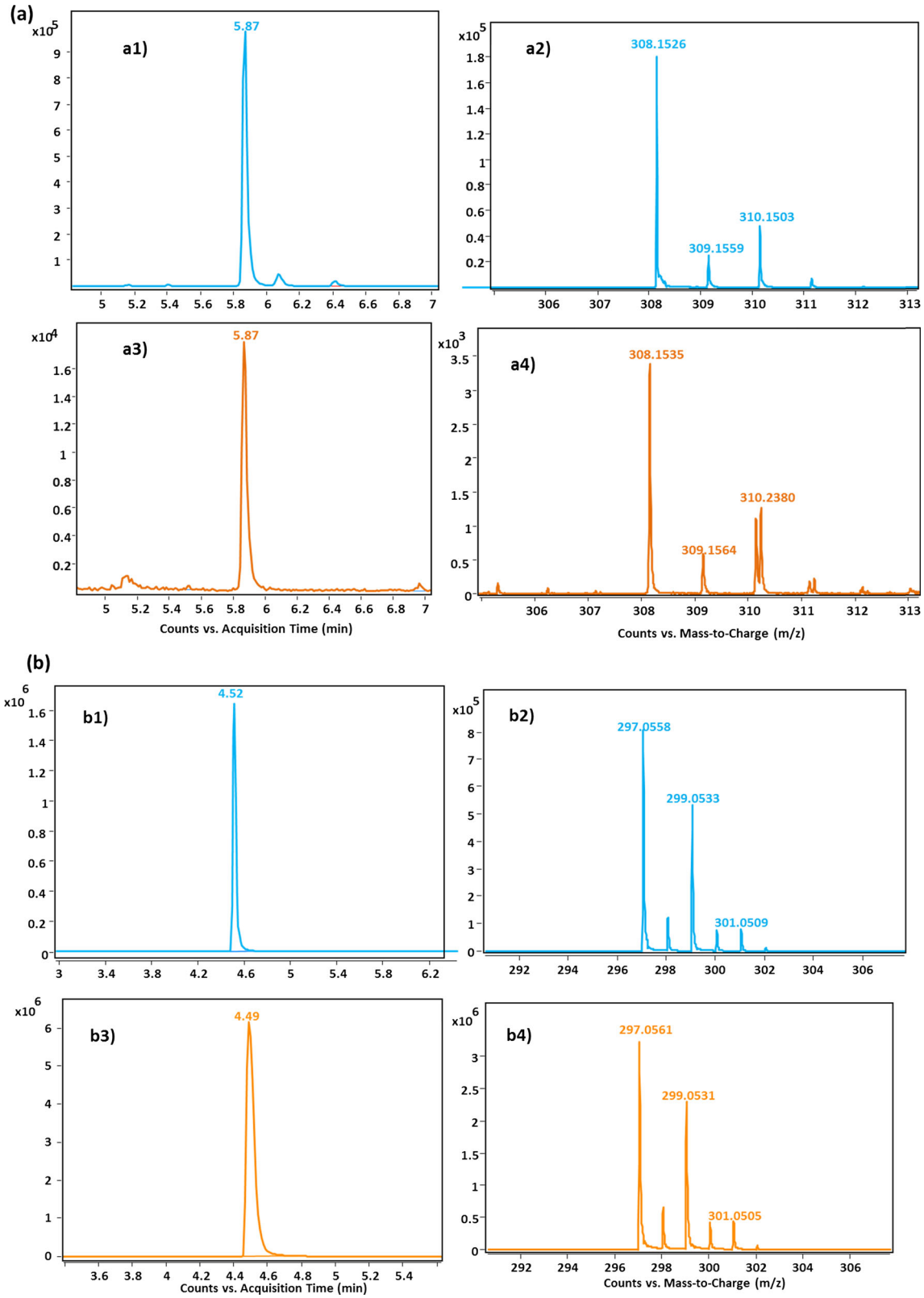


Fig. 7 **a** Extracted ion chromatogram (EIC) of tebuconazole in solvent (20 % methanol) (*a1*), mass spectrum of tebuconazole in solvent (20 % methanol) (*a2*), extracted ion chromatogram (EIC) of tebuconazole in peach jam (*a3*), and mass spectrum of tebuconazole in peach jam (*a4*). **b** Extracted ion chromatogram (EIC) of imazalil in solvent (20 % methanol) (*b1*) and mass spectrum of imazalil in solvent (20 % methanol) (*b2*). Extracted ion chromatogram (EIC) of imazalil in orange (*b3*) and mass spectrum of imazalil in orange (*b4*)

the-art instrumentation in some of the studies. In the case of tomato, despite 75 compounds (18 % out of 411 pesticides included) did not achieve the 10-μg kg $^{-1}$ sensitivity, only 47 were above the MRL value set (10 %), 24 not recovered, and 23 with LOQs above MRLs. Finally, in the case of orange, around 30 % was above the 10-μg kg $^{-1}$ threshold, with 85

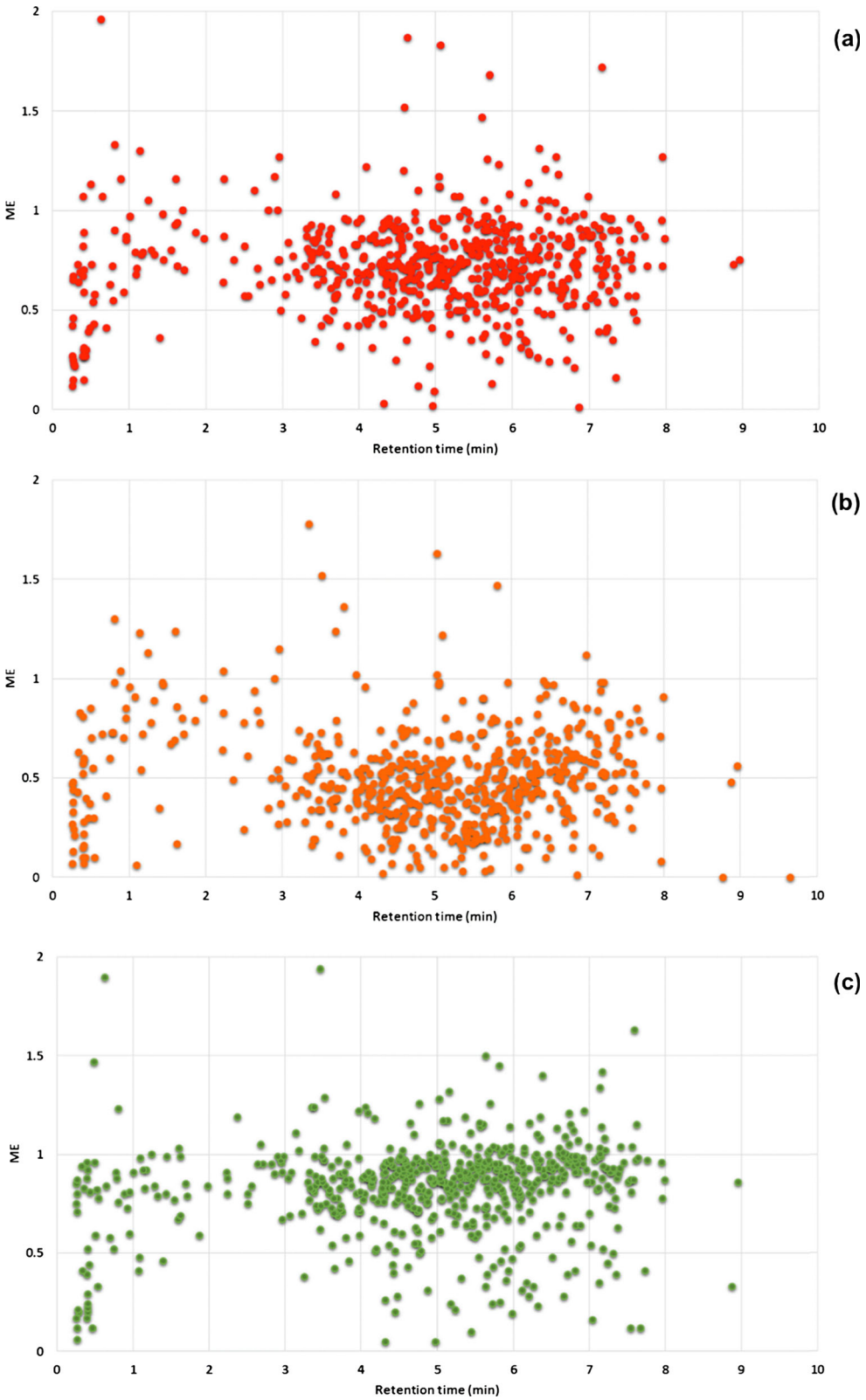


Fig. 8 2D plot representing matrix effects for the different compounds tested in **a** tomato, **b** orange, and **c** baby food. For details, see text

compounds (20 %) not fulfilling the MRL requirements. These results evidence one of the limitations of this type of screening approaches. The sensitivity is yet an issue, and this is more evident as the matrix complexity increases. With the use of state-of-the-art instrumentation, using heated electrospray source providing a remarkable sensitivity increase, there will always be a percentage of "difficult to ionize" compounds that would not fulfill the sensitivity requirements.

Besides the performance in terms of LOQs, matrix effects were also tested. Matrix effects usually occur during ionization step, where the matrix constituents influence the ionization of coeluted analyte(s). Coelution with matrix interferences or with compounds belonged to the same batch could produce signal suppression or enhancement of the target compounds. This fact also could cause mass measurement deviations from theoretical *m/z* values. As an example, Fig. 6b includes the extracted ion chromatograms of a pesticide (metribuzin, 100 μg kg^{-1}) in solvent, tomato, orange, and baby food. Signal suppression was observed in these three matrixes. Orange was the one that produced the highest signal suppression, followed by tomato and baby food. Figure 6c shows EICs for fluquinconazole in solvent and tomato. For this compound, signal enhancement was observed in matrix (200 μg kg^{-1}), although this is not the standard behavior. The same criterion—described previously—was applied for matrix effect evaluation. Slope ratios of matrix/solvent from 0.8 to 1 were considered as soft signal suppression, from 0.5 to 0.8 medium signal suppression, and lower than 0.5 strong signal suppression. Signal enhancement could also be classified as soft (slope ratios of matrix/solvent from 1 to 1.2), medium (slope ratios of matrix/solvent from 1.2 to 1.5), and strong (slope ratios of matrix/solvent from 1.5 to 2). Figure 8 includes a 2D plot representing the matrix effects obtained for all the tested compounds in the three different matrices tested. Table S4 and Fig. S2 (Supplementary data) include the data from the matrix effects displayed by the different classes of compounds, being signal suppression the most common effect produced in tomato, orange, and baby food. Medium signal suppression was the most common effect produced in tomato for pesticides, mycotoxins, veterinary drugs, food-packaging contaminants, and nitrosamines, with the exception of perfluorinated compounds and sweeteners. Results for orange were distinctly worse than the other two matrices, with average suppression of 30–40 % as illustrated in Fig. 8b. These results are consistent with previous studies (Gómez-Ramos et al. 2016) and may be attributed, perhaps, to the complexity of the orange matrix due to its composition and the presence of waxes and citrus oils. Finally, soft signal suppression for pesticides, veterinary drugs, mycotoxins, food-packaging contaminants, and sweeteners was the most common effect produced in baby food. This is consistent with the complexity of each of the matrix revealed by the TIC profiles shown (Fig. 6). As an alternative, the use of longer column (e.g., 100 mm) and longer gradient may help to reduce matrix effects as it would enable a better separation, at the expense of method throughput though.

Conclusions

A screening method using UHPLC-QTOFMS has been developed for the examination of 630 food contaminants, including pesticides, veterinary drugs, food-packaging contaminants, mycotoxins, nitrosamines, perfluorinated compounds, and sweeteners. The method was based on a database with retention time values and mass accurate measurements of the ions of interest. It was found that software parameters such as retention time window and mass error tolerance have a clear influence on the automatic search results. The proposed methodology was also examined in terms of linearity, matrix effect, and limits of quantification in three different matrixes: tomato, orange, and baby food. For most of compounds, signal suppression was the most common matrix effect produced. In general, baby food and orange produced the lowest and the highest matrix effect, respectively. This clearly had an impact on the sensitivity of the method. Limits of quantification were also calculated for the 630 compounds included, and most of them were <10 μg kg^{-1} in tomato, orange, and baby food. However, in the particular case of pesticides with relatively low response factors (ca. 10–20 % of the compounds depending on the complexity of the matrix), the detection was not fulfilling the MRL established for the tested pesticide/commodity combination. This is a drawback of the entire approach that may be partially solved with more sensitive and updated instrumentation, except for the case of compounds not really amenable to electrospray ionization.

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Compliance with Ethical Standards

Conflict of Interest Patricia Pérez-Ortega declares that she has no conflict of interest. Felipe J. Lara-Ortega declares that he has no conflict of interest. Bienvenida Gilbert-López declares that he has no conflict of interest. David Moreno-González declares that he has no conflict of interest. Juan F. García-Reyes declares that he has no conflict of interest. Antonio Molina-Díaz declares that he 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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