RESIDUES AND TRACE ELEMENTS

Identification and Determination of 492 Contaminants of Different Classes in Food and Feed by High-Resolution Mass Spectrometry Using the Standard Addition Method

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The methodology for the identification and determination of 492 different toxicants from a single sample in food and feed by high-resolution quadrupole time-of-flight MS in combination with HPLC has been presented. The sample preparation is easy. The analytes are pesticides of different classes, including mycotoxins, veterinary drugs, and synthetic dyes. A scheme for the identification and determination of toxicants using the standard addition method has been given. The RSDs of the analytical results presented are ≤0.15, with a 40–60 min sample screening time and a 2–3 h for the determination of the detected toxicants.

Food products of plant and animal origin, as well as feed and raw food may contain thousands of toxicants from different sources. These toxicants include mycotoxins, veterinary drug residues, antibiotics, pesticides, etc. Simultaneous identification of these toxicants from a single sample and their determination with minimal effort is a pressing problem in the field of food and feed analytical chemistry.

At present, a considerable number of methods have been proposed for the simultaneous determination (i.e., multicomponent analysis) of one or, in rare cases, several classes of toxicants. These proposed methods for the simultaneous determination of toxicants use HPLC and ultra-HPLC (UHPLC), GLC with fluorescence detection, electron capture detection, quadrupole tandem MS (MS/MS), and time-of-flight (TOF) MS. Detection has included the determination of 12 mycotoxins with HPLC and GLC (1), 26 mycotoxins with UHPLC-MS/MS (2), 11 mycotoxins with HPLC-TOFMS (3), and 39 mycotoxins with HPLC-MS/MS (4). In addition, 120 veterinary drugs residues in kidney (5); 90–180 pesticide residues in vegetables and fruits (6–15); 155–255 veterinary drugs in milk (16, 17); and 100 veterinary drugs in eggs, fish, and meat (18) have been determined by HPLC and GLC with high-resolution MS/MS (HRMS/MS). The same technique has been used for the simultaneous determination of mycotoxins and pesticides in wine (19); spices (20); fruits, grains, and vegetable oil (21); and milk (22).

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Only a few of these papers were devoted to the simultaneous determination of different classes of toxicants. Thus, the methods for the simultaneous determination of aflatoxins, dyes, and pesticides in spices (20); alkaloids, pesticides, antibiotics, and mycotoxins in silage, milk, meat, and liver (23); and pesticides, mycotoxins, plant toxins, and veterinary drugs in feed and food (24) have been proposed.

In the above-cited papers, sample preparation was carried out using the quick, easy, cheap, effective, rugged, and safe (QuEChERS) dispersive SPE method (25). In this method, target components are extracted with acetonitrile in the presence of di- and trisodium citrate and magnesium sulfate. Bondesil PSA, C18, graphite carbon black, and ion exchanger bulk adsorbents and their combinations have been used to purify lipid, fat, and protein extracts. Despite optimization in sample preparation, the proposed methods for the simultaneous determination of toxicants are complicated and require a thorough cleaning of extract from coeluting impurities (proteins, fats, sugars, etc.) not only by dispersive SPE-achieved QuEChERS, but also solid phase extraction. Furthermore, the external standard (calibration curve) technique was used in all the proposed methods to determine the composition of toxic substances. Matrix-matched calibration (9, 14) has been used to eliminate matrix effect in MS methods.

However, we deem such an approach unjustified and expensive. Our study shows that 10–15 targeted toxins (with a maximum value of 18 to 25) could be present in the monitored objects. In this regard, we believe that there is no need to carry out calibration for each of the defined toxicants, as there are >1000 widely distributed toxic substances in foodstuffs and feed.! In our opinion, the standard addition method could be appropriately sufficient to identify (through screening) compounds themselves and as well their composition (26, 27). Additionally, our study shows that the use of HRMS could simplify the sample preparation process considerably, even in comparison to the QuEChERS technique, and matrix effects could be eliminated by diluting extracts with deionized (DI) water.

In our present paper, we combine simple and fast sample preparation with the identification of 492 contaminants of different classes and the determination of identified compounds in raw food and feed using the standard addition method. To our knowledge this is the first such examination. We achieve our objective by high-performance liquid chromatography in combination with quadrupole TOFMS.

Materials and Methods

Chemicals and Standards

The following chemicals and standards were used: standard solutions of mycotoxins in acetonitrile, each containing 100 μg/mL deoxynivalenol, nivalenol, fusarenon X, 15-acetyldeoxynivalenol (15-ADON), 3-acetyldeoxynivalenol (3-ADON), diacetoxyscirpenol, HT-2 toxin (Romer Laboratories Diagnostic GmbH, Tulln, Austria), T-2 toxin, T2-triol, T2-tetraol, neosolaniol, zearalenon, and patulin (StyLab, Moscow, Russia); a mixture of aflatoxins, including B1 (2.0 μg/mL), B2 (0.5 mkg/mL), G1 (2.0 μg/mL), and G2 (0.5 μg/mL) in acetonitrile (TS-108; Trilogy Analytical Laboratory, Washington, MO); a standard solution of aflatoxin M1 (0.5 μg/mL) in acetonitrile (Romer Laboratories Diagnostic GmbH); standard solutions of ochratoxin A (10 μg/mL) in acetonitrile (Romer Laboratories Diagnostic GmbH); and a standard solution of ochratoxin B (10 μg/mL) in acetonitrile (Fluka, Munich, Germany); standard samples of individual pesticides and their mixtures (1 mg/mL) in acetonitrile solution nos. 34, 68, 95, 120, 129, and 173 (Dr. Ehrenstorfer GmbH, Augsburg, Germany); a mixture of 204 iDQuant pesticides (AB Sciex); as well as a variety of veterinary drugs of different classes with ≥85% purity (obtained from Dr. Ehrenstorfer GmbH; Fluka; and Sigma). Stock standard solutions (1 mg/mL) were prepared in acetonitrile or methanol, whereas working solutions were prepared by diluting stock solutions with DI water. We also used methanol, acetonitrile, formic acid, *n*-hexane, and isopropanol (Merck, Darmstadt, Germany).

Instrumentation

An UltiMate 3000 liquid chromatograph (Thermo Scientific, Waltham, MA) combined with a maXis Impact (maXis 4G) quadrupole TOFMS detector (Bruker Daltonics, Bremen, Germany) was used. Separation was carried out on an Acclaim 120 C18 column (150 × 2.1 mm, 2.2 μm; Thermo Scientific) using gradient elution mode in the mobile phase.

Conditions of Chromatographic Separation and Detection

A mobile phase consisting of 0.1% HCOOH in water with the addition of 5 mM $HCOONH_4$ (mobile phase A) and 0.1% HCOOH in acetonitrile (mobile phase B) was used. The gradient elution program was as follows: 0 min 2% B, 15 min 100% B, 20 min 100% B, and 30 min 2% B. The mobile phase flow rate was 0.3 mL/min. The chromatographic column temperature was 40°C with a sample injection volume of 20 μL.

Electrospray ionization (ESI) in an ionBooster ion source (Bruker Daltonics) was used. The following optimum parameters were set: nebulizer voltage of 400 V, capillary voltage of 1000 V, nebulizer gas pressure of 4.76 bar, nitrogen drying gas flow rate of 6 L/min, nitrogen drying gas temperature of 200°C, carrier gas (nitrogen) flow rate of 250 L/h, and a carrier gas (nitrogen) temperature of 250°C.

The range of registered ion masses was 100–1500 Da. HCOONa (10 mM) in an aqueous isopropanol solution (1 + 1) was used as the calibration compound. Calibration was carried out in automatic mode with a positive-ion monitoring range of 3 to 3.5 min and negative-ion monitoring range of 17 to 17.5 min.

Toxicants were identified and determined using TargetAnalysis 1.3 software (Bruker Daltonics). DataAnalysis 4.1 software (Bruker Daltonics) was used to create total ion current chromatograms and mass chromatograms. The isotope distribution pattern for the analytes was built using IsotopePattern software (Bruker Daltonics). Identified antibiotics were determined by by the standard addition method.

The concentration of analytes in the sample was calculated with the following formula:

$$C_x = C_{\text{add}} \Big/ \left(I_{x+\text{add}} / I_x - 1 \right)$$

where C_{add} and C_x are the analyte concentrations to which standard analyte solution was or was not added, respectively; and $I_{x+\text{add}}$ and I_x are the areas or heights of the chromatographic peaks of the analytes (*m/z* peaks) to which standard analyte solution was or was not added, respectively.

Sample Preparation

Milk.—A portion of milk (5.0 g) was placed in a 15 mL centrifuge tube, to which 5 mL acetonitrile and 0.1 mL HCOOH were added. The centrifugetube was vigorously shaken for 5 min and centrifuged for 10 min at 5000 rpm at –4°C. A portion of supernatant (2 mL) was transferred into a 15 mL centrifuge tube, 2 mL hexane (saturated with acetonitrile) added, and the mixture hand-shaken for 2 min. After the separation of phases, 1 mL bottom phase was transferred into a vial, 1 mL DI water added, the mixture stirred and filtered through a membrane filter (0.45 μm) in a microvial, the first 1 mL filtrate disposed, and then chromatography carried out.

Meat, fat, eggs, liver, kidney, and fish.—A portion of homogenized sample (1.00 g) was placed in a 15 mL centrifuge tube, to which 5 mL acetonitrile and 0.1 mL HCOOH were added. The centrifuge tube was vigorously shaken for 8–10 min and centrifuged for 10 min at 5000 rpm at –4°C. A portion of the supernatant (3 mL) was transferred into a 15 mL centrifuge tube, 2 mL hexane (saturated with acetonitrile) added, and the mixture hand-shaken for 2 min. After the separation of phases, 1 mL bottom phase was transferred into a vial, 1 mL DI water added, the mixture stirred and filtered through a membrane filter (0.45 μm) in a microvial, the first 1 mL filtrate disposed, and then chromatography carried out.

Feed and grain.—A portion of homogenized sample (1.00 g) was placed in a 15 mL centrifuge tube, to which 5 mL acetonitrile–water–formic acid (in the proportion 79 + 20 + 1) were added. The centrifuge tube was vigorously shaken for 10 min and centrifuged for 5 min at 2700 rpm. A portion of the supernatant (3 mL) was transferred into a 15 mL centrifuge tube, 1 mL hexane (saturated with acetonitrile) added, and the mixture hand-shaken for 2–3 min. After the separation of phases, 2 mL bottom phase were transferred into a vial, 2 mL DI water added, the mixture stirred and filtered through a membrane filter (0.45 μm) in a microvial, the first 2 mL filtrate disposed, and then chromatography carried out.

Fruit and vegetables.—A portion of homogenized sample (5.0 g) was placed in a 15 mL centrifuge tube, to which 5 mL acetonitrile and 0.1 mL HCOOH were added. The centrifuge tube was vigorously shaken for 8–10 min and centrifuged for

10 min at 5000 rpm at –4°C. A portion of the supernatant (1 mL) was transferred into a 15 mL centrifuge tube, 3 mL DI water added, and the mixture hand shaken for 2 min. The mixture was stirred and filtered through a membrane filter (0.45 µm) in a vial, the first 1 mL filtrate disposed, and then chromatography carried out.

Dispersive SPE QuEChERS.—The test sample was ground with a mixer. A portion of homogenized sample (5.0 g) was placed in a 50 mL centrifuge tube, to which 10 mL acetonitrile (5 mL DI water for feed and grain) and 0.1 mL HCOOH were added. The centrifuge tube was vigorously shaken for 1 min, then 4.0 g $MgSO_4$, 1.0 g NaCl, 1.0 g $Na_3C_6H_5O_7 \times 2H_2O$, and 0.5 g $Na_2C_6H_6O_7 \times 1.5\ H_2O$ were added. The centrifuge tube was vigorously hand-shaken for 1 min (to avoid lump formation) and centrifuged for 5 min at 4500 rpm. A portion of the extract (5 mL) was transferred into a 15 mL centrifuge tube, with a mixture of sorbents, including Bondesil-PSA (0.15 g), C18 (0.15 g), and $MgSO_4$ (0.9 g). The centrifuge tube was vigorously shaken for 1 min and centrifuged for 5 min at 2700 rpm. Extract (1 mL) was transferred into a microvial, evaporated to dryness in nitrogen steam, dissolved in 100 µL mobile phase A, and then chromatography carried out.

Results and Discussion

Identification

Most of the investigated classes of compounds from veterinary drugs, antibiotics, and pesticides under ESI conditions comprise protonated forms, $[M+H]^+$, including aminoglycosides, lincosamides, nitroimidazoles, tetracyclines, sulfonamides, quinolones, anthelmintics, nitrofurans, macrocyclic polyene antibiotics, and dyes (Table 1). Other substances in these classes under these same conditions comprise both protonated and deprotonated forms, $[M-H]^-$, including coccidiostats, amphenicols, nonsteroidal anti-inflammatory agents, penicillins, cephalosporins, and mycotoxins (Table 1). Macrolides and ionophores, under these conditions, form adducts mainly with sodium ions, whereas avilamycin forms adducts with ammonium, sodium, and potassium ions (Figure 1). Aminoglycosides form ions when water is added. Conversely, for coccidiostats, ions form when water is lost and ammonium ions or alkali metals are added. Some mycotoxins form adducts with a formate ion $[M+HCOO]^-$. Doubly charged ions, $[M+2H]^{2+}$, were found in aminoglycosides and spiramycin and polypeptide antibiotics (Table 1). We also found that certain aminoglycosides, nitrofuran metabolites, glyphosate, and glufosinate and its metabolites were not retained in the column, and that one peak appeared in the 1.0–1.4 min range. However, identification of these compounds was easily carried out using their accurate *m/z* ion masses.

Almost all of the investigated pesticides under ESI conditions comprised protonated forms, $[M+H]^+$, and only two pesticides—bromoxynil and ioxynil—comprised deprotonated forms, $[M-H]^-$. Carbofuran and tetramethrin form adducts with ammonium ions, whereas avermectins and glyphosate and its derivatives form adducts with sodium ions (Table 1). The error in determination of ion masses did not exceed ±10 ppm ($n = 3$). We established that signal intensity affects the composition of the mobile phase. Addition of $HCOONH_4$ and CH_3COONH_4 to the mobile phase, which is traditionally used in HRMS, increases analyte peak intensity 2- or 3-fold compared with the aqueous phase. We used acetonitrile containing 0.1% formic acid. An $HCOONH_4$ solution (5 mM) was added to the aqueous phase. Variations of acid concentration from 0.1 to 1% and $HCOONH_4$ concentration from 5 to 20 mM did not result in substantial changes in the chromatographic parameters of the separated analytes. Gradient elution and a column temperature of 40°C allowed us to achieve optimum selectivity of coefficients and peak resolution. The dispersive SPE QuEChERS method substantially reduced sample preparation time. However, we found that purification of fat and protein extracts by this method was insufficient (the area of the total ion current chromatogram from 12 to 17 min, Figure 2a). Fat extraction by hexane, extract desolvation with DI water, and filtration are the simplest and most efficient methods. As can be seen in Figure 2b, the chromatogram by common ion flow is "cleaner" in the retention area of most analytes.

Toxin identification was carried out using TargetAnalysis 1.3 software. Identification parameters were as follows: retention time (±0.2 min), ion mass *m/z* accuracy (±10 ppm), and mSigma (<50). The mSigma parameter corresponds to theoretical and practical isotope distribution. For example, we can see the mass spectrum of the positive avilamicin potassium adduct that was generated by IsotopePattern software (Figure 1). Figure 1 also shows that the features and pattern of isotope ratios coincide.

As can be see by the isotope ratios depicted in Figure 1, the experimental profile of isotopic peak intensities in the area of the molecular ion signal fully mirrors the theoretical estimates for that analyte. The profile of isotope peak are identical with the experimental data, which corresponds to a high degree of identification (100% for three identification parameters), and are reported as "+++" in Figure 3.

Determination

LODs and LOQs were calculated at an S/N of 3 and 10, respectively, for the standard solutions. LODs were 0.0005–100 ng/mL and LOQs were 0.003–250 ng/mL (Figure 4).

We found that that a 5- to 10-fold dilution of the extract was possible due to such a high LOD, and found that the matrix effect (28) was significantly reduced (80–100%). Taking into account that sample preparation and dilution, the lower LOD concentration was 1–500 µg/kg. This limit satisfies the maximum permissible levels for investigated toxins in food, raw foodstuffs, and feed. We established that the extent of analyte extraction would vary between 78 and 110%, depending on the matrix and its character.

In our work, we propose detection of toxicants using the standard addition method (26, 27). This method has the following advantages over the external standard (calibration curve) method: Firstly, there is no need to determine the recovery of analytes; secondly, considerably less expensive reference standards are required and the periodical testing of calibration characteristics is not needed; thirdly, there is increased accuracy of determination; and finally, the matrix effect is neutralized (28). It is well known that the introduction of a single addition depends on the concentration of analyte in the area or height of the chromatographic peak (*m/z* peak). It was found that a linear dependence for the investigated analytes from the LOQ is 500–5000 µg/kg.

Table 1. Main characteristics of the 492 analytes determined by the HRMS method in accurate mass[a]

Analyte	Gross formula	Ion	t_R, min	*m/z*	Δ, ppm	LOD, ng/mL	LOQ, ng/mL
Aminoglycosides (*n* = 10)							
Amikacin	$C_{22}H_{43}N_5O_{13}$	$[M+H]^+$	8.0	586.2930	−0.2	0.05	0.2
Apramycin	$C_{21}H_{41}N_5O_{11}$	$[M+H]^+$	8.9	540.2875	0.2	0.05	0.2
Canamycin	$C_{18}H_{36}N_4O_{11}$	$[M+H]^+$	1.0	485.2453	0.6	0.1	0.4
Dihydrostreptomycin	$C_{21}H_{41}N_7O_{12}$	$[M+2H]^{2+}$	1.0	292.6479	0.1	2	6
		$[M+H]^+$	1.0	584.2886	−0.2		
Gentamicin	$C_{21}H_{43}N_5O_7$	$[M+H]^+$	12.4	478.3235	−0.2	2	5
Hygromycin B	$C_{20}H_{37}N_3O_{13}$	$[M+2H]^{2+}$	1.0	264.6236	−0.4	2	6
		$[M+H]^+$	1.0	528.2399	−0.9		
Neomycin	$C_{23}H_{46}N_6O_{13}$	$[M+H]^+$	7.7	615.3196	8.9	2	5
Paromomycin	$C_{23}H_{45}N_5O_{14}$	$[M+H]^+$	7.8	616.3035	−0.5	0.1	0.4
Spectinomycin	$C_{14}H_{24}N_2O_7$	$[M+H]^+$	1.3	333.1656	−0.3	2	5
		$[M+H_2O+H]^+$	1.3	351.1762	−0.3		
Streptomycin	$C_{21}H_{39}N_7O_{12}$	$[M+2H]^{2+}$	1.0	291.6401	−0.3	2	5
		$[M+H_2O+2H]^{2+}$	1.0	300.6454	−8.9		
		$[M+H_2O+H]^+$	1.0	600.2835	0.1		
Lincosamides (*n* = 2)							
Clindamycin	$C_{18}H_{33}ClN_2O_5S$	$[M+H]^+$	8.9	425.1871	1.2	0.05	0.2
Lincomycin	$C_{18}H_{34}N_2O_6S$	$[M+H]^+$	6.9	407.2210	1.5	1	4
Macrolides (*n* = 12)							
Azithromycin	$C_{38}H_{72}N_2O_{12}$	$[M+H]^+$	8.5, 8.2	749.5158	3.5	0.5	1
Clarithromycin	$C_{38}H_{69}NO_{13}$	$[M+H]^+$	11.1	748.4842	2.1	0.05	0.2
		$[M+Na]^+$	11.1	770.4661	3.3		
Erythromycin	$C_{37}H_{67}O_{13}N$	$[M+H]^+$	10.0, 9.7	734.4690	7.7	0.05	0.1
		$[M+Na]^+$	10.0	756.4583	4.6		
Josamycin	$C_{42}H_{69}NO_{15}$	$[M+H]^+$	11.6	828.4818	0.1	0.3	0.5
		$[M+Na]^+$	11.6	850.4638	5.3		
Roxithromycin	$C_{41}H_{76}N_2O_{15}$	$[M+H]^+$	11.2	837.5318	2.6	0.5	2
Spiramycin I	$C_{43}H_{74}N_2O_{14}$	$[M+2H]^{2+}$	8.6, 8.2	422.2607	1.1	0.01	0.05
		$[M+H]^+$	8.6, 8.2	843.5213	−1.0		
Spiramycin II	$C_{45}H_{76}N_2O_{15}$	$[M+2H]^{2+}$	8.7, 8.5	443.2696	2.0	0.01	0.05
		$[M+H]^+$	8.7, 8.5	885.5318	1.0		
Spiramycin III	$C_{46}H_{78}N_2O_{15}$	$[M+2H]^{2+}$	9.1, 8.9	450.2774	2.1	0.01	0.05
		$[M+H]^+$	9.1, 8.9	899.5475	1.0		
Tilmicosin	$C_{46}H_{80}O_{13}N_2$	$[M+H]^+$	9.3, 9.2	869.5738	0.1	0.05	0.2
Tilvalosyn	$C_{53}H_{87}O_{19}N$	$[M+H]^+$	12.3	1042.5945	6.5	0.1	0.3
Tulathromycin	$C_{41}H_{79}O_{12}N_3$	$[M+2H]^{2+}$	7.6, 6.7	403.7905	3.3	0.05	0.2
		$[M+H]^+$	7.6, 6.7	806.5737	2.1	1	3
Tylosin	$C_{46}H_{77}O_{17}N$	$[M+H]^+$	10.3	916.5270	6.1	0.05	0.2
Coccidiostats (*n* = 15)							
4,4′-Dinitrocarbanilide	$C_{13}H_{10}N_4O_5$	$[M-H]^-$	13.7	301.0567	−0.9	0.1	0.5
Amprolium	$C_{14}H_{18}N_4$	$[M+H]^+$	2.9	243.1604	4.8	0.5	2
Arprinocid	$C_{12}H_9ClFN_5$	$[M+H]^+$	9.9	278.0603	7.8	0.1	0.5
Clopidol	$C_7H_7Cl_2NO$	$[M+H]^+$	6.7	191.9978	0.3	0.01	0.03
Decoquinate	$C_{24}H_{35}NO_5$	$[M+H]^+$	17.1	418.2588	2.8	0.001	0.01
Diclazuril	$C_{17}H_9Cl_3N_4O_2$	$[M-H]^-$	14.4	404.9707	−2.7	0.5	2
Ethopabate	$C_{12}H_{15}O_4N$	$[M+H]^+$	10.0	238.1074	3.3	0.1	0.4
Halofuginone	$C_{16}H_{17}ClBrN_3O_3$	$[M+H]^+$	9.0	414.0215	3.5	0.5	2
Lasalocid	$C_{34}H_{54}O_8$	$[M+Na]^+$	8.1	613.3711	−6.5	0.5	1
Maduramicin	$C_{47}H_{79}O_{17}$	$[M+Na]^+$	17.4	938.5209	7.3	0.3	0.5
Monensin	$C_{36}H_{62}O_{11}$	$[M+Na]^+$	21.6, 16.5	693.4184	6.5	0.3	0.5
		$[M+NH_4]^+$		688.4630			
		$[M+H-H_2O]^+$		653.4259			

Table 1. (*continued*)

Analyte	Gross formula	Ion	t_R, min	*m/z*	Δ, ppm	LOD, ng/mL	LOQ, ng/mL
		$[M+K]^+$		709.3923			
Narasin	$C_{43}H_{72}O_{11}$	$[M+NH_4]^+$	21.8, 20.9, 20.6	782.5412	−7.1	0.5	1
		$[M+H-H_2O]^+$		747.5041			
		$[M+Na]^+$		787.4972			
		$[M+H-2H_2O]^+$		729.4936			
		$[M+K]^+$		803.4706			
Robenidine	$C_{15}H_{13}Cl_2N_5$	$[M+H]^+$	12.0	334.0620	7.3	0.5	1
Salinomycin	$C_{42}H_{70}O_{11}$	$[M+Na]^+$	21.0	773.4810	−10	0.5	2
Toltrazuril	$C_{18}H_{14}F_3N_3O_4S$	$[M-H]^-$	14.8	424.0573	3.1	0.5	1
Amphenicols (*n* = 5)							
Chloramphenicol	$C_{11}H_{12}Cl_2N_2O_5$	$[M-H]^-$	9.8	321.0039	3.1	0.02	0.05
		$[M+H]^+$	9.8	323.0196	0.8	0.2	0.5
Chloramphenicol-succinate	$C_{15}H_{15}Cl_2N_2O_8Na$	$[M-C_5H_6O_3Na]^-$	9.8, 10.1, 10.6	321.0039	1.5	0.01	0.03
		$[M-Na]^-$	10.1, 10.6	421.020	1.0	0.01	0.03
Florfenicol	$C_{12}H_{14}NO_4Cl_2SF$	$[M+NH_4]^+$	9.5	375.0343	−3.1	0.1	0.4
		$[M-H]^-$	9.5	355.9921	1.1	0.1	0.4
Sintomicin (D,L-chloramphenicol)	$C_{11}H_{12}Cl_2N_2O_5$	$[M-H]^-$	9.8	321.0039	1.0	0.02	0.05
Thiamphenicol	$C_{12}H_{15}Cl_2NO_5S$	$[M+NH_4]^+$	7.9	373.0386	0.5	0.1	0.4
		$[M-H]^-$	7.9	353.9964	1.5	0.1	0.4
Nitroimidazoles (*n* = 9)							
Clotrimazole	$C_{22}H_{17}ClN_2$	$[M+H]^+$	11.8	345.1153	3.0	20	60
Dimetridazole	$C_5H_7N_3O_2$	$[M+H]^+$	7.2	142.0611	1.0	0.01	0.03
Ipronidazole	$C_7H_{11}N_3O_2$	$[M+H]^+$	9.8	170.0924	1.3	0.02	0.06
Ipronidazole D3	$C_7D_3H_8N_3O_2$	$[M+H]^+$	9.8	173.1112	−1.7	0.02	0.06
Metronidazole	$C_6H_9N_3O_3$	$[M+H]^+$	6.5	172.0717	2.0	0.005	0.02
Metronidazole-OH	$C_6H_9N_3O_4$	$[M+H]^+$	5.6	188.0666	1.0	0.01	0.03
Ronidazole	$C_6H_8N_4O_4$	$[M+H]^+$	6.8	201.0618	3.3	0.01	0.03
Ternidazole	$C_8H_{11}N_3O_3$	$[M+H]^+$	7.2	186.0873	2.0	0.005	0.02
Tinidazole	$C_8H_{13}N_3O_4S$	$[M+H]^+$	7.9	248.0699	2.3	0.002	0.006
β-Agonists (*n* = 19)							
Brombuterol	$C_{12}H_{18}Br_2N_2O$	$[M+H]^+$	8.6	366.9839	4.7	0.005	0.02
Carazolol	$C_{18}H_{22}N_2O_2$	$[M+H]^+$	9.0	299.1754	8.0	0.01	0.04
Cimaterol	$C_{12}H_{17}N_3O$	$[M+H]^+$	6.2	220.1444	2.6	0.05	0.2
Cimbuterol	$C_{13}H_{19}N_3O$	$[M+H]^+$	6.9	234.1601	8.6	0.01	0.04
Clenbuterol	$C_{12}H_{18}N_2OCl_2$	$[M+H]^+$	8.3	277.0869	1.1	0.01	0.04
Clenpenterol	$C_{13}H_{20}Cl_2N_2O$	$[M+H]^+$	8.8	291.1025	7.4	0.005	0.02
Clenproperol	$C_{11}H_{16}Cl_2N_2O$	$[M+H]^+$	7.9	263.0712	7.4	0.005	0.02
Fenoterol	$C_{17}H_{21}NO_4$	$[M+H]^+$	7.0	304.1543	8.1	0.05	0.2
Formoterol	$C_{19}H_{24}N_2O_4$	$[M+H]^+$	8.3	345.1809	5.3	0.05	0.2
Hydroxymethyl-clenbuterol	$C_{12}H_{18}Cl_2N_2O_2$	$[M+H]^+$	7.8	293.0818	8.2	0.001	0.004
Isoxsuprine	$C_{18}H_{23}NO_3$	$[M+H]^+$	8.7	302.1751	4.8	0.01	0.04
Mabuterol	$C_{13}H_{18}ClF_3N_2O$	$[M+H]^+$	8.9	311.1133	2.8	0.005	0.02
Mapenterol	$C_{14}H_{20}ClF_3N_2O$	$[M+H]^+$	9.4	325.1289	6.8	0.003	0.01
Ractopamine	$C_{18}H_{23}NO_3$	$[M+H]^+$	7.8	302.1751	−0.7	0.01	0.04
Salbutamol	$C_{13}H_{21}NO_3$	$[M+H]^+$	6.1	240.1594	3.8	0.02	0.06
Salmeterol	$C_{25}H_{37}NO_4$	$[M+H]^+$	11.0	416.2795	2.3	0.05	0.2
Tulobuterol	$C_{12}H_{18}ClNO$	$[M+H]^+$	8.2	228.1150	8.0	0.005	0.02
Xylazine	$C_{12}H_{16}N_2S$	$[M+H]^+$	8.2	221.1107	9.5	0.003	0.02
Zilpaterol	$C_{14}H_{19}N_3O_2$	$[M+H]^+$	6.1	262.1550	3.5	0.05	0.2
Sedatives (*n* = 5)							
Acepromazine	$C_{19}H_{22}N_2OS$	$[M+H]^+$	10.4	327.1526	7.1	0.1	0.5
Azaperol	$C_{19}H_{24}FN_3O$	$[M+H]^+$	8.8	330.1976	6.9	0.05	0.1

Table 1. (*continued*)

Analyte	Gross formula	Ion	t_R, min	*m/z*	Δ, ppm	LOD, ng/mL	LOQ, ng/mL
Azaperone	$C_{19}H_{22}FN_3O$	$[M+H]^+$	9.4	328.1820	7.4	0.05	0.1
Chlorpromazine	$C_{17}H_{19}ClN_2S$	$[M+H]^+$	11.4	319.1030	7.1	0.1	0.5
Propionylpromazine	$C_{20}H_{24}N_2OS$	$[M+H]^+$	11.2	341.1682	6.7	0.05	0.1
Nonsteroidal anti-inflammatory agents (*n* = 26)							
5-Hydroxyflunixin	$C_{14}H_{11}F_3N_2O_3$	$[M+H]^+$	12.1	313.0795	1.7	0.5	1
Acetylaminoantipyrine	$C_{13}H_{15}N_3O_2$	$[M+H]^+$	6.48	246.1232	3.4	0.01	0.05
Aminoantipyrine	$C_{11}H_{13}N_3O$	$[M+H]^+$	6.48	204.1126	−0.4	0.1	0.5
Antipyrine	$C_{11}H_{12}N_2O$	$[M+H]^+$	7.43	189.1017	−0.5	0.1	0.5
Caprofen	$C_{15}H_{12}ClNO_2$	$[M-H]^-$	13.6	272.0478	2.8	10	50
Dapsone	$C_{12}H_{12}N_2O_2S$	$[M+H]^+$	8.9	249.0692	1.8	0.01	0.04
Diclofenac	$C_{14}H_{11}Cl_2NO_2$	$[M-H]^-$	12.8	294.0083	−2.7	10	30
Dimethylaminoantipyrine (pyramidon)	$C_{13}H_{17}N_3O$	$[M+H]^+$	6.6	232.1444	2.7	0.1	0.4
Dipyron	$C_{13}H_{16}N_3SO_4$	$[M-H]^-$	8.6	310.0856	3.2	5	20
Flufenamic acid	$C_{14}H_{10}F_3NO_2$	$[M+H]^+$	11.4	282.0736	0.7	20	60
Flunixin	$C_{14}H_{11}N_2O_2F_3$	$[M+H]^+$	13.0	297.0845	2.7	0.1	0.5
Flurbiprofen	$C_{15}H_{13}FO_2$	$[M+H]^+$	6.8	245.0972	−8.9	10	30
Formylaminoantipyrine	$C_{12}H_{13}N_3O_2$	$[M+Na]^+$	6.51	254.0894	−5.1	0.05	0.1
Ibuprofen	$C_{13}H_{18}O_2$	$[M-H]^-$	13.6	205.1229	7.0	10	50
Isopropyl-aminoantipyrine	$C_{14}H_{19}N_3O$	$[M+H]^+$	7.1	246.1601	4.7	0.1	0.5
Ketoprofen	$C_{16}H_{14}O_3$	$[M-H]^-$	9.0	253.0859	2.8	20	60
Mefenamic acid	$C_{15}H_{15}NO_2$	$[M-H]^-$	14.4	240.1025	6.9	0.1	0.5
Meloxicam	$C_{14}H_{13}N_3O_4S_2$	$[M+H]^+$	12.8	352.0420	2.4	0.1	0.4
		$[M-H]^-$	12.8	350.0264	3.5	3	10
Methylaminoantipyrine	$C_{12}H_{15}N_3O$	$[M+H]^+$	8.04	218.1282	4.4	0.5	1
Naproxen	$C_{14}H_{14}O_3$	$[M+H]^+$	7.4	231.1016	2.0	10	50
Niflumic acid	$C_{13}H_9O_2F_3N_2$	$[M+H]^+$	14.0	283.0689	2.0	0.5	2
Oxyphenbutazone	$C_{19}H_{20}N_2O_3$	$[M-H]^-$	11.5	323.1396	4.7	0.1	0.5
Phenylbutazone	$C_{19}H_{20}N_2O_2$	$[M+H]^+$	14.8	309.1598	−3.5	1	4
		$[M-H]^-$	14.8	307.1447	2.8	0.01	0.05
Rifampicin	$C_{43}H_{58}N_4O_{12}$	$[M+H]^+$	12.3, 11.4	823.4124	5.7	10	50
Tolfenamic acid	$C_{14}H_{12}ClNO_2$	$[M-H]^-$	15.0	260.0478	2.6	0.1	0.5
Vedaprofen	$C_{19}H_{22}O_2$	$[M-H]^-$	15.6	281.1542	1.2	20	60
Pleuromutilins (*n* = 2)							
Tiamulin	$C_{28}H_{47}NO_4S$	$[M+H]^+$	10.9	494.3299	2.5	0.001	0.003
Valnemulin	$C_{31}H_{52}N_2O_5S$	$[M+H]^+$	11.4	565.3670	−8.5	0.05	0.2
Quinoxalines and their metabolites (*n* = 4)							
3-Methyl-2-quinoxaline carboxylic acid (a metabolite of olaquindox)	$C_{10}H_8N_2O_2$	$[M-H]^-$	7.6	187.0502	2.5	10	50
Carbadox	$C_{11}H_{10}N_4O_4$	$[M+H]^+$	7.6	263.0775	2.7	0.5	1
Olaquindox	$C_{12}H_{13}N_3O_4$	$[M+H]^+$	6.1	264.0978	−2.5	0.05	0.2
Quinoxaline-2-carboxylic acid (a metabolite of carbadox)	$C_9H_6N_2O_2$	$[M-H]^-$	7.5	173.0346	2.5	10	50
Others (*n* = 20)							
Avermectin B1a	$C_{48}H_{72}O_{14}$	$[M+Na]^+$	18.6	895.4814	−1.2	0.5	1
Avilamycin	$C_{61}H_{88}Cl_2O_{32}$	$[M+K]^+$	14.4	1443.4276	10	10	50
		$[M+Na]^+$		1425.4527	−9.8		
		$[M+NH_4]^+$		1420.4974	5.6		
Baquiloprim	$C_{17}H_{20}N_6$	$[M+H]^+$	5.5	309.1822	3.1	0.005	0.02
Closantel	$C_{22}H_{14}N_2O_2Cl_2I_2$	$[M-H]^-$	18.6	660.8438	2.7	0.5	1
Diaveridine	$C_{13}H_{16}N_4O_2$	$[M+H]^+$	7.1	261.1346	2.7	0.1	0.4
Doramectin	$C_{50}H_{74}O_{14}$	$[M+Na]^+$	19.1	921.4971	−1.3	2	6
Eprinomectin	$C_{50}H_{75}NO_{14}$	$[M+Na]^+$	17.4	936.5079	8.3	0.05	0.1
Haloperidol	$C_{21}H_{23}ClFNO_2$	$[M+H]^+$	10.1	376.1474	6.9	0.01	0.04

Table 1. (*continued*)

Analyte	Gross formula	Ion	t_R, min	*m/z*	Δ, ppm	LOD, ng/mL	LOQ, ng/mL
Imidocarb	$C_{19}H_{20}N_6O$	$[M+H]^+$	6.5	349.1771	4.5	0.5	2
Ionomycin	$C_{41}H_{72}O_9$	$[M+H]^+$	18.8	709.5249	8.8	0.5	1
Isoniazid	$C_6H_7N_3O$	$[M+H]^+$	2.0	138.0662	2.9	0.01	0.04
Ivermectin B1a	$C_{48}H_{74}O_{14}$	$[M+Na]^+$	20.5	897.4977	−1.3	2	6
Methimazole	$C_4H_6N_2S$	$[M+H]^+$	3.7	115.0325	0.1	0.5	2
Nigericin	$C_{40}H_{67}O_{11}$	$[M+Na]^+$	22.7	747.4654	−9.8	0.01	0.03
		$[M+NH_4]^+$		742.5099			
Phenacetin	$C_{10}H_{13}NO_2$	$[M+H]^+$	9.8	447.1333	2.7	2	7
Potassium clavulanate	$C_8H_8NO_5K$	$[M-H]^-$	11.2	235.9906	−7.5	20	60
Reserpine	$C_{33}H_{40}N_2O_9$	$[M+H]^+$	11.3	609.2807	2.7	0.1	0.4
Rifabutin	$C_{46}H_{62}N_4O_{11}$	$[M+H]^+$	12.3	847.4488	5.5	0.01	0.05
Rifaximin	$C_{43}H_{51}N_3O_{11}$	$[M+H]^+$	13.6	786.3596	0.1	0.1	0.4
Trimethoprim	$C_{14}H_{18}N_4O_3$	$[M+H]^+$	7.4	291.1452	8.7	0.05	0.1
Anthelmintics ($n=29$)							
Albendazole	$C_{12}H_{15}N_3O_2S$	$[M+H]^+$	11.3	266.0958	−4.1	0.05	0.2
Albendazole sulfone	$C_{12}H_{15}N_3O_4S$	$[M+H]^+$	8.6	298.0851	0.8	0.1	0.5
		$[M-H]^-$	8.6	296.0705	8.4	0.1	0.5
Albendazole sulfoxide	$C_{12}H_{15}N_3O_3S$	$[M+H]^+$	7.7	282.0901	2.3	0.05	0.1
Amino albendazole-sulfone	$C_{10}H_{13}N_3O_2S$	$[M+H]^+$	7.1	240.0807	2.7	0.5	1
Aminoflubendazole	$C_{14}H_{10}FN_3O$	$[M+H]^+$	9.2	256.0881	1.9	0.1	0.5
		$[M-H]^-$	9.2	254.0730	6.8	0.1	0.5
Clorsulon	$C_8H_8Cl_3N_3O_4S_2$	$[M-H]^-$	9.7	377.8944	4.6	5	15
Cyclopentylalbendazole	$C_{14}H_{17}N_3O_2S$	$[M+H]^+$	12.4	292.1114	2.7	0.05	0.2
Febantel	$C_{20}H_{22}N_4O_6S$	$[M+H]^+$	14.4	447.1333	2.7	0.5	1
Febantel-D6	$C_{20}D_6H_{16}N_4O_6S$	$[M+H]^+$	14.4	453.1709	−3.7	0.01	0.04
Fenbendazole	$C_{15}H_{13}N_3O_2S$	$[M+H]^+$	12.5	300.0806	2.7	5	20
Fenbendazole sulfone	$C_{15}H_{13}N_3O_4S$	$[M+H]^+$	10.5	332.0700	2.7	0.1	0.4
Flubendazol	$C_{16}H_{12}N_3O_3F$	$[M+H]^+$	11.2	314.0941	2.7	0.5	1
Ketotriclabendazole	$C_3H_7Cl_3N_2O_2$	$[M-H]^-$	13.3	326.9489	8.6	0.05	0.1
Levamisole	$C_{11}H_{12}N_2S$	$[M+H]^+$	7.2	205.0794	10.3	0.05	0.1
Mebendazole	$C_{16}H_{13}N_3O_3$	$[M+H]^+$	11.0	296.1029	−3.4	0.05	0.2
Mebendazole-amine	$C_{14}H_{11}N_3O$	$[M+H]^+$	8.9	238.0969	−2.4	1	5
		$[M-H]^-$	8.9	236.0824	7.7	0.1	0.5
Morantel	$C_{12}H_{16}N_2S$	$[M+H]^+$	8.8	221.1107	1.3	0.05	0.1
Niclosamide	$C_{13}H_8Cl_2N_2O_4$	$[M-H]^-$	15.3	324.9778	2.7	1	5
Nitroxinil	$C_7H_3N_2O_3I$	$[M-H]^-$	11.3	288.9105	2.7	1	5
Oxfendazole	$C_{15}H_{13}N_3SO$	$[M+H]^+$	9.6	316.0750	3.3	0.05	0.1
Oxibendazole	$C_{12}H_{15}N_3O_3$	$[M+H]^+$	9.3	250.1191	2.7	0.1	0.5
Oxyclozanide	$C_{13}H_6Cl_5NO_3$	$[M-H]^-$	15.7	397.8712	3.0	0.05	0.1
Parbendazole	$C_{13}H_{17}N_3O_2$	$[M+H]^+$	10.6	248.1394	2.7	0.05	0.2
Praziquantel	$C_{19}H_{24}N_2O_2$	$[M+H]^+$	11.5	313.1910	6.2	100	250
Pyrimethamine	$C_{12}H_{13}ClN_4$	$[M+H]^+$	8.7	249.0902	8.6	0.05	0.1
Rafoxanide	$C_{19}H_{11}Cl_2I_2NO_3$	$[M-H]^-$	18.9	623.8127	−0.2	0.1	0.5
Thiabendazole	$C_{10}H_7N_3S$	$[M+H]^+$	7.2	202.0433	−6.4	0.05	0.2
Triclabendazole	$C_{14}H_9Cl_3N_2OS$	$[M+H]^+$	15.2	358.9574	−8.6	0.05	0.2
		$[M-H]^-$	15.2	356.9417	8.4	0.1	0.3
Triclabendazole sulfoxide	$C_{14}H_9Cl_3O_3SN_2$	$[M-H]^-$	14.4	388.9315	2.7	5	15
Anabolic steroids ($n=2$)							
Trenbolone	$C_{18}H_{22}O_2$	$[M+H]^+$	11.8	271.1693	−2.4	0.001	0.004
Zeranol (α-zearalanol)	$C_{18}H_{24}O_5$	$[M+H]^+$	16.9	321.1697	−5.8	10	30
Hormonal drugs ($n=4$)							
Dienestrol	$C_{18}H_{18}O_2$	$[M+H]^+$	13.5	267.1380	2.3	0.2	0.6
Medroxyprogesterone	$C_{22}H_{32}O_3$	$[M+H]^+$	14.2	345.2424	1.3	10	30

Table 1. (*continued*)

Analyte	Gross formula	Ion	t_R, min	*m/z*	Δ, ppm	LOD, ng/mL	LOQ, ng/mL
Testosterone	$C_{19}H_{28}O_2$	$[M+H]^+$	12.8	289.2162	2.8	20	60
Oxytocin	$C_{43}H_{66}O_{12}N_{12}S_2$	$[M+H]^+$	8.5	1007.4437	0.5	1	5
Glucocorticosteroids (*n* = 4)							
Betamethasone	$C_{22}H_{29}FO_5$	$[M+H]^+$	11.6	393.2072	−8.9	5	20
Dexamethasone	$C_{22}H_{29}FO_5$	$[M+H]^+$	11.1	393.2072	−8.4	5	20
Flumethasone	$C_{22}H_{28}F_2O_5$	$[M-H]^-$	11.2	409.1821	−3.6	8	30
Prednisone	$C_{21}H_{26}O_5$	$[M+H]^+$	10.5	359.1853	1.8	0.01	0.04
Tetracyclines (*n* = 12)							
4-Epichlortetracycline	$C_{22}H_{23}ClN_2O_8$	$[M+H]^+$	8.5	479.1215	−0.4	0.5	1
4-Epidemeclocycline	$C_{21}H_{21}ClN_2O_8$	$[M+H]^+$	8.0	465.1059	0.2	0.1	0.5
4-Epidoxycycline	$C_{22}H_{24}N_2O_8$	$[M+H]^+$	8.6	445.1605	−0.2	0.2	0.7
4-Epioxytetracycline	$C_{22}H_{24}N_2O_9$	$[M+H]^+$	7.2	461.1554	1.1	0.5	1
4-Epitetracycline	$C_{22}H_{24}N_2O_8$	$[M+H]^+$	7.5	445.1605	−0.2	0.5	1
Anhydrotetracycline	$C_{22}H_{22}N_2O_7$	$[M+H]^+$	9.6	427.1499	6.5	0.5	1
Chlortetracycline	$C_{22}H_{23}ClN_2O_8$	$[M+H]^+$	8.9	479.1215	−0.4	0.5	1
Demeclocycline	$C_{21}H_{21}ClN_2O_8$	$[M+H]^+$	8.4	465.1059	0.2	0.1	0.5
Doxycycline	$C_{22}H_{24}N_2O_8$	$[M+H]^+$	9.0	445.1605	−0.2	0.2	0.7
Methacycline	$C_{22}H_{22}N_2O_8$	$[M+H]^+$	8.9	443.1448	−0.2	0.1	0.5
Oxytetracycline	$C_{22}H_{24}N_2O_9$	$[M+H]^+$	7.6	461.1554	1.0	0.5	1
Tetracycline	$C_{22}H_{24}N_2O_8$	$[M+H]^+$	7.9	445.1605	−0.2	0.5	1
Penicillins (*n* = 15)							
Amoxicillin	$C_{16}H_{19}N_3O_5S$	$[M+H]^+$	5.2	366.1118	3.2	0.5	1
Ampicillin	$C_{16}H_{19}N_3O_4S$	$[M+H]^+$	6.8	350.1169	−1.1	0.5	1
Bacampicillin	$C_{21}H_{27}N_3O_7S$	$[M+H]^+$	10.3	466.1642	−2.8	0.1	0.4
Carbenicillin	$C_{17}H_{18}N_2O_6S$	$[M+H]^+$	6.8	379.0958	−2.3	2	5
Cloxacillin	$C_{19}H_{18}Cl\,N_3O_5S$	$[M-H]^-$	11.9	434.0572	8.7	0.5	2
Dicloxacillin	$C_{19}H_{17}Cl_2N_3O_5S$	$[M-H]^-$	12.8	468.0182	2.8	1	3
Flucloxacillin	$C_{19}H_{17}ClFN_3O_5S$	$[M-H]^-$	12.4	452.0478	8.9	0.5	2
Nafcillin	$C_{21}H_{22}N_2O_5S$	$[M+H]^+$	12.2	415.1322	−1.9	0.2	0.7
		$[M-H]^-$	12.2	413.1165	3.6	0.2	0.7
Oxacillin	$C_{19}H_{19}N_3O_5S$	$[M-H]^-$	11.6	400.0962	6.6	1	3
Penicillin G	$C_{16}H_{18}N_2O_4S$	$[M+H]^+$	7.3	335.1060	−0.9	0.5	1
Penicillin V	$C_{16}H_{18}N_2O_5S$	$[M-H]^-$	11.2	349.0853	6.3	0.5	1
Pivampicillin	$C_{22}H_{29}N_3O_6S$	$[M+H]^+$	11.0	464.1849	−3.4	0.05	0.2
Piperacillin	$C_{23}H_{27}N_5O_7S$	$[M-H]^-$	10.0	516.1547	0.8	0.5	1
Sultamicillin	$C_{25}H_{30}N_4O_9S_2$	$[M+H]^+$	9.7	595.1527	−2.5	2	5
Ticarcillin	$C_{15}H_{16}N_2O_6S_2$	$[M+H]^+$	10.1	385.0523	−8.9	2	5
Cephalosporins (*n* = 8)							
Cefalexin	$C_{16}H_{17}N_3O_4S$	$[M+H]^+$	7.1	348.1013	1.6	0.5	2
Cefalonium	$C_{20}H_{18}N_4O_5S_2$	$[M+H]^+$	7.4	459.0791	2.3	1	5
Cefapirin	$C_{17}H_{17}N_3O_6S_2$	$[M+H]^+$	6.3	424.0632	−6.6	0.5	2
Cefoperazone	$C_{25}H_{27}N_9O_8S_2$	$[M-H]^-$	8.7	644.1340	−3.3	10	30
		$[M+H]^+$	8.7	646.1497	4.0	2	6
Cefotaxime	$C_{16}H_{17}N_5O_7S_2$	$[M+H]^+$	7.6	456.0642	−2.6	1	4
Cefquinome	$C_{23}H_{24}N_6O_5S_2$	$[M-H]^-$	7.0	527.1166	−2.4	10	30
Ceftiofur	$C_{19}H_{17}N_5O_7S_3$	$[M+H]^+$	9.5	524.0362	−2.1	1	4
Cefuroxime	$C_{16}H_{16}N_4O_8S$	$[M+H]^-$	8.5	423.0605	−4.5	5	20
Nitrofurans and their metabolites (*n* = 7)							
AGD[a]	$C_3H_5N_3O_2$	$[M-H]^-$	1.8	114.0298	3.5	20	60
		$[M+H]^+$	1.8	116.0454	3.5	20	60
AMOZ[b]	$C_8H_{15}O_3N_3$	$[M+H]^+$	1.3	202.1186	4.1	0.05	0.2
AOZ[c]	$C_3H_6O_2N_2$	$[M+H]^+$	1.6	103.0502	4.1	20	60
Furaltadone	$C_{13}H_{16}N_4O_6$	$[M+H]^+$	6.9	325.1143	0.9	0.2	0.6
Furazolidone	$C_8H_7N_3O_5$	$[M+H]^+$	8.8	226.0458	1.8	1	3

Table 1. (*continued*)

Analyte	Gross formula	Ion	t_R, min	*m/z*	Δ, ppm	LOD, ng/mL	LOQ, ng/mL
Nitrofurantoin	$C_8H_6N_4O_5$	$[M-H]^-$	8.3	237.0254	9.1	2	6
Nitrofurazone (furacilin)	$C_6H_6N_4O_4$	$[M-H]^-$	7.9	197.0305	0.1	10	40
Sulfonamides (*n* = 21)							
Sulfabenzamide	$C_{13}H_{12}N_2O_3S$	$[M+H]^+$	9.9	277.0641	4.9	20	60
Sulfacetamide	$C_8H_{10}N_2O_3S$	$[M+H]^+$	6.4	215.0485	1.6	0.5	1
Sulfachlorpyridazine	$C_{10}H_9ClN_4O_2S$	$[M+H]^+$	9.0	285.0207	2.7	0.2	0.5
Sulfadiazine	$C_{10}H_{10}N_4O_2S$	$[M+H]^+$	6.6	251.0597	2.7	0.1	0.4
Sulfadimethoxine	$C_{12}H_{14}N_4O_4S$	$[M+H]^+$	10.3	311.0808	1.3	0.1	0.4
Sulfadoxine	$C_{12}H_{14}N_4O_4S$	$[M+H]^+$	9.3	311.0808	2.0	0.1	0.4
Sulfaguanidine	$C_7H_{10}N_4O_2S$	$[M+H]^+$	2.5	215.0597	1.5	0.1	0.4
Sulfamerazine	$C_{11}H_{12}N_4O_2S$	$[M+H]^+$	7.6	265.0753	1.8	0.1	0.3
Sulfamethazine	$C_{12}H_{14}N_4O_2S$	$[M+H]^+$	8.2	279.0910	1.8	0.4	1
Sulfamethizole	$C_9H_{10}N_4O_2S_2$	$[M+H]^+$	8.2	271.0318	2.3	0.1	0.4
Sulfamethoxazole	$C_{10}H_{11}N_3O_3S$	$[M+H]^+$	9.4	254.0594	2.1	0.2	0.5
Sulfamethoxy-pyridazine	$C_{11}H_{12}N_4O_3S$	$[M+H]^+$	8.3	281.0703	2.8	0.1	0.4
Sulfamonomethoxine	$C_{11}H_{12}N_4O_3S$	$[M+H]^+$	8.7	281.0703	7.9	0.5	1
Sulfamoxole	$C_{11}H_{13}N_3O_3S$	$[M+H]^+$	8.2	268.0750	8.1	1	5
Sulfanilamide	$C_6H_8N_2O_2S$	$[M+H]^+$	2.5, 3.2	173.0379	3.2	5	15
Sulfanitran	$C_{14}H_{13}N_3O_5S$	$[M-H]^-$	11.3	334.0492	1.6	5	15
Sulfapyridine	$C_{11}H_{11}N_3O_2S$	$[M+H]^+$	7.3	250.0644	1.8	0.1	0.3
Sulfaquinoxaline	$C_{14}H_{12}N_4O_2S$	$[M+H]^+$	10.2	301.0753	1.9	0.1	0.4
Sulfasalazine	$C_{18}H_{14}N_4O_5S$	$[M+H]^+$	8.8	399.0758	1.6	20	60
Sulfathiazole	$C_9H_9N_3O_2S_2$	$[M+H]^+$	7.1	256.0208	2.8	0.07	0.2
Sulfisoxazole	$C_{11}H_{13}N_3O_3S$	$[M+H]^+$	17.4	268.0750	1.6	5	15
Quinolones (*n* = 18)							
Ciprofloxacin	$C_{17}H_{18}FN_3O_3$	$[M+H]^+$	7.7	332.1404	8.9	0.01	0.1
Danofloxacin	$C_{19}H_{20}FN_3O_3$	$[M+H]^+$	7.9	358.1561	8.1	0.001	0.01
Difloxacin	$C_{21}H_{19}F_2N_3O_3$	$[M+H]^+$	8.6	400.1467	8.2	0.01	0.1
Enoxacin	$C_{15}H_{17}FN_4O_3$	$[M+H]^+$	7.3	321.1357	1.2	0.01	0.1
Enrofloxacin	$C_{19}H_{22}FN_3O_3$	$[M+H]^+$	8.1	360.1717	8.1	0.001	0.01
Fleroxacine	$C_{17}H_{18}F_3N_3O_3$	$[M+H]^+$	7.6	370.1373	4.3	1	5
Flumequine	$C_{14}H_{12}FNO_3$	$[M+H]^+$	11.4	262.0873	−7.6	0.0005	0.005
Levofloxacin	$C_{18}H_{20}FN_3O_4$	$[M+H]^+$	7.5	362.1510	−9.6	0.01	0.1
Lomefloxacin	$C_{17}H_{19}F_2N_3O_3$	$[M+H]^+$	7.7	352.1467	0.2	0.001	0.01
Marbofloxacin	$C_{17}H_{19}FN_4O_4$	$[M+H]^+$	7.5	363.1463	9.0	0.01	0.1
Nalidixic acid	$C_{12}H_{12}N_2O_3$	$[M+H]^+$	11.2	233.0920	−7.2	0.0005	0.005
Norfloxacin	$C_{16}H_{18}FN_3O_3$	$[M+H]^+$	7.6	320.1404	−5.6	0.01	0.1
Ofloxacin	$C_{18}H_{20}FN_3O_4$	$[M+H]^+$	7.6	362.1510	9.9	0.01	0.1
Oxolinic acid	$C_{13}H_{11}NO_5$	$[M+H]^+$	9.9	262.0709	−1.0	0.0005	0.005
Pefloxacin	$C_{17}H_{20}FN_3O_3$	$[M+H]^+$	7.7	334.1561	9.8	0.01	0.1
Pipemidic acid	$C_{14}H_{17}N_5O_3$	$[M+H]^+$	6.9	304.1399	−4.7	5	10
Sarafloxacin	$C_{20}H_{17}F_2N_3O_3$	$[M+H]^+$	8.5	386.1310	−0.3	0.001	0.01
Sparfloxacin	$C_{19}H_{22}F_2N_4O_3$	$[M+H]^+$	8.4	393.1733	−1.5	0.01	0.1
Polypeptide antibiotics (*n* = 6)							
Bacitracin	$C_{66}H_{103}N_{17}O_{16}S$	$[M+2H]^{2+}$	9.2	711.8817	−3.4	10	30
Colistin (polymyxin E1)	$C_{53}H_{100}N_{16}O_{13}$	$[M+2H]^{2+}$	7.9	585.3901	1.3	1	3
Colistin (polymyxin E2)	$C_{52}H_{98}N_{16}O_{13}$	$[M+2H]^{2+}$	7.5	578.3822	2.0	1	3
Novobiocin	$C_{31}H_{36}N_2O_{11}$	$[M-H]^-$	14.9	611.2235	−3.6	1	4
Polymyxin B1 + B1-I	$C_{56}H_{98}N_{16}O_3$	$[M+2H]^{2+}$	7.8	522.4076	−1.7	10	30
Polymyxin B2 + B3	$C_{55}H_{96}N_{16}O_3$	$[M+2H]^{2+}$	7.5	515.3998	−2.0	10	30

Table 1. (*continued*)

Analyte	Gross formula	Ion	t_R, min	*m/z*	Δ, ppm	LOD, ng/mL	LOQ, ng/mL
Macrocyclic polyene antibiotics (*n* = 2)							
Amphotericin B	$C_{47}H_{73}NO_{17}$	$[M+H]^+$	11.2	924.4951	−7.4	2	5
		$[M+Na]^+$		946.4770	−9.1		
Nystatin	$C_{47}H_{75}NO_{17}$	$[M+H]^+$	10.8	926.5108	−6.4	2	5
		$[M+Na]^+$		948.4927	−2.0		
Antibiotic dyes and their metabolites (*n* = 13)							
Azure A	$C_{14}H_{14}N_3S$	$[M]^+$	8.5	256.0903	0.9	0.1	0.4
Azure B	$C_{15}H_{16}N_3S$	$[M]^+$	8.9	270.1059	1.0	0.1	0.4
Azure C	$C_{13}H_{12}N_3S$	$[M]^+$	8.0	242.0746	1.9	0.1	0.4
Acriflavine	$C_{14}H_{14}N_3$	$[M]^+$	8.6	224.1182	−2.9	0.01	0.04
Brilliant Green	$C_{27}H_{33}N_2$	$[M]^+$	14.1	385.2638	−9.6	0.01	0.05
Crystal Violet	$C_{25}H_{30}N_3$	$[M]^+$	13.2	372.2434	−8.9	0.01	0.04
Leucobrilliant Green	$C_{27}H_{34}N_2$	$[M+H]^+$	12.9	387.2795	2.3	0.1	0.3
Leucocrystal Violet	$C_{25}H_{31}N_3$	$[M+H]^+$	16.2	374.2591	−2.1	0.1	0.4
Leucomalachite Green	$C_{23}H_{26}N_2$	$[M+H]^+$	17.1	331.2187	1.8	0.1	0.3
Leucomethylene Blue	$C_{16}H_{19}N_3S$	$[M+H]^+$	8.1	286.1372	−0.7	0.1	0.5
Malachite Green	$C_{23}H_{25}N_2$	$[M]^+$	12.1	329.2012	−8.9	0.001	0.005
Methylene Blue	$C_{16}H_{18}N_3S$	$[M]^+$	9.4	284.1216	−9.2	0.01	0.04
Methyl Blue	$C_{24}H_{27}N_3$	$[M]^+$	12.8	358.2277	3.5	0.01	0.04
Mycotoxins (*n* = 24)							
15-Acetyldeoxynivalenol	$C_{17}H_{22}O_7$	$[M+H]^+$	8.4	339.1438	3.5	10	40
3-Acetyldeoxynivalenol	$C_{17}H_{22}O_7$	$[M+H]^+$	8.3	339.1438	3.5	10	40
Aflatoxin B1	$C_{17}H_{12}O_6$	$[M+H]^+$	11.0	313.0707	−0.3	0.01	0.05
Aflatoxin B2	$C_{17}H_{14}O_6$	$[M+H]^+$	10.5	315.0863	−0.3	0.005	0.02
Aflatoxin G1	$C_{17}H_{12}O_7$	$[M+H]^+$	10.5	329.0656	0.6	0.01	0.05
Aflatoxin G2	$C_{17}H_{14}O_7$	$[M+H]^+$	10.1	331.0812	−0.9	0.005	0.02
Aflatoxin M1	$C_{17}H_{12}O_7$	$[M+H]^+$	9.5	329.0656	−1.5	0.01	0.05
Citrinin	$C_{13}H_{14}O_5$	$[M+H]^+$	11.8	251.0914	−6.4	0.5	2
Deoxynivalenol	$C_{15}H_{20}O_6$	$[M+NH_4]^+$	5.2	314.1598	5.0	10	40
		$[M-H]^-$	5.2	295.1176	8.0	10	40
Diacetoxyscirpenol	$C_{19}H_{26}O_7$	$[M+H]^+$	10.9	367.1751	2.1	2	8
Fumonisin B1	$C_{34}H_{59}O_{15}N$	$[M+H]^+$	9.9	722.3957	−1.6	10	40
Fumonisin B2	$C_{34}H_{59}O_{14}N$	$[M+H]^+$	10.9	706.4008	−5.8	10	40
Fusarenon X	$C_{17}H_{22}O_8$	$[M+HCOO]^-$	7.7	399.1297	−2.0	20	60
Neosolaniol	$C_{19}H_{26}O_8$	$[M+NH_4]^+$	8.2	400.1966	−4.9	2	8
Nivalenol	$C_{15}H_{20}O_7$	$[M+HCOO]^-$	6.0	357.1181	3.6	2	8
		$[M+H]^+$	6.0	313.1281	0.3	2	8
Ochratoxin A	$C_{20}H_{18}O_6NCl$	$[M+H]^+$	13.4	404.0901	−4.9	1	3
		$[M-H]^-$	13.4	402.0739	9.9	0.5	2
Ochratoxin B	$C_{20}H_{19}O_6N$	$[M+H]^+$	12.1	370.1285	5.4	0.1	0.5
Patulin	$C_7H_6O_4$	$[M-H]^-$	6.1	153.0182	9.6	10	40
Sterigmatocystin	$C_{18}H_{12}O_6$	$[M+H]^+$	14.1	325.0707	−0.3	0.01	0.05
T2-triol	$C_{20}H_{30}O_7$	$[M+HCOO]^-$	10.1	427.1962	−1.4	2	8
T2-tetraol	$C_{15}H_{22}O_6$	$[M+H]^+$	9.6	299.1489	−0.6	0.05	0.2
Zearalenon	$C_{18}H_{22}O_5$	$[M-H]^-$	11.4	317.1384	3.0	5	20
HT-2 toxin	$C_{22}H_{32}O_8$	$[M+H]^+$	11.3	425.2169	3.3	20	60
T-2 toxin	$C_{24}H_{34}O_9$	$[M+NH_4]^+$	12.8	484.2541	4.5	20	60
Pesticides and their metabolites (*n* = 171)							
6-Chloronicotinic acid	$C_6H_4ClNO_2$	$[M+H]^+$	6.7	158.0003	6.8	20	60
Acephate	$C_4H_{10}NO_3PS$	$[M+H]^+$	5.6	184.0192	2.7	1	4
Acetamiprid	$C_{10}H_{11}ClN_4$	$[M+H]^+$	9.3	223.0745	0.1	5	20
Alanycarb	$C_{17}H_{25}N_3O_4S_2$	$[M+H]^+$	14.5	400.1359	2.3	6	19
Aldicarb	$C_7H_4N_2O_2S$	$[M+H]^+$	9.0	181.0849	8.3	5	20

Table 1. (*continued*)

Analyte	Gross formula	Ion	t_R, min	*m/z*	Δ, ppm	LOD, ng/mL	LOQ, ng/mL
Aldicarb-sulfone	$C_7H_{14}N_2O_4S$	$[M+H]^+$	7.1	223.0747	−6.4	0.3	0.9
Ametryn	$C_9H_{17}N_5S$	$[M+H]^+$	10.5	228.1277	−2.1	10	40
Amitraz	$C_{19}H_{23}N_3$	$[M+H]^+$	17.8	294.1964	3.3	0.005	0.02
Atrazine	$C_8H_{14}ClN_5$	$[M+H]^+$	12.1	216.1010	−2.7	0.1	0.3
Atrazine-desethyl	$C_6H_{10}ClN_5$	$[M+H]^+$	9.1	188.0698	−0.5	0.05	0.2
Atrazine-desethyl-desisopropyl	$C_3H_4ClN_5$	$[M+H]^+$	11.0	146.0228	0.6	1	4
Atrazine-desisopropyl	$C_5H_8ClN_5$	$[M+H]^+$	7.8, 13.5	174.0541	0.1	0.05	0.2
Avermectin B1b	$C_{47}H_{70}O_{14}$	$[M+Na]^+$	19.4	881.4658	2.0	0.5	1
Avermectin B1a	$C_{48}H_{72}O_{14}$	$[M+Na]^+$	18.6	895.4814	−1.2	0.5	1
Azoxystrobin	$C_{22}H_{17}N_3O_5$	$[M+H]^+$	13.9	404.1241	−9.4	1	4
Benalaxyl	$C_{20}H_{23}NO_3$	$[M+H]^+$	15.1	326.1751	−6.4	0.3	1
Benfuracarb	$C_{20}H_{30}N_2O_5S$	$[M+H]^+$	16.6	411.1948	3.8	0.1	0.2
Bentazon	$C_{10}H_{12}N_2O_3S$	$[M+H]^+$	13.4	241.0641	−1.2	20	60
Bitertanol	$C_{20}H_{23}N_3O_2$	$[M+H]^+$	14.3	338.1863	5.4	0.1	0.4
Bromoxynil	$C_7H_3Br_2NO$	$[M-H]^-$	12.6	273.8498	−3.2	5	20
Bromuconazol	$C_{13}H_{12}BrCl_2N_3O$	$[M+H]^+$	13.5	377.9590	10	2	5
Bupirimate	$C_{13}H_{24}N_4O_3S$	$[M+H]^+$	14.9	317.1642	−7.7	0.03	0.09
Buprofezin	$C_{16}H_{23}N_3OS$	$[M+H]^+$	17.3	306.1635	−8.5	0.1	0.4
Carbaryl	$C_{12}H_{11}NO_2$	$[M+H]^+$	6.5	202.0863	1.9	20	60
Carbendazim	$C_9H_9N_3O_2$	$[M+H]^+$	6.5	192.0768	−5.2	0.1	0.3
Carbendazim D	$C_9H_5N_3O_2D_4$	$[M+H]^+$	6.5	196.1019	−4.0	0.1	0.3
Carbofuran	$C_{12}H_{15}NO_3$	$[M+NH_4]^+$	6.4	239.1390	−4.2	20	60
Carbofuran-3-hydroxy	$C_{12}H_{15}NO_4$	$[M+H]^+$	8.7	238.1074	6.4	0.6	2
Chlorantraniliprole	$C_{18}H_{14}BrCl_2N_5O_2$	$[M+H]^+$	12.8	483.9758	0.1	1	2
Chlorbromuron	$C_9H_{10}ClBrN_2O_2$	$[M+H]^+$	7.0, 7.2	292.9687	−1.9	5	20
Chlorfenvinphos	$C_{12}H_{14}Cl_3O_4P$	$[M+H]^+$	15.8	358.9768	−8.9	0.02	0.06
Chloridazon	$C_{10}H_8ClN_3O$	$[M+H]^+$	9.0	222.0429	2.6	0.005	0.02
Chloroxuron	$C_{15}H_{15}ClN_2O_2$	$[M+H]^+$	13.7	291.0895	−1.0	0.002	0.006
Chlortoluron	$C_{10}H_{13}ClN_2O$	$[M+H]^+$	11.9	213.0789	0.7	0.05	0.2
Clethodim	$C_{17}H_{26}ClNO_3S$	$[M+H]^+$	16.5	360.1395	0.4	2	8
Clothianidin	$C_6H_8ClN_5O_2S$	$[M+H]^+$	8.8	250.0160	1.1	5	20
Crimidine	$C_7H_{10}ClN_3$	$[M+H]^+$	8.8	172.0636	−0.5	0.05	0.2
Cyanazine	$C_9H_{13}ClN_6$	$[M+H]^+$	11.0	241.0963	−5.3	0.05	0.2
Cyproconazol	$C_{15}H_{18}ClN_3O$	$[M+H]^+$	13.5	292.1211	−1.3	0.1	0.4
Cyprodinil	$C_{14}H_{15}N_3$	$[M+H]^+$	14.1	226.1339	1.9	0.05	0.2
Cyromazine	$C_6H_{10}N_6$	$[M+H]^+$	2.4	167.1040	−1.2	0.1	0.3
Demeton-*S*-methyl-sulfon	$C_6H_{15}O_5PS_2$	$[M+H]^+$	8.0	263.0172	−0.7	0.01	0.04
Desmedipham	$C_{16}H_{16}N_2O_4$	$[M+H]^+$	13.1	301.1183	−4	0.2	0.6
Diazinon	$C_{12}H_{21}N_2O_3PS$	$[M+H]^+$	16.0	305.1083	4.5	20	60
Diclobutrazol	$C_{15}H_{19}Cl_2N_3O$	$[M+H]^+$	14.0	328.0978	−6.2	1	2
Dicrotophos	$C_8H_{16}NO_5P$	$[M+H]^+$	6.7	238.0839	9.7	0.1	0.5
Dicyclanil	$C_8H_{10}N_6$	$[M+H]^+$	6.1	191.1039	3.8	0.01	0.03
Difenoconazol	$C_{19}H_{17}Cl_2N_3O_3$	$[M+H]^+$	15.5	406.0719	1.7	0.01	0.04
Dimethoate	$C_5H_{12}NO_3PS_2$	$[M+H]^+$	9.3	230.0069	−0.8	5	20
Dimethomorph	$C_{21}H_{22}ClNO_4$	$[M+H]^+$	12.7, 12.9	388.1310	−2.3	0.1	0.4
Dimoxystrobin	$C_{19}H_{22}N_2O_3$	$[M+H]^+$	7.0	327.1703	−1.8	2	6
Diniconazole	$C_{15}H_{17}Cl_2N_3O$	$[M+H]^+$	15.0	326.0821	−1.7	20	60
Dinotefuran	$C_7H_{14}N_4O_3$	$[M+H]^+$	6.9	203.1139	0.5	1	4
Emamectin B1a	$C_{49}H_{75}NO_{13}$	$[M+H]^+$	13.5	886.5316	−9.1	0.05	0.2
		$[M+Na]^+$		908.5131			
Emamectin B1b	$C_{48}H_{73}NO_{13}$	$[M+H]^+$	13.0	872.5155	6.6	0.1	0.4
Epoxiconazole	$C_{17}H_{13}ClFN_3O$	$[M+H]^+$	14.0	330.0803	−8.7	1	3
Etaconazol	$C_{14}H_{15}Cl_2N_3O_2$	$[M+H]^+$	13.7	328.0614	2.2	0.1	0.2

Table 1. (*continued*)

Analyte	Gross formula	Ion	t_R, min	*m/z*	Δ, ppm	LOD, ng/mL	LOQ, ng/mL
Ethirimol	$C_{11}H_{19}N_3O$	$[M+H]^+$	8.4	210.1601	−1.7	1	4
Etoxazole	$C_{21}H_{23}F_2NO_2$	$[M+H]^+$	17.5	360.1770	−5.9	0.05	0.2
Etrimfos	$C_{10}H_{17}N_2O_4PS$	$[M+H]^+$	15.8	293.0719	4.0	0.002	0.006
Fenamidone	$C_{17}H_{17}N_3OS$	$[M+H]^+$	13.7	312.1165	−7.6	0.2	0.5
Fenarimol	$C_{17}H_{12}C_{l2}N_2O$	$[M+H]^+$	13.5	331.0400	−6.6	0.01	0.05
Fenazaquin	$C_{20}H_{22}N_2O$	$[M+H]^+$	18.0	307.1805	−7.1	0.2	0.7
Fenbuconazol	$C_{19}H_{17}ClN_4$	$[M+H]^+$	14.2	337.1215	−6.8	0.01	0.05
Fenoxycarb	$C_{17}H_{19}NO_4$	$[M+H]^+$	11.0	302.1387	−1.9	1	2
Fenpropimorph	$C_{20}H_{33}NO$	$[M+H]^+$	12.8	304.2635	−7.7	0.1	0.4
Fenpyroximate	$C_{24}H_{27}N_3O_4$	$[M+H]^+$	17.4	422.2074	−0.9	0.2	0.7
Fenuron	$C_9H_{12}N_2O$	$[M+H]^+$	8.9	165.1022	−1.8	0.002	0.006
Fludioxonil	$C_{12}H_6N_2O_2F_2$	$[M-H]^-$	13.5	247.0314	1.2	1	3
Fluometuron	$C_{10}H_{11}F_3N_2O$	$[M+H]^+$	11.9	233.0896	0.4	10	30
Fluoxastrobin	$C_{21}H_{16}ClFN_4O_5$	$[M+H]^+$	14.7	459.0866	2.1	0.1	0.3
Flusilazole	$C_{16}H_{15}F_2N_3Si$	$[M+H]^+$	14.1	316.1076	−8.5	0.4	1
Flutriafol	$C_{16}H_{13}F_2N_3O$	$[M+H]^+$	11.9	302.1099	3.3	0.01	0.04
Fonofos	$C_{10}H_{15}OPS_2$	$[M+H]^+$	8.8	247.0374	1.9	0.1	0.5
Forchlorfenuron	$C_{12}H_{10}ClN_3O$	$[M+H]^+$	10.8	248.0585	7.3	1	5
Formetanat	$C_{11}H_{15}N_3O_2$	$[M+H]^+$	4.4	222.1237	−0.8	1	3
Fuberidazole	$C_{11}H_8N_2O$	$[M+H]^+$	8.3	185.0709	−6.3	9	31
Furalaxyl	$C_{17}H_{19}NO_4$	$[M+H]^+$	13.3	302.1387	9.2	0.2	0.7
Furathiocarb	$C_{18}H_{26}N_2O_5S$	$[M+H]^+$	16.7	383.1635	2.7	2	5
Glufosinate	$C_5H_{12}NO_4P$	$[M+H]^+$	1.2	182.0577	1.9	1	4
		$[M+Na]^+$		204.0396			
Glyphosate	$C_3H_8NO_5P$	$[M+H]^+$	1.2	170.0213	2.7	5	20
		$[M+Na]^+$		192.0032			
Hexaconazol	$C_{14}H_{17}C_{l2}N_3O$	$[M+H]^+$	14.3	314.0821	−5.1	2	6
Hexazinone	$C_{12}H_{20}N_4O_2$	$[M+H]^+$	10.3	253.1659	−1.9	0.005	0.02
Hydramethylnon	$C_{25}H_{24}F_6N_4$	$[M+H]^+$	14.8	495.1978	−1.3	0.1	0.2
Imazalil	$C_{14}H_{14}Cl_2N_2O$	$[M+H]^+$	11.0	297.0556	−1.6	0.05	0.2
Imazamethabenz	$C_{15}H_{18}N_2O_3$	$[M+H]^+$	8.5	275.1391	−5.8	0.1	0.3
Imazapyr	$C_{13}H_{15}N_3O_3$	$[M+H]^+$	8.0	262.1186	−5.7	0.1	0.3
Imazaquin	$C_{17}H_{17}N_3O_3$	$[M+H]^+$	10.9	312.1343	−7.0	0.1	0.3
Imazethapyr	$C_{15}H_{19}N_3O_3$	$[M+H]^+$	10.0	290.1499	−6.8	0.1	0.3
Imidacloprid	$C_9H_{10}ClN_5O_2$	$[M+H]^+$	9.0	256.0596	−1.5	0.2	0.6
Ioxynil	$C_7H_3I_2NO$	$[M+H]^-$	13.4	369.8220	10	20	60
Ipconazole	$C_{18}H_{24}ClN_3O$	$[M+H]^+$	15.2	334.1681	−6.1	1	2
Iprovalicarb	$C_{18}H_{28}N_2O_3$	$[M+H]^+$	13.4	321.2173	−7.6	0.1	0.4
Isoproturon	$C_{12}H_{18}N_2O$	$[M+H]^+$	12.2	207.1492	−2.9	0.001	0.005
Kresoxim-methyl	$C_{18}H_{19}NO_4$	$[M+H]^+$	11.5	314.1387	2.0	20	60
Malathion	$C_{10}H_{19}O_6PS_2$	$[M+H]^+$	12.1	331.0433	7.2	2	6
Mandipropamid	$C_{23}H_{22}ClNO_4$	$[M+H]^+$	13.7	412.1310	0.9	5	20
Mebendazole	$C_{16}H_{13}N_3O_3$	$[M+H]^+$	10.4	296.1030	5.7	0.02	0.06
Mefenacet	$C_{16}H_{14}N_2O_2S$	$[M+H]^+$	13.8	299.0849	9.1	0.2	0.7
3-Methylphosphinico-propionic acid (a metabolite of glufosinate)	$C_4H_9O_4P$	$[M+H]^+$	1.2	153.0311	2.1	10	40
Aminomethyl-phosphonic acid (a metabolite of glyphosate)	CH_6NO_3P	$[M+H]^+$	1.2	112.0158	0.8	20	60
Metalaxyl	$C_{15}H_{21}NO_4$	$[M+H]^+$	10.9	280.1543	−7.6	0.4	1
Metamitron	$C_{10}H_{10}N_4O$	$[M+H]^+$	8.7	203.0927	−0.9	0.02	0.06
Metazachlor	$C_{14}H_{16}ClN_3O$	$[M+H]^+$	12.8	278.1055	−0.3	0.005	0.02
Metconazole	$C_{17}H_{22}ClN_3O$	$[M+H]^+$	14.5	320.1524	5.7	0.5	2
Methabenzthiazuron	$C_{10}H_{11}N_3OS$	$[M+H]^+$	11.7	222.0696	−0.9	0.02	0.06
Methoprotryne	$C_{11}H_{21}N_5OS$	$[M+H]^+$	11.4	272.1540	−7.5	0.2	0.5

Table 1. (*continued*)

Analyte	Gross formula	Ion	t_R, min	*m/z*	Δ, ppm	LOD, ng/mL	LOQ, ng/mL
Methoxyfenozide	$C_{22}H_{28}N_2O_3$	$[M+H]^+$	14.1	369.2173	−4.0	2	5
Metobromuron	$C_9H_{11}BrN_2O_2$	$[M+H]^+$	12.6	259.0077	1.1	20	60
Metolachlor	$C_{15}H_{22}ClNO_2$	$[M+H]^+$	14.9	284.1412	−0.3	0.01	0.04
Metoxuron	$C_{10}H_{13}ClN_2O_2$	$[M+H]^+$	10.4	229.0738	−0.8	0.02	0.06
Metribuzin	$C_8H_{14}N_4OS$	$[M+H]^+$	11.2	215.0961	−0.9	0.02	0.06
Mevinphos	$C_7H_{13}O_6P$	$[M+H]^+$	8.8	225.0522	0.1	0.05	0.2
Monocrotophos	$C_7H_{14}NO_5P$	$[M+H]^+$	5.4	224.0682	5.9	0.1	0.4
Monuron	$C_9H_{11}ClN_2O$	$[M+H]^+$	10.8	199.0633	−1.0	10	30
Nicosulfuron	$C_{15}H_{18}N_6O_6S$	$[M+H]^+$	10.3	411.1081	−7.7	1	5
Nitenpyram	$C_{11}H_{15}ClN_4O_2$	$[M+H]^+$	7.5	271.0956	1.3	0.01	0.05
Nuarimol	$C_{17}H_{12}ClFN_2O$	$[M+H]^+$	12.6	315.0695	−4.8	0.1	0.2
Oxadixyl	$C_{14}H_{18}N_2O_4$	$[M+H]^+$	9.6	279.1339	8.2	0.3	0.9
Paclobutrazol	$C_{15}H_{20}ClN_3O$	$[M+H]^+$	13.2	294.1367	−8.8	0.1	0.3
Paraoxon-ethyl	$C_{10}H_{14}NO_6P$	$[M+H]^+$	13.9	276.0632	2.9	5	20
Penconazole	$C_{13}H_{15}Cl_2N_3$	$[M+H]^+$	14.7	284.0718	−2.7	5	20
Pencycuron	$C_{19}H_{21}ClN_2O$	$[M+H]^+$	16.1	329.1415	−9.7	10	40
Pendimethalin	$C_{13}H_{19}N_3O_4$	$[M+H]^+$	17.6	282.1448	−8.8	10	30
Phenmedipham	$C_{16}H_{16}N_2O_4$	$[M+H]^+$	9.6	301.1183	1.7	2	5
Phosalone	$C_{12}H_{15}ClNO_4PS_2$	$[M+H]^+$	16.2	367.9941	−2.7	10	40
Picoxystrobin	$C_{18}H_{16}F_3NO_4$	$[M+H]^+$	15.0	368.1104	−10	0.3	1
Piperophos	$C_{14}H_{28}NO_3PS_2$	$[M+H]^+$	16.4	354.1320	−1.1	1	6
Pirimicarb	$C_{11}H_{18}N_4O_2$	$[M+H]^+$	6.4, 8.4	239.1503	−0.8	0.001	0.005
Pirimiphos-ethyl	$C_{13}H_{24}N_3O_3PS$	$[M+H]^+$	17.7	334.1349	3.8	0.001	0.004
Pirimiphos-methyl	$C_{11}H_{20}N_3O_3PS$	$[M+H]^+$	16.4, 13.9	306.1036	4.2	0.001	0.004
Pirimisulfuron-methyl	$C_{15}H_{12}F_4N_4O_7S$	$[M+H]^+$	14.0	469.0436	−7.6	0.01	0.03
Prochloraz	$C_{15}H_{16}Cl_3N_3O_2$	$[M+H]^+$	13.3	376.0381	0.2	0.01	0.04
Prometryn	$C_{10}H_{19}N_5S$	$[M+H]^+$	11.6	242.1434	−2.8	0.001	0.004
Propazine	$C_9H_{16}ClN_5$	$[M+H]^+$	13.3	230.1167	−1.3	0.002	0.006
Propetamphos	$C_{10}H_{20}NO_3PS$	$[M+H]^+$	12.4	294.1036	−3.1	20	60
Propham	$C_{10}H_{13}NO_2$	$[M+H]^+$	24.7	180.1019	−1.6	10	30
Propiconazole	$C_{15}H_{17}Cl_2N_3O_2$	$[M+H]^+$	15.0	342.0771	0.5	0.005	0.02
Pyraclostrobin	$C_{19}H_{18}ClN_3O_4$	$[M+H]^+$	15.6	388.1059	6.4	0.1	0.4
Pyridaben	$C_{19}H_{25}ClN_2OS$	$[M+H]^+$	18.0	365.1449	−3.8	5	20
Pyriproxifen	$C_{20}H_{19}NO_3$	$[M+H]^+$	16.9	322.1438	−6.4	0.2	0.7
Quinoxyfen	$C_{15}H_8Cl_2FNO$	$[M+H]^+$	16.9	308.0040	8	0.3	1
Sebuthlazin	$C_9H_{16}ClN_5$	$[M+H]^+$	13.2	230.1167	−1.7	0.002	0.006
Siduron	$C_{14}H_{20}N_2O$	$[M+H]^+$	13	233.1648	−0.3	5	20
Simazine	$C_7H_{12}ClN_5$	$[M+H]^+$	10.9	202.0854	−1.4	0.005	0.02
Spinetoram	$C_{42}H_{69}NO_{10}$	$[M+H]^+$	14.4	748.4994	0.5	0.3	0.9
Spinosad	$C_{41}H_{65}NO_{10}$	$[M+H]^+$	12.6	732.4681	−10	20	60
Spirotetramat	$C_{21}H_{27}NO_5$	$[M+H]^+$	12.7	374.1962	4.4	0.1	0.5
Spiroxamine	$C_{18}H_{35}NO_2$	$[M+H]^+$	10.7	298.2741	−6.2	1	4
Tebuconazole	$C_{16}H_{22}ClN_3O$	$[M+H]^+$	14.4	308.1524	3.8	20	60
Tebufenozide	$C_{22}H_{28}N_2O_2$	$[M+H]^+$	14.2	353.2224	−6.4	2	7
Terbuthylazine	$C_9H_{16}ClN_5$	$[M+H]^+$	13.6	230.1167	−1.7	0.001	0.005
Terbuthylazine-desethyl	$C_7H_{12}ClN_5$	$[M+H]^+$	10.8, 11.0	202.0854	−1.4	0.1	0.3
Terbutryn	$C_{10}H_{19}N_5S$	$[M+H]^+$	11.7	242.1434	−2.8	0.001	0.004
Tetramethrin	$C_{19}H_{25}NO_4$	$[M+NH_4]^+$	7.0	349.2121	2.5	10	40
Thiabendazole	$C_{10}H_7N_3S$	$[M+H]^+$	7.2	202.0433	−6.4	1	4
Thiabendazole D	$C_{10}HN_3SD_6$	$[M+H]^+$	7.2	208.0810	−3.3	1	4
Thiacloprid	$C_{10}H_9ClN_4S$	$[M+H]^+$	10.2	253.0309	−5.5	5	20
Thiamethoxam	$C_8H_{10}ClN_5O_3S$	$[M+H]^+$	8.1	292.0267	1.3	0.2	0.6
Thiofanox	$C_9H_{18}N_2O_2S$	$[M+H]^+$	9.6	219.1162	10	1	3
Thiophanate-methyl	$C_{12}H_{14}O_4S_2N_4$	$[M+H]^+$	11.2	343.0529	3.5	1	4

Table 1. (*continued*)

Analyte	Gross formula	Ion	t_R, min	*m/z*	Δ, ppm	LOD, ng/mL	LOQ, ng/mL
Thiram	$C_6H_{12}S_4N_2$	$[M+H]^+$	12.2	240.9956	3.5	0.1	0.4
Triadimefon	$C_{14}H_{16}ClN_3O_2$	$[M+H]^+$	14.1	294.1004	−2.1	1	4
Triadimenol	$C_{14}H_{18}ClN_3O_2$	$[M+H]^+$	13.2, 13.4	296.1160	0.3	1	4
Triasulfuron	$C_{14}H_{16}ClN_5O_5S$	$[M+H]^+$	11.6	402.0633	0.2	1	4
Tricyclazole	$C_9H_7N_3S$	$[M+H]^+$	8.4	190.0433	−2.1	10	30
Trietazine	$C_9H_{16}ClN_5$	$[M+H]^+$	14.6	230.1167	−2.1	5	20
Trifloxystrobin	$C_{20}H_{19}F_3N_2O_4$	$[M+H]^+$	7.3	409.1369	−1.7	1	3
Triflumizole	$C_{15}H_{15}ClF_3N_3O$	$[M+H]^+$	15.5	346.0929	8.4	0.3	0.8
Triticonazole	$C_{17}H_{20}ClN_3O$	$[M+H]^+$	13.5	318.1368	2.1	0.01	0.04
Vamidothion	$C_8H_{18}NO_4PS_2$	$[M+H]^+$	7.3	288.0488	−10	0.1	0.3
			Food dyes ($n=15$)				
Amaranth E123	$C_{20}H_{11}N_2Na_3O_{10}S_3$	$[M-3Na+H]^{2-}$	7.5, 24.9	267.9822	1.3	100	300
Astaxanthin E161j	$C_{40}H_{52}O_4$	$[M+H]^+$	20.3	597.3938	1.1	2	6
Yellow Sunset E110	$C_{16}H_{10}N_2Na_2O_7S_2$	$[M-2Na+H]^-$	7.3	407.0002	2.3	5	20
Green S E142	$C_{27}H_{25}N_2O_7S_2Na$	$[M-Na]^-$	9.1	554.1176	0.9	0.5	2
		$[M-Na+2H]^+$	9.1	555.1254	−1.9	5	20
Indigo carmine E132	$C_{16}H_8N_2Na_2O_8S_2$	$[M-2Na+H]^-$	6.3,7.1	420.9795	1.3	20	60
		$[M+H]^+$	6.3	466.9590	1.3	20	60
Canthaxanthin E161g	$C_{40}H_{52}O_2$	$[M+H]^+$	23.3, 23.7	565.4040	1.0	2	6
Karmazin E122	$C_{20}H_{12}N_2Na_2O_7S_2$	$[M-2Na+H]^-$	8.9	457.0159	1.3	5	20
		$[M+H]^+$	8.9	502.9954	1.0	50	200
Curcumin E100	$C_{21}H_{20}O_6$	$[M+H]^+$	13.5	369.1333	1.9	50	200
Red 2G E128	$C_{18}H_{13}N_3Na_2O_8S_2$	$[M-2Na+H]^-$	8.2	464.0217	0.7	2	6
Allura Red AC E129	$C_{18}H_{14}N_2Na_2O_8S_2$	$[M-2Na+H]^-$	7.8	451.0264	−1.2	5	20
		$[M+H]^+$	7.8	497.0059	2.3	50	200
Patented Blue V E131	$C_{54}H_{64}N_4O_{14}S_4Ca$	$[M-Ca]^{2-}$	11.0	559.1567	0.9	2	6
		$[M-Ca+H]^+$	11.0	1121.3374	−6.3	2	6
Ponceau 4R E124	$C_{20}H_{11}N_2Na_3O_{10}S_3$	$[M-3Na+2H]^-$	24.9	536.9727	3.0	100	300
Brilliant Blue E133	$C_{37}H_{34}N_2O_9S_3Na_2$	$[M-2Na+H]^-$	9.1	747.1510	3.0	2	6
		$[M-2Na+3H]^+$	9.1	749.1656	−2.0	10	40
Tartrazine E102	$C_{16}H_9N_4Na_3O_9S_2$	$[M-3Na+2H]^-$	8.9	466.9961	2.9	10	50
Erythrosine E127	$C_{20}H_8I_4O_5Na_2$	$[M-2Na+H]^-$	14.2	834.6478	−1.3	0.1	0.5
		$[M-2Na+3H]^+$	14.3	836.6623	1.2	20	60
			Synthetic dyes ($n=12$)				
Acridine yellow	$C_{15}H_{15}N_3$	$[M+H]^+$	9.3	238.1339	2.3	0.01	0.04
Dimethyl yellow	$C_{14}H_{15}N_3$	$[M+H]^+$	16.7	226.1339	0.6	0.01	0.04
Methyl red	$C_{15}H_{15}N_3O_2$	$[M+H]^+$	14.6	270.1237	3.1	0.5	2
Para Red	$C_{16}H_{11}N_3O_3$	$[M+H]^+$	16.5	294.0873	1.9	1	3
Direct Red	$C_{35}H_{25}N_7Na_2O_{10}S_2$	$[M+H]^+$	8.8	814.0972	2.1	10	40
Rodamine 6G	$C_{18}H_{31}N_2O_3$	$[M]^+$	9.2	323.2329	0.9	2	8
Sudan I	$C_{16}H_{12}N_2O$	$[M+H]^+$	17.5	249.1022	1.3	1	3
Sudan II	$C_{18}H_{16}N_2O$	$[M+H]^+$	19.3	277.1335	1.8	1	3
Sudan III	$C_{22}H_{16}N_4O$	$[M+H]^+$	20.2	353.1397	1.0	1	4
Sudan IV	$C_{24}H_{20}N_4O$	$[M+H]^+$	18.7, 18.9	381.1710	3.6	1	4
Sudan G	$C_{18}H_{18}N_4O$	$[M+H]^+$	18.8, 19.2	307.1553	0.8	10	40
Hrizoidin	$C_{12}H_{12}N_4$	$[M+H]^+$	9.3	213.1134	1.0	0.5	2

[a] AGD = 1-Aminogidantoin.

[b] AMOZ = 3-Amino-5-morpholinomethyl-2-oxazolidinone.

[c] AOZ = 3-Amino-2-oxazolidinone.

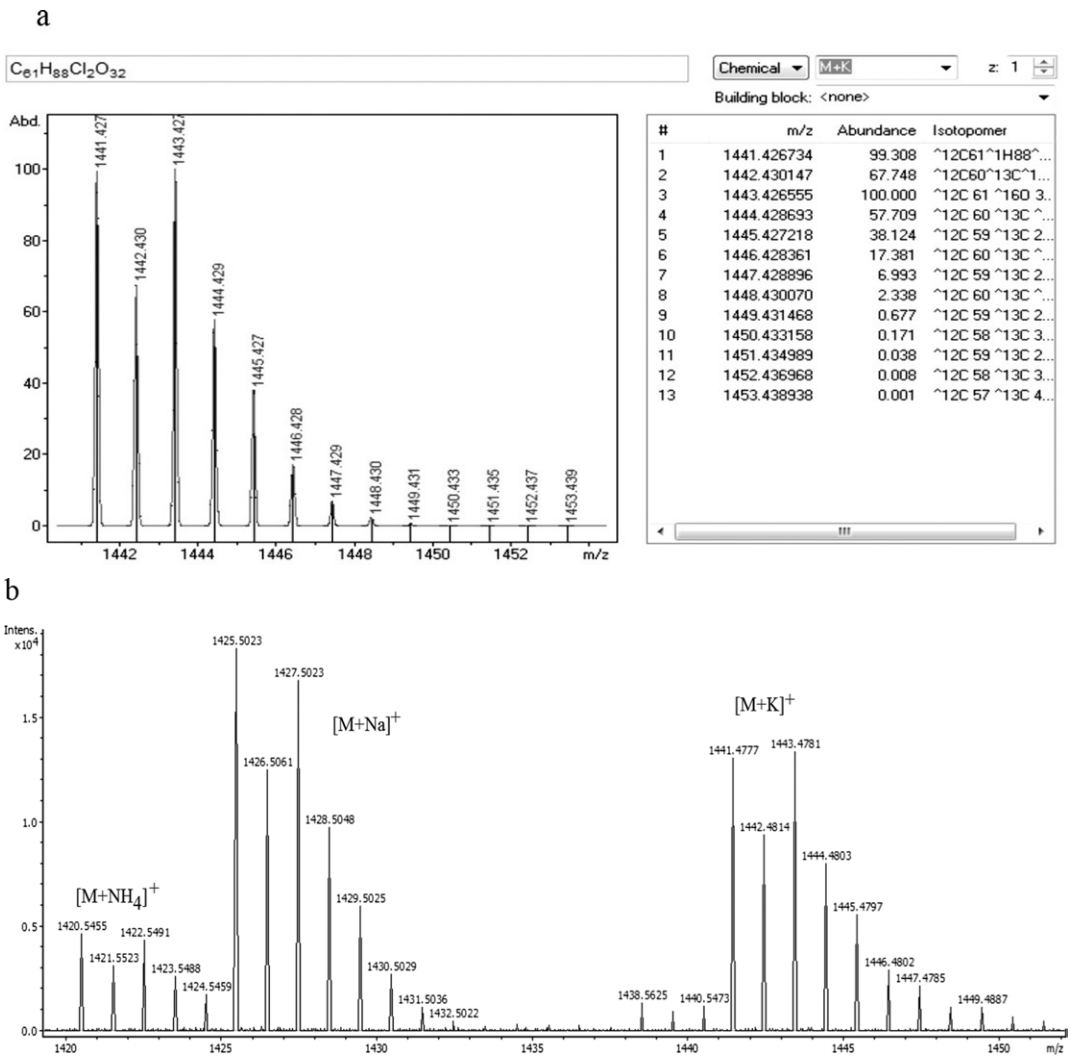


Figure 1. Presented are the (a) mass spectrum of avilamycin potassium adduct and (b) experimentally registered mass-spectrum of avilamycin ammonium, sodium and potassium adducts generated by IsotopePattern software.

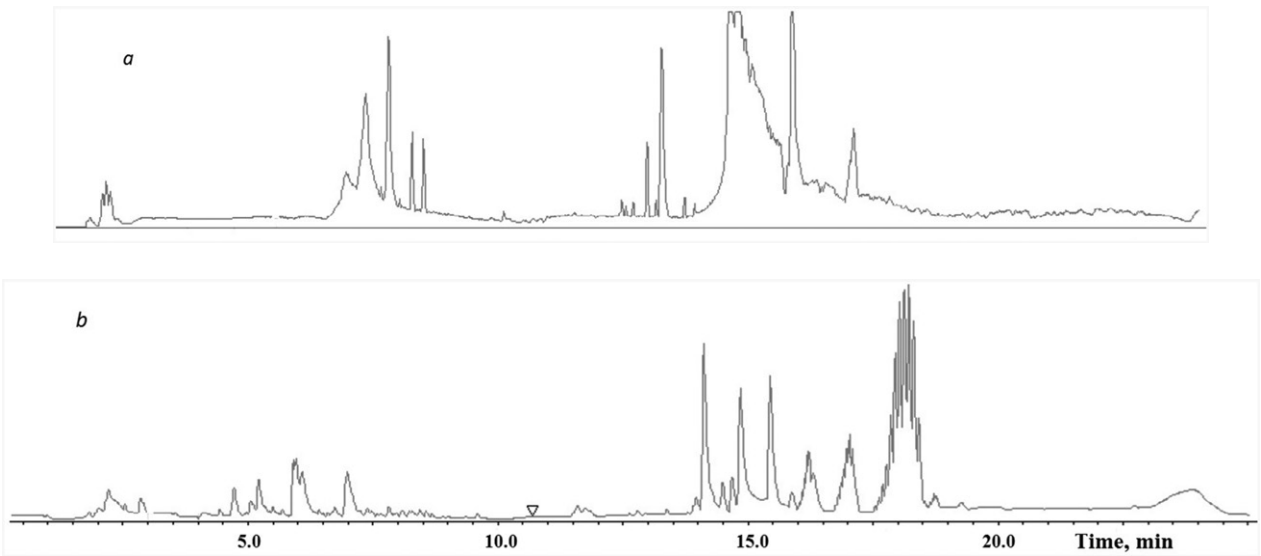
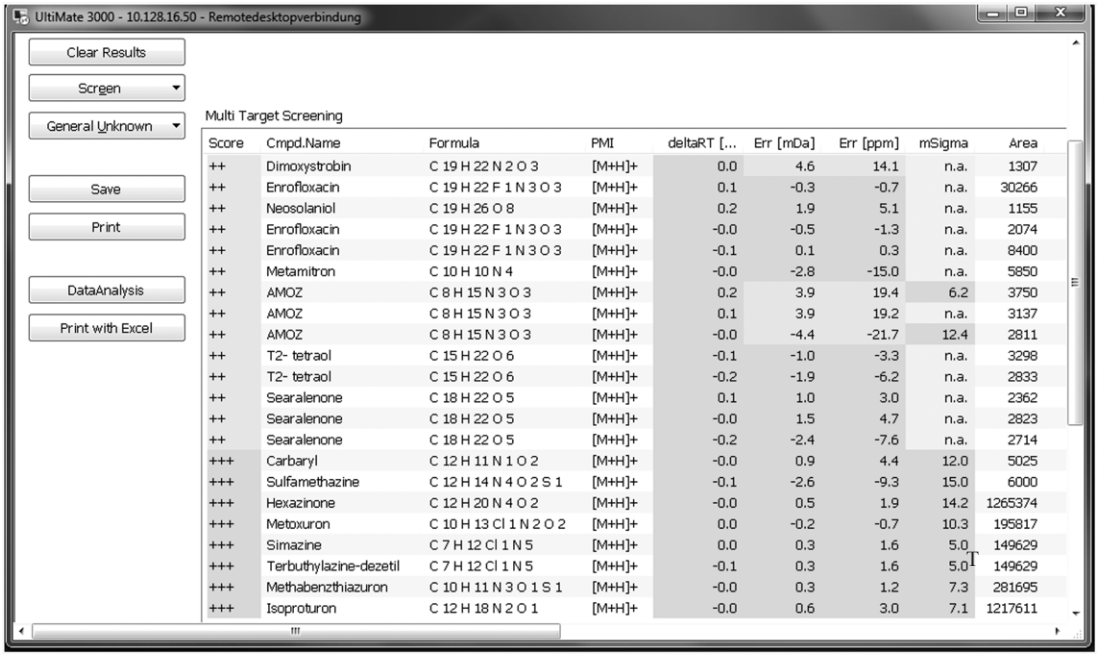


Figure 2. Total ion chromatograms of milk extracts with (a) QuEChERS and (b) the extraction of fat with hexane.



Score	Cmpd.Name	Formula	PMI	deltaRT [...	Err [mDa]	Err [ppm]	mSigma	Area
++	Dimoxystrobin	C 19 H 22 N 2 O 3	[M+H]+	0.0	4.6	14.1	n.a.	1307
++	Enrofloxacin	C 19 H 22 F 1 N 3 O 3	[M+H]+	0.1	-0.3	-0.7	n.a.	30266
++	Neosolaniol	C 19 H 26 O 8	[M+H]+	0.2	1.9	5.1	n.a.	1155
++	Enrofloxacin	C 19 H 22 F 1 N 3 O 3	[M+H]+	-0.0	-0.5	-1.3	n.a.	2074
++	Enrofloxacin	C 19 H 22 F 1 N 3 O 3	[M+H]+	-0.1	0.1	0.3	n.a.	8400
++	Metamitron	C 10 H 10 N 4	[M+H]+	-0.0	-2.8	-15.0	n.a.	5850
++	AMOZ	C 8 H 15 N 3 O 3	[M+H]+	0.2	3.9	19.4	6.2	3750
++	AMOZ	C 8 H 15 N 3 O 3	[M+H]+	0.1	3.9	19.2	n.a.	3137
++	AMOZ	C 8 H 15 N 3 O 3	[M+H]+	-0.0	-4.4	-21.7	12.4	2811
++	T2- tetraol	C 15 H 22 O 6	[M+H]+	-0.1	-1.0	-3.3	n.a.	3298
++	T2- tetraol	C 15 H 22 O 6	[M+H]+	-0.2	-1.9	-6.2	n.a.	2833
++	Searalenone	C 18 H 22 O 5	[M+H]+	0.1	1.0	3.0	n.a.	2362
++	Searalenone	C 18 H 22 O 5	[M+H]+	-0.0	1.5	4.7	n.a.	2823
++	Searalenone	C 18 H 22 O 5	[M+H]+	-0.2	-2.4	-7.6	n.a.	2714
+++	Carbaryl	C 12 H 11 N 1 O 2	[M+H]+	-0.0	0.9	4.4	12.0	5025
+++	Sulfamethazine	C 12 H 14 N 4 O 2 S 1	[M+H]+	-0.1	-2.6	-9.3	15.0	6000
+++	Hexazinone	C 12 H 20 N 4 O 2	[M+H]+	-0.0	0.5	1.9	14.2	1265374
+++	Metoxuron	C 10 H 13 Cl 1 N 2 O 2	[M+H]+	0.0	-0.2	-0.7	10.3	195817
+++	Simazine	C 7 H 12 Cl 1 N 5	[M+H]+	0.0	0.3	1.6	5.0	149629
+++	Terbuthylazine-dezetil	C 7 H 12 Cl 1 N 5	[M+H]+	-0.1	0.3	1.6	5.0	149629
+++	Methabenzthiazuron	C 10 H 11 N 3 O 1 S 1	[M+H]+	-0.0	0.3	1.2	7.3	281695
+++	Isoproturon	C 12 H 18 N 2 O 1	[M+H]+	-0.0	0.6	3.0	7.1	1217611

Figure 3. Report produced by the TargetAnalysis 1.3 software program.

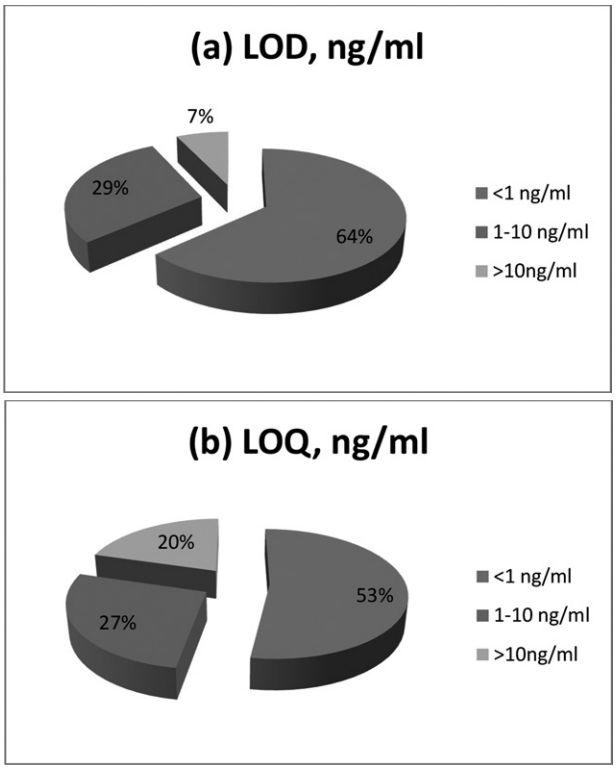


Figure 4. Distribution of (a) LOD and (b) LOQ.

The proposed analysis scheme includes first, the identification of toxicants under positive-and negative-ion monitoring, and second, in the case of detection of the X analyte, the addition of the X analyte to the sample and carrying out a replicate analysis. A 2- to 3-fold increase in the area or height of the chromatographic peak (*m/z* peak) is necessary to increase the accuracy of determination, which has been documented in previous publications (26, 27) and verified by a large number of analyzed samples.

Reference samples from the Food Analysis Performance Assessment Scheme (FAPAS, 2015) were used to confirm the correctness of the identification and determination of our proposed method. Analysis can also be carried out with another method, the All-Russian State Center for Quality and Standardization of Veterinary Drugs and Feed (VGNKI, 2015). Tables 2 and 3 show the results of the comparative analysis of the determination of some of the toxicants in the foodstuffs and feed. As Tables 2 and 3 show, there is satisfactory agreement between the results of analysis ($-2 \leq z \geq 2$), with RSDs ≤ 0.15. The time of sample screening was 40–60 min and time of determination of identified toxicants 2–3 h.

Conclusions

In summary, a scheme for the rational organization of the analytical control of the character and composition of toxicants in food and feeds has been presented. We also showed that

Table 2. Comparison of the determination results of antibiotics in food using the standard addition method and a calibration curve[a]

Matrix	Analyte	Found by the standard addition method, μg/kg	RSD	Found using a calibration curve, μg/kg	RSD
Chicken meat	Ampicillin	3.5±0.1	0.08	4.1±0.2	0.10
Milk	Penicillin G	5.0±0.2	0.09	4.8±0.3	0.12
Chicken egg	Ampicillin	12.3±0.9	0.08	13.5±0.9	0.09
Dry milk	Tetracycline	111±1	0.03	116±2	0.05
	4-Epitetracycline	20±1	0.08	—[b]	—
	Oxytetracycline	12±2	0.09	9±1	0.15
Dry milk	Tetracycline	11.6±0.5	0.07	9.0±0.3	0.10
	4-Epitetracycline	5.5±0.2	0.09	—	—
	Oxytetracycline	10.8±0.3	0.08	7±1	0.16
Dry milk	Tetracycline	15.5±0.3	0.07	15.4±0.5	0.09
	4-Epitetracycline	4.6±0.2	0.09	—	—
	Oxytetracycline	21.6±0.7	0.07	20.0±0.8	0.09
Dry milk	Tetracycline	9.5±0.3	0.09	8.0±0.3	0.16
	Oxytetracycline	1.7±0.1	0.10	2.0±0.2	0.13
Yogurt	Tetracycline	8.0±0.7	0.09	14[c]	—
	4-Epitetracycline	3.1±0.6	0.09		
Yogurt	Tetracycline	10.4±0.4	0.08	13[c]	—
	4-Epitetracycline	6.2±0.2	0.10	16)	17)
Milk	Pirimiphosmethyl	0.032±0.007	0.07	0.036±0.004	0.05
	Carbofuran	0.030±0.009	0.10	0.022±0.002	0.09
	Carbaryl	0.0067±0.007	0.11	0.008	—
Wheat grain	Azoxystrobin	0.06±0.01	0.10	0.044±0.003	0.09
	Diazinon	0.073±0.009	0.10	0.052±0.008	0.10
	Thiabendazole	0.053±0.003	0.05	0.041±0.009	0.10
	Malathion	0.045±0.003	0.06	0.05±0.01	0.10
Beef	Pirimiphosmethyl	0.15±0.03	0.07	0.11±0.09	0.10
Chicken meat	Enrofloxacin	0.022±0.007	0.07	0.018±0.005	0.05
Dumplings	Danofloxacin	0.30±0.05	0.06	0.22±0.06	0.07
	Enrofloxacin	0.43±0.06	0.09	0.504±0.004	0.04
Milk	Danofloxacin	0.06±0.01	0.10	0.044±0.003	0.09
Herring	Danofloxacin	1.23±0.04	0.08	1.142±0.004	0.07
	Lomefloxacin	1.32±0.03	0.05	1.446±0.006	0.03
	Oxolinic acid	0.31±0.07	0.10	0.206±0.005	0.08
	Enoxacin	1.95±0.03	0.04	1.84±0.07	0.02
Cheese	Sulfadiazine	0.21±0.06	0.09	0.11±0.03	0.08
Chicken egg	Enrofloxacin	0.95±0.03	0.03	1.08±0.09	0.08
Chicken meat	AOZ[d]	2.3±0.2	0.15	2[c]	24)
	AMOZ[e]	7.9±0.4	0.10	9[c]	26)
	AGD[f]	5.3±0.4	0.11	—	28)
Shrimp	Malachite Green	9.2±0.2	0.07	6[c]	29)
	Methylene Blue	1.3±0.2	0.11	31)	32)
	Crystal Violet	3.2±0.2	0.12	34)	35)
Fish (trout)	Leucomalachite Green	1.2±0.1	0.11	1[c]	36)
	Malachite Green	0.08±0.01	0.15	37)	38)
Sturgen caviar	Malachite Green	0.30±0.02	0.09	0.5[c]	39)
	Crystal Violet	9.9±0.2	0.03	41)	42)
	Albendazole	1.3±0.1	0.08	0.9±0.1	0.20
	Albendazole sulfoxide	0.60±0.06	0.10	0.73±0.09	0.13

[a] $n = 3$, $P = 0.95$.

[b] Not tested.

[c] Tested by ELISA.

[d] AOZ = 3-Amino-2-oxazolidinone.

[e] AMOZ = 3-Amino-5-morpholinomethyl-2-oxazolidinone.

[f] AGD = 1-Aminogidantoin.

Table 3. Results of the determination of analytes in reference materials using the method of standard addition[a]

Sample	Supplier	Analyte	Assigned concentration value, µg/kg	Found by standard addition method, µg/kg
Corn flour	FAPAS-22110	Nivalenol	122	120 (z=0.1)[b]
		Zearalenon	717	792 (z=0.6)
		Deoxynivalenol	888	1100 (z=1.5)
Corn	FAPAS-04246	Aflatoxin B1	4.9	5.9 (z=0.6)
		Zearalenon	212	250 (z=0.6)
		Ochratoxin A	2.9	3.4 (z=0.6)
Animal feed	FAPAS-22113	Deoxynivalenol	922	966 (z=0.3)
Rice	FAPAS-04255	Aflatoxin B1	2.84	2.99 (z=0.2)
		Aflatoxin B2	1.01	1.42 (z=1.8)
		Aflatoxin G1	1.97	1.62 (z=–0.8)
		Aflatoxin G2	0.95	0.61 (z=–1.6)
Chicken egg	FAPAS-02257	Sulfachlorpyridazine	109	95 (z=–0.8)
		Sulfadoxine	121	133 (z=0.4)
		Sulfathiazole	95	87 (z=–0.4)
Chicken egg	FAPAS-02258	Flumequine	153	88 (z=–2.0)
		Spiramycin	263	192 (z=–1.4)
Animal feed	FAPAS-22116	T-2 toxin	280	266 (z=–0.3)
		HT-2 toxin	411	425 (z=0.2)
Orange	FAPAS-22116	Azoxystrobin	72	88 (z=1.0)
		Aldicarb-sulfone	47	37 (z=–1.0)
		Carbofuran	120	160 (z=1.6)
Animal feed	FAPAS-02252	4,4′-Dinitrocarbanilide	45646	57000 (z=1.3)
		Monensin	119666	101000 (z=–0.9)
		Narasin	48490	47000 (z=–0.2)
Pork liver	FAPAS-02271	Clenbuterol	0.61	0.6 (z=–0.1)
		Ractopamine	0.60	0.7 (z=0.8)
Milk	FAPAS-02274	Phenylbutazone	7.05	9.5 (z=1.6)
		Naproxen	7.64	5.9 (z=–1.0)
Milk	FAPAS-02272	Thiamphenicol	20	21 (z=0.4)
		Chloramphenicol	0.34	0.4 (z=0.9)
Bovine kidney	FAPAS-02232	Oxytetracycline	84.2	74.9 (z=–0.5)
Honey	FAPAS-02236	Chloramphenicol	0.518	0.4 (z=–1.0)
Pear	FAPAS-19187	Metalaxyl	97.5	110.1 (z=0.6)
		Pendimethalin	124.6	142.7 (z=0.7)
		Pyraclostrobin	86.3	107.6 (z=1.1)
Chicken egg	FAPAS-025269	AMOZ	2.18	2.32 (z=0.3)
Honey	FAPAS-02270	Chlortetracycline	8.8	6.7 (z=–1.1)
		Doxycycline	74.2	72.8 (z=–0.1)
Cucumber	FAPAS-19200	Azoxystrobin	74.0	60.2 (z=–0.8)
		Cyprodinil	117	117.7 (z=0.0)
		Difenoconazole	81.3	93.6 (z=0.7)
		Hexaconazole	176	244.9 (z=1.9)
Dry milk	VGNKI-2014	Tetracycline	22	20 (z=–0.4)
		Oxytetracycline	30	22 (z=–1.3)
Dry milk	VGNKI-2014	Tetracycline	148	131 (z=–0.5)
		Oxytetracycline	19	11 (z=2.0)
Dry milk	VGNKI-2014	Tetracycline	13	16 (z=0.3)
		Oxytetracycline	11	11 (z=0.0)
Dry milk	VGNKI-2014	Tetracycline	12	10 (z=–1.0)

[a] n=3, P=0.95.

[b] $z = (x - x_a)/s$, where x is the found concentration, x_a is the assigned concentration value, and s is the SD of the assigned value.

combining identification and determination of compounds by HRMS is efficient, achieved through the preliminary separation of phases by HPCL using the standard addition method for the determination of compounds.

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