

应用纪要

Novel Extraction Techniques with ACQUITY UPLC with 2D Technology: Part I Pesticides Screening in Drinking Water

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Abstract

This application demonstrated the effectiveness of two extraction process, single stage captive and triple stage captive for pesticides screening by 2D LC ToF in drinking water.

Benefits

- Fast 30-minute extraction protocol
- Trace level detection at parts per trillion
- 90 second homogenization

Introduction

Many countries around the world have strict regulatory guide lines for drinking water quality. To satisfy legislative requirements, analytical methods have been developed to monitor a wide range of contaminants at trace levels using analytical techniques such as gas chromatography/mass spectrometry (GC-MS) or liquid chromatography/tandem quadrupole mass spectrometry (LC-MS/MS).

Trace level analysis at ppt (part per trillion) constitute the bulk of the work load for the majority of testing laboratories worldwide. Current analytical techniques use a combination of extraction procedures, often requiring an enrichment process and accurate detection for any given target analyte. As such, large sample volumes are usually extracted using various manual extraction methods (i.e., solid-phase extraction (SPE), liquid-liquid, etc.) and are concentrated into a smaller volume. As an example, a typical extraction method usually starts with a 500 mL of sample and ending up with a final volume of a 100 μ L (5000:1 enrichment ratio). If higher sensitivity is required, the only alternative left is to process larger sample volume but will require an increase in time and manual labor.

In recent years, efforts are now being diverted to investigate effective screening methods with high resolution Time-of-Flight (ToF) instruments and with the capability of reaching sub ppb (part per billion) levels. With current single chromatography separation setup and the inherent low sensitivity of ToF instrument compared to tandem quadrupole MS, this demand is quite difficult to achieve. As

such, a new analytical strategy is needed to reach those goals. This application will discuss the performance of 2D LC-QToF setup for the analysis of pesticides residues in drinking water at sub ppb level. With an enrichment factor of 20:1 from a rapid fractionation sample preparation protocol using two mixed mode sorbents, the gap between method and instrument limits of quantitation (LoQ) can be eliminated with large volume injection. Furthermore, by using an At-column dilution 2D LC configuration, 100% organic solvent extracts can be injected directly, thus eliminating all evaporation and reconstitution steps from any sample preparation protocol.¹⁻⁴

Experimental

Two MRM transitions, quantification and confirmation, for each pesticide were selected and optimized. The MRM conditions are listed in Table 1.

For this application, finding the optimum extraction and chromatographic condition for this multi-residue analysis posed a significant challenge. The chromatographic conditions were tested on several trapping chemistries (Oasis HLB, XBridge C₁₈, and XBridge C₈) and separation chemistries (BEH C₁₈) The loading (low pH, high pH, and neutral pH) and eluting mobile phase (MeOH + 0.5% formic acid and ACN + 0.5% formic acid) were also optimized using an automated 6x6 process.

All pesticides standards were purchased from Sigma Aldrich. The extraction process was performed on pre-conditioned reversed-phase sorbent Oasis HLB SPE Cartridge, 6 cc, 150 mg, (p/n: 186003365) for the captive extraction or a dual mixed-mode Oasis MCX SPE Cartridge, 6 cc, 150 mg (p/n: 186000256) and MAX SPE Cartridge, 6 cc, 150 mg, (p/n: 186000369) for the screening extraction.

Chromatography and MS/MS conditions

Loading conditions

Column:	Oasis HLB Direct Connect HP, 20 µm, 2.1 × 30 mm (p/n: 186005231)
Loading:	MilliQ water (pH 7, no additives)
Flow rate:	2 mL/min

At-column dilution: 5% (0.1 mL/min loading pump and 2 mL/min diluting pump)

UPLC conditions

UPLC system: ACQUITY UPLC with 2D Technology configured for “Trap and Elute” with At-column dilution

Runtime: 10 min

Column: ACQUITY UPLC BEH C₁₈, 1.7 μm, 2.1 × 50 mm (p/n: 176000863)

Column temp.: 60 °C

Mobile phase A: Water + 0.5% formic acid

Mobile phase B: Acetonitrile + 0.5% formic acid

Elution: 5-minute linear gradient from 5% (B) to 95% (B)

Flow rate: 0.500 mL/min (Elution pump)

Injection volume: 100 μL

MS conditions

MS system: Xevo TQ-S

Ionization mode: ESI positive

Capillary voltage: 3.0 kV

Cone voltage: 90.0 V

Source temp.: 150 °C

Desolvation temp.: 550 °C

Desolvation gas: 1100 L/hr

Cone gas: 50 L/hr

Phenyl Urea	MW	Cone (V)	Parent mass	Quant	CID	Qual	CID
Siduron	232.3	30	233.1	137.0	15	94.0	20
Dimefuron	338.8	30	339.0	72.1	25	166.9	20
Chlorobromouron	293.5	30	294.9	205.9	20	182.0	15
Difenoaxurone	286.3	30	287.1	72.1	20	123.1	20
Fluometuron	232.2	30	233.0	72.1	20	46.1	15
Thidiazuron	220.3	30	221.0	102.0	15	128.0	15
Metobromuron	259.1	30	258.9	169.9	20	148.0	10
Chloroxuron	290.7	30	291.0	72.0	20	164.0	15
Thifensulfuron methyl	387.4	30	388.0	167.0	20	204.9	25
Isoproturon	206.3	30	207.2	72.1	15	165.0	20
Monolinuron	214.6	30	215.1	126.1	15	148.1	10
Tribenuron methyl	395.4	30	396.1	155.1	20	181.0	20
Monuron	198.7	30	199.1	72.0	15	46.1	15
Diuron	233.1	30	233.0	72.1	15	46.1	15
Buturon	236.7	30	236.7	84.1	15	126.0	30
Metsulfuron methyl	381.4	30	382.1	167.0	15	199.0	30
Linuron	249.1	30	249.0	159.9	20	182.0	15
Chlortoluron	212.7	30	213.1	72.0	15	46.1	15
Fenuron	164.2	30	165.9	72.1	15	46.1	15
Metoxuron	228.7	30	229.2	72.1	15	46.1	20
Triazole							
Itraconazole	705.6	30	705.1	392.1	30	432.1	30
Fluconazole	306.3	30	307.1	238.1	15	220.1	15
Ketoconazole	531.4	30	531.1	82.1	40	489.1	35
Voriconazole	349.3	30	350.1	127.0	30	281.1	15
Posaconazole	700.8	30	701.3	683.2	30	127.0	60
Ravuconazole	437.5	30	438.0	224.0	20	215.0	20
Difenoconazole	406.3	30	406.1	250.9	30	337.0	15
Propiconazole	342.2	30	342.1	159.0	25	69.1	20
Cyproconazole	291.8	30	292.1	70.0	15	125.0	25
Prothioconazole	344.3	30	344.1	326.0	10	189.0	20
Tebuconazole	307.8	30	308.2	70.0	20	125.0	30
Carbendazim	191.2	30	192.1	160.0	15	132.1	30
Organophosphorus							
Chlorpyrifos	350.6	30	349.8	96.9	30	197.9	20
Parathion methyl	263.2	30	263.9	125.0	20	231.9	15
Azinphos methyl	317.3	20	318.0	132.0	15	125.0	20
Diclotophos	237.2	30	238.0	112.1	15	193.0	10
Diazinon	304.3	30	305.0	169.0	15	153.0	15
Dimethoate	229.3	30	230.1	198.9	10	125.0	20
Azinphos ethyl	345.4	30	346.1	96.9	25	137.0	25
Dichlorvos	221.0	30	220.9	109.0	15	79.0	25
Malathion	330.4	30	331.0	127.1	10	99.1	20
Fenitrothion	277.2	30	277.9	125.1	20	246.1	15
Parathion	291.3	30	292.1	235.9	15	94.0	30
Propetamphos	281.3	30	282.1	138.0	20	156.0	15
Mevinphos	224.2	30	225.0	127.0	15	193.0	5
Carbamate							
Aldicarb sulfoxide	206.3	15	207.1	89.0	15	132.0	5
Oxamyl	219.3	30	242.1	72.0	15	121.0	10
Aldicarb	190.3	30	213.1	89.1	15	116.0	10
Methiocarb sulfone	257.3	30	258.1	122.0	15	201.0	10
Aldicarb sulfone	222.3	30	223.1	86.1	15	148.0	10
Aminocarb	208.3	30	209.2	152.1	15	137.0	20
Carbofuran	221.3	30	222.1	165.0	10	123.1	20
Prosulfocarb	251.4	30	252.1	91.0	15	128.1	10
Methiocarb	225.3	30	226.1	169.0	10	121.0	20
Fenobucarb	207.3	30	208.2	95.0	15	152.0	10
Carbetamide	236.3	30	237.2	118.1	10	192.0	10
Carbofuran-3-cto	235.2	30	236.2	179.0	10	161.0	15
Fenoxycarb	301.3	30	302.1	88.0	20	116.1	10
Carbaryl	201.2	30	202.1	145.0	10	127.0	25
Carbofuran-3-hydroxy	237.3	30	238.2	181.0	10	163.0	15
Methiocarb sulfoxide	241.3	30	242.1	185.0	15	122.1	25
Triazines							
Atrazine-desethyl-desisopropyl	145.6	30	146.1	79.0	15	104.0	15
Propazine	229.7	30	230.2	146.0	20	188.0	15
Ametryn	227.3	30	228.2	186.0	20	96.0	25
Terbutryn	241.4	30	242.2	186.0	20	91.0	25
Trietazine	229.7	30	230.2	99.0	25	132.0	20
Atrazine-desisopropyl 2 hydroxy	155.2	30	156.1	86.0	15	69.0	20
Prometryn	241.4	30	242.2	158.0	25	200.0	20
Atrazine-desethyl	187.6	30	188.1	146.0	15	79.0	25
Terbutylazine	229.7	30	230.2	174.0	15	96.0	25
Simetryn	213.3	30	214.1	124.1	20	96.0	20
Simazine	201.7	30	202.2	132.0	20	124.1	15
Atrazine	215.7	30	216.1	174.0	15	96.0	25
Atrazine desisopropyl	173.6	30	174.1	132.0	20	96.0	15
Others							
Florasulam	359.3	30	360.1	129.0	25	192.0	15
Propyzamide	256.1	30	256.1	189.9	15	172.9	20
Asulam	230.2	30	231.1	156.0	10	92.0	20
Bentazon	240.3	30	241.1	199.0	10	107.1	20
Flufenacet	363.3	30	364.1	152.0	20	194.1	10
Diflufenican	394.3	30	395.1	266.0	25	246.0	35
Pendimethalin	281.3	30	282.2	212.1	10	194.0	20
Flusilazole	315.4	30	316.2	247.0	20	165.0	25
Chloridazon	221.6	30	222.1	103.9	20	92.0	25
Bromoxynil	276.9	30	275.0	129.0	15	234.9	15

2. Mallet, C.R., Botch-Jones, S., *J. Anal. Toxicology*, 1–11, 2016.
 3. Mallet, C.R., Multi-dimensional Chromatography Compendium: Trap and Elute vs. At-column dilution, 720005339EN 2015.
 4. Mallet, C.R., Analysis of Pharmaceuticals and Pesticides in Bottled, Tap and Surface Water Using the ACQUITY UPLC with 2D Technology, Waters Corporation, 720005167EN 2014.
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