Automatic, simultaneous and rapid analysis of pesticides in surface and underground water by online SPE and UHPLC-MS/MS.

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Overview

We here report the quantification of 272 pesticides in water matrix. This method use a SPE-UHPLC-MS/MS from Shimadzu. The performance of the method was evaluated on surface, underground and drinking water. Excellent results were showed independently of the matrix . The obtained LLOQs fits the requirements of the EU guidelines and could also be used to get an agreement in France. Because of its sensitivity, its automation and its adaptability to different waters, this method saves a tremendous amount of time.

1. Introduction

Pesticides are used for crops protection but their intensive use and their slow natural degradation makes them serious contaminants for surface water and underground water. This exposition can be more or less dangerous for animals, humans and ecosystems, with an immediate or long-term impact. Some studies revealed that these compounds cause health problems such as alterations of the nervous system, immune system diseases, fertility and development problems as well as cancer.
Reference separation techniques require tedious pretreatment protocol to reach thresholds set by environmental standards. Shimadzu proposes a new sensitive online SPE-LC-MS/MS method for simultaneous high sensitive quantification of 272 pesticides in surface water and groundwater.

2. Method

To perform this method, we use high quality solvents and reagent for mobile phase (LCMS grade BiosolveTM).

Two surface waters and one groundwater were spiked with standard pesticides purchased from Sigma. Six calibration levels at 1, 10, 20, 50, 100 and 500 ng/L were prepared 3 times in each matrix.

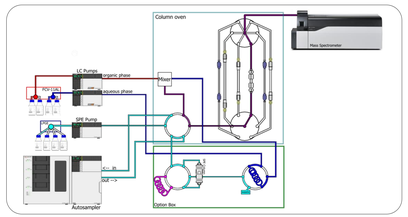

Figure 1. Schema SPE on-line UHPLC-MS/MS (Number of patent : WO 2016/098169 A1).

2-1. SPE-UHPLC conditions : Nexera X2

System: Shimadzu Nexera X2
Column SPE: Mayi-ODS C18
Column LC: C18AQ CS Interchim 2,6µm 150*3 mm
A/B (SPE): water/acetonitrile + 0.002% formic acid + 2mM ammonium formate
A: water + 0.002% formic acid + 2mM ammonium formate
B: 50/50 acetonitrile/Methanol + 0.002% formic acid + 2mM ammonium formate
LC flow: 0.7 mL/min
SPE elution flow: 0.2 mL/min
Oven temperature: 40°C
Injection volume: 1000 µL

2-2. MS conditions : LCMS-8050

System: Shimadzu TQ LCMS-8050
ESI ionization mode: positive and negative
Dwell time: 4 to 199 msec to obtain at least 15 points per peak

Nebulizing gas flow: 2,8 L/min
Heating gas flow: 10 L/min
Drying gas flow: 10 L/min

Desolvatation line: 150°C
Heat block temperature: 300°C
Interface temperature: 350°C

2-3. Typical chromatogram

The different levels prepared on three waters were analysed. Their injection allows to obtain the following chromatogram (Figure 2.)

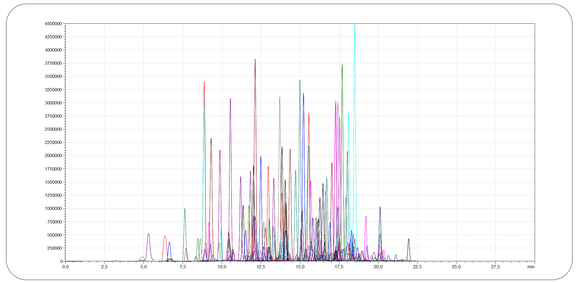

Figure 2. Chromatogram ground water spiked at 100 ng/L.

3. Results

One of the previous matrix spiked at different levels was selected to draw the calibration curve. The other doped water samples were used as controls. The 23 different isotopic standards were added to perform internal calibration. To overcome the matrix effect, ISTD were choose to cover the main families of pesticides: phenylureas, triazines, carbamates, sulphonylureas, organophosphorus compounds ...

3-1. Calibration curves

The limits of quantification were established for each compound by a signal to noise ratio (S/N) greater than 10. The compounds are classified in the following table according to their limits of quantification: 1, 10 and 25 ng/L.
The obtained LLOQs fits the requirements of EU and French guidelines.

Compounds with LOQ at 1ng/L					
4MBC	chlorfluazon	ethidimuron	isoxynil	oxamyl	simazine
acetamiprid	chloridazon	ethiofencarb	IPPMU	oxasulfuron	simazine hydroxy
acetochlor	chlorsulfuron	ethiprole	IPPU	oxazepam	simetryn
acide riflumique	chlortoluron	fenbuconazole	iprovalicarb	oxydemeton-methyl	spirotetramat
alachlore	clethodim	fenobucarb	isoprothiolane	paclobutrazol	sulfometuron-methyl
ametryn	coumafene	fenothiocarbe	isoproturon	penconazole	sulfosulfuron
amidosulfuron	coumatetralyl	fenpyroximate	isoxaben	penoxsulam	tebuconazole
aminocarb	cyanazine	fensulfothion	lufenuron	phosphamidon	tebufenoside
atenolol	cybutrine	fenuron	malaoxon	pinoxaden	tebutam
atrazine	cycloxydim	fipronil sulfone	malathion	pirimicarb	tebuthiuron
atrazine desethyl	cyflufenamid	fluazinam	mandipropamid	pirimicarb desmethyl	teflubenzuron
atrazine-OH	Cyproconazole	flufenacet	mecarbam	pirimicarb II	tepraloxydim
azaconazole	DCPMU	fluometuron	mefluidide	prochloraz	terbumeton
azamethiphos	desmetryn	fluopicolide	mercaptodimethur	progesterone	terbumeton desethyl
azimsulfuron	dichlorophen	fluoxastrobin	metabenzthiazuron	promecarb	terbuthylazine
azinphos ethyl	dicrotophos	flupyrsulfuron methyl	metalaxyl	prometryn	terbuthylazine desethyl
azinphos methyl	diethofencarb	fluridone	metazachlor	propachlore	terbuthylazine hydroxy
azoxystrobin	difenacoum	flurtamone	metconazole	propazine	tetraconazole
bensulfuron methyl	difenoconazole	flusilazole	methomyl	propiconazole	thiabendazole
benthiavalicarb isopropyl	difethialone	fluxapyroxad	metobromuron	propoxur	thiacloprid
bisphenol S	diisobutylphtalate	foramsulfuron	metolachlore	propoxycarbazone	thiazafluron
buturon	dimetachlore	formetanate	metosulam	propyl paraben	thiobencarb
cafeine	dimethenamid	fosthiazate	metoxuron	proquinazid	thiophanate methyl
carbamazepime	dimethomorph	fuberidazole	metribuzin	prosulfuron	triadimefon
carbamazepine epoxyde	dimetilan	halosulfuron methyl	metropolol	pyrazophos	triazamate
carbaryl	dimoxystrobin	hexaconazole	metsulfuron methyl	pyrifenox	tribenuron methyl
carbendazim	diniconazole	hexaflumuron	monolinuron	pyrimethanil	trietazine
carbetamide	dinoseb	hexazinone	monuron	pyroxsulam	trietazine 2OH
carbofuran	dinoterb	hexythiazox	myclobutanil	quizalofop ethyl	trifluralin
carbofuran 3 hydroxy	diuron	hydroxypropazine	neburon	rimsulfuron	trimetoprime
carboxin	econazole	imazapyr	nicosulfuron	rotenone	trinexapac ethyl
chlorantraniliprole	epoxiconazole	imazaquin	oruface	sebuthylazine	triticonazole
chlorbromuron	erythromicine	imidacloprid	oryzalin	siduron	vamidothion

Compounds with LOQ at 10ng/L					
245T Fenoprop	cyprosulfamide	fenarimol	imazamox	metazachlore oa	quizalofop
aldicarbe	Cyromazine	fenoxycarb	imazofulfuron	methidathion	roxythromycine
atrazine desisopropyl	desethyl-Terbutylazine 2-OH	flazasulfuron	iodosulfuron methyl	oxadixyl	tembotrione
bentazone	desmedipham	florasulam	isoprocarb	paraoxon	testosterone
benzafibrate	dia2hydroxy	flufenacet oa	isoxadifen ethyl	phenmedipham	thiencarbazone methyl
brodifacoum	dichlorprop-P	fluroxypyr	lorazepam	phoxim	thiodicarb
bromadiolone	diclofenac	fomesafen	MCPA	propamocarb	tolytriazole
butyl paraben	dimetachlore oa	forchlorfenuron	MCPP	propanolol	triasulfuron
chloroxuron	epitestosterone	haloxyfop	medroxyprogesterone	propyzamide	triazoxide
clofentezine	ethoxysulfuron	haloxyfop methyl	mesosulfuron methyl	prothioconazole	triclopyr
clorsulon	ethyl paraben	imazalil	metamitron	pymetrozine	trietazine desethyl
closantel					tylosine

Compounds with LOQ at 25ng/L					
2,4-D	dea 2 HYDROXY	fluquinconazole	linuron	titrosulfuron	triflumuron

Table 1. Limit of quantification in ng/L for each compound.

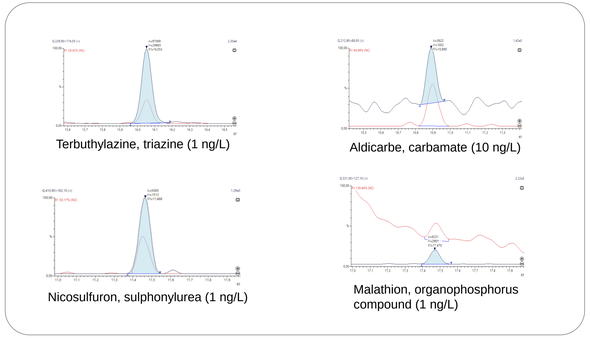

Figure 3. Example of chromatogram at the LLOQ.

3-2. Performance Evaluation

Repeatability is determined at low level of concentration for each water with 3 injections. Whatever the water matrix, the **repeatability** is less than **15%** for all the 272 targeted compounds.
The obtained results show that the calibration standards and the controls were analysed with an **accuracy** between **85 and 115%.**

4. Conclusion

Shimadzu offers a unique, automated and sensitive method to quantify a large number of pesticides in water. Limits of quantification are ranging from
1 to 25 ng/L with 1 mL injection of sample. The accuracy is between 85-115% and the repeatability is less than 15% for the full list.
Finally, this method is consistent with the actual normative environment.
Shimadzu solution with high sensitivity, automation and water matrix adaptability is the most powerful and time saving procedure in harmony with the real customer needs.