TuP 307

Cross validation between LDTD-MS/MS and LC-MS/MS for 5 neonicotinoids insecticides in water

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OVERVIEW

Purpose

- High-throughput detection and quantification of Neonicotinoids insecticides in water

Method

- Salt Assisted Liquid-Liquid Extraction (SALLE) used in the sample preparation
- Direct deposit for LDTD, concentration factor of x5 for HPLC method

Quantification

- Linearity: $r^2 > 0.997$ over the calibration range (0.1 to 100 ng/mL)
- Accuracy ranging from 90.9 to 108.9% using area ratio value
- Precision ranging from 4.4 to 15.0% using area ratio value
- Good agreement in cross validation with LC-MS/MS for runoff water samples
- **Samples analyzed with a run time of 9 seconds using LDTD-MS/MS system**

INTRODUCTION

In recent years, neonicotinoids have become the most widely used class of insecticides in the world. Almost all corn seeds planted in Canada and the USA are coated with one of these compounds. As scientists started to suspect the link between these chemicals to potential collapse disorder in bees, there became increasing need for efficient analytical procedures to study the widespread occurrence of neonicotinoids in the environment.
We developed a method using Laser Diode Thermal Desorption (LDTD) combined to MS/MS to detect the presence of 5 neonicotinoids (Acetamiprid, Clothianidin, Imidacloprid, Thiacloprid and Thiamethoxan) in runoff water samples with analysis in seconds. This method has been cross-validated with a conventional LC-MS/MS method.

LDTD® Ionization Source:

The LDTD uses a Laser Diode to produce and control heat on the sample support **(Figure 1)** which is a 96 wells plate**.** The energy is then transferred through the sample holder to the dry sample which vaporizes prior to being carried by a gas in a corona discharge region. High efficiency protonation and strong resistance to ionic suppression characterize this type of ionization, and is the result of the absence of solvent and mobile phase. This allows for very high throughput capabilities of 9 seconds sample-to-sample analysis time, without carry over.

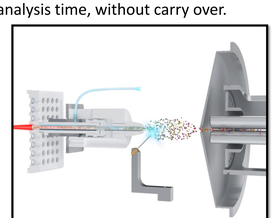

Figure 1 Schematic of the LDTD ionization source

Figure 2 LDTD system on Sciex 5500 QTrap®

METHOD

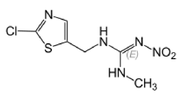

Figure 3 Clothianidin structure

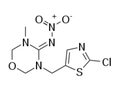

Figure 4 Thiamethoxam structure

Extraction Procedure

0.5 mL of water samples
1 mL of Acetonitrile containing 1 ng/mL Clothianidin-d3 as IS
0.5 mL of NaCl saturated water
Shake on vortex for 1 min and wait for layers separation

LC-MS/MS Analysis

- 500 µL of upper layer evaporated to dryness and reconstituted in 50 µL of MeOH:H2O (75:25)
- 5 µL of the solution is injected
- MPA : 10% MeOH, 90% H2O, 5mM ammonium formate
- MPB : 90% MeOH, 10% H2O, 5mM ammonium formate
- Flow rate: 400 µL /min
- t=0 : 100 % MPA
- t=20 to t=25 min : 100 % MPB
- t=26 to t=35 min : 100 % MPA
- Column : Siliachrom C18 (4.6 x 200 mm, 5 µM)

LDTD-MS/MS Analysis

- 5 µL of upper layer spotted on LazWell plate and dried
- Carrier gas flow : 3 L/min (Air)
- Laser power increased to 55% in 3 seconds, and maintained for 1 second before shut down.
- Sample-to-sample time : 9 seconds

MS Parameters

- Sciex API 5500
- APCI (+)
- Dwell: 25 msec
- MRM mode

Table 1 MRM transitions

Compound	Q1	Q3	CE
Acetamiprid	223	126	28
Clothianidin	250	169	19
Imidacloprid	256	209	21
Thiacloprid	253	126	29
Thiamethoxan	292	211	17
Clothianidin-d3	253	172	19

RESULT

Linearity results

A calibration curve (0.1-100 ng/mL) has been prepared in deionized water and analyzed in triplicate. Correlations were all over 0.9973. **Figure 5** presents a typical calibration curve for Clothianidin.

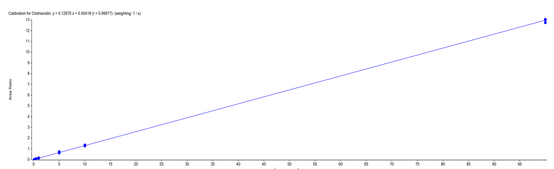

Figure 5 Typical Clothianidin standard curve

Precision/Accuracy results

Inter-run precision/accuracy are calculated. Accuracy ranging from 90.9 to 108.9 % and precision ranging from 4.4 to 15.0% were obtained. Results of Clothianidin were reported in **Table 2**. Similar results were obtained for other Neonicotinoids.

Table 2 Inter-run precision and accuracy of Clothianidin

	QC-Low	QC-Med	QC-High
Conc. (ng/mL)	0.5	5	10
N	6	6	6
Mean (ng/mL)	0.49	5.04	10.01
%RSD	6.6	5.6	4.4
%Nom	98.3	100.9	100.1

Water sample analysis and methods cross validation:

12 runoff water samples collected from different rivers in an agricultural area know for presence of Neonicotinoid compounds were analyzed using LDTD-MS/MS and LC-MS/MS method. Two of the five analyzed neonicotinoids are detected in the river water sample: Clothianidin and Thiamethoxam. Detected concentrations ranged from 0.1 ng/mL to 0.7 ng/mL. Results are reported in **Table 3.**

With the positive samples, a cross validation between the methods was performed. In **Figure 6** and **7**, LDTD-MS/MS and LC-MS/MS correlations higher than 0,98 are obtained.

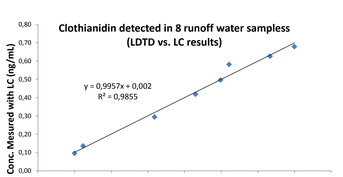

Figure 6 Clothianidin cross validation results

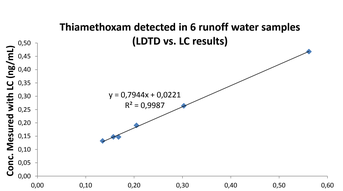

Figure 7 Thiamethoxam cross validation results

Table 3 Runoff water sample results

Water samples	Clothianidin (ng/mL)	Thiamethoxan (ng/mL)
Sample 1	0.12	0.56
Sample 2	0.52	0.16
Sample 3	0.50	0.21
Sample 4	0.43	0.30
Sample 5	< 0.1	< 0.1
Sample 6	< 0.1	< 0.1
Sample 7	< 0.1	< 0.1
Sample 8	< 0.1	< 0.1
Sample 9	0.63	< 0.1
Sample 10	0.32	0.17
Sample 11	0.10	0.14
Sample 12	0.70	< 0.1

CONCLUSION

- **Quantification of Neonicotinoids compounds can be performed in 9 seconds using LDTD-MS/MS**
- **Good Inter-run precision and accuracy are obtained. No carryover was observed**
- **Method Cross validation with correlation value higher than 0.98 for runoff water samples**
- **Ultra fast, precise and accurate LDTD-MS/MS method for Neonicotinoids samples analysis in runoff water.**