

Analysis of Neonicotinoid Pesticides in Honey

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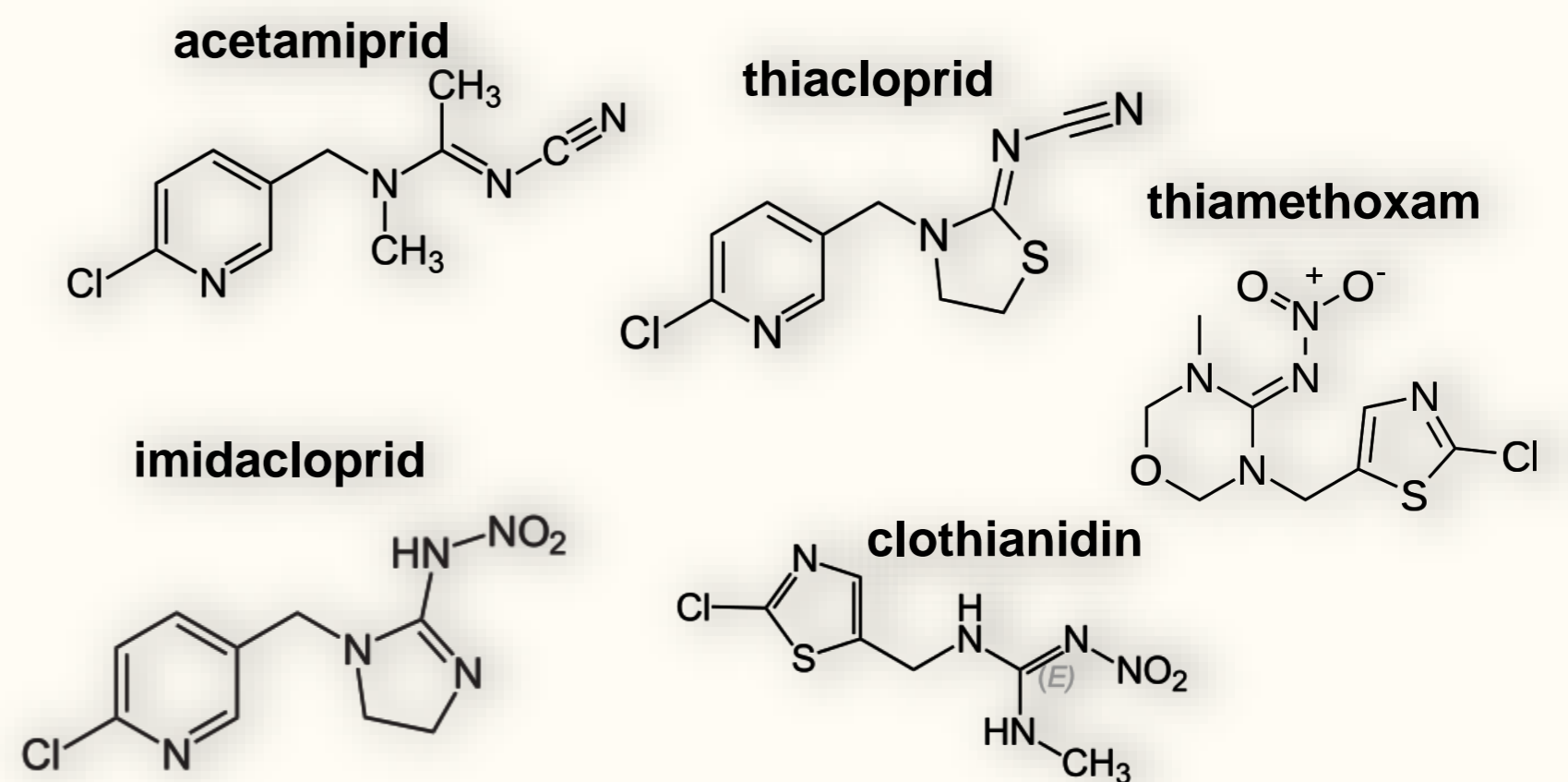
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INTRODUCTION

Neonicotinoids:

- a group of pesticides structurally similar to the nicotine molecule
- used to provide in-plant protection from insects during plant establishment
- linked to honey-bee colony collapses
- very small amounts can have large effects on the bees and bee products
- on the 1st of December 2013 the European Commission banned the use of imidacloprid, clothianidin and thiamethoxam on crops attractive to bees
- Maximum Residue Levels (MRLs) for honey and other apiculture products (EU Pesticide Database):

Neonicotinoid	MRL [ng/g=μg/kg]
Acetamiprid	50
Clothianidin	50
Dinotefuran	10
Fonicamid (sum of fonicamid + TFNA + TFNG)	50
Imidacloprid	50
Nitenpyram	10
Thiacloprid	200
Thiamethoxam	50



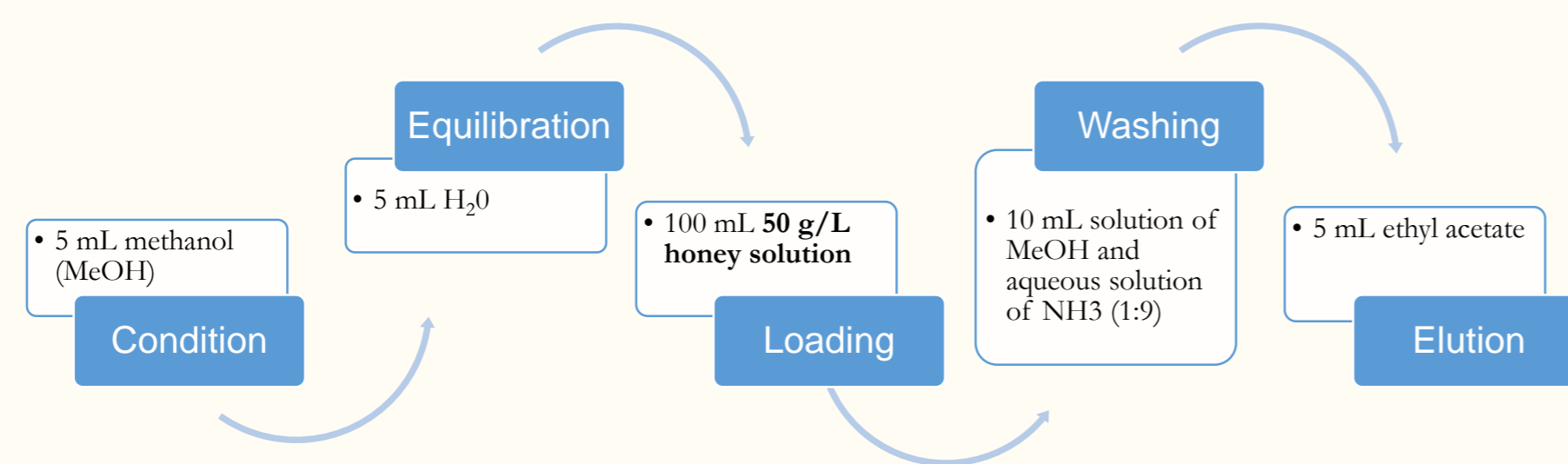
Honey:

- complex, viscous sample with a high sugar content.
- neonicotinoid residues are expected to be present in very low concentrations (<100 ng/g)
- sample clean-up and concentration of the analytes are necessary for successful analysis

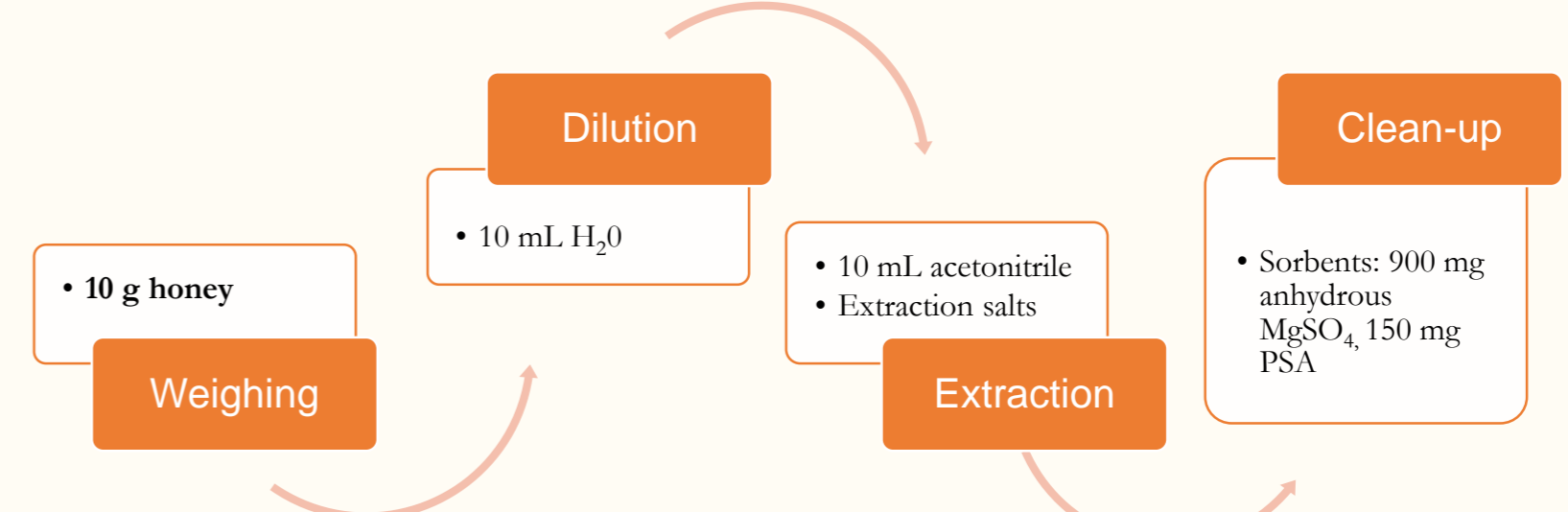
In this study, an analytical method for the determination of residues of five neonicotinoid insecticides in honey using LC-MS/MS was developed. We compared two different approaches of sample preparation in terms of extraction efficiency, matrix removal, repeatability, limit of detection (LOD), and limit of quantification (LOQ). Once validated, we will apply the method to the analysis of a large number of Slovenian honey samples from different geographic regions and farming regimes in order to monitor the effectiveness of the ban.

METHODS

Solid Phase Extraction (SPE)



QuEChERS



A Comparison between SPE and QuEChERS:

	LOD [ng/g]		LOQ [ng/g]		Slope ratio (k_{MMC}/k_{SC}) [%] -matrix effect		Spiking level							
							50 ng/g				10 ng/g			
	QuEChERS	SPE	QuEChERS	SPE	QuEChERS	SPE	RR [%]	RSD [%]	RR [%]	RSD [%]	RR [%]	RSD [%]	RR [%]	RSD [%]
Acetamiprid	0.08	0.07	0.26	0.22	61.6	38.1	85.3	4.7	89.3	2.5	89.8	2.7	113.6	0.9
Clothianidin	0.85	0.97	2.84	3.25	65.1	37.4	84.1	7.0	90.2	1.4	99.9	3.3	70.7	2.5
Imidacloprid	0.70	0.74	2.27	2.48	60.6	36.1	99.4	4.8	83.0	5.9	107.0	7.7	96.3	5.9
Thiacloprid	0.06	0.05	0.19	0.15	68.2	37.3	86.0	3.9	84.4	1.4	83.1	8.0	92.7	6.2
Thiamethoxam	0.30	0.60	1.08	2.00	21.8	11.2	85.9	7.4	74.2	4.0	68.2	4.7	89.2	7.2

Both sample pretreatments procedures provide low limits of detection (LOD) and quantification (LOQ) for all analytes ranging from 0.05 to 0.97 ng/g and from 0.19 to 3.25 ng/g. QuEChERS extraction is more efficient in matrix removal than SPE, which is expressed with slope ratio between matrix-matched calibration and solvent calibration. Both methods give satisfactory recoveries (68.2–113.6 %) and precision (RSDs between 0.9–8.0 %). QuEChERS method is cheaper and not as time-consuming as SPE.

RR=Recovery Rate, RSD=Relative Standard Deviation

Costs* [€]		Time per sample [min]	
QuEChERS	SPE	QuEChERS	SPE
5.8	6.7	15	25

*only cost of cartridges/kits included

RESULTS

Analysis of Honey Samples

Until now, we have analysed 16 honey samples; 11 Slovenian, 1 Croatian, 1 Chinese and 3 others. Acetamiprid, imidacloprid and thiacloprid were found in some samples. See table below:

Honey sample	Concentration [ng/g=μg/kg=ppb]		
	acetamiprid	imidacloprid	thiacloprid
Floral (SLO)	<LOD	<LOD	0.6
Chestnut (SLO)	<LOD	<LOD	0.8
Acacia (China)	0.7	detectable	<LOD
Floral (Ukraine)	0.5	<LOD	1.4



Sampling sites of different honey samples in Slovenia

CONCLUSION

- In the present study:
- two different sample preparation techniques (SPE and QuEChERS) were tested. Both of them showed to be reliable for preparation of honey matrices.
 - analysis of real honey samples revealed the presence of neonicotinoid pesticides in four analysed samples in very low amounts.
- In the further research we plan to test more honey samples to get representative information about the presence of neonicotinoids in Slovenian honey.

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