SAMPLE PREPARATION TECHNIQUES BASED ON EXTRACTION FOR ANALYSIS OF PESTICIDES IN FOOD SAMPLES

Tatjana M. Trtić-Petrović,
Ksenija Kumrić, Jelena Đorđević, Aleksandra Dimitrijević
Laboratory of Physics
„Vinča" Insitute of Nuclear Sciences
University of Belgrade, Belgrade, Serbia

Outline

1. Introduction
2. Two-phase membrane extraction in a single hollow fiber
   - Experimental set-up
   - Results of optimization of extraction parameters
   - Method validation
   - Analysis of the targeted pesticides in fruit juices samples
3. Ionic liquid based liquid-liquid microextraction
   - Experimental set-up
   - Results of optimization of extraction parameters
   - Method validation
   - Analysis of the targeted pesticides in fruit juices samples
4. Conclusion

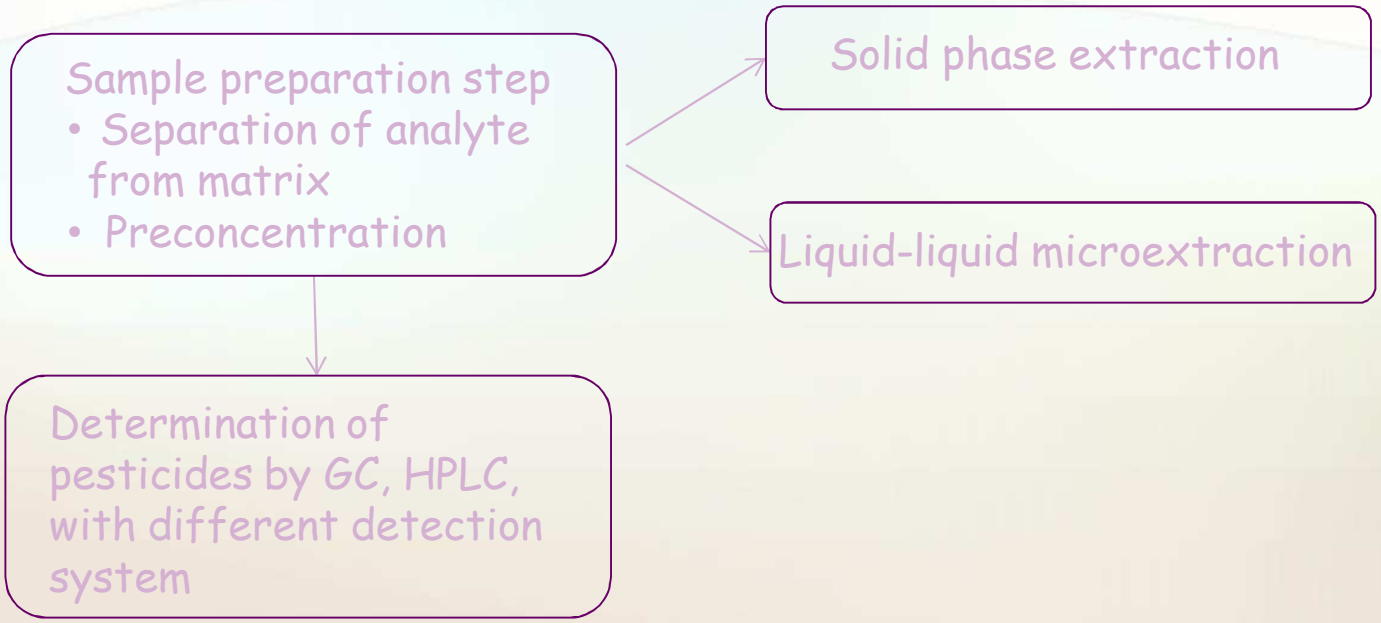
Introduction

- Pesticides are heterogeneous and numerous chemical or biological compounds that are used for the control of different sort of pests.
- More than 1200 compounds have been registrated as pesticides.
- Agricultural production currently, and increasingly, depends on the use of pesticides.
- These compounds and the products of their degradation or metabolism may spread through environment and frequently contaminate surface and ground waters, soil, agricultural products and food.
- Several international organizations have established maximum residue limits (MRLs) for pesticides (EC Regulation No. 396/2005, Off. J. Eur. Commun. L70, 1-16; U.S. Department of Agriculture, Foreign Agricultural Service, Maximum Residue Limit Database)




Phases in analysis of pesticides

In order to control and monitor pesticides and the products of their degradation, analytical methodologies must identify and quantify very low concentration of the pesticides in very complex samples.



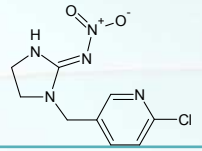
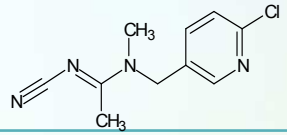
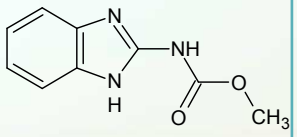
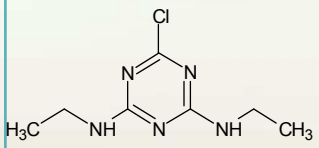
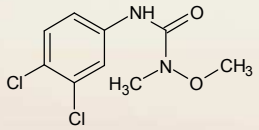
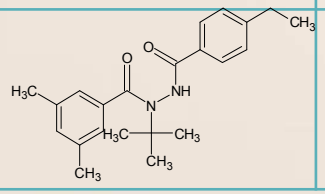
Aim

The aim of this research is investigation of two sample preparation methods based on liquid/liquid microextraction for determination of the selected pesticides in fruit juices:

1. Two-phase membrane extraction in a single hollow fibre,
2. Ionic liquid based liquid-liquid microextraction



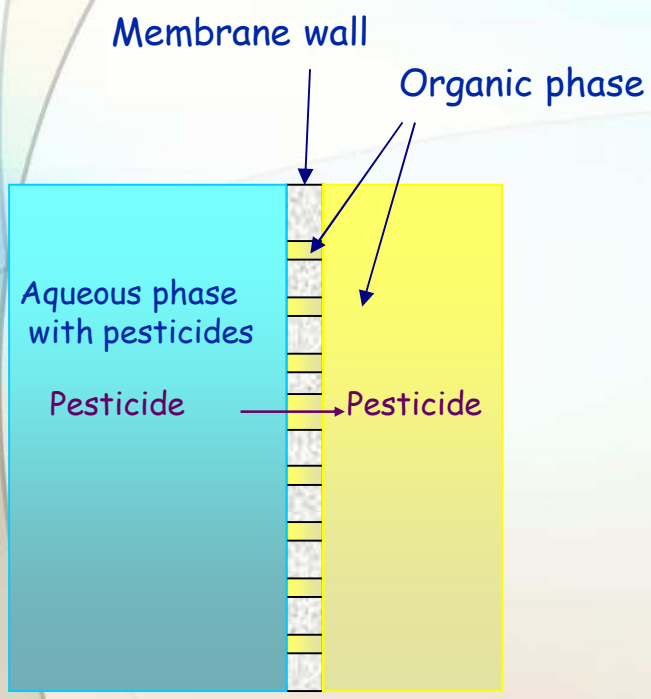

Selected pesticides

Pesticide (shortcut)	Chemical group (Activity)	Chemical structure	Partition coef. (oct/aq) logP* pH 2-8.5	Fruit / fruit juice	Average** /maximal concentration (µg/L)
Imidaclopride (IMI)	Neonikotinoid (insekticid)		0.46	Grapes	72 / 2300
Acetamiprid (ACE)	Neonikotinoid (insekticid)		1.55	Strawberries Apple juice	12 / 670 4 / 25
Carbendazime (CAR)	Benzimidazole (fungicide)		-0.16 – 1.52	Strawberries Apple juice Blueberries	29.9 / 930 4 / 25 2 / 1500
Simazine (SIM)	Triazine (herbicide)		2.26	Blueberries	0.2 / 120
Linuron (LIN)	Fenilurea (herbicide)		3.12	Carrot	18.7 / 330
Tebufenozid (TEB)	Diacilhidrazin (insekticid)		4.38	Blueberries	5.5 / 1000

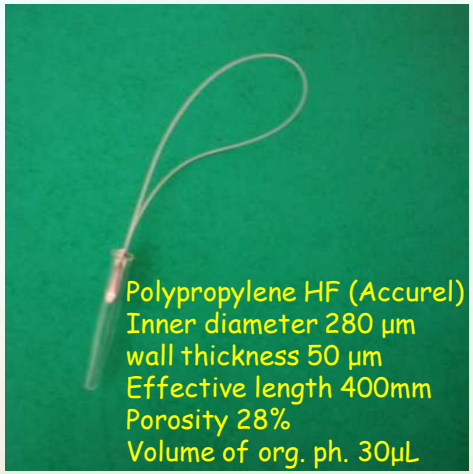
*determined by ACD/Labs PhysChem
**http://www.ams.usda.gov

Two-phase membrane extraction in a single HF

Schematic of two-phase membrane extraction



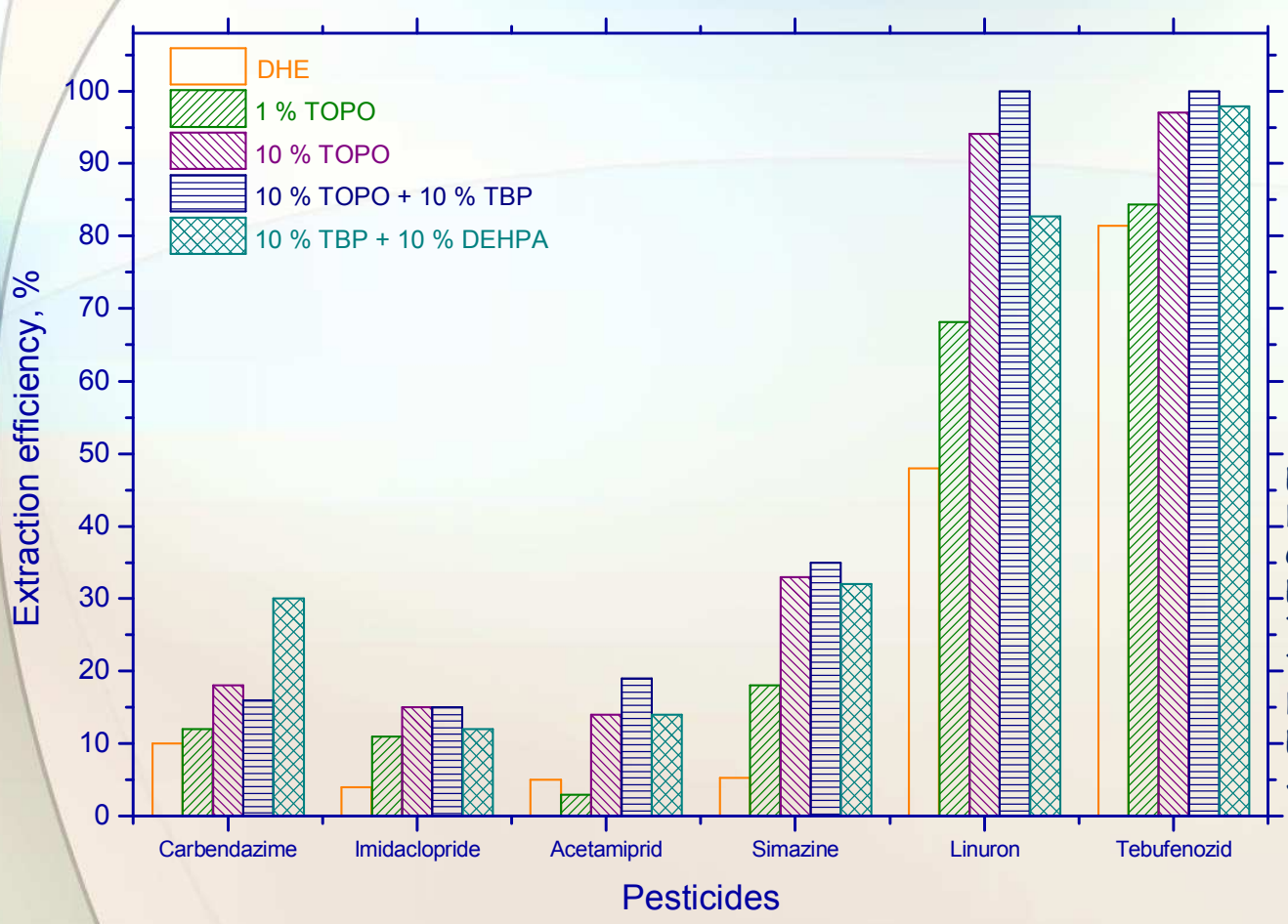
Experimental set-up



Parameters influencing extraction:

- Organic phase
- Extraction time
- Sample volume

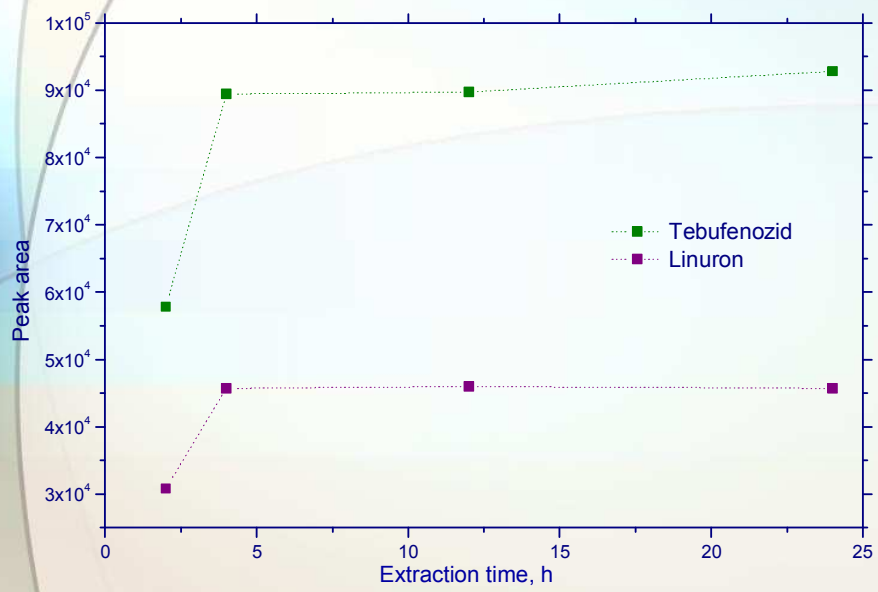
Effect of different extractants on the extraction efficiency of the pesticides from the aqueous sample



Extraction conditions:
Donor: 50 cm^3 water
$C_{pesticide}$= 0.1 mg dm^{-3}
Extractants: DHE - dihexyl ether,
TOPO - tri-n-octylphosphine oxide
TBP - tri-n-butyl phosphate
DEHPA - di(2-ethylhexyl)phosphoric acid
Extraction time: 120 min
Shaking rate: 100 rpm

Optimal organic phase: 10% TOPO + 10% TBP in DHE

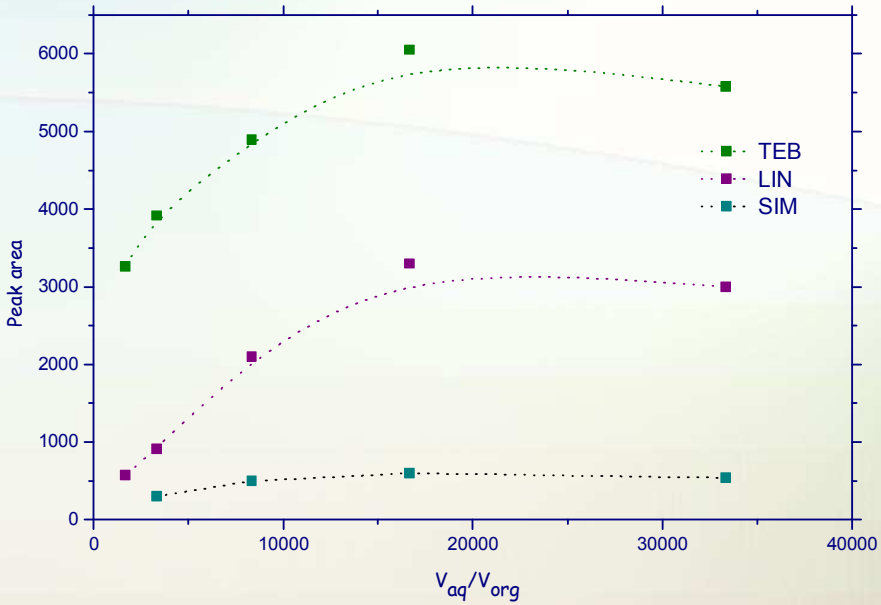
Effect of the extraction time



Extraction conditions: donor – 50 mL water (pH 5.8) spiked at 0.1 mg dm^{-3} of each pesticide, Extractants: 10% TOPO and 10% TBP in DHE, shaking rate: 100 rpm.

Optimal extraction time: 4 h

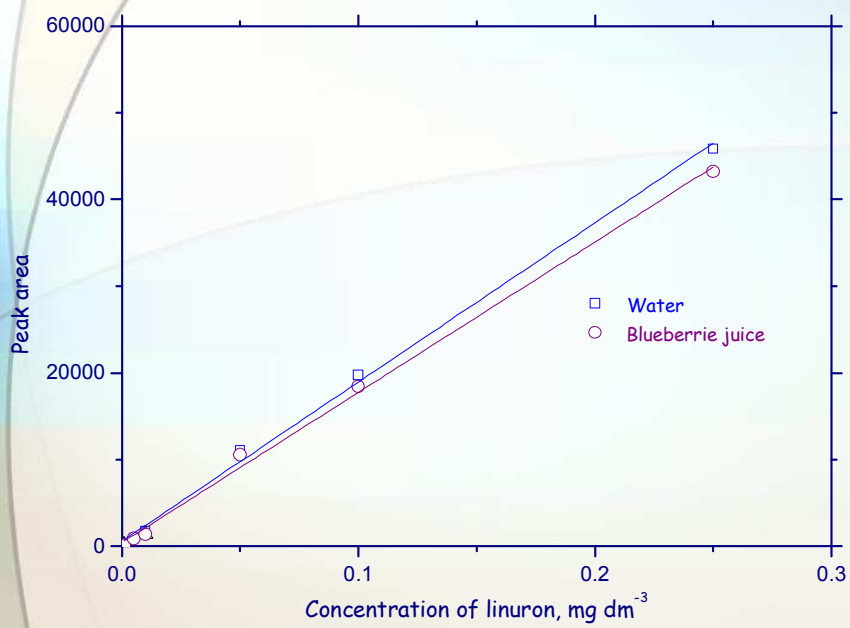
Effect of the sample volume



Extraction conditions: donor – 50 - 1000 mL water (pH 5.8) spiked at 0.1 mg dm^{-3} of each pesticide, Extractants: 10% TOPO and 10% TBP in DHE, shaking rate: 100 rpm. Extraction time: 4 h.

Optimal volume of aqueous phase 500mL and organic phase 30 µL

Calibration curve of linuron from water and blueberry juice



The selected parameters of the calibration curves

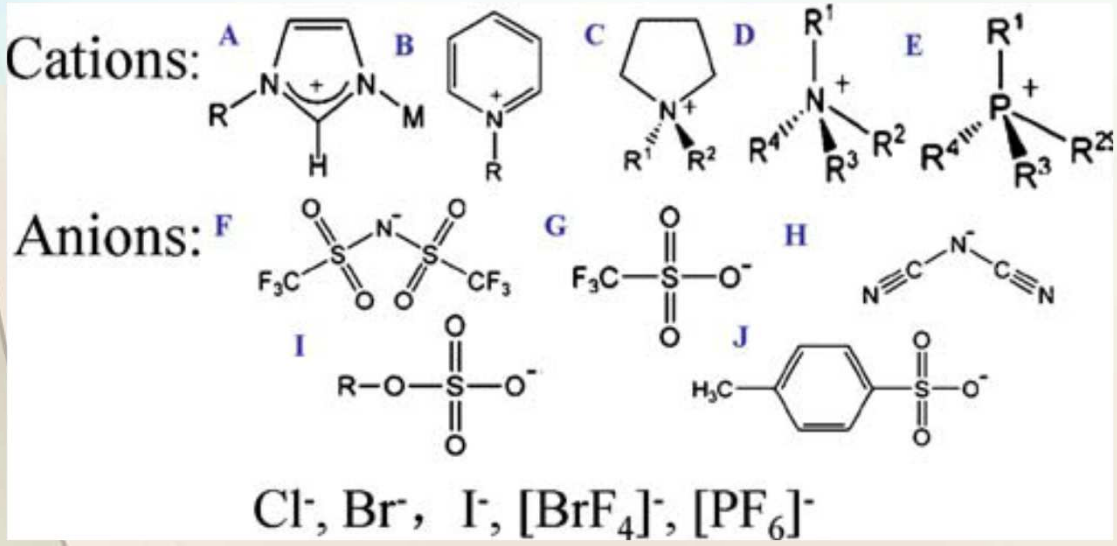
Pesticides	Concentration range (mg dm^{-3})	r^2	LOD (µg dm^{-3})
SIM	0.05 - 1.0	0.9985	57
		0.9975	61
TBF	0.001 – 0.25	0.9997	2.1
		0.9991	2.9
LIN	0.001 – 0.25	0.9987	6.3
		0.9986	6.8

r^2 – correlation coefficient

- The extraction procedure is cheap, selective, and simple;
- no additional sample treatment is needed before the application of the two-phase HF-LPME
- low volume of organic solution
- good linearity, low detection limits for the pesticides with log P > 2

Ionic liquid (IL)

- Ils are salt
- Ils content of organic cations and inorganic or organic anions
- Ils are liquid at RT
- The properties of ILs can be tunable depend on the cation and the anion



Cations:
A: 1-alkyl-3-methyl-imidazolium
B: 1-alkyl-pyridinium
C: 1,1-dialkyl-pyrrolidinium
D: tetraalkyl-ammonium
E: tetraalkyl-phosphonium

Anions
F: bis(trifluoromethylsulfonyl)imide
G: trifluoromethylsulfonate
H: dicyanaimide
I: alkyl sulphate
J: tosilate

Ionic liquid vortex assisted based liquid-liquid microextraction (IL-VALLME)

Ionic liquids: 1-heksil-3-metilimidazol bis(trifluorometilsulfonil)imid $[C_6MIM][(CF_3SO_2)_2N]$

- Density 1.33 g ml^{-1}
- Solubility in water 0.34 g dm^{-1}

Experimental set-up:

- Aqueous solution / fruit juice with pesticides
- Addition of IL
- Shaken using a vortex agitator
- IL was separated from aqueous solution by centrifugation at 1000 rpm
- Determination of pesticides in IL using HPLC/DAD

Parameters influencing extraction:

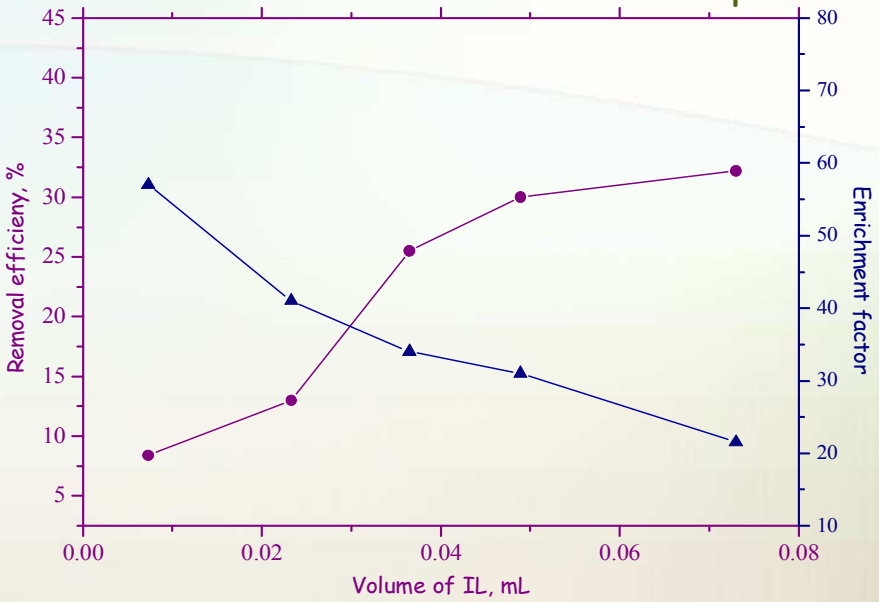
- Volume of IL
- Sample volume
- Extraction time

Optimization of the extraction conditions

Partition coefficient

Pesticide	logP (IL/aq)	logP (oct/aq)
Imidacloprid	1.61	0.46
Acetamiprid	1.65	1.55
Carbendazime	1.64	0.72
Simazine	1.60	2.26
Linuron	3.5	3.12
Tebufenozid	4.13	4.38

Effect of volume of IL on removal efficiency and enrichment factor of imidacloprid

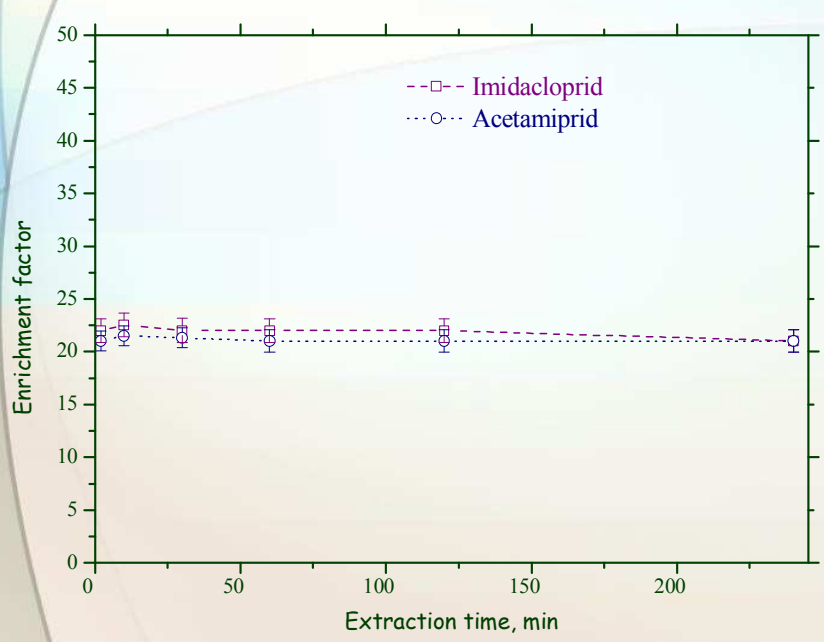


Extraction conditions: sample 5 mL water (pH 5.8) spiked at 0.1 mg dm^{-3} of each pesticide, shaking rate: 100 rpm, extraction time: 60 min.

Optimal volume of IL: 40 µL

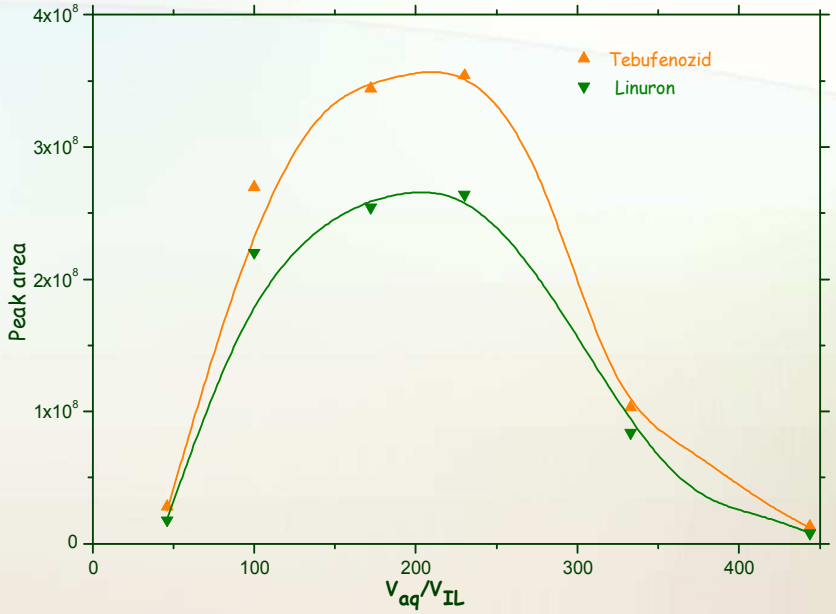
Optimization of the extraction conditions

Effect of the extraction time



Optimal extraction time: 2 min

Effect of the volume ratio of sample and IL



Optimal ratio of V_{aq}/V_{IL}: 200

Results

The selected parameters of calibration curves of the pesticides from water and blueberry juice

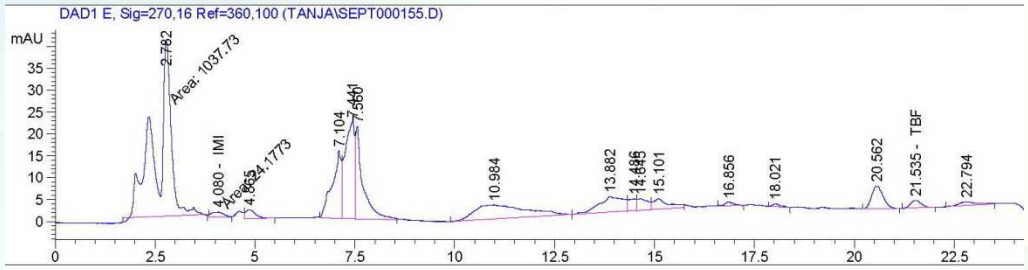
Pesticides	r^2	LOD (μg dm^{-3})
Imidacloprid	0.9985	7.1
	0.9964	9.5
Acetamipride	0.9981	5.5
	0.9963	6.4
Carbendazime	0.9993	3.5
	0.9988	4.3
Simazine	0.9988	5.4
	0.9975	6.3
Linuron	0.9997	2.1
	0.9991	2.9
Tebufenozid	0.9998	1.7
	0.9986	3.0

(Concentration range 0.005 – 0.25 mg dm^{-3})

Optimal extraction conditions:

- volume of sample: 10 mL
- IL: 0.04 mL $[C_6MIM][(CF_3SO_2)_2N]$
- extraction time 2 min
- shaking rate 2500rpm (Vortex)
- separation: centrifugation for 2 min at 1000 rpm

Chromatogram of "real sample"



C_{IMI} = 2.3 μg dm^{-3}
C_{TBF} =1.8 μg dm^{-3}

- Method is fast and simply,
- low consumption of IL,
- simultaneous extraction of the low polar and more polar compounds,
- direct injection in HPLC,.

Concluding remark

This work shows that the two-phase membrane extraction and ionic liquid based microextraction procedures can be considered as a sound alternative to other extraction techniques as the sample pre-treatment before HPLC determination of pesticides in fruit juices.

Thank you for your attention!