MINISTÈRE
DE L'ÉCONOMIE,
DES FINANCES
ET DE LA SOUVERAINETÉ
INDUSTRIELLE ET NUMÉRIQUE

Liberté
Égalité
Fraternité

SCL
Service commun des laboratoires

Multi-residue in essential oils

Experience in SCL

Joint EURL Workshop, 18-20 October 2023
Stuttgart

DG CCRF

DOUANES & DROITS INDIRECTS

Multi-residue in Essential Oil (EO)

I. Context

II. Analytical objectives

III. Sample clean-up method

IV. Quantitation results

V. Real samples analysis and perspectives

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Joint Laboratory Service (SCL)

Facts and Figures

- **National competence service** :
  - General Directorate of Customs and Excise (DGDDI)
  - General Directorate for Competition Policy, Consumer Affairs and Fraud Control (DGCCRF)

17 NRL mandates

200 000 analyses every year

Diverse, complementary missions

Consumer protection : product compliance, product authenticity, detection of illicit substance

Consumer safety : chemical contaminants, compliance with safety standards, ensuring toys comply with standards…

Economic : tariff classification, fair pricing of foodstuffs

Taxation : tax classification of alcohols, wines, petroleum products

Crisis management : horsegate, fipronil, radioactive leaks, …

400 scientific staff

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Montpellier Laboratory

Facts and Figures

- Molecular biology control
- Wine control
- Meat product control
- Pesticide residues control

4 NRL mandates

7 scientific domains

40 scientific staff

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Context

Use of essential oil

- Foodstuff and beverage

- Perfumery and cosmetic

- Medicine, aromatherapy

Mondial market =
110 000 tons every year

Context

Control request

- Import increasing in France for organic EO
- Short timeframe of analysis method implementation
- 2 over 10 scientific staff dedicated to this project

Analytical objectives

- Preparation method applicable for the most wide spectrum of essential oils
- Same LC, GC and MS conditions than usual samples
- Target list : usual findings in LC-QTOF (ESI +), GC-MS/MS and LC-MS/MS (ESI -)

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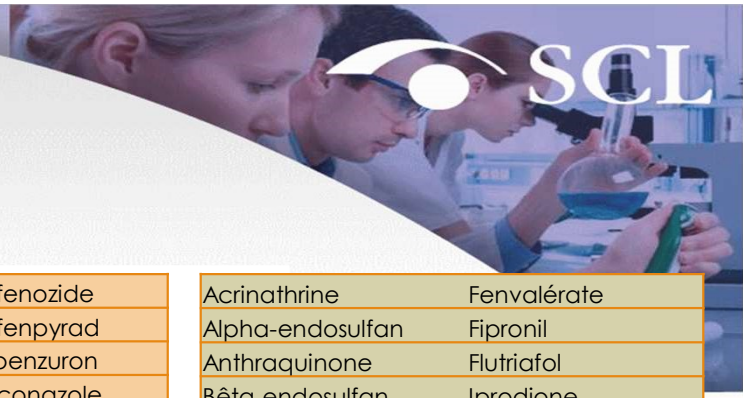

Analytes included

Acephate	Chlorpyriphos-methyl	Ethirimol	Fluxapyroxade	Methomyl	Propamocarb	Tebufenozide
Acetamiprid	Clofentezine	Etofenprox	Fosthiazate	Methoxyfenozide	Propiconazole	Tebufenpyrad
Aclonifen	Clothiandin	Etoxazole	Hexaconazole	Metoxuron	Propoxur	Teflubenzuron
Acrinathrin	Cyantraniliprole	Fenamidone	Hexythiazox	Metrafenone	Propyzamide	Tetraconazole
Aldicarb	Cyazofamid	Fenbuconazole	Imazalil	Monocrotophos	Proquinazid	Thiabendazole
Ametoctradin	Cyflufenamid	Fenhexamid	Imidacloprid	Myclobutanil	Prosulfocarb	Thiacloprid
Azoxystrobin	Cymoxanil	Fenoxycarb	Indoxacarb	Omethoate	Pymetrozine	Thiamethoxam
Benalaxyl	Cyproconazole	Fenpropathrin	Iprovalicarb	Oxadixyl	Pyraclostrobin	Thiophanate-methyl
Bitertanol	Cyprodinil	Fenpropimorph	Isoprothiolane	Oxamyl	Pyridaben	Tolfenpyrad
Boscalid	Cyromazine	Fenpyrazamine	Kresoxim-methyl	Penconazole	Pyrimethanil	Triadimenol
Bupirimate	Deltamethrin	Fenpyroximate	Linuron	Pencycuron	Pyriproxyfen	Triazophos
Buprofezin	Diazinon	Fipronil	Malathion	Phenmedipham	Quinoxyphen	Tricyclazole
Carbaryl	Difenoconazole	Flonicamid	Mandipropamide	Phosalone	Spinosad A	Trifloxystrobin
Carbendazim	Diflubenzuron	Fludioxonil	Mepanipyrim	Phosmet	Spirodiclofen	Zoxamide
Carbofuran	Dimethoate	Flufenoxuron	Metalaxyl	Piperonylbutoxide	Spiromesifen	
Chlorantraniliprole	Dimethomorph	Fluopicolide	Metconazole	Pirimicarb	Spirotetramate	
Chlorfenvinphos	Diuron	Fluopyram	Methamidophos	Pirimiphos-methyl	Spiroxamine	
Chlorpropham	Epoxiconazole	Flusilazole	Methidathion	Prochloraz	Tau Fluvalinate	
Chlorpyriphos	Ethion	Flutriafol	Methiocarb	Profenophos	Tebuconazole	

Acrinathrine	Fenvalérate
Alpha-endosulfan	Fipronil
Anthraquinone	Flutriafol
Bêta-endosulfan	Iprodione
Bifenthrine	Lambda-cyhalothrine
Biphényle	Lindane
Bromopropylate	op'-DDE
Chlordane cis	Orthophénylphénol
Chlordane trans	Oxadixyl
Chlorfénapyr	Oxyfluorfène
Chlorothalonil	Perméthrine
Chlorpyriphos-éthyl	pp'-DDE
Chlorthal-diméthyl	Procymidone
Cyfluthrine	Tau-fluvalinate
Cyperméthrine	Téfluthrine
Deltaméthrine	Tétraméthrine
Diafenthiuron	Tolylfluanide
Dieldrine	Vinchlozoline
Diphénylamine	
Endosulfan sulfate	
Fenpropathrine	

2,4-D	Dichlorprop	MCPA
2,4-DB	Dithianon	Mecoprop
Bentazone	Fluazinam	Meptyldinocap
Bixafen	Flubendiamide	Triclopyr
Bromoxynil	Fludioxonil	Tritosulfuron
Chlorfluazuron	Hexaflumuron	
Dicamba	Ioxynil	

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Essential oils included

Foil distilate based oil	Fruit distillate based oil	Flower distillate based oil	Zest extract based oil
Mint eucalyptus	Litsee (exotic vervein)	Ylang ylang	Lemon
Lemon eucalyptus			Grapefruit
Lemongrass			Orange
Patchouli			Green mandarin
Niaouli			

Sample clean-up method

QU[illegible]ERS?

Litterature research : **PhD of Yohann Fillatre in GIRPA**

Evaporation vs direct dilution

	Dilution + freezing + 2nd dilution before injection	Dilution + freezing + direct injection
Percentage of analytes detected when spiked at 0,010 mg/L		
Lemon	62%	73%
Mint eucalyptus	39%	80%
Niaouli	60%	81%
Lemon eucalyptus	41%	62%
Ylang ylang	52%	74%
Lemongrass	45%	63%

Evaporation : time consuming, possible degradation

Signal extinction due to big matrice effects

2nd dilution before injection > less matrice effect ?

too much sensitivity loss…

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Final clean-up method

SPIKE LEVEL	0,010 ppm	0,020 ppm	0,10 ppm
EO Type	*Percentage of analytes detected*		
Lemon	73%	78%	90%
Mint eucalyptus	80%	81%	90%
Niaouli	81%	82%	92%
Lemon eucalyptus	62%	67%	76%
Ylang ylang	74%	76%	88%
Lemongrass	63%	65%	75%
Litsee (exotic vervein)	61%	70%	84%
Orange	75%	79%	89%
Grapefruit	67%	77%	88%

I. 1 mL EO + 3 mL MeOH 1%AF:ACN 1:3

II. 1 min agitation

III. Freezing in liquid N_2

IV. Centrifugation (3,5 min/2500 rpm)

V. Take upper phase, filtration with PTFE

VI. Injection
in LC-QTOF (2 µL) and LC-MS/MS (5 µL)
GC results to come

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Quantitation results

Lemon ☺

Estimated LOQ of **0,010 ppm** for **47 %** of tested pesticides

Estimated LOQ of **0,020 ppm** for **61 %** of tested pesticides

Litsee ☹

Estimated LOQ of **0,010 ppm** for **31 %** of tested pesticides

Estimated LOQ of **0,020 ppm** for **49 %** of tested pesticides

Estimated LOQ :

70-120 % recovery criteria

+

< 20% shift between std addition value and recalculated one

Real sample analysis

Organic samples purchased for validation !

Residues detected !

- « Organic » orange

Pesticide	Estimated concentration
Fluxapyroxade	0,030 mg/L
Hexythiazox	0,010 mg/L
Imazalil	0,008 mg/L
Pyriproxifen	0,016 mg/L
Pyriméthanil	0,035 mg/L

Estimated concentration :

3 points standard addition

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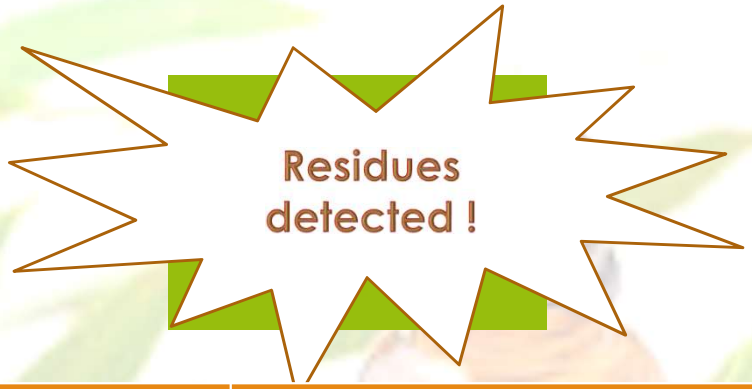
Real sample analysis

Organic samples purchased for validation

- « Organic » grapefruit,
  mandarin
  lemon



Pesticide	Estimated concentration
Acetamiprid *(mandarin)*	From **< 0,010 mg/L** to **0,042 mg/L**
Chlorpyriphos ethyl *(lemon)*	
Etofenprox *(lemon)*	
Fluxapyroxade *(grapefruit, mandarin)*	
Propyzamide *(lemon)*	
Pyriproxyfen *(lemon, grapefruit)*	
Pyriméthanil *(orange)*	

Estimated concentration :

3 points standard addition

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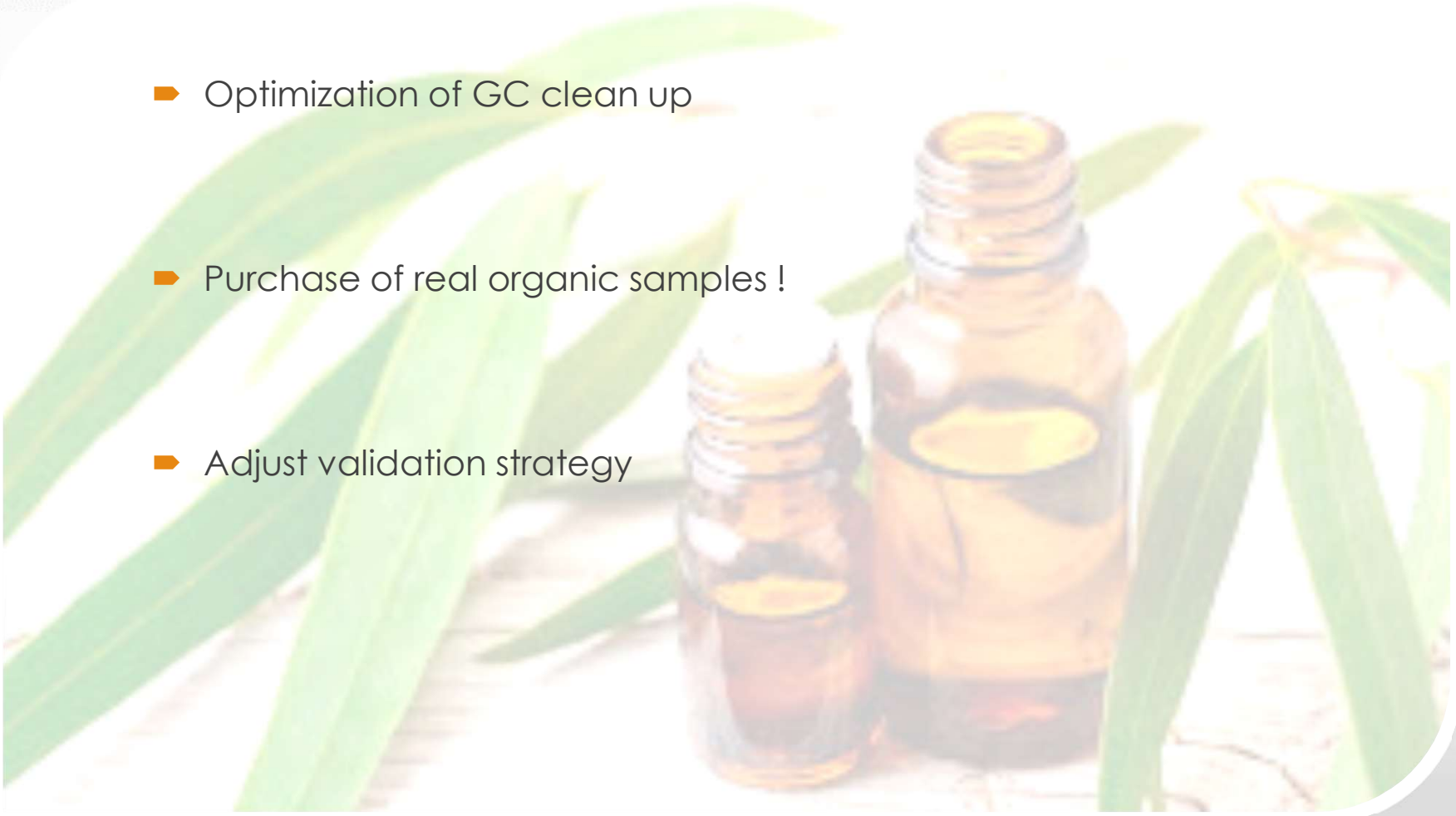
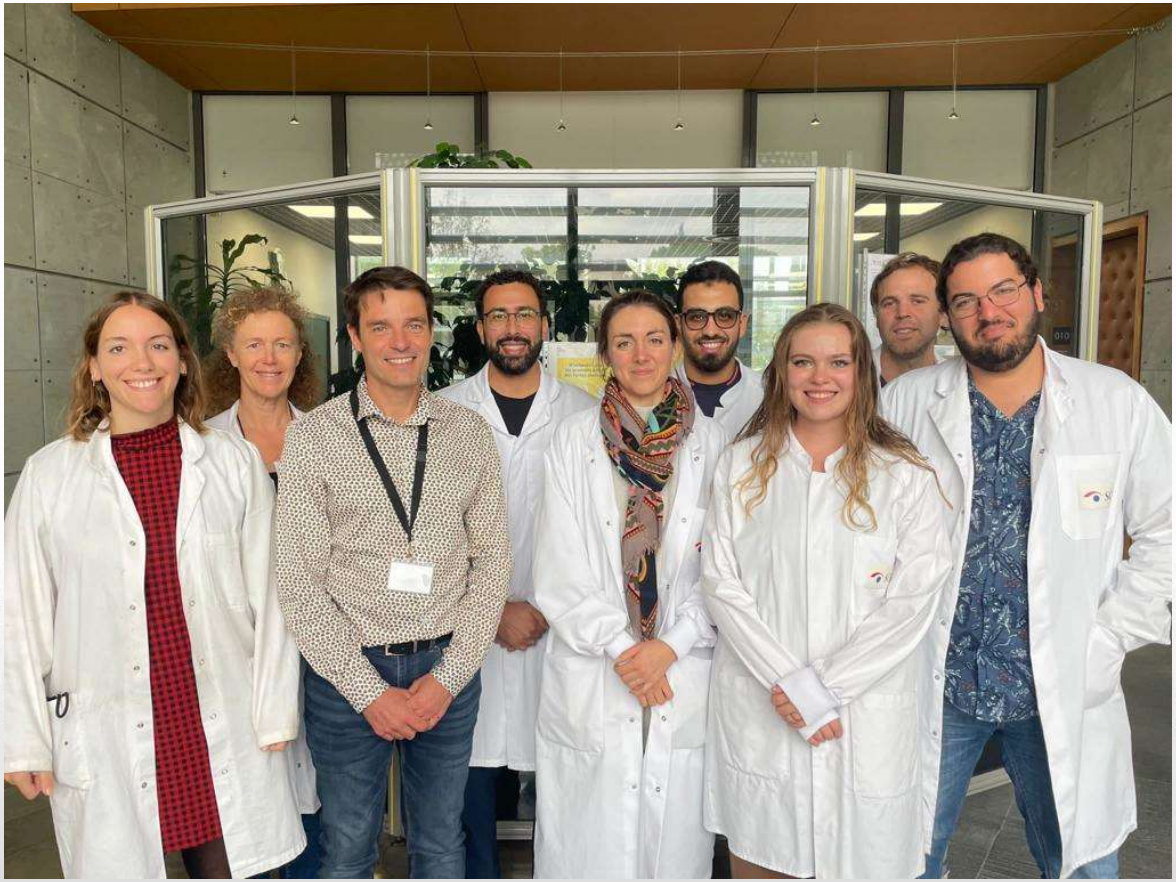
Perspectives

- Optimization of GC clean up
- Purchase of real organic samples !
- Adjust validation strategy



Thank you



for your attention !

Further information :

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We will be happy to answer ☺