Walloon Agricultural Research Centre, Gembloux, Belgium

DEPIPEST

Screening of counterfeit pesticides by Mid-InfraRed spectroscopy (MIR) and confirmation by chromatography (GC, LC, MS)

Juan Antonio Fernández Pierna, Quentin Arnould, Delphine Delhotte, Vincent Baeten
Quality and Authentication of Products Unit (U12)

Pierre Hucorne, Gilles Rousseau, Sébastien Fourmanoir, Laurent Laduron, Jérôme Bodart, Diego Lagasse De Locht, Olivier Pigeon
Protection, Control Products and Residues Unit (U10)

CIPAC Symposium, Galway, Irland, 17 June 2025

The **DEPIPEST** project is funded by the Belgian Federal Public Service Health, Food Chain Safety and Environment

The project goal

Demonstrate the feasibility of a coordinated fight against counterfeit pesticides

- ➢Regulatory aspects
- ➢Screening by MIR and Raman spectroscopy → Transfer to the field (portable spectrometers)
- ➢Confirmation by GC-MS, LC-MS, LC-HRMS (Q-TOF) screening / profiling
- ➢Establishment of a spectral database of legally authorized formulations

Regulatory instruments against the trade of illegal and counterfeit pesticides

Which administrative information should be available when lauching an official control ?

Which rights are violated when a pesticide is marketed illegally ?

A single definition of counterfeiting ?

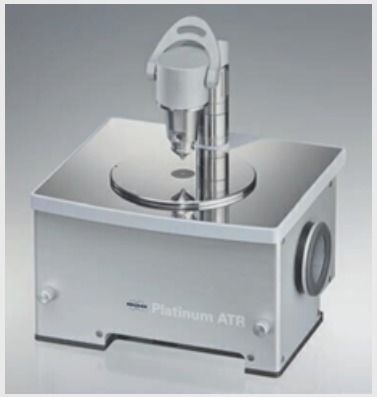
Survey of the following topics :
- Types of rights, types of authorizations
- Legislations, guidance documents
- Competences of international, European and MS institutions (BE)
- Databases
- Procedures

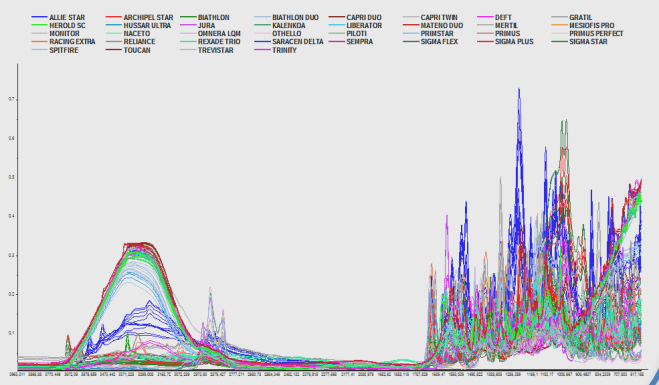
(Review article / guidance document commented by the Croplife Europe Anti-counterfeiting Expert Group and FASFC)

https://www.cra.wallonie.be/en/regulatory-instruments-against-the-trade-of-illegal-and-counterfeit-pesticides-1

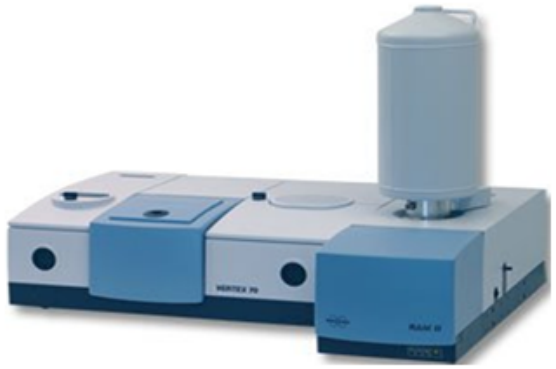
Screening by vibrational spectroscopic methods

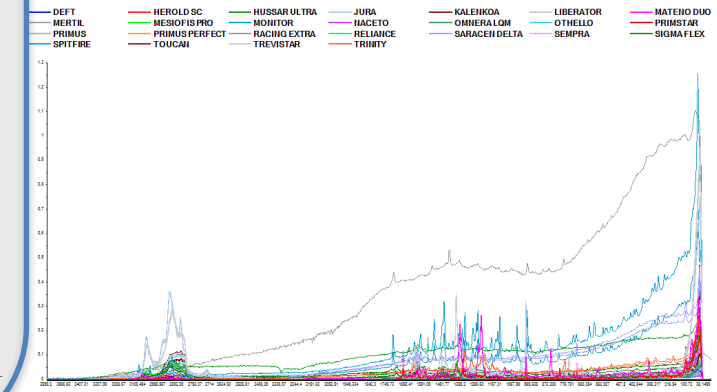
MIR-ATR



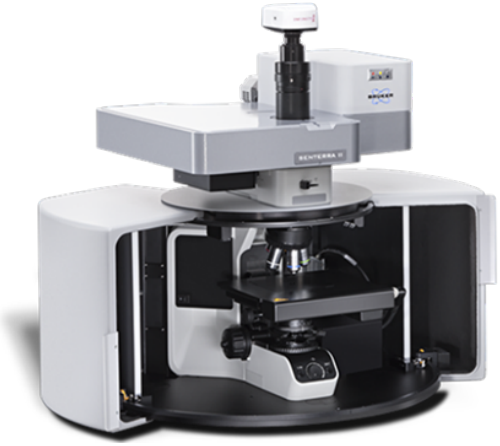


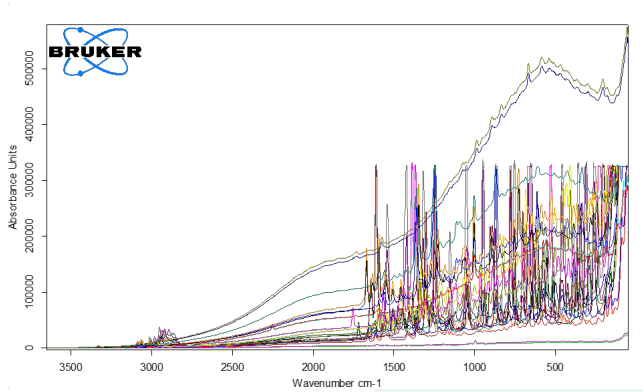
FT-Raman



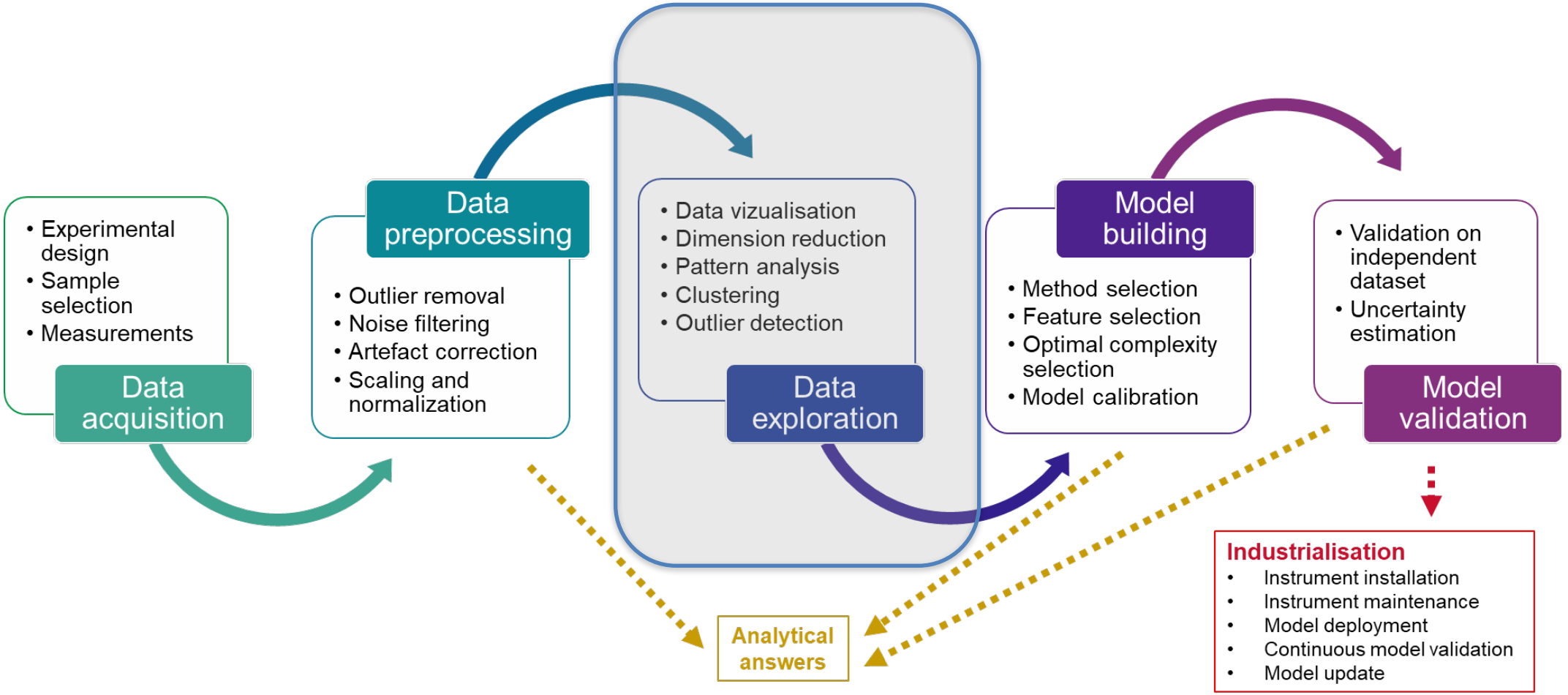


Raman Microscopy

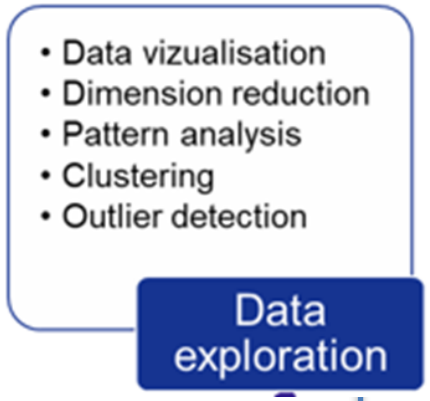




Treatment of data - Chemometrics



A three-steps processing / chemometrics protocol



1 - OPUS / LOCAL APPROACH
2 - PCA
2 - t-SNE

+ visualisation of spectra

OPUS / LOCAL APPROACH

Bruker Optics' new peak based search algorithm

Bruker Optics' new peak based algorithm can be used for both: searching for a pure component or searching for a single component within a mixture.

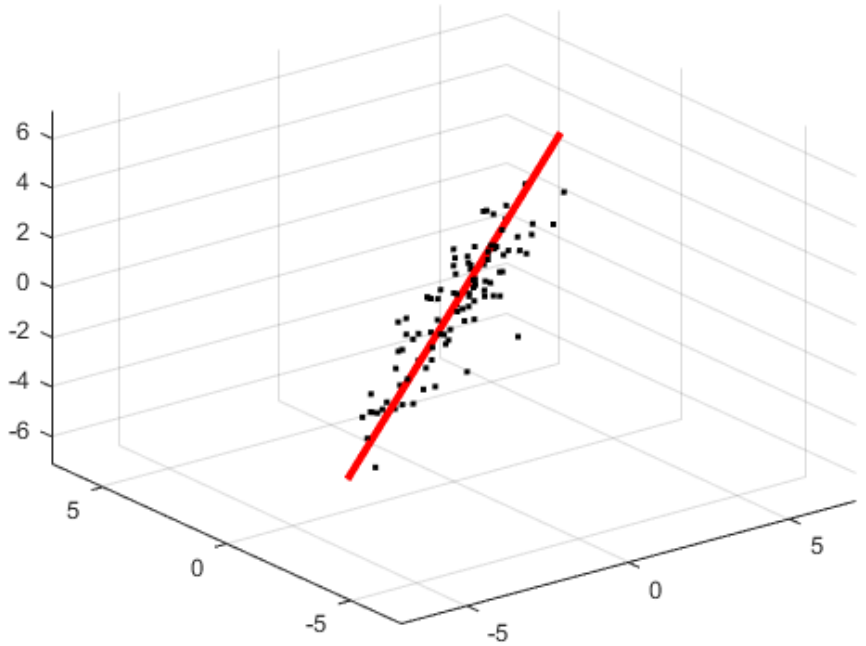
A unique three level database search compares the peak position, relative intensities and the peak half width.

Creation of an index/score. Spectra with score above 990 are considered as correct/consistent, while those below are problematic samples.

PCA : Principal Component Analysis

With PCA we create new variables (PC's) as linear combinations of the original variables

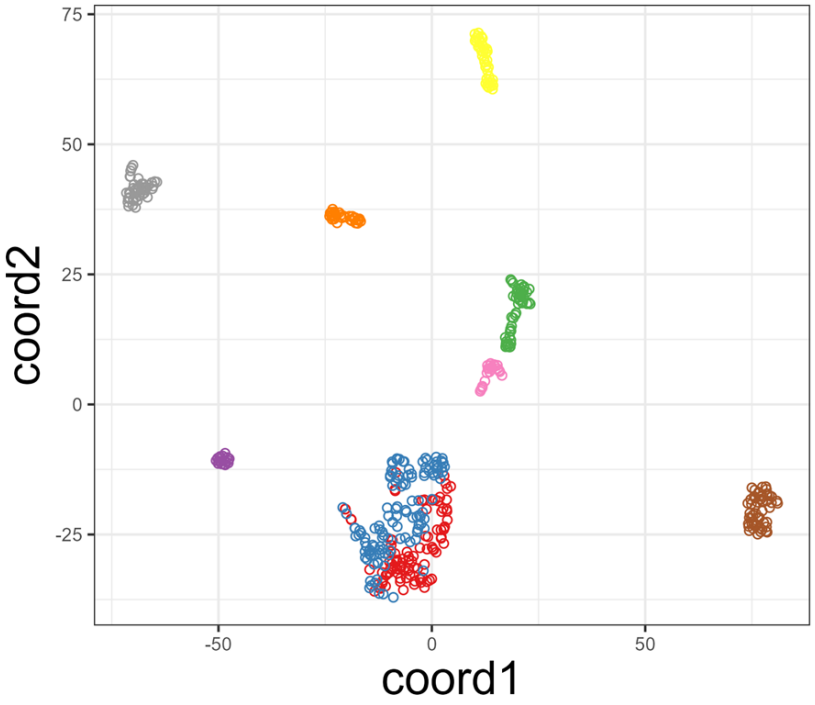
The PC's are uncorrelated and ordered so that the first few retain most of the variation present in all the original variables



t-SNE : t-distributed stochastic neighbour embedding

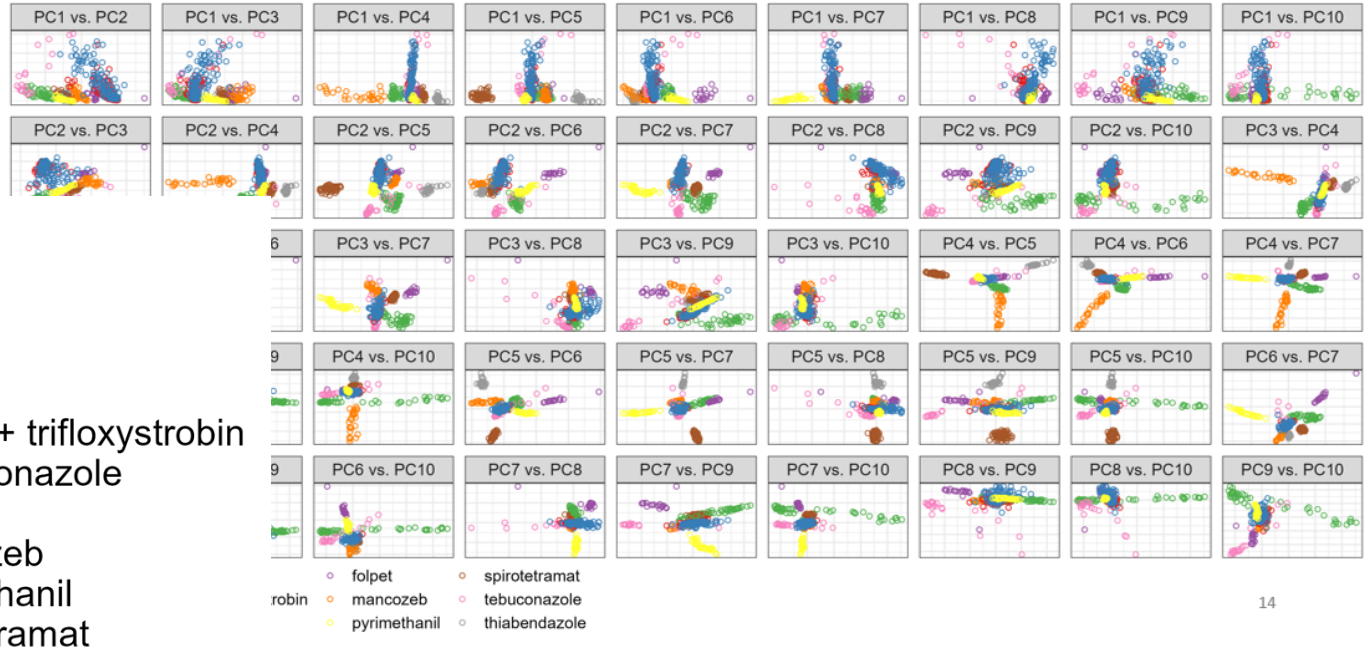
You do not always have to choose which factor to show for data exploration !

→ Visualization method t-SNE displays the structure of a multivariate dataset into a single 2D plot, where the proximity of points indicates the degree of similarity of their spectra



pesticide

- captan
- captan + trifloxystrobin
- difenoconazole
- folpet
- mancozeb
- pyrimethanil
- spirotetramat
- tebuconazole
- thiabendazole



Use of t-distributed stochastic neighbour embedding (t-SNE) in vibrational spectroscopy

F. Stevens[a], V. Baeten[a], J.A. Fernández Pierna[a]

Screening / profiling by chromatographic / mass spectrometric methods

UHPLC-DAD + MS-QDA

Column : Kinetex XDB-C18
Diluting solvent : acetonitrile

Detectors : Diode Array Detector and
Single Quadrupole Mass Spectrometer (molecular mass of parent ions)

Confirmation of known compounds (e.g. active substances standards)

GC-MS

Columns: DB-Wax, HP-5
Diluting solvents :
acetone, hexane

Screening of volatile compounds (co-formulants)
Link to a public DB of mass spectra of various compounds

GC-FID
HPLC-DAD

LC-HRMS (QTOF)

Column : Acquity HSS T3,
Diluting solvent : methanol

Detector: High resolution Mass Spectrometer (Q-TOF)

High resolution mass spectrometry,
Exploratory method

Results and cases

Selection and collection of samples

Goal : several sample types, as representative of research subjects :
a.s. identity and content, a.s. identification based on functional groups, batch profiles, co-formulants content, prohibited coformulants, comparison of similar formulations

Year 1

Around 210 samples have been collected in the CRA-W (**reference formulations**)
- 95 samples of herbicides (35 formulations containing diflufenican, 25 formulations containing florasulam, 35 samples of sulfonylurea herbicides
- 121 samples of fungicides (benzovindiflupyr, bixafen, fluxapyroxad, metconazole, prothioconazole and azoxystrobin, alone or in combination with other active substances)

Around 145 samples have been submitted by FASFC.

Year 2

48 biocides containing deltamethrin, clothianidin, bendiocarb, teflubenzuron, pirimiphos-methyl, DDT (**large series of batches of the same formulation**) previously analysed at CRA-W for quality control. All active substances and phys-chem results available at origin and after accelerated storage

Around 109 samples have been submitted by FASFC.

Samples of reference formulations

	A	B	C	D	E	F	H	K	L	M	N	O	P	Q	R	S	T	U	V
1	N° interne	Nom Commercial	Origine	Nature	Formulation	Annee	N°autorisation	diflufenican	flufenacet	aclonifen	prosulfocarb	iodosulfuron-methyl	mefenpyr-diethyl	mesosulfuron-methyl	chlorotoluron	pendimethalin	florasulam	metsulfuron-methyl	
2	ADV-17-070	JURA	U3- CRA	Herbicide	EC	2017	10633 P/B	14			667								
3	ADV-18-017	JURA	U3- CRA	Herbicide	EC	2018	10633 P/B	14			667								
4	ADV-18-018	JURA	U3- CRA	Herbicide	EC	2018	10633 P/B	14			667								
5	ADV-19-009	JURA	U3- CRA	Herbicide	EC	2019	10633 P/B	14			667								
6	ADV-20-029	JURA	U3- CRA	Herbicide	EC	2020	10633 P/B	14			667								
7	DQ230090-047	Jura	AFSCA	Herbicide	EC	2022	10633 P/B	14			667								
8	ADV-22-007	TRINITY	U3- CRA	Herbicide	SC	2022	10572 P/B	40							250	300			
9	DQ230090-180	TRINITY	AFSCA	Herbicide	SC	2023	10572 P/B	40							250	300			
10	ADV-18-006	OTHELLO	U3- CRA	Herbicide	OD	2018	9873 P/B	50				2,5	22.5	8					
11	ADV-18-062	OTHELLO	U3- CRA	Herbicide	OD	2018	9873 P/B	50				2,5	22.5	8					
12	ADV-22-006	MATENO DUO	U3- CRA	Herbicide	SC	2022	11094 P/B	100		500									
13	ADV-22-017	MATENO DUO	U3- CRA	Herbicide	SC	2022	11094 P/B	100		500									
14	ADV-18-038	LIBERATOR	U3- CRA	Herbicide	SC	2018	9681 P/B	100	400										
15	ADV-20-016	LIBERATOR	U3- CRA	Herbicide	SC	2020	9681 P/B	100	400										
16	ADV-22-010	LIBERATOR	U3- CRA	Herbicide	SC	2022	9681 P/B	100	400										
17	ADV-17-069	KALENKOA	U3- CRA	Herbicide	OD	2017	10247 P/B	120				7,5	27	9					
18	ADV-18-061	KALENKOA	U3- CRA	Herbicide	OD	2018	10247 P/B	120				7,5	27	9					
19	ADV-18-073	KALENKOA	U3- CRA	Herbicide	OD	2018	10247 P/B	120				7,5	27	9					
20	ADV-17-024	NACETO	U3- CRA	Herbicide	SC	2017	10603 P/B	200	400										
21	ADV-18-022	NACETO	U3- CRA	Herbicide	SC	2018	10603 P/B	200	400										
22	ADV-20-027	NACETO	U3- CRA	Herbicide	SC	2020	10603 P/B	200	400										
23	DQ230090-124	naceto	AFSCA	Herbicide	SC	2021	10603 P/B	200	400										
24	ADV-18-029	RELIANCE	U3- CRA	Herbicide	SC	2018	10719 P/B	200	400										
25	ADV-18-030	RELIANCE	U3- CRA	Herbicide	SC	2018	10719 P/B	200	400										
26	ADV-19-002	RELIANCE	U3- CRA	Herbicide	SC	2019	10719 P/B	200	400										
27	ADV-20-024	MERTIL	U3- CRA	Herbicide	SC	2020	10833 P/B	200	400										
28	ADV-21-017	MERTIL	U3- CRA	Herbicide	SC	2021	10833 P/B	200	400										
29	ADV-15-009	HEROLD SC	U3- CRA	Herbicide	SC	2015	9533 P/B	200	400										
30	ADV-19-017	HEROLD SC	U3- CRA	Herbicide	SC	2019	9533 P/B	200	400										
31	ADV-21-008	HEROLD SC	U3- CRA	Herbicide	SC	2021	9533 P/B	200	400										
32	ADV-22-013	HEROLD SC	U3- CRA	Herbicide	SC	2022	9533 P/B	200	400										
33	DQ230090-106	HEROLD SC	AFSCA	Herbicide	SC	2021	9533 P/B	200	400										
34	ADV-19-003	SEMPRA	U3- CRA	Herbicide	SC	2019	10088 P/B	500											
35	ADV-20-021	SARACEN DELTA	U3- CRA	Herbicide	SC	2020	10386 P/B	500									50		
36	DQ230090-092	DIFLANIL500 SC	AFSCA	Herbicide	SC	2021	9408 P/B	500											
37	ADV-17-016	TOUCAN	U3- CRA	Herbicide	SC	2017	9653 P/B	500											
38	ADV-17-020	TOUCAN	U3- CRA	Herbicide	SC	2017	9653 P/B	500											
39	ADV-17-038	TOUCAN	U3- CRA	Herbicide	SC	2017	9653 P/B	500											
40	ADV-18-024	TOUCAN	U3- CRA	Herbicide	SC	2018	9653 P/B	500											
41	DQ230090-140	TOUCAN	AFSCA	Herbicide	SC	2021	9653 P/B	500											
42	ADV-18-079	PILOTI	U3- CRA	Herbicide	WG	2018	10180 P/B	600										60	

Samples containing 14 to 600 g/L **diflufenican**

Several batches of the same formulation

Several formulation types (SC, OD, EC, WG)

Same a.s. composition but different formulations (HEROLD, MERTIL and NACETO)

Same formulation, either bought by CRA-W, or collected by FASFC (ex : JURA)

Same a.s. alone, different formulations (DIFLANIL 500SC, SEMPRA, TOUCAN)

Samples of reference formulations

Nom Commercial	Origine	Nature	Annee	N° autorisation	Colonne1	IODOSULFURON-METHYL-SODIUM	MEFENPYR-DIETHYL	MESOSULFURON-METHYL	THIENCARBAZONE-METHYL	TRIBENURON-METHYLE	METSULFURON-METHYL	AMIDOSULFURON	SULFOSULFURON	THIFENSULFURON-METHYL	PROPOXYCARBAZONE-NA	TRITOSULFURON	FLUROXYPYR
SIGMA MAXX	U3- CRA	herbicide	2019	10409P/B		2	30	10									
MESIOFIS PRO	U3- CRA	herbicide	2020	1215P/P		2	30	10									
SIGMA STAR	U3- CRA	herbicide	2018	10636P/B		9	135	45	23								
SIGMA STAR	U3- CRA	herbicide	2018	10636P/B		9	135	45	23								
SIGMA STAR	U3- CRA	herbicide	2019	10636P/B		9	135	45	23								
SIGMA STAR	U3- CRA	herbicide	2020	10636P/B		9	135	45	23								
SIGMA PLUS	U3- CRA	herbicide	2018	10410P/B		10	90	30				50					
ARCHIPEL STAR	U3- CRA	herbicide	2018	10634P/B		45	135	45	38								
ARCHIPEL STAR	U3- CRA	herbicide	2018	10634P/B		45	135	45	38								
ARCHIPEL STAR	U3- CRA	herbicide	2019	10634P/B		45	135	45	38								
ARCHIPEL STAR	U3- CRA	herbicide	2019	10634P/B		45	135	45	38								
ARCHIPEL STAR	U3- CRA	herbicide	2020	10634P/B		45	135	45	38								
HUSSAR ULTRA	U3- CRA	herbicide	2014	9576P/B		100	300										
HUSSAR ULTRA	U3- CRA	herbicide	2016	9576P/B		100	300										
HUSSAR ULTRA	U3- CRA	herbicide	2021	9576P/B		100	300										
MONITOR	U3- CRA	herbicide	2018	9158P/B									800				
RACING EXTRA	U3- CRA	herbicide	2018	10021P/B							70			680			
SIGMA FLEX	U3- CRA	herbicide	2018	10623P/B			90	45							68		
SIGMA FLEX	U3- CRA	herbicide	2018	10623P/B			90	45							68		
OMNERA LQM	U3- CRA	herbicide	2020	10645P/B							5			30			135
OMNERA LQM	U3- CRA	herbicide	2021	10645P/B							5			30			135
GRATIL	U3- CRA	herbicide	2016	8316P/B								750					
DEFT	U3- CRA	herbicide	2020	9552P/B							200						
BIATHLON	U3- CRA	herbicide	2017	9779P/B												714	
ALLIE STAR	U3- CRA	herbicide	2016	9795P/B						222	111						
ALLIE STAR	U3- CRA	herbicide	2017	9795P/B						222	111						

Samples containing
sulfonylurea herbicides

Validation of our methodology

- Validation on independent dataset
- Uncertainty estimation

Model validation

Reference samples were already available in our spectral database

Preparation of adulterated samples of known composition **(case 1)** and couples of original / counterfeit **(case 2)** **sent in blind** (U10)

Samples are analysed by MIR and Raman spectroscopy (U12)

Samples are identified according to the complete protocol (OPUS / LOCAL + PCA + t-SNE) (U12)

Screening / profiling by chromatography / mass spectrometry of suspected samples (U10)

The identification of the samples is checked versus their actual composition (debriefing U12 – U10)

Simulation Scenario

Study case 1 : Validation of the method with adulterated samples

Database of legitimate reference formulations

	A	B	C	E	F	G	H	I	J	K
1	N° interne	Nom Commercial	Origine	Nature	Annee	N° autorisation	Formulation	metconazole	fluxapyroxad	mepiquat chloride
2	DQ230090-084	CARYX	AFSCA	Fongicide	2021	10182P/B	SL	30		210
3	DQ230090-114	LIBRAX	AFSCA	Fongicide	2021	10177P/B	EC	45	62.5	
4	MAL-21-031	LIBRAX	U3- CRA	Fongicide	2021	10177P/B	EC	45	62.5	
5	MAL-21-057	LIBRAX	U3- CRA	Fongicide	2021	10177P/B	EC	45	62.5	
6	DQ230090-125	plexeo 60	AFSCA	Fongicide	2021	10724 P/B	SL	60		
7	DQ230090-083	CARAMBA	AFSCA	Fongicide	2021	8883 P/B	EC	60		
8	MAL-21-059	SIMVERIS	U3- CRA	Fongicide	2019	10817P/B	EC	90		
9	MAL-21-043	CARAMBA 90 EC	U3- CRA	Fongicide	2021	10922P/B	EC	90		
10										

Simulation Scenario

Study case 1 : Validation of the method with adulterated samples

Preparation of the adulterated samples

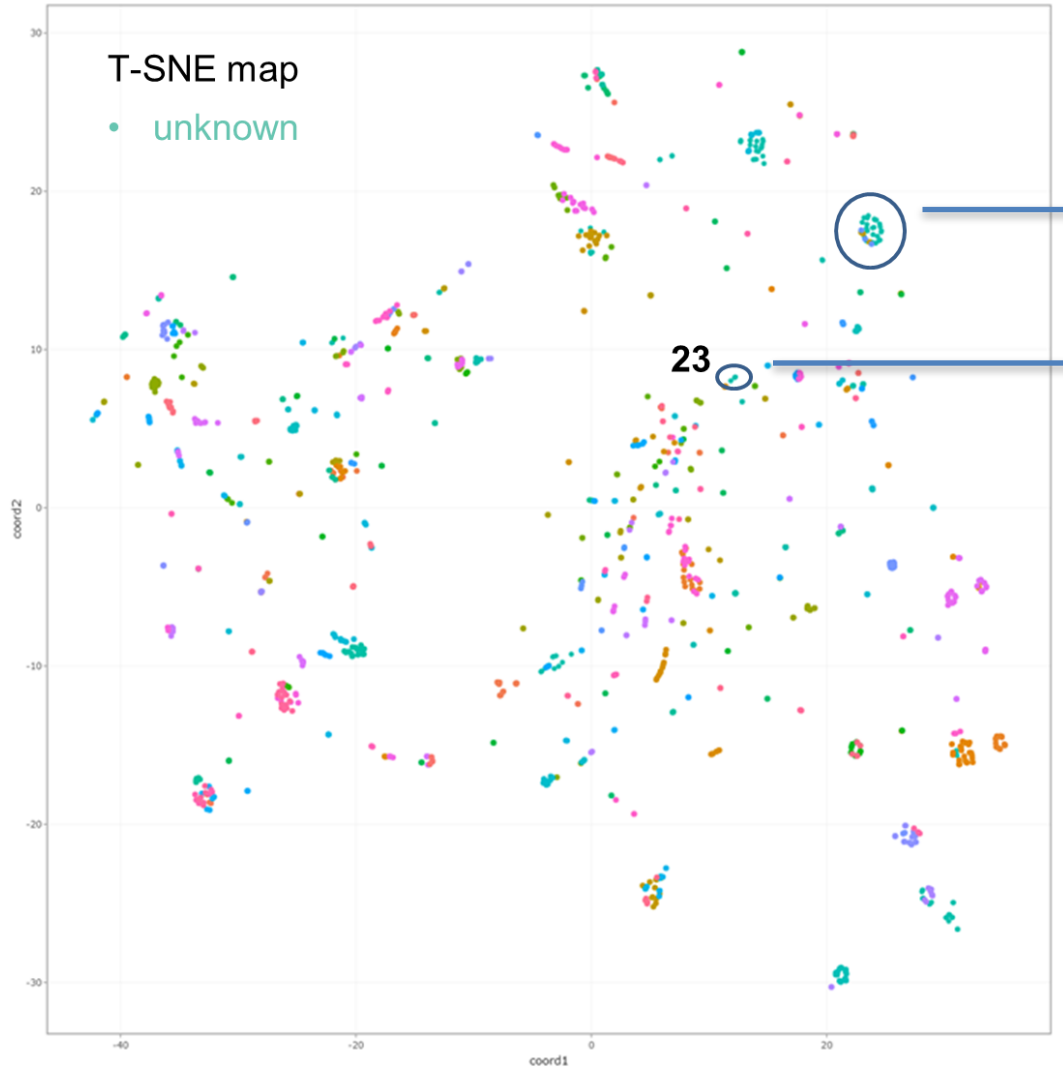
Emulsifiable concentrate and soluble concentrate fungicide formulations containing metconazole, fluxapyroxad and mepiquat chloride

	Sample name/number	Formulation code	metconazole (g/L)	fluxapyroxad (g/L)	mepiquat chloride (g/L)	Adulterated or not	Percentage of adulteration	Aim of this adulteration
1	LIBRAX (batch 2)	EC	45.0	62.5	-	original	100% formu	Evaluating the similarity between batches 2 and 6 and batches of LIBRAX previously analysed (spectra available in the database)
11	LIBRAX (batch 6)	EC	45.0	62.5	-	original	100% formu	
2	CARYX (batch 7)	SL	30.0	-	210.0	original	100% formu	Evaluating the similarity between batch 7 and batches of CARYX previously analysed (spectra available in the database)
12	REMOCCO 60 (batch 3)	EC	60.0	-	-	original	100% formu	Evaluating the similarity between batches 1, 3, 4, 5 and batches of CARAMBA previously analysed (spectra available in the database)
3	REMOCCO 60 (batch 5)	EC	60.0	-	-	original	100% formu	
13	CARAMBA (batch 1)	EC	60.0	-	-	original	100% formu	
4	CARAMBA (batch 4)	EC	60.0	-	-	original	100% formu	
14	LIBRAX (batch 2)	EC	40.5	56.3	-	adulterated	90% formu + 10% xylene	Identifying the formulation and the nature / extent of the adulteration (solvent used / small or large addition)
5	LIBRAX (batch 2)	EC	22.5	31.3	-	adulterated	50% formu + 50% xylene	
15	LIBRAX (batch 2)	EC	40.5	56.3	-	adulterated	90% formu + 10% DMSO	
6	LIBRAX (batch 2)	EC	22.5	31.3	-	adulterated	50% formu + 50% DMSO	
16	LIBRAX (batch 2)	EC	40.5	56.3	-	adulterated	90% formu + 10% iso-octane	
7	LIBRAX (batch 2)	EC	22.5	31.3	-	adulterated	50% formu + 50% iso-octane	
17	CARYX (batch 7)	SL	27.0	-	189.0	adulterated	90% formu + 10% water	
8	CARYX (batch 7)	SL	15.0	-	105.0	adulterated	50% formu + 50% water	
18	LIBRAX (batch 6)	EC	40.5	56.3	-	adulterated	90% formu + 10% iso-octane	
9	REMOCCO 60 (batch 3)	EC	54.0	-	-	adulterated	90% formu + 10% iso-octane	
19	REMOCCO 60 (batch 5)	EC	54.0	-	-	adulterated	90% formu + 10% iso-octane	
10	CARAMBA (batch 1)	EC	54.0	-	-	adulterated	90% formu + 10% iso-octane	
20	CARAMBA (batch 4	EC	54.0	-	-	adulterated	90% formu + 10% iso-octane	
21	xylene (mixture of isomers)	-	-	-	-	-	100% xylene	Identifying the nature of the solvent by means of a published spectral database
22	DMSO (dimethysulfoxide)	-	-	-	-	-	100% DMSO	
23	iso-octane	-	-	-	-	-	100% iso-octane	

Simulation Scenario

Study case 1 : Validation of the method with adulterated samples

Exploratory processing by OPUS / LOCAL and t-SNE approaches



Active compound: metconazol:
CARAMBA, PLEXEO60 (in library)
REMOCCO (not in library)

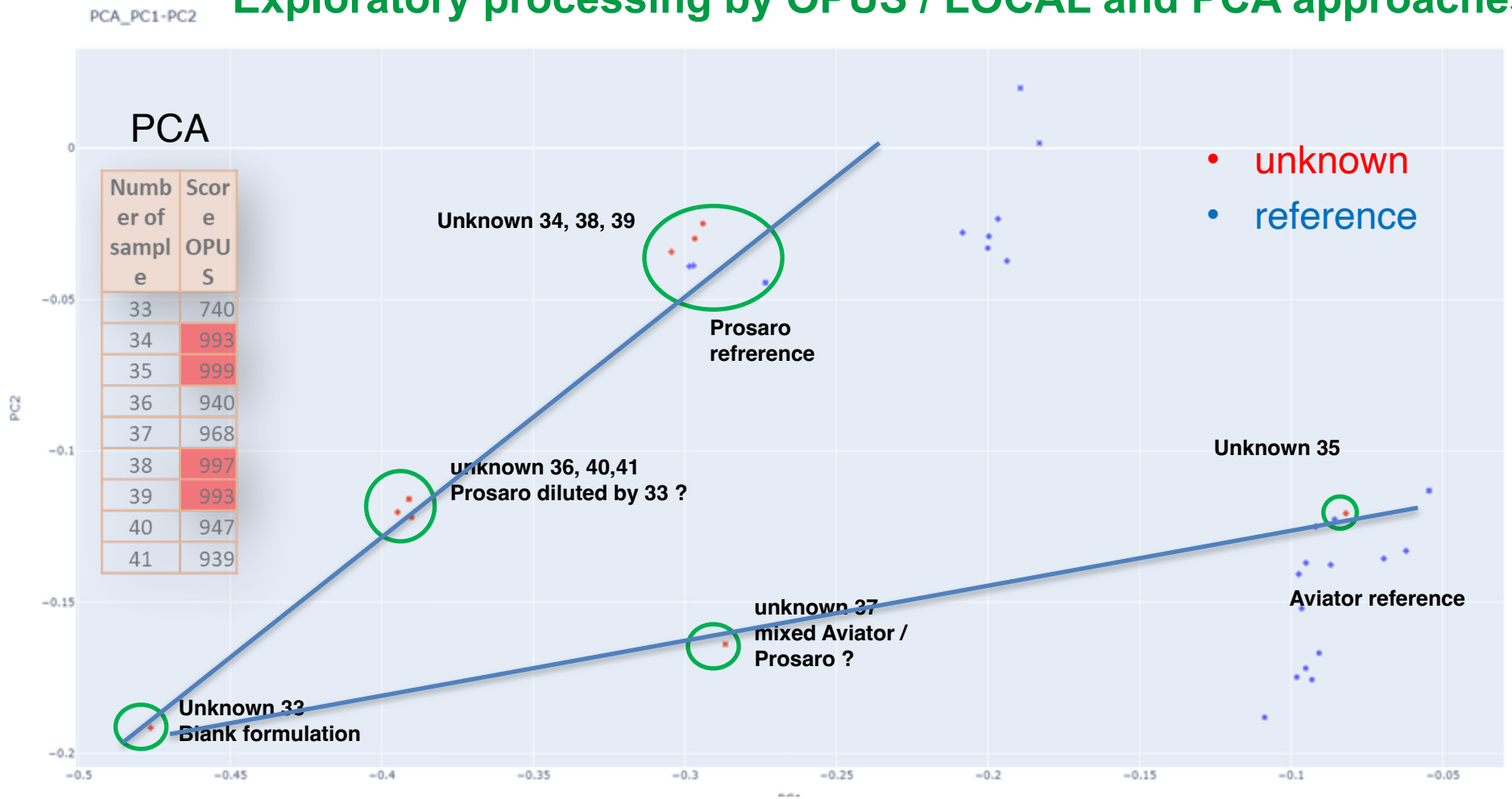
Iso-octane

Sample number	Score OPUS	LOCAL APPROACH
3	999	CARAMBA
4	999	CARAMBA
9	989	CARAMBA
10	989	CARAMBA
12	999	CARAMBA
13	999	CARAMBA
19	989	CARAMBA
20	989	CARAMBA
23	740	Iso Octane

Simulation Scenario

Study case 1 : Validation of the method with adulterated samples

Exploratory processing by OPUS / LOCAL and PCA approaches



Active compound: prothioconazol:
PROSARO, AVIATOR (in library)

Simulation Scenario

Study case 1 : Validation of the method with adulterated samples

Checking of the identification with the actual composition

Sample number	Final results	Sample name/number Batch (U10)	Percentage of adulteration (U10)
1	LIBRAX (pure)	LIBRAX (batch 2)	100% formu
2	CARYX (pure)	CARYX (batch 7)	100% formu
3	CARAMBA/PLEXEO 60 (pure)	REMOCCO 60 (batch 5)	100% formu
4	CARAMBA/PLEXEO 60 (pure)	CARAMBA (batch 4)	100% formu
5	LIBRAX (adulterated by sample 21)	LIBRAX (batch 2)	50% formu + 50% xylene
6	LIBRAX (adulterated by sample 22++)	LIBRAX (batch 2)	50% formu + 50% DMSO
7	LIBRAX adulterated	LIBRAX (batch 2)	50% formu + 50% iso-octane
8	CARYX (dilution ++) – water	CARYX (batch 7)	50% formu + 50% water
9	CARAMBA/PLEXEO 60 (adulterated +)	REMOCCO 60 (batch 3)	90% formu + 10% iso-octane
10	CARAMBA/PLEXEO 60 (adulterated +)	CARAMBA (batch 1)	90% formu + 10% iso-octane
11	LIBRAX (pure)	LIBRAX (batch 6)	100% formu
12	CARAMBA/PLEXEO 60 (pure)	REMOCCO 60 (batch 3)	100% formu
13	CARAMBA/PLEXEO 60 (pure)	CARAMBA (batch 1)	100% formu
14	LIBRAX (adulterated)	LIBRAX (batch 2)	90% formu + 10% xylene
15	LIBRAX (adulterated by sample 22)	LIBRAX (batch 2)	90% formu + 10% DMSO
16	LIBRAX (dilution)	LIBRAX (batch 2)	90% formu + 10% iso-octane
17	CARYX (dilution +)	CARYX (batch 7)	90% formu + 10% water
18	LIBRAX	LIBRAX (batch 6)	90% formu + 10% iso-octane
19	CARAMBA/PLEXEO 60 (adulterated +)	REMOCCO 60 (batch 5)	90% formu + 10% iso-octane

Simulation Scenario

Study case 1 : Validation of the method with adulterated samples

Checking of the identification with the actual composition

Sample number	Final identification	Sample name/number Batch (U10)	Percentage of adulteration (U10)
20	CARAMBA/PLEXEO 60 (adulterated +)	CARAMBA (batch 4	90% formu + 10% iso-octane
21	Contaminant (of sample 5)	xylene (mixture of isomers)	100% xylene
22	Contaminant (of sample 6 et 15)	DMSO (dimethysulfoxide)	100% DMSO
23	Contaminant	iso-octane	100% iso-octane
25	MONITOR (adulteration ?)	Sulfosulfuron 75 WG (batch 2)	100% formu
26	MONITOR (adulteration ?)	Sulfosulfuron 80 WG (batch 3)	100% formu
27	MONITOR + CAPRI	Sulfosulfuron 80 WG (batch 3)	50% formu + 50% CAPRI TWIN
28	MONITOR (pure)	MONITOR (batch 1)	100% formu
31	MONITOR + CAPRI	Sulfosulfuron 80 WG (batch 3)	25% formu + 75% CAPRI TWIN
32	CAPRI TWIN (pure)	CAPRI TWIN (without sulfosulfuron, used as blank) (batch 4)	100% CAPRI TWIN
33	Dilution basis?	PROTENDO EXTRA blank (batch 4b, company 1)	100% blank
34	PROSARO (pure)	PROSARO EC (batch 1, company 2)	100% formu
35	AVIATOR (pure)	AVIATOR XPRO (batch 3, company 2)	100% formu
36	PROSARO (adulterated)	PROSARO EC (batch 1, company 2)	50% formu + 50% blank aviator
37	AVIATOR/PROSARO	AVIATOR XPRO (batch 3, company 2)	50% formu + 50% blank prosaro
38	PROSARO (pure)	PROTENDO EXTRA (batch 4, company 1)	100% formu
39	PROSARO (pure)	PROSARO EC (batch 2, company 2)	100% formu
40	PROSARO (adulterated)	PROTENDO EXTRA (batch 4, company 1)	50% formu + 50% blank
41	PROSARO (adulterated)	PROSARO EC (batch 2, company 2)	50% formu + 50% blank

Study case 2 : Comparison by MIR of counterfeit / original products (spirotetramat 100 g/L SC)

REAL CASE SCENARIO

SPIRO PARRALEL 2, parallel trade, equivalent to SPIRO ORIGINAL, potentially counterfeited (8360)

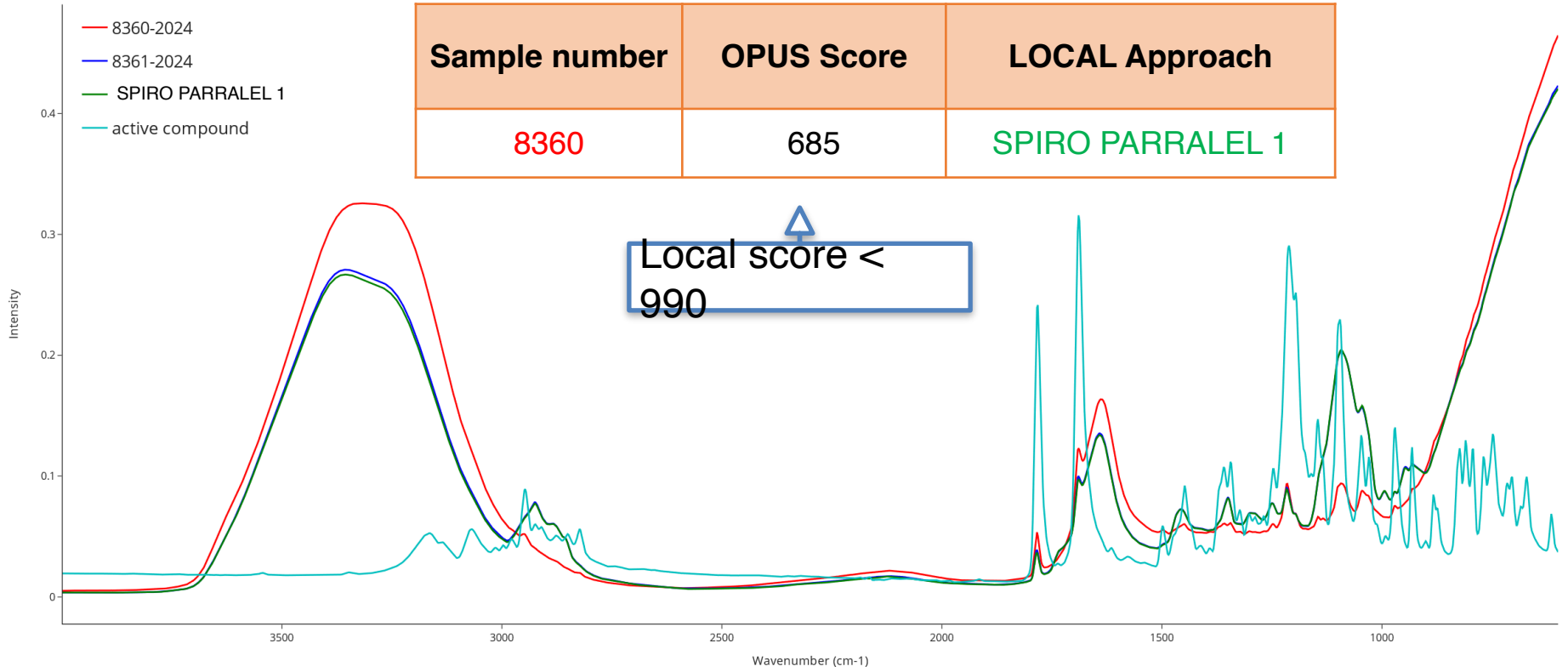
SPIRO ORIGINAL, original submitted by data holder (8361)

SPIRO PARRALEL 1, parallel trade, equivalent to SPIRO ORIGINAL, spectra available in the data base

Analytical standard spirotetramat

Sample number	OPUS Score	LOCAL Approach
8360	685	SPIRO PARRALEL 1

Local score < 990



Study case 2 : Comparison by MIR of counterfeit / original products (spirotetramat 100 g/L SC)

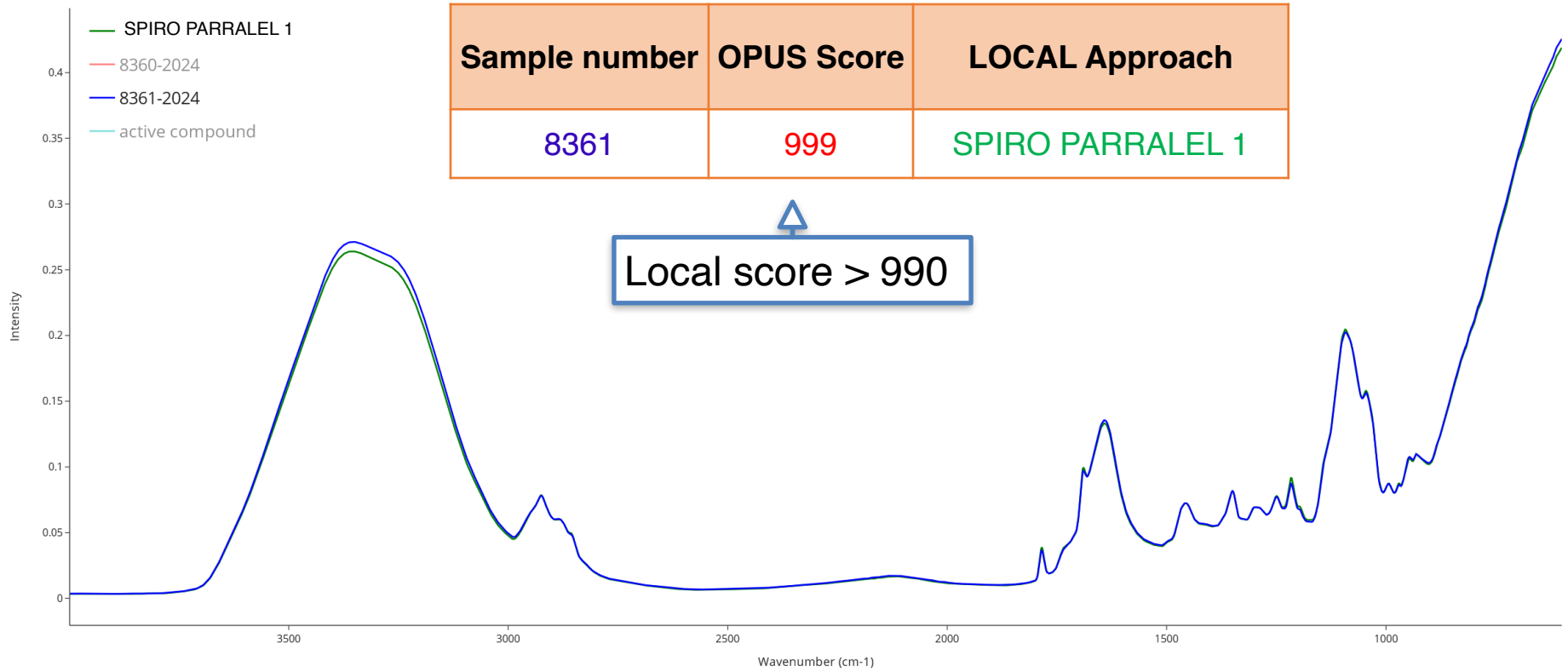
REAL CASE SCENARIO

SPIRO ORIGINAL, original submitted by data holder (8361)

SPIRO PARRALEL 1, parallel trade, equivalent to SPIRO ORIGINAL, spectra available in the data base

Sample number	OPUS Score	LOCAL Approach
8361	999	SPIRO PARRALEL 1

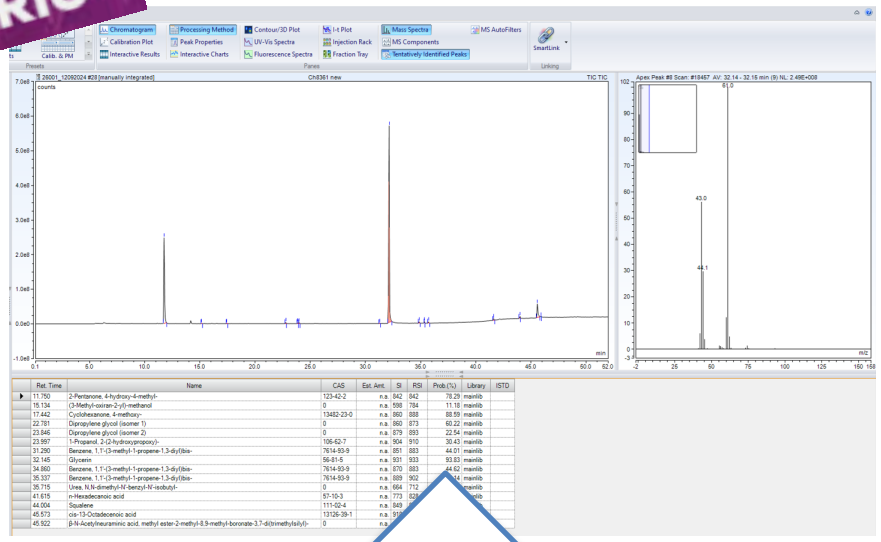
Local score > 990

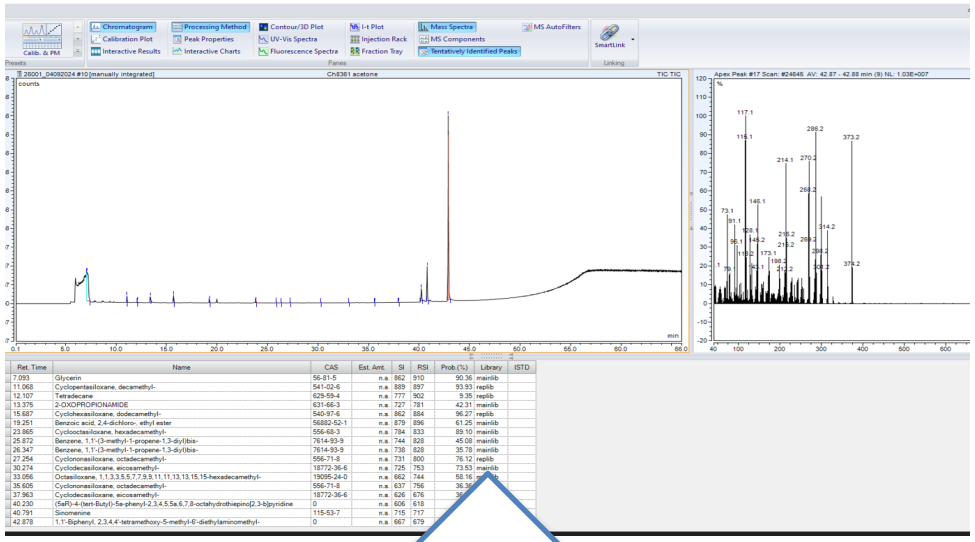


REAL CASE SCENARIO

Case 2 : Confirmation by GC-MS screening

SPIRO ORIGINAL, original submitted by data holder (8361)





Sample 8361 : Glycerin identified
at RT 32.14 min on DB-Wax column
Mass spectra available, with match of 931,
probability 93.8%

Sample 8361: Glycerin identified
at RT 7.09 min on HP5 column
Mass spectra available, with match of 910,
probability 90.4%
(reversed polarity, co-elutes with solvents)

SPIRO PARRALEL 2 parallel trade, equivalent to SPIRO ORIGINAL, potentially counterfeited (8360)

Sample 8360 : glycerin not present; ethylen-glycol present

Case 2 : Confirmation by UHPLC-HRMS (Q-TOF) screening

REAL CASE SCENARIO

SPIRO PARRALEL 2, parallel trade, equivalent to SPIRO ORIGINAL, potentially counterfeited (8360)

SPIRO ORIGINAL, original submitted by data holder (8361)

Sample	Sirotetramat	Spirotetramat cis-enol
8360	557284	11113
8361	610070	1493

2% impurity cis-enol detected in potentially counterfeited sample

a.s. spirotetramat detected in both samples
a.s. content in potentially counterfeited sample is 91% of the original

Nonylphenol Ethoxylate (NPEO) and Octophenol Ethoxylate (OPEO) have not been detected (according to the applicant, the counterfeit contains these coformulants)

Glycerin not detected → not detectable in positive ESI, below mass range of the apparatus (glycerin at 93 DA, apparatus between 100 to 1000 DA)

Conclusion

- Satisfactory demonstration that MIR combined with the defined protocol works well as a screening method for the detection of possible pesticide frauds

- MIR is a non destructive, rapid and cheaper analytical technique, allowing the measurement of many samples in a short time

- Transfer to handheld devices (portable spectrometers)

- Suspicious samples to be sent to the laboratory for further screening / profiling by chromatographic / mass spectrometric methods or reference chemical and physical-chemical methods

Perspectives

Developing a spectral database for one MS, one company, a subset of products

Customs, Police, Food Safety Agencies

Query to SPECTRAL_phytoweb

PPP declared to be CARAMBA, 8883 P/B, according to label, consignements documents, sellor.

Do you confirm?

Answer of SPECTRAL_phytoweb

Sample number	Score OPUS	LOCAL APPROACH
3	999	CARAMBA
4	999	CARAMBA
9	989	CARAMBA
10	989	CARAMBA
12	999	CARAMBA
13	999	CARAMBA
19	989	CARAMBA
20	989	CARAMBA
23	740	Iso Octane

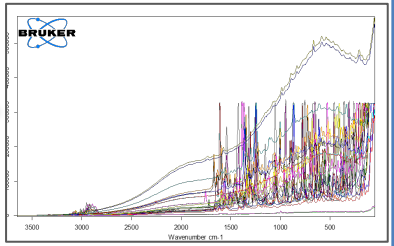
OK for 3,4,12, 13

Chromatographic confirmation needed for 9, 10, 19, 20, 23

SPECTRAL_phytoweb, e-PHY, CTGB, BVL…

Authorized formulations

Nom Commercial	Origine	Nature	Annee	N° autorisation	Formulation	metconazole	fluxapyroxad	mepiquat chloride
CARYX	AFSCA	Fongicide	2021	10182P/B	SL	30		210
LIBRAX	AFSCA	Fongicide	2021	10177P/B	EC	45	62.5	
LIBRAX	U3- CRA	Fongicide	2021	10177P/B	EC	45	62.5	
LIBRAX	U3- CRA	Fongicide	2021	10177P/B	EC	45	62.5	
plexeo 60	AFSCA	Fongicide	2021	10724 P/B	SL	60		
CARAMBA	AFSCA	Fongicide	2021	8883 P/B	EC	60		
SIMVERIS	U3- CRA	Fongicide	2019	10817P/B	EC	90		
CARAMBA 90 EC	U3- CRA	Fongicide	2021	10922P/B	EC	90		



Walloon Agricultural Research Centre, Gembloux, Belgium

DEPIPEST

Innovative screening methodology by vibrational spectroscopy (MIR, RAMAN) and confirmation by chromatographic methods (GC, LC, MS) of counterfeit pesticide formulations

Thank you !

Thanks to the Belgian Federal Public Service Health, Food Chain Safety and Environment for funding this project

Thanks to the Croplife Europe Anti-counterfeiting Expert Group
and the Belgian FASFC for their supply of pesticides samples

Pierre Hucorne (p.hucorne@cra.wallonie.be), Juan Antonio Fernández Pierna (j.fernandez@cra.wallonie.be),
Vincent Baeten (v.baeten@cra.wallonie.be), Olivier Pigeon (o.pigeon@cra.wallonie.be)