Validation of Qualitative Screening Methods

Hans Mol[1], Darinka Stajnbaher[2], Henk van der Kamp[1]

[1] RIKILT – Institute of Food Safety, Wageningen, Netherlands
[2] Public Health Institute, Maribor, Slovenia

hans.mol@wur.nl

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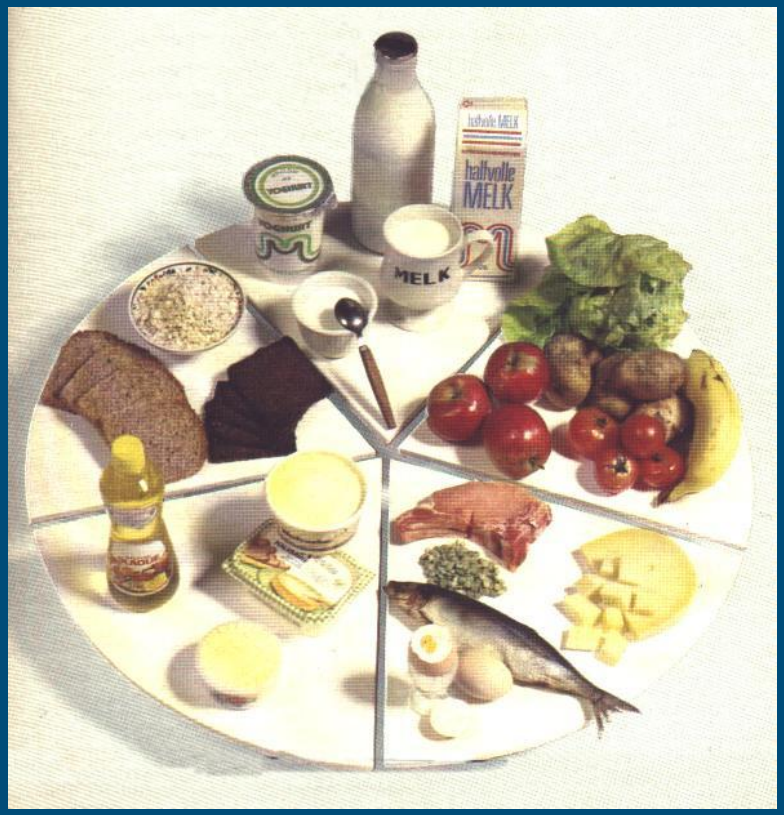
3º Workshop Latinoamericano sobre Residuos de Pesticidas Alimentos y Medio Ambiente

Radisson Montevideo Victoria Plaza Hotel. Montevideo, Uruguay. 8 - 11 Mayo 2011

The pesticide residue issue



Food Safety Authority

Food/feed Industry Retail

Consumer NGOs

Food safety

?

GAP

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Pesticide analysis: the analytical challenge

Pesticide Manual: 1436 pesticides (excl. metabolites)

908 main entries + 528 superseded

380 defined commodities (excl. 'others')

EU Pesticides database

Homepage Search Download

>1200 entries

Active substances

Directive 91/414/EEC

Registered: 366
Out: 813
Pending: 61

Pesticide EU-MRLs

Regulation (EC) No 396/2005

Active substance

Active substance updated on 16/09/2009

Directorate General for Health & Consumers

Products

Pesticides

MRLs updated on 10/09/2009

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>152,000 MRLs set (0.01 mg/kg for all others)

Current practice: quantitative multi-methods

Sample prep

Generic multi-residue extraction/clean up procedure

Analysis

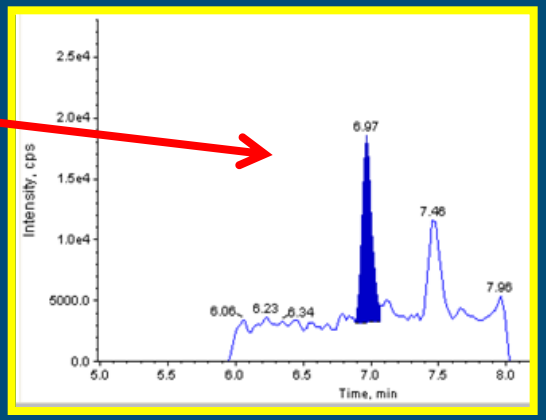
GC-MS (SIM), GC-MS/MS
LC-MS/MS

scope: ever expanding
200-400 pesticides

Data review

Manual verification of peak assignment and integration

Calibration/linearity
Stability of response
Matrix effects
Recovery
Ion ratios/spectra



effort & time increase with # pesticides,

limiting factor in throughput

Validation +
On-going AQC

Various matrices, levels
Recoveries, reproducibility
Measurement uncertainty

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How many residues are actually being found?

Latin American products imported in EU and analyzed in EU labs*

Uruguay

27 pesticides found in 10 products:
Imazalil
ortho-phenylphenol
Prochloraz
Thiabendazole
Chlorpyrifos
Iprodione
Carbaryl
Azinphos-methyl
2,4-D
Captan
Carbendazim
Methidathion

Colombia

52 pesticides found in 12 products:	
Thiabendazole	Captan
Imazalil	Carbofuran
Azoxystrobin	Chlorfenapyr
Carbendazim	Deltamethrin
Difenoconazole	Fenhexamid
Chlorpyrifos	Fentin
Monocrotophos	Imidacloprid
Cypermethrin	Procymidone
Iprodione,	Propamocarb
Myclobutanil	Tetradifon
lambda-Cyhalothrin	Carbaryl
Folpet	Carbofuran, 3-OH
Pyrimethanil	Chlorothalonil
Methamidophos	Dimethoate
Tebuconazole	Dimethomorph
Bitertanol	Malathion
Dithiocarbamates	Omethoate

Brazil

78 pesticides found in 19 products:		
Prochloraz	Ethephon	Pyrimethanil
Imazalil	Gibberellic acid (GA3)	Thiamethoxam
Thiabendazole	Omethoate	Triflumuron
Azoxystrobin	ortho-phenylphenol	Carbofuran, 3-OH
Carbendazim	Phosmet	Chlorfenapyr
Tebuconazole	Captan	Copper
Famoxadone	Carbofuran	lambda-Cyhalothrin
Iprodione	Chlorpyrifos	Cyproconazole
Imidacloprid	Difenoconazole	Dithiocarbamates
Myclobutanil	Dimethomorph	Dodine
Dimethoate	2,4-D	Fenarimol
Pyraclostrobin	Acetamiprid	Fenhexamid
Boscalid	Bifenthrin	Permethrin
Kresoxim-Methyl	Carbaryl	Tebufenozide
Methidathion	Clothianidin	Thiacloprid
Thiophanate-methyl	Cypermethrin	Triadimefon
Zoxamide	Procymidone	Triadimenol

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*Pesticides found at > 0.01 mg/kg, 2007-2010
www.pesticides-online.de (CVUA Stuttgart, Germany)

Current practice: quantitative multi-methods

Sample prep

Generic multi-residue extraction/clean up procedure

Analysis

GC-MS (SIM), GC-MS/MS
LC-MS/MS

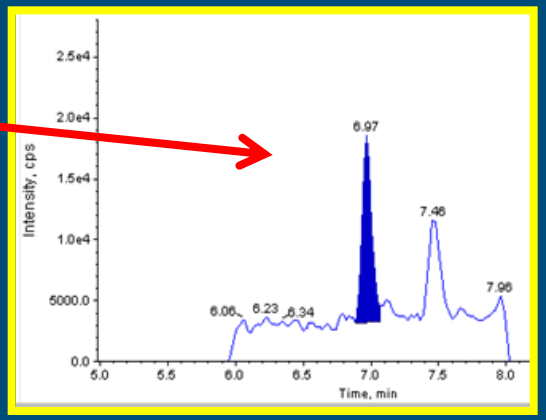
scope: ever expanding
200-400 pesticides

Data review

Manual verification peak
Matrix effects

STOP

doing all this for pesticides seldom found is a waste of effort and time !



effort & time increase with # pesticides,

limiting factor in throughput

Validation +
On-going AQC

Various matrices, levels
Recoveries, reproducibility
Measurement uncertainty

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Maybe less is better.....

Quantitative methods:
focus on frequently occurring/relevant pesticides (25-75)

Prioritize!

Historic perspective: residues/MRL violations found before

Legislative perspective: registered pesticides

Usage perspective: sales/application records

Health perspective: acute toxic pesticides, exceedance of ARfD

Or a smart combination of the above….

Or maybe not.....?

Historic perspective: residue data from past cannot be extrapolated to future

Legislative perspective: use of non-registered (illegal) pesticides ?

Usage perspective: reliability of sales/application records ?

Health perspective: to the consumer any MRL violation is a health issue

Or the worst combination of the above…

>1000 pesticides not likely to occur, but you are never sure and if they are present we want to know about it!

⇒ **Establish fast qualitative screening method**

What is a screening method ?

General: fast, easy, low-tech, low cost, 1 analyte, 1000s samples

Technique: dipstick, sensors (immuno assays)
cut-off at MRL

Purpose: test MRL compliance

Increase efficiency,
reduce workload / need for laborious confirmatory methods

Pesticides: fast, high-tech, >500 pesticides, 100s samples

Technique: chemical methods (chromatography), cut-off at 0.01 mg/kg

Purpose: demonstrate absence/presence unexpected pesticides

Increase efficiency, reduce # pesticides
in quantitative (multi) methods

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Outline of qualitative pesticide screening method

Sample prep	Generic multi-residue extraction/clean up procedure
Analysis	GC-**full scan MS** (single quad, IT, TOF) LC-**full scan MS** (TOF, Orbitrap)
Data review	> 500 pesticides..... ⇒ Only efficient when automated !
Validation + On-going AQC	Procedures only very recently included in EU guideline ⇒Only meaningful for monitoring & enforcement when reliability is known

⇒ key role for software in the overall method

validation of qualitative screening

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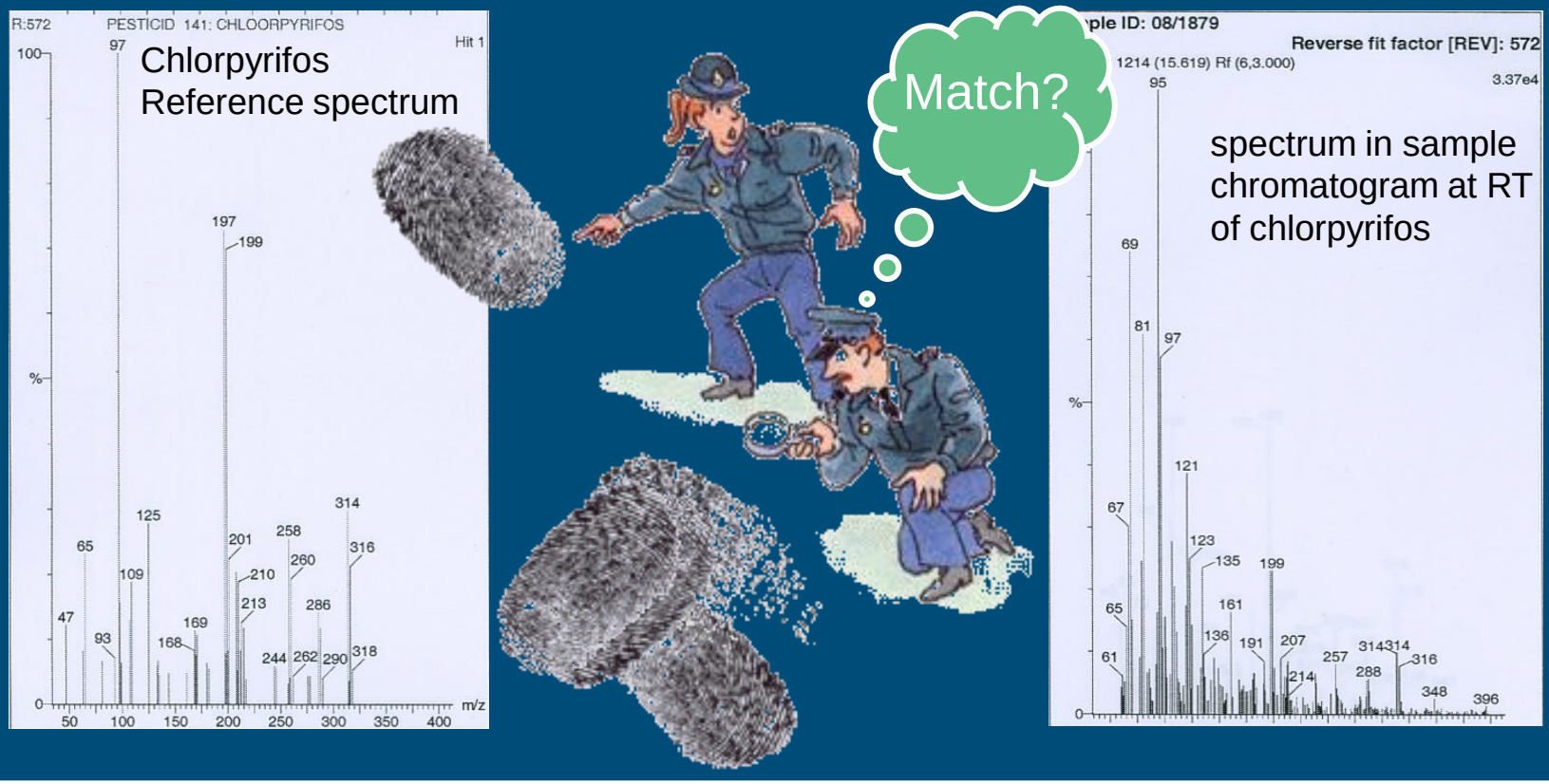
Automated detection by software

Example: GC-single quad MS, full scan acquisition

Comparison of spectra from raw data with reference spectra from library



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Automated detection by software

Example automated library-based detection (DRS, Agilent*):
Software + dedicated target library (926 compounds: spectra + RT)

Automatically performs:
- data pre-processing: deconvolution
- matching of experimental spectra / RT against library spectra / RT
- summary report of compounds detected

MSD Deconvolution Report
Sample Name: std M272/M205 100v
Data File: C:\Documents and Settings\lfs-wyliep\My Documents\My GC_MS Data\Hans Moll Pesticide Analysis\Hans Mol Jan 2006\Mol_Data.D
Date/Time: 11:59 AM Tuesday, May 9 2006

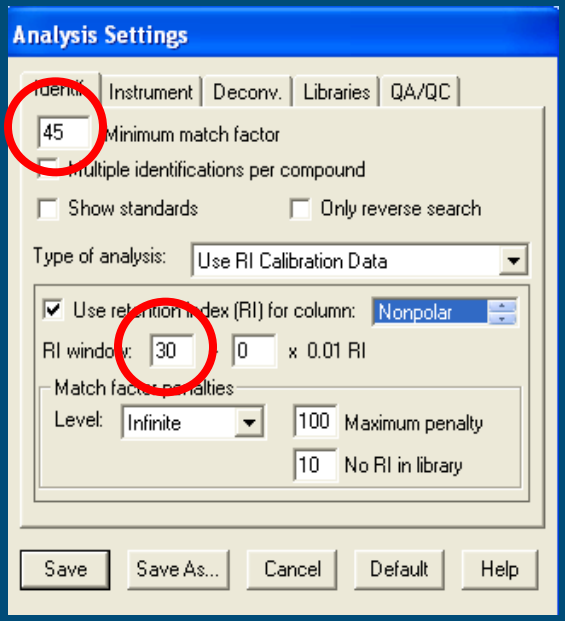
The NIST library was searched for the components that were found in the AMDIS target library.

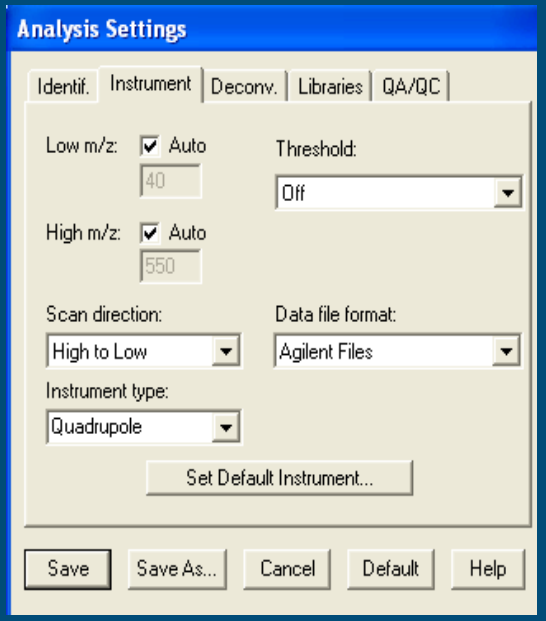
			Agilent	AMDIS		NIST	
R.T.	Cas #	Compound Name	ChemStation Amount (ng)	Match	R.T. Diff sec.	Reverse Match	Hit Num.
9.705	23560590	Heptenophos	0	85	-1.7	82	1
10.330	1918167	Propachlor	0	97	-1.4	94	1
10.3528	114261	Propoxur		93	-0.4	89	3
10.5452	122394	Diphenylamine		96	1.7	92	1
10.713	13194484	Ethoprophos	0	95	-1.5	91	1
11.1186	101213	Chlorpropham		87	4.4	80	2
11.263	4710172	Dichlofluanid metabolite (DMSA)	0	92	6.8	89	1

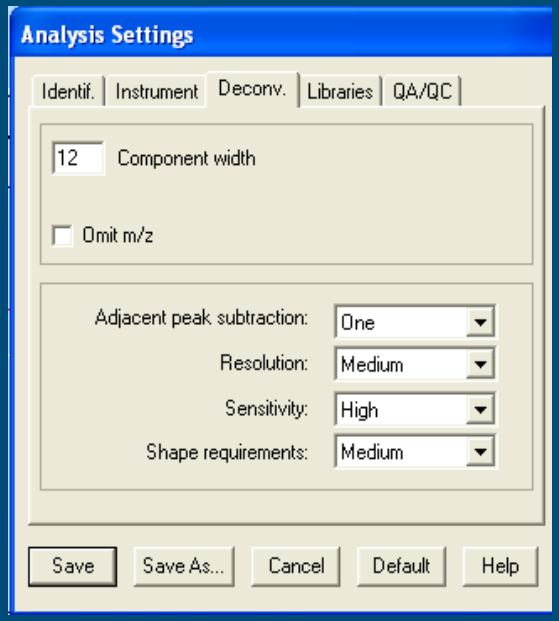
*http://www.chem.agilent.com/Library/applications/5989-5076EN.pdf

Automated detection by software

⇒ Method optimization extends to software







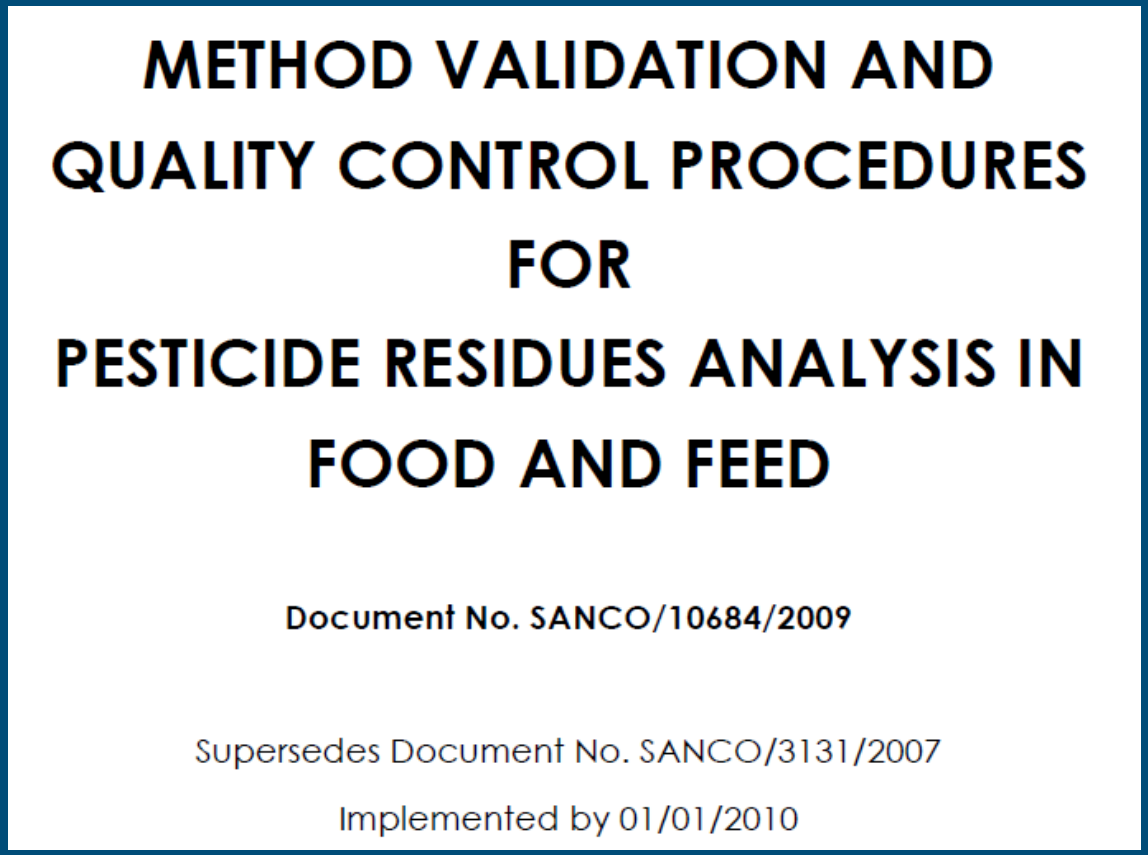
Settings/thresholds too strict: many false negatives

Too loose: many tentative detects needing further follow up (time/effort)

Optimization = compromise between the two

Validation of qualitative screening

EU guidance document for pesticides:



METHOD VALIDATION AND QUALITY CONTROL PROCEDURES FOR PESTICIDE RESIDUES ANALYSIS IN FOOD AND FEED

Document No. SANCO/10684/2009

Supersedes Document No. SANCO/3131/2007

Implemented by 01/01/2010

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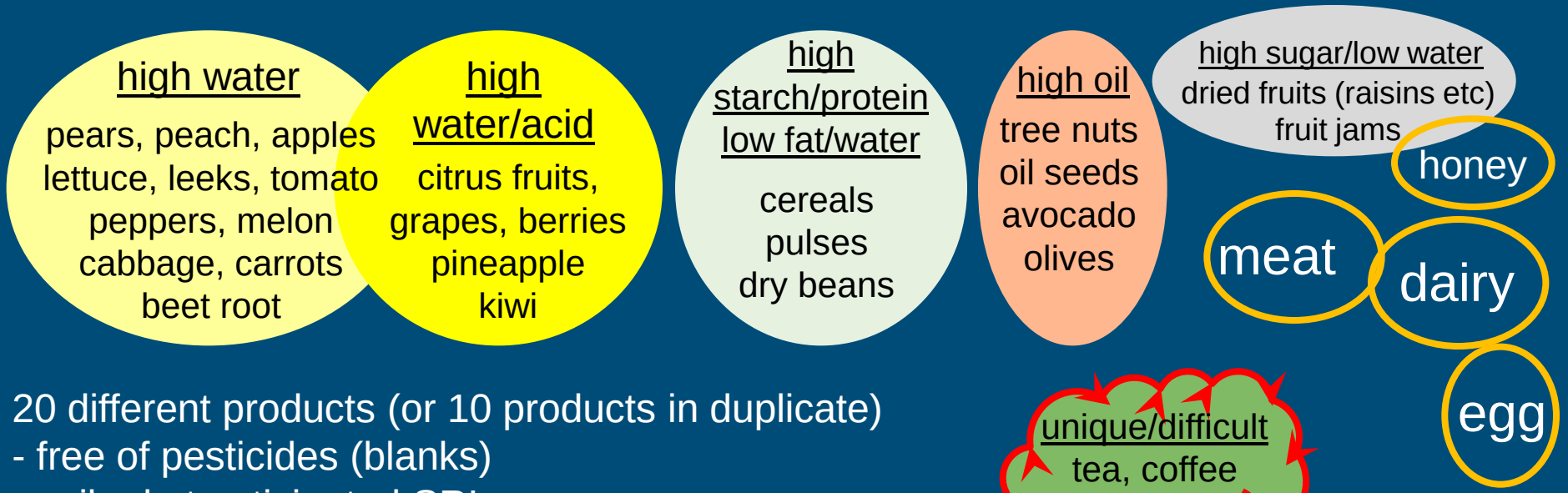
http://ec.europa.eu/food/plant/protection/resources/qualcontrol_en.pdf

Validation of qualitative screening: concept

Initial validation:

To be performed for each pesticide, for each commodity group



20 different products (or 10 products in duplicate)
- free of pesticides (blanks)
- spiked at anticipated SRL

On-going AQC:

During routine analysis:
- spike 1 or more routine sample(s) with pesticides at SRL (e.g. in rolling program)

Validation of qualitative screening

Data evaluation:

Spiked samples: for each pesticide within a commodity group: count # false negatives

Control samples: count # of tentative detects

Criteria:

Focus is on false negatives: ≤ 5%

tentative detects in control samples: no criterion, assuming follow up

On-going AQC:

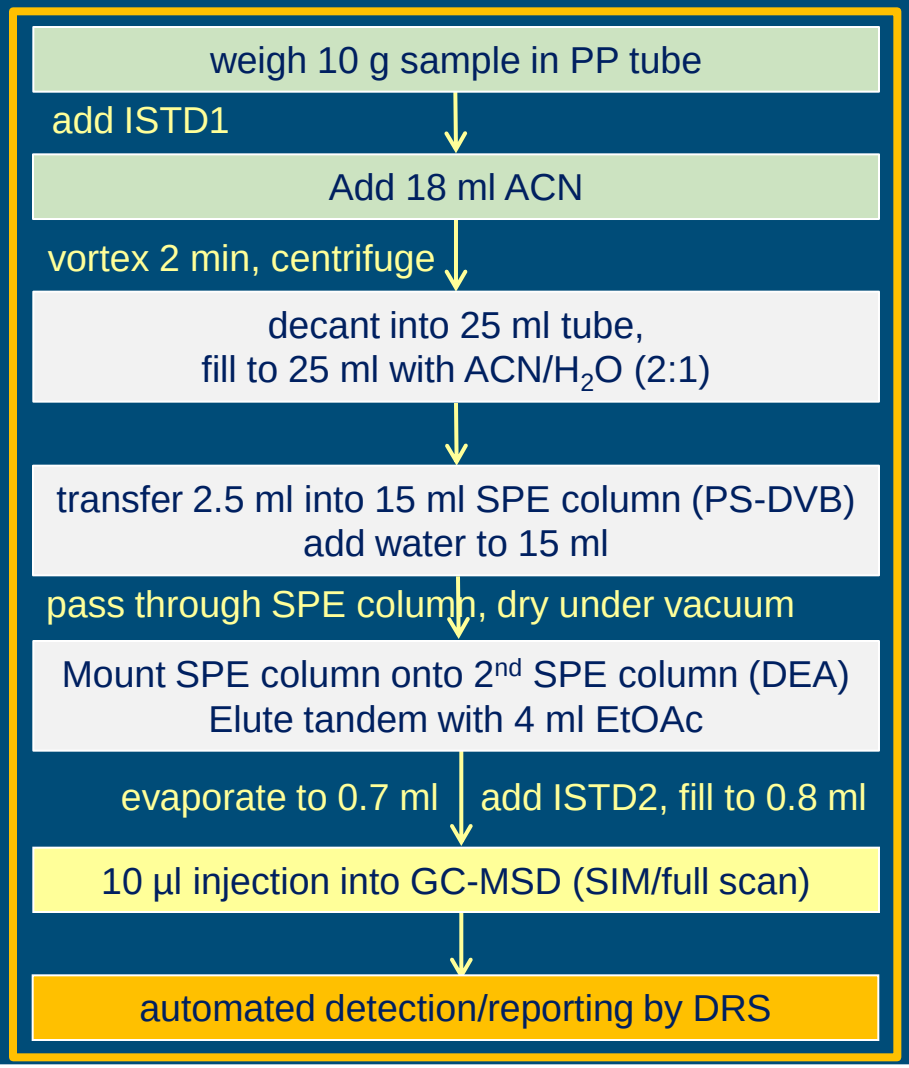
Re-assessment of false negatives over time, including other products

What if false negatives > 5%?

Adjust method or repeat at higher level

Aim validation: establish at which level 95% confidence is obtained

Validation in practice (1)



Retrospective validation:

veg/fruit extracts from routine

12 months, ~40 sequences

spiked with 94 pest/deg products

0.01, 0.02, 0.2, 0.5 mg/kg

Match threshold: 60

RT tolerance: ± 30 sec

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Overview of pesticides found per sequence

date ddmmyy	matrix (0.01 mg/kg)	# pest found out of 94		date ddmmyy	matrix (0.01 mg/kg)	# pest found out of 94
010210	mandarine	42		160710	pepper green	64
150311	lettuce lamb's	48		191010	grape	64
301210	mandarine	50		230710	cucumber	64
100610	cabbage	53		010310	raspberry	65
080610	watermelon	55		080710	watermelon	66
091210	pepper green	55		200510	lettuce	66
170211	beet red in vinegar	56		261110	cabbage	66
031210	pear	57		241110	strawberry	68
300610	lettuce	57		110510	apple	72
180810	pepper green	58		180111	beet	73
020610	strawberry	60		080910	grape	74
151010	lemon	60		081010	lettuce(chichory)	74
201210	apple	60		280111	mandarine	74
290710	melon	60		011010	grape	75
030810	lettuce	61		050510	kiwi	75
021110	lettuce(chichory)	62		010410	apple	76
090810	aubergine	62		270810	apple	77
180610	grape	62		160910	pepper green	79
020311	banana	63		210910	apple	81
110211	orange	63		230410	lettuce	82
160410	leek	64				

Spike level: 0.01 mg/kg

Lower performance for more complex matrices,
but variation in time (condition of GC) also affects performance

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Performance at individual pesticide level

Assessment of reliability

	various vegetables/fruits (incl. high acid)			
	0.01 mg/kg	0.02 mg/kg	0.2 mg/kg	0.5 mg/kg
N	41	40	41	40
confidence level	# out of 94 compounds tested			
>95%	21	43	85	89
>90%	34	57	91	92
50-90%	35	31	3	2
<50%	25	6	0	0

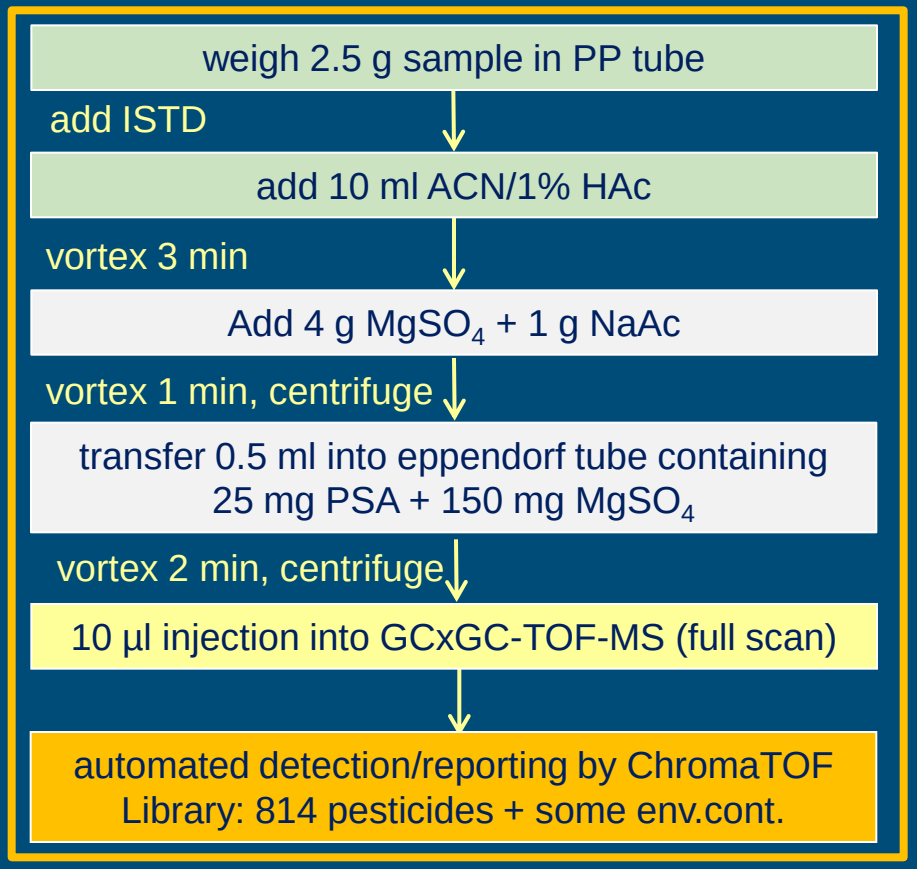
Reasons for false negatives:

- Insufficient selectivity
- Insufficient sensitivity
- Shortcomings in automated detection

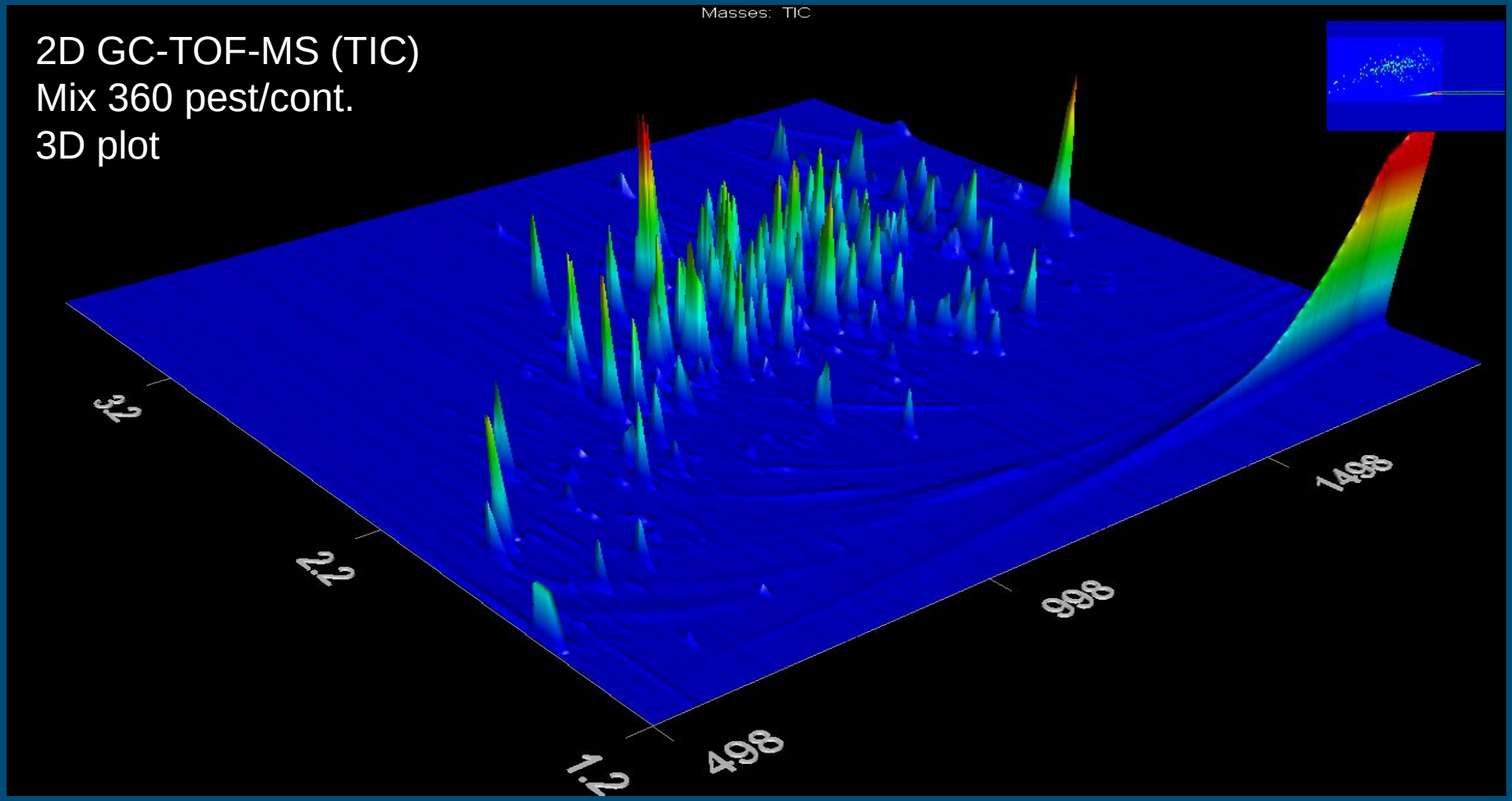
>95% at 0.01 mg/kg		<50% at 0.01 mg/kg	
Bifenthrin	100	Atrazine	49
Diflufenican	100	Bromophos	46
Fenamidone	100	Chlorpropham	46
Quinoxyfen	100	Epoxiconazole	46
Tolclofos-methyl	100	Cyproconazole	44
Dichlobenil	98	Fipronil	44
Diazinon	98	Benfuracarb	41
Dimethenamid	98	Carbofuran-7-phenol	41
Diphenylamine	98	Cinidon-ethyl	41
Flufenacet	98	Fenbuconazole	41
Iprobenfos	98	1-naphthalenol	39
Mepronil	98	Propiconazole	39
Pirimiphos-ethyl	98	Phthalimide	37
Pyridaben	98	Dimethomorph	34
Quinalphos	98	Flurochloridone	32
Spiromesifen	98	Tetrahydrophthalimide	29
Benfluralin	95	Pyrifenox	22
Fenchlorphos-oxon	95	Nitrofen	20
Flutolanil	95	Esfenvalerate	15
Terbuthylazine	95	Profenofos	12
Tetrachlorvinphos	95	Quinoclamine	12
		Tebuconazole	10
		Dicloran	7
		Parathion	7
		Pentachloronitrobenzene	2

Validation in practice (2)

Enforcement GAP through analysis of pre-harvest samples
⇒ leaves



GCxGC-TOF-MS analysis



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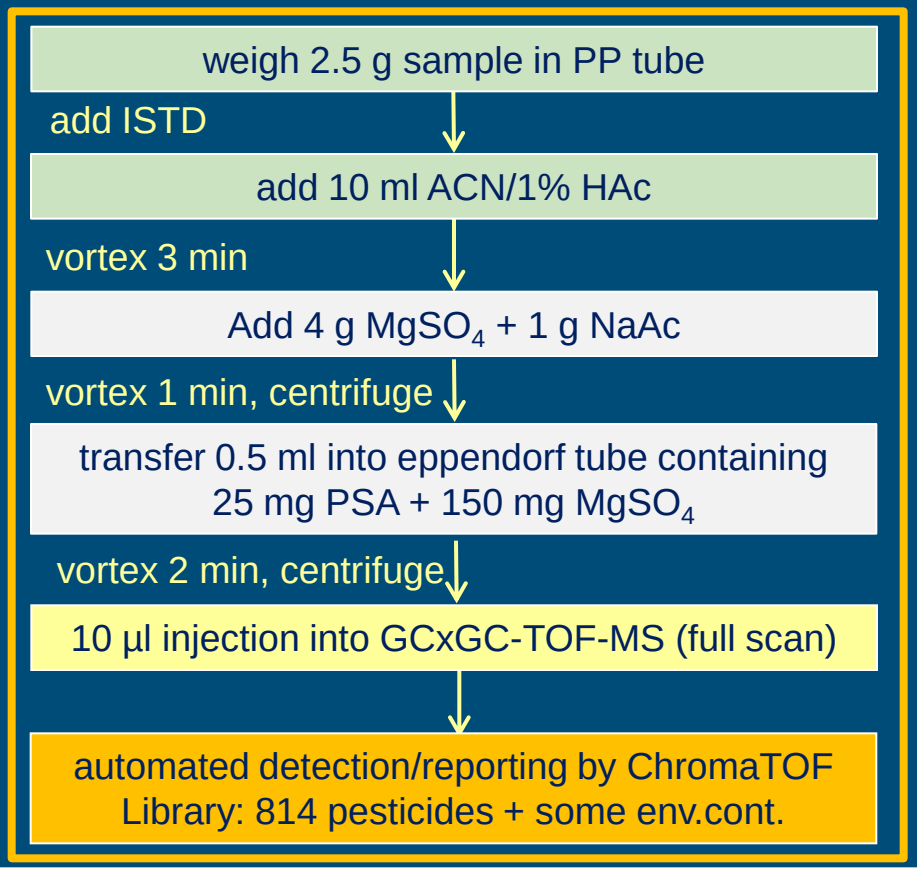
Enhanced chromatographic resolving power
Cleaner spectra, favourable for library matching

Validation in practice (2)

Enforcement GAP through analysis of pre-harvest samples
⇒ leaves



Initial validation :

11 types of leaves, 2x analyzed
Control + spiked at 0.01 mg/kg
235 pesticides

On-going AQC

18 months, 31 sequences
Fixed QC (rose) 0.05 and 0.2 mg/kg
Random QC 0.05 mg/kg
235 pesticides

Match threshold: 600

RT tolerance: ± 20 sec

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Mol et al, JAOAC 2011, accepted for publication

Overview of pesticides found per sequence

0.05 mg/kg level

Overview suggest improved performance after 2008

No clear effect of matrix

Varying performance for same type of matrix in time

year	seq.	product class	leaf matrix (0.05 mg/kg)	# pest found out of 235
2009	23	vegetables	potato	155
2010	21	ornamentals	chrysanths (Chrysanthemum)	162
2008	29	ornamentals	rose	165
2008	30	ornamentals	lisianthus (Estoma)	175
2009	5	ornamentals	geranium	175
2010	13	ornamentals	chrysanths (Chrysanthemum)	184
2008	27	ornamentals	rose	186
2009	4	ornamentals	tulip	188
2010	4	ornamentals	chrysanths (Chrysanthemum)	188
2008	27	ornamentals	rose	192
2009	2	ornamentals	anthurium	195
2008	29	ornamentals	rose	196
2009	11	vegetables	carrot	196
2009	1	ornamentals	spathiphyllum	201
2009	9	ornamentals	tagetes	201
2009	7	ornamentals	viola	202
2010	3	ornamentals	chrysanths (Chrysanthemum)	205
2010	6	ornamentals	chrysanths (Chrysanthemum)	206
2009	8	ornamentals	anthurium	207
2010	12	ornamentals	tulip	210
2010	21	vegetables	cabbage (white)	211
2009	16	ornamentals (als	sorghum sudan grass	212
2009	12	lawn	grass	213
2009	21	weed	nettle (Urtica)	214
2009	21	weed	nettle (Urtica)	214
2010	20	ornamentals	crocus	214
2010	8	vegetables	leek	216
2009	31	golf course	grass	218
2010	15	ornamentals	chrysanths (Chrysanthemum)	218
2009	32	vegetables	tomato	219
2010	8	ornamentals	tulip	223

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Performance at individual pesticide level

Assessment of reliability for each pesticicde

	various leaves		QC leaf	QC leaf
	0.01 mg/kg	0.05 mg/kg	0.05 mg/kg	0.20 mg/kg
N	22	31	28	62
confidence level	# out of 235 compounds tested			
>95%	83	92	128	185
>90%	100	147	147	197
50-90%	75	65	65	29
<50%	60	23	23	9

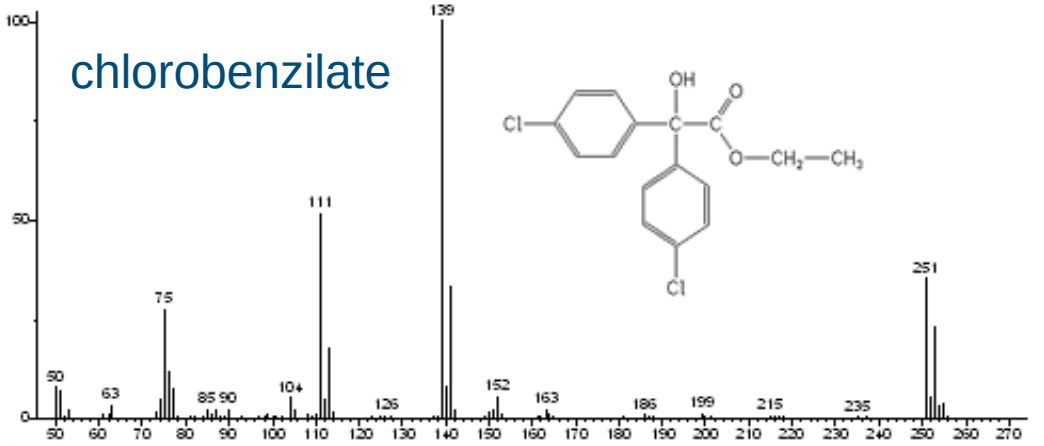
General reasons for false negatives:

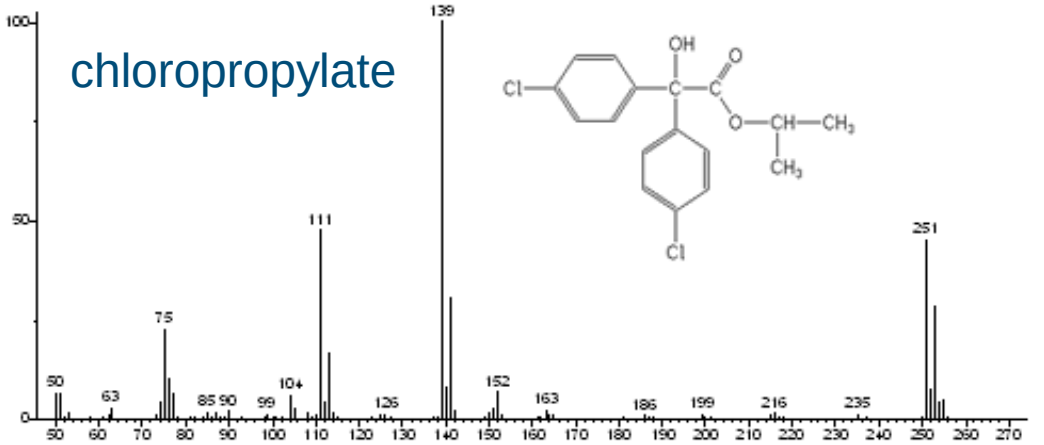
- Insufficient sensitivity
  troublesome GC compounds: degradation, tailing
- Insufficient selectivity
- Shortcomings in automated detection

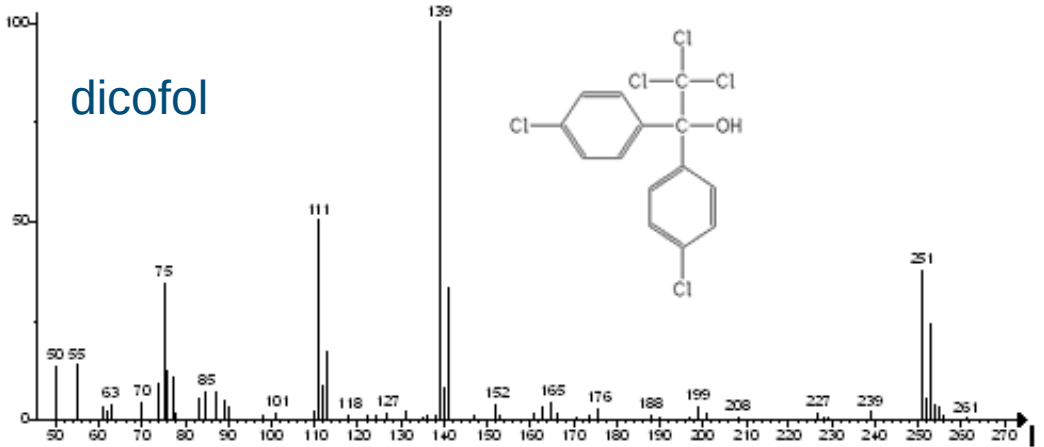
< 50% at 0.05 mg/kg	
Acephate	48
Demeton-S-methyl	48
Metobromuron	48
Monocrotophos	48
Deltamethrin	45
Dimefox	45
Chlorthion	42
Omethoate	42
Pentanochlor	42
Cyromazine	39
Paraoxon	39
Linuron	35
Demeton-O	29
Chlorbromuron	16
Oxamyl	16
Chloropropylate	13 ?
Dazomet	13
Tebuthiuron	10
Ethoxyquin	6
Chlorthiamid	6
Aziprotryne	0
Benfuracarb	0
Chlordecone	0

Chloropropylate failure

chlorobenzilate/chloropropylate
only 5 sec RT difference
(dicofol well separated)







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Qualitative screening: possibilities & challenges

+ Once method is established: little time/effort to detect >500 pesticides

+ More comprehensive than quantitative methods:
  extra pesticides are being found in addition to quantitative method

+ Provides safety net for unexpected residues

? Can you use the results to demonstrate absence of residues:
  yes, but only after proper and successful validation

- Safety net but not yet for all pesticides at low (0.01 mg/kg) level

hardware
software

! vendor solutions: very useful
but pesticides screening ≠ black box
skilled personnel essential

Screening performance heavily relies on software capabilities and well optimized thresholds; even then expert judgment outperforms technology
But even experts are not perfect.....:

World cup football 2010
Germany – England: goal detected or not ?

SOUTH AFRICA 2010 FIFA WORLD CUP

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Gracias traductor !

Gracias por su atención

Funding: Dutch Ministry Economic affairs, Agriculture and Innovation

Validation in practice (1): pesticides included

Acrinathrin	Dimethenamid	Mepronil	Propiconazole
Atrazine	Dimethomorph	Metazachlor	Prosulfocarb
Azoxystrobin	Dimoxystrobin	Methidathion	Pyraflufen-ethyl
Benfluralin	Diphenylamine	Methyl parathion	Pyridaben
Benfuracarb	*DMSA*	Metolachlor	Pyridaphenthion
Bifenthrin	Epoxiconazole	Metrafenone	Pyrifenox
Boscalid	Esfenvalerate	*1-naphthalenol*	Pyriproxyfen
Bromophos	Ethion	Napropamide	Quinalphos
Buprofezin	*Ethofumasate, 2-keto-*	Nitrofen	Quinoclamine
Carbofuran-7-phenol	Fenamidone	Parathion	Quinoxyfen
Chlorfenvinphos	Fenarimol	Penconazole	Resmethrine
3-chloroaniline	Fenbuconazole	*Pentachloroaniline*	Spirodiclofen
Chlorobenzilate	Fenchlorphos	*Pentachloronitrobenzene*	Spiromesifen
Chlorpropham	*Fenchlorphos-oxon*	Permethrin	Tebuconazole
Cinidon-ethyl	Fenothiocarb	Phosalone	Tefluthrin
Clomazone	Fepropimorph	Phosmet	Terbuthylazine
Coumaphos	Fipronil	ortho-Phenylphenol	Tetrachlorvinphos
Cyproconazole	*Fipronil-sulfone*	*Phthalimide*	Tetraconazole
Diazinon	Flufenacet	Pirimiphos-ethyl	*Tetrahydrophthalimide, cis-1,2,3,6-*
Dichlobenil	Flurochloridone	Pirimiphos-methyl	Tetramethrin
Dicloran	Flutolanil	Profenofos	Tolclofos-methyl
4,4'-Dichlorobenzophenone	Flutriafol	Prometryn	Tolylfluanid
Diflufenican	Iprobenfos	Propetamphos	
Dimethachlor	Mecarbam	Propham	

Software settings for automated detection

Effect of match threshold on # detects in blanks and false negatives

Match threshold	# detects in control leaves	% pest found at 0.01 mg/kg
> 400	474	84
> 500	161	79
> 600	53	71
> 700	2	58
> 800	0	35
> 900	0	7

compounds found in 11 control samples

Compound	601-700
Cinerin II	10
Fenobucarb	10
Thanite	7
Cinerin I	5
Isoprocarb	5
Jasmolin I	4
Methanimidamide N-(24-	2
Pyrethrin I	2
Benzo(a)pyrene	1
Bifenthrin	1
Carbofuran	1
Carbofuran, 3-hydroxy	1

% detected out of
5170 pest*matrix combinations
(235 spiked pesticides in 2*11 samples)

RIKILT - Institute of Food Safety; part of Wageningen University

Independent research institute

Statutory task for Dutch government

EURL hormones and sedatives

NRL pest-AO, mycotoxins, marine toxins, vet. drugs, dioxins, PAHs, heavy metals, …

OFL pesticides in feed/AO/pre-harvest

Screening and food forensics

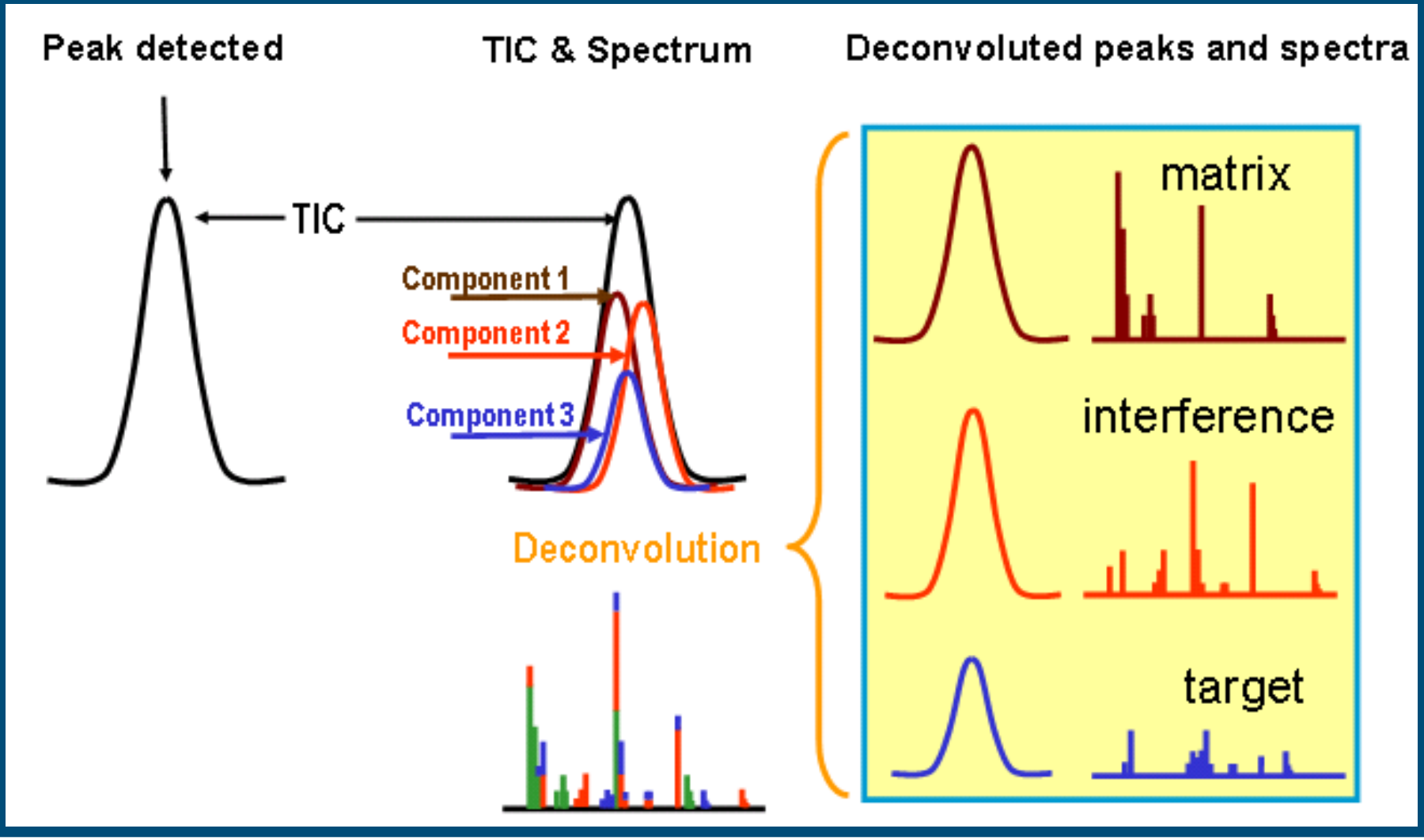
RIKILT WAGENINGEN UR

Holland.

Validation in practice (2): 235 pesticides included

Acephate	Chlormephos	Dicofol metabolite (4,4-Dic	Fluazifop-butyl	Oxadixyl	Pyrimethanil
Alachlor	Chlorobenzilate	Dicrotophos	Flusilazole	Oxamyl	Quinalphos
Aldrin	Chloropropylate	Dieldrin	tau-Fluvalinate	Oxychlordane	Quintozene
Ametryn	Chlorpropham	Diethatyl-ethyl	Fonofos	Paclobutrazol	Quizalofop-ethyl
Anthraquinone	Chlorpyrifos	Difenoconazole	Formothion	Paraoxon	Simazine
Atrazine	Chlorpyrifos-methyl	Dimefox	Fuberidazole	Parathion	Sulfotep
Azinphos-ethyl	Chlorthiamid	Dimethachlor	Furalaxyl	Parathion-methyl	Sulprofos
Azinphos-methyl	Chlorthion	Dimethipin	HCB	PCB 209	o,p'-TDE (DDD)
Aziprotryne	Chlorthiophos	Dimethoate	alpha-HCH	Penconazole	p,p'-TDE (DDD)
Azolamide	Chlozolinate	Dioxathion	delta-HCH	Pendimethalin	Tebuthiuron
Barban	Coumaphos	Diphenylamine	gamma-HCH (Lindane)	Pentachloraniline	Tecnazene
Benalaxyl	Crimidine	Disulfoton	Heptachlor	Pentachloroanisole	Telodrin
Bendiocarb	Crotoxyphos	Ditalimfos	Heptachlor epoxide (iso A)	Pentachlorobenzene	Terbacil
Benfuracarb	Crufomate	Dodemorph	Heptachlor epoxide (iso B)	Pentanochlor	Terbufos
Benodanil	Cyanazine	Edifenphos	Imazalil	Permethrin I	Terbuthylazine
Benzoylprop-ethyl	Cyanofenphos	alpha-Endosulfan	Isodrin	Phenothrin	Terbutryn
Bifenthrin	Cyanophos	beta-Endosulfan	Isofenphos	Phenothrin	Tetrachlorvinphos
Bitertanol	Cycloate	Endosulfan ether	Jodfenphos	Phenthoate	Tetradifon
Bromacil	Cyfluthrin (isomer cluster)	Endosulfan lactone	Lenacil	ortho-Phenylphenol	Tetramethrin
Bromfenvinphos	Cypermethrin (isomer cluster)	Endosulfan sulphate	Leptophos	Phorate	Tetrasul
Bromfenvinphos	Cyprofuram	Endrin	Linuron	Phosalone	Thiabendazole
Bromophos-ethyl	Cyromazine	EPTC	Malathion	Phosphamidon	Thiobencarb
Bromopropylate	Dazomet	Ethiofencarb	Malathion-oxon (Malaoxon)	Piperonyl butoxide	Thiometon
Bupirimate	o,p'-DDE	Ethion	Mecarbam	Pirimicarb	Thionazin
Buprofezin	p,p'-DDE	Ethofumesate	Metalaxyl	Pirimiphos-ethyl	THP (Captan Captafol met
Butralin	o,p'-DDT	Ethoprophos	Metazachlor	Pirimiphos-methyl	Tolclofos-methyl
Carbaryl	p,p'-DDT	Ethoxyquin	Methacrifos	Prochloraz	Triadimefon
Carbetamide	Deltamethrin trans	Etridiazole	Methamidophos	Procymidone	Triadimenol
Carbofuran	Deltamethrin cis	Fenamiphos	Methidathion	Profenofos	Triallate
Carbophenothion	Demeton-O	Fenarimol	Methiocarb	Propachlor	Triazophos
Chinomethionat	Demeton-S-methyl	Fenchlorphos	Methoxychlor	Propargite	Trichloronat
Chlorbenside	Demeton-S-methyl-sulfone	Fenfuram	Metobromuron	Propazine	Trietazine
Chlorbromuron	Desmetryn	Fenitrothion	Metolachlor	Propetamphos	Trifenmorph
Chlorbufam	Diallate	Fenpropathrin	Metribuzin	Propham	Triflumizole
trans-Chlordane	Diallate	Fenson	Mevinphos	Propiconazole	Trifluralin
Chlordecone	Diazinon	Fensulfothion	Mirex	Propoxur	2,3,5-Trimethacarb
Chlordimeform	Dichlobenil	Fenthion	Monocrotophos	Propyzamide	3,4,5-Trimethacarb
Chlorfenprop-methyl	Dichlofenthion	Fenvalerate	Monolinuron	Prothiofos	Vernolate
Chlorfenson	Dichlorvos	Fenvalerate	Myclobutanil	Pyrazophos	Vinclozolin
Chlorfenvinphos	Diclobutrazol	Flamprop-isopropyl	Norflurazon	Pyridaben	
Chloridazon	Dicloran	Flamprop-methyl	Omethoate	Pyridaphenthion	

Deconvolution



NIST, AMDIS, http://chemdata.nist.gov/mass-spc/amdis

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Validation of qualitative screening

Data evaluation:

Spiked samples: for each pesticide within a commodity group: count # false negatives

Control samples: count # of provisional detects

Criteria:

Focus on false negatives: ≤ 5%

Initial validation: pesticide should be automatically detected in 19 out of 20 samples

detects in control samples: no criterion, assuming follow up of detects!

But: many detects compromise efficiency of screening method

On-going AQC:

Re-assessment of false negatives over time, including other products

What if false negatives > 5%?

Adjust method or repeat at higher level

Aim validation: establish at which level 95% confidence is obtained