

Extractability of Incurred Residues using QuEChERS



M. Anastassiades,
J. Hepperle,
D. Roux,
I. Sigalov



QuEChERS

>160 000 recov. figures on **SPIKED** pesticides
(Method Validation Database of CRL-DataPool)

but ...

How well
do we extract
INCURRED residues?

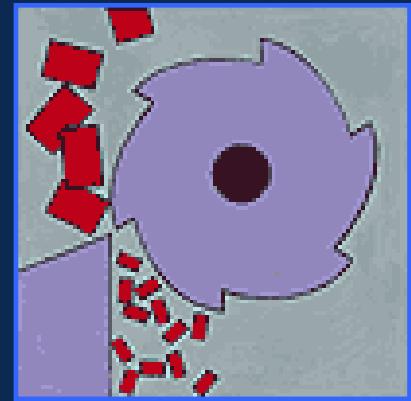
Incurred Residues

not always easily accessible

- enclosed in cells, vacuoles or wax particles
- strong non-covalent interactions with matrix sites

Small sample particles are helpful in extraction

- ☛ Good Sample Commminution needed



QuEChERS

- ACN / Water: 1-phase extraction system
- 1 min extraction by shaking

ACN and ACN-Water mixtures are quite weak in dissolving lipids and penetrating waxes

Extraction **Time** and **Temperature**

- ➔ expected to have an effect

Question:

What are the **minimum agitation times** required to extract incurred residues quantitatively ?



Extraction/ Homogen. equipment employed in this study:



Geno Grinder
Spex Sample Prep



Biosan Multi RS-60



Horizontal shaker



Rotation shaker

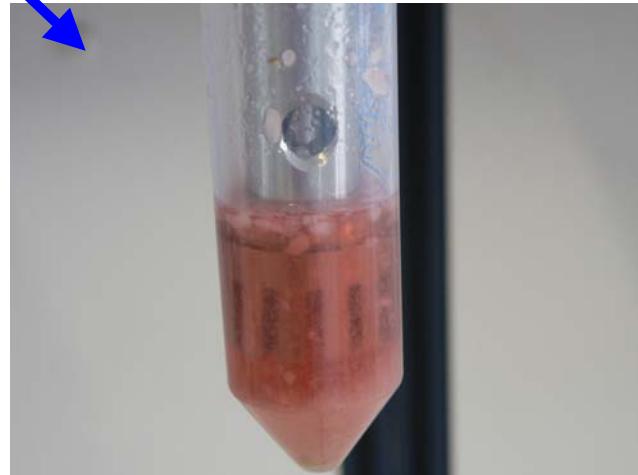
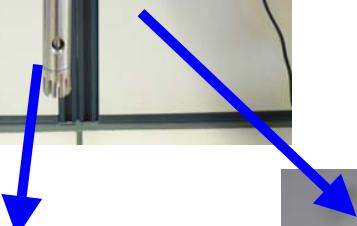


Heidolph Multi Reax



Agytax®

Ultra Turrax



Ultrasonic probe



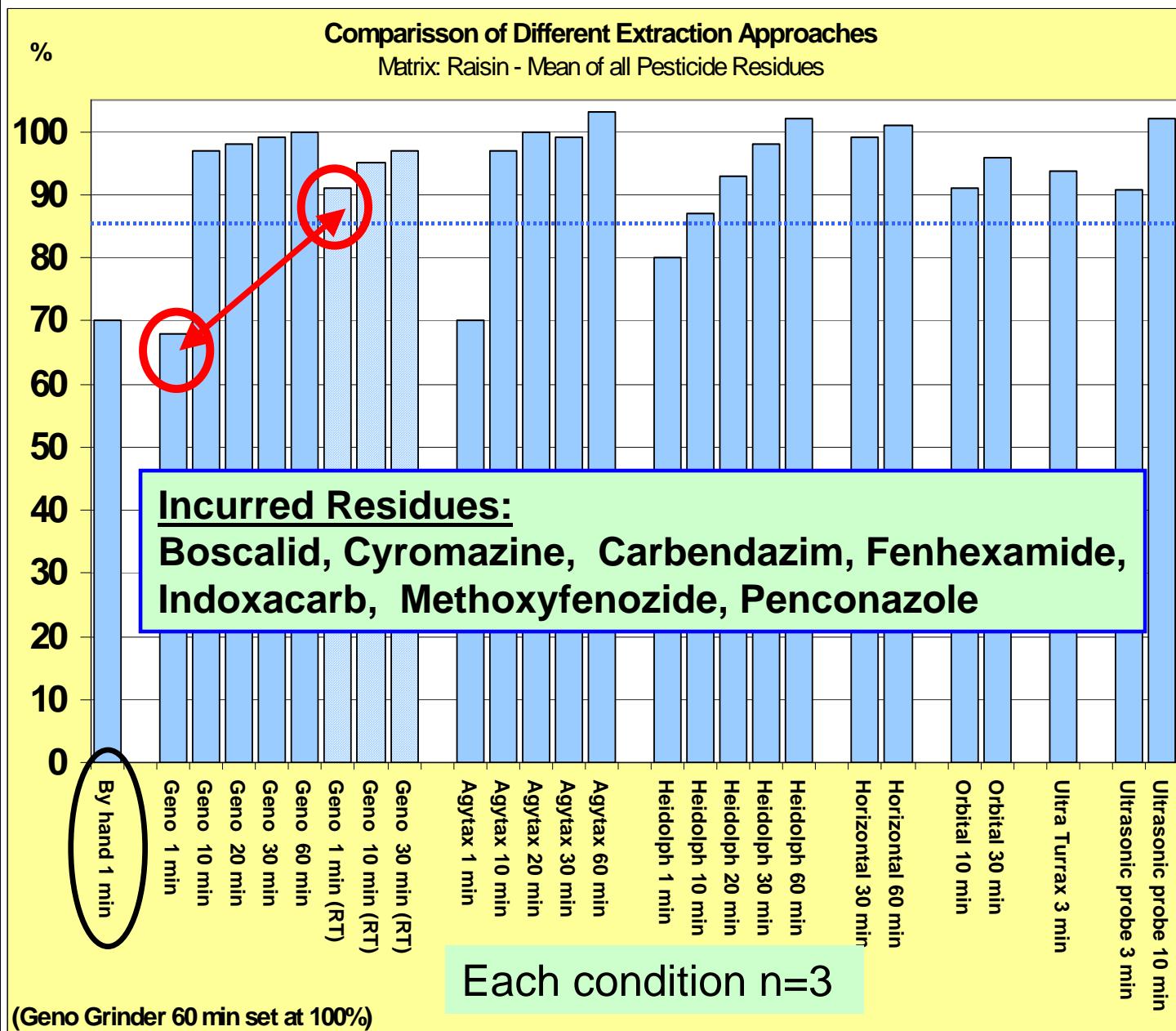
By hand



Sample: RAISINS



Comparison of Different Approaches



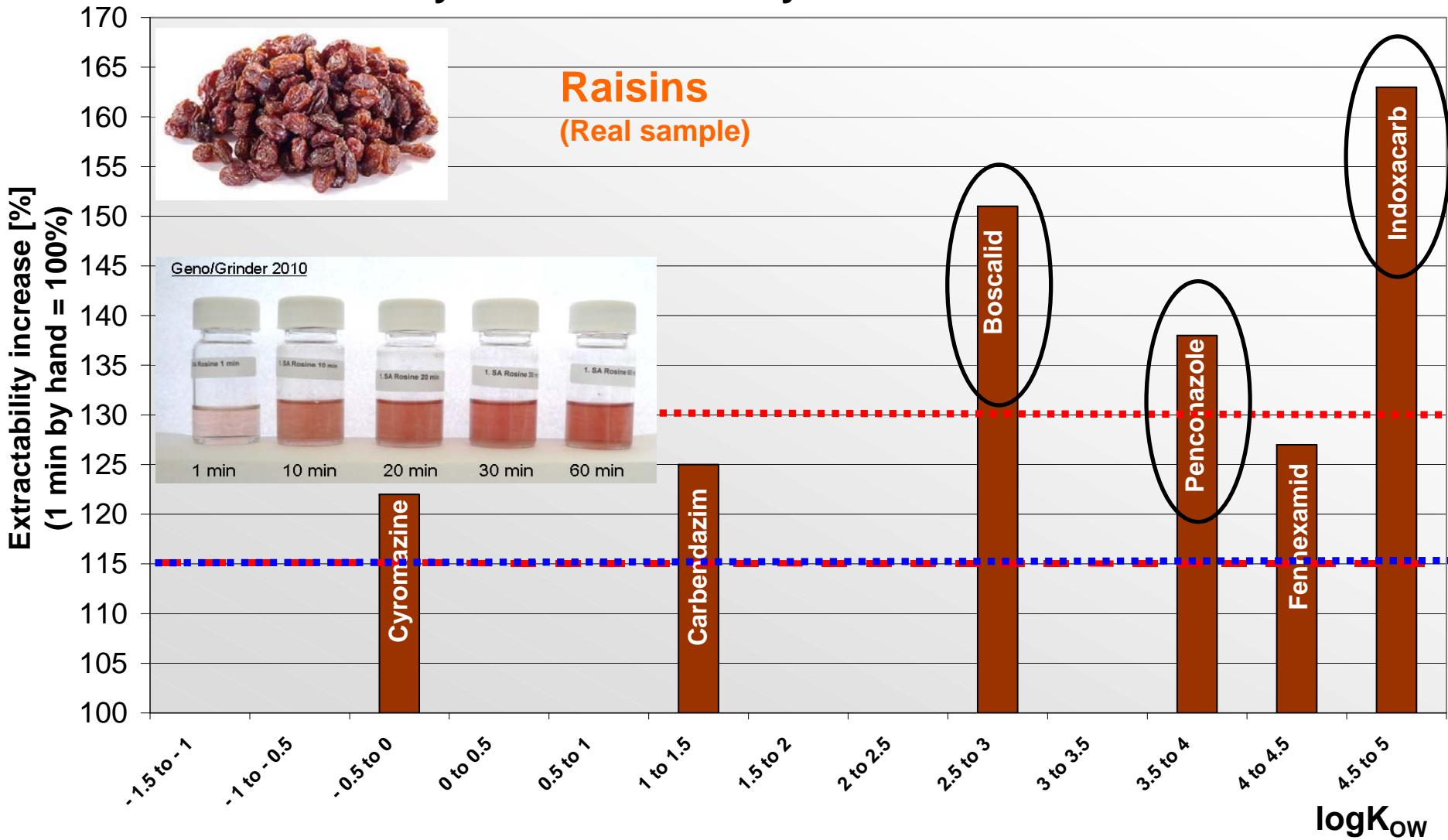
Frozen Material:
10-15 min extraction seem enough to get >90% yields

Material at RT.:
much shorter times needed

NOTES:
% Yields: Average of all listed residues
Times: Refer to 1st extraction step

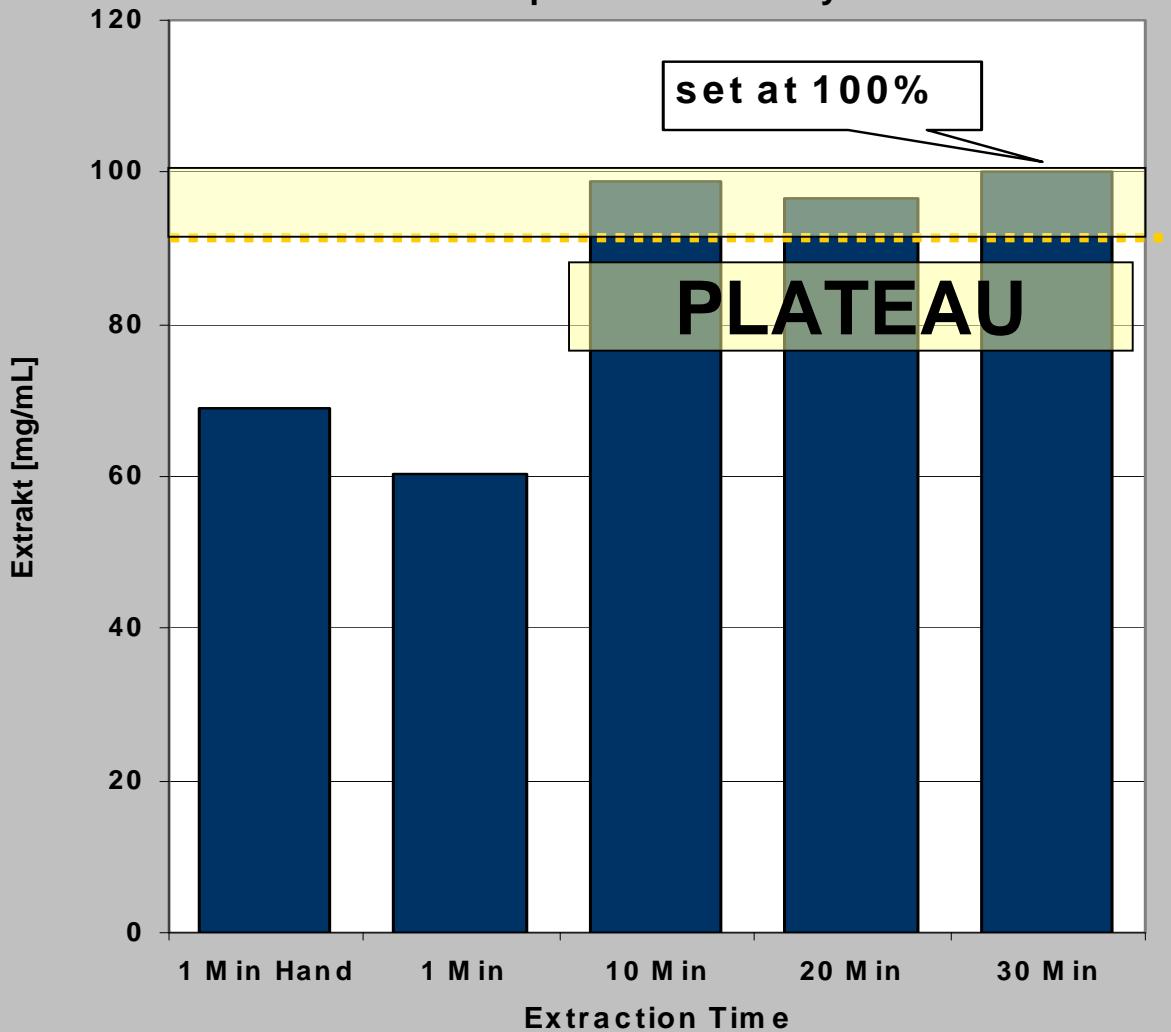
Comparison of extractability using QuEChERS

1 min by hand vs. 20 min by automated shaker



Co-extracted Matrix

Residual extract
after evaporation to dryness

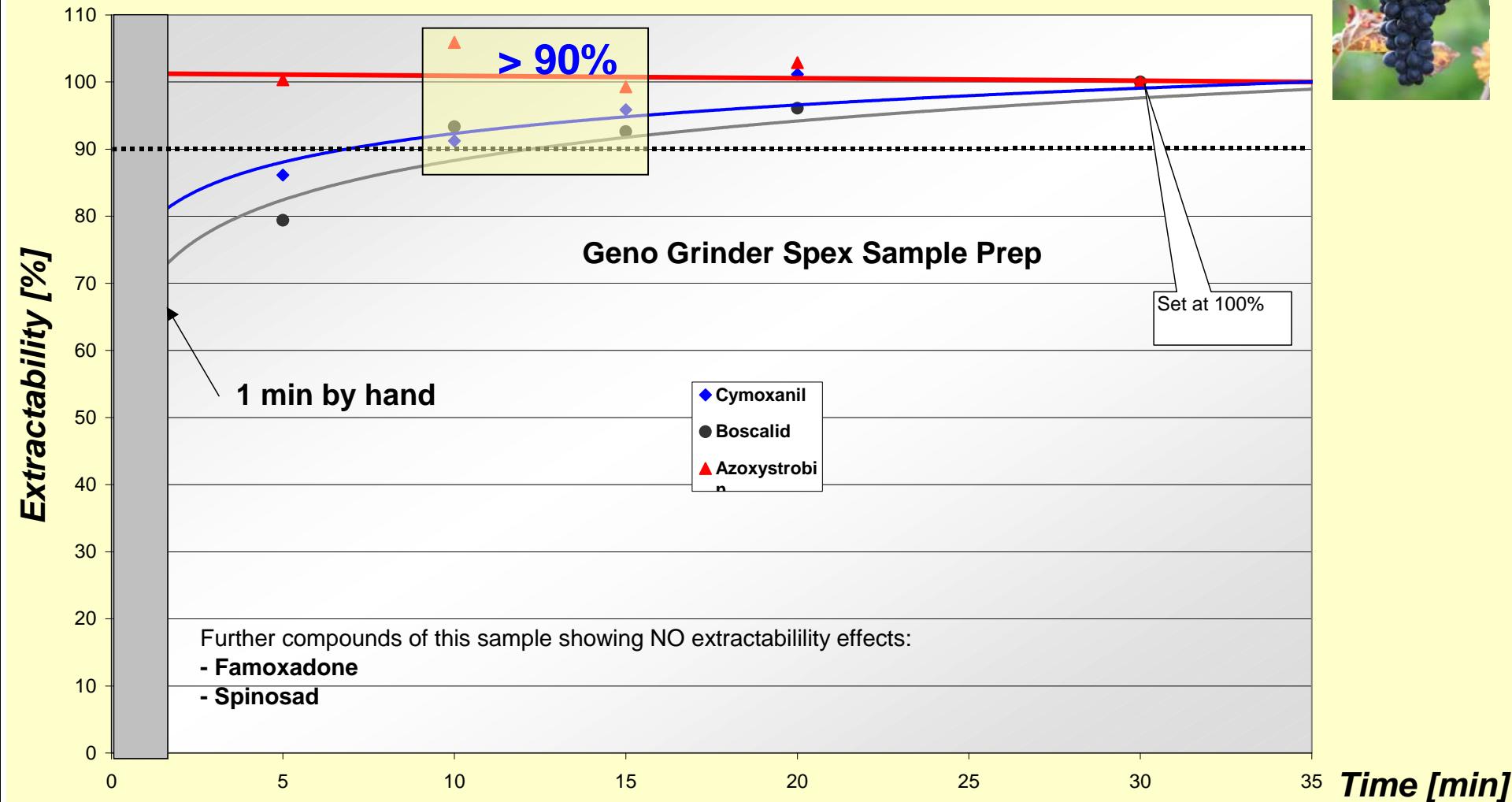


Raisins



Extracted with
Geno Grinder

PT-Grape w. incurred residues



First Conclusions

SHAKERS

- Shaking intensity less important
- Ca. 10-15 min shaking of frozen samples sufficient
- Employing samples at RT accelerates extraction

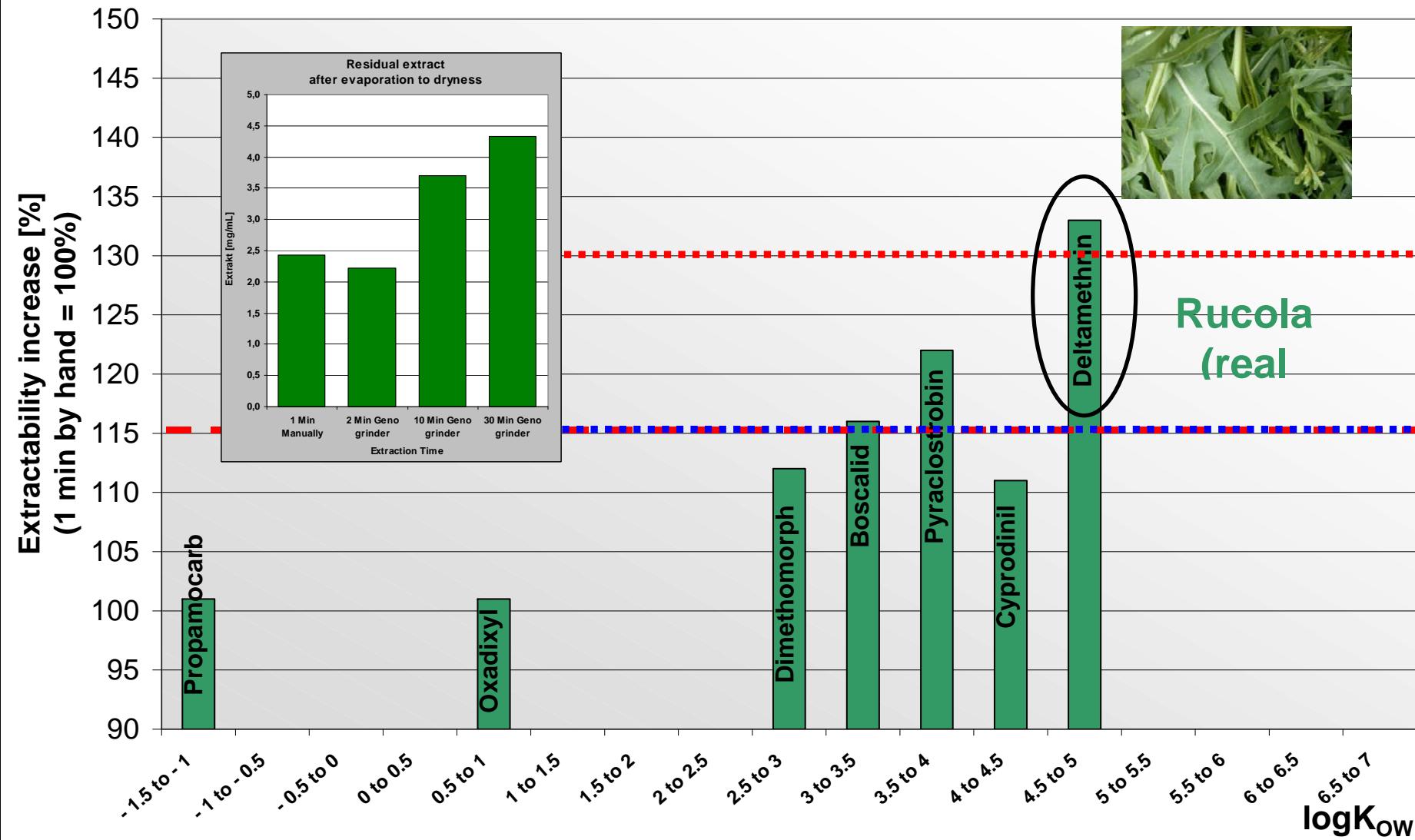
ULTRA-TURRAX AND ULTRASOUND PROBE

- Accelerate extraction, but...impractical for routine work (sequential approach)

Results for further **REAL SAMPLES** (with incurred residues)

Comparison of extractability using QuEChERS

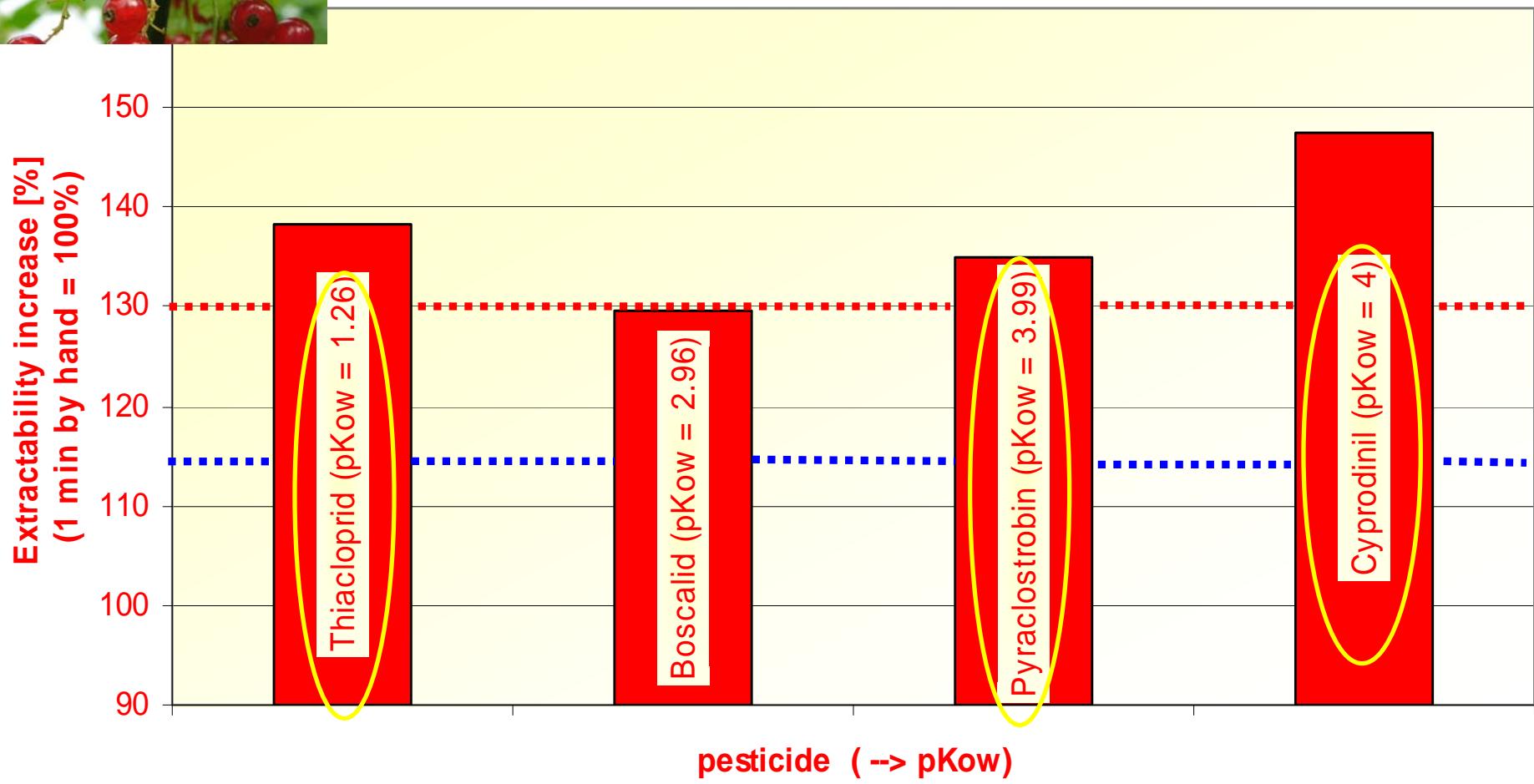
1 min by hand vs. 20 min by automated shaker



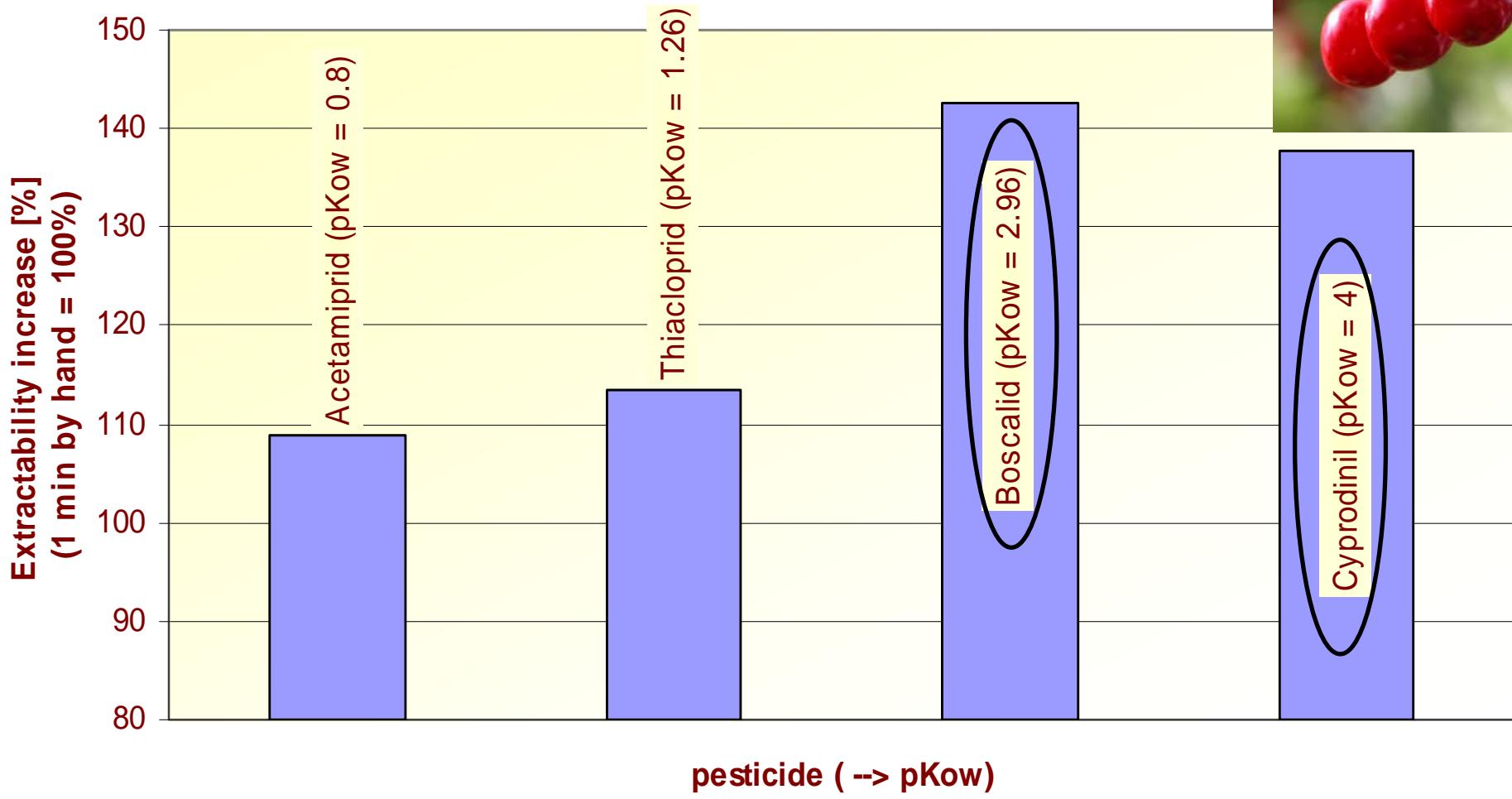


Currant (real sample)

1 min by hand vs. 15 min by automated shaker

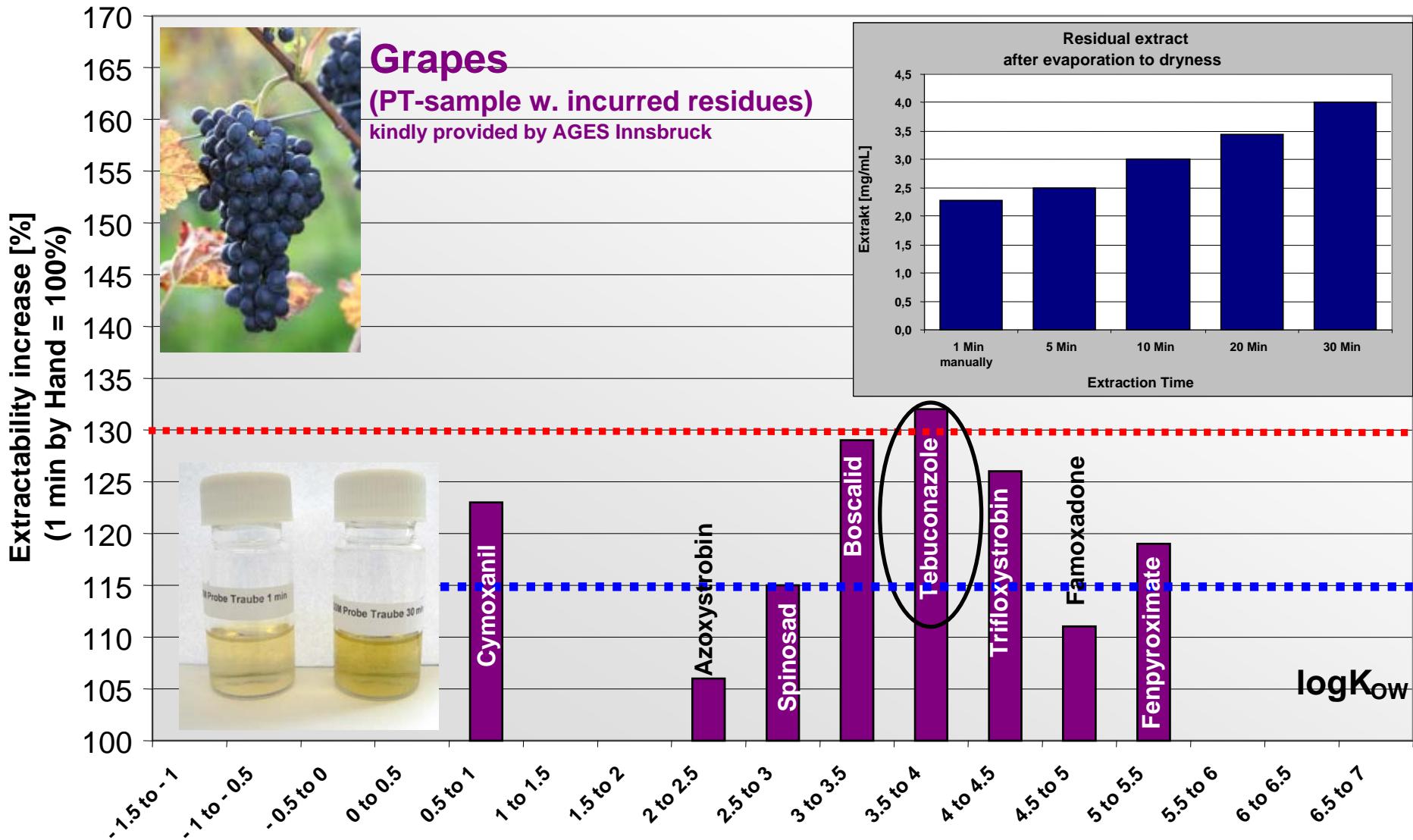


Cherry (real sample) 1 min by hand vs. 15 min by automated shaker



Comparison of extractability using QuEChERS

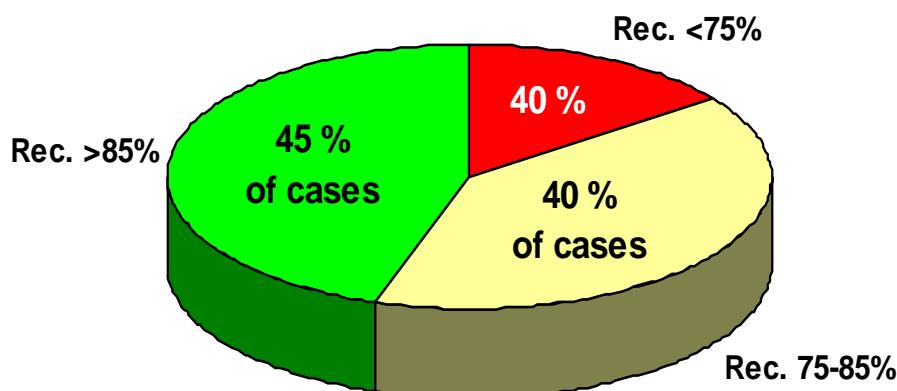
1 min by hand vs. 20 min by automated shaker (Geno Grinder)



OBSERVATIONS:

(typically reached
after 10-15 min)

Extraction yields
at 1 min by hand vs. Plateau



~60% of tested PESTICIDES
showed yields <85%
in at least one case

> 80% of tested SAMPLES (fruits, veg. and cereals) showed yields <85% for at least one of the pesticides contained!!

FURTHER CONCLUSIONS

Pesticides

- The lower the logP the less frequent the effects
 - LogP < 2.5: ~20% of residues showed yields <85%
 - LogP > 2.5: ~65% of residues showed yields <85%, but no clear link between logP and extraction yields

Matrix

- Extraction retardation seems more pronounced in certain commodities
- Natural surface-wax may play a role (slow penetration by extractant)

Examples

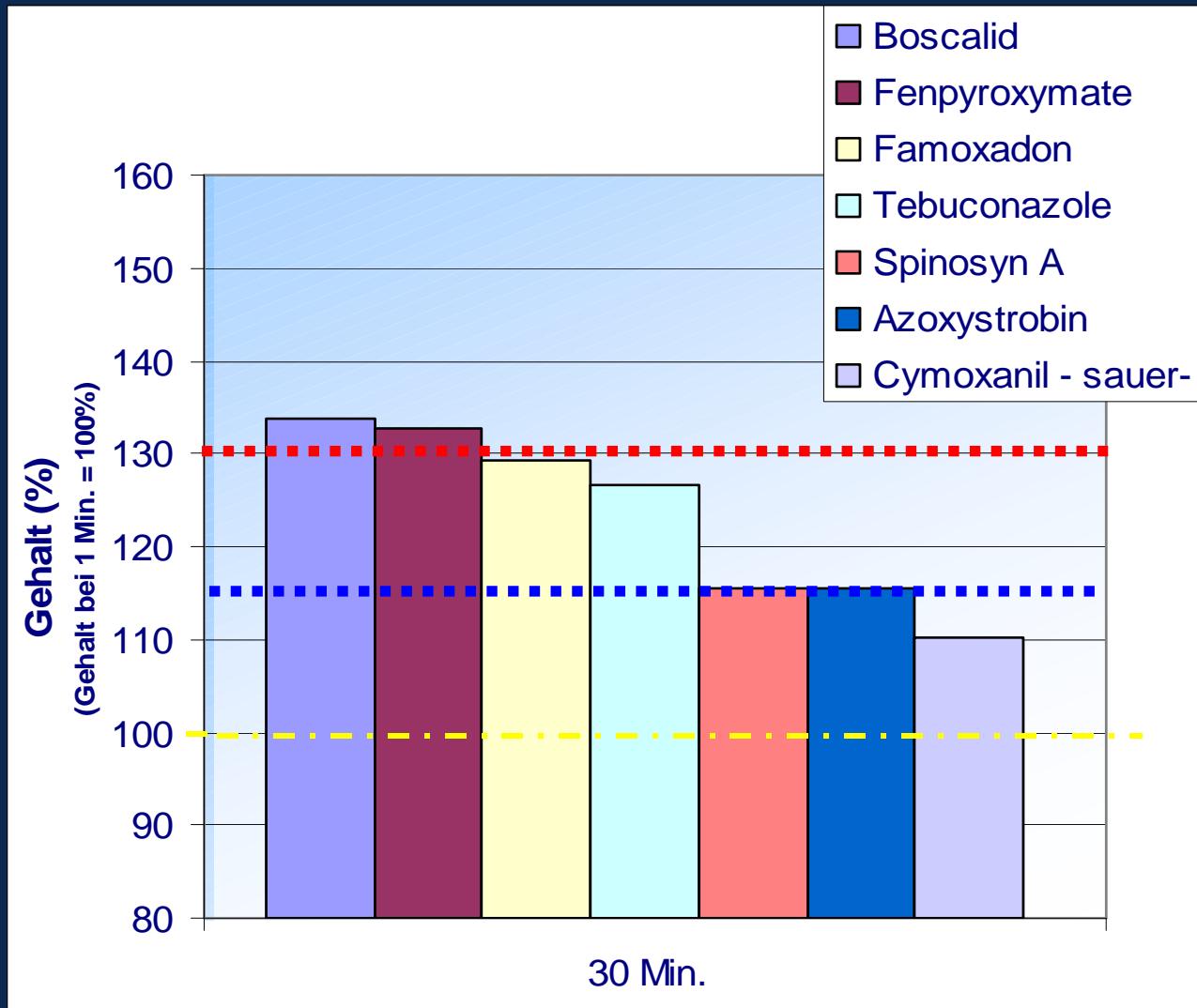
	Lamb's lettuce	Auber-gine	Grape	Raisin	Straw- berry	Ruccola	Red Currant	Cherry
Boscalid (logP = 2,96)	-		+	+		++	+	++
Cyprodinyl (logP = 4)		-			+	-	++	++

- : Minor or no effect : > 85% yield

+ : Intermediate effect : 75-85% yield

++ : Great Effect : <75% yield

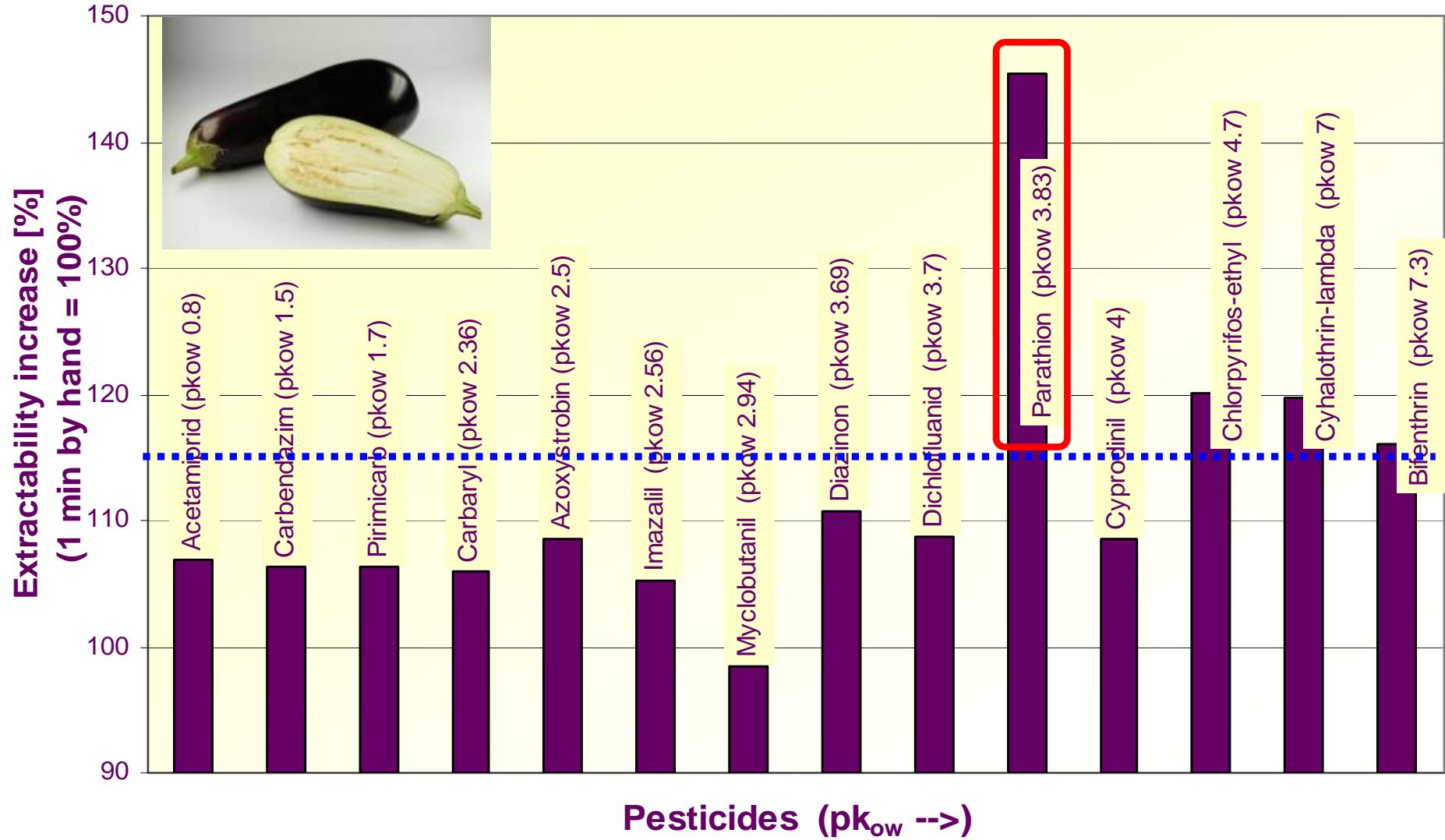
Ethylacetate



Results of EU-PTs samples

Aubergine (EUPF FV 8)

1 min by hand vs. 15 min by automated shaker

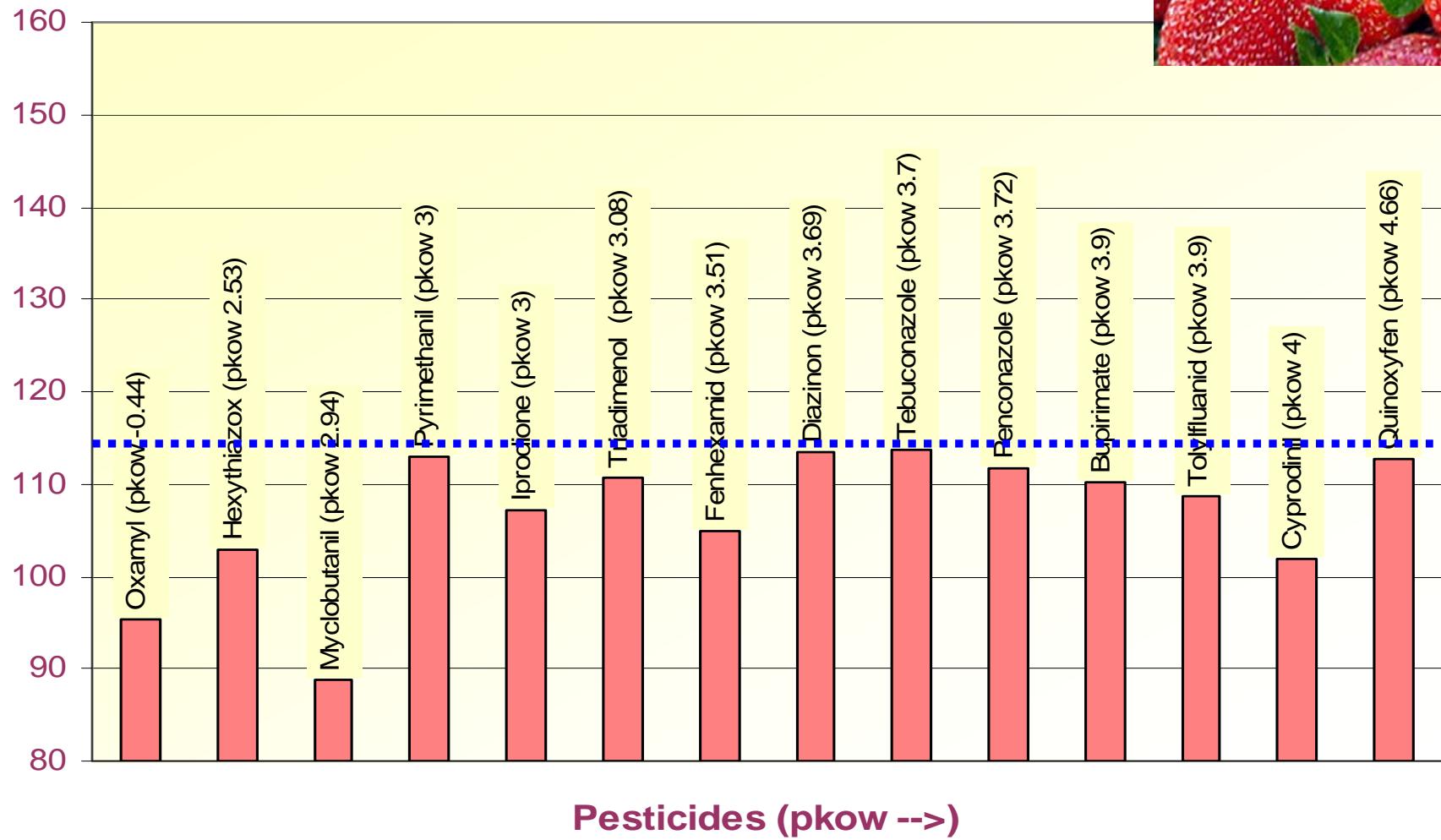


Strawberry (EUPF FV 9)

1 min by hand vs. 15 min by automated shaker



Extractability increase [%]
(1 min by hand = 100%)



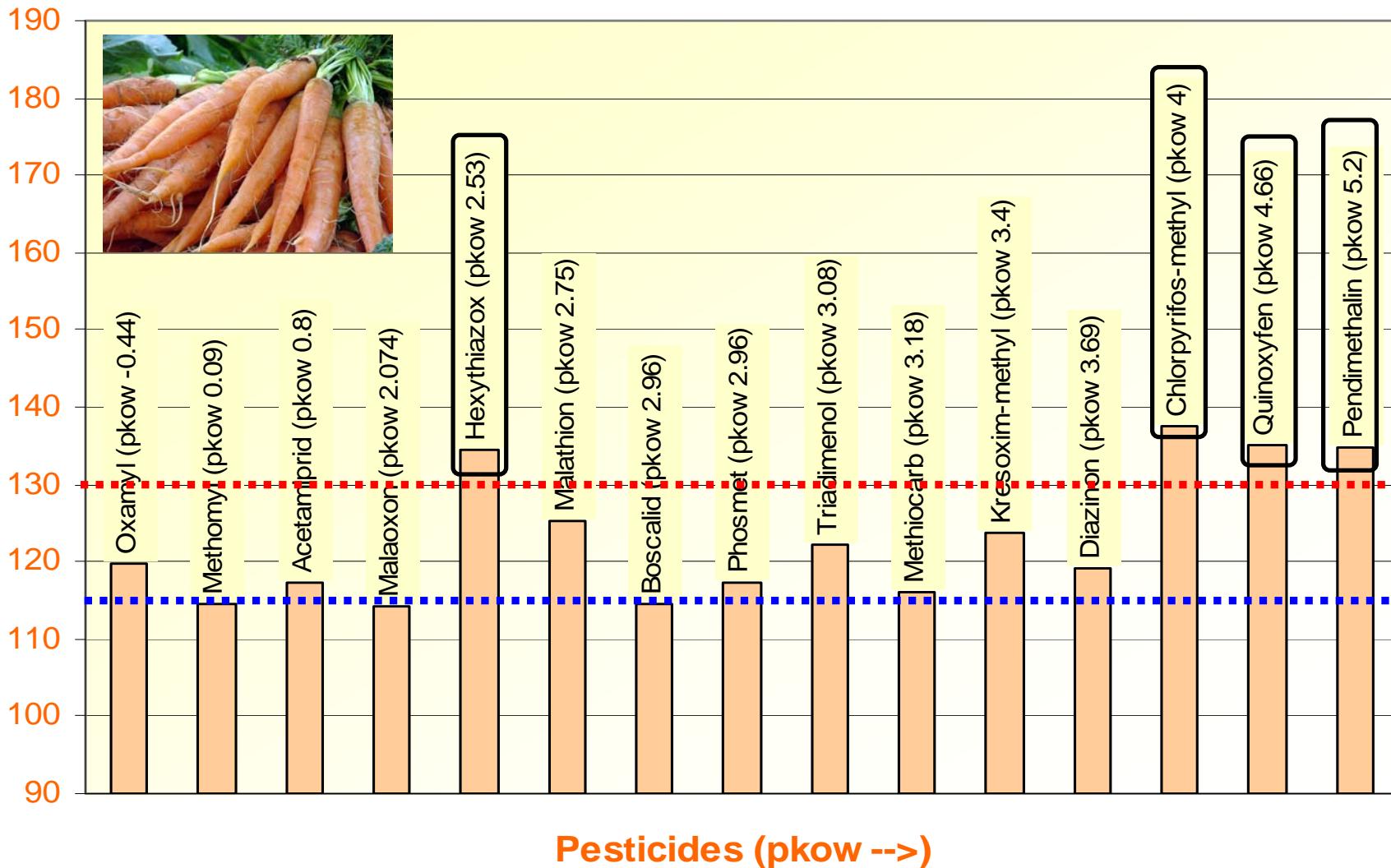
Pesticides (pkow -->)

Carrot (EUPF FV 10)

1 min by hand vs. 15 min by automated shaker

Extractability increase [%]

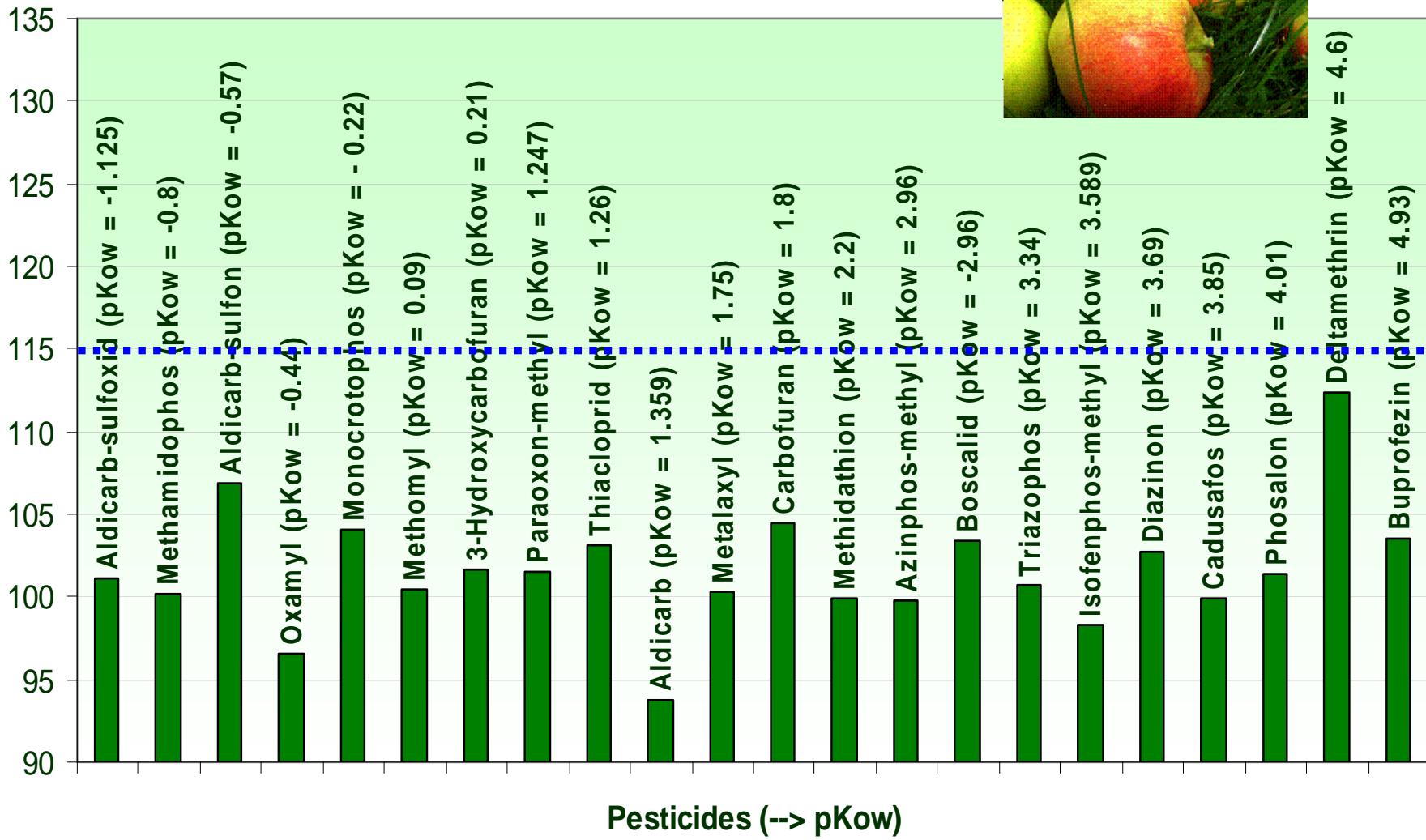
(1 min by hand = 100%)



Apple (EUP-T-FV 11)

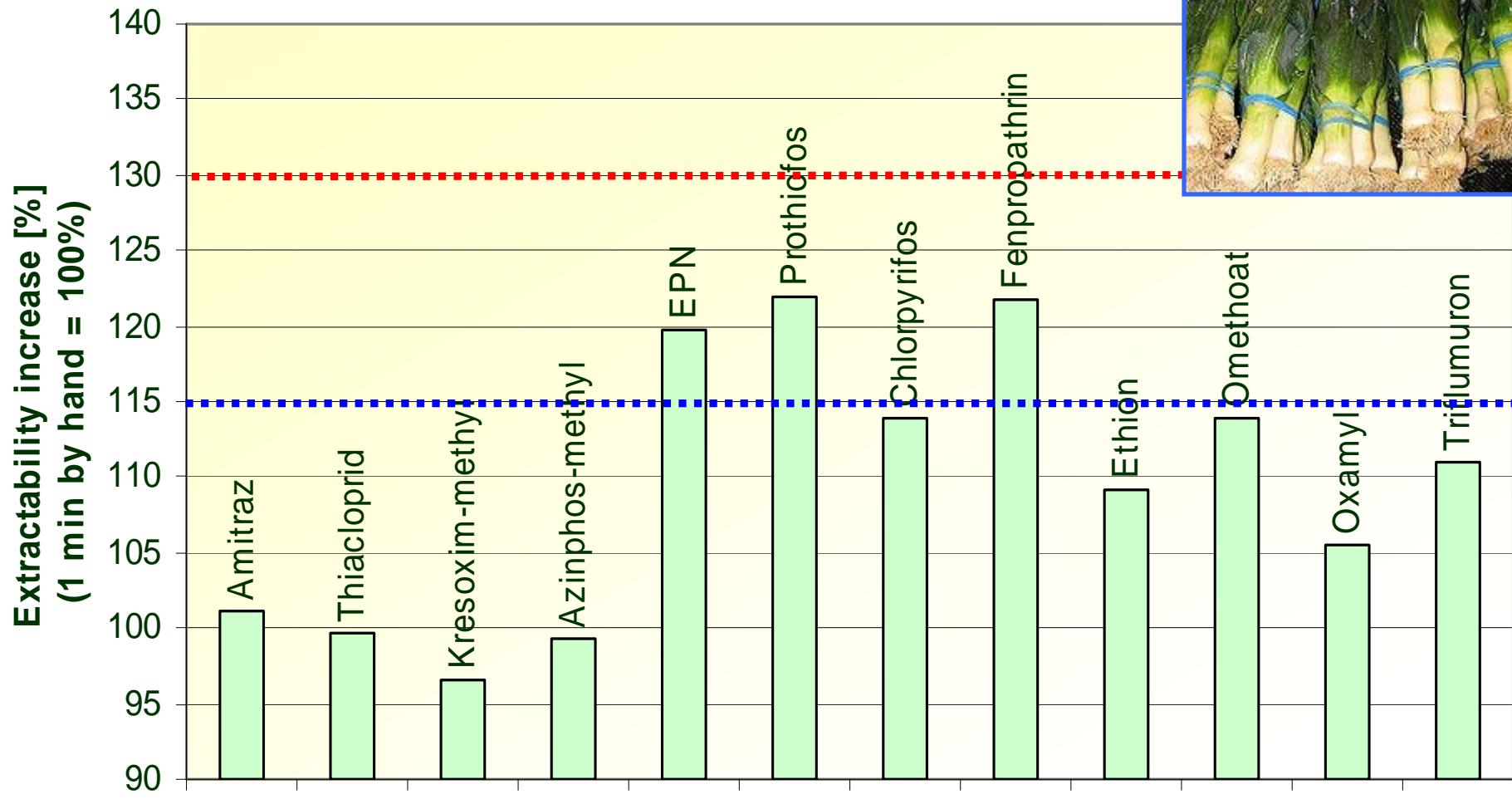


Extractability increase [%]
(1min by hand = 100%)

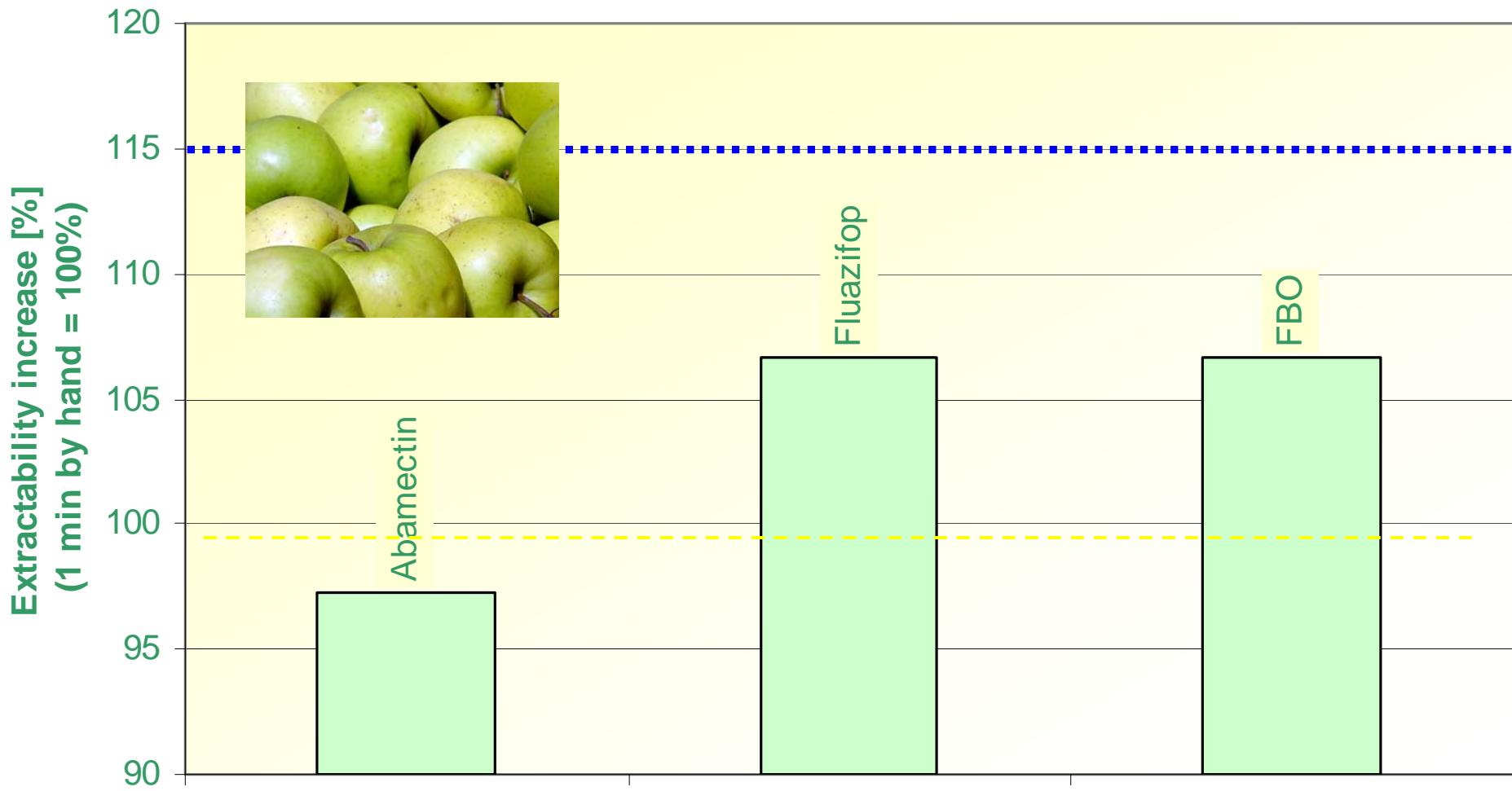


Leek (EUPF FV 12)

1 min by hand vs. 15 min by automated shaker

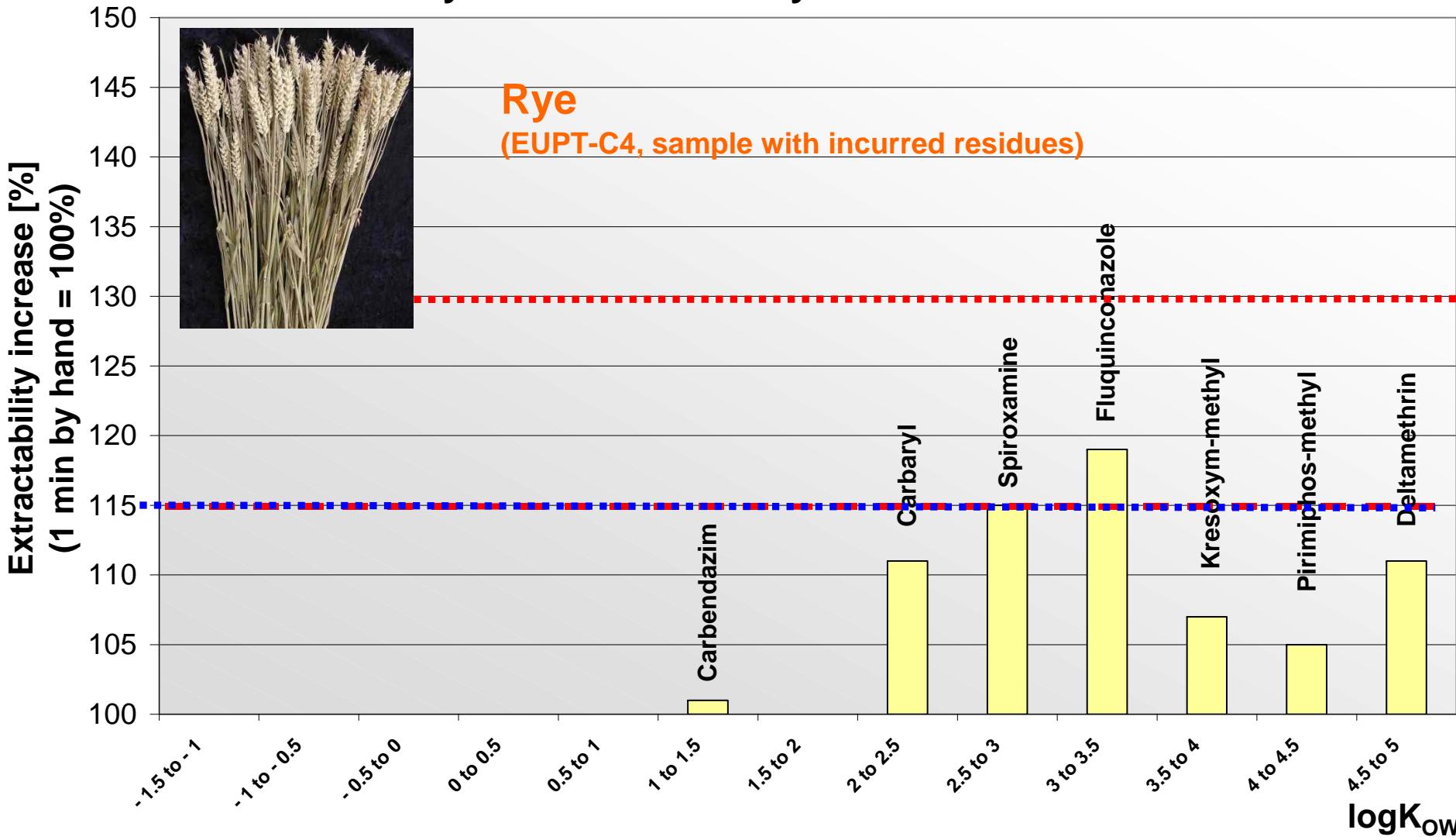


Apple puree (EUPt SRM 5) 1 min by hand vs. 15 min by automated shaker



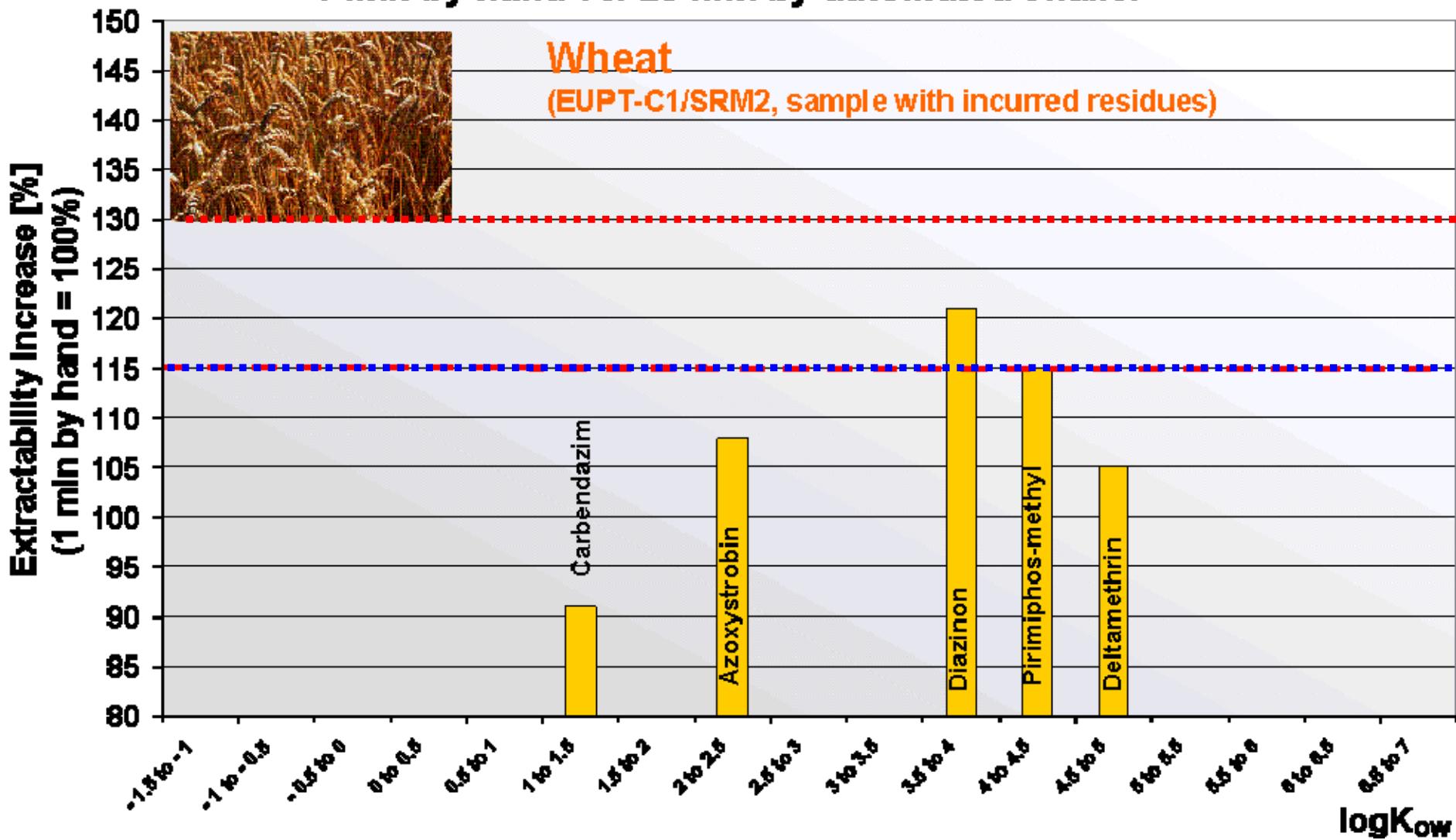
Comparison of extractability using QuEChERS

1 min by hand vs. 20 min by automated shaker



Comparison of extractability using QuEChERS

1 min by hand vs. 20 min by automated shaker



How was Data-Reliability ensured?

We have studied...

IMPACT OF EXTENDED EXTRACTION TIMES ON...

- a) RECOVERIES
- b) MATRIX EFFECTS

Also:

Only sample-compound combinations with good repeatability included in study (RSD <12 % at n=5)

- ☛ good homogeneity,
- ☛ little influence of measurement uncertainty

At least n=3 for each experimental settings

IMPACT OF EXTENDED EXTRACTION TIMES

a) on Recoveries ...

- 430 pesticides tested whether they degrade during prolonged extraction times
- using commodities representing the lower and upper end of the physiological pH range
- Only very few pesticides showed a clear degradation effect e.g. captan, folpet, dichlofluanid, chlorothalonil in the higher pH-range.

IMPACT OF EXTENDED EXTRACTION TIMES

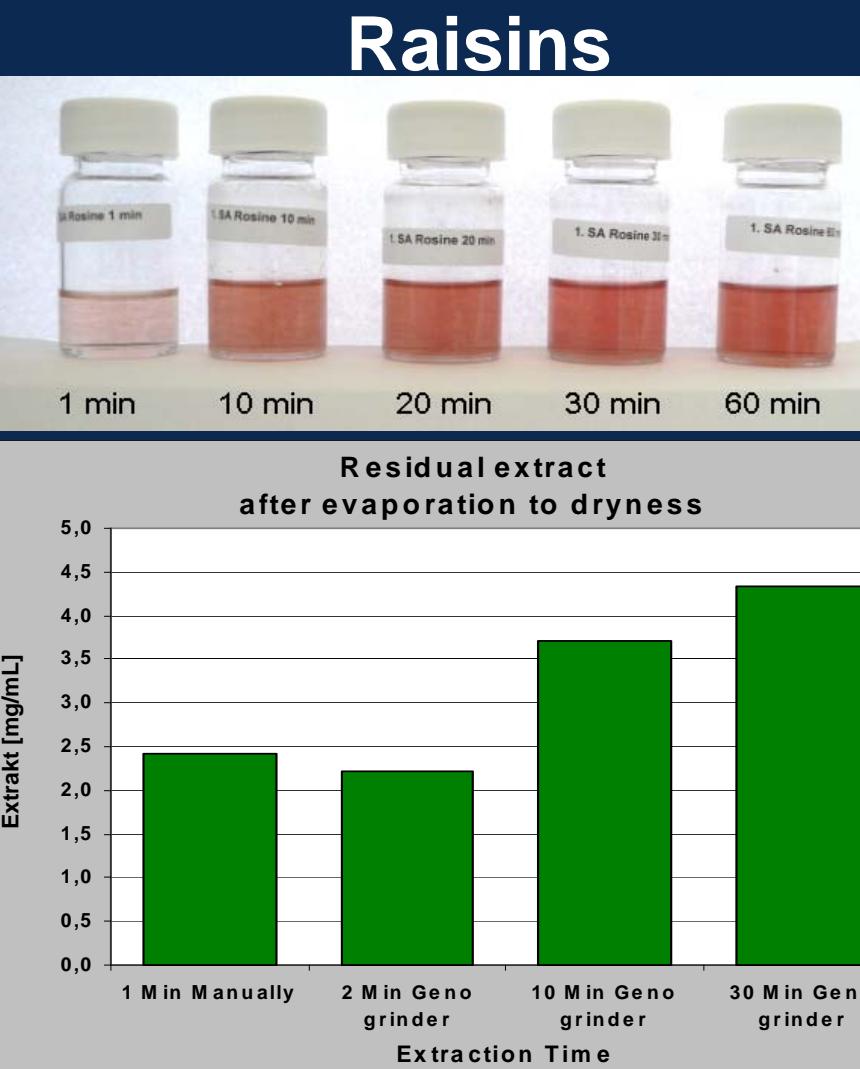
b) On Matrix Effects...

Extended extraction times resulted in :

- a) deeper coloured extracts
- b) higher dry residue

However...

- ☛ Impact on matrix-effects was insignificant
(compounds responsible for matrix effects are obviously rather quickly extracted)



Compound	1 min Extraction by Hand	30 min Extraction with GenoGrinder				Notes
		BEFORE adding partitioning buffering salts		AFTER adding partitioning buffering salts		
	Rec. %	Deviation %	Rec. %	Deviation %	Rec. %	
1-Naphthalene acetamide	101	2	103	98	-2	
1-Naphthylessigsaeure	108	-6	102	88	-18	
2,4,5-T	103	-2	100	104	1	
2,4,5-TP	106	-4	102	99	-7	
2,4-D	98	0	98	96	-2	
2,4-DB	110	-3	107	91	-17	
2,4-DP	101	2	103	91	-10	
2-Naphtoxy acetic acid	103	-7	96	97	-6	
3-Hydroxycarbofuran	104	0	104	95	-8	
4-CPA	95	-8	88	103	8	
Acephat	82	11	91	81	-2	
Acetamiprid	102	-5	97	95	-7	
Acibenzolar-S-methyl	100	2	102	101	1	
Aciflourfen	102	-4	98	90	-12	
Acrinathrin	101	5	106	99	-2	
a-Endosulfan	112	-10	101	105	-6	
Aldicarb	108	19	129	70	-35	Oxidation prone, plus other problems with measurement ??
Aldicarb-sulfon	94	-9	86	89	-6	
Aldicarb-sulfoxid	86	15	100	94	9	
Aminocarb	89	3	92	95	6	
Amitraz	27	-8	25	28	5	Always low recovery if extract not stabilized (requires D-SPE w. PSA w/o acidification)
Ancymidol	91	13	103	99	8	
Anilophos	101	2	102	101	0	
Aspon	104	2	106	95	-8	
Azaconazole	101	-4	98	103	2	
Azinphos-methyl	108	-23	83	80	-26	Oxidation to the oxon?
Azoxystrobin	99	3	102	97	-3	

Compound	1 min Extraction by Hand	30 min Extraction with GenoGrinder				Notes	
		BEFORE adding partitioning/buffering salts		AFTER adding partitioning/buffering salts			
		Rec. %	Deviation %	Rec. %	Deviation %		
Benalaxyl	101	108	7	102	1		
Benazolin	95	98	3	93	-2		
Bendiocarb	112	104	-7	96	-14		
b-Endosulfan	98	99	1	97	-1		
Benfluralin	104	107	3	102	-2		
Benfuresate	102	106	4	102	0		
Bensulide	104	104	0	100	-3		
Bentazon	102	99	-2	93	-8		
Benthiavalicarb-isopropyl	102	101	-1	98	-4		
Benzoylprop-ethyl	97	103	6	99	2		
Bifenazat	108	102	-6	100	-7		
Bifenthrin	99	102	4	96	-2		
Bitertanol	96	99	3	99	3		
Bitertanol	106	97	-8	96	-10		
Bixafen	106	111	5	104	-3		
Boscalid	99	95	-4	97	-3		
Boscalid	100	96	-4	86	-13		
Bromacil	106	92	-14	104	-3		
Bromoxynil	104	93	-10	90	-14		
Brompropylat	106	111	4	104	-2		
Bromuconazole	96	105	8	96	-1		
Bupirimat	105	116	10	105	0		
Buprofezin	104	103	-2	96	-8		
Butafenacil	104	101	-4	99	-5		
Butamifos	102	102	0	100	-2		
Butylat	100	108	8	102	2		
Butylate	107	103	-3	97	-9		

Compound	1 min Extraction by Hand	30 min Extraction with GenoGrinder				Notes	
		BEFORE adding partitioning/buffering salts		AFTER adding partitioning/buffering salts			
		Rec. %	Deviation %	Rec. %	Deviation %		
Cadusafos	94	90	-4	92	-3		
Cafenstrole	104	103	-1	100	-4		
Captan	119	89	-25	80	-33	Degrades at high pH	
Carbaryl	103	105	2	95	-7		
Carbendazim	94	97	3	95	1		
Carbofuran	104	104	0	99	-5		
Carboxin	69	67	-3	68	-2	Always low recoveries	
Carfentrazone-ethyl	105	103	-2	98	-6		
Chlorantraniliprole	107	99	-8	99	-8		
Chlorfenapyr	107	112	5	104	-2		
Chlorfluazuron	100	98	-2	88	-13		
Chlorpyrifos	103	103	0	102	-1		
Chlorpyrifos-methyl	106	101	-5	107	1		
Chlorthalonil	136	118	-13	111	-18	Degrades at high pH, plus measurement problems??	
Chlozolinat	108	111	3	108	0		
Chromafenozide	100	97	-3	100	0		
Cinidon-ethyl	99	104	5	96	-3		
Clodinafop-propargyl	103	103	0	97	-5		
Clofentezin	97	92	-5	95	-2		
Clopyralid	79	85	7	90	14		
Clothianidin	97	102	5	100	3		
Coumachlor	100	100	1	102	2		
Cyanophos	101	103	3	101	0		
Cyazofamid	92	110	19	90	-2		
Cycloxydim	99	92	-6	97	-1		
Cyenopyrafen	113	117	3	108	-5		
Cyflufenamid	108	112	4	102	-5		
Cyfluthrin	107	111	4	106	-1		
Cymoxanil	135	156	15	92	-32	Measurement problems ???	
Cypermethrin	109	116	7	102	-6		
Cyprazine	102	103	1	98	-4		
Cyproconazole	99	96	-3	104	5		
Cyprodinil	103	105	2	95	-8		

Compound	1 min Extraction by Hand	30 min Extraction with GenoGrinder				Notes	
		BEFORE adding partitioning/buffering salts		AFTER adding partitioning/buffering salts			
		Rec. %	Deviation %	Rec. %	Deviation %		
Daimuron	102	101	0	98	-4		
Dalapon	66	74	12	76	14	Always low recoveries	
DEET	98	99	2	104	6		
Deltamethrin	106	110	4	105	-1		
Demeton-S-methyl	113	101	-10	100	-11		
Demeton-S-methyl-sulfon	94	99	6	101	7		
Dicamba	107	98	-8	100	-7		
Dichlofuanid	97	28	-71	87	-10	Degrades at high pH	
Dichlorbenzophenon 4,4	86	88	2	84	-2		
Dichlormid	104	102	-2	99	-5		
Dichlorvos	95	112	17	91	-5		
Diclobutrazole	92	102	10	98	7		
Dicloran	100	101	2	94	-6		
Dicrotophos	91	91	0	87	-4		
Dieldrin	106	118	11	102	-4		
Difenconazole	95	99	4	99	5		
Difenoquat methylsulfate	101	100	-1	98	-3		
Diflubenzuron	98	101	3	97	-1		
Diflufenzoxypr	101	102	1	93	-8		
Dikegulac	98	101	3	99	1		
Dimethoat	96	89	-7	91	-6		
Dimethomorph	100	98	-3	93	-7		
Dimethylvinphos	101	102	1	97	-4		
Dimoxystrobin	104	102	-2	98	-5		
Diniconazole	97	98	1	105	8		
Dinocap	96	97	1	95	-1		
Dinotefuran	91	98	7	98	7		
Dioxacarb	101	97	-4	95	-6		
Dioxathion	103	107	4	100	-3		
Diphenamid	99	104	5	99	0		
Disulfoton	82	89	8	107	30		
Disulfoton-sulfon	96	96	0	87	-10		
Disulfoton-sulfoxid	98	92	-6	93	-5		
Dithiopyr	103	103	0	95	-7		
DMST	111	108	-3	92	-17		
Dodine	113	112	-1	105	-7		

QuEChERS - Citrate buffered No cleanup, always n=2, matrix = cucumber	1 min Extraction by Hand	30 min Extraction with GenoGrinder				Notes
		BEFORE adding partitioning/buffering salts		AFTER adding partitioning/buffering salts		
		Rec. %	Rec. %	Deviation %	Rec. %	Deviation %
Edifenphos	103	104	1	96	-7	
Endosulfansulfat	100	112	12	106	6	
EPN	97	102	5	99	2	
Epoxiconazole	98	98	0	97	0	
EPTC	117	106	-9	98	-16	
Eprocarb	99	102	2	99	0	
Etaconazole	111	102	-8	114	2	
Ethalfluralin	105	109	3	103	-2	
Ethiofencarb	143	103	-28	71	-50	Oxidation prone, plus problems w. stability of standard??
Ethiofencarb-sulfon	168	131	-22	98	-42	Problems w. stability of standard??
Ethiofencarb-sulfoxid	166	128	-23	100	-40	Oxidation prone, plus problems w. stability of standard??
Ethiprole	97	98	0	109	11	
Ethirimol	93	98	5	95	2	
Ethoprophos	103	105	2	101	-2	
Etofenprox	95	101	7	93	-2	
Etoxazole	101	103	1	96	-5	
Etridiazol	107	100	-6	100	-6	
Famoxadone	93	95	2	99	6	
Famphur	101	109	8	106	4	
Fenamiphos	96	99	3	100	5	
Fenamiphos sulfon	100	98	-2	107	7	
Fenamiphos sulfoxid	113	97	-14	104	-8	
Fenarimol	99	100	0	94	-6	
Fenbuconazole	103	100	-3	107	3	
Fenhexamid	99	102	3	105	6	
Fenitrothion	101	108	7	103	3	
Fenobucarb	98	99	1	100	2	
Fenothiocarb	96	96	-1	98	2	
Fenoxyprop-P	103	97	-6	93	-10	
Fenoxy carb	95	94	-1	88	-7	
Fenpiclonil	104	115	11	109	5	
Fenpropidin	102	106	3	103	1	
Fenpropimorph	97	97	1	102	5	
Fenpyroximat	99	94	-5	92	-7	

Compound	1 min Extraction by Hand	30 min Extraction with GenoGrinder				Notes
		BEFORE adding partitioning/buffering salts		AFTER adding partitioning/buffering salts		
		Rec. %	Rec. %	Deviation %	Rec. %	Deviation %
Fensulfothion	102	105	3	100	-2	
Fensulfothion	100	89	-11	92	-8	
Fensulfothion-sulfon	91	99	9	98	8	
Fenthion	92	99	7	96	5	
Fenthion-oxon	87	98	12	85	-2	
Fenthion-oxon-sulfoxid	98	91	-8	90	-9	
Fenthion-sulfon	102	101	0	96	-6	
Fenthion-sulfoxid	102	91	-11	89	-12	
Fenthio-oxon-sulfon	93	105	13	89	-4	
Eipropril	116	96	-17	90	-22	Oxidation??
Eiproprildesulfinyl	94	96	2	99	5	
Eiproprilsulfide	103	92	-11	90	-13	
Eiproprilsulfon	109	97	-11	93	-15	
Flonicamid	97	102	6	98	2	
Florasulam	100	100	-1	94	-7	
Fluacrypyrim	102	107	5	102	0	
Fluazifop	104	102	-2	93	-11	
Fluazinam	103	97	-6	96	-7	
Fluazuron	104	107	3	99	-4	
Flubendiamide	88	103	17	94	7	
Flucycloxuron	102	101	-2	90	-12	
Flucythrinate	108	112	3	105	-3	
Fludioxonil	92	93	1	89	-4	
Flufenoxuron	100	98	-2	103	2	
Flumetralin	112	107	-4	105	-6	
Flumioxazin	101	110	9	100	-1	
Fluopicolide	106	110	4	103	-3	
Fluopyram	108	112	4	102	-5	
Fluorochloridon	103	105	2	102	-1	
Fluoxastrobin	104	102	-2	99	-5	
Fluquinconazole	107	100	-7	103	-4	
Fluroxypyr	101	105	5	96	-4	
Flurprimidol	101	99	-2	97	-4	
Flurtamone	104	95	-9	89	-15	
Flusilazole	102	100	-2	109	6	
Flusulfamide	102	101	-1	101	-1	
Flutolanil	98	100	2	99	1	
Flutriafol	95	98	4	97	2	
Folpet	117	100	-15	84	-28	Degrades at high pH
Fomesafen	109	102	-7	96	-13	
Forchlorfenuron	100	101	1	101	1	
Formetanate	89	97	9	83	-7	
Fosthiazat	99	105	6	97	-3	
Fuberidazole	85	96	13	103	21	
Furathiocarb	103	105	2	97	-5	

Compound	1 min Extraction by Hand	30 min Extraction with GenoGrinder				Notes	
		BEFORE adding partitioning/buffering salts		AFTER adding partitioning/buffering salts			
		Rec. %	Deviation %	Rec. %	Deviation %		
Gibberellic	100	104	3	98	-2		
Halfenprox	100	101	1	98	-2		
Halofenozide	100	99	-1	100	-1		
Haloxyfop	104	94	-10	95	-8		
Heptachlorepoxyd Summe	107	112	5	103	-4		
Hexachlorbenzol	103	98	-5	99	-4		
Hexaconazol	102	99	-3	102	1		
Hexaflumuron	102	99	-3	90	-12		
Hexythiazox	95	95	0	94	-1		
Imazalil	95	95	0	97	2		
Imazamox	97	90	-7	92	-5		
Imazapyr	93	105	13	93	0		
Imazaquin	103	92	-11	91	-11		
Imazethapyr	94	94	0	99	5		
Imibenconazole	96	105	9	104	8		
Imidacloprid	98	101	2	104	6		
Inabenfide	99	98	-2	102	3		
Indoxacarb	96	94	-2	93	-3		
Ioxynil	114	98	-14	106	-7		
Iprobenfos	102	101	-1	99	-4		
Iprodion	92	101	11	94	2		
Iprovalicarb	98	93	-5	91	-7		
Isocarbophos	110	106	-4	102	-7		
Isofenphos	105	106	1	102	-2		
Isofenphos-Methyl	102	107	5	101	-1		
Isoprocarb	97	98	1	97	0		
Isoxadifen-ethyl	102	103	0	99	-4		
Isoxathion	101	103	1	99	-3		
Kresoxim-methyl	98	103	5	99	1		
Lactofen	104	103	-1	100	-4		
Lambda-Cyhalothrin	98	103	5	97	-1		
Landrin	97	99	2	97	1		
Lenacil	104	94	-9	103	-1		
Linuron	95	99	4	102	7		
Lufenuron	97	99	2	93	-5		

Compound	1 min Extraction by Hand	30 min Extraction with GenoGrinder				Notes
		BEFORE adding partitioning/buffering salts		AFTER adding partitioning/buffering salts		
		Rec. %	Rec. %	Deviation %	Rec. %	Deviation %
Malaoxon	97	100	3	97	0	
Malathion	89	103	16	90	1	
Mandipropamid	110	99	-10	105	-4	
MCPA	100	95	-5	97	-2	
MCPB	96	93	-3	94	-3	
MCPP (Mecoprop)	108	94	-12	96	-11	
Mefenacet	102	103	0	98	-4	
Mefenpyr-diethyl	104	106	2	100	-4	
Mefluidide	99	108	9	94	-5	
Mepanipyrim	98	102	4	88	-11	
Mepronil	101	106	6	103	2	
Metalaxyl	103	105	2	100	-4	
Metconazole	100	98	-2	99	-1	
Methamidophos	77	83	7	79	2	
Methidathion	106	109	3	95	-10	
Methiocarb	103	105	2	99	-4	
Methiocarb-sulfon	132	138	4	95	-28	Degrades at high pH, plus problems w. stability of standard??
Methiocarb-sulfoxid	150	128	-15	95	-37	Degrades at high pH, oxidation prone, plus problems w. stability of standard???)
Methomyl	102	103	1	90	-12	
Methoxyfenozide	96	97	1	95	-2	
Metolcarb	102	101	-1	94	-8	
Metrafenone	92	98	6	94	2	
Mevinphos	98	98	1	99	1	
Monocrotophos	91	88	-4	92	1	
Propoxy-carbazone-sodium	110	97	-11	98	-10	
Propyzamid	104	101	-3	97	-7	
Proquinazid	105	110	5	101	-3	
Prothioconazole desthio	99	108	9	108	9	
Pymetrozin	56	66	17	51	-9	Always low recoveries
Pyraclostrobin	102	104	3	99	-3	
Pyrafluofen-ethyl	102	104	1	97	-6	
Pyrazophos	103	110	7	103	-1	
Pyrethrin Pyrethrin 1+2	101	93	-8	99	-2	
Pyributicarb	104	102	-2	96	-8	
Pyridaben	97	101	4	93	-4	
Pyridafenthion	100	101	2	98	-2	
Pyridalyl	105	106	1	102	-2	
Pyrifenoxy	105	108	2	101	-4	
Pyrimethanil	101	104	3	95	-6	
Pyrimidifen	104	103	-1	98	-5	
Pyriproxyfen	95	103	8	93	-2	

QuEChERS - Citrate buffered No cleanup, always n=2, matrix = cucumber	1 min Extraction by Hand	30 min Extraction with GenoGrinder				Notes	
		BEFORE adding partitioning/buffering salts		AFTER adding partitioning/buffering salts			
		Rec. %	Deviation %	Rec. %	Deviation %		
Quinalphos	95	104	9	92	-3		
Quinoxifen	100	102	3	96	-4		
Quizalofop	105	92	-12	93	-12		
Rabenazazole	100	98	-2	99	-1		
Rotenon	94	87	-8	97	3		
Schradan	102	111	9	100	-1		
Siduron	101	105	4	98	-3		
Silafluofen	101	105	4	101	1		
Spinosyn	96	105	9	100	4		
Spirodiclofen	116	116	1	110	-5		
Sprioxamine	96	102	5	99	2		
tau-Fluvalinat	103	115	11	105	1		
TCMTB	89	80	-11	84	-6		
Tebufenozide	97	95	-2	97	0		
Tebufenpyrad	97	101	4	96	-2		
Tecloftalam	97	101	4	87	-11		
Teflubenzuron	106	91	-15	88	-17		
Tefluthrin	104	119	15	101	-3		
Tefluthrin	107	111	5	104	-3		
Terbacil	110	96	-12	97	-11		
Terbufos	93	91	-2	93	0		
Terbufos-sulfon	103	88	-14	89	-13		
Terbufos-sulfoxid	97	91	-6	98	0		
Tetraconazole	109	103	-5	105	-4		
Tetradifon	106	111	5	104	-2		
Tetramethrin	117	102	-13	115	-2		
Thenylchlor	100	102	2	97	-2		
Thiacloprid	99	99	0	97	-2		
Thiamethoxam	97	104	7	99	2		
Thiazopyr	104	103	-1	97	-6		
Thiobencarb	103	106	3	108	5		
Thiocyclam	83	68	-18	81	-3		

Compound	1 min Extraction by Hand	30 min Extraction with GenoGrinder				Notes	
		BEFORE adding partitioning/buffering salts		AFTER adding partitioning/buffering salts			
		Rec. %	Deviation %	Rec. %	Deviation %		
Thiodicarb	146	101	-31	71	-51	Degrades to methomyl, plus other problems (w. stability of standard??)	
Thiophanat-methyl	103	106	3	89	-13		
Thiosultap	28	33	18	30	10	Always low recoveries at high pH	
Tolfenpyrad	101	101	0	103	2		
Tolyfluanid	101	42	-58	92	-9	Degrades at high pH	
Triadimefon	102	100	-2	99	-2		
Triadimenol	101	96	-5	100	-1		
Triazamte	101	101	0	97	-4		
Triazophos	102	104	1	98	-5		
Triazoxide	111	124	12	95	-14		
Trichlorfon	124	126	1	94	-24	Degrades to dichlorvos plus other problems (w. stability of standard??)	
Triclopyr	103	91	-12	94	-9		
Tricyclazole	98	100	3	98	0		
Trifloxystrobin	103	106	2	93	-10		
Trifloxsulfuron	105	104	-1	100	-4		
Triflumizol	98	114	16	101	3		
Triflumuron	101	101	0	101	0		
Triflusulfuron-methyl	157	137	-13	147	-6	Measurement problems ???	
Triforine	96	102	7	99	4		
Trinexapac-ethyl	106	112	6	102	-4		
Triticonazole	100	104	4	115	15		
Uniconazole	94	96	1	101	7		
Vernolate (Pebulate)	104	104	-1	98	-6		
Vinclozolin	103	100	-3	101	-2		
Zoxamide	97	98	1	109	12		

SUMMARY

Experiments with real samples
have shown the need for

PROLONGED EXTRACTION TIMES

(e.g. 10-15 min)

to increase the recoveries of incurred residues.

The use of
MECHANICAL SHAKERS
is indicated



Thank you very much...