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From pesticide quality control to textile chemistry-

Experiences with the draft CIPAC wash method for LN

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What are LN formulations (Long-lasting insecticidal net)?

"**Manual on development and use of FAO and WHO specifications for pesticides**

(March 2006 revision of the First edition)"

"A slow- or controlled-release formulation in the form of netting, providing physical and chemical barriers to insects. LN refers to both bulk netting and ready-to-use products, for example mosquito nets."

(source: press release Syngenta)

Why insectical coated nets?

The insecticide on the net kills or keeps away mosquitoes

Combination of physical barrier with an insecticide

1. net
2. pyrethroid, rapid knock down

Two types of nets (polymer fibre - influences the LN technology)

- **HDPE** → incorporated insecticide
- **Polyester** → insecticide coated with a „binder“

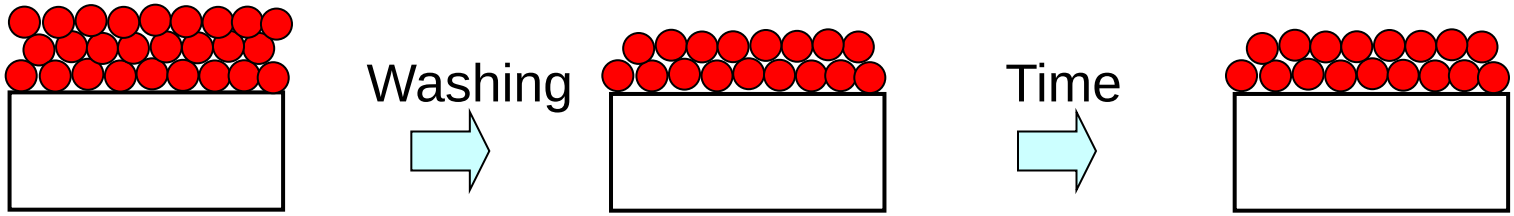
Coating or Integration- Pros and Cons

- **Coating:** more insecticide bioavailable, but good wash resistance and homogeneity more difficult to achieve.

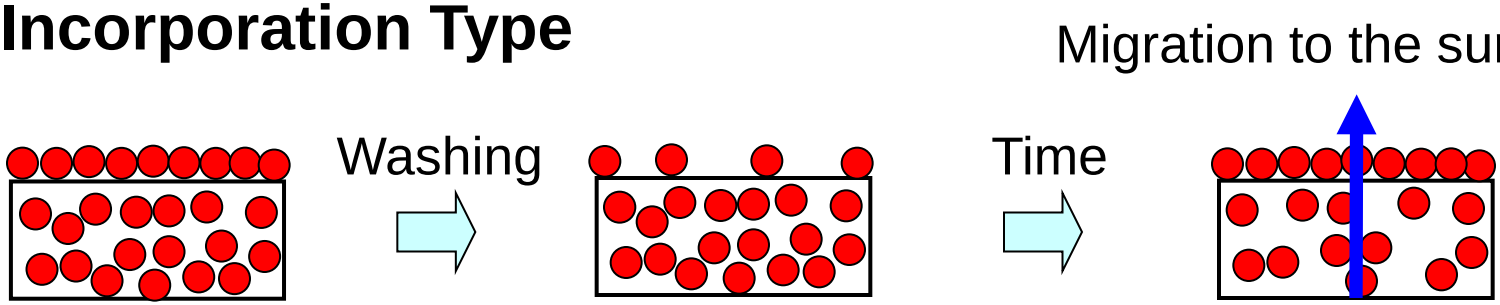
- **Integration:** inherently more homogeneous, but surface replenishment difficult to show by chemical analysis.

Effects of washing

Coating Type



Incorporation Type



From a presentation of Sumitomo

Test design to anwser the question:

- Quality of immobilisation of insecticide
- long term behaviour during repeated washing steps

Don‘t forget…

No laboratory test design can
replicate in detail
all kinds of
possible

Consumer Reality

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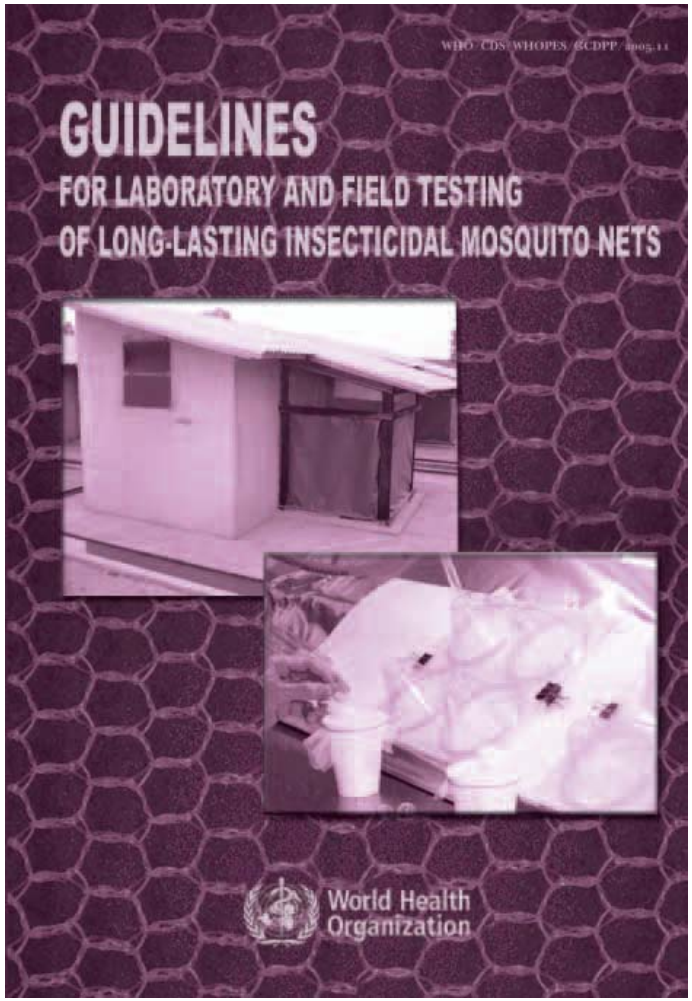
History



- WHO recommended nets for public health
- WHO wash method in combination with a bioassays (2005)

The WHO wash method

- Net samples (25 x 25 cm) are put in a 1-l beaker containing 0.5 l deionised water with 2g/l „Savon de Marseille“ (pH 10-11)
- 10 min shaking at 30°C and 155 beats per minute (bpm)
- Rinsed twice with deionised water, same conditions
- Dried at room temperature, stored at 30°C in the dark between the wash steps
- The regeneration time between the washes at 30°C was determined before with another standard test (comparing 1 and 3 days)
- The washed net samples are then tested with a bioassay after 0, 1, 5, 10, 15 and 20 wash cycles

WHOPES criteria for a recommendet net

- Efficacy after 20 washes: KD (>95% 1 h) and mortality (>80% 24 h)
- Minimum 3 years usable under field conditions

	Wash No.	Surface active ingredient (mg/kg*)	KD (%)	Mortality (%)
PermaNet	0	73.2	100	100
	1	70.9	100	100
	3	66.6	100	100
	5	62.5	100	100
	10	53.4	100	97
	15	45.7	100	78
	20	39.0	87	23
Hiking	0	41.6	100	95
	1	40.5	98	57
	3	38.5	54	8
	5	36.7	35	2
	10	32.3	51	6
	15	28.5	12	5
	20	25.1	1	1

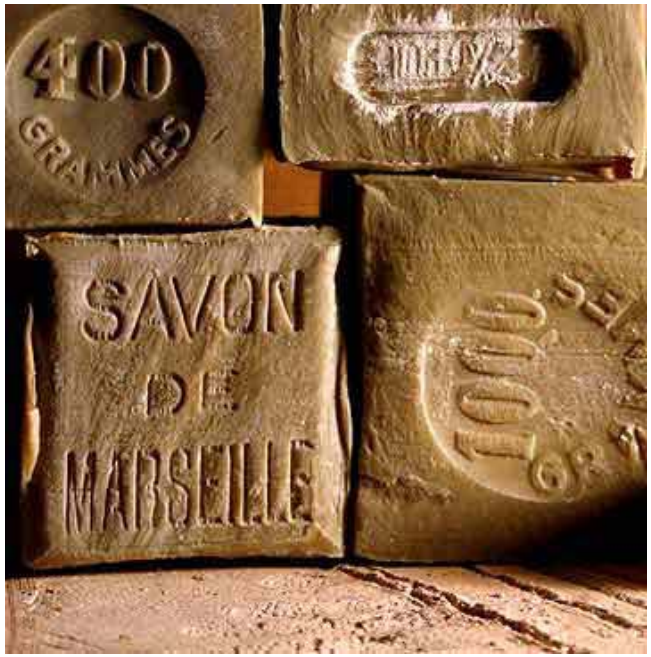
Source: Report of the eleventh WHOPES working group meeting 2007

WHOPES procedure

- Time consuming
- Specialised lab (bioassay)
- “Savon de Marseille” not readily available and not standardised
- Not easily transferable to a quality control lab

Definition „Savon de Marseille“

Marseille soap or ***Savon de Marseille*** is a traditional soap made from vegetable oils that has been made around Marseille, France, for about 600 years, the first recorded soapmaker in the area in about 1370. By 1688, *Louis XIV* introduced regulations (*Edict of Colbert*) limiting the use of the name *savon de Marseille* to soaps made in and around the Marseille area,[1] and only from olive oil. Today this law still stands (although the regulations now allow other vegetable oils to be used).
(Source Wikipedia)



Why a new standard wash method?

- Further standardization ... is necessary“ (recommendation 11th WHOPES meeting)
- “Savon de Marseille” → standard soap
- amplitude of movement
- drying and storage conditions

Goals

- Useable for retention/release index determination
- For comparison with WHOPES Phase I efficacy results
- Standardized sampling and sub sampling
- Method for quality and market control
- Usable in standard analytical pesticide control labs
- One wash method for all nets

The draft CIPAC wash method

- Net samples (25 x 25 cm) put in a 1-l beaker containing 0.5 l deionised water with **2.5 g/l IEC A*** standard detergent
- 10 min shaking at 30°C and 155 bpm and defined **amplitude (15 mm)**
- Rinsed twice with deionised water by the same conditions
- Nets are dried at room temperature (protected from sunlight) for **30 min and then stored at 40°C in the dark for 22 hours**
- The content of the insecticide is analysed in the unwashed and 4 times washed net

CIPAC draft method

$$\text{Retention index: } \sqrt[4]{\frac{\text{content } t4}{\text{content } to}}$$

WHO interim specification

$$\text{Retention index: } \frac{\text{content } t3}{\text{content } t2}$$

Our experiment in a pesticide quality control lab

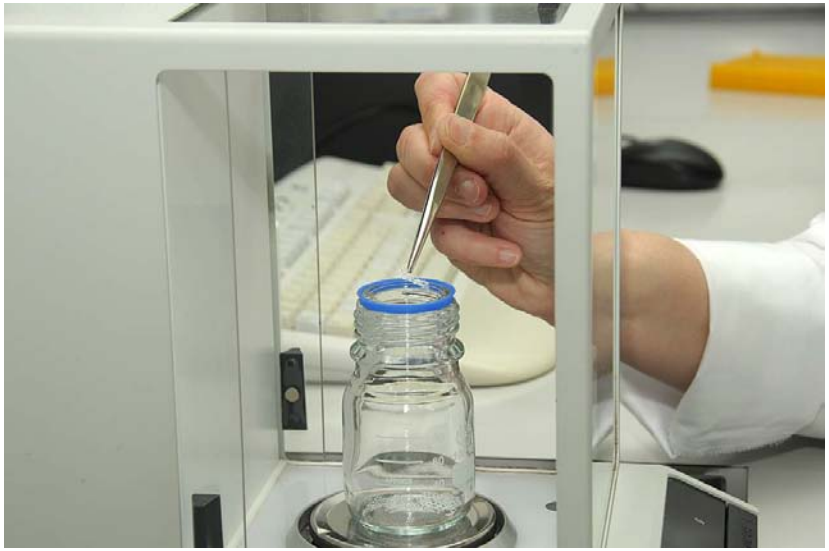
- 4 nets containing deltamethrin from 2 different manufacturers
- 5 wash steps, **5g/l IEC A* instead of 2.5 g/l**,
- Amplitude **50 mm instead of 15 mm**
- After each wash step determination of the total remaining deltamethrin content

CIPAC HPLC – method for LN formulation

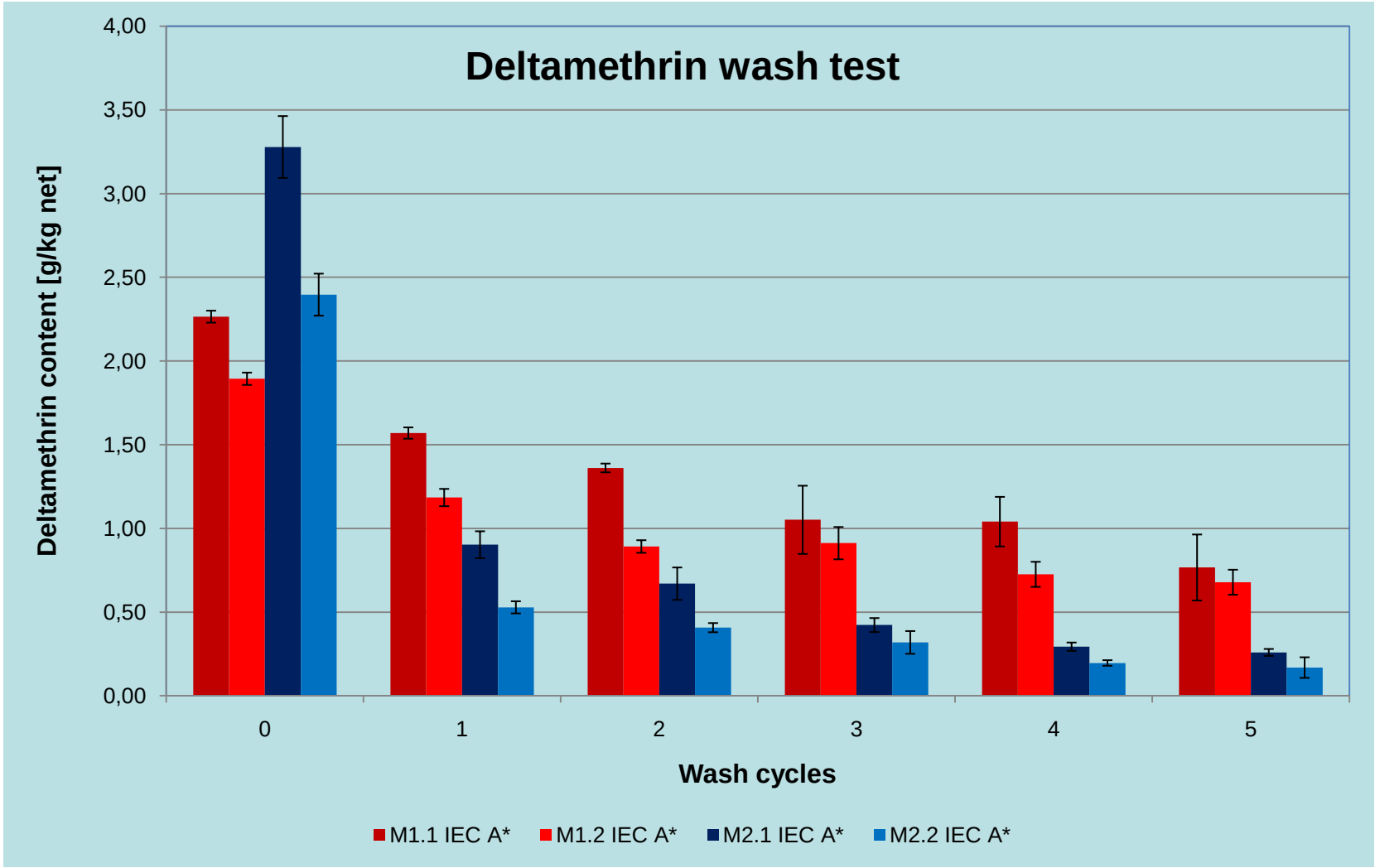
- **Column:** Nucleosil 100 CN, 5 µm, 250 x 4 mm, 35°C
- **Eluent:** isooctane : dioxane with 0.15% water; 94:6 (v/v)
- **Flow:** 1.5 ml/min
- **Detection:** UV 230 nm
- **Injection vol.:** 20 µl
- **Runtime:** 7 minutes

Sample preparation

- Cut small pieces
- Weigh sufficient sample to contain about 0.5 mg deltamethrin
- Add ISTD and 14 ml isooctane : dioxane 80:20
- 15 min 80°C ultrasonic bath, then 30 min shaker (150 – 200 bpm room temp.)
- Filter and analyse



First results



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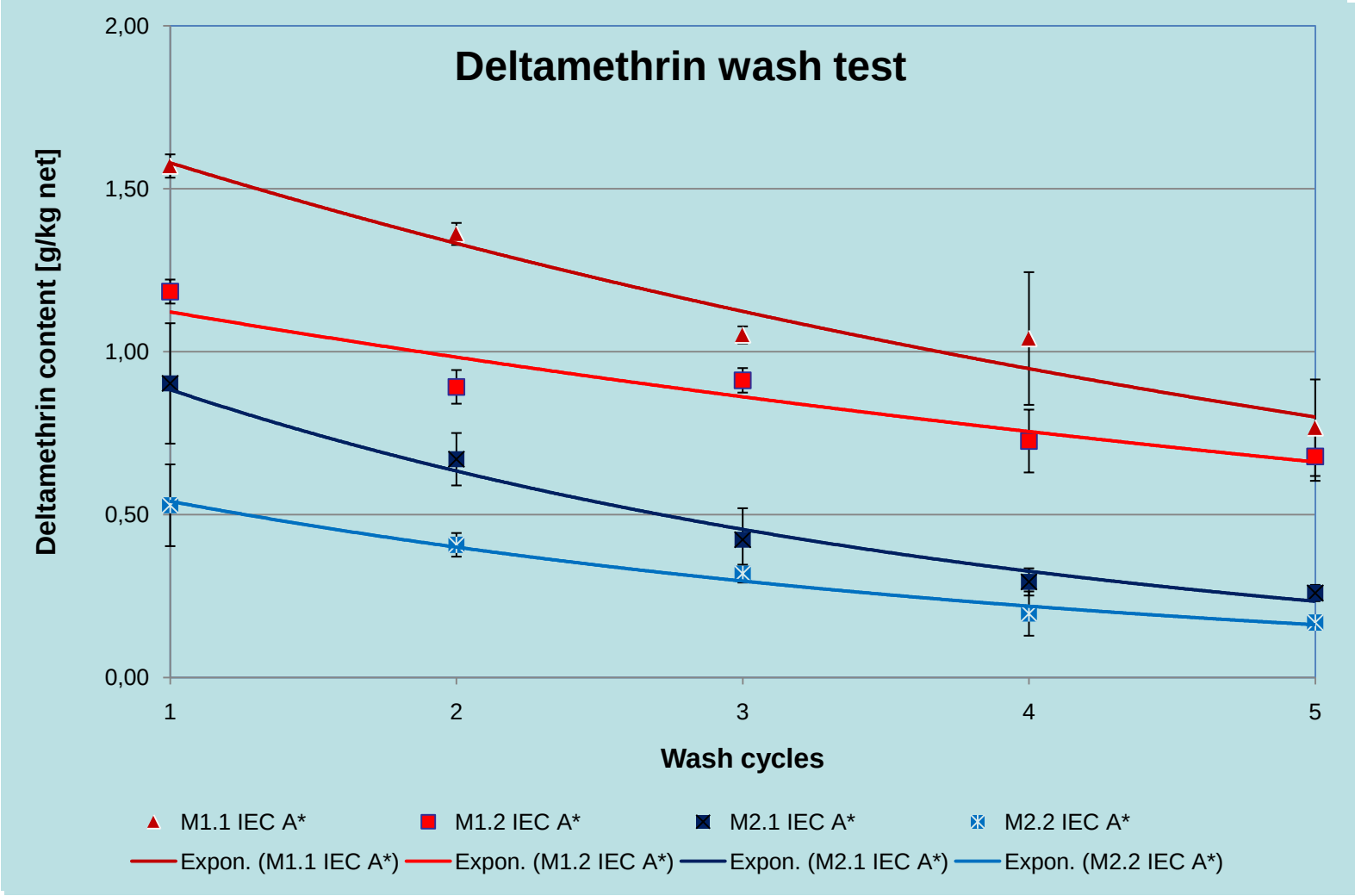
First results



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Interpretation of the results

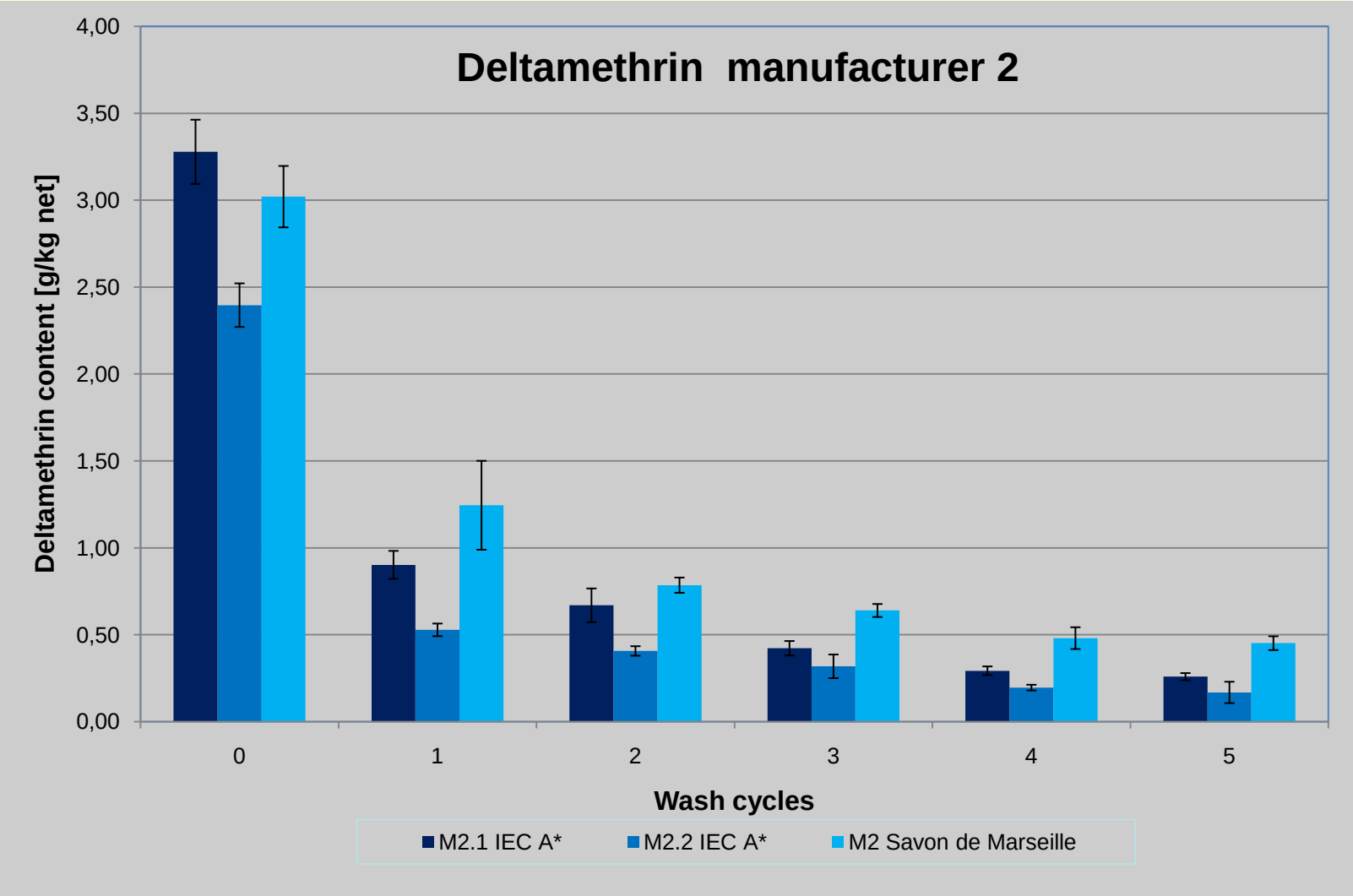
	Retention-index	
	CIPAC	WHO
M1	0.82	0.77
	0.79	1.02
M2	0.55	0.63
	0.53	0.78

- Retention-index lower than in standard WHOPES wash test
- Differences between the two manufacturers products

Next step

- Wash with “Savon de Marseille” (2 g/l)
- Regeneration 30°C 22 h similar to WHO method

Results incl. „Savon de Marseille“



Results incl. „Savon de Marseille“

Retention-index				
soap/detergent	CIPAC	WHO	4	5
M1.1 (IEC A*)	0.82	0.77	0.99	0.74
M1.2 (IEC A*)	0.79	1.02	0.80	0.94
M1 (Savon de Marseille)	0.88	0.81	0.98	0.90
M2.1 (IEC A*)	0.55	0.63	0.69	0.88
M2.2 (IEC A*)	0.53	0.78	0.62	0.86
M2 (Savon de Marseille)	0.63	0.81	0.75	0.94

Conclusion

- IEC A* wash more harsh
- Zeolite has a presumed abrasive behaviour
- But…

Open questions

Net coated alpha-cypermethrin						
Wash step soap	[g/kg] 0	2	3	4	Retention-index CIPAC	WHO
Savon de Marseille	7.11	7.02	7.15	5.59	**0.94**	**1.02**
IEC A* 2g/l	7.11	6.96	5.62	5.78	**0.95**	**0.81**
IEC A* 3g/l	7.11	7.49	6.90	6.31	**0.97**	**0.92**
IEC A* 5g/l	7.11	6.83	6.40	5.56	**0.94**	**0.94**

Net incorporated alpha-cypermethrin						
Wash step soap	[g/kg] 0	2	3	4	Retention-index CIPAC	WHO
Savon de Marseille	5.30	4.99	5.41	4.95	**0.98**	**1.08**
IEC A* 2g/l	5.30	4.91	5.05	5.05	**0.99**	**1.03**
IEC A* 3g/l	5.30	5.31	5.48	5.19	**0.99**	**1.03**
IEC A* 5g/l	5.30	5.02	5.11	5.02	**0.99**	**1.02**

Source: Retention/release characteristics Study N 22018 Dr. ir. Olivier Pigeon, CRA-W Gembloux

Higher amplitude? **Other insecticide?**

Next step

- Question: Is IEC B more similar to „Savon de Marseille” than IEC A*?
- Wash test with 5g/l IEC B

Composition IEC A* and IEC B

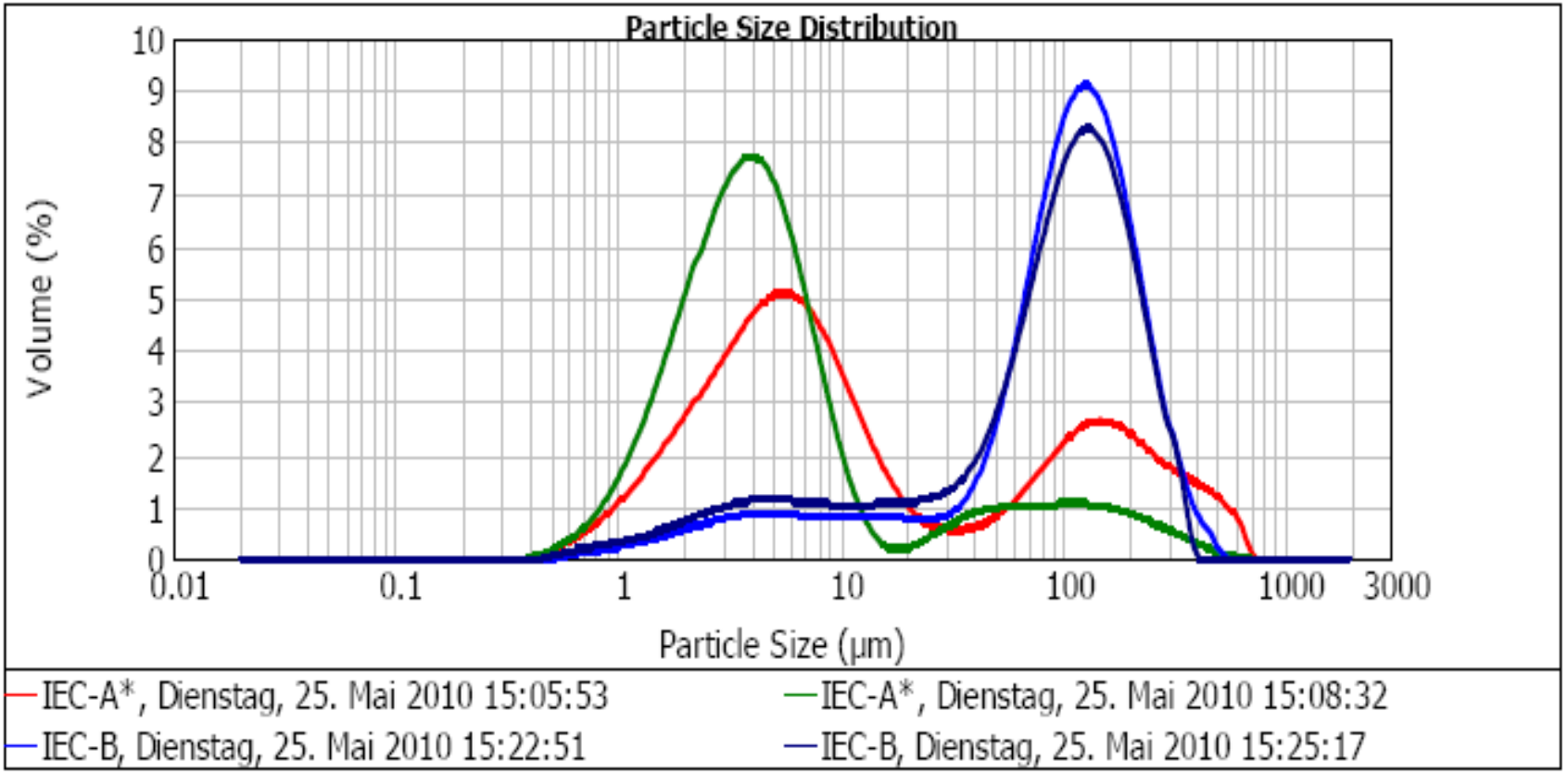
Component	IEC-B	IEC-A*
LAS (linear alkylbenzene sulfonate; detergent)	6.4	8.8
Nonionic	2.3	4.7
Soap	2.8	3.2
Anti foam		3.9
Phosphate	35.0	2.8
Zeolite (alkali aluminium silicates)		28.3
Carbonate		11.6
Acrylic acid, Maleic acid		2.4
Na-Silicate	6.0	3.0
Mg-Silicate	1.5	
CMC (carboxy methyl cellulose)	1.0	1.2
EDTA (ethylenediaminetetraacetic acid)	0.2	
Optical brightner	0.2	0.2
Sulphate	16.8	6.5
Protease		0.4
Water/Misc.	7.8	
Perborate (bleacher)*	20.0	20.0
TAED (bleacher activator: N,N,N',N'-tetraacetylethylenediamine)*		3.0

*Bleacher pack not included in tests

Particle size analyses by Laser Diffraction

Particle size distribution of the three tested wash solutions by laser diffraction

Particle Size analyses by Laser Diffraction



Malvern Mastersizer 2000 (Syngenta EZA Münchwilen)

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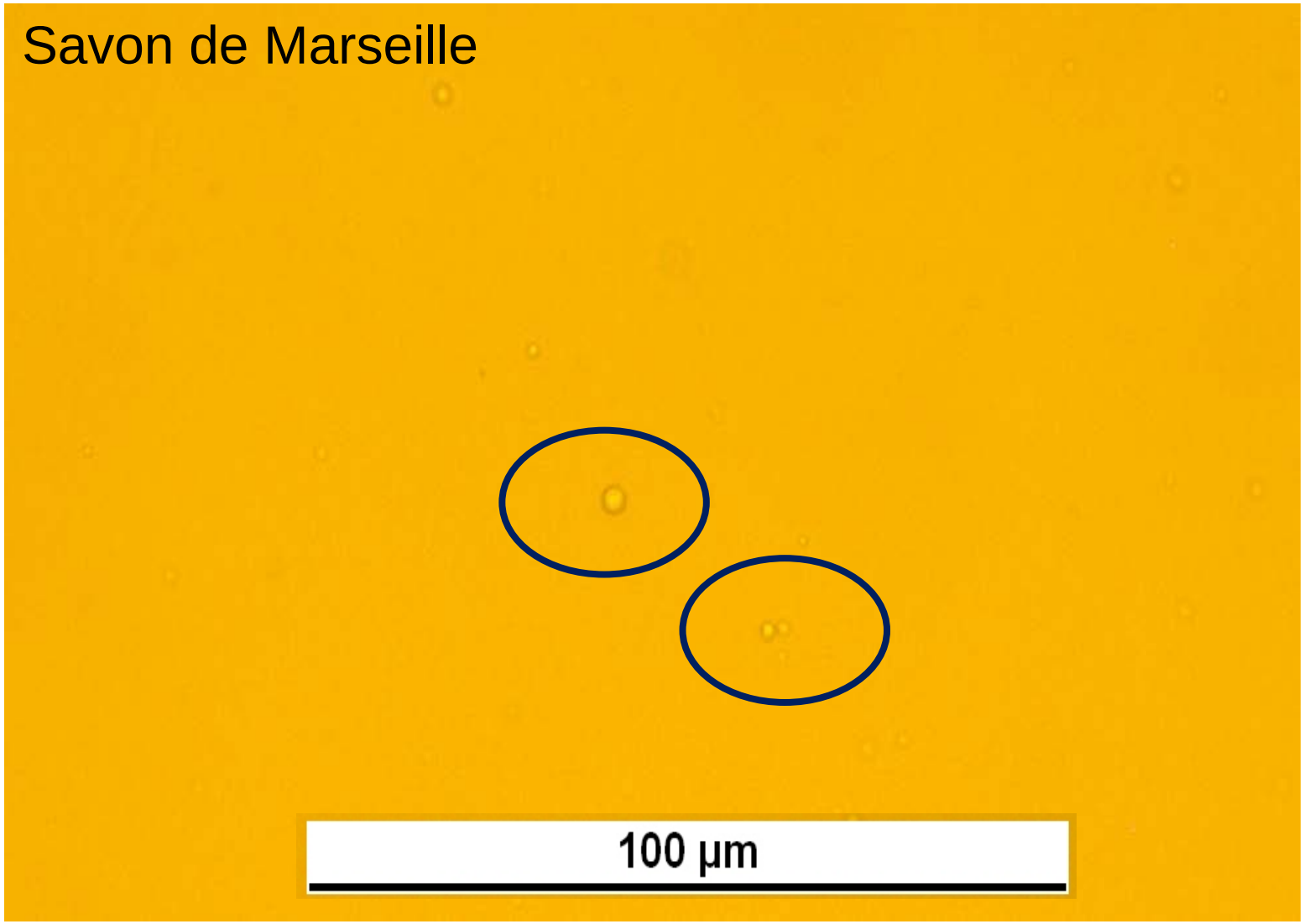
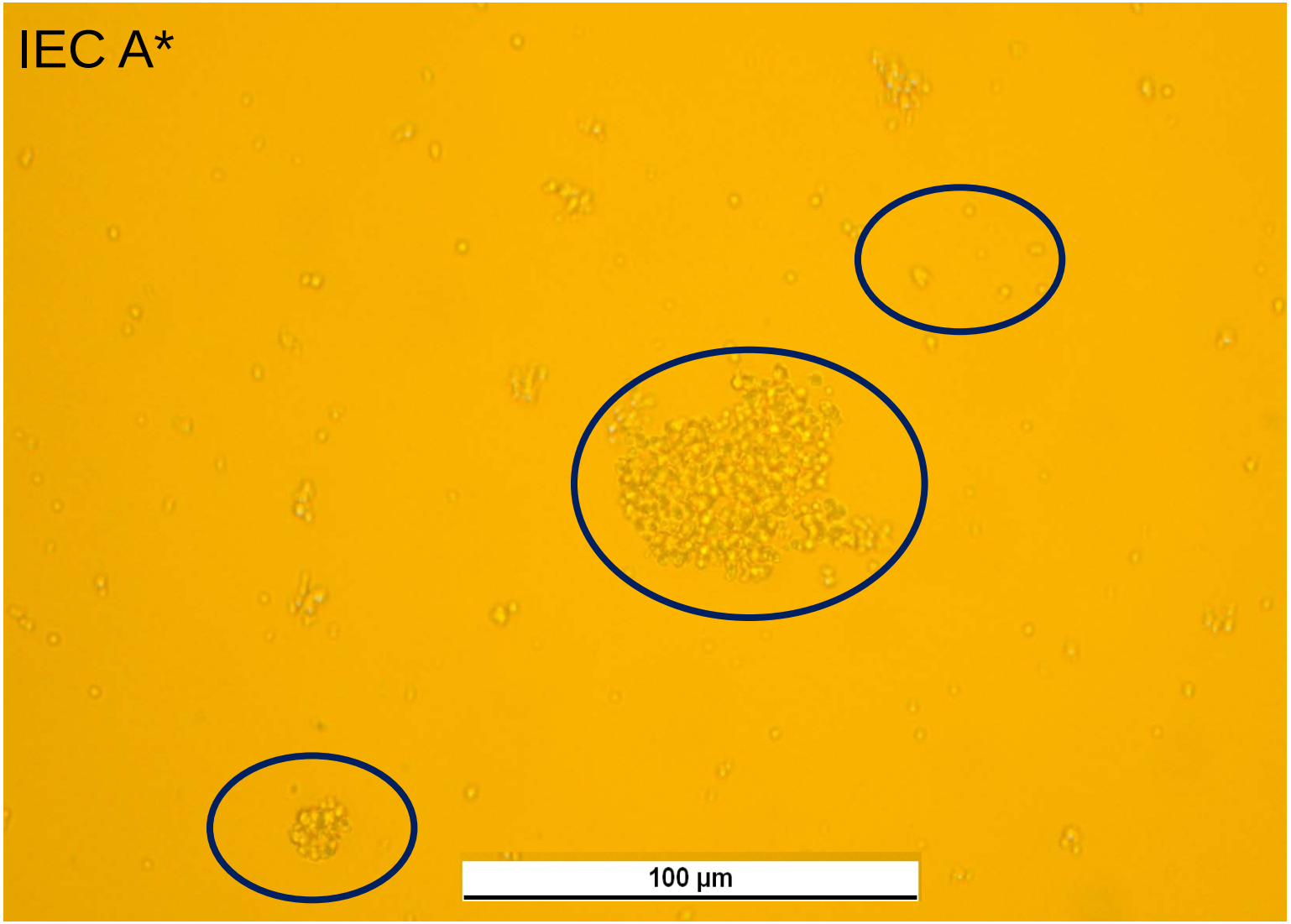
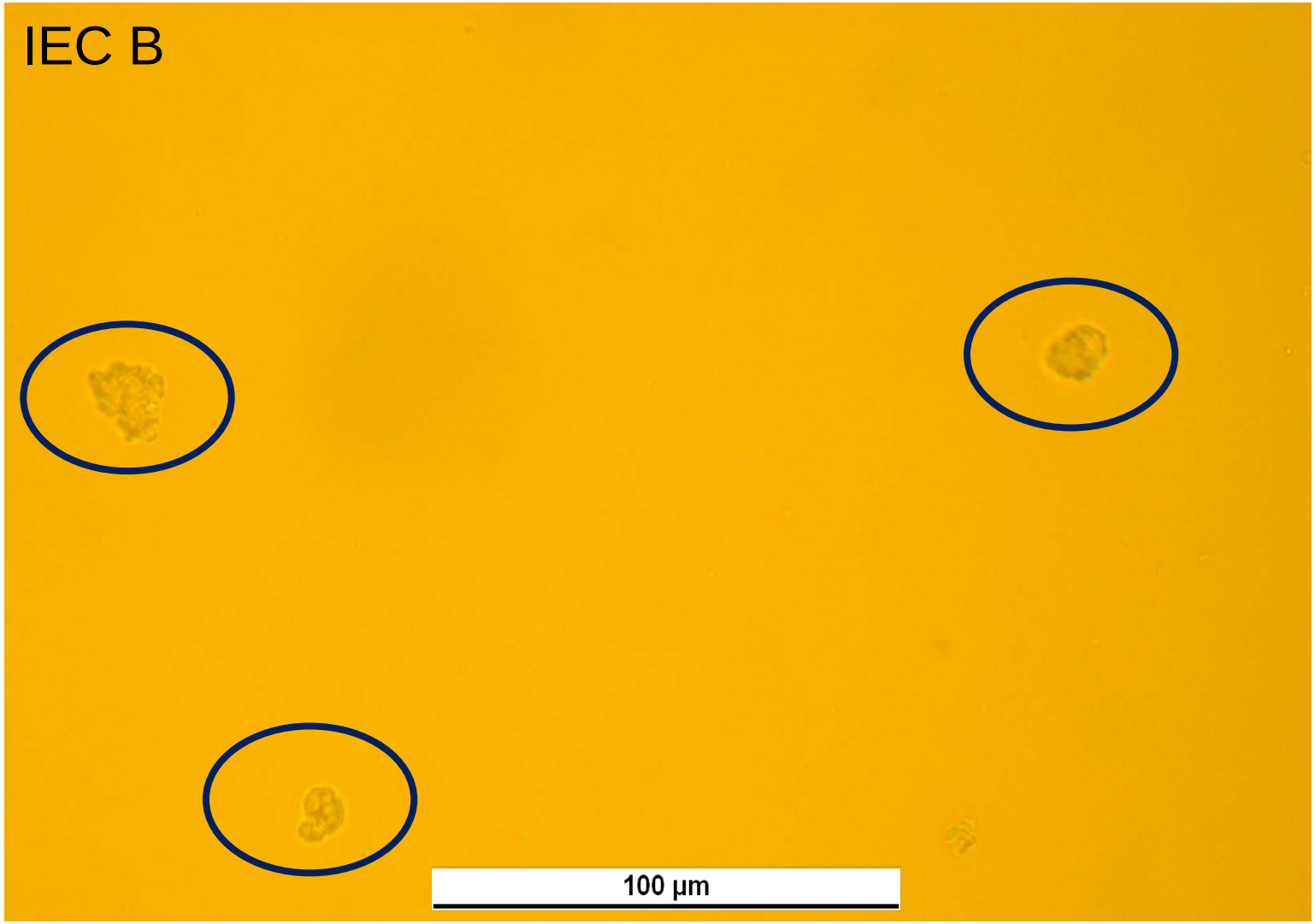
Under the microscope



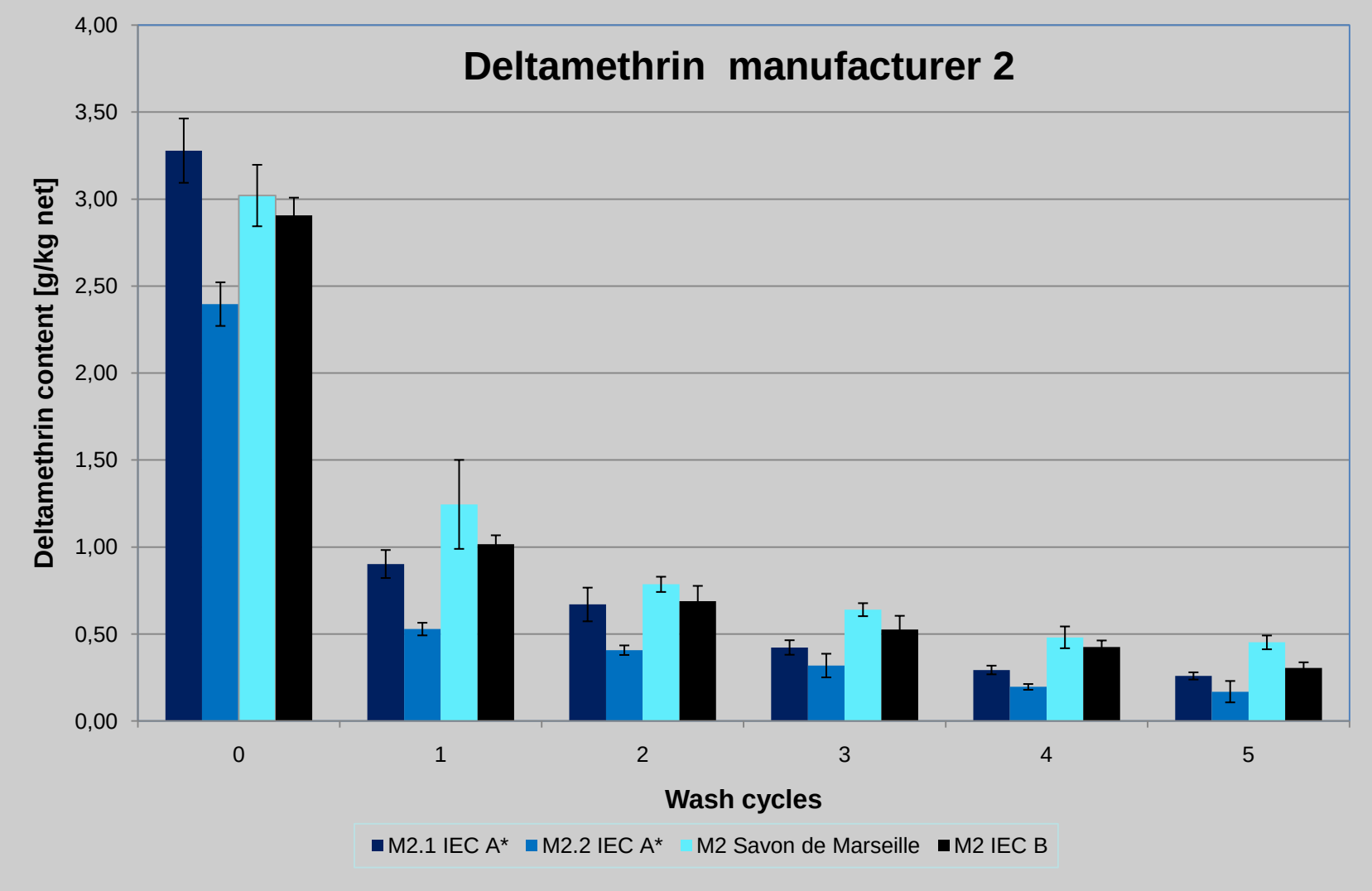
Under the microscope



Under the microscope



Results incl. IEC B



Results incl. IEC B

Retention-index				
Soap	CIPAC	WHO	4	5
M1.1 (IEC A*)	0.82	0.77	0.99	0.74
M1.2 (IEC A*)	0.79	1.02	0.80	0.94
M1 (IEC B)	0.82	0.78	1.00	0.90
M1 (Savon de Marseille)	0.88	0.81	0.98	0.90
M2.1 (IEC A*)	0.55	0.63	0.69	0.88
M2.2 (IEC A*)	0.53	0.78	0.62	0.86
M2 (IEC B)	0.62	0.76	0.81	0.71
M2 (Savon de Marseille)	0.63	0.81	0.75	0.94

Preliminary conclusions

- IEC B wash more similar to IEC A* than “Savon de ...”
- But IEC B seems to better mimic “Savon de Marseille”

Remarks to the calculation methods

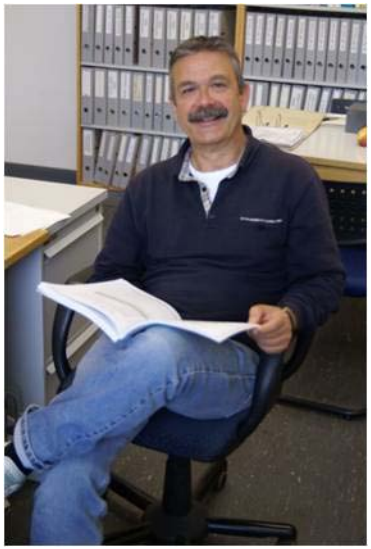
Retention-index					
Soap	CIPAC	WHO	4	5	T5/T1
M1.1 (IEC A*)	0.82	0.77	0.99	0.74	0.84
M1.2 (IEC A*)	0.88	1.02	0.80	0.94	0.87
M1 (IEC B)	0.82	0.78	1.00	0.90	0.87
M1 (Savon de Marseille)	0.88	0.81	0.98	0.90	0.90
M2.1 (IEC A*)	0.55	0.63	0.69	0.88	0.73
M2.2 (IEC A*)	0.53	0.78	0.62	0.86	0.75
M2 (IEC B)	0.62	0.76	0.81	0.71	0.74
M2 (Savon de Marseille)	0.63	0.81	0.75	0.94	0.78

- CIPAC calculation method well suited
- For calculation of the retention-index, only two measurements necessary (t0 t4) as for WHO calculation

Overall conclusion

- CIPAC wash method easy to implement in a pesticide quality control lab
- IEC A* household detergent leads to less retention than „Savon de Marseille“
- IEC B seems to better mimic “Savon de Marseille” than IEC A*. Further work is needed to confirm this finding
- IEC A* and IEC B are not directly comparable with “Savon de Marseille”
- The wash method allowed to differentiate between nets of different qualities
- Calculation of the retention index: The CIPAC draft calculation method seems to have certain advantages

Involved team



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Thank you for your attention!