FATE OF PLANT PROTECTION AGENTS DURING HOP PROCESSING

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LEGISLATION

- Pesticide residues and maximum residue levels (MRLs) are fixed in e.g. Regulations EC 839/2008 and 750/2010 for (dried) hops, but:

  How to judge residues in hop products?

- Regulation EC 396/2005; Chapter III, Article 20:

  "MRLs applicable to processed and/or composite products
  1. Where MRLs are not set … taking into account changes in the levels of pesticide residues caused by processing and/or mixing.
  2. Specific concentration or dilution factors for certain processing and/or mixing operations or for certain processed and/or composite products may be included in the list in Annex VI. …"

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FOCUS ON

Extraction with CO_2

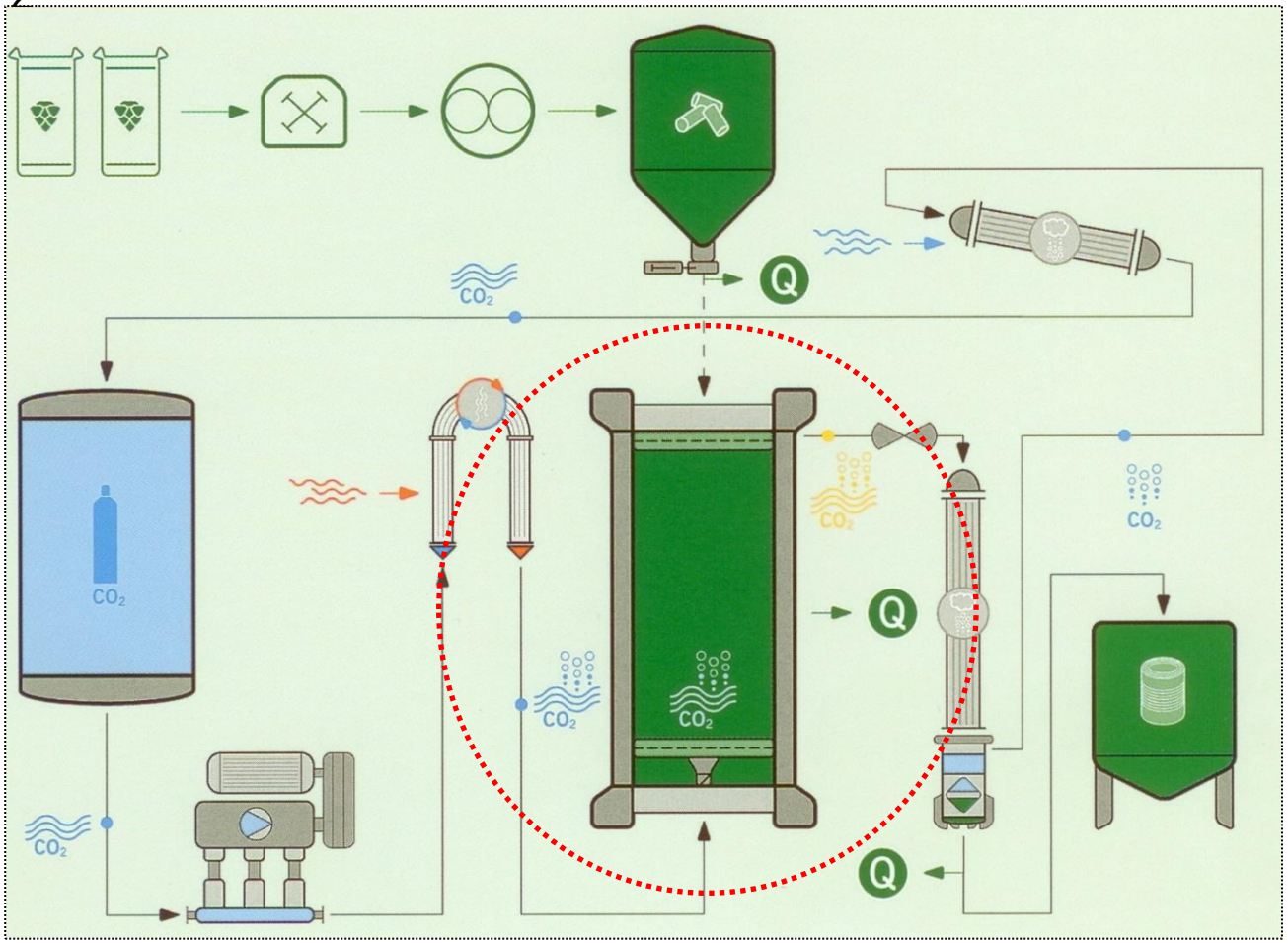
Extraction with ethanol

Production of lupulin-enriched pellets

MAIN PRODUCTION STEPS

Extraction with CO_2:

- Starting
- Extraction
- Decrease in pressure
- Evaporation
- Separation
- Condensation
- Homogenising
- Filling
- Packaging



source: CMA „The spirit of beer“

EXTRACTION WITH CO_2

"Definite non-polar residues could be detected in the resin extract quantitatively" and "Polar active agents remained in the spent hops"
(Forster et al.; Poster EBC Congress 1991, Lisbon)

Solubility is the most important parameter. But the scenery of active agents has changed since then totally. Therefore the following active agents (fungicides) with actual relevance were monitored during the extraction process:

azoxystrobin (Ortiva ®)	quinoxyfen (Fortress ®)
dimethomorph (Forum ®)	tolylfluanid (Euparen ®)
folpet (Folpet ®)	triadimenol (Bayfidan ®)
myclobutanil (Systhane ®)	trifloxystrobin (Flint ®)

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RESULTS (mg/kg) FOR ONE BIG EXTRACTION BATCH

active agent	MRL (EU)	hops (pellets)	CO_2-extract	mg/kg α
azoxystrobin	20	0.5	3.6	6
dimethomorph	50	< 0.1	0.2	<1
folpet	150	11.5	27	47
myclobutanil	2	0.3	2.5	4
quinoxyfen	0.5	0.2	0.6	1
tolylfluanid	50	0.1	0.6	1
triadimenol	10	0.3	3.2	5
trifloxystrobin	30	< 0.05	0.2	<1

residues in spent hops: <0.1 mg/kg or not detected

ENRICHMENT BY CO_2-EXTRACTION

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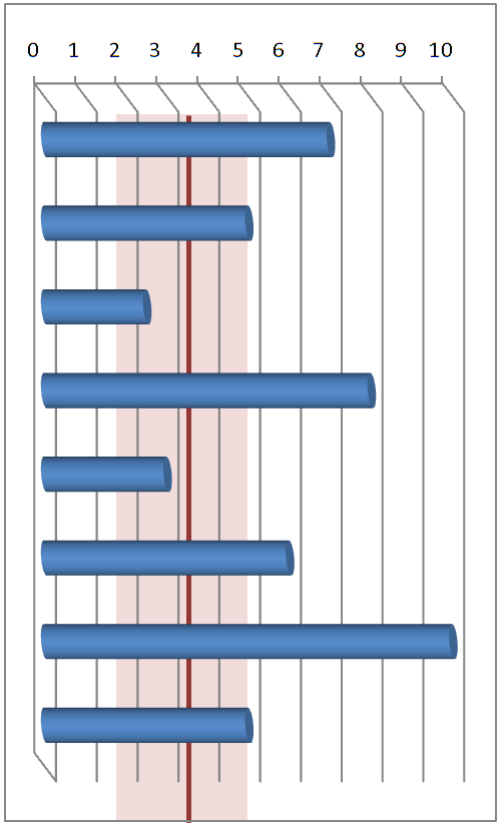
active agent	enrichment factor
azoxystrobin	7
dimethomorph	5
folpet	2.5
myclobutanil	8
quinoxyfen	3
tolylfluanid	6
triadimenol	10
trifloxystrobin	5
alpha acids (HPLC)	3.2



examples for US hops	boscalid	pyraclostrobin	spirodiclofen
enrichment factor	1.8 – 6.4	3.1 – 5.1	2.4 – 7.1

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RESIDUES IN CO_2-EXTRACTS 2009 (when applied and detected)

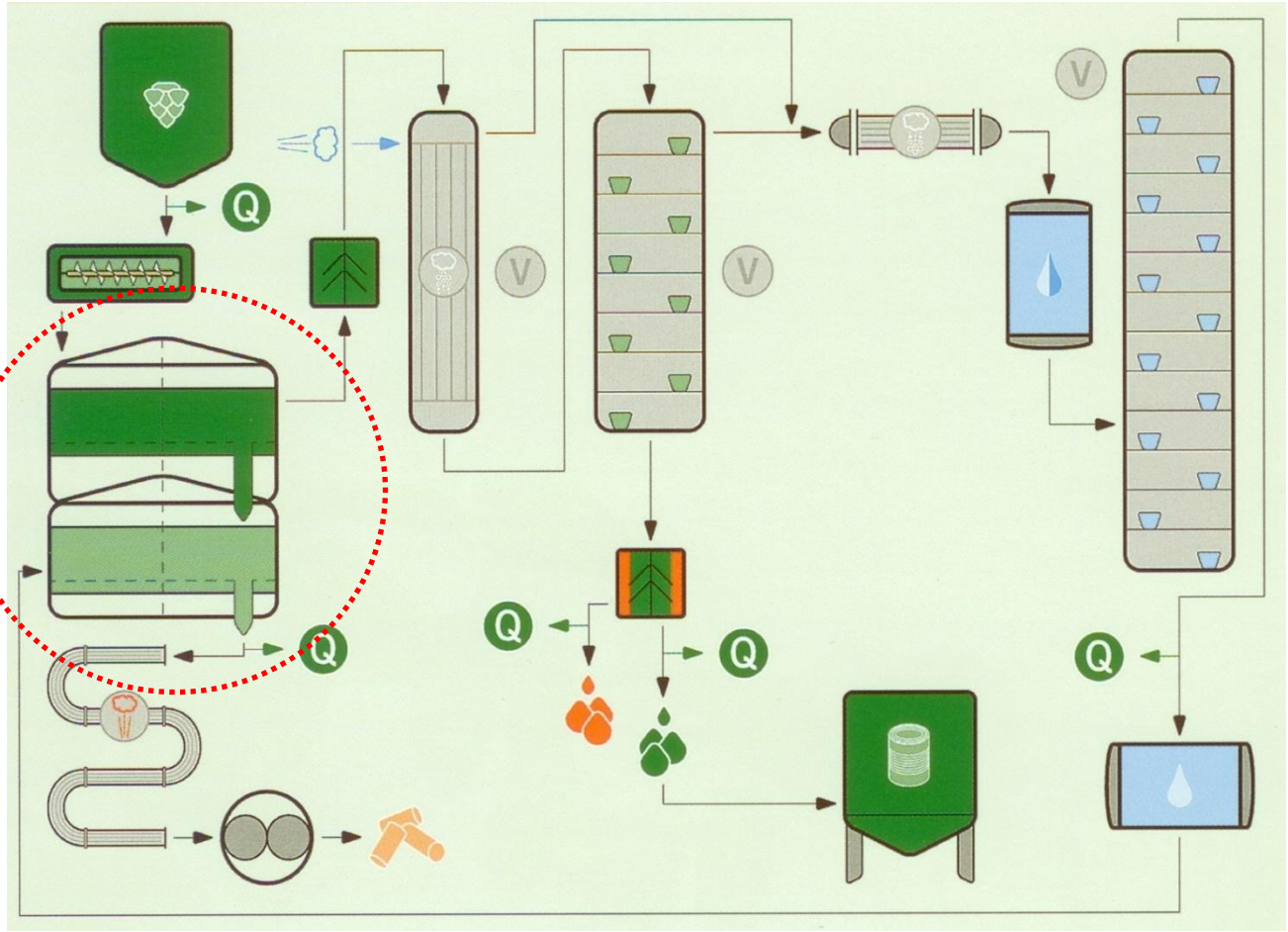
active agent [mg/kg]	range of residues in CO_2-extract	MRL in EU (for hops)	max in extract / MRL (for hops)
azoxystrobin	1.6 – 8.4	20	0.42
dimethomorph	2.5 – 7.1	50	0.14
folpet	9.1 – 173	150	1.15*)
myclobutanil	0.5 – 2.4	2	1.2*)
quinoxyfen	0.2 – 1.5	0.5	3.0*)
triadimenol	1.1 – 1.2	10	0.12
trifloxystrobin	14.4 - 77	30	2.57*)

*) no breach of regulations!

MAIN PRODUCTION STEPS

Extraction with ethanol:

- Extraction
- Evaporation
- Homogenising
- Filling
- Packaging



source: CMA „The spirit of beer“

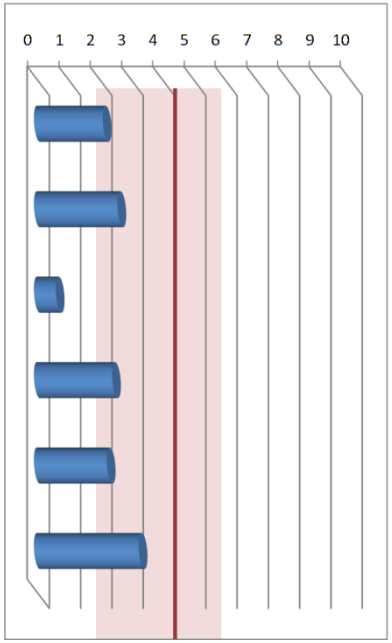
RESULTS (mg/kg) FOR ONE BIG EXTRACTION BATCH

active agent	MRL (EU)	hops	EtOH-extract	recovery	mg/kg α
azoxystrobin	20	1.9	4.2	55 %	9
dimethomorph	50	0.9	2.4	66 %	5
folpet	150	21.0	14.6	17 %	32
myclobutanil	2	0.2	0.5	62 %	1
quinoxyfen	0.5	0.3	0.7	58 %	1
trifloxystrobin	30	1.7	5.7	83 %	13

source: Hopsteiner

ENRICHMENT BY ETOH-EXTRACTION

active agent	enrichment factor
azoxystrobin	2.2
dimethomorph	2.7
folpet	0.7
myclobutanil	2.5
quinoxyfen	2.3
trifloxystrobin	3.4
alpha acids (LCV)	4.0



source: Hopsteiner

CONCLUSION FOR EXTRACTS

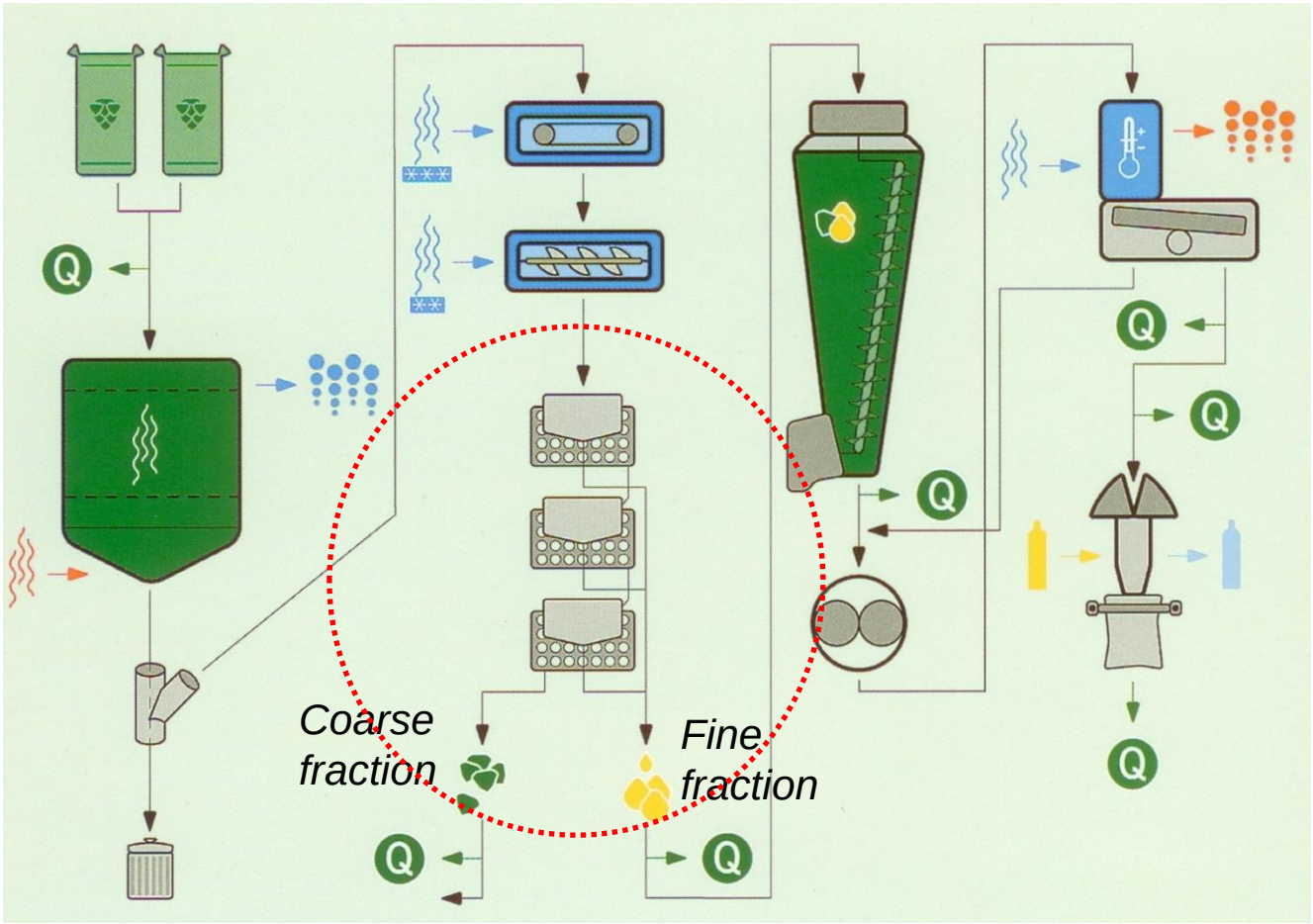
- For all analysed active agents the „yields“ are comparable to the yields or the enrichment of the alpha level.
- For judging pesticide residues in CO_2 and EtOH extracts the enrichment factor given by the extraction process must be taken in account. Depending on the hop variety (different alpha levels) the enrichment factor can vary from 2.5 to 10.
  To cover most varieties the proposal is to use 5 as factor.
- The states of the two publications*) from the 1990ies must be revised for the actually used active agents.

*) Brauwelt 130, 930-939, 1990 and Proceedings of the 23rd EBC Congress Lisbon, 193-200, 1991

MAIN PRODUCTION STEPS

Production of lupulin-enriched pellets:

- Drying
- Cleaning
- Deep freezing
- Milling
- Sieving
- Standardising
- Homogenising
- Pelletising
- Cooling
- Packaging



source: CMA „The spirit of beer“

PRODUCTION OF LUPULIN-ENRICHED PELLETS

Traditionally: “Type 45” = 45kg pellets produced from100 kg hops

Nowadays: Flexible enrichment of alpha-acids (standardization of alpha acid contents) determines the yield of the product quantity.

Example	Hops	Pellets
Alpha content	8.7 %	12.0 %
Quantity	10 000 kg	7 250 kg
Yield (Quantity)	-	72.50 %
Enrichment factor	-	1.38

27.50 % from whole quantity removed as coarse fraction

CALCULATION OF THE DISTRIBUTION

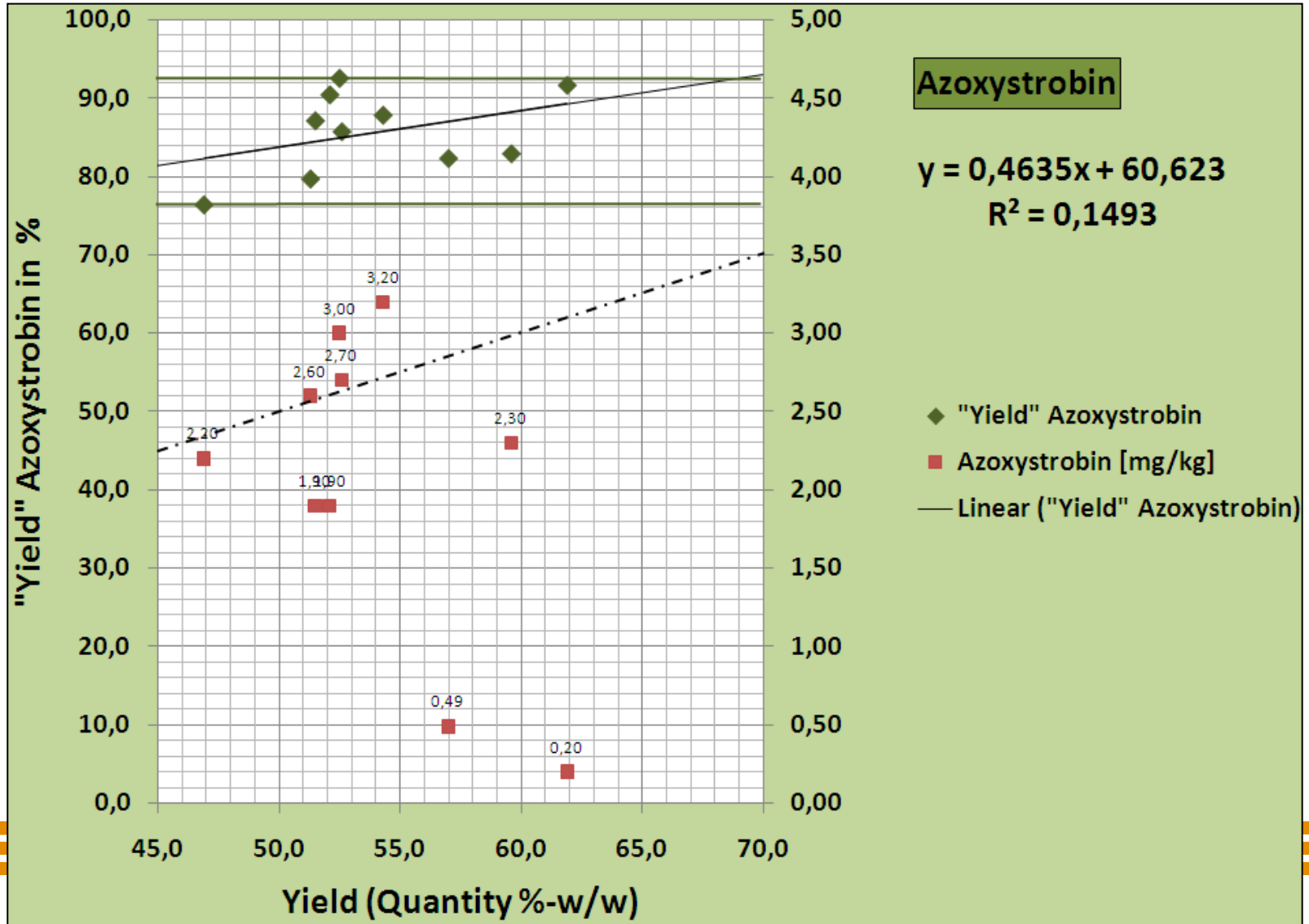
- Recovery in the fine fraction (=pellets):
  How much of the residues of each active agent (total of residues in both fractions) can be found in the pellets?
- Depending on the yield (enrichment factor with regard to alpha)
- When distribution is even, both percentages must be the same.
  On the other side it means:
  - 100%: whole quantity of the residues in the fine fraction
  - 0%: whole quantity of the residues in the coarse fraction

YIELD AND “YIELDS”

The yields (quantity) of ten different pellet production lots compared with the “yields” of the active agents (examples):

Yield (Quantity %-w/w)	46.9	51.3	51.5	52.1	52.5	52.6	54.3	57.0	59.6	61.9
azoxystrobin [mg/kg]	*2.20*	*2.60*	*1.90*	*1.90*	*3.00*	*2.70*	*3.20*	*0.49*	*2.30*	*0.20*
"Yield" azoxystrobin	76.4	79.7	87.1	90.4	92.5	85.7	87.8	82.3	82.9	91.6
dimethomorph [mg/kg]	*1.30*	*1.30*	*0.44*	*3.30*	*2.20*	*5.00*	*3.20*	*9.70*	*0.19*	*0.53*
"Yield" dimethomorph	75.7	79.2	82.4	83.7	88.7	82.2	86.4	87.1	73.7	79.0

RESIDUES AND RECOVERY IN THE FINE FRACTION (EXAMPLE)



RECOVERIES

Yield (Quantity %-w/w)	46.9	51.3	51.5	52.1	52.5	52.6	54.3	57.0	59.6	61.9
azoxystrobin	76.4	79.7	87.1	90.4	92.5	85.7	87.8	82.3	82.9	91.6
dimethomorph	75.7	79.2	82.4	83.7	88.7	82.2	86.4	87.1	73.7	79.0
flonicamid						58.1				57.1
folpet	90.4	94.4	92.8	84.0	85.9	92.8	94.1	90.9	80.0	79.0
myclobutanil	78.0	78.4	77.3	85.3	84.4	87.5		90.3	68.6	72.1
quinoxyfen	68.5	74.9	93.3	81.3	76.4	73.5			60.7	73.9
spiroxamin									94.8	
tolylfluanid	72.6									
triadimenol	57.0	51.3	97.0			76.0			84.9	
trifloxystrobin	77.3	76.5	88.0	80.4	84.4	86.3	89.1	92.7	83.0	76.1
pymetrozin								87.7		
copper	60.8							80.5		
phosphoric acid				57.0		100.0				
imidacloprid					100.0				100.0	

CONCLUSION FOR PELLETS

- For all analysed active agents the „yields“ are higher then the yields with regard to alpha.
- The attempt to draw lines of best fits fails because of their bad regressions.
- For the comparison of residues in lupulin-enriched pellets and the MRL‘s the enrichment factor has to be taken into account.
  To cover most cases the proposal is: to use 2 as factor.
- The states of the two publications*) from the 1990ies must be revised for the actually used active agents.

*) Brauwelt 130, 930-939, 1990 and Proceedings of the 23rd EBC Congress Lisbon, 193-200, 1991

SUMMARY

- According to the regulations EC 839/2008, EC 750/2010 and EC 396/2005 the question was:

  How to judge residues in hop products?

- Proposals:
  - For extracts (CO_2 and EtOH): 5 * MRL (hops)
  - For lupulin-enriched pellets: 2 * MRL (hops)

- Although these factors are proposed usually the use of hop products reduces the input of active agents into the brewing process.

COMPARISONS

active agent	ADI (mg/70kg)	Beer *) [mg/l] „worst case“	strawberries MRL [mg/100g]	grapes MRL [mg/100g]	tomatoes MRL [mg/100g]
azoxystrobin	14	0.018	1	0.2	0.3
dimethomorph	3.5	0.033	0.005	0.3	0.1
folpet	7	n.d.	0.3	0.002	0.02
myclobutanil	2.1	0.002	0.1	0.1	0.03
quinoxyfen	14	n.d.	0.03	0.1	0.002
tolylfluanid	7	n.d.	0.5	0.5	0.3
triadimenol	3.5	n.d.	0.05	0.2	0.1
trifloxystrobin	7	0.002	0.05	0.5	0.05

*) 14 + 7 g α/hl spiked pellets dosed with residues = MRL
Schmidt et al., EBC Poster 2007, Venice (I)

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THANK YOU!

Joh. Barth & Sohn
hops are our world

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... for your attention!