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Disinfestation of table grapes with pure phosphine – residues and quality aspects

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Institute for Stored Product Protection; Dagmar Klementz

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Nov. 2005

Federal Biological Research Centre for Agriculture and Forestry (BBA)

Berlin, Germany

www.bba.de



Fumigation station of the Institut for Stored Product Protection



- two steel grain bins (10t capacity)
- 340m³ fumigation hall
- a gas analytical lab
- a biological lab
- two 0.5m³ and one 3m³ vacuum fumigation chambers
- three walk-in climatic rooms

Background:

Fumigation of agricultural products for pest control in trade and for quarantine

Methyl bromide (MB) established for:

1. quick pest control prior to shipment
2. fulfilment of the requirements of trade and quarantine to obtain phytosanitary certificates

Phase OUT of MB, replacement? By phosphine??

The main question:

Is the use of phosphine

- especially in pure form from cylinders -

a good candidate

for replacing methyl bromide as

a pest control agent for perishables ?

Disinfestation of table grapes with pure phosphine – residues and quality aspects

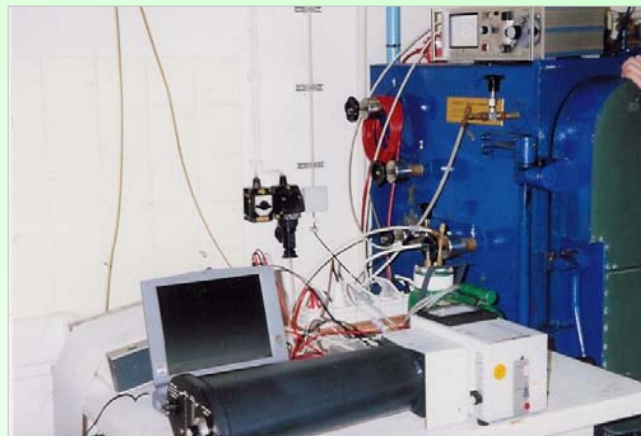
Questions:

- 1. Can we find any residues of phosphine in fumigated table grapes?**
- 2. If so, are they above the maximum residue limit (MRL)?**
- 3. Are there any quality losses in fumigated table grapes?**
- 4. If so, which kind of quality changes can be detected and are they tolerable?**

Material and methods - chemistry



Fumigation chambers



Detection of phosphine with
a Miran Infrared Analyser



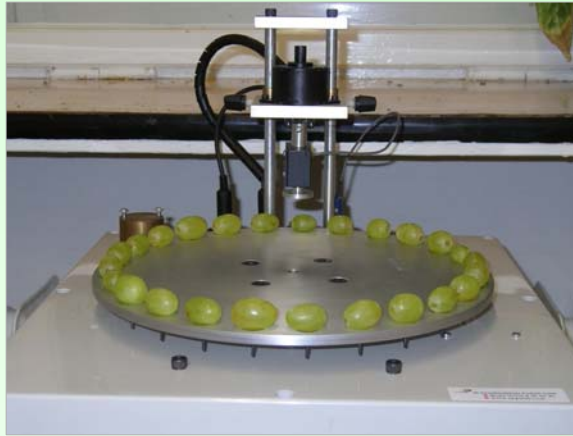
Equipment for the residue
detection of gases

- 1. Method for residue detection of phosphine**
- 2. Fumigation in chambers or in test vessels**
- 3. Phosphine residues after fumigation with headspace technique (GLP permission according to OECD since April 2004)**

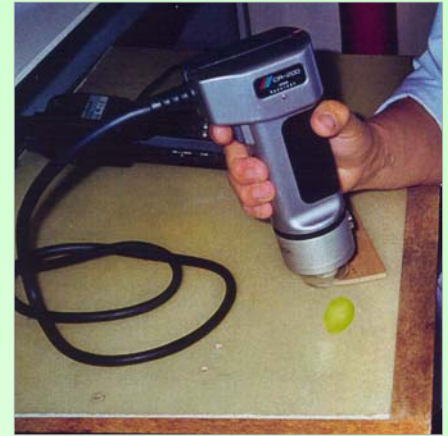
Material and methods - quality



Digital Refractometer



Fruit Firmness Tester (Firmtec)



Colorimeter (Minolta)

Identification of several quality aspects of fumigated and unfumigated grapes

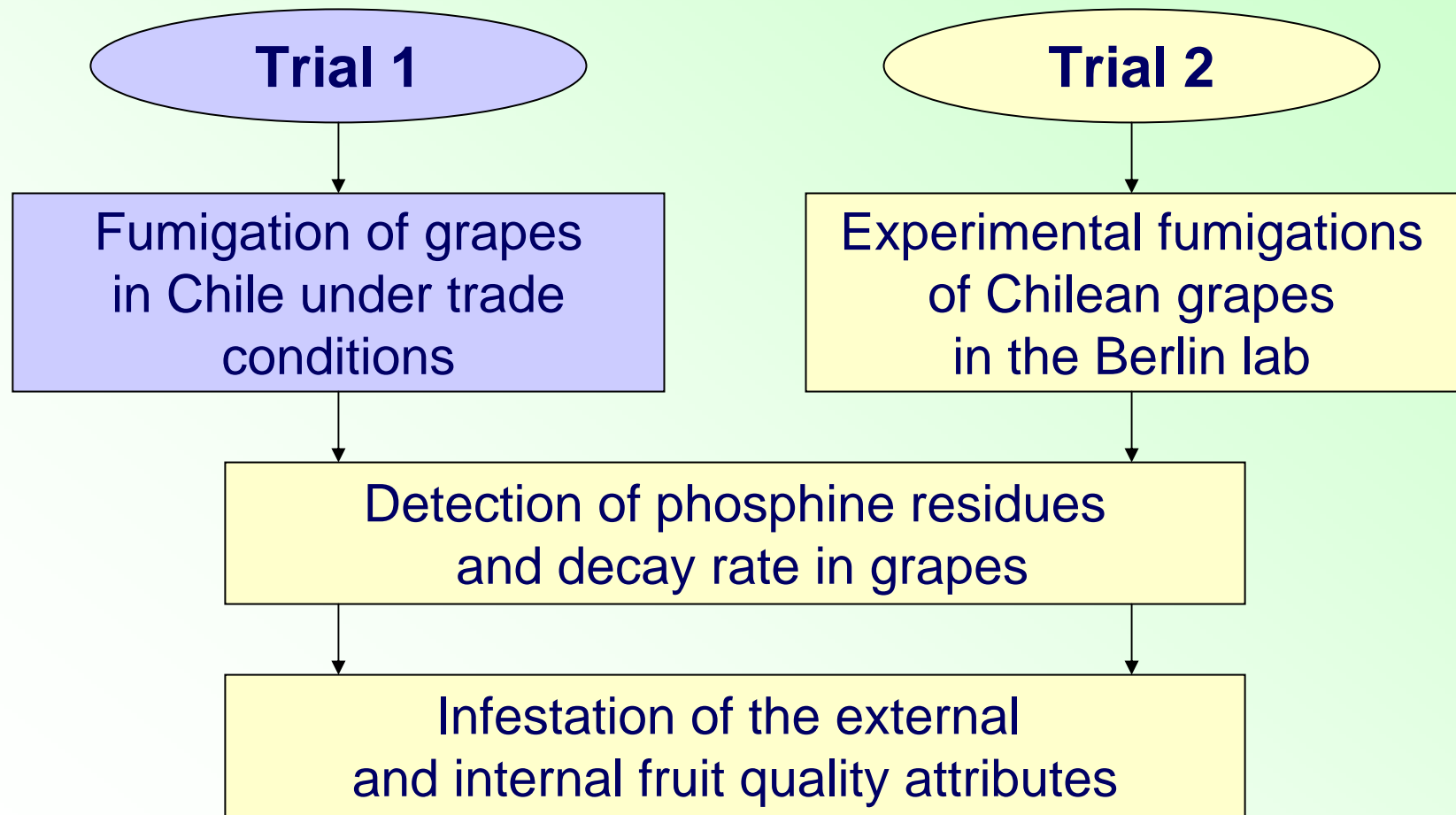
external:

maturity,
fruit peel colour,
firmness

internal:

fresh and dry weight,
juice yield (%), sugar content (°Brix),
organic acids (tartaric acid %),
sugar/acid ratio

Investigations of phosphine residues and quality aspects in fumigated grapes



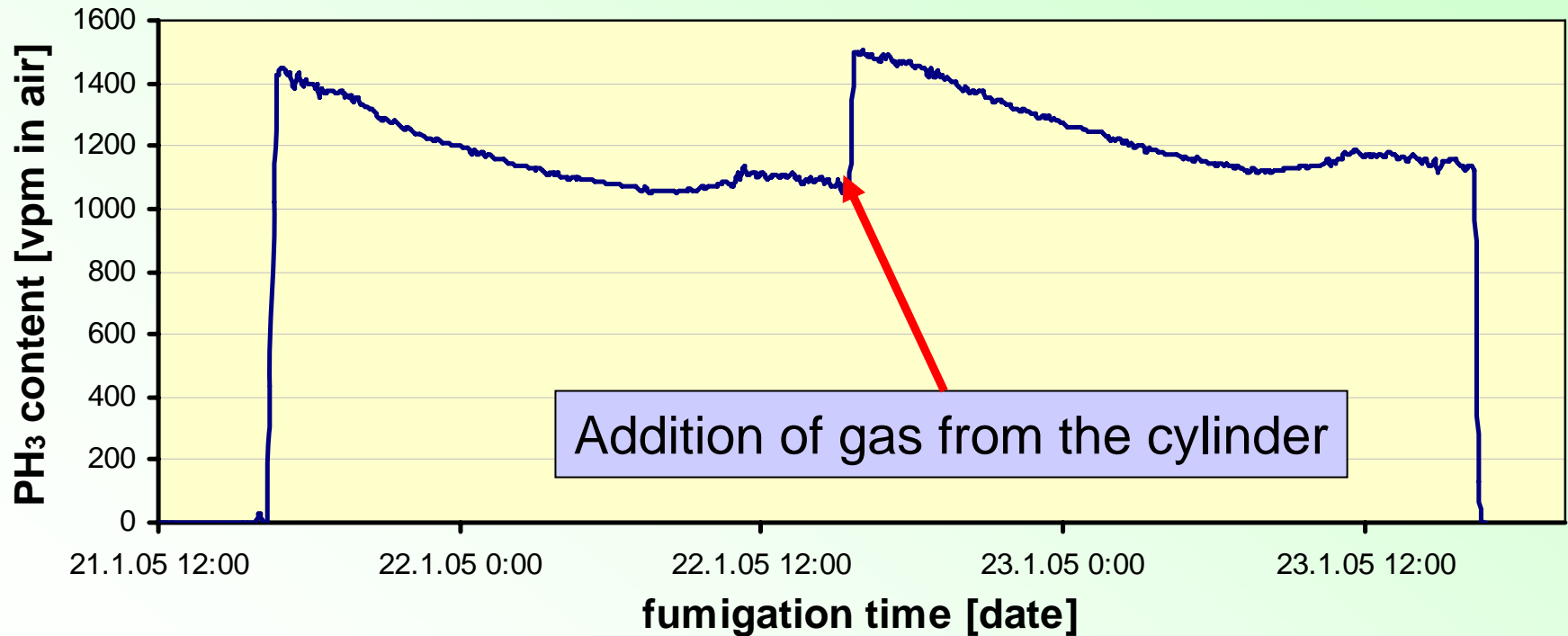
Parameter of fumigations

fumigation	Trial 1*)	Trail 2A	Trial 2B	Trial 2C
fumigation place	Chile	laboratory in Berlin		
gas development	Horn dilution system	magnesium phosphide		
active gradient	pure cylindered PH ₃	PH ₃ (95%)		
fumigation time (h)	50	48		
temperature (°C)	0	0		
store volume	344 m ³	20 l	6 l	20 l
phosphine content during fumigation (vpm)	ca. 1400	2533	1812	1815
fumigated grape varieties	'Red Globe' 'Thompson seedless' 'Flame seedless'	'Regulap'		
transport temperature (°C)	0	0		
waiting period after fumigation (days)	9	0, 1, 3, 7	not investigated	0, 1, 3, 7

*) Details according to Fosfoquim S.A.

Trial 1:

Fumigation parameter in Chile (provided by Fosfoquim S.A.)



Fumigation with 2g phosphine/m³

Trial 1:

Results after a fumigation in Chile with pure cylindered phosphine

1. PH₃-residues in grapes

- ✓ no residues above the detection limit of 0.003 mg/kg

None of the samples contained PH₃-residues above the European maximum residue limit (MRL) of 0.01 mg/kg.

Trial 1:

2. Fruit colour and texture

- ✓ only a slight variety-specific response
- ✓ no significant differences in 'Flame Seedless' grapes
- ✓ insignificantly lower fruit firmness of the treated 'Thomson Seedless' and 'Red Globe' grapes

3. Juice yield

- ✓ insignificantly lower juice yield of treated grapes of all varieties

4. Sugar/acid ratio

- ✓ no significant differences in all grape varieties

Parameter of fumigations

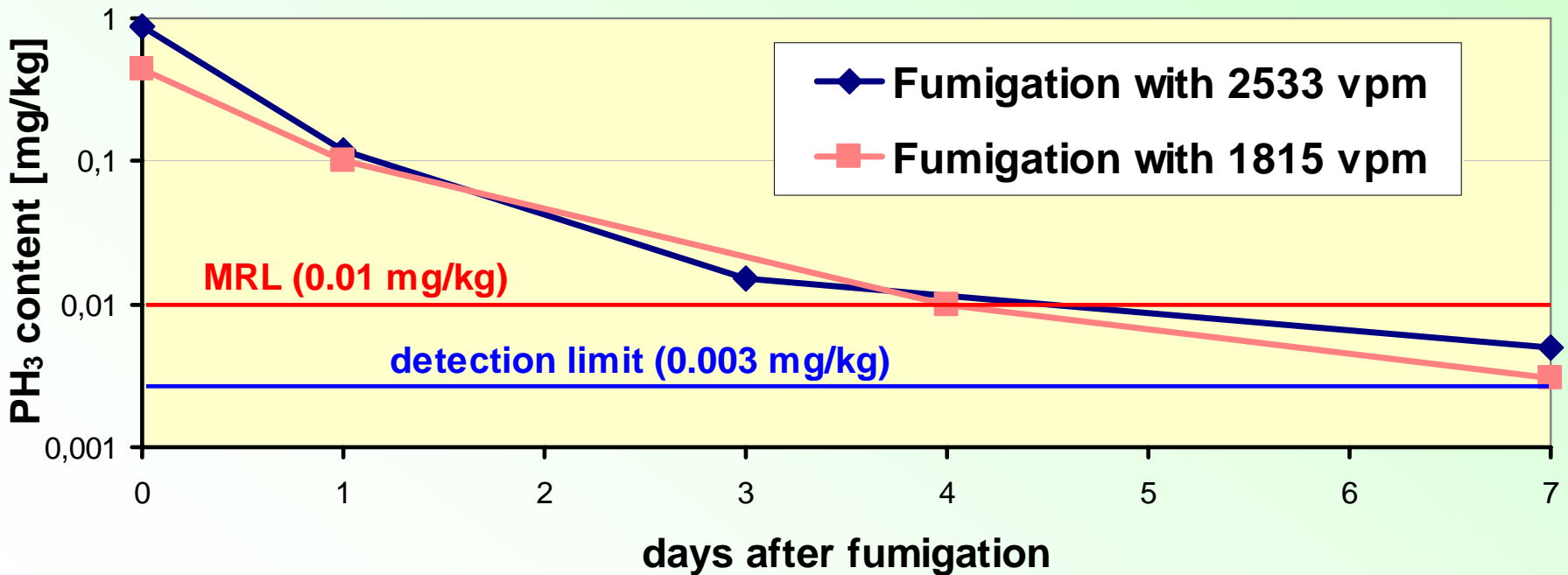
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fumigation time (h)	50	48		
temperature (°C)	0	0		
store volume	344 m ³	20 l	6 l	20 l
phosphine content during fumigation (vpm)	ca. 1400	2533	1812	1815
fumigated grape varieties	'Red Globe' 'Thompson seedless' 'Flame seedless'	'Regulap'		
transport temperature (°C)	0	0		
waiting period after fumigation (days)	9	0, 1, 3, 7	not investigated	0, 1, 3, 7

*) Details according to Fosfoquim S.A.

Trial 2:

Results after fumigation with phosphine from Mg_3P_2 of 'Regulap' grapes in Berlin

1. PH_3 -residues in grapes



MRL = maximum residue limit

Trial 2:

2. Fruit colour

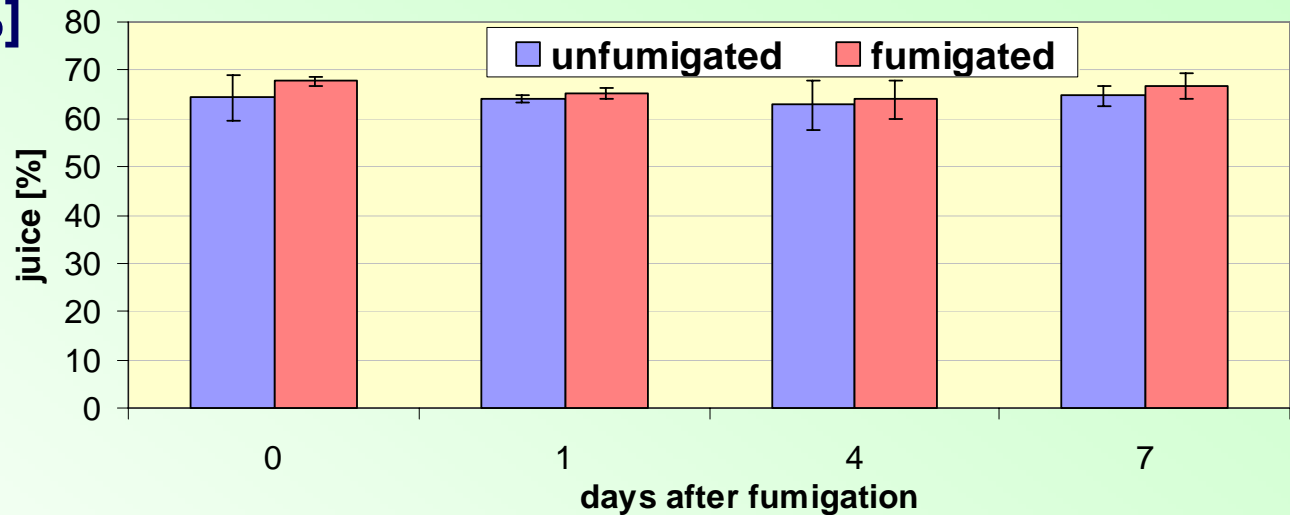
- ✓ no significant differences between fumigated and unfumigated grapes
- ✓ green and yellow colour remained nearly unchanged
- ✓ tendency: loss of the berries lightness

3. Texture

- ✓ considerably higher firmness immediately after fumigation!
- ✓ during storage of seven days the fumigated grapes lost firmness slightly more than the untreated grapes

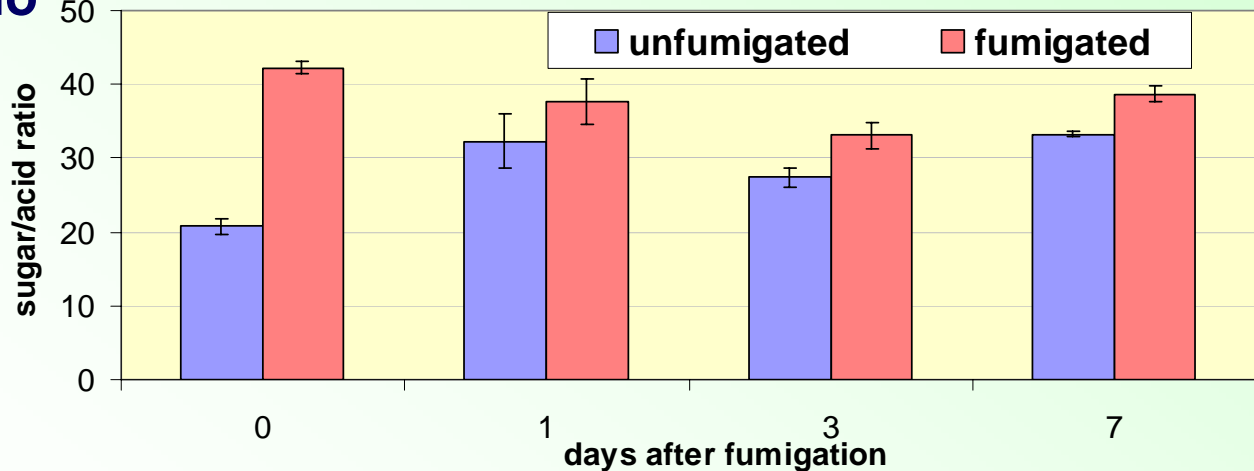
Trial 2:

4. Juice yield [%]



Fumigation with 1812 vpm
(Trial 2B; 18.1.2005)

5. Sugar/acid ratio



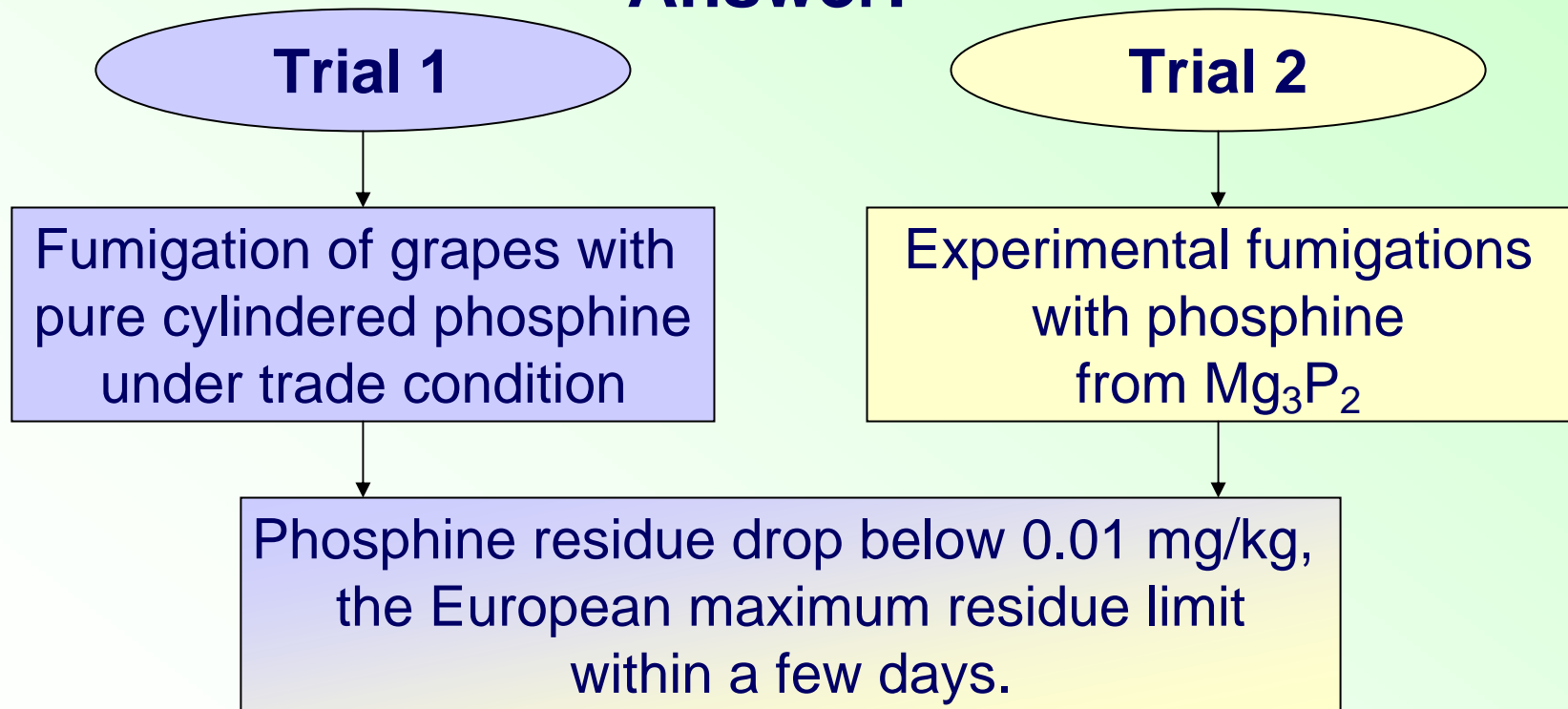
Fumigation with 2533 vpm
(Trial 2A; 8.1.2005)

CONCLUSIONS - chemistry

Question:

Phosphine residues in grapes after fumigation? MRL problems?

Answer:

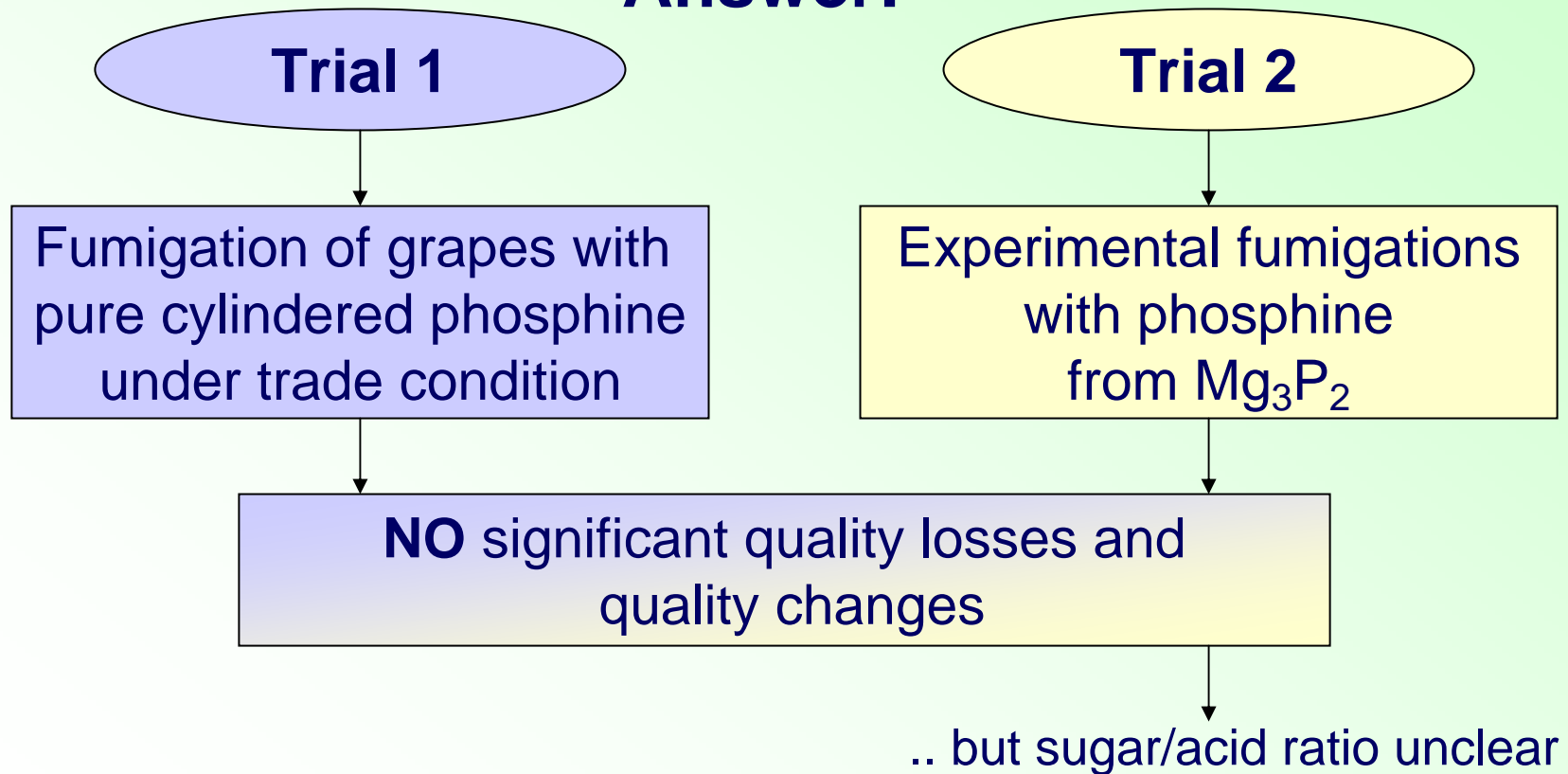


CONCLUSIONS - quality

Question:

Quality losses or quality changes tolerable?

Answer:



CONCLUSION

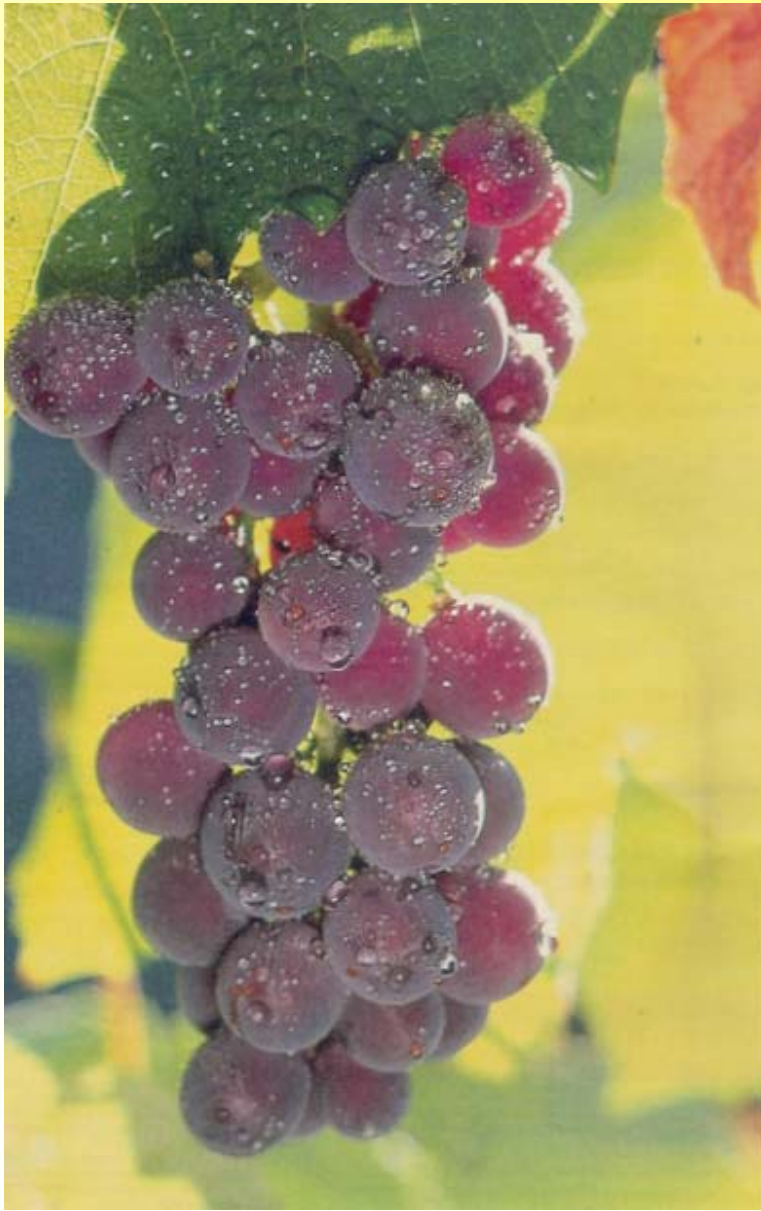
Main question:

Use of phosphine a good candidate for replacing MB?

Answer:

Yes !

The study indicated opportunities for the replacement of MB for pest control in perishable products with pure cylindered phosphine including quarantine.



THEREFORE

TO DO

- we have to ..
 - .. establish the fumigation method for various other perishable products, like kiwi fruits, strawberries, cherries
 - .. determine the lethal dosages for the related pests in the lab and under field conditions
 - .. check the suitability for export and quarantine: length of transport, quality aspects
- we should ..
 - .. implement the new results into national and international import and export legislation



➤ want to ...

.. say THANK YOU
to all colleagues
from the BBA and
the Humboldt University

.. say THANK YOU to
Dr. Franziskus Horn and
his Team of Fosfoquim

.. say THANK YOU to all my domestic and
overseas 😊! friends



Mrs. Huyskens-Keil



Mr. Reichmuth



Mrs. Reichmann





Thank you
for
your attention



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Development of a method for detection of phosphine residues in table grapes



experiment No	PH ₃ dosage in air [vpm]	desorption after "x" days
1 and 4	1500	1, 2, 6, 13
2	1500	6, 13
3	1000	13
5	1500	2, 6, 13
6	1500	6, 13

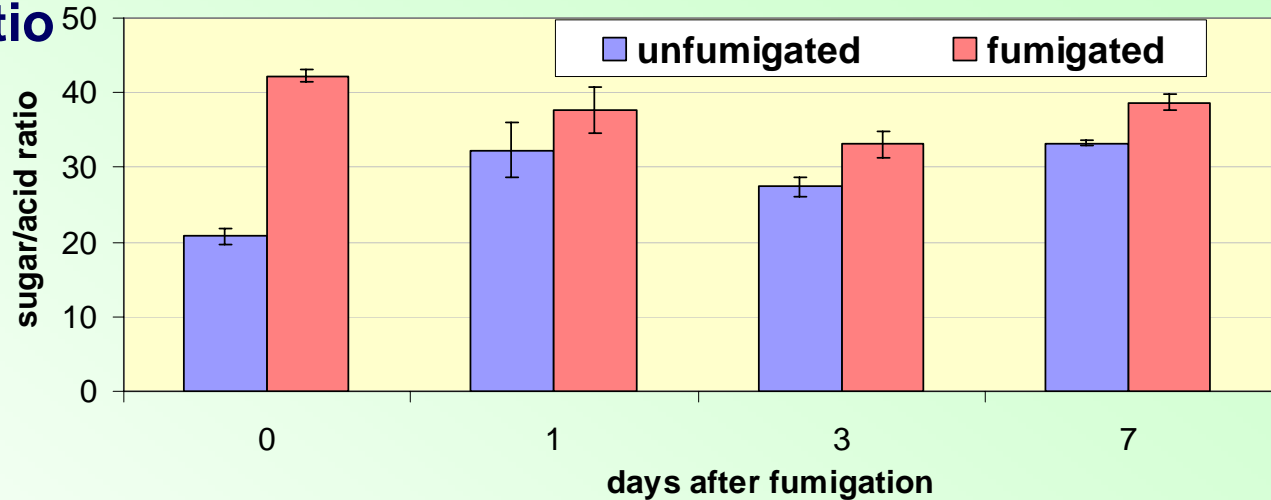
0.01 mg/kg = maximal residue limit (MRL)

0.005 mg/kg = quantitative detection limit

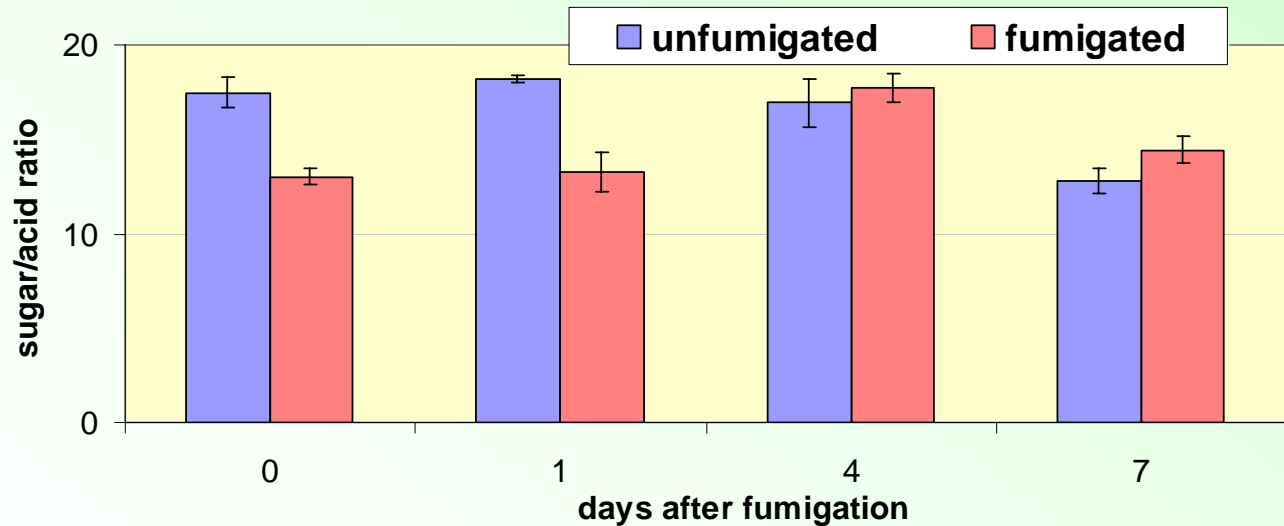
0.003 mg/kg = qualitative detection limit

Trial 2:

5. Sugar/acid ratio



Fumigation with 2533 vpm
(Trial 2A; 8.1.2005)



Fumigation with 1812 vpm
(Trial 2B; 18.1.2005)