

MBAO-Tagung in San Diego, CA, USA , 2005

**Fumigation of table grapes with pure phosphine for pest control –
residues and quality aspects**

**Klementz, D.¹⁾ Heckemüller, H.^{1/2)}; Reichmuth, Ch.¹⁾; Huyskens-Keil, S.²⁾;
Büttner, C.²⁾; Horn, F.³⁾; Horn, P.³⁾**

¹⁾ Federal Biological Research Centre for Agriculture and Forestry, Institute for Stored Product Protection, Königin-Luise-Straße 19, 14195 Berlin, Germany

²⁾ Humboldt University Berlin, Institute for Horticultural Sciences, Section Quality Dynamics/Postharvest Physiology, Lentzeallee 55-57, 14195 Berlin, Germany

³⁾ Fosfoquim, Santiago, Chile

Project:

Phosphine of high purity in mixtures with air is discussed as a replacement fumigant for the ozone depleting methyl bromide against *Pseudococcus spp*, *Cydia pomonella*, *Proeulia spp.*, *Naupactus xanthographus* and *Ceratitidis capitata*. These pest insects occur on perishable products like table grapes. In contrast to methyl bromide, phosphine does not remain a stable residue in fumigated fruit, and after its release into the ambient atmosphere by photolytic processes it is transformed into harmless amounts of phosphoric acid and phosphates.

The present study reports on results of fumigant residues and fruit quality during storage of various table grapes after treatment with pure phosphine in air.

Experiments:

Trial 1

Fumigation in Chile under practise conditions

The study comprised table grapes of the varieties 'Red Globe', 'Thompson Seedless' and 'Flame Seedless'. The fumigant consisting of pure phosphine (PH₃) is commercially known as VAPORPH₃OS and available from the Canadian company Cytec. The application uses a dilution system with air, distributed by the Chilean company Fosfoquim. In Chile, 2.0g phosphine/m³ in air (about 1500vpm phosphine in air) served to fumigate the grapes for 48h at 0°C.

Phosphine detection

Within 9 days after the fumigation, the fumigated grapes and untreated reference samples arrived at the laboratory in Berlin. During transportation, they were continuously kept at 0°C. Using a head space technique, the grapes were processed to release the possible phosphine residues. The determination of the residues by gas chromatography and mass selective detector had a quantitative determination limit of 0.005mg/kg and a qualitative detection limit of 0.003mg/kg.

Trial 2

Experimental fumigation and residue determination in the laboratory

Untreated Chilean table grapes of 'Regulap' were exposed in three different trials for 48h at 0°C to 2533vpm, 1812vpm and 1815vpm phosphine in air. Phosphine was developed from magnesium phosphide.

Again, the temperature of 0°C was kept constant during transport from Chile, fumigation and storage in Berlin.

Analysis of Fruit Quality

Beside the phosphine residues, both trials investigated external and internal fruit quality attributes of the grapes according to EU quality standards. The investigation was conducted in trial 2 after 0, 1, 3 (4) and 7 days of storage. The quality assessment included the fruit peel colour (L*a*b*-system [McGuire, 1992], fruit firmness (Firmtec, UP GmbH, Germany), fresh and dry weight, juice yield (%), sugar content (%Brix), organic acids (tartaric acid %), sugar/acid ratio.

Results and discussion

Trial 1 (fumigation in Chile)

In all grape varieties investigated, the phosphine residues were below the detection limit of 0.003mg/kg. So, none of the samples contained residues above the European maximum residue limits (MRLs) of 0.01mg PH₃/kg after nine days' transport from Chile to Germany at 0°C.

Concerning fruit colour and texture, a variety-specific response to fumigation was observed. The untreated 'Thomson Seedless' and 'Red Globe' grapes had a slightly higher fruit firmness compared to the fumigated grapes of the same varieties. No significant differences in colour and textural properties could be determined in 'Flame Seedless' grapes. The juice yield of treated grapes was lower than in the untreated reference samples of all varieties.

The sugar/acid ratio showed no significant differences between the grape varieties and treatments.

Trial 2 (fumigation in the laboratory)

Phosphine contents in the grapes were in the range of 0.44mg/kg (fumigation with 1815vpm) and 0.88mg/kg (fumigation with 2533vpm) on day "zero", which took place immediately after the fumigation and a 15-minute ventilation. Figure 1 shows that as soon as three days after storage the residues had dropped down to about 0.01mg/kg. After seven days, the PH₃-values were below the quantitative detection limit of 0.005mg/kg (fumigation with 2533vpm) and the qualitative detection limit of 0.003mg/kg (fumigation with 1815vpm) respectively, altogether below the legal maximum residue limit (MRL) in Europe of 0.01 mg/kg.

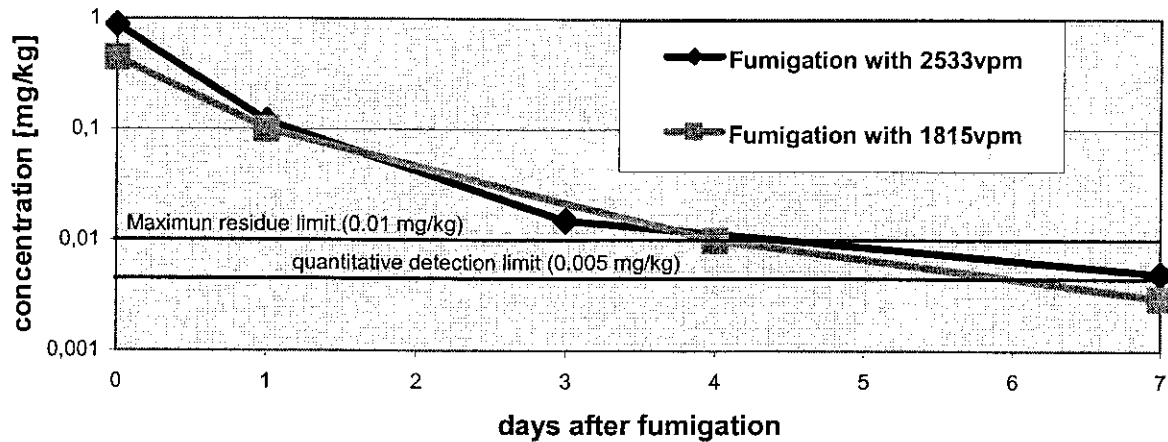


Fig. 1: PH₃-contents in table grapes 'Regulap' following a 48h treatment with phosphine (2533vpm and 1818vpm phosphine in air) developed from magnesium phosphide at 0°C

Most of the quality attributes did not differ significantly between fumigated and unfumigated grapes, e.g. the colour of the fruits ($L^*a^*b^*$). As a tendency, the lightness of the berries dropped after fumigation with no changes of the green and yellow colour values.

The firmness of 'Regulap' fruits was considerably higher in fumigated samples when using phosphine from magnesium phosphide compared to untreated grapes. During the subsequent storage of seven days, untreated and treated grapes slightly lost textural strength, especially the fumigated ones. Similar results and tendencies were observed for juice yield and sugar/acid ratio: slightly higher values for the yield (Fig. 2) and higher ratio of sugar/acid (Fig. 3) were found in fumigated grapes, presumably due to the lower acid content in fumigated grapes compared to untreated fruits.

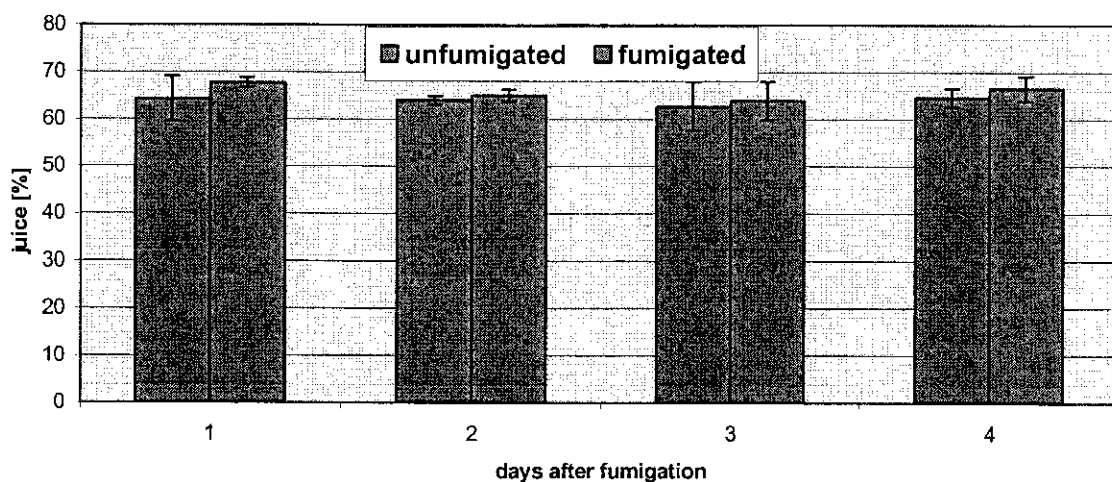


Fig. 2: Juice yield of phosphine treated and untreated 'Regulap' grapes; (treatment with 1812vpm phosphine in air)

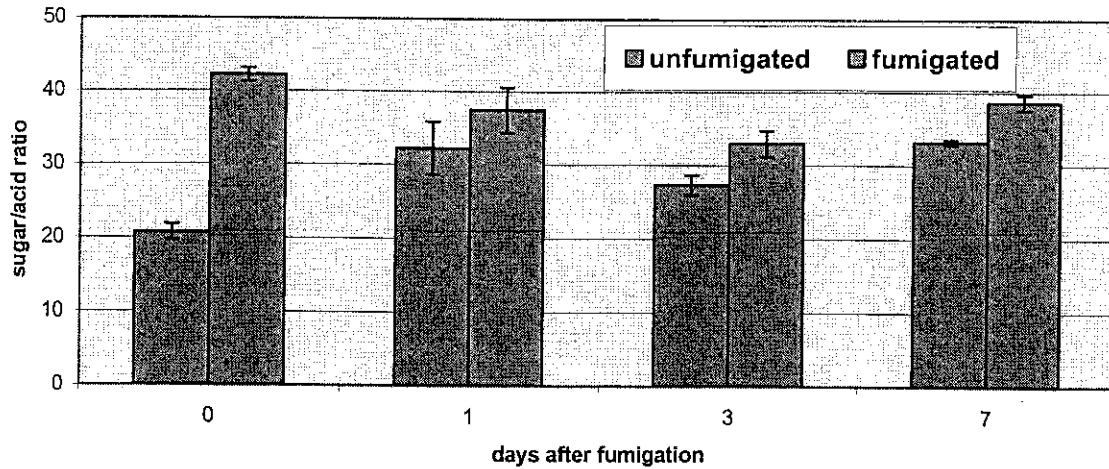


Fig. 3: Sugar/acid ratio in phosphine treated and untreated 'Regulap' table grapes; (treatment with 2533vpm phosphine in air)

Conclusion

The present investigation evidenced that pure phosphine in air is suitable to disinfest various varieties of table grapes from certain pests within 48 hours with 2g phosphine/m³ at 0°C, without changing the quality of fruits significantly. Moreover, the residues of the fumigant dropped below the legal MRL in Europe of 0.01mg/kg within a few days after the treatment. This opens opportunities to replace methyl bromide as a fumigant for these perishable products, even for quarantine purposes and other products as well.