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METHYL BROMIDE AND ETHYLENE OXIDE AS FUMIGANTS

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METHYL BROMIDE

FAO (1) published a tentative method for the detection and measurement of resistance against methyl bromide and phosphine employing adults of some major pest species of stored cereals. After exposure periods (5 hours for methyl bromide, 20 hours for phosphine), responses were determined 14 days following termination of the exposure. With reference strains of known susceptibility base-line data were established. Survival in these tests indicates resistance. Thompson (2) gave a synopsis concerning the use of fumigants, regulations, precautionary measures, and problems, culminating in the Health and Safety at Work etc. Act 1974.

During 1973 and 1974, wheat imported into the Soviet Union had to be fumigated with methyl bromide on arrival at the ports. Where no ventilation system was available, the grain was removed temporarily to a depth of 2 m during fumigant introduction. Post-fumigation ventilation was achieved by pneumatic exhausts, the time necessary to remove the gas was reduced to one half (3).

With special reference to the Soviet Union, the author reviews the main pests (Sitophilus granarius and S. oryzae) responsible for losses, precautionary measures for the disinfection of storage premises (insecticides), and the fumigation of infested grain. Main fumigants used were methyl bromide, chloropicrine, methallyl chloride and dichloroethane. Malathion is being increasingly applied as protectant (4).

Wheat fumigation with methyl bromide at a concentration-time product (CT) ranging from 4 to 20 times that used in normal practice caused a significant increase in maximum resistance to extension of dough and decrease in loaf volume. Germination was reduced but not significantly different from that of the control, except for CT values above 220 mg.h/litre (5). Containers holding 48 bags of flour were fumigated repeatedly (3 to 5 times) with methyl bromide at 15-27°C until the tolerance level of 125 ppm was reached. Residues increased with increasing temperature even though the dose was reduced (6). Repeated fumigation reduced the germination of cereal seeds corresponding directly with the number of treatments. Methyl bromide was most phytotoxic, followed by phosphine and carbon disulfide. Single fumigations had no influence on the germination of maize seeds, single treatment is therefore recommended (7).

Melons can be fumigated against the melon fly with methyl bromide (32-48 g/m^3) for 2-4 hours without effects on taste and aroma. Bromine remains below the tolerance limit (8). Methyl bromide was considered for use as an eradicant for rats infesting the wall insulation of a commercial frozen meat store. Trials under the condition of low temperature indicated that the penetration into the wrapped insulation material was virtually unimpeded. No difference was noticed in odor and flavor of fat or lean of grilled lamb chops and roast beef, even if treated at three times the level necessary for rodent control. If treated at ten times this level, results were unacceptable with regard to flavor and odor (9).

Susceptible granary weevil were repeatedly crossed with individuals from a strain resistant to methyl bromide. The progeny attained resistance prior to fumigation, which increased compared to the parent generation when subjected to methyl bromide. Resistant insects absorbed slightly less fumigant than susceptible ones during the first few hours of exposure. Resistance could not be related to rate or degree of uptake of fumigant (10).

The effectiveness of phosphine and methyl bromide against the various stages of Trogoderma variable increased with the exposure period and/or temperature. Eggs, one day old, and full grown larvae were the stages most resistant to phosphine. With methyl bromide, there was little difference in the susceptibility, although eggs of 2 days appeared to be most resistant (11). A high tolerance of acarid mites to various fumigants is generally known. Methyl bromide is the fumigant most commonly used for their control, particularly in Poland where Acarus siro is an important pest of stored products. Three periods of sensitivity were distinguished in eggs (12). Methyl bromide may be used as a fumigant for dry bulbs of Narcissus against the bulb scale mite, a CT product of 2oo-25o mg.h/litre is recommended (13).

Laboratory tests examined the penetration of methyl bromide into wheat at freezing temperatures. In columns of wheat (51 and 33-42 cm high) methyl bromide (49-5o and 32-34 mg/litre, respectively) was applied at -o.5 to -3.3°C. Penetration was better at the higher temperature but the difference was not significant (14).

In soils fumigated with methyl bromide, problems arise in connection with the remaining bromide residues. Hydrogen bromide formed on decomposition of methyl bromide in water and under soil conditions is absorbed by plants in its dissociated form. Under natural conditions, the soil has about 1-5 ppm of bromide ion. Higher levels of 8oo ppm exist for instance in Japanese volcanic soils. During soil treatment with bromine containing pesticides, the supply of bromine reaches 17o kg/ha with ethylene dibromide, 6o kg/ha with dibromo=chloropropane, and 4oo-5oo kg/ha with methyl bromide. The bromine remaining in the soil varies from 3 to 5o ppm. A level of 1oo ppm can be reached in plants, depending on the species, plant organs, general growth, soil conditions, method of application, and the amount of methyl bromide used. Foliage vegetables show the highest concentration. The uptake of bromide can be reduced by soil irrigation immediately after treatment (15).

The bromide ion content of foodstuffs is determined by a method using a bromide specific electrode. For low levels (below 1o mg/kg) and for accurate work, bromide was extracted with water and separated from interfering compounds by ion-exchange chromatography before estimation. Bromide ion can be estimated approximately by direct measurement on the aqueous extracts. The method was checked against standard methods and has been used to determine the bromide and chloride contents occurring naturally in wheat, maize, copra, soya beans and sorghum (16).

ETHYLENE OXIDE

In a greenhouse and an insectary, ethylene oxide has been tried with success to inactivate the nuclear polyhedrosis and granulosis virus, but with the cytoplasmic polyhedrosis virus only partial denaturation occurred (17).

The residual hydrins in brown rice after fumigation with a mixture of ethylene oxide and methyl bromide (85-86%) were investigated. A minute amount of the gases penetrated into the rice tissue but residues were not detectable after 48 hous of fumigation with 1o g/m^3. Hydrins (ethylene chloro- and bromohydrin, 1.o-1.4 ppm) could only be detected after fumigation with 21 g/m^3 but neither with 15.75 g/m^3 and 1o.5 g/m^3 nor after actual warehouse fumigations with 1o.5 g/m^3 (18).

American foulbrood disease recurred within two seasons in 22% of the colonies established on ethylene oxide fumigated equipment but in only 8% when the bees had received oxytetracycline initially. No recurrence has been seen with bees from infected colonies if they hived on fumigated equipment and received oxytetracycline or on uncontamined equipment (19).

Extreme shortening of the time-consuming process of eliminating the toxic substances after cold sterilization with ethylene oxide could be achieved by vacuum forced gas exchange. The sterilized material can be used 72 hours after the beginning of the sterilization process (2o).

A specific and sensitive method for the determination of ethylene oxide at the ppm level in sterilized material has been described (21). The method is simpler than others, more rapid (5o analyses per 8 hours), and more sensitive (limit 5o ppb). The ethylene oxide in the sample is volatized into the gaseous head space of an enclosed vial, and a portion of the gas is analyzed by a previously calibrated gas chromatograph.

Residues in dates fumigated with ethylene oxide showed the presence of ethylene oxide and ethylene chlorohydrin, but not of ethylene glycol or diethylene glycol. The ethylene oxide disappeared gradually when the fruit was exposed to the atmosphere, remaining less than 5o ppm after 2-3 days. Ethylene glycol and ethylene chlorohydrine in dates fumigated with a tenfold dose rose gradually as there was a slow conversion of ethylene oxide into these chemicals. In dates fumigated with the recommended dose, amounts of ethylene chlorohydrin varied between 0 and 1oo ppm (22).

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