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HYDROGEN CYANIDE FOR INSECTICIDE PHYTOQUARANTINE TREATMENT OF PACKAGE WOOD

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ABSTRACT

Currently hydrogen cyanide (HCN) is industrially produced in the Czech Republic (Lucebni zavody Draslovka Kolin) and is extensively used for Czech mill fumigation. Therefore we evaluated the potential of HCN fumigant for treatment of wooden transport packages (pallets). We tested the penetration of HCN trough wooden pallet materials using gas chromatography. The preliminary results on biological efficacy of HCN on eggs, larvae, pupae and adults of 2 test species (*Hylotrupes bajulus* and *Tribolium castaneum*)- placed in wooden chambers are presented. The results obtained can be used to establish alternative timber fumigation technologies and protocols to methyl bromide. The research was funded by a grant (QI111B065 - Ministry of Agriculture, Czech Republic.)

Key words: Fumigation, hydrogen cyanide, HCN, regulated pests, phyto-quarantine, timber, wood, pallets, *Hylotrupes bajulus*.

INTRODUCTION

There is a permanent threat of the introduction and spread of many pest organisms via infested wooden products and wood packages due to extensive international trade. The traditional regulated pests of processed wood include *Sirex*, spp. and *Urocerus* spp. However, European plant health organizations (EPPO and EFSA) have recognized several emerging wood infesting pests as a new threats, that have reached the status of regulated (phytoquarantine) organisms. They include dangerous cerambycids (*Anoplophora* sp.) and nematodes (*Bursaphelenchus* spp.). These species have been recorded in France, Germany, Austria, Italy and Portugal. However, the available phytoquarantine technology for wood treatment is very limited. The fumigant methyl bromide has been prohibited for wood phytoquarantine purposes due to its negative environmental impacts. Although the fumigant sulfuryl fluoride has been successfully tested (Buckley et al., 2010), it is not yet registered for wood phyto-quarantine . The only non-fumigant option is a heat treatment that requires chamber technology and is logistically and energy demanding. Hydrogen cyanide (HCN) is one of the remaining potential fumigation alternatives.

Hydrogen cyanide is a colorless liquid that evaporates immediately if in contact with air. Pure hydrogen cyanide with a concentration greater than 2 $g.m^{-3}$ smells of bitter almonds. As an industrial insecticide HCN is a fast-acting fumigant (respiratory poison) with a broad range of pest-control applications. Hydrogen cyanide impairs the metabolism of the pests. Historically, HCN has been extensively used to control scale insects on citrus trees starting from 1866. The development of resistance to hydrocyanic acid has been described for scale insects (Quayle 1922, 1938). Later HCN fumigation structural technology has been developed for mill disinfestations. The first mill HCN-fumigation was performed in USA in 1889 and the first industrial mill fumigation was performed in Europe in 1917. HCN was also marketed in Great Britain and USA for the purpose of grain admixture fumigation. It was a solid formulation of calcium cyanide (e.g. Cyanogas G, Cyanogas A dust).

In Germany, according to Wikipedia, "Ferdinand Flury developed Zyklon A at Degesch in 1920 and Walter Heerdt was named the official inventor of Zyklon B in a Degesch patent application from 20 June 1922. Its development was a major advance over previous methods of delivering hydrocyanic acid for pest control because of its improved chemical stability and the presence of a warning odorant. The main invention in Zyklon B consisted of the absorption of liquid hydrocyanic acid into a highly porous adsorbent. Initially, heated diatomite (diatomaceous earth) was used as an adsorbent. Later, high-porosity gypsum pellets called Ercodice (described by eye witnesses as "crystals") as well as disks made from wood fiber were also used. The adsorbed hydrocyanic acid was very safe in handling and storage when placed in inexpensive airtight cans of various sizes. From 1929 onwards the U.S. used Zyklon B to disinfect the freight trains and clothes of Mexican immigrants entering the US."

Nowadays the only available HCN canned formulation for pest control fumigation is produced in the Czech Republic by Lucebni zavody Draslovka a.s. Kolin under the trade name URAGAN D2 (Stejskal and Adler, 1997). URAGAN D2 is stabilized, liquid hydrogen cyanide (HCN) fully soaked in porous material and sealed in gastight tins. It is stabilized with phosphoric acid (0.1%) and sulfur dioxide (0.9 – 1.1 %). URAGAN D2 is packaged in 0.40-0.45 mm thick tins. One tin contains 1.5 kg of hydrogen cyanide absorbed in cardboard paper reels with a diameter of 145 mm, with a central opening of 30 mm and a thickness of 4 mm.

In Europe, HCN has been traditionally used for structural fumigation. HCN was employed for insecticide fumigation of wooden parts of historical buildings, churches in particular. HCN fumigation method has been used to treat parts of the gallery as well as the structural woodwork, which had been infested by various wood pests. This method does not provide protection against pest reoccurrence. Despite the toxicity of the substance, no accidents have been reported for this type of structural fumigation (Germar, 2003). Cases of damage to the facilities themselves have also been very rare. The only exception was discoloration of some type of plaster. The highly reactive cyanide ion combines with iron ions to form, among other things, the complex salt known as Prussian Blue (Grosser and Roßmann 1974, Emerling 1995, Germar, 2003).

Because of HCN's good insecticidal and fumigation properties and commercial availability we evaluated the potential of HCN fumigant for treatment of wooden transport packages (pallets). We tested the penetration of HCN through wooden pallet materials using gas chromatography. The preliminary results on biological efficacy of HCN on eggs, larvae and adults of 2 test species placed in wooden chambers, *Hylotrupes bajulus* (L.) and *Tribolium castaneum* (Herbst), - - are presented.

MATERIAL AND METHODS

Fumigation chamber, HCN formulation and concentration estimation

All experiments were performed in the hermetic fumigation chamber (volume 650 L) with air circulation located at Lucebni zavody Draslovka a.s. Kolin, Czech Republic. Ambient temperatures were 20-25°C. HCN was used in a cooled (5°C) and liquid form (stabilized 0,01% H_2SO_4) and applied in a fumigation chamber by syringe via a rubber septum. Fumigation chamber HCN-in-air concentrations (inside / outside = headspace / wooden-spruce block) were estimated by GC (Shimadzu GC-17A, RT-QPLOT, 30m, ID 0,53mm, GC Software Clarity DataApex v. 2.6.6).

HCN wood penetration and desorption

Five spruce (*Picea alba*) wooden blocks (100 x 100 x 150 mm; Fig. 1) were placed in the 650-L experimental fumigation chamber. The required dose (20 $g.m^{-3}$) of HCN was injected into the fumigation chamber and the HCN rate of penetration into the central cavity of each spruce block during a 50-h exposure was assessed. Air samples were taken from the central spruce block cavity (see "extraction chamber" in Fig. 1) using a syringe via the block's rubber septum, as well from the fumigation chamber headspace. After the 50-h exposure the chamber was quickly ventilated and closed. Then we continually measured HCN concentrations (i.e. desorption from the spruce blocks) outside (headspace) and inside blocks.

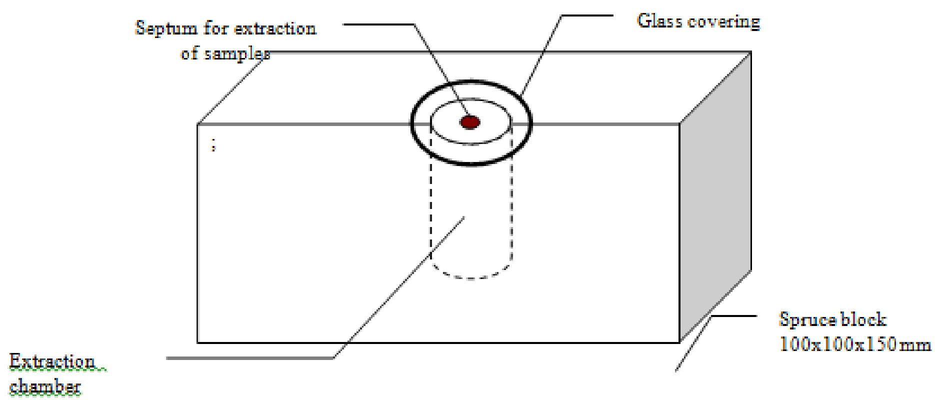

Fig. 1- Experimental spruce block (100 x 100 x 150 mm). It is equipped with an extraction chamber and rubber septum enabling continual air sampling for HCN concentration from the central part of the wooden block.

Efficacy of HCN on *Tribolium castaneum* (Tenebrionidae)

Experimental individuals of *Tribolium castaneum* were taken from insecticide susceptible RICP strain (Crop Research Institute, Drnovska 507, 161 06 Prague 6, CZ). We estimated the effect of exposure period (15, 60, 120 and 180 min) on mortality of eggs, larvae, pupae and adults of *T. castaneum* at the HCN dosage of 20 $g.m^{-3}$. After exposure the insects were transferred into Petri dishes. Experimental conditions were 22ºC ± 1ºC, 60% r.h. We checked adult and larvae mortality after 48 h and pupal and egg mortality after 288 h (12 days). We compared mortality for each exposure period and insect stage by Kruskal-Wallis using Statistica Version 10.

Efficacy of HCN on Long horn beetle *Hylotrupes bajulus* (Cerambycidae)
The test was performed in the fumigation chamber at Lucebni zavody Draslovka a.s. Kolin with HCN at 2% (concentration 24 g.m^{-3}) for 24 h. All stadia were taken from the laboratory *Hylotrupes bajulus* stocks; they were cultivated and provided by the personnel of Timber Institute s. e. (Na Florenci 7-9, 111 71 Praha 1- Czech Republic). **Larvae:** Larvae (6/block) were fixed in 10 wooden blocks. Two untreated blocks were taken as control. The size of each block was 150±2 x 100±2 x 25±2 mm. The mortality check was made after 24 h of wooden block ventilation. **Adults:** We tested 10 adults (5 males, 5 females) and 2 adults were left untreated as a check. The mortality check of the exposed adults was made after 24 h of wooden block ventilation. **Eggs:** 10 batches of eggs (laid by 10 females) were divided as follows: 1/3 of each batch served as untreated controls and the remaining 2/3 were used for fumigation treatment. After the 24-h exposure the treated eggs were transferred to the Timber Institute s. e. laboratory and left to see if larvae emerged.

RESULTS

HCN wood penetration and desorption
It took about 15 h for HCN to penetrate into the spruce blocks to about half the chamber concentration level (Fig. 2). Desorption of HCN from 5 spruce blocks after fumigation and the short headspace ventilation is shown in Fig. 3.

Efficacy of HCN on *Tribolium castaneum*
The results are summarized in Table 1. We found significant differences among various tested stages for the 15-min exposure period ($N = 48$, $H = 37.81$; $p = 0.0001$) and the 60-min exposure period ($N = 48$, $H = 20,04$; $p = 0,0002$). The multiple comparison test revealed that pupae were statistically more tolerant than the other stages. No significant difference was evident for the 120-min exposure period ($N = 48$, $H = 3.00$; $p = 0.3916$) or for the 180-min exposure period which achieved total kill.

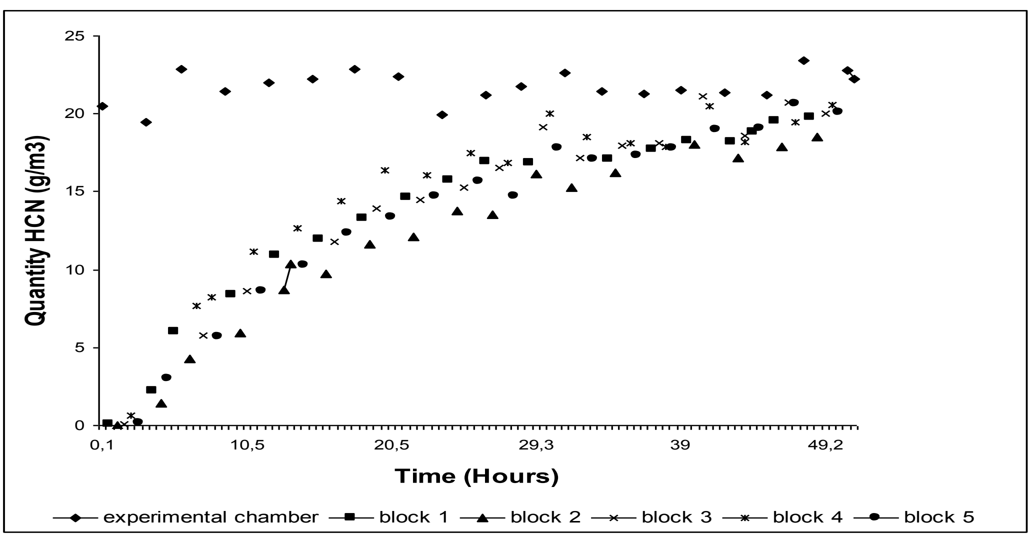

Fig. 2- Temporal dynamics of HCN concentration in the headspace and in the center of the experimental spruce blocks. Five blocks were used per fumigation chamber (650 L). (Explanations: "experimental chamber" = HCN concentration in the headspace of fumigation chamber; "block" = HCN concentration in the center of spruce block 100 x 100 x 150 mm).

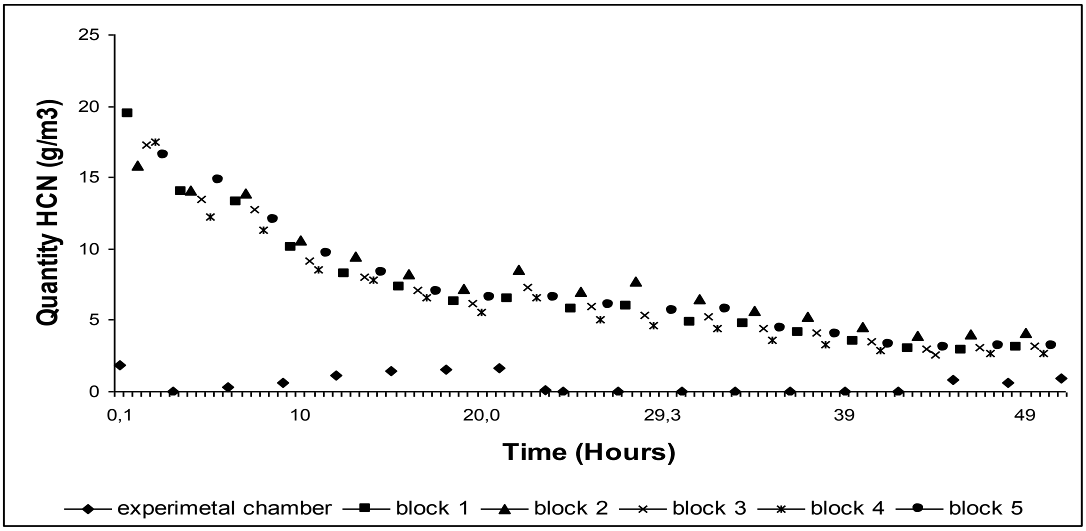

Fig. 3- Desorption of HCN from 5 spruce blocks after fumigation treatment and short headspace active ventilation (Explanations: "experimental chamber" = HCN concentration in the headspace of fumigation chamber, "block" = HCN concentration in the center of spruce block 100 x 100 x 150 mm).

Table 1. Mortality of various stages of *Tribolium castaneum* after various exposures of HCN (dose 20 g m^{-3})

Tabulka	Exposition time (min)				
	15	60	120	180	Control
Imago	100.0±0.0	100.0±0.0	100.0±0.0	100.0±0.0	0.0±0.0
Egg	98.3±1.1	100.0±0.0	100.0±0.0	100.0±0.0	42.5±8.0
Larva	97.5±1.8	100.0±0.0	100.0±0.0	100.0±0.0	5.0±3.4
Pupa	48.3±5.9	90.8±3.1	98.3±1.7	100.0±0.0	10.8±2.6

Efficacy of HCN on long horn beetle *Hylotrupes bajulus*
The results are summarized in the Table 2. The 24-h HCN exposure achieved 100% mortality of all test samples (i.e. eggs, larvae, male and female adults) of *H. bajulus*.

Table 2. Mortality of various stages of *Hylotrupes bajulus* after a 24-h exposure to HCN (dose 20 g m^{-3})

Tabulka

	Experiment	Control
Imago	100.0±0.0	0.0±0.0
Egg	100.0±0.0	2.0±1.3
Larva	100.0±0.0	0.0±0.0

DISCUSSION

In this study we have confirmed 100% biological efficacy of a 24-h exposure period to 2% HCN (concentration 24 g.m^{-3}) on all tested stages of *Hylotrupes bajulus* treated inside the small wooden blocks. With the other test species *Tribolium castaneum,* 100% mortality was reached for all developmental stages, including eggs and pupae after 180 min of HCN exposure in the fumigation chamber. The most tolerant stage was the pupa; its survival was recorded after 120 minutes of HCN exposure.

In the past HCN has been used for special stored product fumigations. However, only few studies are available on HCN absorption and penetration in different commodities: Kunz et al. (1964) studied the penetration of HCN through a grain sorghum bulk. Although HCN has been employed for structural wood fumigation in historical buildings, only one study has been published concerning the rate of HCN absorption by timber (Capoun and Krykorova, 2008). They determined considerably higher HCN absorption in spruce wood than in pine wood. The highest HCN content was determined at a depth of approximately 1.5 cm while content of HCN was low in the surface layer because of desorption between the time of exposure to the fumigant and sampling. However, this study did not provide any HCN measurements from the fumigated headspace. We showed that HCN required (under normal room pressure and temperatures) almost 50 h to reach the central part of the exposed spruce blocks (100 x 100 x 150 mm) at the concentration that was equal to the head space concentration (Fig. 2). Ren et al. (2011) compared rate of penetration of four industrial fumigants (SF, PH_3, C_2N_2, CH_3Br) into pinewood (*Pseudotsuga menziesii*) blocks (10 cm × 10 cm × 30 cm). Each fumigant penetrated to all parts of the block, but the speed and extent of penetration were different. The fumigants that most rapidly achieved an even concentration throughout the block and chamber were PH_3 and C_2N_2. We cannot compare our results for HCN directly with this work since Ren et al. (2011) used a different type of wood. Nevertheless, it seems that the rate of HCN penetration in spruce blocks (obtained in our experiments) was similar to the rate of sulfuryl fluoride penetration into pinewood obtained by Ren et al. (2011).

SUMMARY

In our work we showed high efficacy of HCN on various stages of the serious timber pest *Hylotrupes bajulus* and *Tribolium castaneum*, and described the temporal rate of HCN penetration inside spruce blocks. The results can be used to establish alternative timber fumigation technologies and protocols to methyl bromide.

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