ETHYL FORMATE AS A SAFE GENERAL FUMIGANT

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ABSTRACT

Ethyl formate has been successfully used for individual package fumigation for many years and in tests reported here it has shown promise as a safe general fumigant for stored foods in large quantities. Studies on the use of ethyl formate for the control of stored grain pests have shown that dosages of 300–400 gm/m^3 in an exposure period of 48–72 hours control all stages of insects in stored grain and their products. Large scale disinfestation has been carried out on various agricultural commodities including cereals, pulses, spices, dry fruits, nuts and dried tubers. Fumigation methods have been suggested. The residues of ethyl formate or formic acid are much below the permissible limit of the 250 ppm prescribed. Simple methods of detection of the above have been developed.

INTRODUCTION

Ethyl formate (EF) is a low boiling point liquid insecticidal fumigant with a pleasant aromatic odour. It is used as an intermediate in the synthesis of pharmaceuticals, as an additive of synthetic flavours, production of resins and other compounds. The specifications and physical properties are shown in Table 1 (ANNONYMOUS 1971).

Ethyl formate has been successfully used for individual package fumigation of dry fruits since 1927. The usual dosage for a 11.4 kg box of raisins ranges from about 4 ml in hot weather to 7 ml in cold weather (318–556 mg/l) (SIMMONS AND FISHER, 1945).

Ethyl and methyl formates (MF) were tested by NEIFERT *et al.*, (1925), COTTON AND ROARK, (1928) and ROARK AND COTTON (1929). SHEPARD *et al.*, (1937) found them to be more toxic than carbon disulphide to *Tribolium confusum* Duv., and *Sitophilus granarius* L. VINCENT *et al.*, (1972) have evaluated EF against insects infesting dates and other dried fruits and compared it with phosphine.

Ethyl formate is being produced as a by product in the manufacture of explosives by M/s IDL chemicals Ltd., Hyderabad, India. Therefore a project was initiated at the Central Food Technological Research Institure, Mysore to find a good use for EF. The product had no free formic acid.

MATERIALS AND METHODS

Insect toxicity tests

The toxicity of EF was determined in the laboratory against all life stages of *Sitophilus oryzae* L. and *Tribolium castaneum* Herbst. The insects were reared respectively on *Sorghum vulgare* and whole wheat flour with 5% yeast at 25°C and 70± 10% r.h. For immature stages of *S. oryzae*, about 500 unsexed adults were allowed to oviposit on 500 g of sorghum for 48 hours. The insects were sieved out and the infested grain was held at the rearing conditions till the developing stages attained the required age. Then the grain was weighed into 25 g aliquots for fumigation. Pre-adult stages of *T. castaneum* were obtained from regular cultures. Similarly 2-3 week old unsexed adults of both species of insects obtained from established cultures were tested. In these cases there were 30 insects in each replicate. In each age group 5-11 doses were tested with 4-9 replicates per dose. All fumigations were carried out for 24 hours at the laboratory conditions of 27.4 ± 2.2°C and 60-80 r.h. in 850 ml desiccators provided with septum caps on the lid for fumigant dosing.

EF was drawn as a vapour in a 20 ml gas-tight syringe from a gas-wash bottle containing excess liquid to obtain a saturated concentration (BROWN, 1951). The vapour was injected into the desiccators through the septum caps after establishing a slight vacuum to draw the vapour in.

Following treatment, mortality of the immature stages of *S. oryzae* was assessed based on the number of adult emergences and that of *T. castaneum* on development to the next metamorphic stage. Adult mortality was assessed 10 days after the treatment. The data were corrected for natural control mortality and analysed statistically by the method of LITCHFIELD and WILCOXON (1949) (Table 2).

Effective doses of ethyl formate in foods

Three hundred gm each of 27 commodities were fumigated in triplicate in 850 ml desiccators with EF to ascertain the effective dose required in a 24 hour treatment. The test insects were *T. castaneum* adults in open end glass tubes with cloth diaphragm closures. The EF was administered as a liquid to give dosages ranging from 300-500 mg/L. The sorption ratios were calculated by dividing the effective commodity dose (LD_{100}) by the LD_{95} dose (32.2 mg/L; upper limit) (Table 3).

Penetration of ethyl formate in grain columns

The penetration of EF was studied in 1-5 meter tall 20.25 cm diameter (i.d) air tight mild steel (pipe) columns fitted with spouts and stopcocks at the top, middle and bottom locations. Each spout contained 40 kg of wheat and insect exposure tubes containing 30 *T. castaneum* adults. The lethal CT

product was determined when there was cessation of all movement of the insects.

EF at dosages of 100, 200 and 300 mg/L was administered as a liquid in a syringe at the top spout. Mortality time was noted at each of the three locations (Table 4).

Trials on paddy rice

EF and MF were poured over seed paddy in 0.5 tonne galvanised iron (GI) bins, carrying an infestation of *Sitotroga cerealella* moth. Mixtures of EF and ethylene dibromide (EDB) absorbed in pieces of chalk were also probed to different depths of the bin using a hollow metal probe. Table 5 depicts the details of these tests.

Penetration of EF through sealed flexible packs

Cereal based "Energy food" (100g) in sealed flexible pouches were fumigated separately in 2.5 L desiccators with Ef at a dosage of 300 mg/L with an exposure of 48 hours. Each pouch had 30 *T. castaneum* adults in glass tubes with cloth diaphragm closures. The penetration of EF into the packages was computed by estimating the residual gas concentration by gas chromatography, as described in this paper, and deducing the quantity that penetrated the packages from concentration of EF in a control desiccator with no packages. The data are shown in table 6.

Determination of EF in air and as residue in foods

1 Qualitative tests:

Blue litmus paper (E. Merck) (pH 4.5 red:8.3 blue), methyl red treated paper strips (pH 4.2 red:6.2 yellow), bromo creso green treated paper strips (pH 3.8 yellow: 5.4 blue) were placed inside 250 ml gas bubblers and vapour of EF to give a concentration of 100 ppm (the T.L.V. in air Torkelson et al 1966) was injected into the gas bubbler after creating a slight vacuum. The change in colour of the strips was recorded after 30 minutes of exposure.

2 Quantitive tests:

Quantification of the blue litmus colour change was attempted by using a Reflectance meter (Table 7).

2.1 Colourmetric method: Alzarin; 1,2 - dihydroxy anthraquinone was used as the reagent and the pinkish violet colour developed was read at 520 nm in a Bausch & Lomb Spectronic 20 colorimeter.

Reagents: (a) 1ml of 1% sodium hydroxide solution:

(b) 0.5 ml of 0.1% alizarin

(c) EF standard solution:

The final volume was made up to 10 ml in distilled water.

Procedure: A standard solution of EF consisting of 20 mg EF in 1 ml of methyl alcohol was prepared and 1-10 ml was taken in separate tubes. 0.5 ml alizarin solution and 1 ml of 1% sodium hydroxide was added and shaken well before taking the reading. Beer's law was applicable in the range of 20-80 µg of EF.

2.2 Interferometric analysis: A "Riken 18" interferometer was calibrated for EF. The soda lime scrubber was replaced with a paper towelling scrubber to avoid reaction of EF. Known concentrations of the vapour were prepared in a 100 ml syringe attached to the intake end of the interferometer and the concentrations were analysed. The interferometer was used in all field experiments along with a bioassay method to monitor the concentrations.

2.3 Gas chromatography: AIMIL gas chromatograph model 5580 with an FID mode was employed under the following conditions for analysis of EF-

Detector temperature	105 - 112°C
Oven temperature	34 - 42°C
Injector temperature	77 - 84°C
Balance current	x 100
Attenuation	x 16
Carrier gas flow(Nitrogen)	60 ml/min
Hydrogen	40 ml/min
Column	2 m, 1/8" dia SS loaded with 80-100 mesh chromosorb W coated with 5% dinonyl phthalate.
Retention time	40-45 seconds
Sensitivity	1 µg EF.

Table 8 gives the standard curve for EF.

2.4 Detector tube method: Methyl red solution (0.1g in 18.6 ml of 0.02 N sodium hydroxide made up to 250 ml; PH 4.2 red; 6.2 yellow) was impregnated on 30-50 mesh celite, dried at room temperature and packed into 17.8 cm x 0.2 cm (i.d.) glass tubes with a rubber septum cap for injecting samples from a syringe (MUTHU AND MAJUMDER, 1973). The tube was tested for both EF (60 ml air sample) and formic acid (100 ml air sample) with encouraging results.

Table 9 dipicts the calibration between quantity of vapour of EF and formic acid and the length of the red band formed. There were three replicates per concentration of each vapour. A regression line was drawn for EF whereas for formic acid, as there was perfect correlation between quantity of sample and band length, no further statistical treatment was applied.

Determination of residues in foods

Residue as EF

Fourteen commodities were fumigated in 100 gm lots in 210 ml gas washing bottles with three replicates per commodity. EF was dosed at the rate of 300 mg/L with an exposure period of 3 days and an aeration of one week under static conditions. The head space gas was analysed by gas chromatography as described earlier after keeping the gas-wash bottles in a water bath for 30 minutes at 80°C to desorb the EF sorbed. The calculated values are shown in Table 10.

Residue as formic acid: As the tolerance of 250 ppm as total or combined formic acid is the residue stipulated by the food and Drug Administration of USA (Federal Register, 1979) it is important to estimate this in foods.

Blue litmus paper was again used to determine the formic acid in vapour form. Graded concentrations of formic acid vapour were established in 210 ml gas bubblers with blue litmus paper strips in each of them (4-5 replicates per concentration). The colour formed was read in the Reflectance meter (ELICO REFLECTOMETER CL-28). Data are shown in Table 11 along with the regression equation. The residues determined by the above method in certain foods are given in Table 12.

Large scale fumigation trials

Attempts to use EF for large-scale fumigations have been rather sporadic. PELIKH *et al.*, (1940, 1941) found it effective against warehouse insects at a dosage of 250 g/m^3. Surface treatment of wheat infested by *R. dominica* and *Latheticus oryzae* at dosages of 454-568 ml per 0.84 square meter proved in-effective (WILSON and MILLER 1946). NEIFERT *et al.*, (1925) found it quite effective for grain fumigation in box-cars. Wheat germination was not adversely affected (COTTON and ROARK, 1928).

In view of lack of enough data on EF for large scale treatments several trials were conducted on bag stacks of wheat, pulses, spices, dried tapioca chips and deoiled copra cake.

Fumigations were mostly carried out under gas-proof sheets (rubberised fabric tent, low density polyethylene sheet tent, high density polyethylene laminated on ether side with low density polyethylene sheets, neoprene coated

nylon sheet (balloon cloth). A wheat stack was enveloped by both a rubberised fabric tent and a 1000 gauge low density black polyethylene tent. The gas-proof sheets were sealed to the floor by mud-plaster or sand.

Arecanuts (betel nuts) were fumigated in a brick masonry room with wooden ceiling made airtight by mud plaster sealing. The doors and windows were sealed using gummed paper strips.

Fumigation distribution: The fumigant distribution system consisted of dichotomously branched rubber pressure tubing laid on top of the stack before covering, and secured with strings to prevent 'whipping' at the time of discharge of the fumigant. At the exit ends of the branches gunny sacking was placed to absorb and vaporise the liquid EF. The main fumigant feeder tubes were brought out of the stack at the floor level and connected to a sprayer pump. After pressurizing the unit the fumigant was discharged into the tubes.

Unglazed baked clay pans were also used for distributing the liquid EF in some fumigantions especially on stacks in rooms. They were distributed on top of the stacks.

Test insects

The test insects consisting of 30, 2-3 week old *T. castaneum* adults were placed in glass tubes plugged with cotton wool which, in turn, were inserted in brass perforated capsules that were screwed on to 1M long galvanised iron probes (GI) with a 'T' handle. A gas sampling tube ran inside the core of the tube, with the sampling nipple in the middle of the 'T'. The probes were randomly thrust into the top, middle and bottom strata of the stack into the bags.

Gas concentrations

EF concentrations were determined during exposures at the top, middle and bottom locations from the probes using the Riken-18" interferometer. The concentrations were plotted against the exposure times and the concentration time (CT) curves drawn. The areas encompassed by the curves represent the integrated CT products expressed as mg. hrs/L. This gave an indication of the effectiveness of gas distribution and toxicity to insects.

Bio-assay of gas concentrations

The bioassay method for assaying gas concentrations (MUTHU *et al*, 1971) was also tried. Fifty ml capacity U-tubes with stoppers and side spouts containing 30 *T. castaneum* adults were scrubbed with the gas samples connected to the interferometer intake line so that the reading on the

interferometer denoted the concentration in the U-tube as well. After taking the reading the U-tubes were closed and the time of sampling noted. The knock-down time was recorded to arrive at the total time that had elapsed from the time of sampling. The EF concentrations as determined by the interferometer multiplied by the knock-down times give an estimate of the CT products that could be employed for determining the concentrations by the bio-assay method.

Aeration was done at the end of the exposure periods by cross ventilation. About 500 gm of samples were drawn from the top, middle and bottom locations of the stacks and sieved to gauge the mortality suffered by the resident infestation. The commodity samples were incubated in the laboratory for a period of one month at 25-27°C and sieved every week to determine the effect of the treatment on the pre-adult stages of insects (on emergence). Germination tests were conducted on samples of wheat drawn before and after fumigation. Residues as EF were determined in some of the samples after fumigation.

RESULTS AND DISCUSSION

Insect Toxicity tests

Eggs of both *S. oryzae* and *T. castaneum* were found to be most susceptible and pupae most tolerant. The maximum CT product *viz* 1110 mg hrs/L, the LD_{95} for *S. oryzae* pupae, is much below that of 1,1,1 Trichloroethane (Methylchloroform) which requires a CT product of over 33,300 mg hrs/L (PICL REPORT 1977-79) and carbon tetrachloride which is effective against all stages of *S. oryzae* at 22,000 mg.hrs/L (PICL Report 1974-76)

Effective doses of EF in foods

Rice bran required the highest dose of 500 mg/L followed by copra cake and semolina (400 mg/L). Split pulses, walnuts, pepper and copra needed 150-200 mg/L. followed by ginger, paddy and coriander (100 mg/L). All the rest could be effectively treated at 50-75 mg/L with the exception of green gram which showed the least sorption (30 mg/L being sufficient for the treatment). SIMMONS and FISHER (1945) have recommended a dosage of 4 ml per 25 lt box of raisins which works out to a dose of 318 mg/L. This could compensate for sorption and leakage losses from the containers.

Penetration of EF in grain columns

The data show that a dosage of 300 mg/L is required for adequate penetration of EF through the grain and this took about 8 hrs. It would be possible to fumigate wheat in farm bins with EF, extrapolating these results.

Seed paddy in bins

An examination of table 5 shows that for paddy a dosage of 712 g/m^3 of EF is necessary to control *S. cerealella*. Mixtures of 1.5:1 (W/W) of EF and EDB absorbed in pieces of chalk is also equally effective. Mixture, of EF-MF, 1:1 (V/V) at 300 ml for 2 quintals of paddy gave only partial control of *S. cerealella*. MF did not control the insect even at the effective dose of EF, *viz.* 712 g/m^3 (600 ml). The bin lids were found to be illfitting although efforts were made to seal them well with gum-paper strips. MF having a lower boiling point (31.5°C) might leak out if the system is not air tight. Germination of seed paddy (12%m.c) was not hampered by the treatments.

Penetration of EF through sealed flexible packs

It appears that EF can penetrate sealed flexible packs, especially low density polyethylene, and kill the resident infestation. The fumigant may not pose problems of toxic residues by the time it is delivered to the consumers as the quantity of residual EF would be low due to outward diffusion. The technique used is a new approach to in-package fumigation as presently understood and simplifies the procedure considerably.

Determination of EF in air and as residue in foods

1. Qualitative tests: Blue litmus, methyl red and bromocresol green paper strips were equally effective in signalling EF at 100 ppm, the TLV in air.

2. Quantitative tests:

(1) Reflectance meter readings (Table 7) were linear between 100-500 ppm of EF.

(2) Colorimetric method using alizarin also proved promising.

(3) In the Interferometric analysis one division on the ocular scale of 0-10 corresponded to 8 mg/L EF. Concentrations down to 0.16 mg/L could be read on the vernier scale, carbon dioxide concentration interfered with the reading at concentrations above 1%.

(4) Gas Chromatographic method could analyse concentrations down to 1 µ gm EF and proved useful in residue determination.

(5) The Detector Tube Method could be employed in determining air concentrations of EF as well as its residue in foods as EF or formic acid.

Residues as formic acid

The residue as formic acid in the foods fumigated with EF were far below the stipulated level of 250 ppm by the method used. Although the method of residue determination may not account for all the residual formic acid present it serves to indicate the presence of low levels. The saturation concentration

of formic acid is around 134 mg/L at 30°C. The natural formic acid occurring in several foods and beverages far exceeds the residue levels from fumigation with EF (fruits 20–40 ppm, coffee roasted 1350–2200 ppm/. Cheese, 20–30 ppm Evoporated milk 30–40 ppm; FDA, 1976). In the FEDERAL REGISTER (1979) the following comments are made "the agency proposes to affirm the generally recognised as safe (GRAS) status of ethyl formate as a direct human food ingredient and of formic acid and its sodium salt as indirect human food ingredient..." current good manufacturing practice results in a maximum level, as served, of 500 ppm in baked goods, 400 ppm in chewing gum, hard candy and soft candy, 200 ppm in frozen dairy desserts, 300 ppm in gelatins, puddings and fillings and 100 ppm in all other food categories.

No adverse effect attributable to formate were found in five successive generations of rats given up to 200 mg of calcium formate per kg of body weight daily (FDA 1976).

Large scale fumigation trials

Wheat bag stacks: When EF was applied to stacks about 20 minutes were required to discharge the fumigant and there was a faint smell of EF in the vicinity. Integrated CT products of 2573–4054 mg hrs/L were obtained with 100% mortality of *T. castaneum* adults at top middle and bottom locations in the probes (Table 13). The effective CT product estimated by the bio-assay method using *T. castaneum* adults worked out to 123 mg hrs/L at 32–35°C (Table 14). The smell of EF dissipated rapidly and the pest control personnel did not feel any discomfort during the degassing operations.

Incubation tests

The data on insect emergences from the grain at the end of each week and the associated life stages are shown in Table 15. Although a good control of insects was observed as evidenced by the incubation tests the integrated CT product of 2573 mg. hrs/L appeared inadequate as denoted by some surviving insects at the top; CT products of over 3000 mg. hrs/L appeared to be necessary for an overall 100% effect. Good gas-tight covers and a dose of 400 gm/m^3 may be necessary to achieve this. Germination of the seed was unaffected.

The residues determined after 9 months storage were negative to EF.

Fumigation of turmeric

The data are shown in Table 16. There was 100% mortality of both test insects and resident insects in the turmeric samples (*Stegobium paniceum;* all stages). Integrated CT products of 2690 and 2570 mg. hrs/L were recorded at the top and bottom locations.

Fumigation of field beans and coriander

Unglazed baked clay pans were used to distribute EF on the top of the bag stacks in this trial. 100% mortality of *T. castaneum* adults used as test insects and the resident infestation of *Collosobruchus chinensis* and *S. paniceum* in all their stages of development was obtained. Integrated CT product of 2394 mg hrs/L was estimated in a 48 hrs exposure (Table 17).

Fumigation of arecanuts (Areca catechu)

Fifteen clay pans were used to distribute EF in a go down with wooden plank ceiling. The pans were spaced uniformly on the 300 bags. A dosage of 300 g/m^3 with an exposure of 70 hrs was given. Results are shown in Table 18. The mortality of test insects (*T. castaneum*) adults were inconsistent with integrated CT products obtained. However the nuts remained insect free on incubation. There was also no "off" taste in the nuts when chewed.

Fumigation of tapioca chips

High moisture tapioca chips (750 bags; 50 tonnes) infested by *Araecerus fasciculatus*, the coffee bean weevil, was fumigated under a balloon cloth gas proof sheet for 42 hrs at 30°C. As the interferometer could not be relied upon to give accurate values for EF due to a high carbon dioxide build-up from fungal infection, only bio-assay with *T. castaneum* adults was attempted. The results are shown in Table 19. Heavy mortality of *A. fasciculatus* was observed as well as 100% mortality of the test insects. The incubated samples were found insect free. It was learnt later that the fumigated lot was passed for shipment as the quality was found excellent compared to the unfumigated lots.

Fumigation of expeller copra cake

Four hundred bags with a volume of 48 m^3/m. were fumigated using a dosage of 500 gm/m^3 with an exposure of 70 hrs at 26.7°C. The results shown in Tables 20 and 21 indicate that there was 100% mortality of *T. castaneum*, *S. paniceum*, *Necrobia rufipes* and *cryptolestes* sp. in the samples sieved after fumigation. The residue as formic acid in a composite sample was 2.3 ppm as determined by the detector tube method, described earlier. No live insects were seen in the incubated samples drawn after fumigation. Heavy infestation was observed in the "before fumigation" sample.

CONCLUSION

A total of 27 field bioassay results, on analysis showed the mean CT product of 154 $\pm$ 42 mg. hrs/L. could be used as a working CT product to determine approximate concentrations of EF in the field.

Dosages of 400 g/cu.m may be required as a blanket dosage for most commodities at an exposure period of 72 hrs. as at 300 g/cu.m survivers were seen at the top. It is imperative that good gas proof sheets are used for better fumigant retention as EF has a vapour pressure of 312 mm Hg at 30°C.

No fire hazard is likely if proper precautions are taken like no-smoking or sparks from electrical short-circuits etc., even internal heating of commodity to nearly 40-50°C met with in the fumigation of wet tapioca chips did not "spark off" an explosion.

For bag stacks the best method of application appears to be the use of branched tubings with properly aligned manifolds for proper fumigant distribution with empty gunny sacking being kept at the exit points to take care of the liquid splash. A hand compressor sprayer could be used as a pressure source. The filling of this can be done in the open to avoid vapour build up in enclosed spaces. For room fumigation the shallow unglazed baked clay pans used could aid rapid evaporation of the liquid due to the porosity and extended surface area for quick evaporation. Liquid soaking of the commodities could thus be avoided and any formic acid produced by hydrolysis of EF would remain in the pans.

Normal precautions of establishing good cross ventilation before degassing appears to be adequate. At the end of the exposure period concentrations around 16-30 mg/L might remain and these would dissipate quickly due to the high vapour pressure and diffusion characteristics of the compound. The smell is pleasant and well tolerated compared to the halogenated hydrocarbon fumigants (ethylene dibromide, ethylene dichloride, carbon tetrachloride etc.).

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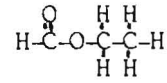
TABLE 1

Physical Properties and specifications of Ethyl Formate
(Ethyl Methanoate, Formic Ether; $HCOOC_2H_5$)

Structural formula		
Molecular weight(calc.)	...	74.08
Boiling point at 760 torr	...	54.1°C
Vapour pressure at 20°C	...	200 torr(mm Hg.)
Freezing point	...	-80°C
Density of liquid at 20°C	...	0.917 g/ml
Specific gravity 20/20°C	...	0.924
Density of gas at 25°C	...	1 g/Litre
Vapour density (Air=1)	...	2.56
Specific heat at 32°C	...	0.478 cal/g(°C)
Auto/ignition temp. in air	...	455°C
Explosive limits in air(approx.)	...	2.8%-16.5% by vol.
Solubility in water at 25°C	...	14.5% by wt.
Specifications:		
Ethyl formate(min)	...	98% by wt.
Acidity(max)	...	0.1% by wt. as formic acid.
Odour:	...	aromatic, non-residual
Suspended	...	Substantially free
Distillation range: Initial B.P.	(min)	52.0°C
98%	(max)	54.5°C

Ethyl formate is miscible with alcohol and ether and gradually hydrolyses with water to formic acid and ethanol (5 days). Anhydrous sodium sulphate and calcium chloride minimise this.

TABLE 2

Toxicity of Ethyl formate to the Life Stages of S. oryzae and T.castaneum

Species	Stage	LD_{50}(Mg/L) Value	95% limits	LD_{95}(Mg/L) Value	95% limits	c x t (mg.hrs/L)
S. oryzae:						
	Egg	6.2	5.6, 6.8	11.8	10.0, 14.0	283
	Larvae					
Age	5 days	9.0	8.5, 9.6	16.0	14.8, 17.4	384
Age	9 days	10.4	9.6, 11.2	21.1	19.0, 23.5	506
Age	13 days	15.7	14.6, 16.8	30.3	27.1, 33.9	727
Age	16 days (pre-pupa)	20.0	19.01 21.1	44.2	39.6, 49.3	1060
Age	24 days (pupae)	13.7	13.2, 14.2	46.3	44.0, 48.8	1110
	Adults 2-3 week old	14.3	13.4 15.3	24.5	19.2 30.6	588
T.castaneum:						
	Egg	2.5	2.3, 2.9	6.4	5.3, 7.8	154
	Larva	8.8	7.4, 10.5	24.6	17.4, 30.6	590
	Pupa	18.2	16.6, 20.1	27.6	23.5, 32.4	662
	Adults 2-3 week old	19.5	18.8 20.3	26.8	22.3 32.2	643

TABLE 3

Effective Dose of Ethyl formate in Foods

Commodity	LD_{100} (actual dose: mg/L)	Sorption ratio commodity dose: LD_{95} dose
Paddy	100	3.1
Rice	75	2.3
Wheat	75	2.3
Bengal gram	50	1.6
Green gram	30	1.0
Cow pea	75	2.3
Peas	50	1.6
Bengal gram splits	150	4.7
Groundnut kernel	75	2.3
Cashew kernel	75	2.3
Almond kernel	75	2.3
Copra	150	4.7
Raisins	50	1.6
Dates	50	1.6
Walnuts	200	6.2
Turmeric	50	1.6
Ginger	100	3.1
Cumin	75	2.3
Tobacco	75	2.3
Tamarind pulp	75	2.3
Green gram splits	200	6.2
Pepper	200	6.2
Coriander	100	3.1
Rice bran	500	15.6
Copra cake	400	12.5
Copra cake powder	400	12.5
Semolina (wheat)	400	12.5

TABLE 4

Stratification of Ethyl formate in Wheat Denoted by Knock-down (k.d.) Time of T.castaneum Adults:(Hrs.)

Dose Mg/L	Knock-down time		
	Top (Surface)	Middle (0.75m)	Bottom (1.5m)
100	4.8	8.0	No mortality even after 1 week
200	1.1	3.0	-do-
300	1.0	1.0	8

TABLE 5

Fumigation of seed paddy with Ethyl formate, Methyl formate and Ethyl formate+Ethylene dibromide

Bin No.	Variety	Quantity quintals (100 kg)	Fumigant	Dosage g/m^3	Remarks
1	Madhu	5	EF+EDB (1.5:1 w/w)	700 280 EDB 420 EF	S.cerealella controlled
2	Madhu	5	EF	356	S.cerealella living
3	Madhu	4	EF	712	Good control
4	Vani	2	EF+Methyl formate (MF) (1:1 v/v)	300ml	Partial control
5	Vani	5	MF	600ml (840 mg/L)	Not controlled

TABLE 6

Penetration of Ethyl formate into Flexible packs

Package type	Amount Penetrating (mg)	Mortality of T.castaneum adults (%)	Remarks
1 HDPE 200 (gauge)	99.6	98	
2 HDPE 300 (gauge)	90.1	98	
3 LDPE 300 (gauge)	115.0	100	Quantities of
4 MSAQ Cellophane	114.2	98	over 115 mg.
5 MST cellophane	95.9	98	are associated
6 Aluminium foil laminate	80.9	90	with 100% effect. Exposure of 72 hrs
7 Polycel	115	100	may help

1 HDPE : High density polyethylene
3 LDPE : Low density polyethylene
4 MSAQ : Moisture proof, sealable, anchored, opaque
5 MST : Moisture proof, sealable, transparent
6 60 gm paper /0.02mm foil/ 150 LDPE
7 Polycel : Polyethylene-cellophane laminate
LDPE 150 (gauge) / Cellophane 300 gm.

TABLE 7

Determination of Ethyl formate using Blue Litmus Paper: Reflectance Measurements

Ethyl formate ppm	mg/L	Reflectance %	Remarks
0	0	37	
50	0.15	39.5	Curve linear
100*	0.30	43	between 100-500
250	0.75	44	ppm
500	1.50	45	

* TLV

TABLE 8

Gas Chromatography of Ethyl Formate: Standard Curve

Ethyl formate (µgm)	Peak height (cms)
1.14	0.67
5.70	3.05
11.40	5.70
17.40	9.70
22.80	12.40

TABLE 9

Detector tube method for Determination of Ethyl formate and Formic acid

Ethyl formate		Formic acid	
mg (x)	Band length:cms (Y_p)	µg	Band length (cms)
0.25	1.4	1	0.15
0.50	1.7	2	0.2
1.0	2.3	4	0.4
2.0	3.4	8	0.8
3.0	4.6	12	1.2
4.0	5.7		
5.0	6.8		

Regression equation:

$Y_p = 3.7+1.13\ (x-2.25)$

TABLE 10

Residue of Ethyl formate in Fumigated Foods

Commodity	Ethyl formate (ppm)	Permissible Levels (ppm) (FEDERAL REGISTER, 1979)
Cardamom	12.75	100
Cashewnut	1.17	15
Cow pea	0.27	100
Bengal gram	1.62	100
Bengal gram splits	Not detected	100
Groundnut seeds	0.49	100
Green gram	4.62	100
Raisins	39.32	250
Rice (polished)	9.45	100
Sorghum	6.32	100
Turmeric rhizomes (dried)	8.65	100
Cumin	7.70	100
Wheat	0.88	100

TABLE 11

Estimation of Formic acid with Blue Litmus Paper

Formic acid: /μ gm (X)	Y_p	Reflectance: % (Y)	Regression Equation
0	43	41	
62.5	44	44	
125	45	47	$Y_p = 46.4 + 0.0184 (x - 187.5)$
250	47.6	49	
500	52.0	51	

TABLE 12

Residue of Formic acid in Ethyl formate Fumigated Foods: Blue Litmus Paper Strip Method

Commodity	Reflectance %	Formic acid µ gm	Residue ppm
Bengal gram	48	250	2.5
Bengal gram splits	41	0	0
Cashew nuts	44.5	80	0.8
Cow pea	45	120	1.2
Cumin	45	120	1.2
Groundnut seeds	47	220	2.2
Field beans	40	0	0
Turmeric	47.5	250	2.5
Wheat	44.5	80	0.8

TABLE 13

Concentration of Ethyl formate, c.t. products and Mortality of T.castaneum Adults in Probes

Exposure: Hrs	Concentration of Ethyl formate (mg/L)		
	Top	Middle	Bottom
1	20	84	80
19	54.4	76	80
27	52.8	66.4	66.4
42	40.0	41.6	46.4
72	25.6	26.6	26.2
Integrated c.t. Product: mg.hrs/L	2573	3919	4054
Mortality of T.castaneum adults (%)	100	100	100

TABLE 14

Bioassay of Ethyl formate concentrations in the wheat bag stack at the end of 19 hrs. of exposure. Temperature: 32-35°C

Location	Knock-down time:Hrs.	Conc. of Ethyl formate: mg/L	c.t. product mg.hrs/L
Top	2.5	54.4	136
Middle	1.5	76.0	114
Bottom	1.5	80.0	120
			123(mean)

TABLE 15

Effect of Ethyl formate Fumigation on the Life Stages of Stored Product Insects in Wheat

Date of Screening	Location of Sampling and insects			Life Stages
	Top	Middle	Bottom	
18.9.78 immediately after degassing	Tribolium:1 Rhyzopertha:1 Psocids	*Nil	Tribolium:1 Rhyzopertha:1	Adults
25. 9.78	Nil	Nil	Nil	Pupae
4.10.78	Cryptolestes 2	Nil	Nil	Larvae
13.10.78	Cryptolestes 3	Nil	Nil	Larvae
17.10.78	Nil	Nil	Nil	Eggs

* From two damaged bags on top of the stack.

TABLE 16

Fumigation of 26 bags of Turmeric with Ethyl formate under a balloon cloth: Gas concentrations and Insect Mortality - Temperature 32°C Dose: 300 g/m^3

Exposure Hrs.	Gas concn. mg/L (Interferometer) Top	Bottom
5	Beyond scale	Beyond scale
21	68.8	60.5
50	37.6	38.0
Integrated c.t. product mg.hrs/L	2690	2570
Mortality of test insects T.castaneum	100	100

The control of insects was 100% even in the incubated samples.

TABLE 17

Fumigation of Field Beans and Coriander

Field beans: 320 bags (100 kg each)

Coriander: 60 bags (40 kg each)

Stack volume: 65 cu.m; one side against a wall

Gas proof sheet: HDPE Woven polyethylene laminated with LDPE

Fumigant distribution: in mud pans, 6 nos. on top of the stack equally distributed before draping cover.

Dosage: 300 gm/cu.m (19.5 kg)

Exposure: 48 hrs

Gas sampling: only from middle probe

Integrated c.t. product: 2394 mg. hrs/L

100% mortality of test insects (T.castaneum adults) and immature stages in incubated samples.

TABLE 18

Gas concentrations and Mortality of Insects in Fumigating Arecanuts with Ethyl formate

Exposure: (hrs)	Location(mg/L)			Bioassay:(k.d. time Hrs)		
	Top	Middle	Bottom	Top	Middle	Bottom
5	26.4	27.2	34.9			
21	38.2	40	45.0	5	4	2.5
47	42.6	44.6	49.0	c.t:191	160	112
68	37.4	37.0	40			
Integrated c.t. product mg.hrs/L	2636	2710	3006			
Mortality of test insects T.castaneum adults (%)	50	100	98			

TABLE 19

Bio-assay of Gas Concentrations and Mortality of Test Insects in Fumigating Tapioca chips

Exposure (Hrs)	Bio-assay: Knock down time (k.d.)		
	Top	Middle	Bottom
19	5	5	12
43	40	40	17
Mortality of T.castaneum (probes)	100	100	100

TABLE 20

Fumigation of Copra Cake with Ethyl formate

(a) Gas Concentration (Interferometer): mg/L			
Exposure(Hrs)	Top	Middle	Bottom
3.7	44	37	8
22.5	80	54	36
45.5	77	61	48
69.8	65	59	55
Integrated c.t. product mg.hrs/L	5017	3989	3147

TABLE 21

Bio-assay using T.castaneum Adults: Copra Cake Fumigation

Exposure (Hrs)		Knock-down time (Hrs)	Concn. (mg/L)	c.t. product mg. hrs/L
22.5	Top	1.25	80	100
	Middle	2.75	54	148
	Bottom	24	36	864(90%* mortality)
45.5	Top	1.3	77	100
	Middle	2.25	61	137
	Bottom	2.5	48	120

* Defective sampling.