The Use of Chloropicrin for Beet-Seed Warehouse Fumigation and Other Purposes[1]

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Chloropicrin, commonly called "tear gas" because of its lachrymatory effect, is different from the true tear gas in general use at the present time. Pure chloropicrin is a colorless liquid, although the commercial preparation is frequently yellowish in color. It has an oily appearance and a Swedish, not unpleasant odor. A few of the commonly accepted physical and chemical properties, as compiled from a number of references on the chemical, are as follows:

Formula (tricloronitromethane)	CCI_3NO_2
Molecular weight	164.88
Specific gravity (at ordinary temperatures)	1.65
Theoretical specific gravity of vapor (air — 1)	5.7
Boiling' point	112.4 ° C.
Freezing point	—64° C
Vapor pressure	5.7 mm. at 0° C. and 18.3 mm. at 20° C.
Solubility in water	0.14 percent
Heat of vaporization	6.77 Kg Calories per gram molecule at 35° C.
Weight per gallon	13.75 lb.
Fluid ounces per pound	9.15 oz.
Cubic centimeters per pound	273 cc.
Drops per cubic centimeter	118
Solubility	Soluble in the usual organic solvents
Flash point	None
Bleaching effect	None

Chloropicrin has been scientifically known for almost 100 years, but it became available commercially in this country only during 1925. For fumigation purposes it has gradually replaced the use of carbon disulfide, because of the fire and explosion hazard, and hydro-cyanic-acid gas, because of its quick action and lack of warning which endangered human life. Chloropicrin was first adopted as a fumigant by the milling and grain industry and has since found acceptance in most fields where gas control of insects and rodents is practiced. The toxicity of chloropicrin to the lower forms of animal life is well established. Roark (17) lists some 236 references on the use of chloropicrin as a fumigant.[3]

It is difficult to make an accurate comparison between the toxicity of different fumigants, because the relationship continually varies with the environmental factors and the material concerned. A comparison of time-proved dosages under practical fumigation con-

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ditions would seem a fair comparison. The following information gives the ordinary commercial rates of application, in a tight building, at a temperature of 80° F., for a few common fumigants (1) :

Chemical	Dosage per 1000 en. ft.	Percentage gas—volume concentration
Chloropicrin	1 lb.	0.24
Hydro-cyanic acid	½ lb.	0.72
Ethylene oxide	1½ lb.	1.33
Carbon disulfide	5 lb.	2.60
Ethylene dichloride	10 lb.	4.00

If gas-volume concentration may be used as an index, chloropicrin is 3 times as effective as hydro-cyanic-acid gas and 10 times as effective as carbon disulfide. Actually, Moore (14) calculated that, molecule for molecule, chloropicrin is 283 times as toxic as carbon disulfide. One of the chief factors affecting results from chloropicrin fumigation is the penetrating ability of the gas. Johnson (10) states that at the proper concentration it kills insect life in all stages throughout warehouses containing 140-pound sacks of flour, standard cases of tobacco, and sacks of rice. Tn bulk-grain fumigation, penetration is effected to kill the weevil egg, larva, and pupa hidden within the grain. It was the only fumigant among those tried by the California Termite Commission (2) which killed all termite life in sections of telephone poles in vault fumigations.

Rodents have always been more or less of importance in sugar-beet-seed warehouses. Mice, in particular, have caused a great deal of damage to both bags and seed. Each company and every factory, where beet seed is stored, has had to contend with this nuisance. Lambert and Jackson (13) give lethal concentrations of chloropicrin for rats at various exposure-times as follows:

7.4 mg. per liter	3 minutes
1.0 mg. per liter	15 minutes
0.5 mg. per liter	30 minutes

The usual commercial recommendation, according to Johnson (10). for the control of rats and mice is ¼ pound of chloropicrin per 1,000 cubic feet of warehouse space. Chloropicrin irritates the rodents, causing them to leave their hiding places to die in the open. There is no odor to the dead bodies, indicating that the gas kills the organisms causing putrefaction.

Such a highly toxic, penetrating fumigant would be desirable for use in beet-seed warehouses if it could be handled safely and would not have a detrimental effect on the seed. According to Witherspoon and Garber (21), the average person is conscious of the presence of chloropicrin in concentrations as low as 1 ppm., and, at 2 to 3 ppm., tears are produced. As the concentration increases, irritation of the membranes in nose, throat, and bronchial tubes occur progressively, accompanied by such reactions as coughing and sneezing. Experimental work indicates the limit of human voluntary toleration for a 2-minute period as about 22 ppm. According to Witherspoon and Garber, the lowest lethal concentration for dogs is over 120 ppm. which is 5 times the maximum voluntary toleration by humans, and the exposure for dogs is ½ hour as compared to only 2 minutes for humans. Thus it would appear that chloropicrin is far from being a rapid poison, which would be a valuable safety factor in case of accidental severe exposure. Since the gas is detectable in such minute concentrations and cannot be tolerated voluntarily in concentrations sufficiently strong to cause injury, it should be quite safe to use.

Knight (12) presents data on the effect upon germinations and states that the viability of the seeds of corn, oats, wheat, and soybeans, with moisture content low enough for safe storage, was not significantly affected by chloropicrin fumigation with dosages necessary for complete insect control in sacked grain. He used from 1 to 6 pounds per 1,000 cubic feet for grain stored in cloth bags. Thus it would appear that the recommended commercial rate of ¼ pound per 1,000 cubic feet for the control of rodents would be safely applicable to stored beet seed.

Beet-Seed Warehouse Fumigation

In order to determine the effect of chloropicrin fumigation on sugar-beet seed, an experiment was conducted using sealed glass bottles and concentrations of chloropicrin up to 1 pound per 1,000 cubic feet. Germinations were run on the treated seed after 40 hours exposure, and they showed no detrimental effect on the seed as a result of the treatment.

Mice had infested our seed room at the experiment station at Sheridan, and in order to make a practical application, chloropicrin was applied to this room, in the fall, at the rate of ¼ pound per 1,000 cubic feet. The application was made on Saturday evening, and the building remained closed until Monday morning. This single application was sufficient to kill all of the mice in the building. It remained free of mice until late the following spring when it was necessary to have the building open a great deal and mice had an opportunity to come in from the outside. Germinations after exposure showed no detrimental effect upon the seed.

In large warehouse fumigation, the application of chloropicrin is relatively simple, and a number of methods have been used successfully. In general, the more finely the liquid is broken up, the more readily it passes from a liquid to a vapor form, and the quicker a maximum concentration is reached within the building. Any method of application may be evaluated by this criterion. The most common method of application for large warehouses is by sprinkling with an ordinary watering can, or by bottles equipped with sprinkler corks, on empty burlap sacks spread out either under foot or over the material to be fumigated. Hand-compressor sprayers, blowers, and atomizers have also been used successfully. Usually men wear gas masks equipped with canisters, designed for protection from acid gases and organic vapors, when they are making the application.

Following our initial experiments, the Sheridan factory warehouse, which was heavily infested with mice, was fumigated in the late fall. This building is constructed of corrugated iron siding nailed to open studding. The volume of the warhouse was calculated, including the space in the gables and not deducting for the space occupied by the seed. An amount of chlolopicrin was measured out to make an application of ¼ pound per 1,000 cubic feet. The liquid was placed in a garden hand-compressor sprayer, and a man wearing a gas mask climbed over the large stacks of bagged seed spraying in the atmosphere and on the upper layer of sacks. As soon as the application was well underway, observers on the outside of the building noticed many mice coming out of crevices and holes in the sides of the building. By the time the application was complete the mice were tumbling pell-mell out of any opening they could find. A count was made of the number coming out of one crevice formed by a lap of the corrugated iron, and a total of 21 mice came out during the observation. A few of the mice apparently escaped, after having only a light exposure, and were able to move some 15 feet away from the building where they sat up, pawed vigorously at their noses, and soon toppled over and died. No mouse was seen to escape. The building was closed over the week end and then opened to allow any remaining fumes to escape. Examination of the building revealed many dead mice. They were lying about in the corners and wedged between sacks of seed, indicating that they had attempted without success to avoid the penetrating fumes.

Following this initial application, the bases of the large stacks were sprayed with chloropicrin, using ¼ of the above amount at intervals of about 1 month, to avoid reinfestation until time to remove the seed in the spring. No live mice were seen in the warehouse after the initial application in the fall. At the time the seed was removed, dead mice were found wedged between sacks in all parts of the large stacks indicating that the fumes had penetrated the stacks thoroughly.

Formerly, hydro-cyanic-acid gas had been used as a fumigant in our seed warehouses with only partial success in mouse control. Due to our success in keeping the warehouses free of mice by using chloropicrin, it has been adopted for use in all our beet-seed warehouses. The procedure is to calculate the entire volume of the house and make the initial application, at the rate of ¼ pound of chloropicrin per 1,000 cubic feet, in the fall after all seed has been stored in the warehouse for the year. This same rate is applied again in the spring following the period when the seed is issued to the farmers, at which time the warehouse normally is open a great deal. Between these 2 strong applications, which normally are about 6 months apart, 2 light applications of ¼ the above amount, each, or 1/16 pound per 1,000 cubic feet, are made as a precaution against reinfestation. Thus, there are 6 fumigations a year at approximately 2-month intervals. Following the strong applications, the building normally may be left closed for quite some time and, when opened, thorough ventilation usually is unnecessary, so that sufficient traces of the gas remain to act as a repellent to rodents but are not noticeable to workmen. By the addition of the light applications, reinfestation is avoided. The warehouses are open sufficiently in the fall during receipt of The seed and again in the spring during the issuance of the seed, thus no traces of the gas are noticeable to the workmen.

Following the above procedure for the Sheridan factory warehouse, which is -10 by 80 feet by 16 feet high, plus a 10-foot gable (a total of 67,200 cubic feet), it would require 16.8 pounds for a strong application and a total of 50.4 pounds per year. The cost of our latest shipment of the chemical was 77.18 cents per pound, fob. Sheridan. Wyoming, which would make the annual cost of the chemical $38.90. This amounts to approximately 58 cents per 1,000 cubic feet per year. Comparing this with the cost of an equal number of applications of hydro-cyanic-acid gas, as formerly used, it required 12 pounds of sodium cyanide at 24 cents per pound and 18 pounds of acid at 22 cents per pound, or $6.84 per application—a total cost of $41.04 per year for 6 applications. This would show a decrease in the cost of the chemical of $2.14 for the year, but the cyanide actually was applied more frequently and was only partially successful, being particularly less effective during cold weather. Data in regard to the actual number of fumigations per year with cyanide or the loss of bags and seed from rodent activity are not available, but this additional cost would show a. decided saving in the use of chloropicrin.

Greenhouse Soil Sterilization

During the past few years the use of the fumigant chloropicrin, for partial sterilization of soils, has been receiving increasing attention as the knowledge of its value for this purpose has increased and better methods of application have developed. G. II. Godfrey and co-workers have done much to increase our knowledge in this use of chloropicrin. Their work has been primarily on the control of root-knot nematode, and a good deal of this work was done in the pineapple fields of Hawaii. In a comparison of a light application of chloropicrin with carbon disulfide, Godfrey (5) reports:

Nellar and Allison (15) of the Everglades Experiment Station of

Chemical	Rate (pounds per acre)	Reduction of root knot nematode (percentage)	Increase in yield of pineapple (percentage)
Chloropicrin	150	83	52
Chloropicrin	170	90	52
Carbon disulfide	750	48	29

the University of Florida, have developed a machine for the subsurface treatment of soils with chloropierin and carbon disulfide. They report complete control of root-knot nematode on okra in peaty soil at 405 pounds of chloropicrin per acre.

Chloropierin not only is a nematicide but also an efficient fungicide. The control of a rather large number of pathogens has been reported. Godfrey (4) reports the control of *Fusarium-* sp. from gladiolus, *Phytophthora cactorum* from snapdragons, *Rhizoctonia solani* from sugar beets, *Sclerotium rolfsii* from sugar beets. *Verticillum albo-atrum* from strawberry, *Dematophora* sp. from apple roots, and *Armiliaria mellea* from prune roots by an application of 400 pounds per acre.

The use of chloropicrin on soils results in a stimulated plant growth such as that reported following "partial sterilization" of soils. Howard (9) reports increases in crop yields from the use of chloropicrin, at the rate of 154 pounds per acre, on a series of field-crop plots which had been used for 30 years in a rotation study. This increase was 22 percent" for cabbage, 52 percent for carrots, 65 percent for mangels, 46 percent for millet. 88 percent for rutabagas, 43 percent for onions, 46 percent for tomatoes, 104 percent for peppers, and 206 percent for eggplant.

Johnson (11) made an extensive series of pot experiments comparing 42 chemicals for soil treatment and found that at anywhere near equivalent applications, no oilier chemical produced the stimulation in growth that resulted with the use of chloropicrin, nor did any of them appear to be a practical rival for soil treatment. Amounts of chloropierin as small as 2 grams per cubic foot of soil produced results similar to those obtained from steaming the soil.

Johnson (11) discusses the phenomena observed as a result of partial sterilization of soil and a number of the theories advanced by other workers. Howard (8) reports no unfavorable change in the physical structure or the chemical composition of the soil.

The use of chloropicrin for partial sterilization of greenhouse soils has been well outlined, giving the requirements for good results and the materials and equipment necessary, by Godfrey and Young (7), Stark (19) (20), Howard (8), and Newhall (16). 'Godfrey (6) reports that better results may be obtained by confining the gas adequately in the soil. His results show that animal glue is durable and highly efficient for confining chloropicrin. The glue is cheap and may be used as a sizing on paper to produce a relatively gas-tight covering material applicable for general fumigation purposes. When using gas-impervious containers Godfrey (4) found that 2½ cc. per cubic foot were very efficient in killing injurious soil fungi, nematodes, garden centipedes, wireworms, sowbugs, and the like, and even weed seeds to some extent. Since chloropicrin is relatively insoluble in water, the diffusion of the gas through water is very low. This may be made use of in utilizing a water seal for confining the gas. For gas retention, when using a hand applicator, Howard (8) states that as an area is finished a water "seal" should be created by watering so as to wet the surface soil.

We have been utilizing chloropicrin for sterilization of greenhouse soil for the past 3 years. We have successfully utilized applications of from 2 cc. to 8 cc. per square foot. From our results, it is apparent that the depth of application and frequency or spacing of points of injection, as well as the amount of material to apply, will vary with each specific set of conditions. The amount of material required apparently varies with the organic content of the soil, more material being required as the organic material present is increased. As a general plan of fumigation, from which we deviate according to specific conditions under consideration, we have adopted the practice of applying chloropicrin, when the moisture content of the soil is such that the soil is in optimum working condition (culturally), at the rate of 6 cc. per injection, to a depth of 8 inches, at points of injection 20 inches apart in 10-inch rows, and thoroughly wetting the surface with water immediately to prevent the rapid escape of the gas. This procedure has given satisfactory control of harmful soil micro-organisms and insects, and has not affected adversely soil structure or chemical composition. We have controlled, as shown by cultures from diseased sugar beets, *Phoma* sp., *Stemphylium* sp., and *Fusarium* sp. Where the greenhouse is well ventilated and the surface of the soil thoroughly wet at the time of application, a gas mask has been found unnecessary. Small concentrations of the gas are toxic to living plants, and therefore no living plants remain in the greenhouse during the treatment. Applications normally are made in the evening and the building tightly closed overnight. The gas escapes as the surface of the soil dries, and plantings normally are made 2 weeks after application. On heavier types of soil, working of the soil may be necessary for escape of the gas. The above rate of application would require 15.82 pounds per 1,000 square feet. At a cost of 77.18 cents per pound, this would amount to $12.21 per 1,000 square feet of treated surface.

According to the Chemical Warfare School (3), the maximum possible concentration of gas obtainable at 20° C. and standard pressure is 0.164 gram per liter of air. Using this figure it would require 3.28 cc. per cubic foot for saturation. However, using Godfrey's (4) figure of 40-percent air space in soil, it would require only 1.312 cc. per cubic foot. This might indicate that we have been utilizing an excess of material, but the additional amount seems warranted to take care of the diffusion below the first foot and the loss into the atmosphere. By utilizing a gas-impervious paper instead of a water seal, a smaller amount of chloropicrin may be found equally effective.

Other Uses

We investigated the possibility of utilizing chloropicrin as a fumigant to control aphids on living sugar-beet plants in our greenhouse. Concentrations of from 1 pound per 24,000 cubic feet up to 1 pound per 1,000 cubic feet were tested. Severe burning of the plants was obtained where only a few aphids were killed, and where all aphids were killed, the plants also were killed. These results are in agreement with those of Spencer (18) and others who conclude that chloropicrin cannot be used for greenhouse fumigation because of its deadly effect on living plants.

Although adequate trials have not been conducted to establish proper treatment, we have utilized chloropicrin successfully for sterilization of root cellars and storage crates, at the rate of 1 pound per 1,000 cubic feet. We also have controlled sugar-beet nematode in field trials by applications of 6 cc. per square foot of treated area. A similar application destroyed perennial European bindweed. Bedbugs were thoroughly controlled in labor houses by 2 applications, at a 2-week interval, of 1 pound per 1,000 cubic feet.

Summary

The use of chloropicrin as a fumigant for beet-seed warehouses answers a need for a highly toxic, penetrating, safe, efficient fumigant for rodent control. The cost of the chemical for this control is only about 58 cents per 1,000 cubic feet per year.

Chloropicrin is a convenient fumigant for effective partial sterilization of greenhouse soils for the control of harmful micro-organisms and soil insects.

Chloropicrin may be utilized to sterilize root cellars and storage crates. It is useful in the control of nematode and bindweed. It may be used effectively to eliminate bedbugs from labor houses.

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