

## Validation of Colorimetric Detector Tubes for Compliance Monitoring of Chloropicrin in Fumigated Structures

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**Abstract.** A standard detector tube and pump apparatus for chloropicrin (CP) gas measurement was modified with a hypodermic needle to detect airborne ppm-level CP concentrations after evaporation of one fluid oz CP per 15 Mcf (Mcf = thousand cubic feet) of airspace in 22 structures ranging in volume from 4.5 Mcf to 123.5 Mcf. Chloropicrin readings were taken from four sides of each structure at 0, 0.5, 1.0, and 6.0 hours, and at termination of the fumigation (mean of 22 hours). No false positive reading of CP occurred at 0 hr. A total of 347 readings were positive for CP after CP introduction, while only one reading, at 0.5 hours, gave zero CP measurement. This study validates the use of colorimetric detector tubes as a regulatory inspection tool. The use of CP detector tubes is expected to yield greater compliance of CP-use regulations by the structural fumigation industry.

### Introduction

Although the addition of chloropicrin (CP) warning agent is a requirement of the sulfuryl fluoride (SF) label for structural fumigations (Anonymous 2006, 2007), the proper application of CP may be difficult or impossible to verify by regulatory agencies such as the Florida Department of Agriculture and Consumer Service (FDACS). Because CP is not used as an active ingredient in structural fumigations, it is not monitored during the fumigation or during the post-aeration clearance procedure.

Currently, the only means by which a regulatory inspector can determine compliance with the CP application procedure is to witness a certified operator or a special identification licensee dispensing the required volume of CP within the structure. This would require that the inspector enter the structure with protective gear while the CP is being dispensed. More typically, the inspector must rely on the presence of the CP evaporation pan(s) at the fumigation site to indicate that CP will be or had been applied. Because the CP evaporates long before the fumigation is concluded, it is impossible for an inspector to determine if the label-mandated fluid volume of CP (Anonymous 2006, 2007) was poured into the pan.

Because working concentrations of SF are odorless, the use of CP is one of the essential elements in preventing human or animal entry into a fumigated airspace. Likewise, CP application can be used to warn humans inside buildings that SF application is eminent. The inability for an inspector to verify the application of CP compromises his or her ability to conduct a complete safety inspection of an active fumigation site. The purpose of this study was to validate a simple, inexpensive, and reliable device and procedure for detection of CP from the exterior of an airspace undergoing fumigation.

### Materials and Methods

CP Measurement. Chloropicrin was measured from outside the structure using Kitagawa gas detector tubes for CP detection (tube no. 172S, 0.05 – 16 ppm, Matheson Safety Products, E. Rutherford, NJ). These tubes are used in series with an accompanying “pretreat” tube connected by a rubber sleeve (included in tube box) to an graduated indicator (detector) tube that is connected to a specifically designed air pump (Matheson model No. 8014-400A). This tube apparatus was modified for behind-tarpaulin sampling by the addition of a 14-gauge hypodermic needle attached with another rubber sleeve to the pretreat tube (Figure 1A). During sampling, the needle was used to penetrate a tarpaulin, polyethylene, or tape seal to obtain a sample of fumigated airspace that is, in series, pulled through the detector tube (Figure 1). Measurement of CP concentration followed the manufacturer’s instructions that accompany the tubes. A positive reading and its magnitude is indicated by the pink color which forms in the calibrated section of the detector tube (Figure 1B). Tubes were stored per manufacturer’s recommendations except during transport and field use. Manufacturer’s lot numbers were recorded for all tubes.

Test Structures. Twenty-two buildings were used to validate the above method. Buildings were selected from sites to be fumigated in cooperation with two companies: Dead Bug Edwards (Plantation, FL) and Hammerhead Termite Control (Big Pine Key, FL). Locating structures and securing permission for experimental trial was obtained by the fumigation company. Each building was graphed and measured for volume by the research personnel who advised the fumigator in charge of how much CP to apply. In each structure, CP was released at the lowest label rate of 1 fluid ounce/15,000 cubic feet of fumigated volume.

CP was measured from tube readings (ppm) in sets of four readings, one each, from the north, east, west, and south side of each structure. The approximate location of each measurement site was marked and a wireless temperature/humidity sensor (WS 2010, La Crosse, Technology Ltd., La Crescent, MN) was placed at each of the four locations before the structure is sealed per standard industry practice (Scheffrahn et al. 2005). For some structures, SF monitoring lines (0.25 inch ID) were also be placed at each location before sealing in order to measure SF concentration using a thermal conductivity detector (Fumiscop®). Immediately before taking a tube measurement, the temperature, humidity, and SF concentration was recorded at each site. The first set of measurements (controls) was taken from each site of each structure before either CP or SF was released into the structures. Four additional sets of four measurements were taken at 0.5, 1.0, and 6.0 hours after CP release and 20 minutes before the structure was aerated.

## **Results and Discussion**

The volume, environmental conditions, and mean chloropicrin concentrations measured for each of the 22 structures tested in this study are summarized in Table 1 and Figure 2. For the study overall, the fumigated volumes ranged from 4.5 Mcf (4,500 ft<sup>3</sup>) to 123.5 Mcf. Temperatures and humidities of the fumigated spaces ranged between 57.2 to 105.6 °F and 25-93 % RH, respectively. Fumigations were terminated (start of aeration) at between 16-26 hours after CP introduction (mean fumigation duration 22 hours). Before chloropicrin was released, all tube readings detected 0 ppm CP. Of the 348 measurements taken after the release of CP, only a single reading (structure 5, east side) measured 0 ppm CP, however the south, west, and north side of the building gave positive CP detection. Fumigation temperature did not affect tube performance as the detector tube reaction of CP with CrO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> is rapid even at low

temperature. Relative humidity also did not affect tube performance because the pretreat tube scrubs water from the air sample before arriving at the detector tube.

In every structure studied, the 0.5-hour reading was less than the 1.0-hour reading, which, in turn was less than the 6-hour reading. The final reading was always less than the 6-hour reading. This follows the expected behavior of CP after release: evaporation, followed by maximum airborne concentration, followed by sorptive and diffusive loss. Quantitative statistical analyses of data herein are difficult because each structure was an unreplicated unique entity.

## **Conclusions**

The method of CP detection validated herein is a reliable and effective means of determining label compliance of sulfuryl fluoride in structural fumigations. The method uses standard detector tube equipment and procedures with the exception of the hypodermic needle attached to the pretreat tube using a tube connector. The needle is inserted into the tarpaulin (polyethylene or tape) before the air sample is drawn.

Concentration of CP varies greatly (Figure 2) depending on type of structure, contents of structure, and unknown variables. Therefore, ppm-level readings should not be used to confirm or question compliance. The presence of CP in airspace alone verifies that the fumigator in charge did actually release CP. The new Vikane label (Anonymous 2006) offers optional CP-rate calculation as a function of volume and underseal. In larger buildings the optional CP rate may be less than one ounce/15 Mcf.

Based on the results of this study, the follow procedures are applicable for use of CP detector tubes in determining CP use compliance:

- 1) Earliest sample should be taken no earlier than 1 hour after CP introduction.
- 2) Last sample should be taken no later than 22 hours after CP introduction.
- 3) If first tube gives a positive CP reading, CP release is in compliance
- 4) If no chloropicrin is detected using the first tube, additional readings at other sides of the structure should be taken. If second, third, and fourth readings are negative, CP was not added at the correct label rate.

The results of this study validate the use of colorimetric detector tubes as a tool for regulatory compliance. The availability of these tubes by FLDACS inspectors should result in greater compliance of CP-use regulations for the structural fumigation industry

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## **References**

Anonymous. 2006. Vikane Gas Fumigant. Specimen Label. DowAgrosciences, Indianapolis, IN. EPA accepted 04/13/2006

Anonymous. 2007 Zythor. Specimen Label. Ensystex II, Inc. Fayetteville, NC

Scheffrahn, R.H., B.J. Cabrera, and W.H. Kern, Jr. 2004. Florida Fumigation Manual. University of Florida Institute of Food and Agric. Sci. Extension Publ. No. SP-340, 137 pp.

Table 1. Volume, temperature and humidity ranges, and mean (n=4) chloropicrin concentrations for 22 structures. All structures were on concrete slab foundations except for nos. 2, 4, and 17 which were crawlspace foundations. Structure no. 1 was a 35' boat.

Structure No.	Volume Mcf	Temp.		RH		Mean chloropicrin concentration			
		Min	Max	Min	Max	1/2 hr.	1 hr.	6 hr.	Final
1	4,500	70.3	83.8	63	83	1.55	2.75	3.15	0.95
2	7,200	71.6	105.6	40	80	4.38	5.88	3.50	1.35
3	11,100	66.3	88.3	25	73	1.18	1.88	1.73	0.58
4	15,800	77.4	92.4	47	64	2.18	3.48	6.33	3.80
5	16,905	61.5	80.4	44	85	0.88	1.58	2.40	0.81
6	17,700	66.3	83.6	57	82	3.38	5.83	5.03	2.08
7	20,000	60.9	76.2	49	79	2.43	4.23	4.23	1.98
8	22,486	67.8	95.3	39	86	3.00	4.98	4.38	1.40
9	22,700	74.1	89.6	48	67	3.38	4.18	3.48	1.40
10	24,400	68	91	60	84	0.69	2.63	4.75	0.94
11	25,000	74.3	91	36	66	2.73	3.85	5.00	1.78
12	32,500	64	87.4	28	70	1.68	2.50	4.58	2.68
13	35,000	57.2	81.8	35	73	1.68	2.53	3.90	1.13
14	35,201	73.2	97.1	39	80	5.25	8.25	6.25	4.00
15	38,000	73.2	82.2	53	91	3.68	5.53	6.28	1.95
16	40,000	72.8	95.5	30	72	2.25	3.98	7.00	3.48
17	46,300	73	90.3	36	63	3.78	5.88	6.98	4.03
18	52,100	67.6	83.8	35	67	2.18	3.25	5.15	2.73
19	56,600	69.9	87.2	41	87	3.30	4.45	4.13	1.57
20	91,982	80.9	93.3	44	93.3	2.86	3.70	3.63	1.78
21	114,100	67.6	79.7	37	69	2.90	4.50	4.73	2.43
22	123,500	76.2	86.5	36	56	0.50	0.73	1.63	1.15



Figure 1. Chloropicrin was measured through the tarpaulin seal of a fumigated structure using a 14-gauge hypodermic needle (A) connected by rubber sleeve to the “pretreat” tube. Another sleeve was used to connect the pretreat tube to the measuring tube (B) which was attached to the pump apparatus.

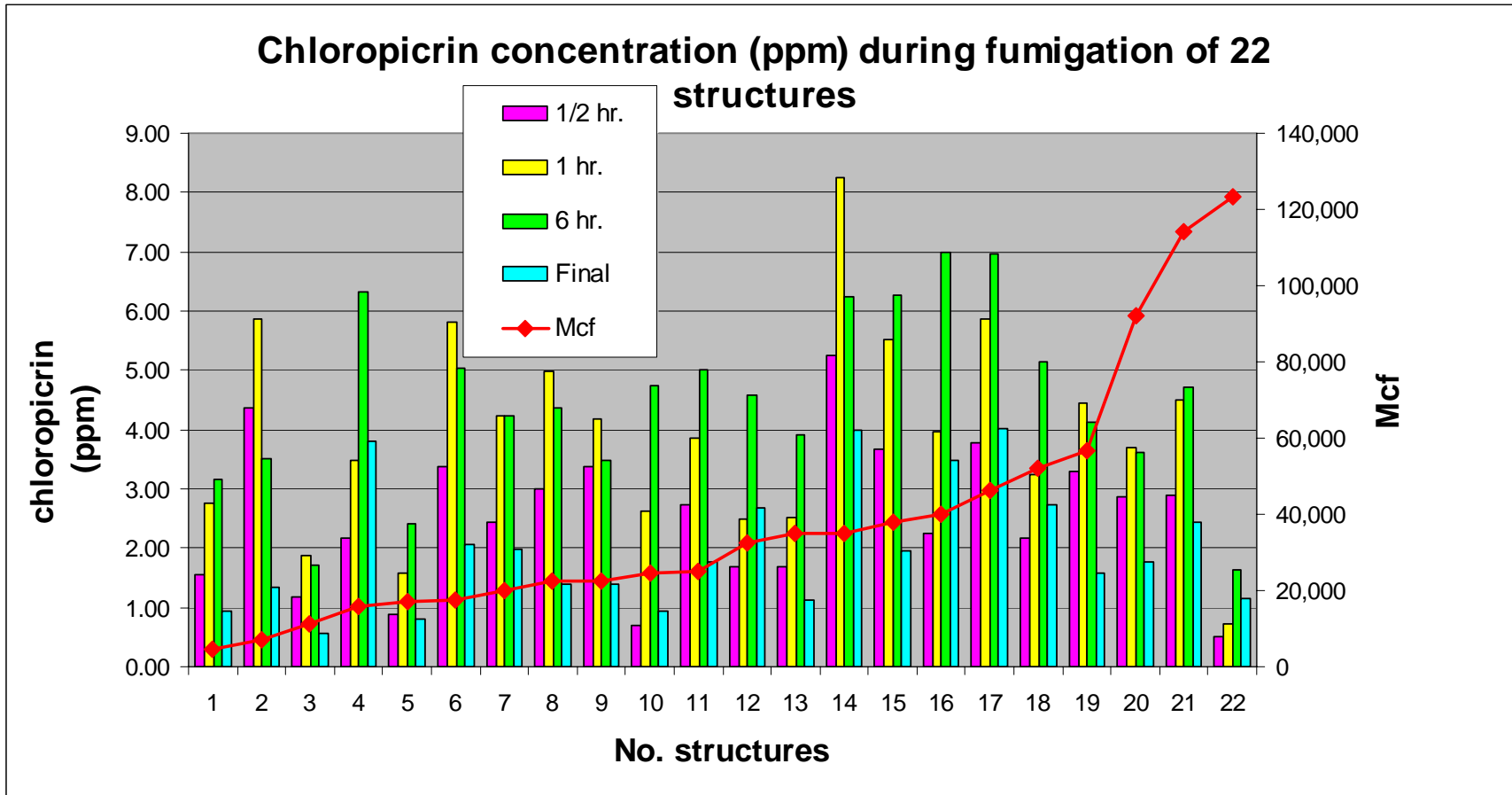


Figure 2. Volumes and mean (n=4) chloropicrin concentrations at 0.5, 1.0, 6.0 hours, and at termination (16-26 hrs) of 22 fumigated structures tested. At 0 hrs, 1 fluid ounce/15Mcf of chloropicrin was released into each structure.