A STUDY OF THE LEVELS OF METHYL BROMIDE AND CHLOROPICRIN IN THE AIR DOWNWIND FROM A FIELD DURING AND AFTER A PREPLANT SOIL FUMIGATION (SHALLOW INJECTION) - A PRELIMINARY REPORT

by

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SUMMARY

The levels of methyl bromide and chloropicrin in the downwind air were monitored during and after a preplant soil fumigation (shallow injection) in Orange County in 1982. In general, the levels of methyl bromide fluctuated throughout the day and were all below the Cal/OSHA 8-hour Permissible Exposure Limit (PEL) of 15 ppm for the workplace, ranging from below the detectable limit (22 ppb) up to 634 ppb. The data on chloropicrin showed levels increasing after the fumigation ended. These levels slightly exceeded the PEL of 100 ppb for chloropicrin twice during the day and ranged from below the detectable limit (1.0 ppb) up to 106 ppb. Only one day's fumigation was monitored because of erratic weather and other work commitments.

INTRODUCTION

Methyl bromide and chloropicrin are Toxicity Category I pesticides. Mixtures of the two chemicals are registered for use in California as a preplant soil fumigant. The mixture is used to kill weed and grass seeds, nematodes and other soil-borne organisms.

Methyl bromide is a colorless, tasteless, nonflammable gas which is odorless except at extremely high concentrations (2). It is known to cause damage to the lungs, nervous system, kidneys, and skin with sufficient dosage. The onset of symptoms from overexposure can be delayed for up to several hours. The PEL for methyl bromide is 15 ppm for an 8-hour TWA in the workplace environment. There is no standard for nonworkplace environments. The Cal/ OSHA ceiling level (not to be exceeded) for methyl bromide is 50 ppm.

Chloropicrin is a heavy nonflammable liquid. The odor threshold is reported from 0.78 to 1.1 ppm (3,4). Concentrations of 0.3 ppm result in painful irritation to the eyes in three to 30 seconds (1). No threshold level for eye irritation was found in the literature. The 8-hour PEL for chloropicrin is 0.1 ppm in the workplace environment. There are no standards for non-workplace environments. No Cal/OSHA exposure ceiling has been set for chloropicrin, but using the guidelines in Title 8, Section 5155 of the California Administrative Code, 0.3 ppm would be the recommended maximum exposure concentration. The American Conference of Governmental Industrial Hygienists have recommended a Threshold Limit Value (the TLV is the same as the PEL) of 0.1 ppm and a Short-Term Exposure Limit (STEL) of 0.3 ppm (1). These recommendations were made to provide freedom from eye irritation and prevent potential pulmonary changes.

APPLICATION

The major use period of the methyl bromide/chloropicrin mixture as a soil fumigant to fallow fields is from early July to early October. The methyl bromide and chloropicrin are premixed in compressed gas cylinders by the registrant. The mixture is shank-injected into the soil approximately eight inches deep using a positive pressure closed system (pressurized with nitrogen gas). A one mil polyethylene tarp is automatically laid down over the soil behind the shanks. The tarp reduces the dissipation rate of the gases into the air which lessens the hazards to the workers and increases the overall efficacy of the gases.

MATERIALS AND METHODS

Air samples were collected 25 feet downwind from the application site. Site adjustments were made as shifts in the wind direction became apparent (see Chart 1). The sampling periods lasted for approximately 45 minutes each. A 15 minute time period elapsed between sampling periods for each site [a period of 30 minutes occurred once between sampling periods at site A (see Graphs 1 and 4)].

Methyl bromide was trapped on charcoal sorbent tubes (SKC #226-09, Lot 120), while the chloropicrin was trapped on two XAD-4 resin tubes (SKC #226-30-11-04, Lot 146) connected in series. Separate MSA model C-210 portable pumps were used with each type of tube. The pumps were calibrated to draw approximately 200 ml of air per minute. The counters on the C-210 portable pumps were also calibrated to determine the ml/count ratio. The counters were read before and after each sample period. The net count was multiplied by the ml/count ratio to determine the volume of air (in ml)/sample.

All samples were capped and placed on dry ice and shipped to the department's laboratory for analysis. In the laboratory, the sampling tubes were divided into sections to determine if breakthrough occurred, indicating non-quantitative trapping of methyl bromide or chloropicrin. The charcoal tubes were separated into front and back sections with each analyzed separately. See Appendix 1 for the analytical method for methyl bromide. The chloropicrin sample was analyzed in three parts to check for migration through the tubes and to detect the amount of breakthrough, if any, into the third section. The first section was the whole first tube, the second was the front of the second tube, and the third section was the back portion of the second tube. See Appendix 2 for the analytical method for chloropicrin.

RESULTS

The data shows the levels of methyl bromide in the downwind air to be significantly below the PEL of 15 ppm. In fact, all were below 1 ppm, with the highest level being 634 ppb. The corresponding data for chloropicrin showed the peak levels slightly above the PEL of 100 ppb. The highest chloropicrin level found was 106 ppb. See Table 1 for a summary of the data.

DISCUSSION

Concerns had been raised about the hazards of methyl bromide and chloropicrin exposure to people living adjacent to fumigated fields. The objective of the study was to determine the concentrations of methyl bromide and chloropicrin in the downwind air from a fumigated field. Unpredictable fall weather and other work commitments prevented more than one day of sampling. The fumigation was done between 8:30 a.m. and 5:00 p.m. with a noon break for lunch. The operation was moving away from the sampling sites (see Chart 1). The data obtained showed the overall concentrations of chloropicrin in the air to have steadily increased from 4:00 p.m. to 9:45 p.m. (see Graphs 5 and 6). The data on the concentrations of methyl bromide showed a trend of rising as the day progressed, but was more erratic than the chloropicrin data (see Graphs 1 to 3).

The results from this field indicate that the concentrations of methyl bromide in the air are low relative to the PEL of 15 ppm. The highest concentration found was 634 ppb (approximately 4 percent of the PEL) which occurred when the fumigating operation was close to the sampling site. The air concentrations of chloropicrin, on the other hand, peaked at concentrations slightly above the PEL of 100 ppb. Graph 6 clearly shows increasing concentrations of chloropicrin in the air from 3:00 p.m. to 8:45 p.m., before the wind direction changed slightly and concentrations dropped to less than detectable levels. Sample Site B shows chloropicrin concentrations (Graph 5) remaining fairly stable from 4:00 p.m. to 7:00 p.m. before rising steadily through the last three sampling periods.

The data from this preliminary study shows a possible problem with the airborne levels of chloropicrin while showing no potential problems with the airborne concentrations of methyl bromide. This is encouraging because methyl bromide is odorless at acceptable exposure levels while chloropicrin acts as its own warning agent. At very low concentrations chloropicrin can be slightly irritating to the eyes. Problems with irritation due to field fumigations have been known to occur to people living close to those fields (according to the Orange County Agriculture Department).

The analysis of the samples showed breakthrough is not a serious problem. Only two of eighteen methyl bromide samples showed more than 10 percent (11.8 and 11.4 percent) breakthrough into the back section of the charcoal tube. Breakthrough into the third section of the chloropicrin sampling trains was negligible (all were down near the limit of detectability) while four of 18 samples had greater than 10 percent in the second section.

Concentrations of methyl bromide and chloropicrin in the breathing zone of the fumigation workers was also monitored. The results are in report HS-1076.

CONCLUSIONS

The data indicates the concentration of methyl bromide in the downwind air from field fumigations should not pose a health hazard under normal conditions. The data also indicates the concentration of chloropicrin in the downwind air may cause minor irritation (most likely to the eyes) to humans under some conditions. More data is needed to further characterize concentrations of chloropicrin during and after fumigation. Future sampling should include before, during, and after fumigation samples. Sampling should be continued until measurable levels of the fumigants have subsided.

TABLE 1

Concentrations of Methyl Bromide and Chloropicrin in the Downwind Air During and After a Preplant Soil Fumigation (Shallow Shank).

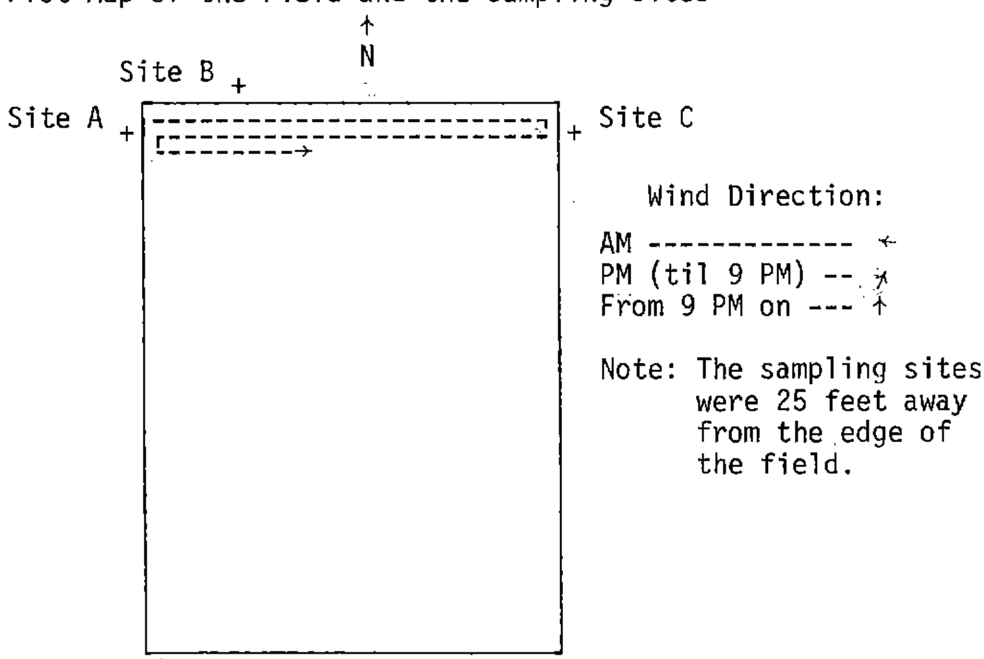
Time	Methyl Bromide (ppb)			Chloropicrin (ppb)		
	Site A	Site B	Site C	Site A	Site B	Site C
0900-0945	634	---	---	33	---	---
1015-1100	62	---	---	7	---	---
1115-1200	437	---	---	ND(1)	---	---
1400-1445	---	257	---	---	80	---
1500-1545	---	252	122	---	102	28
1600-1645	---	253	455	---	32	66
1700-1745	---	284	296	---	36	73
1800-1845	---	193	317	---	22	78
1900-1945	---	336	560	---	37	97
2000-2045	---	455	488	---	64	106
2100-2145	---	361	ND(2)	---	76	ND

(1) MDL = 1.0 ppb.

(2) MDL = 22 ppb (0.2 ug/sample and assuming a 9 liter sample).

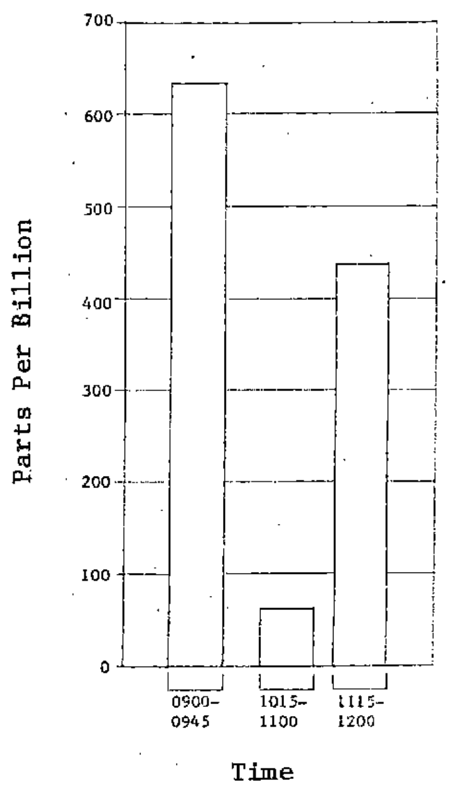
CHART 1

Plot Map of the Field and the Sampling Sites



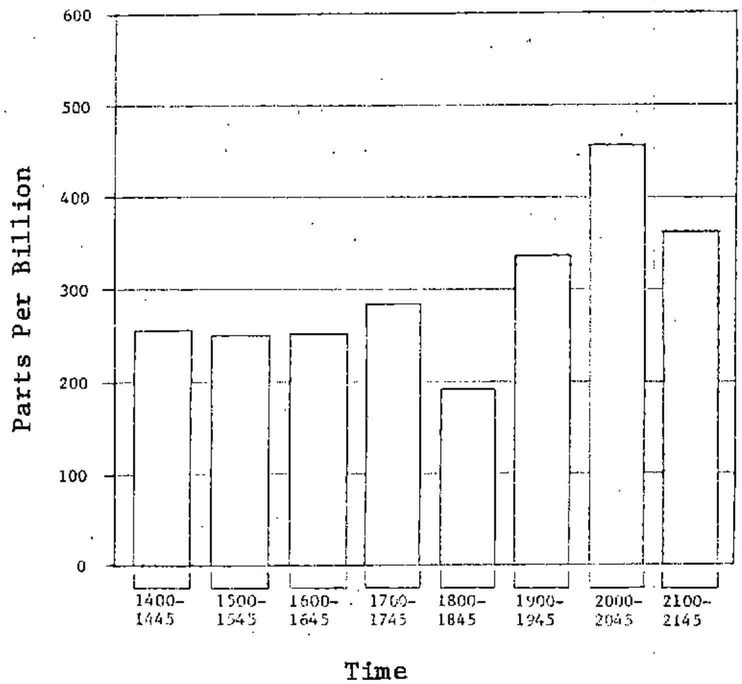
GRAPH 1

Measured Concentrations of Methyl Bromide in the Downwind Air at Site A During fumigation



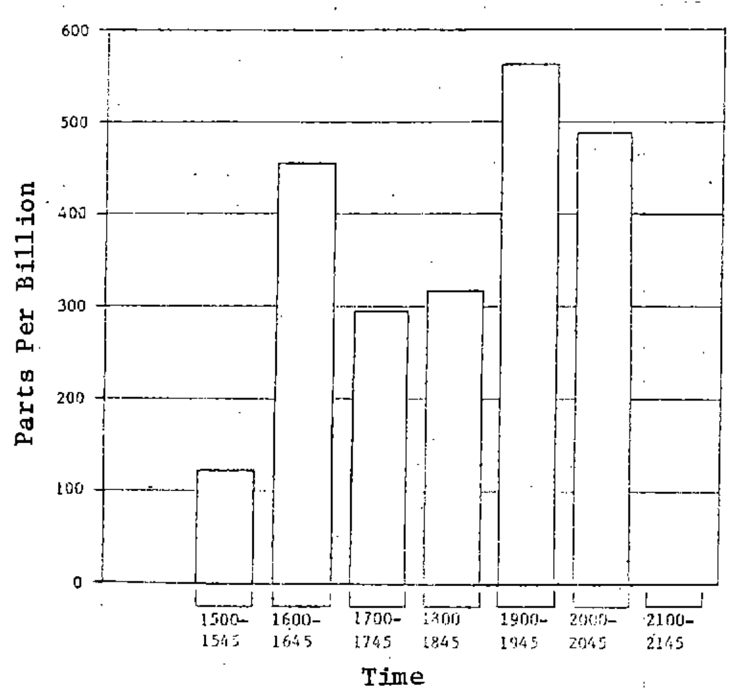
GRAPH 2

Measured Concentrations of Methyl Bromide in the Downwind Air at Site B During and After Fumigation



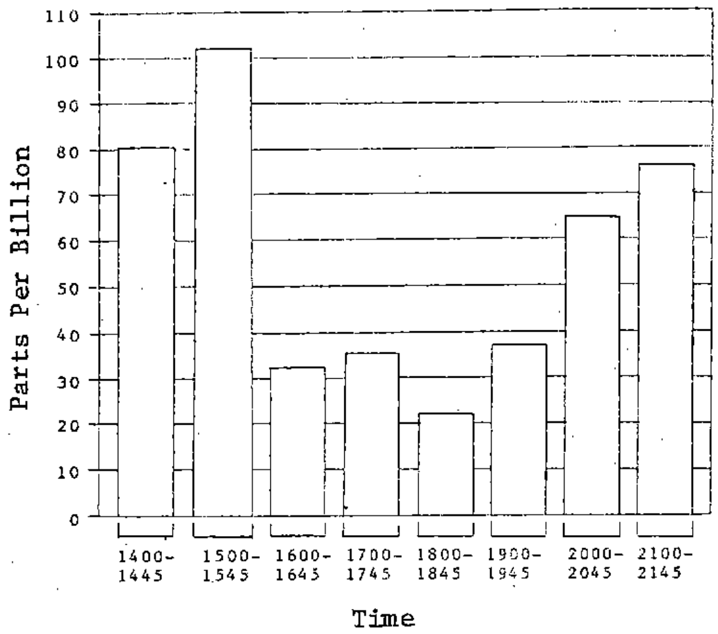
GRAPH 3

Measured Concentrations of Methyl Bromide in the Downwind Air at Site C During and After Fumigation



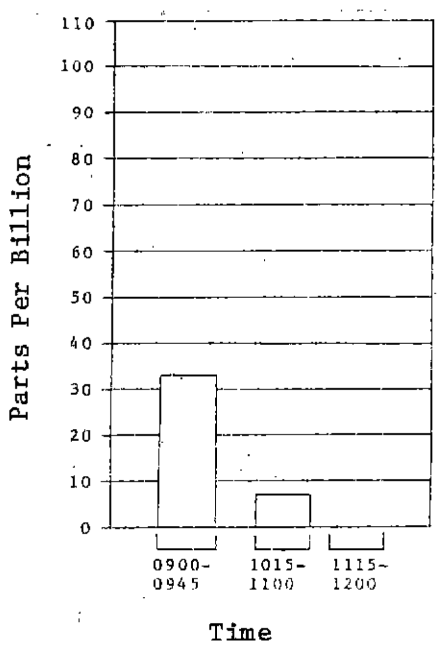
GRAPH 5

Measured Concentrations of Chloropicrin in the Downwind Air at Site B During and After Fumigation



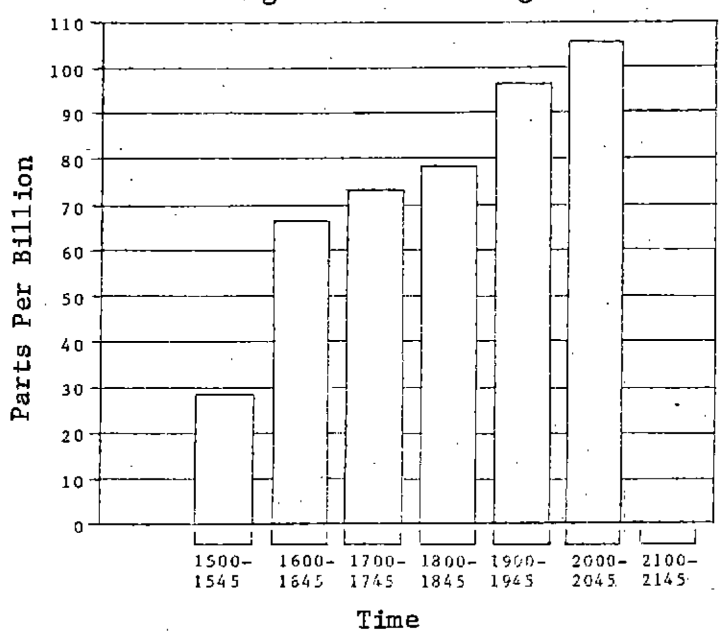
GRAPH 4

Measured Concentrations of Chloropicrin in the Downwind Air at Site A During Fumigation



GRAPH 6

Measured Concentrations of Chloropicrin in the Downwind Air at Site C During and After Fumigation



REFERENCES

1. American Conference of Governmental Industrial Hygienists. 1980. Chloropicrin. Documentation of the Threshold Limit Values (4th Edition). Cincinnati.

2. American Conference of Governmental Industrial Hygienists. 1980. Methyl Bromide. Documentation of the Threshold Limit Values (4th Edition). Cincinnati.

3. Amoore, J.E. and E. Hautala. Odor as an Aid to Chemical Safety: Odor Thresholds Compared with the Threshold Limit Values and Volatilities for Industrial Chemicals (In Press).

4. National Institute for Occupational Safety and Health/Occupational Safety and Health Administration. 1981. Occupational Health Guidelines for Chloropicrin. Occupational Health Guidelines for Chemical Hazards. Washington D.C.

DETERMINATION OF METHYL BROMIDE ON CHARCOAL TUBES

Scope

This method is for the desorption and analysis of methyl bromide from charcoal air sampling tubes. It is intended solely for the use of the California Department of Food and Agriculture, Chemistry Laboratory Services.

Principle

Methyl bromide (MeBr) that has been adsorbed from the air onto activated charcoal is desorbed from the charcoal with ethyl acetate, diluted as needed and analytically determined by gas chromatography using flame ionization or electron capture detection.

Reagents and Equipment

1. Ethyl acetate, nanograde.
2. Analytical grade methyl bromide.
3. Approved and calibrated personal sampling pump.
4. Charcoal tubes--SKC #226-09.
5. Developing vials with teflon liners--SKC #226-02.
6. Assorted microsyringes for preparing standards and gas chromatography.
7. Assorted pipets.
8. Volumetric flasks.
9. Small triangular file for scoring glass tubes.
10. Gas sampling bulb--Supelco 500 ml. with septum (#2-2148).

Analysis

Interferences: High humidity may affect trapping efficiency.

1. Score each charcoal tube with a file in front of the first section of charcoal.
2. Break open the tube. Remove and discard the glass wool.

3. Transfer the charcoal in the upstream section to a labeled desorption vial which contains a known amount of nanograde ethyl acetate. 2-4 ml. is suggested. Adding solvent to the charcoal may cause loss of MeBr.

4. Remove and discard the foam partition from the tube.

5. Transfer the second section of charcoal to a second labeled desorption vial which contains a known amount of nanograde ethyl acetate.

6. Allow the samples to desorb for one hour while rotating at 30 rpm.

7. Transfer an aliquot to a sample storage vial, label, and freeze until analysis time.

8. Determine by GLC.

Determination of Desorption Efficiency

1. Inject a known amount of MeBr (1 microgram to several milligrams) into the charcoal with a syringe and cap the tube with the supplied caps. The tube should be from the same lot that was used for the samples.

2. At least five tubes (preferably at levels covering the expected range) should be prepared in this manner and allowed to stand at least overnight to assure complete desorption. A blank tube should be treated the same way except that no sample is added.

3. Analyze the tubes by the analytical procedure.

4. Desorption efficiency = $\frac{\text{Response sample-response blank}}{\text{Response standard}}$

   The standard(s) should be the same amount as injected into the charcoal tubes. This eliminates standard variation errors.

Calculations

1. Determine weight of MeBr present on charcoal tube sections by GLC analysis.

2. Correct this total weight of MeBr by subtracting any blank value present on the blank tube.

3. The corrected weight is divided by the desorption efficiency to obtain the final weight of MeBr present.

4. The volume of air sampled is converted to standard conditions of 25°C and 760 mm Hg.

$$VS = \frac{V \times P \times 298}{760 \times (T+273)}$$

Where VS = Volume of air at standard conditions.
V = Volume of air as measured.
P = Barometric pressure in mm Hg.
T = Temperature of air in °C.

5. Calculate ppb in air from the above data.

$$\text{ppb (volume basis)} = \frac{ng \times 24.45}{VS \times 94.9} = \frac{ng}{VS} \times 0.2576$$

24.45 is the mole volume of MeBr at 25° and 760 mm.
94.9 is the molecular weight of MeBr.

Gas Chromatographic Conditions

Gas chromatograph with Ni^{63}, H^3, or flame ionization detector.

Temperature - Injector: 125°C.
Detector: Follow manufacturer's suggestions.

Column: 20' x 1/8" O.D. nickel tubing.
10% SP-2100 on 100/120 Chromosorb W-HP.
70°C, 10 ml/min N_2 carrier gas.
MeBr retention time approximately 1.9 minutes.

Column: 6' x 2 mm I.D. glass.
80/100 Poropak Q
130°C, 30 ml/min N_2 carrier gas.
MeBr retention time approximately 1.4 minutes.

Column: 20' x 1/8" O.D. nickel tubing
10% FFAP on 100/120 Chromosorb W-HP.
70°C, 25 ml/min N_2 carrier gas.
MeBr retention time approximately 1.9 minutes.

References

1. NIOSH Manual of Analytical Methods, Second Edition. Method S372. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

2. Determination of EDB on Charcoal Tubes, California Department of Food and Agriculture, Chemistry Laboratory Services, 3292 Meadowview Road, Sacramento, California 94832.

3. Malone, B., Analysis of Grains for Multiple Residues of Organic Fumigants. AOAC, 52, p. 800, 1969.

4. Clower, M., Modification of the AOAC Method for Fumigants in Wheat. FDA Laboratory Information Bulletin #2169, August 1978.

5. Mr. Mario Fraccia, Air and Industrial Hygiene Lab, California Department of Health, Berkeley, California. Personal Communication.

THE ANALYSIS OF AIR SAMPLES FOR CHLOROPICRIN

Scope

This analysis is for the determination of chloropicrin on XAD-4 resin air sample tubes.

Principle

Chloropicrin is trapped on XAD-4 tubes at the sampling site, frozen during transport to the lab, desorbed with ethyl acetate, and analyzed on a capillary GLC using electron capture detection.

Reagents and Equipment

1. Ethyl acetate--pesticide grade, checked for interferences.

2. Appropriate glassware.

3. Gas Chromatograph.

   Instrument: Hewlett Packard 5880 with ECD detector at 300°C.

   Column: 30 M x .25 mm J & W 1701 at 40°C. Operated in split mode--approximately 100:1 split.

   Column pressure: 20 psi.
   Split flow: 40 ml/min.

   Injector: Split injector liner at 220°C.

Under these conditions chloropicrin elutes in 6.5 minutes.

Analysis

Break the XAD-4 tubes and place the resin in 5 ml vials containing 4 ml ethyl acetate. Desorb tubes for an hour on a rotator. Proceed to the GLC with no further preparation.

Desorption Coefficient

The desorption coefficient is 94 percent at the two microgram/spl level.

Calculations

Results should be reported in ppb and mg/m^3 using the appropriate air sample calculations. The molecular weight of chloropicrin is 164.4.

Discussion

At the present time, a single sample consists of two tubes in series. The entire first tube is treated as the "front" section, and the second tube is treated as two additional sections. This system was used to check out breakthrough. If the sample size is kept to 10 L or less, and the sample flow rate is about 200 ml/min, the breakthrough will be 10 percent or less. Recoveries are 94 percent for levels of about 30 ppb, or 2 ug/spl.

References

Guide to Chemicals Used in Crop Production, Information Canada, p. 118, 1973.

NIOSH Manual of Analytical Methods, Method S212, S104, 260.