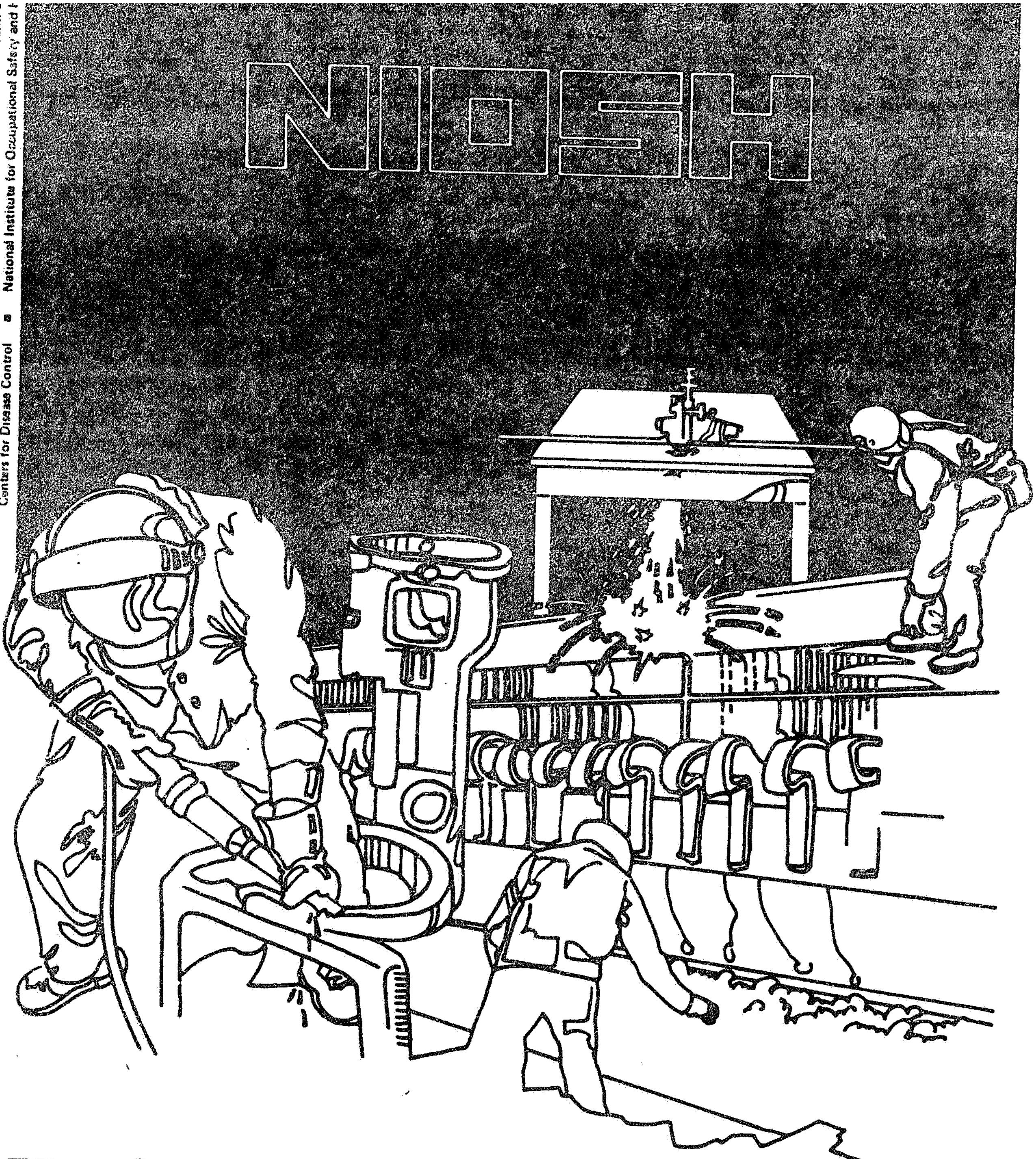
U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES ■ Public Health S
Centers for Disease Control ■ National Institute for Occupational Safety and H



Health Hazard Evaluation Report

HETA 84-194-1549
AMERICAN FEDERATION OF GRAIN MILLERS, LOCAL 118
SUPERIOR, WISCONSIN

HETA 84-194-1549
JANUARY 1985
AMERICAN FEDERATION OF GRAIN MILLERS, LOCAL 118
SUPERIOR, WISCONSIN

NIOSH INVESTIGATORS:
Steven H. Ahrenholz, C.I.H.

I. SUMMARY

On February 17, 1984, the National Institute for Occupational Safety and Health (NIOSH) received a request from Local 118 of the American Federation of Grain Millers and Congressman David Obey's office to evaluate a railway grain shipment for grain fumigants. A grain elevator worker opening the railroad cars to conduct routine fumigant testing had become ill raising concerns that this shipment had been heavily treated with chemicals to eradicate insects. (The railcars were located in a railroad yard, waiting to be unloaded.) In anticipation of the grain being unloaded into a grain elevator, the request focused on identification of fumigants and determination of the levels present. No workers were evaluated in this study, as none were required to handle the grain at the time of our survey.

On February 18 and 19 a NIOSH industrial hygienist conducted a field survey. The environmental methodology involved sorbent tube sampling both above the grain and in the grain for chlorinated hydrocarbons (e.g. carbon tetrachloride, chloroform, ethylene dichloride, and 1,2-dichloroethylene), carbon disulfide, methyl bromide, and ethylene dibromide. Bulk samples of grain were also collected. A total of seven of 26 cars in the train were sampled, selected in a systematic manner.

All seven bulk grain samples contained carbon tetrachloride and carbon disulfide with small amounts of chloroform and methylene chloride. Concentrations of fumigants in the grain (from air samples pulled through the grain mass) had the following ranges: carbon tetrachloride - 0.75 to 61 parts per million (ppm); carbon disulfide - nondetectable (ND) to 6.5 ppm; chloroform - ND to an estimated maximum of 0.14 ppm. Fumigant concentrations in air samples obtained one to eight inches above the grain mass were as follows: carbon tetrachloride - ND to 0.46 ppm; carbon disulfide - all ND; chlorofrom - all ND. No other halogenated compounds were identified. No methyl bromide or ethylene dibromide were detected in any of the samples collected. Chloroform and methylene chloride were considered to be present as impurities. No occupational exposure criteria is considered applicable to this data, since the intended purpose of the data collection was compound identification.

Data obtained from this investigation demonstrated the presence of both carbon tetrachloride and carbon disulfide in this grain shipment. No ethylene dibromide or methyl bromide was found. Since no unloading of the grain was taking place and no workers were working around the shipment during the survey, no direct evaluation of worker exposure could be undertaken in this investigation. However, the results of the survey identify the possible exposure responsible for the acute illness of the worker first opening the railcars. Exposures of grain inspectors and grain elevator workers to fumigants are evaluated in two subsequent NIOSH HETA reports (HETA 83-375 and HETA 84-311). Recommendations include personal protective equipment and reporting of fumigant usage on inbound grain shipments.

KEYWORDS: SIC 5153 (Grain), grain fumigants, carbon disulfide - CAS #75-15-0, carbon tetrachloride - CAS # 56-23-5, ethylene dibromide - CAS #106-93-4

II. INTRODUCTION

On February 17, 1984, the National Institute for Occupational Safety and Health (NIOSH) received a request from Local 118 of the American Federation of Grain Millers and Congressman David Obey's office to evaluate a rail shipment of grain for fumigant concentrations. The grain shipment was located in the Chicago and North Western - Superior Wisconsin railroad yard. A NIOSH investigator conducted a site visit and environmental monitoring February 18-19, 1984. The purpose of this survey was to conduct sampling in and around the unit train shipment for the purpose of identifying the fumigants present in the grain and obtaining an indication of fumigant concentrations. Sampling railroad hopper cars containing fumigated grain was conducted February 19, 1984.

Local 118, Congressman Obey's office, and representatives of Peavey Company's Globe Elevator (the elevator to whom the shipment was consigned) were notified directly of preliminary sampling results as they became available. A letter report sent to the above parties March 15, 1984, presented all results obtained during this survey.

This final report will present the findings of the NIOSH investigator along with more information on the sampling and analytical methods used.

III. BACKGROUND

A. Basis of the Request

On Monday, February 13, 1984, a member of Local 118 was reported by the union to have become ill after opening several grain-filled railroad cars. The worker experienced acute health affects during the routine opening and fumigant sampling procedures conducted on inbound railroad shipments. All railroad cars are routinely checked for the presence of fumigants upon delivery to the elevators. The immediate concern in this instance was the identification and evaluation of fumigant concentrations in this shipment. Direct reading indicator tube samples obtained by the elevator workers and OSHA had not provided sufficient information to answer this question.

Local 118 expressed additional concerns about this shipment which included the extent of exposure to fumigants associated with dumping and handling this grain in the elevator, the exposure of grain inspectors conducting "sniff tests" to fumigants, and whether in-the-grain or above-the-grain sampling makes a difference in determining when grain fumigant levels are acceptable for unloading and loading purposes. (Note: a sniff test is part of the grading process conducted on a grain sample. This test requires the grain inspector to smell the grain directly for musty or sour odors).

B. Problem Description

Efforts to evaluate fumigant exposures associated with the handling of treated grain are fraught with variables beyound the control of any single group. The identification of treated, unplacarded grain shipments before an overexposure incident occurs can be enhanced by screening grain samples but fumigant identity may not be known before the sample is taken, possibly resulting in inappropriate sample collection. The loss of placards on fumigated rail shipments may contribute to worker fumigant exposures through the assumption that the grain has not been treated. Likewise, failure to remove placards from untreated grain shipments (present from previous ladings) further reduces the value of using placards alone to indicate fumigated cargo. Difficulty in identifying the source of fumigated grain complicates efforts to identify substances used on grain shipments. This essentially insures that the application rate (amount used) of the fumigant will remain unknown as well as the identity of specific fumigants used. The multiple fumigation of grain during its storage and shipment may result in higher residual fumigant levels in recently loaded grain shipments, even though the grain was not directly treated prior to the last transfer of grain into the railcar. Temperatures influence the release of volatile fumigants from the grain and in the case of phostoxin, may inhibit phosphine gas release at low ambient temperatures. Currently there is no consensus as to what constitutes sufficient aeration or handling of fumigated grain which renders it "safe" for conducting a sniff test. Additionally, information is lacking on how grain should be tested to determine if it is free of fumigants or at least will not present a health hazard to workers handling the grain. Another question that is raised is whether different grain behave similarly or differently when fumigated as far as fumigant retention and release are concerned. Lastly, there does not appear to be any reliable method of predicting increased movement of fumigated grain. Essentially grain shipments come into the elevator "as is" with no historical information on the grain or shipment. The time and location of fumigant application often is not known.

IV. METHODS AND MATERIALS

Thirty-one railroad hopper cars were reported to be of concern in this instance, however, at the time sampling was conducted only 26 were located. Therefore, sampling was limited to this identified group of cars. No personal exposure monitoring was conducted since the grain was not being dumped or inspected and no workers were present. Two sets of samples were obtained for each of seven railroad cars containing fumigated grain. One set was obtained by burying a small inverted box (ie bottom open) about 8 inches down in the grain. Sampling tubes were inserted through holes in the top and the entire assembly buried in a mound of grain (submerged or in-the-mass samples). The second set was obtained by suspending sampling trains one to eight inches above the grain (above-the-mass samples), in the same location as the submerged sample set. A bulk sample of the grain was also taken from these locations. The sampling rate used for sorbent tubes was 1 liter per minute. Except for the methyl bromide samples (which used Qazi Ketchum tubes) all air samples were collected using standard coconut shell charcoal tubes. Cars were selected by taking the first (southern most) connected rail car on track number 3 and subsequently sampling every fourth car.

The analytical methods used for bulk grain samples and sorbent tube samples for chlorinated hydrocarbons, carbon disulfide, methyl bromide, and ethylene dibromide are presented in Appendix I. Bulk grain samples were desorbed both with carbon disulfide and 1% methanol in benzene.

VI. RESULTS

Analysis of seven bulk grain samples by solvent extraction indicated the presence of carbon tetrachloride and carbon disulfide with much smaller amounts of chloroform and methylene chloride. Fumigant concentrations in the grain (air samples pulled through the grain mass) had the following ranges: carbon tetrachloride - 0.75 to 61 parts per million (ppm); carbon disulfide - nondetectable to 6.5 ppm; chloroform - nondetectable to an estimated maximum of 0.14 ppm. Fumigant concentrations in the air one to eight inches above the grain mass were as follows: carbon tetrachloride - nondetectable to 0.46 ppm; carbon disulfide - all nondetectable; chloroform - all nondetectable. No other halogenated compounds were identified. No ethylene dichloride (1,2-dichloroethane) or 1,2- dichloroethylene was detected on any of the chlorinated hydrocarbon air samples. No methyl bromide was detected in any of the samples collected. Chloroform and methylene chloride were identified as present in small amounts relative to carbon tetrachloride and carbon disulfide concentrations (i.e. most likely as an impurity). Analyses for ethylene dibromide were negative.

Ethylene dibromide, if present, was not above the analytical detection limit of 100 nanograms (0.0001 milligrams) per sample. This means that EDB, if present, was below 0.0004 ppm or less than 0.003 milligrams (3 micrograms) per cubic meter. (For reference NIOSH's recommended short term personal exposure limit (breathing zone) for EDB is 0.13 ppm in any 15 minute period.)

As mentioned previously all results presented here and in Table I should not be interpreted as worker exposures because these samples were collected for fumigant identification purposes, are more appropriately considered process samples, and were taken at locations considered unrealistic for a worker's breathing zone (e.g. submerged in the grain). Air temperature during the survey was about 42° Farenheit and 40% relative humidity.

VII. DISCUSSION AND CONCLUSIONS

The fumigants identified as present on the grain in question were carbon tetrachloride and carbon disulfide. Trace quantities of methylene chloride and chloroform appear to be present as contaminants of the carbon tetrachloride rather than specific components of the fumigant. The difference between submerged and headspace values confirms the belief that levels of fumigant measured above the grain do not represent fumigant levels in the grain. This is especially pertinent in regard to determining the presence of fumigants on grain that will be "sniff tested". The data presented here identifies fumigants for which potential exposures may exist.

Limitations associated with sampling at one point near the top of the hopper cars are: the non-uniformity of fumigant concentrations throughout the grain; the absence of air contact and dilution deep in the car until dumping occurs at which time the grain/interstitial fumigant equilibrium is disturbed permitting increased release of fumigants; warming of grain as it passes through the elevator (especially during colder seasons) increasing the rate of fumigant vaporization from the grain; and the unknown effectiveness of aeration procedures for a relatively solid mass (the undisturbed grain) at atmospheric temperatures and pressures. All of these considerations prevent equating independent levels found in grain or above grain with any quantitative worker exposure Data on fumigant levels in grain provides a more conservative means of deciding whether the grain is acceptable for handling by workers. Determination of worker exposure associated with handling fumigated grain needs to be obtained through personal exposure monitoring, however caution should be applied when handling all fumigated grain for the reasons previously mentioned. The limitations currently associated with evaluating the fumigated grain, as received, prevent assurance that worker exposures or overexposures to fumigants will not occur.

An additional factor influencing the fumigant concentrations observed in the samples collected during this survey is that the hopper cars had been left open and efforts to aerate the grain undertaken between the time of the triggering event (worker illness) and when samples could be collected. (See Section III: Background). Re-creation of the transient circumstances occurring during incidents of this type is not possible.

Sampling in the grain mass (submerged samples) for fumigants appears to be a more conservative approach for determining the presence of chemical contaminants in a grain shipment. At the present time there does not appear to be any criteria to which such sampling data can be directly compared in determining the potential health hazard associated with handling treated grain. NIOSH investigators have conducted surveys involving exposure monitoring of workers handling fumigated grain and for potential fumigant exposures at different contact and transfer points during the sampling, inspection, and dumping of treated grain. The reader is referred to these final HETA reports (HETA

83-375-1521, Federal Grain Inspection Service, Portland, Oregon[1] and HETA 84-311 American Federation of Grain Millers, Local 118, Superior, Wisconsin[2]) for the findings, discussions, and recommendations concerning worker exposures.

VIII. RECOMMENDATIONS

A. Interim Recommendations

These recommendations are intended to be amenable to more immediate implementation. Due to the varying circumstances affecting worker exposures to grain fumigants, some situations do not lend themselves to a simple or expedient solution.

1. Workers required to open fumgated railcars should have self-contained breathing apparatus (SCBA) to use during the initial opening of the shipment(s). This is necessary due to the variables preventing identification and evaluation of fumigant levels in unopened marked and unmarked railcars. An alternative is the use of a gas mask which is approved for use against organic vapors and phosphine. The latter eliminates some of the problems associated with use and maintenance of an SCBA program, although the protection provided is not as great.

2. Fumigant placards should be placed on top of the cars by the hatch or doors in addition to being attached to the side of the car. (Sec 174.208 para (b) of the Hazardous Material Transportation Act regulations state that a railcar with treated lading"...must be placarded on each door (or as close as possible to the door if it is not possible to placard the door) ..." Possible alternates include incorporation of an additional tag designating fumigated lading on the hatch door seals.

3. Workers need to be informed that the designated opening dates and times given on placards do not refer to the car's safety for entry or absence of fumigant vapors after that time period.

4. Workers using indicator tubes to assess fumigant concentrations should be trained in the use of such equipment and also be made aware of its limitations.

5. Elevator managers and operators should routinely elicit information on fumigant treatment of incoming grain prior to its arrival at the elevator.

B. Long-Term Recommendations

The following recommendations are considered appropriate in addressing the long-term solution of this problem.

1. Institute a method of tracking grain fumigation during a shipment's passage through the grain handling system with the burden of assurance that a shipment does not exceed acceptable fumigant levels upon the shipper and/or owner.

2. Develop a uniform approach mutually agreed upon and honored by the elevators concerning how fumigated grain shipments should be handled. This could serve as a deterrent to shipping heavily fumigated grain or of shippers searching among elevators for those with the most lenient policies for incoming fumigated grain.

3. Development of a registry of grain handlers and inspectors along with descriptive job element which will permit long term surveillance of the group tied in with occupational history.

C. Research Needs

Development of methods which assure quick, effective, and economical removal of fumigants from treated grain.

Determination of the best approach in evaluating fumigated grain, to insure that a health risk to workers handling the grain will not occur. An example of this is the question of sampling in-the-grain mass versus above-the-grain mass in deciding if fumigated grain presents a health hazard.

Development of both equipment and strategies for evaluating incoming suspect grain shipment for the identification and quantitation of fumigant content.

IX. References

1. Ahrenholz S.H. Health hazard evaluation - Portland, Oregon: Report No. 83-375-1521. Cincinnati, Ohio: National Institute for Occupational Safety and Health, 1984.

2. Ahrenholz SH. Health hazard evaluation-Superior, Wisconsin - Duluth, Minnesota: Report No 84-311--____ Cincinnati, Ohio: National Institute for Occupational Safety and Health, (in preparation).

X. AUTHORSHIP AND ACKNOWLEDGEMENTS

Evaluation Conducted and Report Prepared by: Steven H. Ahrenholz, M.S., C.I.H.
Industrial Hygienist
Industrial Hygiene Section

Laboratory Analyses: Ardith A. Grote
Chemist
Division of Physical Sciences and Engineering

Arthur D. Little, Inc.
Boston, Massachusetts

Originating Office:	Hazard Evaluations and Technical Assistance Branch Division of Surveillance, Hazard Evaluations, and Field Studies
Report Typed By:	Patty Johnson Secretary Hazard Evaluations and Technical Assistance Branch Connie L. Kidd Clerk-Typist Industrial Hygiene Section

XI. DISTRIBUTION AND AVAILABILITY OF REPORT

Copies of this report are currently available upon request from NIOSH, Division of Standards Development and Technology Transfer, Publications Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days, the report will be available through the National Technical Information Service (NTIS), 5285 Port Royal, Springfield, Virginia 22161. Information regarding its availability through NTIS can be obtained from NIOSH Publications Office at the Cincinnati address. Copies of this report have been sent to:

1. American Federation of Grain Millers, Local 118
2. Peavey Company - Globe Elevator
3. Congressman David Obey
4. Chicago and North Western Transportation Company
5. Food and Allied Services Trades AFL-CIO
6. NIOSH, Region V
7. OSHA, Region V

For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

Table I

Grain Fumigant Concentrations Determined by In-Grain and Ambient Air Sampling

Grain Millers Local 118
Superior, Wisconsin
HETA 84-194

February 19, 1984

Sample Description*		Fumigant Concentration in mg/m^3 (ppm)**					
		CCl_4		CS_2		$CHCl_3$	
Car Number	Duration (min)	Submerged	Headspace	Submerged	Headspace	Submerged	Headspace
CNW 182210	33	5.2 (0.83)	Trace+	Trace	-	N.D.	N.D.
CNW 753765	54	18 (2.9)	Trace	N.D.	-	N.D.	N.D.
CNW 752816	41	114 (18)	N.D.++	20 (6.5)	N.D.	Trace***	N.D.
CNW 752396	36	14 (2.2)	0.86 (0.14)	15 (4.7)	N.D.	N.D.	N.D.
CNW 178069	53	383 (61)	2.9 (0.46)	19 (6.2)	N.D.	0.66 (0.14)***	N.D.
NAHX 489594+++	55	4.7 (0.75)	Trace	8.6 (2.8)	N.D.	N.D.	N.D.
CNW 173910	38	42 (6.7)	Trace	Trace	N.D.	N.D.	N.D.
OSHA PEL (See Note 1)		(10 ppm) 8 hr. shift (25 ppm) ceiling (200 ppm) 5 min in 4 hr		(20 ppm) 8 hr. shift (30 ppm) ceiling (100 ppm) 30 min		240 (50 ppm) ceiling	
NIOSH Recommended Limit (See Note 1)		(2 ppm) 1 hr ceiling		(1 ppm) 8-10 hr. shift (10 ppm) ceiling		(2 ppm) 1 hr. ceiling	
Analytical Limit of Detection in micrograms (ug) per sample:		4		6		4	

* Sample description gives car number and an average sample duration.
** Fumigant concentration is given in milligrams per cubic meter (mg/m^3) and parts per million (ppm) are given in parentheses.
Fumigants listed are carbon tetrachloride = CCl_4; carbon disulfide = CS_2; and chloroform = $CHCl_3$.
Submerged = sample values obtained by sampling in the grain mass.
Headspace = sample values obtained by sampling above the grain mass 0.5 to 6 inches.
\+ Trace indicates compound was identified as present but could not be quantified, i.e., it fell below the limits of quantitation but above the limit of detection.
++ N.D. indicates none detected. Compound, if present, was below the analytical limit of detection given at bottom of table.
*** Trace values for chloroform were seen only on the samples having the greatest amount of carbon tetrachloride present. Values given should be considered maximal.
+++ This car was being aerated during approximately the first 30 minutes of the sample period.
Note 1: OSHA and NIOSH exposure values are given for reference purposes. This data is not to be interpreted as worker exposures associated with handling the grain. OSHA and NIOSH values apply to personal breathing zone exposure data collected over specified time periods.

Appendix I
Analytical Methods
American Federation of Grain Millers, Local 118
Superior, Wisconsin
HETA 84-194

Chlorinated Hydrocarbons: Bulk and Sorbent Tube Samples

All charcoal tubes were desorbed with 1 mL carbon disulfide and analyzed by gas chromatography (equipped with a flame ionization detector, FID) using a 30 meter DB-1 bonded phase fused silica capillary column (splitless mode). Standards were prepared containing carbon tetrachloride and chloroform. Two of the charcoal samples were further analyzed by gas chromatography (GC)/mass spectroscopy to identify components.

Unweighed portions of each of the bulk grain samples were extracted with several milliliters of carbon disulfide. These extracts were also screened by GC-FID using the same conditions as for the charcoal tubes. Bulk sample analyses were strictly qualitative in nature.

Carbon Disulfide: Sorbent Tube Samples

The following gas chromatograph/flame photometric detector (FPD) conditions were used for the analyses:

Instrument:	Varian 2700 with FPD
Column:	10% Carbowax 20 m (10 ft glass)
Carrier Gas:	Helium at 30 mL/min
Column Temperature:	55°C isothermal
Injector Temperature:	150°C
Detector Temperature:	200°C
Injection Volume:	1 uL
Attenuation:	$64 \times 10^{-7} \times 4$

The front and back sections of the charcoal tubes were desorbed for at least 1 hour with 10 mL of benzene.

Methyl Bromide: Bulk and Sorbent Tube Samples

Two Qazi Ketchum tubes in series were used for methyl bromide sample collection.
The following GC/electron capture detector (ECD) conditions were used:

Instrument:	Hewlett-Packard 5840 GC with ECD
Column:	10% SP-1000 on 80/100 Supelcoport (20 ft x 12 in. stainless steel)
Carrier Gas:	Helium at 30 mL/min

Column Temperature:	65°C isothermal (5 min), 10°/min up to 110°C(10 min)
Injector Temperature:	200°C
Detector Temperature:	250°C
Injection Volume:	1 uL
Attenuation:	2^6

The front and back sections of the charcoal tubes were desorbed for at least 2 hours with 10 mL of 1% methanol in benzene. One gram of each grain was also desorbed in 10 mL.

Ethylene Dibromide: Sorbent Tube Samples

The following GC/ECD conditions were used:

Instrument:	Varian Vista
Column:	FSCC with DB-1
Carrier Gas:	Helium - 2 mL/min
Column Temperature:	50°C isothermal
Injector Temperature:	215°C
Detector Temperature:	250°C
Injection Volume:	1 uL
Attenuation:	16

The front sections of the charcoal tubes were desorbed for at least 1 hour with 10 mL of 1% methanol in benzene. The back sections were desorbed in 1 mL of this solution.