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EXPOSURE TO PHOSPHINE GAS DURING APPLICATION OF MAGNESIUM PHOSPHIDE IN STORED PRODUCT WAREHOUSES

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A thesis submitted in partial fulfillment of the
requirements for the degree of Master of Science
at Virginia Commonwealth University

by

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Exposure To Phosphine Gas During Application of Magnesium Phosphide In Stored Product Warehouses

ABSTRACT

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The use of phosphine gas requires that respiratory protection be used if exposures exceed the OSHA permissible exposure limit. As with other chemical exposures limits many of the references used to establish occupational health guidelines date back to the 1930's and 1940's. This is quite common and is the case with phosphine gas. Initial planning for fumigations involving magnesium phosphide requires that a hazard assessment be performed. Expected worker exposures based on previous monitoring or test data was not readily available. Many current practices and procedures for fumigations are based on recommendations from applicators who used the product in the 1950's and 60's. Unfortunately, many of the recommendations were based on personal opinion and experience rather than actual exposure monitoring data. Not until the 1980's were comprehensive applicator exposure assessments being conducted for

different tasks involving magnesium phosphide. As a result, it is necessary to generate current applicator exposure data and compare the data to current occupational exposure limits for phosphine gas.

INTRODUCTION

One of the most common methods of safely generating phosphine during a warehouse fumigation is through the use of magnesium phosphide. Magnesium phosphide (Mg_3P_2) products exhibit two main hazards that must be carefully taken into account during its use. The first is a potential for fire due to its high reactivity. The magnesium phosphide may flash or burn if it comes in contact with water. The second hazard, and the most important in terms of applicator exposure, is the inhalation of toxic phosphine gas (1-4).

Magnesium phosphide is a highly acute toxic substance. Phosphine gas is liberated by the reaction of magnesium phosphide with water molecules in the air. The chemical reaction is represented by: (5,6).

$$Mg_3P_2 + 6H_2O \dashrightarrow 3Mg(OH)_2 + 2PH_3$$

At the present time limited data are available with regard to applicator exposure to phosphine gas during the application of magnesium phosphide in stored product warehouses. For this reason it is critical to determine the potential exposures to applicators of magnesium phosphide products during a warehouse fumigation. The purpose of this study was to conduct personal air monitoring on individuals applying magnesium phosphide fumigants in warehouses. This data will be used to characterize applicator exposures and compare these levels to the current Occupational Safety and Health Administration's (OSHA) (29 CFR 1910.1000) Permissible Exposure Limit (PEL) of 0.3 ppm for phosphine gas.

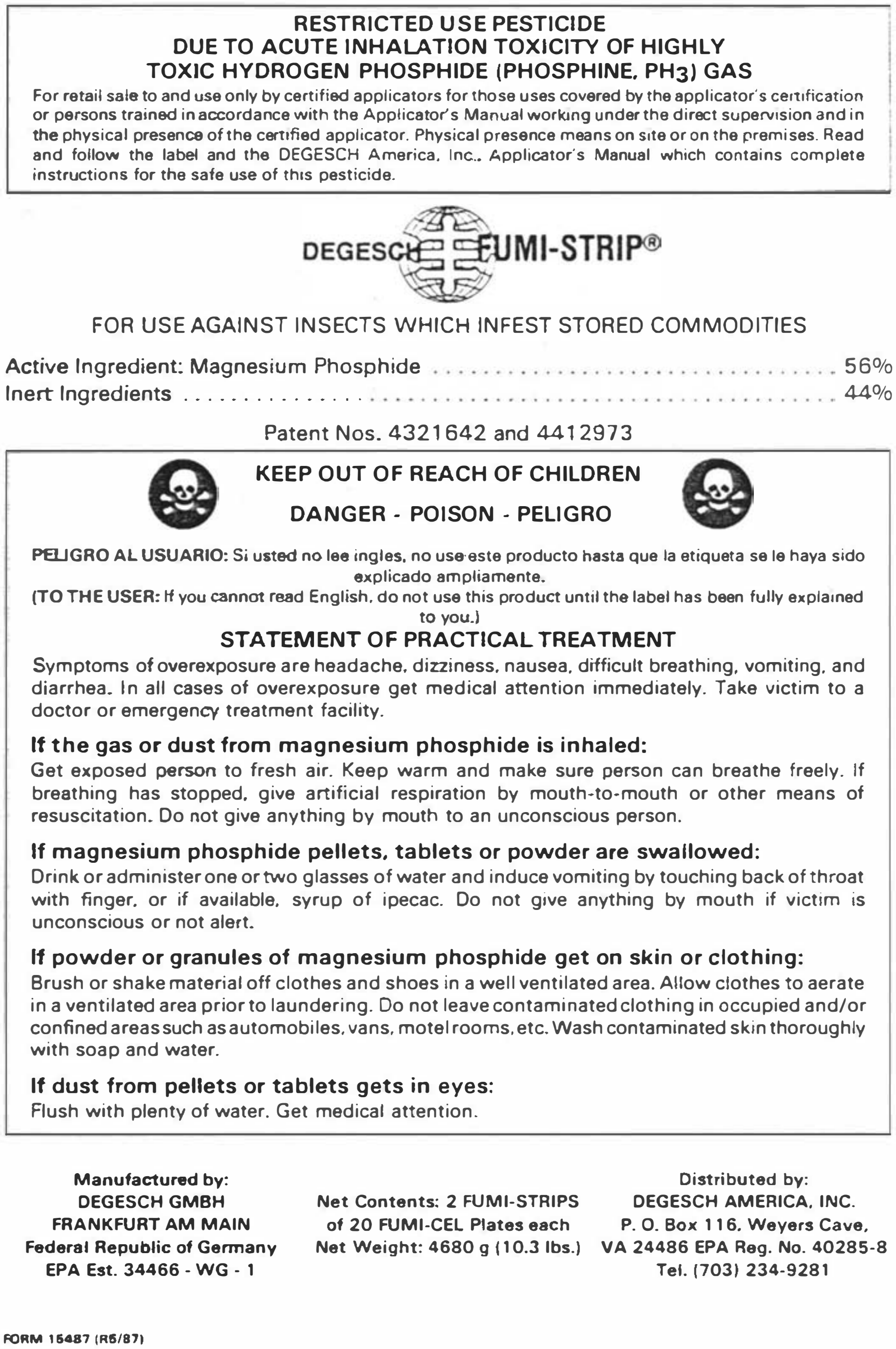
LITERATURE REVIEW

Phosphine gas (PH_3) is an effective fumigant for the cigarette beetle as well as many other insects that infest many different types of stored commodities. This gas has been found to be effective against the adult as well as the preadult stages - that is, eggs, larvae and pupae.

Insects that are commonly controlled with the use of phosphine include the: almond moth, bean weevil, bees, raisin moth, spider beetles, fruit flies, maize beetle, European grain beetle as well as many others (7).

Magnesium phosphide is classified as a restricted use product by the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA). Section (3)(d)(1)(c)(i) of the Act states " If the Administrator classified a pesticide, or one or more uses of such pesticide, for restricted use because of a determination that the acute dermal or inhalation toxicity of the pesticide presents a hazard to the applicator or other persons, the pesticide shall be applied for any such use to which the restricted classification applies only by or under the direct supervision of a certified applicator ". It's use is limited to licensed pesticide applicators and must be applied per the label

FIGURE - 1
MAGNESIUM PHOSPHIDE WARNING LABEL



RESTRICTED USE PESTICIDE DUE TO ACUTE INHALATION TOXICITY OF HIGHLY TOXIC HYDROGEN PHOSPHIDE (PHOSPHINE, PH_3) GAS

For retail sale to and use only by certified applicators for those uses covered by the applicator's certification or persons trained in accordance with the Applicator's Manual working under the direct supervision and in the physical presence of the certified applicator. Physical presence means on site or on the premises. Read and follow the label and the DEGESCH America, Inc., Applicator's Manual which contains complete instructions for the safe use of this pesticide.

DEGESCH FUMI-STRIP®

FOR USE AGAINST INSECTS WHICH INFEST STORED COMMODITIES

Active Ingredient: Magnesium Phosphide	56%
Inert Ingredients	44%

Patent Nos. 4321642 and 4412973

KEEP OUT OF REACH OF CHILDREN

DANGER - POISON - PELIGRO

PELIGRO AL USUARIO: Si usted no lee ingles, no use este producto hasta que la etiqueta se le haya sido explicado ampliamente.

(**TO THE USER:** If you cannot read English, do not use this product until the label has been fully explained to you.)

STATEMENT OF PRACTICAL TREATMENT

Symptoms of overexposure are headache, dizziness, nausea, difficult breathing, vomiting, and diarrhea. In all cases of overexposure get medical attention immediately. Take victim to a doctor or emergency treatment facility.

If the gas or dust from magnesium phosphide is inhaled:
Get exposed person to fresh air. Keep warm and make sure person can breathe freely. If breathing has stopped, give artificial respiration by mouth-to-mouth or other means of resuscitation. Do not give anything by mouth to an unconscious person.

If magnesium phosphide pellets, tablets or powder are swallowed:
Drink or administer one or two glasses of water and induce vomiting by touching back of throat with finger, or if available, syrup of ipecac. Do not give anything by mouth if victim is unconscious or not alert.

If powder or granules of magnesium phosphide get on skin or clothing:
Brush or shake material off clothes and shoes in a well ventilated area. Allow clothes to aerate in a ventilated area prior to laundering. Do not leave contaminated clothing in occupied and/or confined areas such as automobiles, vans, motel rooms, etc. Wash contaminated skin thoroughly with soap and water.

If dust from pellets or tablets gets in eyes:
Flush with plenty of water. Get medical attention.

Manufactured by:
DEGESCH GMBH
FRANKFURT AM MAIN
Federal Republic of Germany
EPA Est. 34466 - WG - 1

Net Contents: 2 FUMI-STRIPS
of 20 FUMI-CEL Plates each
Net Weight: 4680 g (10.3 lbs.)

Distributed by:
DEGESCH AMERICA, INC.
P. O. Box 116, Weyers Cave,
VA 24486 EPA Reg. No. 40285-8
Tel. (703) 234-9281

FORM 15487 (R5/87)

instructions (8). A copy of the label is attached as Figure 1.

Fumi-Cel and Fumi-Strip, made by Degesch America, Inc., are the trade names for the magnesium phosphide products used in this survey (9).

Some studies have been undertaken by the manufacturers of phosphide products in order to meet certain requirements for reregistration of the pesticide. This was undertaken through authority granted by the Environmental Protection Agency (EPA) to perform a reassessment of the potential hazards resulting from the use of phosphide products (10).

The use of magnesium phosphide products in the fumigation of tobacco warehouses typically results in short periods of exposure to the applicator. Because of this variability it is necessary to characterize the potential exposure to phosphine for the applicators.

The primary route of exposure to phosphine gas is limited to inhalation. Exposure to high concentrations of phosphine gas does not require the use of protective clothing. Dermal absorption for phosphine gas is minimal (11).

Background

The rate of phosphine gas production is directly related to the ambient temperature and percentage of moisture in the air. For this reason the summer is an ideal time for fumigation of stored products. Typical ambient conditions during this period consist of temperatures around 90 degrees F. and relative humidities ranging from 80 - 90 percent.

Worker exposure to phosphine during the fumigation in the warehouse is dependent upon time of exposure. The fumigation takes place in two steps; first a crew of individuals begin to place the unopened foil pouches in the warehouses. Afterwards, a second crew begins the opening procedure. This increases the efficiency of application and reduces the time between warehouses.

Typically, the fumigant is placed inside the warehouse from the back to the front. The packs are opened, starting at the rear of the warehouse, and work towards the front door. This procedure minimizes the actual time of exposure to the gas. However, it is very difficult to determine the total amount of phosphine gas that the individual is exposed to because of the variability in work practices between applicators and the time of exposure. Work practices may include: ease of opening the foil bag, time required to place the fumigant and applicator experience.

The requirement for respiratory protection while working with phosphine gas is determined by the eight hour PEL of the applicator. Respiratory protection must be worn if the applicator is exposed to levels of phosphine gas greater than the OSHA 0.3 ppm PEL averaged over an eight hour period or the 1.0 ppm STEL averaged over a 15 minute period.

Work practices during the application of magnesium phosphide is typified by multiple periods of short duration exposure. Time of exposure during fumigant application averages about 2 - 2 1/2 minutes per warehouse. These times represent application inside warehouses that average approximately 1 1/2 - 2 million cubic feet of space. There may be short periods of time between the next exposure period (warehouse) or an extended period of time depending upon delays between warehouses.

Under these circumstances one would expect that occupational exposures would be minimal. However, the applicator is required to lean directly over the Fumi-Cels as they are being placed in the warehouse. The rate of phosphine gas evolution is highly variable and the number of Fumi-Cels applied per warehouse will vary from as little as 708 up to 1600. The number of Fumi-cels used per warehouse is based on volume. This equates to about 35 to 75 Fumi-Strips that may be applied in a given warehouse. These quantities represent a single warehouse. The maximum number of warehouses on a single complex in this survey was 51. If all of these warehouses are fumigated a total of approximately 56,200 Fumi-Cels would be applied.

Refer to Figures 2 - 4, for a layout diagram of each warehouse complex. The application sequence varies between complexes due to the number of houses and their arrangement.

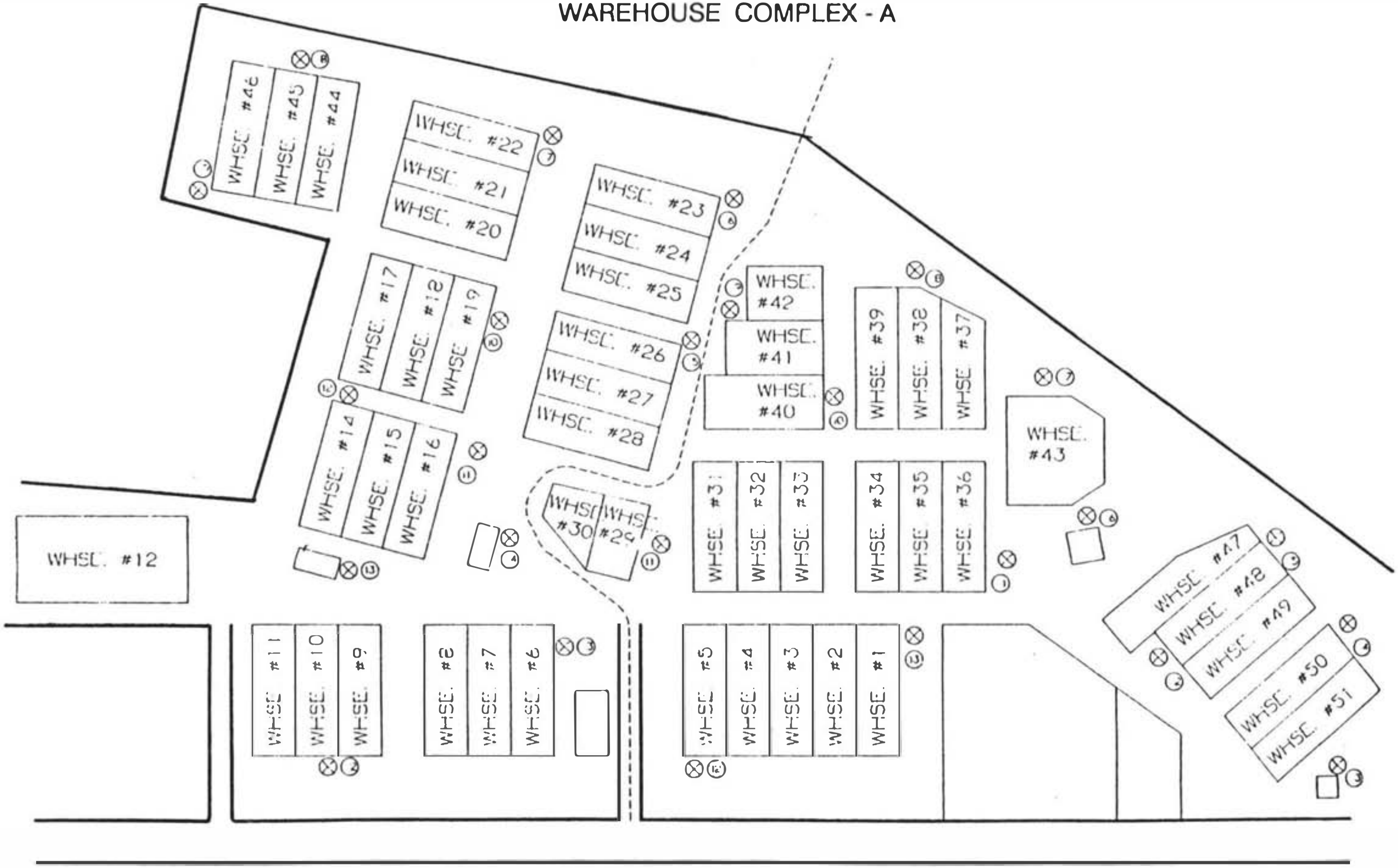
Hypothesis

As is typical with fumigations and related pest control activities the time required for actual application of the product seldom coincides with an eight hour permissible exposure limit. Based on the duration of exposure and the number of magnesium phosphide cells that are placed in the warehouses the possibility exists that the action limit, expressed as 1/2 the PEL value, as well as the eight hour permissible exposure limit for phosphine may be exceeded. Characterization of applicator exposure levels and comparison with the OSHA action limit and PEL will determine if potential overexposure to phosphine exists and if existing health standards adequately protect the workers.

Sampling and Analytical Methodology

All field samples collected to determine personal exposures were conducted according to the sampling procedures contained in the National Institute for Occupational Safety and Health (NIOSH) method S-332. This method is attached as

FIGURE - 2
WAREHOUSE COMPLEX - A



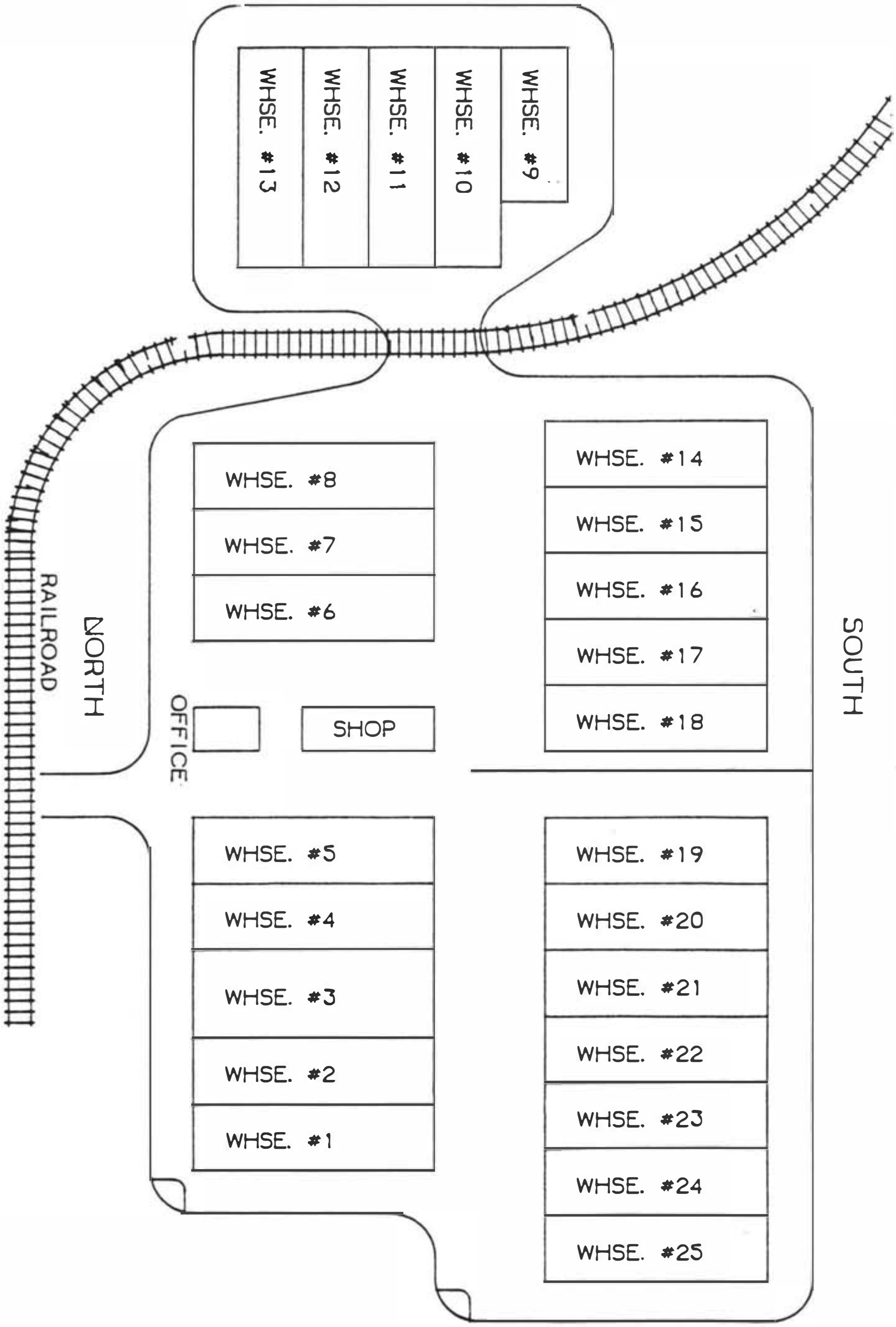
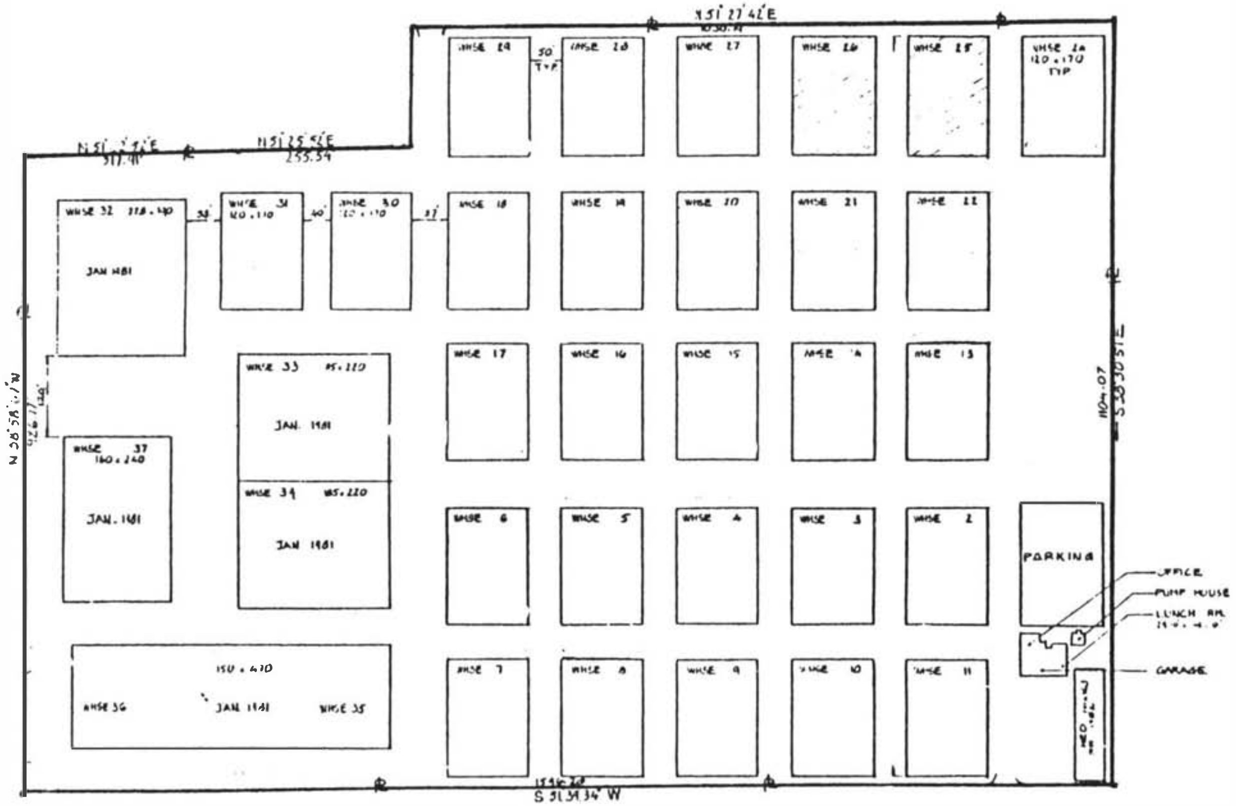


FIGURE - 3
WAREHOUSE COMPLEX - B

FIGURE - 4
WAREHOUSE COMPLEX - C



Appendix A. The laboratory used to prepare as well as perform the analysis on the sample tubes is Clayton Environmental Laboratories, Novi, Michigan. Clayton Environmental Laboratories, an AIHA accredited laboratory, employed NIOSH analytical method S-332 for the analysis.

A brief description of the method is as follows: A known volume of air is drawn through a tube containing mercuric cyanide impregnated silica gel to capture the phosphine. The phosphorus is extracted and oxidized to phosphate using a hot, acidic permanganate solution.

The extracted sample is analyzed for phosphate by formation of phosphomolybdate complex, extracted into a mixture of isobutanol and toluene and reduction using stannous chloride. The absorbance of the reduced phosphomolybdate complex is measured at 625 nm on a spectrophotometer. The analytical method requires measurement of the absorbance of the phosphomolybdate complex one minute after reduction with stannous chloride.

The sample tube measures 12 cm in length with a 6 mm O.D. and a 4 mm I.D. Contained inside the tube is two sections of mercuric cyanide treated silica gel (40/60 mesh). The front absorbing section contains 300 mg of treated silica gel and the back section contains 150 mg. A small wad of silylated glass wool is placed between the front and back sections. These glass wool plugs are held in place by other additional plugs (12).

All samples were collected using either the Gilian LFS-113 or Sipin SP-15 low range constant flow sample pumps. All sample pumps were calibrated before and after each sample period. A primary standard utilizing the Mast model 823-1 or Buck model M-5 bubble meter was used to calibrate the sample pumps. The sample pumps were calibrated to draw the recommended flowrate of 50cc/min through the sample tube.

The sample period was based on the length of time required to apply the magnesium phosphide strips. Potential exposure existed only during the actual process of opening the sealed pouches and applying the strips. Once the applicator leaves the warehouse the exposure ceases. The total time required for application averaged from 2 - 4 hours per complex.

Warehouse Description

The warehouses range in age of construction from approximately the mid 1950's up to the present day (1989). The construction materials vary from about 80 % wood / 20 % sheet metal in the older warehouses to solid concrete floor, cinder block wall and sheet metal siding.

Extensive effort has been expended, particularly on the older warehouses, to seal any unwanted openings in the structure. Phosphine gas is very mobile (vapor density 1.12) and disperses readily within the warehouse (13,14).

The criteria used to determine a successful fumigation is dependent upon holding a specified amount of gas for a period of time. As mentioned above some of the older warehouses may have wooden floors, walls and ceilings which presents a concern with fire as well as increased potential for gas leakage.

The volume inside the warehouses also varies greatly with the age of the warehouses. The volume of the warehouses range from 400,000 in the older warehouses up to 2,300,000 cubic feet in the newer ones.

The volume (cubic feet) of each warehouse is critical because it directly determines the dosage rate. The manufacturer provides average dosage rates in their applicators manual for magnesium phosphide products. The allowable dosage rates is one Fumi-Cel (33 gms of hydrogen phosphide) per 1000 cubic feet or one Fumi-Strip (660 gms of hydrogen phosphide) per 20,000 cubic feet (15).

Application Procedures

The application of Fumi-Strips begins after the warehouses are sealed and turned over to the contractor. The applicator is contractually responsible for the fumigation from the point of initial gas application until final air clearance of the commodity has been approved.

The exact amount of fumigant is determined by the cubic footage of the warehouse. The appropriate numbers of

Fumi-Strips are then deposited at each warehouse.
The Fumi-Cel plates and Fumi-Strip have a polyethylene matrix which is impregnated with magnesium phosphide along with some inert ingredients. The plate measures about 6-3/4 by 11 inches and is 5/32 inches in thickness. The Fumi-Strip is formed by attaching together, end to end, 20 of the Fumi-Cel plates. The strip measures 18 feet 4 inches in length and will liberate 660g of phosphine gas.
Strips and plates are packaged individually in gas-tight aluminum foil pouches. These pouches are not re-sealable. The pouches, in turn, are packed in tins, 40 plates or 2 strips per tin. The tins are packed 3 tins per case. Each case contains 120 plates or 6 strips, has a net weight of 14 kg and will evolve a total of 3960 grams of phosphine (16).

The aluminum pouches are carried into the warehouse by the first crew and placed next to metal racks that elevate them off the floor. This is a permit requirement of the local fire department in the event of water leakage during heavy rainstorms. The pouches are placed over the length of the warehouse and care is taken to avoid placement under skylights or other potential leakage areas.

The applicator crew then follows behind and begins to open pouches at the rear of the warehouse working their way to the exit door located in the front of the warehouse. The Fumi-Strips are placed on the metal racks in an accordion fashion. Attention to given to insure that air spaces are present between the individual plates so that gas will not pocket and possibly ignite. The crews move very rapidly once the opening begins. A 1.5 million cubic foot warehouse would require about 75 Fumi-Strips be placed inside.

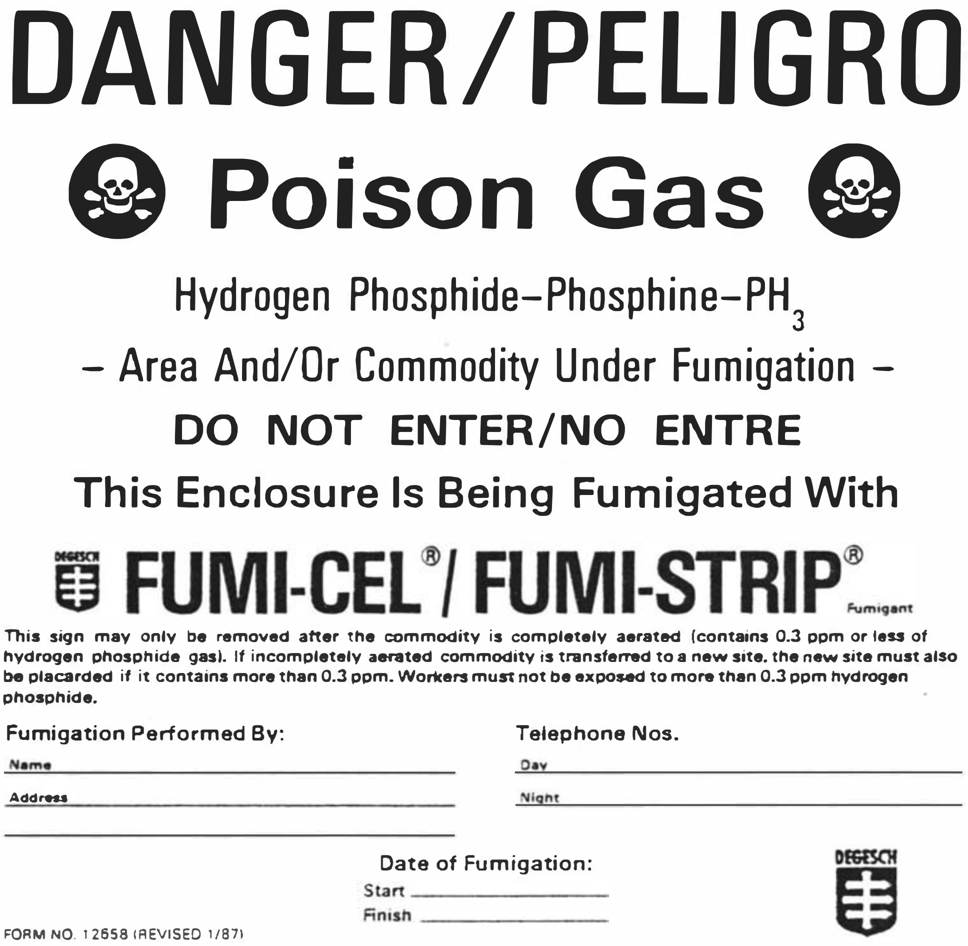
Application times were recorded to determine an average time from start to finish per warehouse. The average application per warehouse is between 2.5 and 3 minutes.

As the last man leaves the warehouse a verbal call is made to insure that no one is still inside. Depending on the particular warehouse either the personnel door is closed, taped and a warning sign is taped on any entrance into the warehouse or a polyethylene seal covering the door is taped and the sliding metal doors are closed. A copy of the warning sign is included as Figure 5.

Preparation before the start of the fumigation allows the crew to continue to the next warehouse and repeat the procedure until the fumigant has been placed in all designated warehouses.

As mentioned earlier the average total application times of 2 - 4 hours is dependent only on the number of warehouses requiring fumigation. On certain occasions as few as 5 - 10 warehouses may need to be fumigated. These can be treated in as little as 30 - 40 minutes.

FIGURE - 5
HYDROGEN PHOSPHIDE WARNING PLACARD



DANGER/PELIGRO

☠ Poison Gas ☠

Hydrogen Phosphide–Phosphine–PH_3

– Area And/Or Commodity Under Fumigation –

DO NOT ENTER/NO ENTRE

This Enclosure Is Being Fumigated With

DEGESCH **FUMI-CEL®/ FUMI-STRIP®** Fumigant

This sign may only be removed after the commodity is completely aerated (contains 0.3 ppm or less of hydrogen phosphide gas). If incompletely aerated commodity is transferred to a new site, the new site must also be placarded if it contains more than 0.3 ppm. Workers must not be exposed to more than 0.3 ppm hydrogen phosphide.

Fumigation Performed By:

Name ______________________

Address ______________________

____

Telephone Nos.

Day ______________________

Night ______________________

Date of Fumigation:

Start ______________

Finish ______________

DEGESCH

FORM NO. 12658 (REVISED 1/87)

Exposure Standards

The Occupational Safety and Health Administration (OSHA) eight hour Permissible Exposure Limit (PEL)-Time Weighted Average (TWA) concentration for exposure to phosphine gas is 0.4 mg/m^3. The Short Term Exposure Limit (STEL) is 1.0 mg/m^3 averaged over a fifteen minute period and this level should not be exceeded at any time during a work day even if the eight hour TWA is within the PEL. Exposures at the STEL should not be repeated more than four times per day. Other safety and health guidelines for occupational exposure also support this level. They include the: American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) of 0.3 ppm (17,18).

The United States' PEL/TLV for phosphine is one of the highest when compared to levels for other countries. Listed on Table - 1, are 8 hour exposure limits for phosphine from 25 other countries. The limits are listed as mg/m^3.

Table - 1
Worldwide Phosphine Exposure Limits

Austria	0.15	Italy	0.40
Belgium	0.40	Mexico	0.40
Brazil	0.30	Netherlands	0.40
Bulgaria	0.30	PR. of China	0.30
Chile	0.32	Poland	0.10
Czechoslovakia	0.10	Rep. of China	0.40

Denmark	0.15	Sweden	0.40
France	0.13	Switzerland	0.40
FRG	0.15	United Kingdom	0.40
GDR	0.10	USSR	0.10
Hungary	0.10	Venezuela	0.40
India	0.40	Yugoslavia	0.10
Indonesia	0.40		

Exposure levels appear to cluster around 0.10, 0.30 or 0.40 mg/m^3. Approximately half of the levels are greater than 0.30 mg/m^3 and half are below 0.30 mg/m^3 (19).

Listed on Table - 2, is RTECS animal and human toxicity data related to phosphine.

Table - 2
RTECS Phosphine Toxicity Data

ihl-hmn LCLo:1000ppm/5M

ihl-rat LC50:11 ppm/4H

ihl-mus LCLo:380 mg/m^3/2H

ihl-cat LCLo:70 mg/m^3/2H

ihl-rbt LCLo:2500 ppm/20H

ihl-gpg LCLo:140 mg/m^3/4H

ihl-mam LCLo:1000 ppm/5M

The Immediately Dangerous to Life and Health (IDLH) level for phosphine gas is about 190 ppm for one hour (20-22).

Information regarding the odor threshold and warning properties for phosphine seems quite variable. Odor thresholds as low as 0.02 and 0.03 ppm have been reported. An odor threshold at these levels would provide an adequate warning for phosphine considering the PEL/TLV of 0.3 ppm. Pattys states a limit of detection much higher, ranging from 1.0 to 3.0 ppm. Information provided by May from experience of industrial users supports the lower odor thresholds (23).

Phosphine Case Histories

Cases of illness or death over the years have been attributed mainly to aluminum phosphide products. One article reports that during the time period from about 1900 up to 1958, 59 cases of phosphine poisoning were reported. Of these reported cases 26 of the effected people died.

Also reported was a single incident on board a grain freighter that was being fumigated during transport. Twenty nine of the thirty one crew members became acutely ill and one child died. The most common symptom associated with both of the incidents were: headache, fatigue, nausea, vomiting, cough and shortness of breath. In the second case the child who died showed signs of jaundice, anesthesias, ataxia, pulmonary edema and widespread small-vessel injury (24-26).

Signs and symptoms of low level chronic exposure include: headache, dizziness, tremors, general fatigue, GI tract distress, burning substernal pain and effect on the CNS including blurred vision, speech and motor disturbances. Serious effects may be seen upon exposure to 5 to 10 ppm over several hours (27,28). These low level effects to phosphine exposure have not been clearly defined, however, several authorities mention the possibility of phosphorus poisoning from chronic exposure to phosphine.

The majority of cases reported in the United States involving phosphine gas poisonings were associated with treatment of grain storage and grain freighters using aluminum phosphide products. The primary cause of these poisonings resulted from improper handling procedures while applying the product (29).

Fumigant Chemistry

Metal phosphide fumigants are acted upon by atmospheric moisture to produce hydrogen phosphide (phosphine, PH_3) gas. The Fumi-Cel and Fumi-Strip contain magnesium phosphide (Mg_3P_2) as their active ingredient and will liberate hydrogen phosphide by way of the following reaction:

$$Mg_3P_2 + 6H_2O \dashrightarrow 3Mg(OH)_2 + 2PH_3$$

Phosphine gas is highly toxic to insects, burrowing pests, humans, and other forms of animal life. In addition to its toxic properties, the gas will corrode certain precious metals and may spontaneously ignite in air at concentrations above its lower flammable limit of 1.8 % or about 18,000 ppm. Phosphine is a colorless gas identified as a garlic, fishy like odor. It has a molecular weight of 34 and a density of 1.529. The boiling point is - 85° C and the melting point is -133.5° C. It is slightly soluble in water and is soluble in alcohol and ether (30-32).

Toxicology of Phosphine

Because of the physical properties required of a fumigant they are often chemically simple molecules but they can exert a complex range of biochemical effects on target organs.

Phosphine is an acutely toxic gas and a severe pulmonary irritant. The primary route of exposure into the body is by way of the lungs. The responses of the lung to toxic agents may be divided into four general categories. The two responses generally associated with phosphine exposure include the following.

1. Irritation of the passages, which results in constriction of the airways. Edema often occurs and secondary infection frequently compounds the damage.

2. Damage to the cells lining the airways, which results in necrosis, increased permeability, and edema. This edema is, in general intraluminal (within the airways) rather than interstitial (within the cells of the airway).

The degree of cellular response and potential tissue damage is dependent upon the agent and amount of exposure (dose). The water solubility of a gas plays an integral part in its point of absorption and degree of irritation within the lung. Ammonia and chlorine are examples of gases that are highly water soluble and rapidly irritate the upper airway upon inhalation. Phosphine, on the other hand, affects the lower airways and alveoli due to its relatively low solubility in water (33,34).

Exposure to phosphine may lead to pulmonary edema resulting in an increase in cell permeability and release of edema fluid into the lumen of the airway and alveoli. The production of major edema may take several hours to develop so that seriously damaging or fatal exposures may occur without the individual being aware of it at the time of exposure (35).

The liver may also be affected by high exposures to phosphine gas as evidenced by the yellow discoloration of the skin present in phosphine poisoned victims. This may result from reduced bile activity due to phosphorous exposure (36). The phosphorous portion of phosphine gas may adversely effect kidney function. Consumption of alcohol is not recommended if exposure to phosphine gas is suspected. The portions of the kidney responsible for secretion and absorption of fluids (distal tubules) may be adversely affected by the accumulation of phosphorous (37).

One important property of a fumigant used on stored food products is its water solubility. The water solubility of the gas determines the amount of absorption into a product and may adversely effect its taste or palatability. Phosphine gas is only slightly soluble in water and this makes it a desirable fumigant to use on stored food commodities (38).

Mechanism of Toxicology

The chemistry of phosphine is similar to arsine, but it does not lyse red blood cells. It exerts its effect on the body, primarily, by way of the respiratory system (39,40).

Biochemically, the mode of action for phosphine is very similar to that of hydrogen cyanide (HCN). HCN was first used extensively as a fumigant in California in 1886. The first study on the toxic effects of cyanide were first studied in 1781 (41).

As the biochemical details of the respiratory processes became known it was found that the enzyme cytochrome-c oxidaze played a important part in respiration. Cytochrome-c oxidaze contains copper and haem groups which are vital in the biochemistry of respiration. Phosphine and HCN inhibit other enzymes in the respiration process but cytochrome oxidaze is the most sensitive. Oxidization of co-factors NADH and FADH by way of redox reactions using oxygen occurs during aerobic respiration. The mitochondria carries out this process and generates Adenosine Triphosphate (ATP). Cytochrome-c oxidase is the final electron acceptor site for this reaction. Direct interference with respiratory oxygen will prevent oxidative phosphorylation and production of energy will cease (42,43).

Exposure to phosphine has been shown to inhibit AMP stimulation and mitochondrial oxygen uptake in the rat liver. Experiments using isolated mitochondria from rat liver, mouse liver and housefly flight muscle show that, in vitro phosphine is a powerful inhibitor of mitochondrial respiration and that inhibition of cytochrome-c oxidaze was responsible (44).

A recent study by Chaudhry and Price suggests that direct inhibition of cytochrome-c is not the primary mechanism of toxicity in humans or mammals exposed to phosphine (45).

Their study looks at two blood proteins: hemoglobin and myoglobin which are present only in humans and mammals and not found in insects. Phosphine appears to remove oxygen from the two oxygenated haem proteins. With prolonged exposure to phosphine the process of deoxygenation occurs to the two blood proteins, hemoglobin and myoglobin. This appears to result in a slow decrease in the amount of oxygen available to the various body organs and tissue (46). Death from phosphine overexposure is slow, unlike deaths associated with more toxic, faster acting gases such as hydrogen cyanide. The toxic effect of phosphine on humans is consistent with the current IDLH of 190 ppm/1 hour.

With regard to insects, which lack the oxygen-carrying haem proteins, the toxic action of phosphine, which requires the presence of oxygen, may involve a direct interaction of the dissolved gases which would then result in the deoxygenation of haemproteins that are sensitive to oxygen depletion (47). The route of entry for insects when exposed to phosphine is through the spiracles located on each side of the abdomen (48).

Although phosphine currently has not been identified as a carcinogen or mutagen, one recent study raises the question about the effects of phosphine exposure. In a preliminary study by Garry, et.al., data generated appears to suggest that pesticide workers who are involved in the application of phosphine showed a significant increase in stable chromosome rearrangements. These rearrangements primarily involved translocations in G-banded lymphocytes. There was a significant difference between the exposed group of applicators and a non-exposed control group. The study was continued six months after the pesticide application season ended to determine if the alterations were permanent. The number of alterations were no longer significant when compared to the control group. The significance of the alterations due to phosphine exposure is not clearly understood at this time. These types of chromosome rearrangements have also been associated with exposures to other types of chemical agents (49).

The effects of phosphine overexposure on humans is consistent with signs and symptoms which appear to be non-specific and general in nature. These include headache, dizziness, tremors, general fatigue, GI tract distress, blurred vision and speech and motor control disturbances. These symptoms are consistent with exposure to other agents that produce anoxia which is characterized by a slow, gradual depletion of oxygen to the body organs and tissues. Death does not result from the lack of, or displacement of, atmospheric oxygen, instead phosphine appears to deoxygenate the blood proteins. As expected, death from overexposure to phosphine is not immediate, but usually occurs hours or days later.

RESULTS

Other exposure studies have been conducted using aluminum phosphide products in other applications. One other application involves personal and area monitoring on workers applying aluminum phosphide in grain elevators and the results for personal full shift samples ranged from < 0.01 ppm up to 1.66 ppm. Significant differences exist between the application of phosphide products in grain elevators and in warehouses.

In this study all of the sample results represent only personal exposures during the application of magnesium phosphide fumigants in warehouses. A total of 53 (n=53) samples were collected during various fumigations. The fumigations were conducted during both summer and winter months and represent three (3) years of data collection (1987-1989).

Actual exposure to phosphine gas occurs only during the application of the magnesium phosphide products in the warehouse. The sample times varied from 76 minutes up to 460 minutes. The average sample time was 211 minutes. These are typical exposure times for this type of operation.

As a result it would not be appropriate to compare the sample results against the 8-hour OSHA PEL of 0.3 ppm.

One approach that presents the data on an equivalent basis is to calculate the results as dose x time. The PEL is based on 0.3 ppm averaged over an 8-hour period. 0.3 ppm times 480 minutes equals 144 ppm-minutes. The action limit for phosphine is half the PEL or 0.15 ppm. As with the PEL, calculation at the action limit equals 0.15 ppm times 480 minutes or 72 ppm-minutes. Listed on Table-3, are the sample results in ppm-min vs the OSHA action limit level and the PEL level in ppm-min.

None of the personal exposures for the applicators were above the 8-hour 144 ppm-minute level. The highest ppm/minute concentration was 113 ppm-minute with a low value of 2.3 ppm-min. The average for the group was 28.0 ppm-minute with a standard deviation of 25.9 (see Table-4).

Considering the poor warning properties of phosphine gas and the delayed biological effects it causes, it may be more appropriate to use the action limit as a upper limit of exposure. The ppm-minute level for the action limit is 72.0. Of the 53 personal samples collected 50 (94.34 %) were below the ppm-minute action limit. Only 3 samples (5.66 %) were above the 72.0 ppm-minute action limit (see Table-5). Utilizing the action limit as a trigger mechanism the potential for applicator overexposure is minimal.

TABLE - 3
PHOSPHINE APPLICATOR EXPOSURE DATA

OSHA PEL (0.3PPM) X 480 min. = 144 ppm/min
ACTION LIMIT (0.15PPM) X 480 min. = 72 ppm/min

DATE	ACTUAL CONC. (ppm)	EXPOSURE TIME (min.)	PPM X MIN	ACTION LIMIT LEVEL PPM/MIN	OSHA PEL LEVEL PPM/MIN
JULY 1987	0.2	303	60.60	72	144
JULY 1987	0.2	303	60.60	72	144
JULY 1987	0.3	303	90.90	72	144
JULY 1987	0.2	101	20.20	72	144
JULY 1987	0.3	101	30.30	72	144
JULY 1987	0.8	101	80.80	72	144
JULY 1987	0.4	147	58.80	72	144
JULY 1987	0.3	151	45.30	72	144
JULY 1987	0.1	142	14.20	72	144
JULY 1987	0.08	460	36.80	72	144
JULY 1987	0.1	458	45.80	72	144
JULY 1987	0.1	445	44.50	72	144
JULY 1987	0.2	190	38.00	72	144
JULY 1987	0.3	187	56.10	72	144
DECEMBER 1987	0.09	221	19.89	72	144
DECEMBER 1987	0.07	221	15.47	72	144
DECEMBER 1987	0.09	221	19.89	72	144
DECEMBER 1987	0.12	221	26.52	72	144
DECEMBER 1987	0.07	221	15.47	72	144
DECEMBER 1987	0.19	221	41.99	72	144
DECEMBER 1987	0.16	221	35.36	72	144
DECEMBER 1987	0.27	221	59.67	72	144
DECEMBER 1987	0.21	221	46.41	72	144
DECEMBER 1987	0.21	221	46.41	72	144
DECEMBER 1987	0.3	221	66.30	72	144
DECEMBER 1987	0.3	221	66.30	72	144
DECEMBER 1987	0.51	221	112.71	72	144
JULY 1988	0.1	120	12.00	72	144
JULY 1988	0.03	76	2.28	72	144
JULY 1988	0.03	120	3.60	72	144
JULY 1988	0.03	76	2.28	72	144
JULY 1988	0.03	120	3.60	72	144
JULY 1988	0.03	76	2.28	72	144
JULY 1988	0.03	76	2.28	72	144
JULY 1988	0.03	76	2.28	72	144
JULY 1988	0.03	264	7.92	72	144
JULY 1988	0.05	264	13.20	72	144
JULY 1988	0.05	285	14.25	72	144
JULY 1988	0.1	265	26.50	72	144
JULY 1988	0.1	266	26.60	72	144
JULY 1988	0.03	266	7.98	72	144
JULY 1989	0.07	163	11.41	72	144
JULY 1989	0.07	174	12.18	72	144
JULY 1989	0.07	173	12.11	72	144
JULY 1989	0.07	174	12.18	72	144
JULY 1989	0.07	173	12.11	72	144
JULY 1989	0.07	173	12.11	72	144
JULY 1989	0.02	266	5.32	72	144
JULY 1989	0.02	266	5.32	72	144
JULY 1989	0.03	237	7.11	72	144
JULY 1989	0.02	247	4.94	72	144
JULY 1989	0.02	267	5.34	72	144
JULY 1989	0.02	267	5.34	72	144

ALL RESULTS REPRESENT PERSONAL EXPOSURES DURING APPLICATION

Table - 4
Phosphine Applicator Exposure Data
vs. OSHA PEL Level

Upper	144 ppm/min	Count	53	+3.0 sigma	105.842
Nominal	0	Mean	28.072	Mean	28.072
		Sigma	25.923		

Observed beyond spec: 144 ppm/min

High	0.000 %
Low	0.000 %

Estimated beyond spec:

High	0.000 %
Low	0.000 %

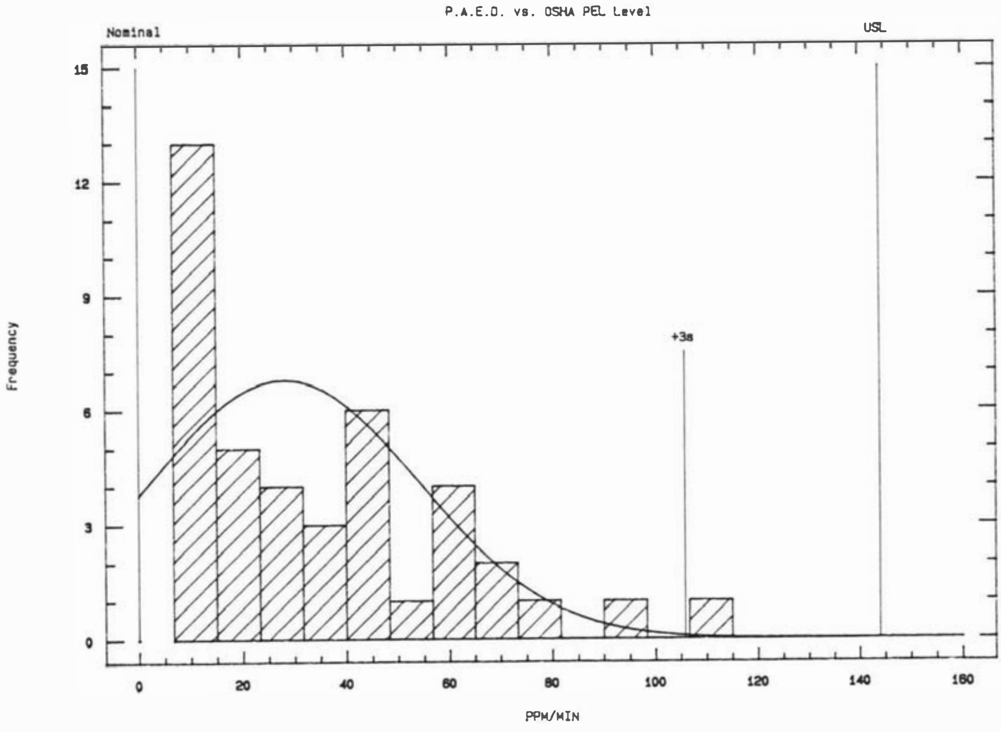


Table - 5
Phosphine Applicator Exposure Data vs. Action Limit Level
July 87 to July 89

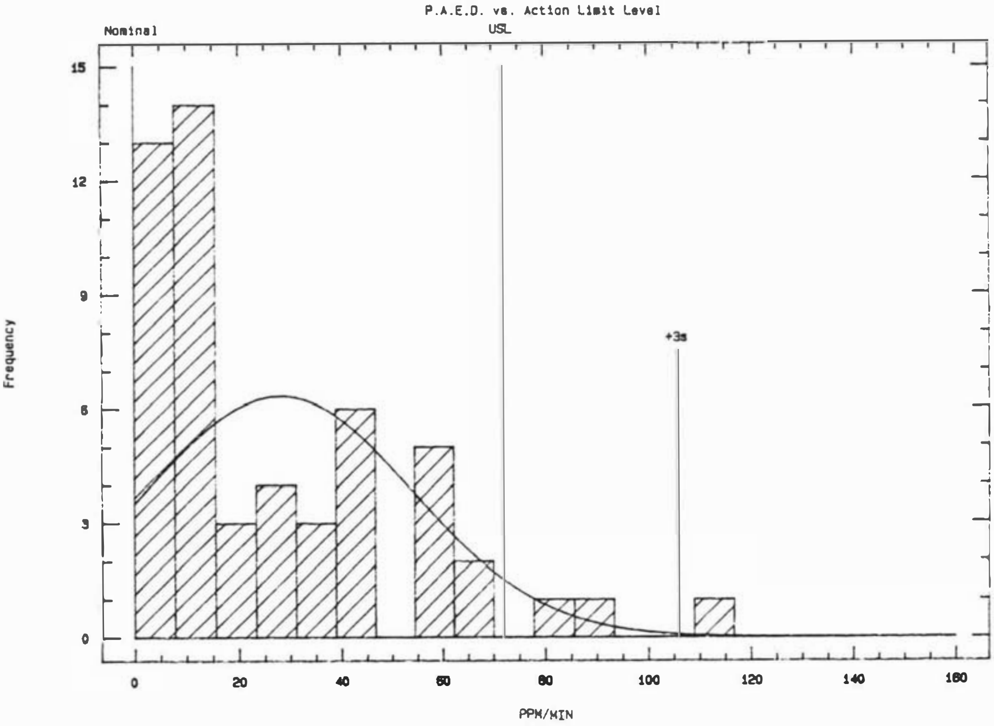
Upper	72 ppm/min	Count	53	+ 3.0 sigma	105.842
Lower	0	Mean	28.073	Mean	28.073
		Sigma	25.923		

Observed beyond spec: 72 ppm/min

High	5.660 %
Low	0.00 %

Estimated beyond spec:

High	4.508 %
Low	0.00 %



DISCUSSION AND CONCLUSION

Based on these sample results collected during the application of magnesium phosphide in stored product warehouses, the potential for applicator overexposure appears minimal. However, there are two important factors that play an integral part in determining the duration and degree of applicator exposure.

The following two items must be given serious consideration: (1) The standard operating procedure for a fumigation must be very detailed and (2) the applicator must be experienced and an expert at his job. Well qualified applicators will adhere to strict procedures and their expertise will show up in the time it takes to apply the gas. Fast, efficient applicators will minimize their exposure time and reduce the potential dose of phosphine received.

Data listed on Table - 6, very clearly illustrates this point. Data variables are presented for the total group (n=53) as well as for each individual sample period: July 87, December 87, July 88 and July 89. All data variables in each successive sample group decrease as well as the range of exposure levels. Table - 8, presents the data listed on

Table - 6
Phosphine Applicator Exposure Data
By Sample Period

Variable	PPMxMIN	July 87	December 87	July 88	July 89
Sample Size	53	14	13	14	12
Average	28.073	48.779	44.03	9.079	8.789
Median	15.47	45.55	41.99	5.76	9.26
Mode	2.28	60.6	15.47	2.28	12.11
Standard Dev.	25.923	21.278	27.610	8.579	3.417
Minimum	2.28	14.2	15.47	2.28	4.94
Maximum	112.71	90.9	112.71	26.60	12.18
Range	110.43	76.7	97.24	24.32	7.24

Table - 7
Phosphine Applicator Exposure Data
vs. Action Limit Level
July 88 to July 89

Upper	72 ppm/min	Count	26	+ 3.0 sigma	28.716
Lower	0	Mean	8.945	Mean	8.945
		Sigma	6.590		

Observed beyond spec: 72 ppm/min

High 0.00 %
Low 0.00 %

Estimated beyond spec:

High 0.00 %
Low 0.00 %

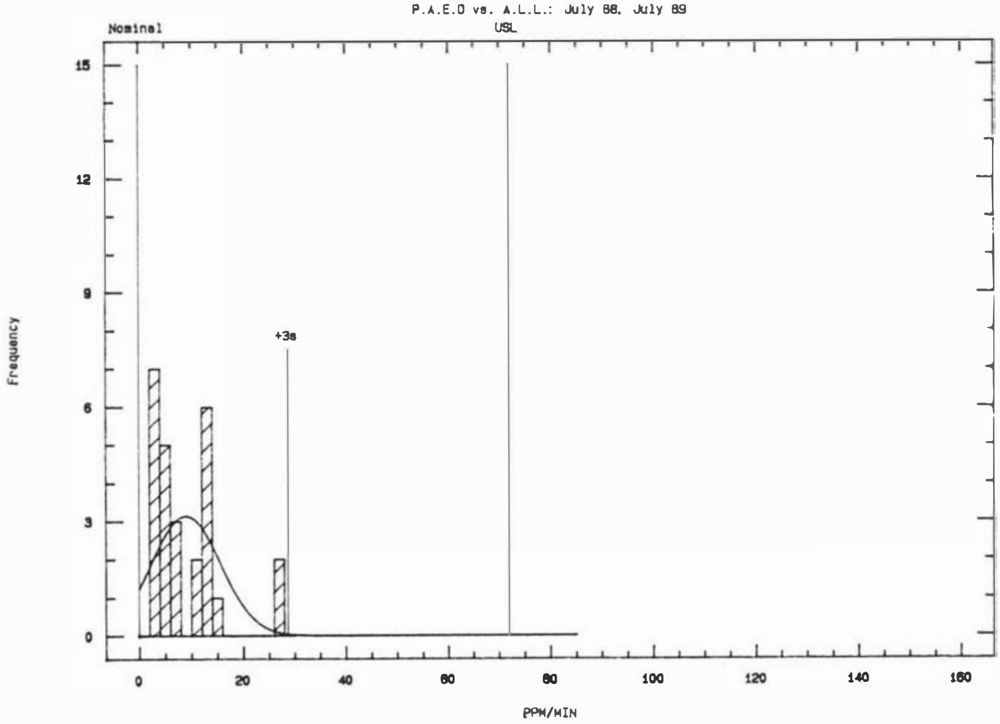


TABLE - 8
PHOSPHINE APPLICATOR DATA
YEARS 1987 - 1989

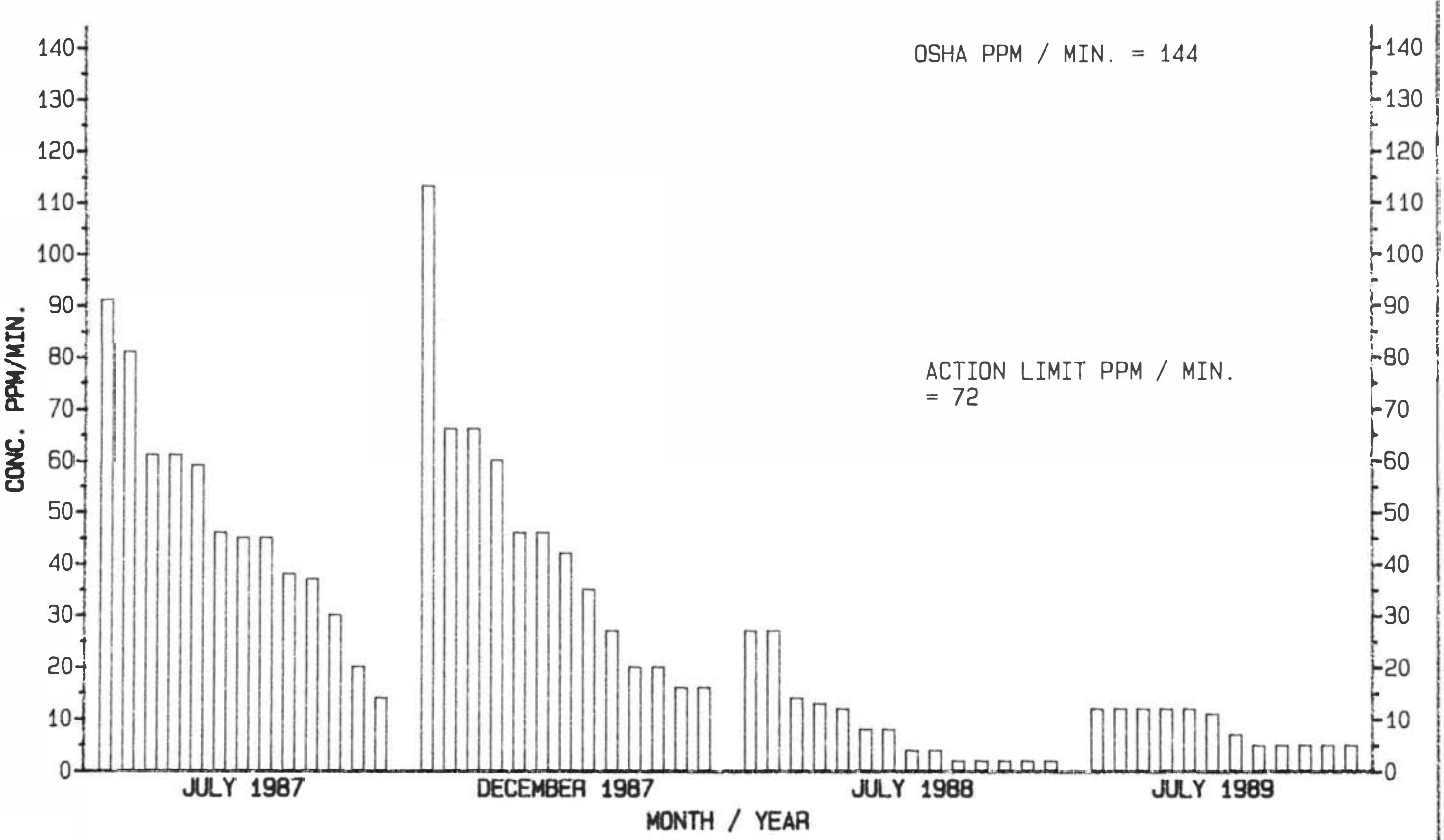


Table - 6, in graphic form. Table - 7 combines the last two sample periods (July 88, July 89) and compares the sample results to the action limit level of 74 ppm-min. The highest level measured was 26.6 ppm-min which is well below the action limit ppm-min level. Comparison of values on Table - 7 for July 88 and July 89 vs Table - 5, for all sample periods clearly indicates a downward trend in the average concentration, range, standard deviation, etc.

This demonstrates the advantage of utilizing well prepared procedures and a qualified contractor to perform the fumigation. Once the operational learning curve for each warehouse complex is overcome both application time and worker exposures will decrease.

No data were presented in this study comparing applicator exposures against the OSHA STEL. Attempts were made to conduct STEL monitoring but problems arose with sampling equipment.

At the time of this study the sample tubes were hand made. Later, phosphine tubes were available from SKC, Inc., however the same problem was encountered. In order to collect sufficient volume a flowrate of approximately 1.0 liter per minute was required. The resistance through the sample tube was too great and as a result the sample pump would shut off. Various attempts were made to sample at the STEL, but were not successful.

There is another facet to this study that should be seriously considered. This study is a typical industrial hygiene exercise to characterize the exposures of a known chemical agent to a group of workers. These types of studies are important as they address areas that may not have been adequately evaluated in the past. Also, the data may be useful to others in the determination of employee exposures in similar types of applications.

One obvious limitation to these studies is that they usually fall short in providing beneficial data with regard to predictable biological effects and setting exposure limitations.

As mentioned earlier, recent work by Garry, et.al., has demonstrated that applicators exposed to phosphine gas have a significant increase in rearrangements of G-banded lymphocytes. However, they were unable to draw a conclusion from their data. This recent information is very important. If industrial hygiene exposure characterizations can accurately determine worker exposures and the data is representative for the given task then this information becomes more valuable to the laboratory investigator.

Instead of generating exposure characterizations in the field and researchers discovering information in the laboratory the two must become integrated if they are to offer significant information. Field research can provide real world data for lab personnel to correlate with biological effects. Changes at the cellular level may be occurring with many chemical exposures that are well below the current PEL/TLV.

The data in this study would be of far greater value if specific airborne concentrations of phosphine gas could be shown to produce the G-banded lymphocyte rearrangements. Future exposure levels could be set that reduce the probability of genetic damage from long term low level phosphine exposure.

The data presented in this study indicates that with proper procedures and qualified applicators the potential for overexposure to the OSHA 0.3 ppm PEL is minimal. However, at these current acceptable exposure levels the question remains as to how much chromosome rearrangement is occurring in the workforce and what are the long term effects from this type of exposure.

As field surveys and laboratory studies become more integrated, biological monitoring in conjunction with field exposure assessments will be used to determine acceptable exposure concentrations for future occupational health standards.

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APPENDIX

Phosphine

Analyte:	Phosphate	Method No.:	S332
Matrix:	Air	Range:	0.195-0.877 mg/cu m
OSHA Standard:	0.3 ppm (0.4 mg/cu m)	Precision ($\overline{CV}_T$):	0.091
Procedure:	Collection on coated silica gel, permanganate, extraction, colorimetry	Validation Date:	3/17/78

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1. Synopsis

1.1 A known volume of air is drawn through a tube containing mercuric cyanide impregnated silica gel to trap the phosphine. The phosphorus is extracted and oxidized to phosphate using a hot, acidic permanganate solution.

1.2 The extracted sample is analyzed for phosphate by formation of the phosphomolybdate complex, extraction into a mixture of isobutanol and toluene and reduction using stannous chloride. The absorbance of the reduced phosphomolybdate complex is measured at 625 nm.

2. Working Range, Sensitivity and Detection Limit

2.1 This method was validated over the range of 0.195-0.877 mg/cu m at an atmospheric temperature and pressure of 19.0°C and 765.3 mm Hg, respectively, using a 16-liter sample. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used. The upper limit of the range of the method depends on the adsorptive capacity of the mercuric cyanide treated silica gel. This capacity may vary with the concentration of phosphine and other substances in the air. When an atmosphere at 90% relative humidity containing 0.957 mg/cu m of phosphine was sampled at a flow rate of 0.2 liter per minute, breakthrough was determined to occur at a sampling volume of 20.75 liters (capacity = 19.86 μg PH_3). To minimize the probability of overloading the sampling tube, the sample size recommended is less than two-thirds the 5% breakthrough capacity at >80% RH at twice the OSHA standard.

2.2 Sampling at 0.2 liter per minute for 80 minutes will yield a 16-liter sample with 6.4 μg of PH_3 collected at the OSHA standard level. The sensitivity of the method obtained from the slope of the absorbance vs μg of phosphine calibration curve is 0.0524 absorbance units per μg of PH_3.

2.3 The detection limit of the method determined from twice the standard deviation for the absorbance of six blank treated silica gel tubes corresponds to 0.19 μg PH_3 (or 0.0119 mg/cu m for a 16-liter sample).

3. Interferences

3.1 When two or more compounds are known or suspected to be present in the air, such information, including the suspected identities, should be transmitted with the sample.

3.2 The colorimetric determination of phosphate is subject to interference by any species which also forms a molybdate complex which is extractable into the isobutanol-toluene mix and absorbs at similar wavelengths.

3.3 Any phosphorus compound which is retained by the mercuric cyanide-coated silica gel tube and oxidized to phosphate by hot aqueous permanganate solution will be a major interference. Possible interfering species include PCl_3 and PCl_5 vapors and organic phosphorus compounds. Particulate H_3PO_4, P_4O_{10} and P_4S_{10} are also possible interferents unless a prefilter is used in conjunction with the sorbent tube. Although a prefilter has not been tested with the method, its use is recommended.

3.4 If the possibility of interferences do exist, modification of the analytical procedure must be made to circumvent the problems or an alternative procedure should be used.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total sampling method in the range 0.195-0.877 mg/cu m was 0.0908. This value corresponds to a standard deviation of 0.0363 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.

4.2 On the average, the concentration obtained at the OSHA standard level using the overall sampling and analytical procedure was 0.2% higher than the average taken concentration for a limited number of laboratory experiments. Any difference between the found and taken concentrations may not represent a bias in the sampling and analytical method but rather a random variation from the experimentally determined taken ("true") concentration. Also, collected samples, stored for at least seven days, are stable, thus no recovery corrections should be applied to the final result.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable and involves no liquids.

5.2 The precision of the method is affected by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for only one tube.

5.3 The analytical method requires measurement of the absorbance of the phosphomolybdate complex one minute after reduction with stannous chloride. This may present an inconvenience since the samples need to be handled individually.

5.4 A disadvantage of the method is that the amount of sample which can be collected is limited by the number of micrograms of phosphine that the tube will hold before overloading. When the amount of phosphine found on the backup section exceeds 25% of that on the front, the probability of sample loss exists.

6. Apparatus

6.1 Personal Sampling Pump. A calibrated personal pump whose flow rate can be determined within ±5% of the recommended flow rate. The pump must be calibrated with a representative tube in the line.

6.2 Treated Silica Gel Tube. Glass tube with both ends flame sealed 12-cm long with a 6-mm O.D. and a 4-mm I.D. containing two sections of treated silica gel (45/60 mesh, SKC, Inc.). The absorbing section contains 300-mg of the treated silica gel and the backup 150-mg. A small wad of silylated glass wool is also placed between the front adsorbing section and the backup section; a plug of silylated glass wool is also placed in the front of the adsorbing section and at the end of the backup section. The pressure drop across the tube must be less than 2 inches of mercury at a flow rate of 0.2 liter per minute.

The silica gel is coated according to the following procedure:

6.2.1 Dry one hundred grams of silica gel at 90°C for 2 hours.

6.2.2 Prepare a 2% w/v mercuric cyanide solution in water (2 g $Hg(CN)_2$ in 100 mL H_2O).

6.2.3 Add the dried silica gel to the mercuric cyanide solution and let set for 15 minutes with occasional stirring.

6.2.4 Drain the excess mercuric cyanide solution and dry the remaining silica gel at 90°C for 3 hours.

6.2.5 Cool the silica gel to room temperature in a covered beaker.

6.2.6 Expose the silica gel to a humid atmosphere (>80% RH) for 24 hours.

6.3 A spectrophotometer capable of measuring absorbance or transmittance at 625 nm.

6.4 Two matched 5-cm silica cells with tight fitting caps.

6.5 Separatory funnel, 125-mL.

6.6 Beakers, 50-mL.

6.7 Volumetric flasks, 10, 25, 100 and 1000-mL.

6.8 Pipets, 0.2, 10 and 25-mL and other convenient sizes to make standard dilutions.

6.9 Graduated cylinders, 10-mL.

6.10 Water bath (maintained at 65-70°C).

6.11 Syringes, 0.5 and 1.0-mL.

6.12 Balance.

6.13 Barometer.

6.14 Thermometer.

6.15 Stopwatch.

7. Reagents

All reagents should be ACS reagent grade or better.

7.1 Water, distilled or deionized.

7.2 Potassium dihydrogen phosphate, anhydrous, KH_2PO_4.

7.3 Sulfuric acid, concentrated.

7.4 Ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$.

7.5 Ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2$.

7.6 Potassium permanganate, $KMnO_4$.

7.7 Stannous chloride, $SnCl_2$.

7.8 Glycerol.

7.9 Toluene.

7.10 Isobutanol.

7.11 Methanol.

7.12 Standard phosphate solution. Prepare by dissolving 200 mg of KH_2PO_4 in 1 L of distilled water. (1.00 mL = 49.94 μg PH_3).

7.13 Molybdate solution. Prepare by dissolving 49.4 g of $(NH_4)_6 Mo_7O_{24}.4H_2O$ and 112 mL of concentrated H_2SO_4 in water to a total volume of 1 L.

7.14 Toluene-isobutanol solvent. Mix equal volumes of toluene and isobutyl alcohol.

7.15 Alcoholic sulfuric acid solution. Add 50 mL of concentrated H_2SO_4 to 950 mL of methyl alcohol.

7.16 Ferrous solution. Prepare by dissolving 7.9 g of $Fe(NH_4)_2(SO_4)_2$ and 1 mL of concentrated H_2SO_4 in water with a total volume of 100 mL.

7.17 Stannous chloride reagent. Prepare by dissolving 0.4 g of $SnCl_2$ in 50 mL of glycerol (heat to dissolve).

7.18 Acidic permanganate reagent. Prepare by dissolving 0.316 g of $KMnO_4$ and 6 mL of concentrated H_2SO_4 in a total volume of 1 L H_2O.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should be initially soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, 6 M nitric acid, tap water, distilled water in that order and then dried.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative sampling tube in the line. The tube is described in Section 6.2. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the two ends of the silica gel tubes to provide an opening of at least one half of the internal diameter of the tube (2-mm).

8.3.2 The treated silica gel tubes should be placed in a vertical direction during sampling to minimize channeling through the sorbent bed.

8.3.3 Air being sampled should not be passed through any hose or tubing before entering the tube.

8.3.4 A sample size of 16 liters is recommended. Sample at a known flow rate between 0.2 and 0.01 liter per minute. The flow rate should be known with an accuracy of at least ±5%.

8.3.5 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available, record the elevation.

8.3.6 The treated silica gel tubes should be labeled appropriately and capped with supplied plastic caps. Under no circumstances should rubber caps be used.

8.3.7 With each batch or partial batch of 10 samples, submit one treated silica gel tube which had been handled in the same manner as the sample tubes (break, seal, transport) except that no air is sampled through this tube. This tube should be labeled as blank.

8.3.8 Capped treated silica gel tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis each treated silica gel tube is scored with a file and broken open. The glass wool is removed with care and discarded making sure that no silica gel is lost in the process. The silica gel in the front section is transferred to a 50-mL beaker. The separating section of glass wool is removed and discarded. The backup section of silica gel is transferred to another container. These two sections are analyzed separately.

8.4.2 Extraction of the Samples. Prior to analysis, 10 mL of the acidic permanganate reagent is pipetted into each beaker containing the silica gel. The extraction is carried out for 90 minutes at 65-70°C in a water bath. After extraction the acidic permanganate solution is drained into a 10-mL volumetric leaving the silica gel. The volumetric is made to volume with distilled water. The silica gel is washed twice with 3 mL portions of distilled water and the contents drained into another 10 ml volumetric containing 1 mL of ferrous solution. The flask is made up to volume with distilled water and mixed thoroughly.

8.4.3 Spectrophotometer Operation. Turn on the spectrophotometer and allow sufficient time for warmup. Follow the instrument manufacturer's recommendations for specific operating parameters. Adjust the wavelength to 625 nm and set the zero and 100% transmittance scale using 5-cm cells filled with distilled water. Check these settings prior to making any measurement to check on instrument drift.

8.4.4 Analytical Procedure

1. Add the contents of both 10-mL volumetric flasks (extract and washings) to a 125-mL separatory funnel.

2. Add 7.5 mL of molybdate reagent and 25 mL of toluene-isobutanol solvent. Shake for 60 seconds. Allow 60 seconds for the aqueous and nonaqueous layers to separate and discard the lower (aqueous layer).

3. Pipet 10 mL of the nonaqueous layer into a 25-mL volumetric containing 10 mL of the alcoholic sulfuric acid solution.

At this stage steps 4 through 6 must be performed within 1 minute.

4. Add 0.5 mL (25 drops) of stannous chloride reagent and make to volume using alcoholic sulfuric acid solution. Mix thoroughly.

5. Transfer the sample into 5-cm cells and stopper immediately.

6. Measure the absorbance or transmittance at 625 nm using water as a blank.

9. Calibration and Standardization

9.1 Add 10 mL of acidic permanganate solution, 1 mL of ferrous reagent to the separatory funnel.

9.2 Add 20 to 400 μL of the standard phosphorus solution to cover the range of 1 to 10 μg of PH_3. Add 8 to 9 mL of H_2O to make the total volume of the permanganate solution, ferrous solution, phosphorus solution and water to 20 mL. Prepare at least six calibration standards. A blank containing no phosphorus should also be analyzed.

9.3 Proceed as in Sections 8.4.4.2 to 8.4.4.6.

9.4 Prepare a calibration curve by plotting the absorbance of the standards after subtraction of the blank versus the amount of each standard in μg of PH_3 added on linear graph paper.

10. Calculations

10.1 Correction for the blank (obtained by extraction and analysis of the treated silica gel tube marked "blank") must be made for each sample

$$A_C = A_S - A_B$$

A similar procedure is followed for the backup tube.

10.2 The amount of phosphine present in the front tube, corrected for the blank, is found by reading the amount corresponding to A_C from the standard curve. The amount of phosphine found in the backup tube is similarly determined.

10.3 Add the amounts present in the front and backup tubes for the same sample to determine the total weight in the sample.

10.4 Determine the volume of air sampled at ambient conditions based on the appropriate information, such as flow rate (L/min) multiplied by sampling time (min). If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}\right)$$

where:

f = sampling flow rate

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air samples (°K)

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m, which is numerically equal to µg/L, by

$$\text{mg/cu m} = \frac{\text{Total mg (Section 10.3)}}{\text{Air Volume Sampled (L)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{34.00} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
34.00 = molecular weight of phosphine
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, Washington, D.C., Order No. 017-33-00231-2.

11.2 Backup Data Report for Phosphine, S332, prepared under NIOSH Contract No. 210-76-0123, 3/17/78.

Vita

[redacted]