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ANALYSIS OF PHOSPHINE WITH DIFFERENT TECHNIQUES

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ABSTRACT: Phosphine is commonly used as an insecticide and rodenticide compound. It is considered hazardous air pollutant and suspected to cause serious health effects, such as reproductive effects, birth defects and adverse environmental effects. Phosphine is a Colorless metal hydride gas with the chemical formula PH_3. It is slightly soluble in water and soluble in most organic solvents. The risks of phosphine to human health and the environment vary considerably depending upon the type and extent of exposure. Different techniques available for its examination are: flame photometry, infrared spectroscopy, mass spectrometry and gas chromatography. Gas chromatography is the most sensitive method for the determination of the phosphine content in air samples. Phosphine derivatives such as magnesium phosphide and zinc phosphide are used as formulations prepared for fumigation in pest control and powder or paste used as a rodenticide respectively. The purpose of this paper is to introduce some methods for the examination of phosphine by using laboratory techniques.

Keywords: Phosphine, Rodenticide, Gas chromatography.

INTRODUCTION:

Phosphine is also known as hydrogen phosphide, phosphorous hydride, phosphorated hydrogen and lying in physical state of gas with molecular weight 33.99.

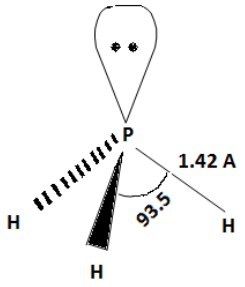

Fig. 1: Structural formula of Phosphine

It is flammable and explosive in air and can auto ignite at ambient temperatures so it is necessary to keep the sources of sparking flames and ignition away from it. The pyrophoric nature of phosphine makes it more dangerous to handle when it comes in contact with air. It may occur naturally in the anaerobic degradation of phosphorus-containing organic matter viz; in the production of marsh gas. Naturally occurring phosphides are extremely rare. It is stable at room temperature and begins to decompose at about 375 ^{0}C. Phosphine reacts vigorously and is a strong reducing agent and incompatible with oxidizing materials. Threat to the environment and human life can be reduced if handling is done carefully and with proper control.

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It is used in the synthesis of organophosphines, organic phosphonium derivatives and as doping agent in the manufacture of semiconductors in the electronics industry. Formulations of aluminium or magnesium phosphide are available for fumigation in pest control. Zinc phosphide is used as a rodenticide in the form of a powder or a paste containing 2.5- 5% zinc phosphide, which is incorporated in bait at 1 part in 10.

CHEMICAL PROPERTIES:

Phosphine is a strong reducing agent and reacts vigorously with oxidizers such as potassium permanganate, sodium hypochlorite, oxygen, ozone, chlorine, fluorine, and nitric oxide and also has some reaction with the alkali metal. It is incompatible with oxidizing materials, members of the halogen family, acids, and other combustible materials.

ALL BRAND NAMES/TRADE NAMES:

Celphide, Celphine, Celphos, Delicia Gas toxin, Detia Gas Ex-B/P/T, L-Fume, Phosphine, Phostex, Phostoxin, Quickfos and Zedesa

TOXICOLOGICAL EFFECTS;

Phosphine is toxic by inhalation however the effects are not completely understood till now .It mainly harms to central nervous system (CNS), creates depression and causes lung irritation, responsible for pulmonary edema, dilation of the heart and hyperemia of the visceral organs. Inhalation can cause coma and convulsions leading to death within 48 hours. However, most cases recover without after-effects. Chronic poisoning, characterized by anemia, bronchitis, gastrointestinal disturbances and visual, speech and motor disturbances, may result from continued exposure to very low concentrations. Once the phosphine is inhaled it is absorbed readily through the lungs and produces early symptoms in the brain and liver and also affects the other parts of the body. Phosphine inhibits the cytochrome oxidase and the organs with the greatest oxygen requirements including brain, kidneys, heart and liver are the most sensitive and soft targets to damage. Phosphine is not normally present in the environment and diluted and oxidized up to great range to minimize its effects. It is released in order to reduce the level of pests and has been demonstrated to be effective against many species of arthropod. Major accidental release of stored phosphine presents serious toxic and explosive fire hazards for man and even animals. The diagnosis of phosphine poisoning is easy, but the clinical manifestations of phosphine and the phosphides may be similar to those of other toxic chemicals such as arsenic sulphide and calcium oxide. A silver nitrate impregnated paper test can be used for the breath and gastric fluid of the patients exposed to phosphine/phosphide. Silver nitrate and phosphine/phosphides react to form silver phosphide which confirms the diagnosis. Other laboratory investigations such as cell blood counts, haemoglobin, haematocrit, arterial blood gas analyses, renal and liver function tests and cardiopulmonary monitoring and investigations (ECG and chest X-ray) are essential for the assessment of organ effects and the management of phosphine/phosphide poisoning.

COLOR TEST FOR PHOSPHINE:

Silver nitrate impregnated paper test can be used for the breath and gastric fluid of the patients exposed to phosphine/phosphides.

PROCEDURE:

To the 5 ml of blood add 2ml of conc. HCl solution. Filter paper dipped in $AgNO_3$ solution is placed over the lid of the test tube which results in the dark black color indicating the presence of Phosphine in the sample.

DIFFERENT METHODS FOR ANALYSIS OF PHOSPHINE:

1. Distillation Method: It is one of the important methods for the analysis of phosphine. The different steps involved are as follows:

1. 10 ml blood is taken in the round bottom flask.
2. 2ml of 1N H_2SO_4 or Tartaric acid (5% w/v) in water is added to it and diluted the content with 30 ml water.
3. Content of the round bottom flask fitted with water condenser is heated to collect the distillate (Figure 1).
4. The distillate is allowed to react with the 2ml 1% $AgNO_3$ in a test tube.
5. The black precipitate in test tube shows the presence of phosphine.

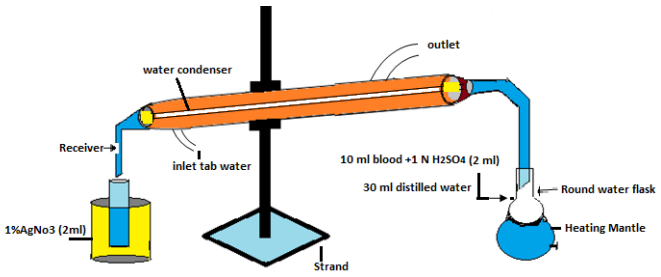

Figure 1: Schematic diagram for distillation of phosphine from blood

2. Mercuric bromide Test

1. 10-15gm of the stomach content /intestinal parts is taken in a conical flask.
2. 3-5 gm of the cadmium chloride salt and few drops of the concentrated sulphuric acid & 5ml of the water are added to it.
3. A strip of the filter paper dipped and dried in 10% $HgBr_2$ stick with the glass lid is fitted on the mouth of the conical flask.
4. The above setup is heated for 10 min.
5. The yellowish color of the filter paper indicates the presence of the phosphine.

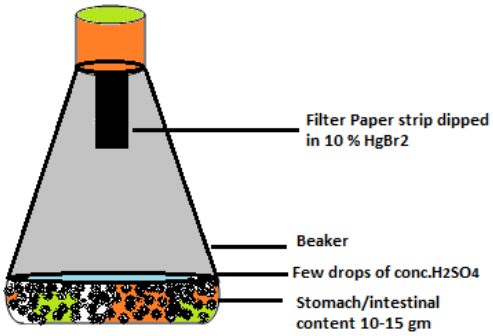

Figure 2: Schematic diagram of test of phosphine by $AgBr_2$ method

3. Silver Nitrate Test

1. 25gm of the biological material is taken in a conical flask.
2. A few ml of cadmium sulphate solution is added.
3. Few drops of dilute sulphuric acid is added to it.
4. The neck of conical flask is plucked with cotton soaked and dried with saturated solution of lead acetate.
5. After the above step, conical flask's mouth is covered by filter paper soaked and dried with saturated solution of AgNO3 solution.
6. The mixture is heated gently on the water bath at 40-60C.
7. The gas evolved is allowed to come in contact with $AgNO_3$ paper.
8. The grey or yellowish brown or black coloration of $AgNO_3$ paper indicates the presence of the phosphine.

4. Ammonium molybdate Test

1. The colored $AgNO_3$ paper obtained from the above silver nitrate test is dried and cut into the pieces and dissolved in the dilute HNO_3.

2. The filtrate is collected and the residue is again dissolved in HNO3 solution.

3. All the filtrates are collected and evaporated to dryness.
4. The residue is taken in a few drops of the conc. Nitric acid (HNO_3) and 1ml of ammonium molybdate solution is added and warmed.
5. The formation of the canary yellow precipitates confirms the presence of the phosphine

5. Silver diethyl-dithiocarbamate (SDDC) method: This method is based on reaction of phosphine with SDDC in pyridine or chloroform which forms a red coloured complex. This method has a drawback under the circumstances of arsenic in high concentration will interfere in the reaction and give the same red coloured complex.

1. In the reaction vessel of the apparatus 10ml of blood or 10gm of finely homogenized tissue is taken.
2. 30ml of distilled water is added to it.
3. One end of the absorption tube (U tube) is plugged with cotton soaked with saturated solution of lead acetate. And other end of U tube is filled with 4 ml SDDC solution and tube is secured to the reaction vessel.
4. Briefly lifting the absorption tube and added 5.0 ml of the conc. HCl to the reaction vessel and the tube is fitted to the reaction vessel.
5. Approximately 3 g of zinc granules are added to the reaction vessel.
6. The reaction flask fitted with absorption tube is placed in a water bath at 50 ^{0}C for 30 minute.
7. A blank is run simultaneously in another reaction vessel containing the distilled water only.
8. Colour of the SDDC changes from yellow to red which confirms the presence of phosphine.
9. This can be further confirmed by measuring optical density of the SDDC at the 465 nm in UV-vis spectrophotometer.
10. For quantification similar reaction can be run for known amounts (10, 20, 30 and 40 µg zinc/ aluminium phosphide) for calibration curve.

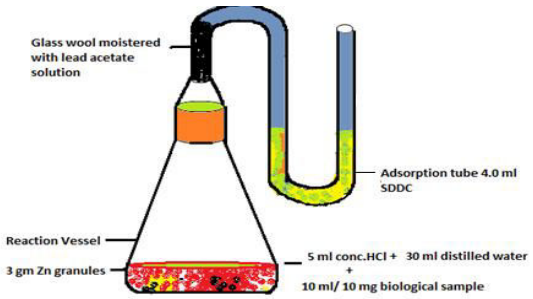

Figure 3: Schematic diagram for test of phosphine by SDDC method

6. **Phosphorous Determination Method:** This test is an indirect method of phosphide estimation. In the reaction distilled water is used in place of SDDC reagent, wherein phosphine gas is absorbed.A known amount of this water with dissolved phosphine is oxidized with addition of potassium permaganate. Excess of permagnate is reduced with addition of hydroxylammonium hydrochoride and phosphorous is determined by the molybdic acid-ANSA reagent.

1. In the reaction flask 10 gm of finely homogenized tissue or blood /unknown sample (containing about 30 µg of phosphide) is taken.
2. Then added 30 ml of the distilled water to the reaction flask.
3. To the absorption tube of the apparatus 4.0 ml of distilled water and 5.0 ml of conc HCl is added and the tube is fitted to the reaction flask.
4. Then 3.0 gm of the Zn granules is added to the reaction vessel and reaction is allowed to progress for 30 min. (if there is enough phosphine gas evolving without the addition of the Zn, this step should be avoided).
5. The reaction flask is placed into the water bath at 50 ^{0}C for 30 min.
6. The distilled water is quantitatively transferred to a test tube and 0.5 ml of 6% aq $KMnO_4$ is added. The tube is shaken well and excess of $KMnO_4$ is reduced by the addition of the 0.2 ml of 20% hydroxyl ammonium hydrochloride and solution becomes colorless.
7. One ml of distilled water aliquot from the above reaction is taken for phosphorous estimation. Then 1 ml ammonium molybdate reagent and 7 ml distilled water is taken in each tube. After the tubes are well shaken 4 ml, 1-amino-2-naphthol-4-sulphonic acid reagent is added.
8. Solution becomes coloured which confirms the presence of phosphorous and hence phosphine.
9. This can be further confirmed by measuring optical density of the above coloured complex formed at the 660 nm by colorimeter.
10. For quantification similar reaction can be run for known amounts (10, 20, 30 and 40 µg zinc/ aluminium phosphide) and the resultant phosphorous is estimated. The amount of phosphorous released is plotted against the known amount of zinc/aluminium phosphide in a calibration curve.

7. **Gas Chromatography Headspace Method:**

The Gas chromatograpy headspace technique using nitrogen phosphorous detector (HS-GC/NPD) play promising role for the analysis of phosphine from samples of lungs, liver, kidney, heart, brain, stomach etc. A procedure using HS-GC coupled with mass spectrometry (MS) for investigation and detection of phosphine from post mortem materials has also been reported. The condition for the analysis of phosphine by GC-HS is given bellow:

Column: HP-Plot Q GC (30 m ×0.32 mm; ID film thickness 20 µm)
Carrier gas: H_2 (4 psi, 12 s splitless, split 1/30; injection volume 0.1 ml)
Flame photometric detector: (P mode)
Oven temperature: 70 ^{0}C for 0.5 min followed by 15 ^{0}C/min up to 100 ^{0}C with an 8 min hold.
Injector temp. : 150 ^{0}C
Detector temp. : 310 ^{0}C

PREPARATION OF REAGENTS

1. Preparation of the 1 N H_2SO_4

2.6 ml of con. sulphuric acid is added in a 100ml of the volumetric flask and then make-up it with distilled water.

2. Preparation of the SDDC reagent

a. 300 mg silver diethyldithiocarbamate is dissolved in pyridine or chloroform and make-up it to 100ml.
b. If dissolved in chloroform 1ml of morpholene is added before making it up to 100 ml.
c. The reagent is stored in the amber colored bottle and is stable for the one month.

3. Preparation of the ammonium molybdate reagent

a. 10 N sulphuric acid is prepared from lab reagent.
b. 2.5 gm ammonium molybdate is dissolved in 30 ml of distilled water + 20 ml of the solution (a), the solution is made up to the 100 ml, Heat slightly to dissolve, if necessary.

4. Preparation of the 1-amino 2-napthol 4 sulphonic acid (ANSA reagent)

a. Sodium metabisulphate 15% (w/v) in distilled water.
b. Sodium sulphate 20 % (w/v) in distilled water.
c. 195 ml of solution (a) is mixed with 0.5 gm 1-amino 2-napthol 4 sulphonic acid (ANSA) .then 5 ml of sol (b) is added and stored in a dark bottle

CONCLUSION:

The use of phosphine has constantly been growing and this usage is expected continue to escalate throughout the world and the issue of the safe handling of phosphine is a very important and relevant topic today Different methods has been discuss employed for its examinations.

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