

carb, promecarb, Mesurol, and carbaryl can be classified as strong inhibitors, and aldicarb and formetanate (HCl) can be classified as weak inhibitors of pig liver esterases catalyzing the hydrolysis of IPA.

Since the colorimetric procedure used includes incubation of pesticides before the addition of substrates, it can be used directly to assay enzyme activities from insecticide-treated organisms.

IPA used as a substrate of pig liver esterases has certain advantages over other esterase substrates. It can be used in tlc and colorimetry without involving complex preparations. IPA solution is stable, particularly when stored at 4°. The product indophenolate ion can be measured directly with a spectrophotometer. It has a high extinction coefficient; therefore, it is detectable at a small concentration.

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Detector for Phosphine at Permissible Levels in Air

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A paper-strip detector has been developed for detecting maximum acceptable concentrations (0.05–0.3 ppm) of phosphine in air. The strips are prepared by dipping them in a 1% solution of mercuric chloride in methyl yellow. The papers turn red from the yellow. Ammonia interferes with

the proper development of color. The strips are useful for personal protection against phosphine in fumigation and degassing operations, and to detect traces of phosphine in fumigated commodities.

Phosphine (PH₃) gas generated from aluminum phosphide [Phostoxin (Federal Republic of Germany), Delicia (GDR), Celphos (India)] tablets is being used extensively for fumigating food grains and products. Its detection in air at permissible levels is important because of its very high toxicity rating and lack of warning odor at toxic levels. It can be detected by smell at 5 ppm (Singh *et al.*, 1967). Subacute poisoning has been reported at this threshold level (Klimmer, 1969). Sniff tests conducted by a five-man panel could detect 0.002 mg/l. or 1.3 ppm (Berck, 1968). But the carbide-like odor cannot be relied upon to signal toxic levels of the gas, as the commodities preferentially absorb the odor principal (Bond and Dumas, 1967). The maximum allowable concentration for prolonged exposure is 0.05 ppm according to the Second International Symposium, Paris, 1963 (Truhaut, 1964). The threshold limit is set at 0.3 ppm by the American Conference of Government Industrial Hygienists (1964) (Monro, 1969).

Commercially available phosphine detector tubes (Dumas and Monro, 1966) are not always freely available in all countries and are also expensive. Several types of

chemically treated papers have been developed for detecting PH₃ in air (Lugg, 1962). Of all these, silver nitrate-impregnated papers have been found to be the most sensitive. Narrow range (BDH) pH papers (pH 2.5–4.0) treated with mercuric chloride have also been found sensitive to 0.05 ppm and above (Muthu, 1970), but the color change is not very apparent and hence is hard to evaluate. In the present method, advantage is taken of the reaction of PH₃ with mercuric chloride where the hydrochloric acid formed is responsible for the change in color of a stain sensitive to the pH change and is shown by the reaction $\text{PH}_3 + 3\text{HgCl}_2 \rightarrow \text{P}(\text{HgCl})_3 + 3\text{HCl}$.

MATERIALS AND METHODS

Preliminary experiments using several pH-indicating stains on mercuric chloride-impregnated paper strips indicated the suitability of methyl yellow, which turned from yellow to red as the pH was lowered from 4 to 2.9.

Preparation of the PH₃ Detector Strips. Filter paper strips, 10 cm long and 0.5 cm wide, were cut from a Whatman No. 1 sheet dipped in methyl yellow (*p*-dimethyl aminobenzene) (CAUTION: carcinogenic) solution (0.05% in ethanol) and dried in a draught of air. A drop of a 1% solution (pH 4) of mercuric chloride was allowed to creep along the strip, which was dried again. The strips

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Table I. Detection of PH₃ at Permissible Levels in Air by Mercuric Chloride–Methyl Yellow-Treated Paper

| Concentration of PH ₃ , ppm | Time taken for change in color, min | Color | Standard color (according to the Dictionary of Color, Maerz and Paul, 1950) |
|--|-------------------------------------|---|---|
| 0.00 | | Yellow | |
| 0.05 ^a | 7 | Pink edges; body slowly turning yellowish-red | Between primuline and Ta-Ming (Plate 10) |
| 0.10 ^b | 2 | Pink edges; body slowly turning yellowish-red | Ta-Ming (Plate 10) |
| 0.30 ^c | Immediate | Saffron turning red | Between Ta-Ming (Plate 10) and Spanish Y Golden Y |
| 0.05 (Vault) (100 ml syringe) | 10 | Saffron turning red | Blaze Sheik (Plate 3) |

^aThreshold concentration, Second International Symposium, Paris, 1963 (Truhaut, 1964). ^bPermissible limit in fumigated foods (Dietrich *et al.*, 1967). ^cThreshold concentration, American Conference of Government Industrial Hygienists (1964) (Monro, 1969).

Table II. Influence of Mixtures of Ammonia and Phosphine on the Development of Color in Mercuric Chloride–Methyl Yellow-Treated Paper

| PH ₃ at 0.3 ppm | |
|---|---------------------------------------|
| PH ₃ –NH ₃ (v/v) | Color |
| 1:0 | Saffron turning red |
| 1:3 (stoichiometric ratio as evolved from ALP + NH ₄ NH ₂ CO ₂ compressed tablets) | Pink edges with pink infiltration |
| 1:6 | Pink edges with dirty yellow interior |
| 0:0.9 | Yellow |

were exposed at a temperature of 30° and a relative humidity of 50%.

Testing of Strips. Vacuum desiccators of 10.4-l. capacity provided with rubber septum caps on the lids were partially evacuated by using a rubber bulb aspirator and dosed with PH₃ generated from aluminum phosphide (Phostoxin) tablets (mixture of aluminum phosphide and ammonium carbamate) inside a gas burette containing distilled water (Bond *et al.*, 1969). A stock concentration of 0.75 mg/l. (500 ppm) was established by injecting 6.5 ml (7.8 mg) of PH₃ into the 10.4-l. desiccator through the septum cap (density of PH₃ was estimated to be 1.2 g/l. over water in the gas burette at 30° and 696.5 mm pressure). An aliquot of 1 ml from the stock concentration equivalent to 0.00078 mg (0.00065 ml) of PH₃ injected into the 10.4 l. test desiccator gave a concentration of 0.00075 mg/l. equivalent to 0.05 ppm. Concentrations of 0.1 and 0.3 ppm were also established by dosing 2- and 6-ml

quantities of the stock concentration in separate 10.4-l. desiccators. The strips were fixed to paper clips and hung on the hooks of the test desiccator stoppers, which were quickly replaced. The time taken for change in color was noted in each case in a span of 10 min. The standard color charts in the Dictionary of Color of Maerz and Paul (1950) were matched with the color developed on the detector strips. There were five replicates per concentration. A treated paper strip without PH₃ served as a control. The data are given in Table I.

Another set of three desiccators was dosed with 0.3 ppm of PH₃ and mixtures of PH₃ and ammonia (NH₃) to give proportions of 1:3 (stoichiometric proportion as generated from Phostoxin tablets), 1:6, and NH₃ alone at 0.9 ppm. Ammonia from a cylinder was pressure filled into a 100-ml all-glass syringe and the tip was closed with a rubber septum cap. The required quantities were withdrawn using a 10- μ l gas-tight syringe (density of NH₃ was estimated to be 0.65 g/l. at 30° and 696.5 mm). 2 μ l of the gas in 10.4 l. corresponded to 0.15 ppm (0.0001 mg/l.). The test paper strips were exposed as before. The data are shown in Table II.

Field Trials. A 6.2 m³ volume atmospheric vault was dosed with 2 mg of freshly powdered aluminum phosphide tablet to obtain a concentration of 0.05 ppm. After an interval of half an hour the paper strip was placed inside a 100-ml syringe and the atmosphere was sampled by attaching the syringe to the gas sampling line. The time taken for the changes in color was noted (Table I).

The strips were distributed in hoods where aluminum phosphide + ammonium carbamate compressed tablets were being manufactured and also at different points radially from the hoods. The distances were 1, 3, 8, 16, 32, and 60 m from the source. After an exposure of 10 min,

Table III. Monitoring of Atmosphere in a Phosphine Tablet-Formulating Plant with the Mercuric Chloride–Methyl Yellow-Treated Paper Strips

| Sample no. | Point of sampling | Distance from the source, m | Strip indicator color | Time taken for reaction, min | Remarks |
|------------|--------------------------------------|-----------------------------|---------------------------|------------------------------|---|
| 1. | Within the hood | 1 | Yellow | Immediate | Interference of NH ₃ |
| 2. | Outside the hood | 3 | Yellow saffron | Immediate | Slight interference of NH ₃ |
| 3. | Near the entry of the shed | 8 | Saffron to red | | No interference of NH ₃ |
| 4. | Outside the processing shed | 16 | Saffron to red | 5 | No interference of NH ₃ |
| 9. | Road in front of the processing shed | 32 | Saffron; streaks of black | 10 | Interference from unknown industrial atmospheric contaminants |
| 12. | Near the factory gate | 60 | Blackish | 10 | Interference from unknown industrial atmospheric contaminants |

the strips were examined for color change. The results are given in Table III.

In similar trials the strips were used for noting the time required for aerating a ship hold and a warehouse where wheat bags were fumigated with aluminum phosphide tablets.

RESULTS AND DISCUSSION

At 0.05 and 0.1 ppm, the edges of the strip showed a thin red margin, and the body of the paper turned yellowish-red slowly (Table I). At 0.3 ppm, the change was rapid and occurred in 1 min. The color was a deeper saffron, which became red in 30 min. A concentration of 0.05 ppm in the atmospheric vault (Table I) also gave the characteristic red color in the exposed strip.

With concentration of NH_3 present along with PH_3 (Table II), the color development was suppressed, denoting the shifting of pH to the alkaline side. This was also amply demonstrated when the atmosphere in the aluminum phosphide manufacturing plant was tested (Table III). The papers turned markedly red at distances away from the tableting point as concentrations of NH_3 dwindled. At the tableting point and the immediate vicinity, high concentrations of NH_3 from the ammonium carbamate were responsible for the interference in the color development; the papers remained yellow when exposed inside the exhaust hoods where the tableting was in progress. However, it is unlikely that such high concentrations of NH_3 will be met with in actual fumigation and degassing operations.

At 0.3 ppm, which is the accepted (threshold) permissible limit for prolonged exposure (Monro, 1969), the change in color is very perceptible and can caution fumigation operators quickly. The operators can wear badges containing the indicator strips (similar to the radiation exposure badges) to signal the presence of PH_3 . It is also possible to use the strips to indicate exhaustion of gas mask canisters. The strips can be used in phosphine detector tubes (Singh *et al.*, 1967) and also to determine whether the fumigated materials (Dietrich *et al.*, 1967) are free from residual vapors (Tornow, 1942). The strips developed are more efficient than silver nitrate-treated paper strips, as they are not affected by light.

They were subsequently effectively used to detect leaks and residual gas in ship holds offshore and in a warehouse where fumigated bagged wheat was being aired. Traces of PH_3 could be detected even after 1 hr in the interspaces of bags. The change in color is almost instantaneous at high concentrations of PH_3 (0.3 ppm).

Detector tubes containing chromogenic reactants respond to the threshold concentrations only after several pumping operations of the aspirator bulb or bellows of the detector device. The HgCl_2 -methyl yellow paper strips, however, are easier to prepare, less expensive, not affected by light, and more versatile in that they can be placed at various check points and left there to indicate even traces of PH_3 . After this investigation was completed, another refinement was made for treating the filter paper strips: 1% mercuric chloride solution was prepared in the methyl yellow stain. The strips were dipped and dried before use.

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Dynamics of a Salt of (2,4-Dichlorophenoxy)acetic Acid in Fish, Water, and Hydrosol

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The uptake, distribution, and dissipation of ^{14}C -labeled dimethylamine salt of (2,4-dichlorophenoxy)acetic acid (DMA-2,4-D) from water by three species of fish was studied concurrently with the dissipation of DMA-2,4-D from water and hydrosol. Fish were exposed to 0.5, 1.0, or 2.0 mg/l. concentrations of herbicide for up to 84 days. Radioactive residues of 2,4-D were determined by radiometric procedures in eight or more

tissues and organs. Residues of 2,4-D were determined in muscle and whole-body extracts by gas chromatography. Radioactive residues were found in all fish tissues and organs analyzed, but actual 2,4-D content was negligible in muscle, indicating that most of the ^{14}C -residue was a metabolite(s) of 2,4-D. Residues of 2,4-D declined in water to less than 0.1 mg/l. after 35 days and in hydrosol to less than 0.1 mg/kg after 14 days.

The widespread occurrence and uncontrolled growth of various aquatic plants, especially in the southeastern

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United States, have caused many problems, including blocked navigation ways, obstructed water flow, poor fishing, and impaired recreational values. In addition, the water hyacinth [*Etchornia crassipes* (Mart.) Solms.] provides an ideal breeding ground for mosquitoes. Water hyacinth presently is controlled by the use of the dimethylamine salt of (2,4-dichlorophenoxy)acetic acid (DMA-2,4-D). Wojtalik *et al.* (1971) reported that DMA-2,4-D ap-