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## *Note*

# A simple spectrophotometric method for the determination of some organophosphorus insecticides

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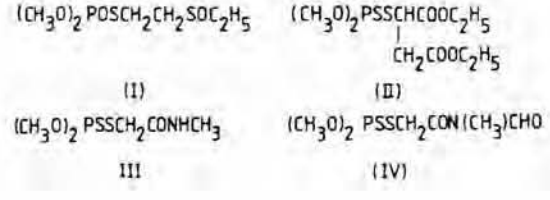
A photometric titration method for the determination of organophosphorus insecticides in their commercial formulations has been developed. In the present method potassium hydroxide hydrolyses oxydemton-methyl, malathion, dimethoate and formothion smoothly and quantitatively in aqueous *tert*-butanol and the residual alkali is instantaneously transformed into bright yellow potassium benzyl trithiocarbonate (through reaction with carbon disulphide and benzyl mercaptan) showing $\lambda_{max}$ at 430 nm.

Organoderivatives of thiophosphoric $(RO)_2POSH$ and dithiophosphoric $(RO)_2PSSH$ acids are widely used for pest control because of their low mammalian toxicity and high insecticidal activity. Oxydemton - methyl (**I**), malathion (**II**), dimethoate (**III**) and formothion (**IV**), well known insecticides, are the derivatives of above acids.

The methods[1] commonly employed for the analysis of these insecticides in their commercial formulations are tedious, time-consuming and require a strict control of experimental conditions and a special apparatus. The increasing use of above insecticides in agriculture necessitates the development of convenient, reliable, rugged and cost-effective methods for their analysis particularly for ensuring the quality of technical and commercial products of these insecticides. In the present work, advantage has been taken of the following observations to evolve a sensitive photometric titration method for the determination of above insecticides.



(I)



(II)



III



(IV)

i) In aqueous *tert*-butanol and in the presence of potassium hydroxide, these insecticides hydrolyse smoothly and quantitatively to form potassium salts of mono/dithiophosphoric acids.

ii) In the same medium, the residual alkali can be measured by adding carbon disulphide and titrating the resulting solution photometrically at 430 nm against standard benzyl mercaptan. The titration is based on the smooth and quantitative transformation of potassium hydroxide into bright yellow potassium benzyl trithiocarbonate showing $\lambda_{max}$ at 430 nm. The absorbance at this wavelength in these titrations goes on increasing till it attains a maximum value corresponding to the quantitative transformation of potassium hydroxide into the above trithiocarbonate. Thereafter, it attains almost constant values indicating no more formation of trithiocarbonate. The end point is found by extrapolation of the linear segments.

## Experimental

Carbon disulphide A R (Merck) was used as received. *tert*-Butanol A R (Extrapure) was used as such for preparing its 80% solution (by mixing solvent and water in the ratio 4:1). Benzyl mercaptan was distilled before use. Its standard solution was prepared by dissolving a little more than the calculated amount of the compound in 80% tertiary butanol and standardising the solution by the reported method[2]. The standard solution of potassium hydroxide was prepared in 80% *tert*-butanol. The analytical standard of each organophosphorus insecticide (Poly Science, USA) was used. The purity of each standard was checked by the reported methods[1]. Beckman DU-6 and Bausch and Lomb (Spectronic -20 D) spectrophotometers were used for absorbance measurements.

### *Procedures*

#### *Photometric titrations*

*Determination of potassium hydroxide*—Aliquots of solutions in 80% *tert*-butanol of KOH were taken and diluted to 5 ml with the same solvent. Each solution was mixed with a drop (~50µl) of carbon disulphide and the resulting solution titrated with standard benzyl mercaptan photometrically at 430 nm

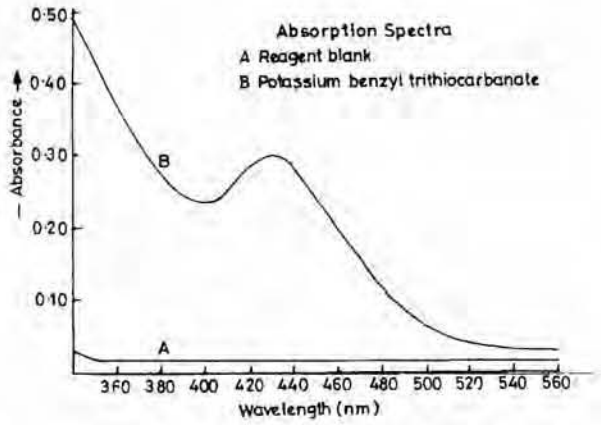



Fig. 1—Absorption spectrum of potassium benzyl trithiocarbonate

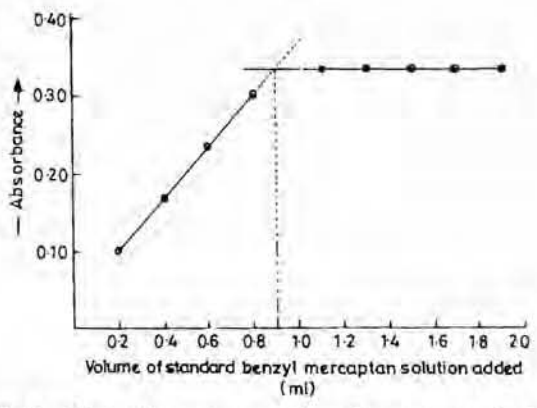



Fig. 2—Absorption spectrum of benzyl merceptan solution

at room temperature (~23°) against a reagent blank (the spectrum of the bright yellow potassium benzyl trithiocarbonate solution is illustrated in Fig.1). Dilution corrections were applied and titration curves were plotted in the usual way. The end point was found by extrapolation of linear segments (Fig. 2).

*Determination of insecticides*—Aliquots of solutions of each insecticide in 80% *tert*-butanol were taken and mixed with standard KOH (3 ml, 0.01*N* in 80 % *tert*-butanol) and kept for 5 min to ensure completion of the reaction. Each solution was mixed with a drop (~ 50µl) of carbon disulphide and the volume made to 5 ml with 80% *tert*-butanol. The photometric titrations were performed with standard benzyl mercaptan in the same manner as described above.

*Formulation analysis*—One formulation each of oxydemton-methyl, malathion, dimethoate and formothion containing 25%, 50%, 30% and 25% active ingredients respectively, all Emulsifiable concentrates (ECs) were used. A single large sample of each formulation was weighed and dissolved in known volume of 80% *tert*-butanol (all formulations are freely soluble in 80% *tert*-butanol). Suitable aliquots of each formulation were taken and processed for analysis by phtotometric titrations in the same manner as described above. The results are given in Table 1.

Table 1—Assay results of some commercial formulations of oxydemton-methyl, malathion, dimethoate and formothion

| Insecticide Formulation | | Based on active Ingredient (%) | Active ingredient found*, (%) Present method | Comparison method[1] |
|---|---|---|---|---|
| Oxydemton-methyl | (I) | 25 | 24.9 (0.3) | 24.5 (0.4) |
| | (II) | 25 | 24.6 (0.2) | 24.4 (0.5) |
| Malathion | (I) | 50 | 49.5 (0.5) | 49.2 (0.6) |
| Formothion | (I) | 25 | 24.7 (0.4) | 24.6 (0.5) |
| Dimethoate | (I) | 30 | 29.8 (0.3) | 24.2 (0.6) |
| | (II) | 30 | 29.7 (0.4) | 24.3 (0.4) |

*Values are mean of five determinations with standard deviation (±)

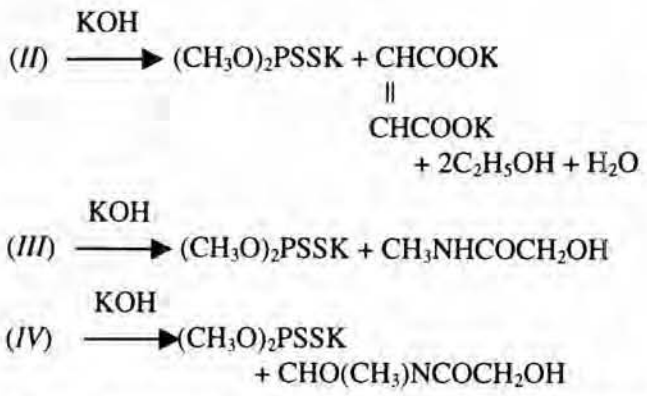
## Results and discussion

That mercaptans react with carbon disulphides and potassium hydroxide in 1:1:1 molar ratio to form bright yellow potassium alkyl/aryl trithiocarbonates, has been found to be reaction of considerable analytical utility in our laboratory.

$$RSH + CS_2 + KOH \longrightarrow RSCSSK + H_2O$$

Based on this reaction, we have already described new methods for the determination of mercaptans[3] and carbon disulphide[4,5]. Using benzyl mercaptan as the titrant, this reaction has been found extremely useful for the photometric titrimetric determination of potassium hydroxide. The alkali in the range 0.5 to 2.25 mg could be determined with a maximum relative standard deviation (RSD) of 0.7%. The method has subsequently been applied to four organophosphorus insecticides viz. **I, II, III** and **IV** which hydrolyses in the presence of potassium hydroxide to form potassium salt of mono/dithiophosphoric acid.

$$(I) \xrightarrow{KOH} (CH_3O)_2POSK + C_2H_5SOCH_2CH_2OH$$



The analysis is concluded by measuring the residual alkali by photometric titration method. The maximum RSDs calculated from the pooled data of all the titrations performed with 1 and 2 mg of **I, II, III** and **IV** were 0.7, 0.8, 0.8 and 0.7% respectively. When applied to the analysis of commercial formulations of above insecticides, the RSDs were in the range 0.2-0.5% (Table 1).

The smooth and quantitative transformation of potassium hydroxide into potassium benzyl trithiocarbonate and instantaneous development of yellow colour and its stability are special attributes of the present method.

**Acknowledgement**

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