Indirect Determination of Malathion Using Atomic Absorption

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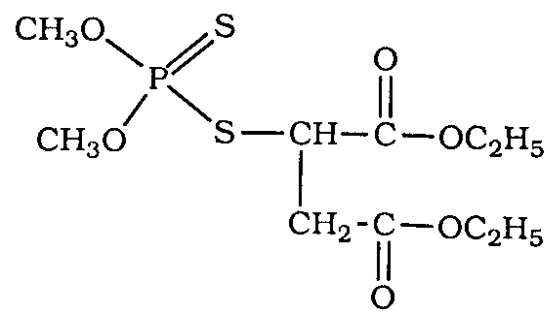
Summary: The organophosphate pesticide malathion is hydrolysed in alkaline medium to dimethyl dithiophosphate (DMDSP) sodium fumarate and ethanol. The DMDSP reacts with bismuth (III) to form a complex which is extracted in methyl isobutyl ketone (MIBK). The bismuth is determined in organic phase using air acetylene flame atomic absorption. The concentration of bismuth is proportional to malathion in solution. The linear calibration range and detection limits for DMDSP were evaluated. Finally a commercial sample of malathion was analysed for the contents of malathion.

Introudction

The organophosphorous pesticide malathion (O,O-Dimethyl-S-[1,2-diethoxycarbonyl) ethyl] phosphodithioate] is conveniently determine by gas chromatography [1-3] or by spectrophotometry [4-7]. The spectrophotometric methods are based on decomposition of malathion by alkali (Fig. 1) to dimethyl dithiophosphate (DMDSP), sodium fumarate and ethanol. The DMDSP is then converted into copper(II), bismuth(III) or palladium(II) complex. These DMDSP metal chelates are soluble in organic solvents such as carbon tetrachloride or *n*-hexane. The colour intensity of metal chelate in organic phase is proportional to the concentration of (DMDSP) and it is measured spectrophotometrically. The color of copper complex is stable for shorter time, but its bismuth complex is stable for longer time (> 24 hour) (5). Recently a method has been proposed for the determination of malathion by atomic absorption spectrophotometry by the formation and extraction of palladium chloride malathion complex [8]. In the present work DMDSP obtained by alkaline hydrolysis is complexed to bismuth (III). The bismuth complex is extracted in methyl isobutyl ketone (MIBK) and concentration of bismuth is determined using atomic absorption. The concentration of bismuth is proportional to malathion in the sample. Moreover the use of malathion standard is not neeessary, because the hydrolysis of malathion to DMDSP is reported to the quantitative [5].



Malation

Fig.1 Structural Diagram of Malathion

Results and Discussion

The extraction of bismuth DMDSP complex in MIBK using different amounts of 3.04×10^{-3}M w/v DMDSP was checked and compared spectrophotometrically with that of carbon tetrachloride. Both the solvents indicated a similar absorbance with λ_{max} at 325 nm (n = 3). Thus MIBK was selected for the extraction of bismuth complex, for quantitative determination using atomic absorption. The linear calibration was obtained in the range of 6.0×10^{-5}- 4.56×10^{-4}M with average relative standard deviation within 1.9%. The detection limit for DMDSP measured as three times the standard deviation of the blank (n = 4) was $2.x10^{-5}$M (w/v). The analysis of malathion samples from the calibration curve prepared from DMDSP was 57.93% w/w (RSD 1.1%). The expected results are 57% w/w.

Experimental

Freshly prepared dimethyl dithiophosphoric acid by a reported method [9] was used for the

preparation of solution 3.04×10^{-3}M (w/v) in ethanol. A bismuth solution containing 0.45 mg/ml in 0.1M nitric acid was prepared from bismuth oxide (Bi_2O_3) (Merck).

Hitachi 220 spectrophotometer and an atomic absorption spectrometer Spectra AA-20 (Varian) with air-acetylene/flame atomizer were used.

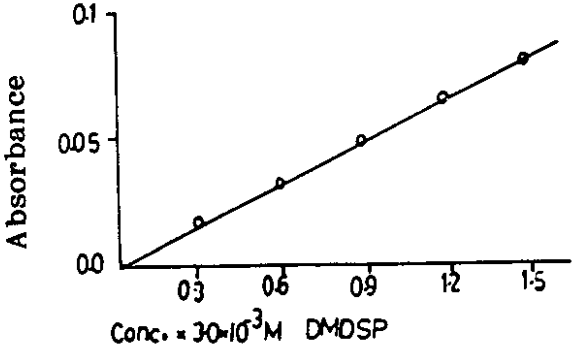


Fig.2 Calibration curve of DMDSP using atomic absorption with bismuthcathode lamp at 223.1 nm. Solvent MIBK.

Calibration curve for the extraction of DMDSP

To a separating funnel containing water (9 ml) was added DMDSP (0.2-1.5 ml of 3.04×10^{-3}M w/v) followed by MIBK (10 ml) and bismuth solution (1 ml). The funnel was stoppered and shaken for about 2 min. The organic layer was allowed to separate and was collected in a flask. The extract was nebulized to air acetylene flame atomizer, after adjusting the instrumental zero with MIBK. The absorption of bismuth was measured at 223.1 nm.

Analysis of malathion

Malathion sample (A/S Cheminova, Lemving, Denmark: Distributors Jaffer Bros. (Pvt Ltd.) (0.1 ml) diluted to 100 ml of ethanol and 2 ml of solution was further diluted to 10 ml with ethanol. Finally (1-3 ml) was transferred to a separating funnel, followed by sodium hydroxide (1 ml, 6N) and the mixture was swirled for 1 min. Distilled water (10 ml) was then added and the solution was made acidic with hydrochloric acid (2-4 ml, 7N). The acidic solution was added MIBK (10 ml) and bisnmuth (1 ml). The remaining procedure was followed as above.

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