Development of A Simple Method for
The Detection of Phosphorus Insecticides

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In this study, a detection method was developed for phosphorus insecticides. At first phosphomolybdate was formed by using standard phosphate solution and ammonium molybdate and then it was reduced to obtain molybdenum blue. According to the earlier experiments, *m*-phenylenediamine, which hadn't been used classically as a reductant, was tested and at the first part of this study a phosphate detection method was developed by using this reductant. The optimum pH range was found for the reduction of phosphomolybdate as 1-1.5 and as 5-6 for the formation of molybdenum blue, respectively. The maximum absorbance was measured between 705 nm and 710 nm and the molar absorptivity coefficient was calculated in terms of phosphorus as 2.95×10^{-3} L/mol cm. At the second part of this study, developed method was used for the detection of two pesticides, dimethoate and methyl parathion. Before reacting with ammonium molybdate, pesticides were degraded in alkaline conditions with hydrogen peroxide to form phosphate.

Key Words: Phosphorus pesticides, Molybdenum blue, *m*-Phenylenediamine, Phosphate.

INTRODUCTION

Organophosphorus pesticides (OPs) are widely used in agriculture to control many kinds of pests. Although they are less persistent in the environment when compared with organochlorine pesticides, they affect nervous system inhibiting the activity of acetylcholinesterase.

Many of organophosphorus pesticides are considered controlled substances and strict application instructions for the workers. Others may be controlled indirectly by the governmental bodies in developed countries, who set maximum allowable concentration standards for organophosphorus pesticides in drinking water, for instance[1].

Therefore it is important to detect and determine the residues of phosphorus insecticides which are the most frequently used type of organophosphorus pesticides[1,2]. In this connection a great variety of methods such as spectroscopy, gas chromatography, gas-liquid chromatography, supercritical fluid chromatography, high pressure liquid chromatography, gas chromatography-mass spectroscopy and liquid chromatography-

mass spectroscopy, have been described. Some of which are expensive and analysis cannot be carried out easily in every conventional laboratory. The formation of heteropoly complexes with molybdenum is an example of spectroscopical methods. The method can be applied in two ways; one without reduction and the other with reduction of heteropoly complex by a reductant such as ascorbic acid[3], tin(II) chloride[4], ascorbic acid and tin(II) chloride[5], hydroquinone[6], 1-amino-2-naphthol-4 sulfonic acid[7], hydrazine sulfate[8,9]. Metals such as Al, Pb, Mo, Cu, Zn, Cd and Hg and substances such as B_2H_6, $NaBH_4$, H_2S, SO_2, SO_3^{2-}, $S_2O_3^{2-}$, $MoCl_5$, Mohr salt, ethanol, thiourea are the other examples of reductants used so far[10].

EXPERIMENTAL

Methyl parathion (85 %) and dimethoate (98 %) were supplied by Hektas T.A.S (Turkey). All the other reagents used were analytical grade and supplied by Merck. The solutions were prepared by distilled water as follows:

Ammonium molybdate, 5 % solution: The solution was prepared by dissolving 50 g of recrystallized (in the presence of alcohol) ammonium molybdate in water on heating. After the solution was cooled and diluted with water up to 1 L.

Standard phosphate solution: A sample of potassium dihydrogen phosphate weighing 0.4393 g was dissolved in water and diluted with water up to 500 mL. The solution contained 0.2 mg of phosphorus in 1 mL.

m-Phenylene diamine, 0.07 M solution: 0.736 g *m*-Phenylene diamine was dissolved in 8 mL of 60 % perchloric acid and water was added up to 100 mL.

Perchloric acid, 1.25 M solution: In order to prepare the solution of 1.25 M perchloric acid, 13.63 mL of d = 1.53 g/mL, 60 % perchloric acid was pippetted and water was added to make 100 mL.

Buffer solutions: Citrate and acetate buffers[9] were prepared by the given methods for pH ranged between 1.1 and 6.0 and adjusted with 0.1 N NaOH.

Methyl parathion solution: A sample of methyl parathion weighing 0.3822 mg was dissolved with ethanol and diluted with ethanol up to 50 mL.

Dimethoate solution: A sample of dimethoate weighing 0.1304 mg was dissolved with ethanol and diluted with ethanol up to 50 mL.

Analyses were performed by ATI Unicam UV-VIS spectrophotometer.

In the experiments, at first phosphomolybdate was formed by using potassium dihydrogen phosphate and ammonium molybdate solutions and then phospho-molybdate was reduced to obtain molybdenum blue. In the earlier experiments, *m*-phenylenediamine, which hadn't been used classically as a reductant, was tested and the first part of this study for detection method was developed by using this reductant.

At the second part of this study, developed method was used for the detection of two pesticides, dimethoate and methyl parathion. 5 mL 10 % NaOH and 2 mL of 35 % H_2O_2 solutions were added to 10 mL of pesticides solutions and heated up to dryness. After cooling, $HClO_4$ was added and boiled, in order to eliminate excess

of H_2O_2. Cooled solutions were diluted up to 50 mL, after the pHs were adjusted to 4.0-5.0. 1.5 mL of 1.25 M $HClO_4$ and 7.5 mL of 5% of ammonium molybdate were added to 7.5 mL of each decomposed solutions of pesticides and the volume of solutions were diluted to 50 mL. After 1 mL of 0.07 M *m*-phenylene diamine was added to 7.5 mL of final solutions, pHs were adjusted about 5.0 with 1 M NaOH solution and then the volume of solutions were diluted with buffer solutions (pH 5). Absorbances of solutions were measured at 708 nm.

RESULTS AND DISCUSSION

At first, the optimum conditions of forming molybdenum blue with standard phosphate solutions were investigated when *m*-phenylene diamine was used as a reductant.

Completion of reduction reaction was found that pH was maintained between 1.1 and 1.5. Experiments showed that pH would be between 5 and 6 after reduction in order to form blue colour. Otherwise, the formation of blue colour wouldn't occur (Table-1). Occurrence of blue colour and measurable absorbance was obtained from pH 4. With the increase of pH, blue colour became darker and with respect to this absorbance of solutions increased. At pHs 5.0, 5.5 and 6.0 absorbances were measured approximately the same. Orange color was obtained when the experiments carried out at higher pHs such as 8.0. After pH was decreased between 5.0 and 6.0, blue colour occurred again.

TABLE-1
CHANGE OF ABSORBANCE WITH pH

pH	Absorbance	Colour
1.1	0	Colourless
1.5	0	Colourless
2.0	0	Colourless
2.,5	0	Colourless
3.0	0	Colourless
3.4	0	Colourless
4.0	0.049	Light blue
4.5	0.093	Blue-purple
5.0	0.111	Blue-purple
5.5	0.111	Blue-purple
6.0	0.109	Blue-purple

Amount of *m*-phenylene diamine per atom-g phosphorus was investigated. It can be seen from Fig. 1 that 4 mmol *m*-phenylene diamine was necessary per atom-g phosphorus, but using more than 4 mmol *m*-phenylene diamine didn't interact the reaction.

It can be seen from Table-2 that absorbance did not change within 1 h, so that it wasn't necessary to measure the absorbance in a limited time.
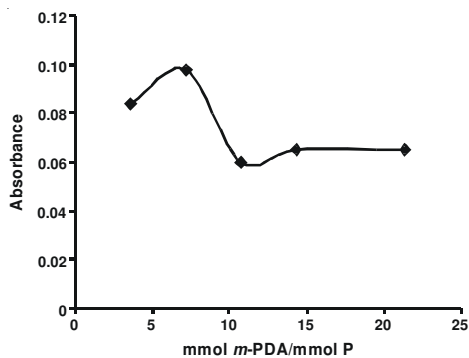
Fig. 1. Change of absorbance with mmol *m*-PDA/ mmol P in solutions containing 3.6 ppm P
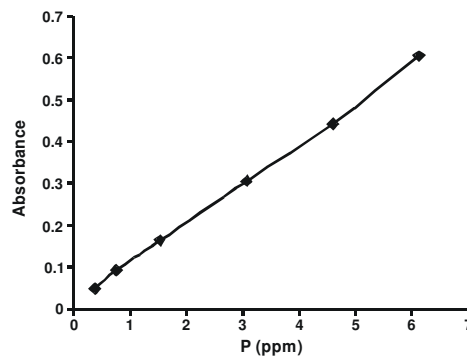
Fig. 2. Change of absorbance with respect to P

TABLE-2
CHANGE OF ABSORBANCE WITH TIME

Time (min)	Absorbance	Time (min)	Absorbance
0	0.111	40	0.113
10	0,112	50	0.113
20	0.113	60	0.113
30	0.113	–	–

Amount of molybdenum per atom-g phosphorus was also investigated. It's known that stoichiometric molar ratio of Mo/P is 12 in ammonium phosphomolybdate molecule, $(NH_4)_3[PMo_{12}O_{40}]$. It can be seen from Table-3 that formed phosphomolybdate would be less than phosphorus, so that this would prevent the formation of blue colour below this ratio. Blue colour occurred, when Mo/P mmol ratio was higher than stoichiometric ratio. When this ratio was 36 or more, absorbance didn't change approximately.

TABLE-3
CHANGE OF ABSORBANCE WITH mmol Mo/mmol P

mmol Mo/mmol P	Absorbance	mmol Mo/mmol P	Absorbance
04.61	0.000	36.18	0.175
08.94	0.000	54.27	0.189
18.12	0.113	72.35	0.180

It can be seen from Fig. 2 that the change in absorbance with respect to the phosphorus, given range, was linear. The equation of the graphic was found as y = 0.09534x + 0.01492 and r was calculated as 0.9996. As it can be seen from the results that the modified method can be used for quantitative determination of phosphate. However, the aim of this study wasn't determination of phosphate. That is why many experiments weren't held to calculate standard deviation and give limit of detection for phosphate.

After dimethoate and methyl parathion had been decomposed in alkaline conditions with hydrogen peroxide, developed detection method was applied using *m*-phenylene diamine as a reductant. UV-VIS spectrums and the colours of the solutions can be seen from Figs. 3 and 4. By the use of methyl parathion, the colour of the solution was green, since the yellow colour of *p*-nitrophenol, which is the decomposition product of methyl parathion. By using this method detection limits of methyl parathion and dimethoate were 7.05×10^{-6} M and 5.02×10^{-6} M, respectively.
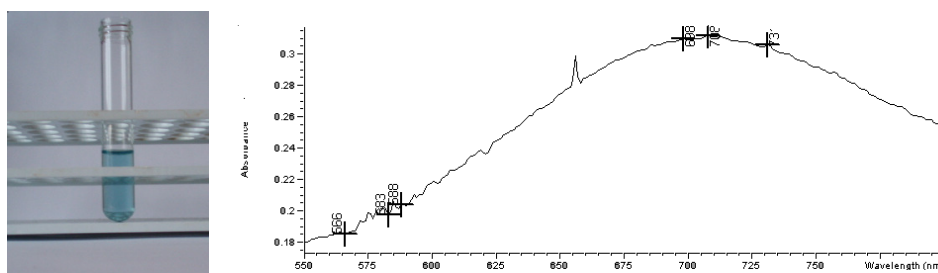

Fig. 3.   Photo and UV-Vis spectrum of dimethoate which was decomposed in alkaline condition with hydrogen peroxide
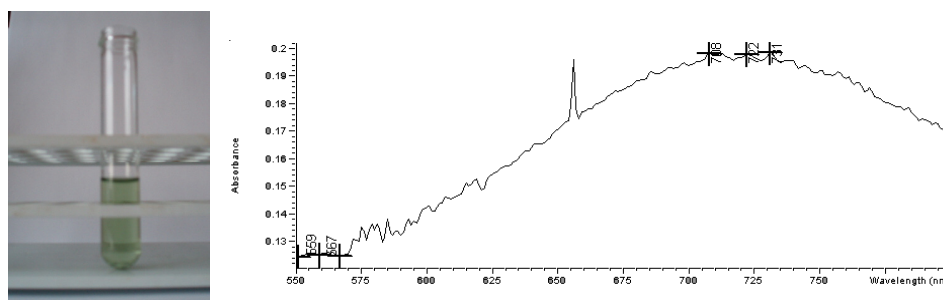

Fig. 4.   Photo and UV-Vis spectrum of methyl parathion which was decomposed in alkaline condition with hydrogen peroxide

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