Investigation of Spectrophotometric Method for Determination of Organophosphorus Pesticides

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Summary: A new decomposition method for the release of phosphorus was investigated and the molybdenum blue method for phosphorus determination in organics was modified. The modified method was applied for the determination of organophosphorus pesticide (dimecron) in commercial samples of dimecron. The commercial samples were found to contain 0.2 g/ml of pesticide instead of 1.0g/ml as shown by the label. Limit of detection of the method was investigated and was found to be 0.282 ppm for dimecron. The method was applied successfully to other organophosphorus pesticides.

Introduction

Environmental pollution due to the indiscriminate use of various types of pesticides is becoming a common problem. These compounds are known to display various kinds and types of acute toxicity [1] and as a result the availability of safe drinking water and food products have become a matter of special concern [2]. Owing to the continuing need for the employment of pesticides, there is a need to monitor the presence of pesticides in samples of environmental importance.

A variety of analytical techniques may be used to determine pesticides in different types of samples. Among these TLC [3,4], HPLC [5,6] and GC [7,8] together with various clean up techniques are preferred methods for organic pesticides.

A number of spectrophotometric methods have also been utilized for the determination of pesticides [9-14]. Most of these methods are modifications of the spectrometric method introduced by Norris *et al* [9].

As most of the methods mentioned above need expensive instrumentation and expensive chemicals apart from exhaustive and lengthy procedures, there is a need for simple, sensitive and cheap method, which could be applied for the determination of pesticides in ordinary laboratory. In this paper, we are presenting a new indirect method for determination of organophosphorus pesticides based on modified molybdenum blue method.

Results and Discussion

i) Investigation of decomposition parameters

A number of reagents and acids individually and acid mixtures were tried for the decomposition of organophosphorus pesticides. Among the oxidizing reagents hydrogen peroxide was tried and was found to be ineffective. Sulphuric acid, nitric acid, hydrochloric acid individually and their mixture were also investigated. In the case of nitric acid it was observed that the reducing agent instead of reducing phosphomolybdic acid itself got oxidized and no colour specific for molybdenum blue method was observed. Even after neutralizing nitric acid, the colour could not be developed because of the presence of nitrate ion in the solution. Therefore, the use of nitric acid was abandoned.

The mixture of hydrochloric acid and sulphuric acid was found to be the most suitable decomposition agent. Therefore, further studies were conducted to find out the optimum ratio of the mixture for decomposition and subsequent release of phosphorus. For this purpose different volumes of hydrochloric acid and sulphuric acid were used keeping all the experimental conditions the same. It was observed that 0.4 ml of hydrochloric and 0.1 ml of sulphuric acid were found to be the optimum volumes for decomposition of organophosphorus pesticides. In general it could be concluded that hydrochloric acid and sulphuric acid mixture in 4:1 ratio is the best mixture for the decomposition of organophosphorus pesticides.

ii) Investigation of decomposition time

For optimization of decomposition time the investigations were carried out by varying the heating time as 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 hours. The results are shown diagrammatically in Figure 1. From Figure 1 two hours were found to be the optimum decomposition time for organophosphorus pesticides.

iii) Investigation of reducing agent

For the selection of suitable reducing agent different reducing agents like ferrous sulphate, ascorbic acid, ferrous ammonium sulphate and hydrazinium sulphate were investigated. Ferrous sulphate was found to be the most effective and strong reducing agent. For optimization of ferrous sulphate quantity different volumes of 10% ferrous

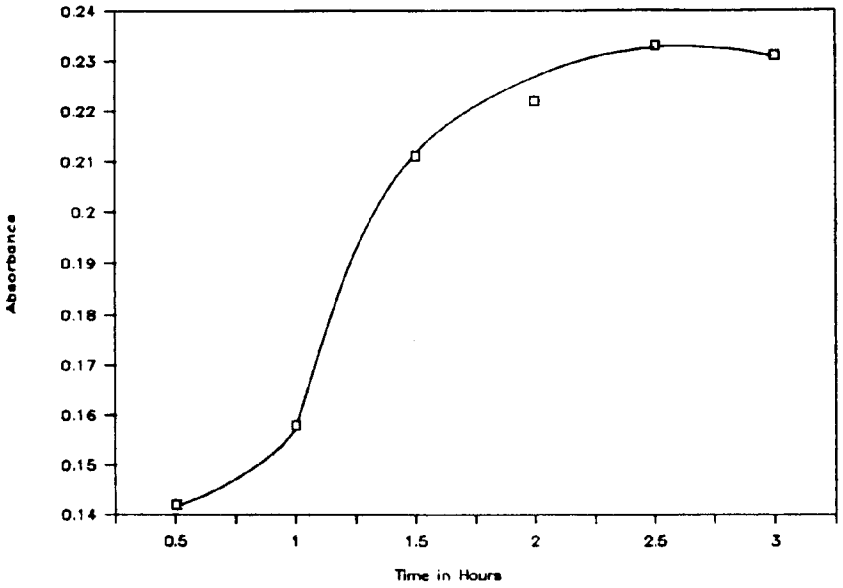

Fig. 1: Optimization of heating time.

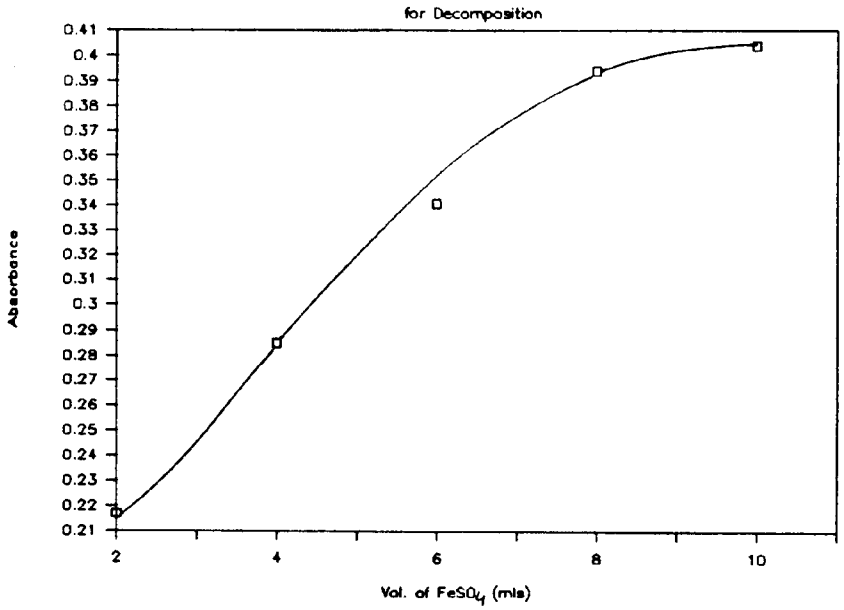

Fig. 2: Optimization of $FeSO_4$ quantity.

sulphate were tried. The observations are shown diagrammatically in Figure 2. From the Figure 8 ml of 10% ferrous sulphate was found to be the optimum quantity for determination of phosphorus by this method.

iv) Investigation of sodium molybdate quantity

For optimization of sodium molybdate quantity its different volumes were used in the range of 0.5 to 12 ml. The results are shown diagrammatically in Figure 3. The results show that absorbance increases as the molybdate volume increases but beyond 10 ml the increase was not proportional to molybdate volume. Therefore, 10 ml of sodium molybdate was taken as optimum volume.

Effect of concentration

The effect of concentration of organophosphorus pesticides on the absorbance of molybdenum blue method was studied in the range of 0.3 to 80 ppm. The results are shown diagrammatically in Figure 4. It was observed that the relationship between absorbance and concentration was linear upto 16 ppm. When the concentration was increased beyond 16 ppm a nonlinear behaviour was observed as can be seen from Figure 4. The method was applied for determination of pesticide contents in commercial sample of dimecron. The commercial sample was found to contain 0.2 g/ml of the pesticide instead of 1.0 g/ml as shown by the label. Limit of detection of the method was found to be 0.3 ppm. This limit indicates the usefulness of optimized method for determination of organophosphorus pesticides by molybdenum blue method.

Determination of insecticide contents in commercially available insecticides by molybdenum blue method

The method based on determination of phosphorus was applied for the determination of insecticide contents in the commercially available insecticides. The results are given in Table 1. From the actual amount of insecticide calculated by indirect method, it was found that the concentration of the active ingredient of insecticide was lower than the label value given on the bottle.

Experimental

Apparatus

Spectronic 20 D Milton Roy and Jasco. UVIDEC-1, digital double beam spectrophotometer were used during this investigation.

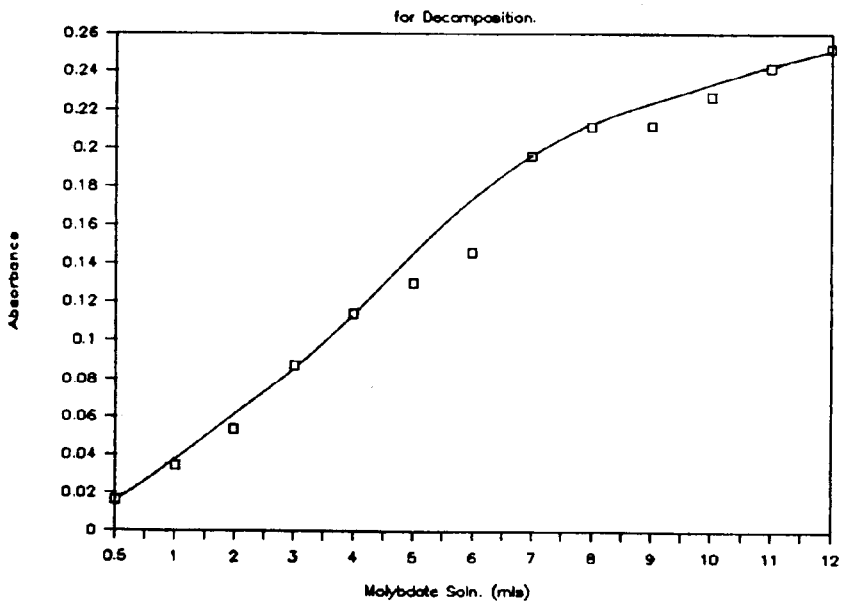

Fig. 3: Optimization of molybdate solution.

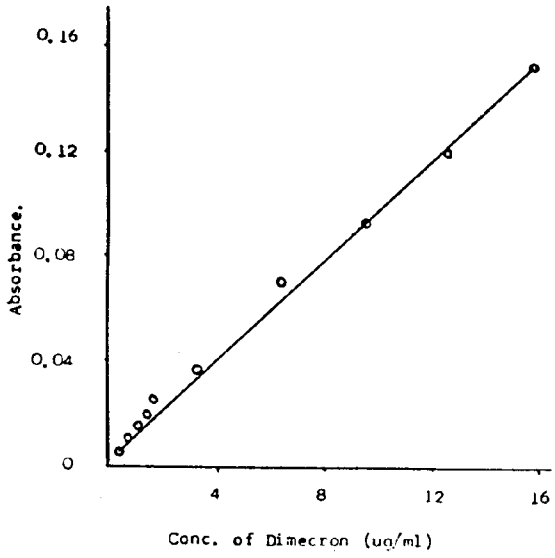

Fig.4: Effect of pesticide concentration on absorption behaviour, using molbdenum blue method.

Table 1: Determination of insecticide contents in commercially available insecticides by molybdenum blue method

Pesticides	Active ingredient On label g/ml	Found g/ml
Anthio	0.25	1.07×10^{-4}
Sumithion	0.10	0.06
Dichlorovos	1.00	0.03
Dimecron	1.00	0.20

Reagents

Samples of dimecron, nogos, sumithion and anthio were obtained commercially. Sodium molybdate, ferrous sulphate, sodium dihydrogen phosphate and concentrated sulphuric acid were purchased commercially and were used without further purification.

Solution

Preparation of sodium molybdate solution

0.05 M sodium molybdate solution was prepared by dissolving 12.5 g of sodium molybdate in minimum amount of 5M sulphuric acid and diluting upto 500 ml with 5M sulphuric acid.

ii) Stock solution of phosphorus

50 ppm stock solution of phosphorus was prepared by dissolving 0.25 g of sodium dihydrogen phosphate in minimum amount of distilled water. The solution was diluted upto one litre.

Procedure

For spectrophotometric determination of dimecron using molybdenum blue method 0.1, 0.2, 0.3, 0.4 and 0.5 ml of dimecron were taken. To each of them 0.1 ml of concentrated sulphuric acid and 0.4 ml of concentrated hydrochloric acid were added and heated in a water bath for two hours. Then 10 ml of sodium molybdate were added to them and again heated for 12 to 13 minutes followed by the addition of 8 ml of freshly prepared 10% ferrous sulphate solution. The resulting solutions were diluted upto the mark. These solutions were allowed to equilibrate for half an hour and their absorbance was noted at 825 nm (λ_{max}), using synthetic blank carrying all the reagents except pesticide as a reference solvent.

Conclusion

The optimized molybdenum blue method is fast, simple and cheap. The method could be applied in routine laboratory for determination of pesticides residue in samples of environmental importance and also for checking the purity of commercially available pesticides. The sensitivity of the method is of the same level as of sophisticated chromatographic and other available methods.

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