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Short communication

Indirect liquid chromatographic determination of malathion in formulations, based on the formation of palladium(II)–dimethyldithiosphate complex

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Abstract

High-performance liquid chromatographic methods for the determination of an organophosphorous pesticide have been developed, based on alkaline hydrolysis of malathion to dimethyldithiophosphate (DDTP) followed by complexation with palladium(II). The complex is extracted in chloroform and eluted from LiChrosorb Si 100 (5 μm), Hypersil ODS, (3 μm) or YMC Pack ODS (5 μm) columns with chloroform or methanol–acetonitrile–water (80:10:20, v/v/v). Detection was by UV at 295 nm. Linear calibration is obtained with 24–120 μg/ml and detection limits of 2.4 μg/ml DDTP. The methods are applied for the determination of malathion in commercial formulations. The separation of copper(II) and palladium(II) complexes of DDTP and selectivity of the reaction of DDTP towards copper(II) and palladium(II) are examined by reversed-phase HPLC.

Keywords: Complexation; Derivatization, LC; Malathion; Pesticides

1. Introduction

The development of selective and sensitive methods for the determination of pesticides is desirable, because of their increasing use in agriculture and the quality control of different formulations. The organophosphorous pesticides comprise a major group. Malathion, a member of this group, is commonly used for the control of sucking and chewing insects.

Malathion is hydrolysed quantitatively in alkaline media to dimethyldithiophosphate (DDTP), alkali fumarate and ethanol. The reaction is reported to be selective and some thiophosphate pesticides interfere negatively, which may be due to interferences in the extraction of the complex [1]. An analytical method suitable for the determination of DDTP could be used for the estimation of malathion. A number of procedures have been reported for the determination of DDTP, which includes chromatographic [2], spectrophotometric [2–10] and atomic absorption spectrometric techniques [1,11–15]. Visweswriah and Jayaram [3] have determined malathion spectrophotometrically by acid hydrolysis and complexation of the hydrolysed product with palladium. Hernandez Mendez et al. [15] have determined malathion by atomic absorption spectrometry by formation and extraction of the palladium chloride–malathion complex at pH 3. The organic extract is mineralized and the palladium is determined in the aqueous phase. Clark and Qazi [5] and Jimenez de Blas et al. [13]

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have observed hydrolysis of malathion to DDTP only in alkaline media. In the present work DDTP after complexation with palladium(II) and extraction in the organic phase has therefore been examined by spectrophotometry and HPLC with UV detection.

2. Experimental

Freshly prepared DDTP [16] was used to prepare 120 μg/ml DDTP in ethanol. Palladium(II) and copper(II) solutions (1.0 mg/ml) were prepared from palladium(II) chloride and copper(II) chloride.

Spectrophotometry was carried out on a Hitachi 220 spectrophotometer. A Hitachi 655A liquid chromatograph connected with a variable-wavelength UV monitor, a Rheodyne 7125 injector and a Hitachi D2500 Chromato-integrator was used.

Hypersil ODS, 3 μm (150×4.6 mm I.D.) (Shandon, USA), YMC Pack ODS-AQ, S-5 μm (150×4.6 mm I.D.) (YMC, Japan) and LiChrosorb Si 100, 5 μm (250×4 mm I.D.) columns were used.

2.1. Extraction procedure

In a well-stoppered test tube was transferred 0.2–1.0 ml solution containing 24–120 μg DDTP and the volume was adjusted to 2 ml with ethanol. Palladium(II) solution (1 ml) containing 1 mg/ml, 7 *M* hydrochloric acid (1 ml) and chloroform (2 ml) were added. The contents were mixed well and layers were allowed to separate. For normal-phase LC the extract (2 μl) was injected on LiChrosorb Si 100 and the complex was eluted with chloroform. Detection was by UV at 295 nm. For reversed-phase LC exactly 1 ml of chloroform was transferred to a sample vial and solvent was evaporated. The residue was dissolved in methanol (1 ml). Solution (2 μl) was injected on Hypersil ODS or YMC Pack ODS-AQ and the complex was eluted with methanol–acetonitrile–water (70:10:20, v/v/v) using a flow-rate of 0.6 ml/min. Detection was by UV at 295 nm.

2.2. Determination of malathion

Malathion sample as used for agricultural formulations (1) (Cheminova Lemuing, Denmark; 0.1 ml) was diluted to 50 ml in methanol and (2) emulsifiable insecticide dust (Malacheme, Iran; 0.1 g) was dissolved in 100 ml ethanol. The solutions 0.2 ml and 0.4 ml from 1 and 0.1 ml and 0.2 ml from 2 were transferred to well-stoppered test tubes and the volume was adjusted to 2 ml with methanol. A 2-ml volume of 6 *M* sodium hydroxide was added and the contents were mixed well for 5–7 min. To the solution, 7 *M* hydrochloric acid (4 ml), and palladium(II) solution (1 ml) containing 1 mg/ml were added. The remaining procedure was the same in Section 2.1. The amount of malathion was evaluated from calibration curves prepared from known amounts of DDTP.

2.3. Study of selectivity of reaction of DDTP toward copper(II) and palladium(II)

To a well-stoppered test tube was added 72 μg DDTP and a mixture containing copper(II) and palladium(II) 0.5 mg and 1 mg; 1 mg and 1 mg or 1 mg and 0.5 mg, respectively. The extraction procedure was as in Section 2.1. The solution (2 μl) was injected on column Hypersil ODS and eluted as described in section 2.1. The amounts of DDTP–copper(II) and DDTP–palladium(II) complexes formed were evaluated from calibration curves prepared using copper(II) or palladium(II) individually.

2.4. Spectrophotometric studies

Solution (0.2–1.0 ml) containing 23–116 μg DDTP was transferred to a separating funnel and volume was adjusted to 2 ml. This was followed by the procedure in Section 2.1, but 5 ml chloroform was added. The organic layer was collected in a 10-ml volumetric flask and extraction was repeated with chloroform (3 ml). The final volume was adjusted to the mark. The absorption spectrum was recorded against chloroform.

Emulsifiable insecticide dust (Malacheme) was also analysed using spectrophotometry. The procedure in Section 2.2 was used, but extraction with chloroform was repeated and final volume was adjusted to 10 ml with chloroform.

3. Results and discussion

In the presence of excess of palladium, DDTP reacts to develop a golden colour in acidic media.

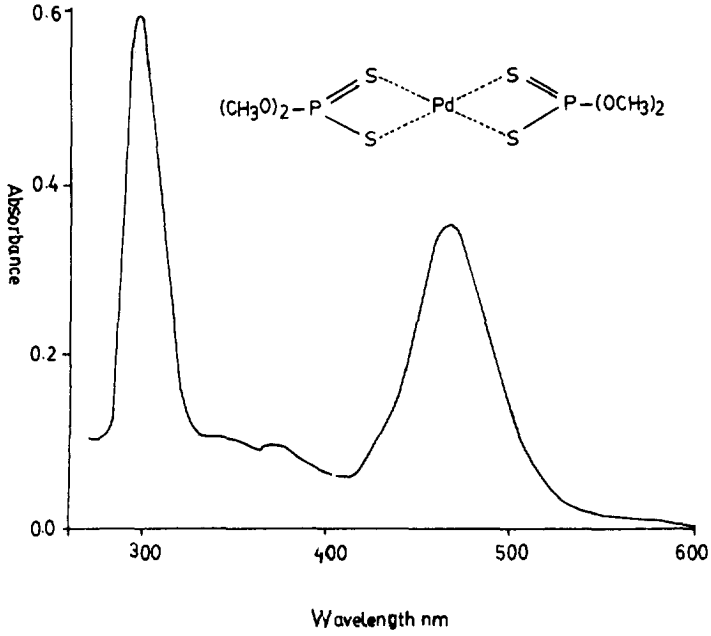

Fig. 1. Absorption spectrum of DDTP–palladium(II) complex at a final concentration of 6.9 μg/ml DDTP.

The complex indicates maximum absorbance at 460 nm and 298 nm (Fig. 1). The complex did not show any change in absorbance within 24 h. The complex obeys Beer's law at a final concentration up to 2.3–11.6 μg/ml DDTP.

DDTP as a palladium(II) complex easily eluted from HPLC columns. It was eluted from a LiChrosorb Si 100 (250×4 mm) column with chloroform using a flow-rate of 0.9 ml/min with capacity factor $k'=0.13$. But from reversed-phase HPLC column Hypersil ODS (150×4.6 mm) it was eluted with methanol–water or methanol–acetonitrile–water (70:10:20, v/v/v) using a flow-rate of 0.6 ml/min. Detection in each case was by UV at 295 nm (Fig. 2). Linear calibration curves by plotting average peak heights (five data points, each point calculated from three replicates) versus concentration of DDTP were obtained with 24–120 μg/ml. The correlation coefficients (r) using normal- and reversed-phase LC columns were 0.994 and 0.999, respectively. The detection limit, measuring at least three times the background noise, was 2.4 μg/ml corresponding to 4.8 ng/injection of 2 μl for normal- and reversed-phase modes.

DDTP also forms complexes with copper(II) which is extractable in chloroform and elutes from a

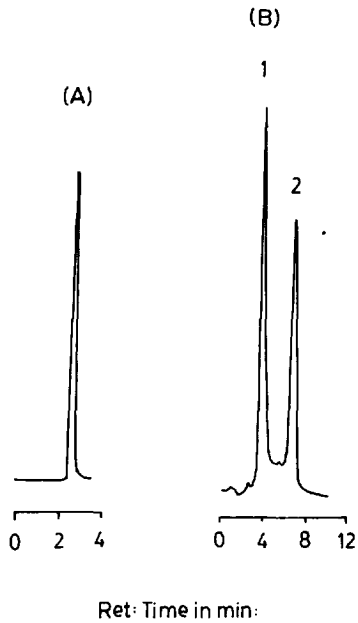

Fig. 2. (A) HPLC elution of DDTP–palladium(II) complex from LiChrosorb Si 100 (250×4 mm I.D.) column with chloroform at a flow-rate of 0.9 ml/min and UV detection at 295 nm. (B) Separation of (1) palladium(II) and (2) copper(II) complexes of DDTP from YMC Pack ODS (150×4.6 mm I.D). Elution with methanol–acetonitrile–water (70:10:20, v/v/v) with a flow-rate of 0.6 ml/min and UV detection at 295 nm.

reversed-phase HPLC column [17]. Therefore, the separation of copper(II) and palladium(II) complexes of DDTP on Hypersil ODS and YMC Pack ODS columns was investigated. The copper(II) and palladium(II) complexes were prepared separately and were mixed together before injecting on the HPLC column. DDTP–copper(II) complex was prepared following the procedure in Section 2.1, as for DDTP–palladium(II) complex, but instead of palladium(II), copper(II) was added. The optimal and complete separation (R_s=1.54) was obtained when eluted with methanol–acetonitrile–water (70:10:20, v/v/v) with a flow-rate of 0.6 ml/min. Detection was by UV at 295 nm. The capacity factors calculated for palladium(II)– and copper(II)–DDTP complexes were 1.22 and 2.86 (Fig. 2).

Selectivity of the reaction of DDTP towards copper and palladium was checked by varying the concentrations of copper/palladium and complexes were eluted at conditions optimized for their separation. Each time, two peaks corresponding to palladium and copper complexes were obtained. The amounts of copper(II) and palladium(II) complexes formed were calculated as 65% and 35%, 53% and 47% or 45% and 55%, respectively using copper/palladium ratios 2:1, 1:1, or 1:2 respectively. It shows that complexation of DDTP with both palladium(II) and copper(II) is fairly rapid, but has a slightly higher selectivity for copper(II).

A commercial sample of malathion formulation was analysed using both normal- and reversed-phase HPLC. The amounts of malathion found with normal-phase LC was 38.0% (v/v) and using reversed-phase LC it was 38.5% (v/v). The relative standard deviations (R.S.D.) (n=3) observed were 4.6% and 5.3%, respectively.

Emulsifiable insecticide malathion dust was also analysed by reversed-phase HPLC and the amount found was also 52.6% with R.S.D. (n=3) 5.2%. The malathion sample was also analysed using spectrophotometry and the amount obtained was 53.5% with R.S.D. 2.4%.

4. Conclusion

Simple LC methods have been developed for organophosphorous pesticides, based on the alkaline hydrolysis of malathion, followed by complexation of dimethyl dithiophosphate with palladium(II) and isocratic elution from normal- or reversed-phase HPLC column. Detection was at 295 nm. The detection limits were observed at 4.8 ng/injection. The copper(II)–DDTP separates completely from Pd–DDTP and could be identified. The methods were applied to the determination of malathion in malathion formulations.

References

[1] O. Jimenez De Blas, J.L. Pereda De Paz and J. Hernandez Mendez, Talanta, 38 (1991) 857.
[2] C.M. Deshpande and S.S. Bhende, Indian J. Environ. Prot., 2 (1982) 145.
[3] K. Visweswriah and M. Jayaram, Agric. Biol. Chem., 38 (1974) 2031.
[4] R.T. Sane and S.S. Kamat, J. Assoc. Off. Anal. Chem., 65 (1982) 40.
[5] E.R. Clark and I.A. Qazi, Analyst, 104 (1979) 1129.
[6] E.R. Clark and I.A. Qazi, Analyst, 105 (1980) 564.
[7] E.R. Clark and I.A. Qazi, Water Res., 14 (1980) 1037.
[8] U. Venkatadri Naidu, T. Gnaugaiah, P. Ramadevi, K. Seshaiah and G.R.K. Naidu, Talanta, 37 (1990) 761.
[9] P. Chiranjeevi, Indian J. Environ. Prot., 9 (1989) 580.
[10] M.H. Jones and T.J. Woodcock, Anal. Chem. Acta, 87 (1976) 463.
[11] F. Sanchez Rasero, J. Assoc. Off. Anal. Chem., 64 (1981) 75.
[12] J. Hernandez Mendez, O. Jimenz de Blas, V. Rodriguez Martin and E. Sanchez Lopez, Anal. Lett., 18 (1985) 2069.
[13] O. Jimenez de Blas, J.L. Pereda de Paz and J. Hernandez Mendez, Analyst, 114 (1989) 1675.
[14] M.Y. Khuhawar, A.H. Channar and I.A. Qazi, J. Chem. Soc., 16 (1994) 194.
[15] J. Hernandez Mendez, O. Jimenz de Blas and V. Rodriguez Martin, Microchim. J., 37 (1988) 275.
[16] M.I. Kabachnik and T.A. Mastryukova, Invest. Akad. Nauk. S.S.S.R, Otidel. Khim. Nauk, 121 (1953); C.A., 47 (1954) 3244e.
[17] M.Y. Khuhawar, A.H. Channar and S.N. Lanjwani, Chromatographia, 42 (1996) 680.