AYMAN A. GOUDA[1]
ALAA S. AMIN[2]
RAGAA EL SHEIKH[1]
MAGDA A. AKL[3]

[1]Chemistry Department, Faculty of Science, Zagazig University, Zagazig, Egypt
[2]Chemistry Department, Faculty of Science, Benha University, Benha, Egypt
[3]Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

SENSITIVE SPECTROPHOTOMETRIC METHODS FOR DETERMINATION OF SOME ORGANOPHOSPHORUS PESTICIDES IN VEGETABLE SAMPLES

Three rapid, simple, reproducible and sensitive spectrophotometric methods (A, B and C) are described for the determination of two organophosphorus pesticides, (malathion and dimethoate) in formulations and vegetable samples. The methods A and B involve the addition of an excess of Ce^{4+} into sulphuric acid medium and the determination of the unreacted oxidant by decreasing the red color of chromotrope 2R (C2R) at a suitable λ_{max} = 528 nm for method A, or a decrease in the orange pink color of rhodamine 6G (Rh6G) at a suitable λ_{max} = = 525 nm. The method C is based on the oxidation of malathion or dimethoate with the slight excess of N-bromosuccinimide (NBS) and the determination of unreacted oxidant by reacting it with amaranth dye (AM) in hydrochloric acid medium at a suitable λ_{max} = 520 nm. A regression analysis of Beer-Lambert plots showed a good correlation in the concentration range of 0.1-4.2 µg mL^{-1}. The apparent molar absorptivity, Sandell sensitivity, the detection and quantification limits were calculated. For more accurate analysis, Ringbom optimum concentration ranges are 0.25-4.0 µg mL^{-1}. The developed methods were successfully applied to the determination of malathion, and dimethoate in their formulations and environmental vegetable samples.

Key words: spectrophotometry; malathion; dimethoate; ceric sulfate; N-bromosuccinimide; vegetable samples.

Organophosphates are organic esters of phosphoric acid, thiophosphoric acid and other phosphoric acids, which are widely used as insecticides and acaricides. Organophosphorus compounds exhibit a wide range of toxicity to mammals. They work on central nervous system inhibiting its normal function resulting in convulsions, paralysis and death. Malathion is 2--(dimethoxyphosphinothioylthio) butanedioic acid diethyl esteran organophosphate parasympathomimetic which binds irreversibly to cholinesterase. Malathion is an insecticide of relatively low human toxicity. Dimethoate is *O,O*-dimethyl S-[2-(methylamino)-2-oxoethyl] dithiophosphate, a widely used organophosphate insecticide used to kill insects on contact. Like other organophosphates, dimethoate is an anticholinesterase which disables cholinesterase, an enzyme essential for the central nervous system function [1-5].

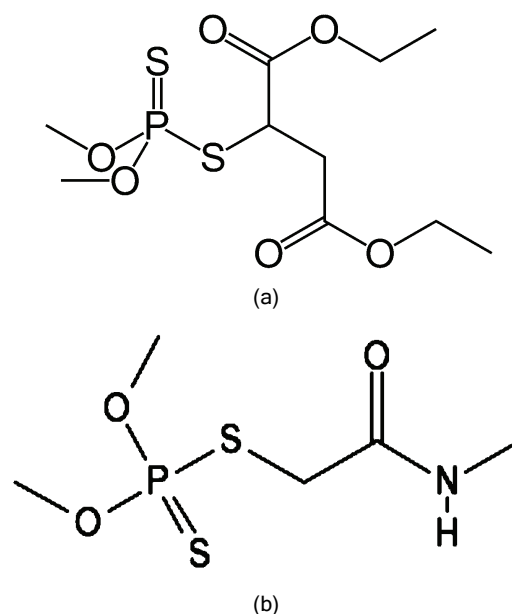The chemical structure of malathion and dimethoate is shown in Figure 1.

(a)

(b)

Figure 1. The chemical structure of malathion (a) and dimethoate (b).

Due to its wide use and toxicity, several methods like liquid chromatography with mass spectrommetry (LC-MS) [6-8], titrimetry [9], voltammetry [10,11], gas chromatography (GC) [12-15], high performance liquid chromatography (HPLC) [16], atomic absorption spectrophotometry (AAS) [17] and spectrophotometry [18-21] have been reported in the literature for the determination of organophosphates. Most spectrophotometric procedures involve the determination of organophosphorus insecticides by total phosphorus measurement, based on the formation of molybdenum blue using various reducing agents [4,19].

Some of these methods suffer from poor sensitivity, instability of color or involve extraction where as others suffer from the interference with arsenic and copper, blank absorption or longer time required for color development. To overcome these drawbacks, a rapid and sensitive method has been proposed for the determination of the studied organophosphorus insecticides.

Cerium(IV) sulfate and *N*-bromosuccinimide (NBS) are a versatile oxidimetric reagents. Due to its high oxidation potential and excellent solution stability, they were used for the quantitative determination of many compounds [22-27].

Because of its simplicity, speed, sensitivity, reasonable accuracy and precision, and cost-effectiveness, visible spectrophotometry continues to be the preferred technique in laboratories of developing and underdeveloped nations which can afford expensive chromatographic and related techniques.

The present methods are based on the oxidation of the organophosphorus insecticides with slight excess of cerium(IV) sulfate and *N*-bromosuccinimide (NBS) to form oxidation products. The unconsumed cerium(IV) sulfate was measured by a decrease in the red color of chromotrope 2R (C2R) at λ_{max} = 528 nm and a decrease in the orange pink color of rhodamine 6G (Rh6G) at λ_{max} = 525 nm, whereas the unreacted *N*-bromosuccinimide was then estimated with the decrease in the color intensity of amaranth dye (AM) at λ_{max} = 520 nm. The methods have been successfully applied for the determination of malathion and dimethoate in formulations and insecticide residues in various vegetable samples.

EXPERIMENTAL

Apparatus

All absorption spectra were made using Kontron 930 UV-Vis spectrophotometer (German) with a scanning speed of 200 nm/min and a band width of 2.0 nm, equipped with 10 mm matched quartz cells. Hanna pH-meter instrument (Portogal) (HI: 9321) was used for checking the pH measurements.

Reagents and materials

All chemicals were of analytical grade and double distilled water was used throughout the experiment.

Stock solution of organophosphorus insecticides (malathion, and dimethoate) (ONYX/ADCO, Egypt) were prepared by dissolving 100 mg of insecticide (technical forms and formulations) in a minimum amount of glacial acetic acid (Merck) and then diluting to 100 mL with distilled water. Working standards 20 µg mL^{-1} were prepared by the appropriate dilution.

A solution of cerium(IV) sulfate $Ce(SO_4)_2 \cdot 4H_2O$ (May and Baker; 3.0×10^{-3} M) was prepared by dissolving the known weight of $Ce(SO_4)_2$ in the least amount of warm 1.0 M sulfuric acid in a 250 ml calibrated flask, then diluted with the same acid to the mark.

An aqueous solution of 0.01% (w/v) *N*-bromosuccinimide (NBS) (Aldrich) was freshly prepared. A solution of 4.0 M HCl was prepared and standardized prior to use, as recommended previously [23,28].

The aqueous solution of chromotrope 2R (C2R) (Aldrich; 5.0×10^{-3} M) and rhodamine 6G (Rh6G) (BDH; 1.0×10^{-3} M), amaranth (AM) (Merck; 1.0×10^{-3} M) was prepared by dissolving an accurate weight of dye in the least amount of water and completed to the mark in a 100 ml calibrated flask.

Methods

Methods A and B

An aliquot of the sample solution containing 5.0-105 µg mL^{-1} of malathion, and 5.0-90 µg mL^{-1} of dimethoate were transferred into a series of 25 mL calibrated flasks, containing an excess 2.0 mL of 3.0×10^{-3} M Ce^{4+} dissolved in 1.0 M H_2SO_4 and then the solution was boiled in a water bath for 5.0 min. The solution was cooled and 0.8 mL of 5.0×10^{-3} M of C2R was added for method A, or 0.7 mL of 1.0×10^{-3} M of Rh6G was added to the hot solution for method B. The volume was completed to 25 mL with water and a decrease in color intensities of C2R or Rh6G were measured spectrophotometrically at their corresponding maximum wavelengths 528 or 525 nm, respectively against a reagent blank. A blank without insecticide (dye and $Ce(SO_4)_2$) and dye (devoid of insecticide and $Ce(SO_4)_2$) were prepared in a similar manner and its absorbance was measured against distilled water. A decrease in absorbance corresponding to the consumed oxidant which reflects the insecticide concentration was obtained by subtracting a decrease in absorbance of the test solution (dye minus test) from that

of the blank solution (dye minus blank). The concentration range was determined in each case by plotting a decrease in absorbance of the dye (ΔA) against the amount of the insecticide at the corresponding λ_{max}.

Method C

An aliquot of the sample solution containing 2.5-90 µg mL^{-1} of malathion and 5.0-75 µg mL^{-1} of dimethoate were transferred into a series of 25 mL calibrated flasks, to which 3.0 mL of 0.01% (w/v) NBS, 2.0 mL of hydrochloric acid (4.0 M) and 2.0 mL of 1.0% KBr were added successively; the solution was kept aside with occasional shaking for about 10 min at ≈25-30 °C and then 0.75 mL of (1.0×10^{-3} M) of AM. The volume was completed to 25 mL with water. The absorbance was measured at λ_{max} of 520 nm against a reagent blank. A blank without insecticide (dye and NBS) and the dye (devoid of insecticide and NBS) were prepared in a similar manner and its absorbance was measured against the distilled water. A decrease in absorbance corresponding to the consumed oxidant which reflects the insecticide concentration was obtained by subtracting the decrease in absorbance of the test solution (dye minus test) from that of the blank solution (dye minus blank). A calibration graph was prepared by plotting the decrease in absorbance of the dye (ΔA) against the amount of the insecticide.

Assay procedure for formulations

The contents of three bottles of malathion lotion (Quick, 0.5%) were mixed and the average volume for one bottle was determined. An aliquot of the solution equivalent to 10 mg malathion was transferred to 100 mL calibrated flask and dissolved in a minimum amount of glacial acetic acid and made up to the mark with bidistilled water. The above stated procedures described were applied to determine malathion concentration. This solution was further diluted stepwise to the requested concentration with water and then analyzed by the recommended procedure.

RESULTS AND DISCUSSION

These methods involve two steps namely:

1. The reaction of malathion or dimethoate with an excess of oxidant Ce(SO$_4$)$_2$ in acid medium under the effect of heating or NBS giving products involving oxidation.

2. The estimation of the excess oxidant by measuring the decrease in color of C2R or Rh6G using Ce(SO$_4$)$_2$ at λ_{max} 528 or 525 nm for C2R or Rh6G, respectively or amaranth dye (AM) using NBS at λ_{max} 520 nm.

The influence of each of the following variables on the reaction was tested.

Effect of acid concentration

In methods A and B, the most suitable acid to be used with Ce^{4+} was found to be sulfuric acid of 1.0 M if present as 2.0 mL in the total volume of the reaction mixture (25 mL).

In method C, the optimum acid of the examined (sulfuric, hydrochloric, nitric, phosphoric and acetic acids) was hydrochloric acid of 4.0 M concentration. Moreover, 2.0 mL of 4.0 M HCl was chosen as an optimum volume in 25 mL total volume.

Effect of temperature and time

In methods A and B, sample solutions containing organophosphorus insecticides (malathion and dimethoate), Ce^{4+} and H$_2$SO$_4$ were heated at different temperatures ranging from 30 to 100 °C. The results obtained indicated that the reaction is catalyzed by heat and is maximum at 100 °C. The time required to complete the reaction is 5.0 min. In method A, the solution must be cooled for at least 3.0 min before the addition of C2R. In method B, the addition of Rh6G to the hot solution gives the maximum absorbance.

In method C, the reaction takes place completely in the presence of KBr after 10 min of mixing and shaking. Raising the temperature does not accelerate the oxidation process and does not give reproducible results, so the optimum temperature is ambient (25±1 °C). The effect of time after adding the dye indicated that shaking for 1.0 min is sufficient to give reliable results.

Effect of dye concentration

In methods A and B, to establish the optimum concentration of the reagent, different volumes of 5.0×10^{-3} M C2R or 1.0×10^{-3} M Rh6G solution were used (Figure 2). The optimum volume used for the production of maximum and reproducible color intensity is 0.8 mL of C2R or 0.7 mL of Rh6G.

In method C, different volumes (0.2-1.0 mL) of 1.0×10^{-3} M AM dye were used. The optimum volume used for the production of maximum and reproducible color intensity is 0.75 mL (Figure 2).

Effect of sequence of addition

Insecticide-acid-oxidant-KBr-(dye) is the optimum sequence of the addition; other sequences gave lower absorbance values under the same experimental conditions.

Effect of KBr

Two mL of KBr (1.0%) was chosen as the optimum volume in 25 mL total volume to accelerate the oxidation process.
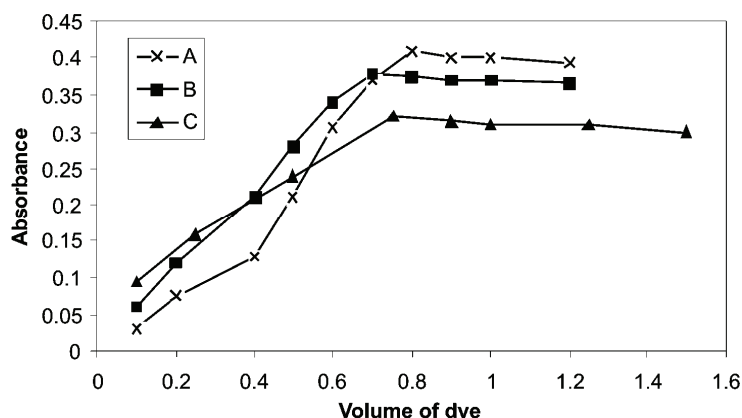
Figure 2. The effect of added dyes on absorbance of 2.0 µg mL^{-1} of malathion using the proposed methods A-C.

Molar ratio

Ce(SO$_4$)$_2$ reacts with organophosphorus insecticides (malathion and dimethoate) with the consumption of 25 mol of Ce(SO$_4$)$_2$ per each mole of organophosphorus insecticides giving a mixture of products. The remaining Ce^{4+} reduces the color intensity of C2R or Rh6G through disruption of the conjugation system in the dye.

NBS reacts with malathion and dimethoate with consumption of 6.0 mol of NBS per each mole of malathion and dimethoate giving a mixture of products. The remaining oxidant reduces the intensity of red color of AM dye through disruption of the conjugation system in the dye.

The remaining colours stay constant in absorbance for at least 48 h, and then slightly decrease afterwards.

Method validation

Linearity

At described experimental conditions for malathion and dimethoate determination, standard calibration curves for malathion and dimethoate with Ce^{4+} or NBS and dyes were constructed by plotting a decrease in absorbencies *vs*. concentrations. The statistical parameters were given in the regression equation calculated from the calibration graphs, along with the standard deviations of the slope (S_b) and the intercept (S_a) on the ordinate and the standard deviation residuals ($S_{y/x}$).

The linearity of calibration graphs was proved by high values of the correlation coefficient (*r*) and small values of the *y*-intercepts of the regression equations. The apparent molar absorptivities of the resulting colored solution and relative standard deviation of response factors for each proposed spectrophotometric method were also calculated and recorded in Table 1. The molar absorptivity of B > A > C method for mala-

thion, whereas for dimethoate, the molar absorptivity for B > C >A was found.

Sensitivity

The detection limits (*LOD*) for the proposed methods were calculated using the following equation [29]:

$$LOD = 3s/k$$

where *s* is the standard deviation of replicate determination values under the same conditions as for the sample analysis in the absence of the analyte and *k* is the sensitivity, namely the slope of the calibration graph. In accordance with the formula, the detection limits were found to be 0.022, 0.045 and 0.021 µg mL^{-1} for malathion, whereas for dimethoate the detection limits were found to be 0.056, 0.037 and 0.031 µg mL^{-1} for A, B and C method, respectively.

The limits of quantitation, *LOQ*, are defined as [29]:

$$LOQ = 10s/k$$

According to this equation, the limit of quantitation were found to be 0.074, 0.15 and 0.07 µg mL^{-1} for malathion, whereas for dimethoate the detection limits were found to be 0.187, 0.123 and 0.103 µg mL^{-1} for A, B and C method, respectively.

Specificity, precision, and accuracy

Specificity of the oxidation-reduction reaction and selective determination of malathion and dimethoate with Ce^{4+} or NBS and dyes could be possible. The percentage relative standard deviation (*RSD*) as precision and percentage relative error (*Er* / %) as accuracy of the suggested methods were calculated. The precision was carried out by six determinations at four different concentrations in these spectrophotometric methods. The percentage relative error was calculated using the following equation:

Table 1. Analytical parameters and optical characteristics of the proposed methods with malathion and dimethoate

Parameters	Malathion			Dimethoate		
	Method					
	A	B	C	A	B	C
λ_{max} / nm	528	525	520	528	525	520
Beer's law limits, µg mL^{-1}	0.2-4.0	0.2-4.2	0.1-3.6	0.4-3.2	0.2-3.6	0.2-3.0
Ringbom limits, µg mL^{-1}	0.4-3.7	0.35-4.0	0.25-3.4	0.6-3.0	0.4-3.5	0.3-2.8
Molar absorptivity×10^4, L mol^{-1} cm^{-1}	6.56	7.839	5.73	2.672	4.582	3.286
Sandell sensitivity, ng cm^{-2}	5.03	4.21	5.76	8.58	5.0	6.98
Regression equation[a]						
Slope (*b*)	0.2127	0.2243	0.1594	0.1179	0.1854	0.1387
Intercept (*a*)	-0.0089	0.0061	0.0053	-0.0016	0.0079	0.0023
Correlation coefficient (*r*)	0.9996	0.9998	0.9997	0.9994	0.9993	0.9991
$S_{y/x}$	0.3585	0.39	0.249	0.0598	0.2847	0.175
SD of slope (S_b)	0.0107	0.069	0.079	0.0242	0.092	0.069
SD of intercept (S_a)	0.241	0.258	0.169	0.051	0.196	0.128
Detection limits, µg mL^{-1}	0.022	0.045	0.021	0.056	0.037	0.031
Quantification limit, µg mL^{-1}	0.074	0.15	0.07	0.187	0.123	0.103
Recovery, %	98.95	99.19	99.22	99.06	99.24	98.76
RSD / %	1.74	1.83	1.23	1.16	1.19	1.30
t[b]	1.062	0.651	0.894	0.972	1.18	1.38
F[b]	1.29	1.17	2.59	2.12	2.02	1.69

[a]A = a + bC, where C is the concentration in µg mL^{-1}; [b]calculated *t* and *F*-values (tabulated *t*- and *F*-values for five degrees of freedom and 95% confidence limits (*p* = 0.05) are 2.57and 5.05

Er [%] = ((found – added)/added)×100

The inter-day precision and accuracy results are shown in (Table 2). These results of accuracy and precision show that the proposed methods have good repeatability and reproducibility.

Robustness and ruggedness

For the evaluation of the method robustness, some parameters were interchanged: Ce^{4+} or NBS concentration, dye concentration, wavelength range, and time. The capacity remains unaffected by small deliberate variations. Method ruggedness was expressed as *RSD* of the same procedure applied by two analysts and in two different instruments on different days. The results showed no statistical differences between different analysts and instruments suggesting that the developed methods were robust and rugged.

Table 2. The evaluation of the inter-day precision and accuracy data for malathion and dimethoate obtained by the proposed methods (mean of five determinations; RSD: relative standard deviation; Er: relative error)

Method	Malathion				Dimethoate			
	Added µg mL^{-1}	Recovery %	Precision *RSD* / %[a]	Accuracy Er / %	Added µg mL^{-1}	Recovery %	Precision *RSD* / %[a]	Accuracy Er / %
A	0.5	100.1	0.084	0.10	0.5	100.09	0.68	0.09
	1.0	99.57	0.092	-0.43	1.0	99.92	0.90	-0.08
	2.0	99.95	0.077	-0.05	2.0	99.70	0.88	-0.30
	3.0	100.20	0.108	0.20	3.0	100.15	1.17	0.15
B	0.5	99.72	0.99	-0.28	0.5	99.20	0.76	-0.80
	1.0	99.15	0.85	-0.85	1.0	100.2	0.57	0.20
	2.0	98.94	1.12	-1.06	2.0	99.90	0.66	-0.10
	3.0	99.45	0.88	-0.55	3.0	100.31	0.39	0.31
C	0.5	100.12	0.76	0.12	0.5	99.70	1.08	-0.30
	1.0	99.85	0.79	-0.15	1.0	98.92	0.54	-1.08
	2.0	99.92	0.81	-0.08	2.0	99.30	0.45	-0.70
	3.0	100.15	1.23	0.15	3.0	100.10	0.61	0.10

Interference

To assess the validity of the proposed method, the effects of various common foreign species and other pesticides associated with organophosphorus insecticides were added in known amounts to the sample and analyzed by the proposed methods. Most of the metallic species like Zn^{2+}, Cu^{2+}, Mn^{2+}, Cd^{2+}, Ni^{2+} had negligible interference. Phenol was the most expected interference (Table 3).

method were compared statistically by student's *t*-test (for accuracy) and variance ratio *F*-test (for precision) with the reported method [21] at the 95% confidence level with five degrees of freedom (Table 4). The results showed that the *t* and *F*-values were less than the critical value [29] indicating that there was no significant difference between the proposed and reported method [21]. Because the proposed methods were more reproducible with high recoveries, they can be

Table 3. The effect of foreign species on the determination of 1.0 µg mL^{-1} of malathion and dimethoate organophosphorus insecticides

Foreign species	Tolerance limit^a, µg mL^{-1}	
	Malathion	Dimethoate
Cu^{2+}, Ni^{2+}	1500	1400
Zn^{2+}, Cd^{2+}	1200	1100
Mn^{2+}	950	900
Fe^{3+}	620	600
Se^{4+}	550	500
Cr^{3+}	220	250
Aniline	260	220
Dithiocarbamate pesticides	45	50
Carbamate pesticides	25	20
Phenol	9	10

^{a}May vary by ±2.0%

Analytical application

The proposed methods were successfully applied to determine malathion and dimethoate in formulations. Six replicate determinations were made. Therefore it is concluded that the excipients in formulations of malathion and dimethoate were not found any interference. The results obtained by the standard addition

recommended for the routine analysis in majority of the insecticide quality control laboratories.

To check the recovery of organophosphorus insecticide, various vegetable samples free from organophosphorus insecticide were taken and treated with known amounts of insecticide and kept for 24 h. The samples were then washed with ethanol and the

Table 4. The application of the standard addition technique for the determination of malathion and dimethoate in formulations using the proposed methods

Method	Taken µg mL^{-1}	Quick lotion (0.5%)			Dimethoate formulation		
		Added µg mL^{-1}	Recovery^a, %	Reported method [21]	Added µg mL^{-1}	Recovery^a, %	Reported method [21]
A	0.5	--	99.80		-	97.85	
		0.5	100.50		2.0	99.50	
		1.0	100.35		4.0	101.00	
		1.5	100.20		6.0	100.25	
		2.0	99.65		8.0	100.60	
		2.5	100.80		10	99.25	
	Mean^a ± *SD* (*p* = 0.05)		100.02 ± 0.43	99.70 ± 0.49		99.81 ± 0.47	99.35 ± 0.36
	t^b		1.10			1.74	
	F^b		1.29			1.70	
B	0.5	--	99.51		-	98.95	
		5.0	99.96		2.0	99.50	
		1.0	100.01		4.0	100.40	
		2.0	99.10		6.0	100.55	

Table 4. Continued

Method	Taken µg mL^{-1}	Quick lotion (0.5%)			Dimethoate formulation		
		Added µg mL^{-1}	Recovery[a], %	Reported method [21]	Added µg mL^{-1}	Recovery[a], %	Reported method [21]
B		2.5	99.85		8.0	99.50	
		3.0	100.30		10	99.90	
	Mean[a] ± *SD* (*p* = 0.05)		99.97 ± 0.35	99.70 ± 0.49		99.80 ± 0.41	99.35 ± 0.36
	t[b]		1.00			1.84	
	F[b]		1.96			1.30	
C	0.5	--	99.60		-	99.35	
		0.5	100.45		2.0	99.70	
		1.0	100.15		4.0	100.40	
		2.0	100.30		6.0	99.20	
		2.5	99.85		8.0	100.50	
		3.0	99.60		10	99.75	
	Mean[a] ± *SD* (*p* = 0.05)		99.89 ± 0.52	99.70 ± 0.49		99.72 ± 0.28	99.35 ± 0.36
	t[b]		0.59			1.81	
	F[b]		1.13			1.65	

[a]Mean of three different experiments; [b]*t*- and *F*-values for five degrees of freedom and 95% confidence limits (*p* = 0.05) are 2.57 and 5.05

washings were collected in a boiling tube. Aliquots of these washings were used for the determination of organophosphorus insecticides by the proposed method. The recoveries range from 93.85 to 96.45 % and the results are summarized in Table 5.

CONCLUSIONS

All the proposed methods were advantageous over other reported visible spectrophotometric methods with respect to their higher sensitivity, simplicity, re-producibility, precision, accuracy and stability of co-lored species. The proposed methods can be applied for the routine analysis and in the quality control laboratories for the quantitative determination of the studied organophosphorus insecticides in raw mate-rials, in formulations and the determination of insec-ticide residue in vegetable samples.

REFERENCES

[1] A.I. Al-Samariee, A.M. Khloud Shaker, M.A. Al-Bassomy, Pestic. Sci. **22** (1988) 189.
[2] J.V. Das, K.N. Ramachandran and V.K. Gupta, Analyst **119** (1994) 1387.
[3] V. Agrawal, V.K. Gupta, Fresenius J. Anal. Chem. **345** (1993) 720.

Table 5. The application of the method on insecticide free vegetable samples

Method	Vegetable sample[a]	Malathion			Dimethoate		
		Amount added, µg	Recovery %	Reported method [21]	Amount added, µg	Recovery %	Reported method [21]
A	Cabbage	2.5	95.20	96.20	2.5	93.85	95.70
		5.0	96.45	95.95	5.0	94.75	95.80
	Spinach	2.5	95.10	95.75	2.5	96.30	96.60
		5.0	95.55	96.00	5.0	94.97	95.65
B	Cabbage	2.5	96.20	96.51	2.5	94.55	96.20
		5.0	95.80	95.90	5.0	95.30	95.45
	Spinach	2.5	95.15	94.90	2.5	95.00	96.10
		5.0	95.05	96.25	5.0	94.95	96.55
C	Cabbage	2.5	95.60	96.85	2.5	94.80	95.55
		5.0	94.90	95.80	5.0	96.00	96.10
	Spinach	2.5	94.70	95.70	2.5	95.25	95.80
		5.0	95.07	96.25	5.0	95.35	96.25

[a]The amount of vegetable samples from fields where organophosphorus insecticides were sprayed was 25 g

[4]   S. Sunita, V.K. Gupta, J. Ind. Chem. Soc. **65** (1987) 114.

[5]   World Health Organization, Safe use of pesticides in public health, 16th Report of the W.H.O. Expert Committee on Insecticides, Geneva, (1987).

[6]   S. Inoue, T. Saito, H. Mase, Y. Suzuki, K. Takazawa, I. Yamamoto, S. Inokuchi, J. Pharm. Biomed. Anal. **44** (2007) 258.

[7]   B. A. Ingelse, R. C. J. van Dam, R. J. Vreeken, H. G. J. Mol, O. M. Steijger, *J. Chromatog. A* **918** (2001) 67.

[8]   M. Liu, Y. Hashi, Y. Song, J.M. Lin, J. Chromatog. A **1097** (2005) 183.

[9]   A.K. Tiwari, B.K. Dubey, I.C. Shukla, J. Ind. Chem. Soc. **80** (2003) 717.

[10] Y. Ni, P. Qiu and S. Kokot, Anal. Chim. Acta **516** (2004) 7.

[11] Z.M. Getenga, J.I.O. Jandiiko, S.O. Wandigo and E. Beck, Bull. Environ. Contam. Toxicol. **64**, (2000) 359.

[12] M.L.C. Cano, J.L.M. Vidal, F.J.E. Gonzalez and M.M. Galera, J. Chromatogr. Sci. **42**, (2002) 322.

[13] H. Tsoukali, G. Theodoridis, N Raikos and I. Grigoratou, J. Chromatogr. B Anal. Technol Biomed Life Sci. **822** (2005) 194.

[14] M.L. Castro Cano, J. L. Martínez Vidal, F.J. Egea González, M. Martínez Galera, J. Chromatogr. Sci. **39** (2001) 345.

[15] F.J. López, E. Pitarch, S. Egea, J. Beltran and F. Hernández, Anal. Chim. Acta **433** (2001) 217

[16] K.N.S. Karim, B.C. Das, M. Khalequzzaman, Pak. J. Zool. **33** (2001) 105.

[17] J. Hernández Méndez, O. Jiménez De Bias, V. Rodriguez Martín, E. Sánchez López, Anal. Lett. **18** (1985) 2069.

[18] H. Ping, Z. Hui, L. Qing, Fenxi Huaxue **28** (2000) 1445.

[19] J. Raju, V.K. Gupta, Microchem. J. **39** (1989) 166.

[20] K. Seshaiah, P. Mowli, Analyst **112** (1987) 1189.

[21] S.B. Mathew, A.K. Pillai, V.K. Gupta, Spectrochim. Acta (A) **67** (2007) 1430.

[22] M.S. Rizk, Y.M. Issa, A.F. Snoukry, E.M. Atia, Anal. Lett. **30** (1997) 2743.

[23] M.M. Ayad, A.A. Shalaby, H.E. Abdel Latef, H.M. El- Said, J. Pharm. Biomed. Anal. **20** (1999) 557.

[24] S.M. Sultan, Y.A.M. Hassan, K.E.E. Ibrahim, Analyst **124** (1999) 917.

[25] A.S. Amin, I.S. Ahmed, H.A. Dessouki, I.A. Gouda, Spectrochim. Acta A **59** (2003) 695.

[26] A.S. Amin, S.A. Shama, I.S. Ahmed, E.A. Gouda, Anal. Lett. **35** (2002) 1851.

[27] A.S. Amin, H.A. Dessouki, S.A. Shama, E.A. Gouda, J. AOAC Int. **92** (2009) 382.

[28] G.H. Jeffery, J. Bassett, J. Mendham, R.C. Denney, Titrimetric Analysis. In Vogel's a Text Book of Quantitative Inorganic Analysis, 5th ed., ELBS, London, 1989, p. 286.

[29] J.C. Miller and J.N. Miller, Significance tests. In Statistics in Analytical Chemistry, 3rd ed., Ellis Horwood, Chichester, 1993.

AYMAN A. GOUDA[1]
ALAA S. AMIN[2]
RAGAA EL SHEIKH[1]
MAGDA A. AKL[3]

[1]Chemistry Department, Faculty of Science, Zagazig University, Zagazig, Egypt
[2]Chemistry Department, Faculty of Science, Benha University, Benha, Egypt
[3]Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

NAUČNI RAD

OSETLJIVE SPEKTROFOTOMETRIJSKE METODE ZA ODREĐIVANJE NEKIH ORGANOFOSFORNIH INSEKTICIDA U UZORCIMA POVRĆA

U radu su opisane tri brze, jednostavne, reproduktivne i senzitivne spektrofotometrijske metode (A, B i C) za određivanje dva organofosforna pesticida (malationa i dimetoata) u formulacijama i uzorcima povrća. Metode A i B su zasnovane na dodatku viška Ce^{4+} u sredini zakišeljenoj sumpornom kiselinom i određivanjem neizreagovanog oksidanta merenjem intenziteta hromotropne crvene boje na λ_{max} = 528 nm za metodu A ili narandžasto-ljubičaste boje rodamina 6G na λ_{max} = 525 nm. Metoda C se zasniva na oksidaciji malationa ili dimetoata malim viškom N-bromosukcinimida i određivanjem neizreagovanog oksidanta sa amarant bojom u hlorovodnočnoj kiselini na λ_{max}= 520 nm. Regresiona analiza Beer-Lamberovih grafika je pokazala dobru korelaciju u opsegu koncentracije od 0,1 do 4,2 μg mL^{−1}. Izračunata je molarna apsorpivnost, Sandelovi indeksi i limiti detekcije i kvantifikacije. Za tačnije određivanje optimalni Ringbom koncentracijski opsezi su 0,25-4,0 μg mL^{−1}. Razvijene metode uspešno su primenjene za određivanje malationa i dimetoata u formulacijama i uzorcima povrća.

Ključne reči: spektrofotometrija; malation; dimetoat; ceri-sulfat; N-bromsukcinimid; uzorci povrća.