Environmental Science
An Indian Journal

Trade Science Inc.

Current Research Papers

Polarographic determination of insecticide imidacloprid at DME

N.V.S.Naidu*, K.Purushotham Naidu, C.Swarna, M.Sulochana, K.Saraswathi
Department of Chemistry, S.V. University, Tirupati - 517 502, Andhra Pradesh, (INDIA)
E-mail : nvsn69@gmail.com

ABSTRACT

A simple polarographic method is developed for the determination of imidacloprid. It is a neonicotinoid group of insecticide and chemically known as 1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine. This insecticide was analyzed in sodium acetate buffer of p^H 7.2 in methanol water medium in the concentration range from 1×10^{-4} to 5.2×10^{-4} M. The developed method is applied for the determination of imidacloprid in pesticide formulations and spiked water samples. These obtained results are compared with UV –Vis Spectrophotomerty. The developed method is simple, easy and inexpensive, thus making of an excellent tool for the routine analysis of pesticides.   © 2011 Trade Science Inc. - INDIA

KEYWORDS

INTRODUCTION

Imidacloprid[1-(6-Chloro-3-pyridylmethyl)-N-Nitroimidazollidin-2-ylideneamine] (Figure 1) belongs to the new class of insecticide known as neonicotinoid insecticides, and acts on the nicotinic acetylcholine receptor and, therefore have specific activity against the insect nervous system. Imidacloprid is marketed under variety of names including Gaucho, merit, Admire, Confidor, Macho and Winner. Imidacloprid p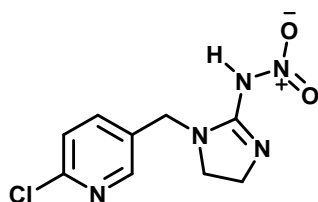hysical, chemical and toxicological properties have been summarized in a pesticide manual[1]. This unique mode of action makes them highly desirable for controlling insects that are developing resistance to conventional organophosphate, carbamate and phyrethorid insecticides[2]. Imidacloprid is a systematic and contact insecticide, effective in controlling aphid's, thrips, potato, battle and other harmful pest species[2,3]. Although imidacloprid has been in use for a relatively short period compared to other common pesticides, it is considered to be used in the largest volume globally of all insecticides[4-6]. The mechanism of Imidacloprid action has been studied extensively, and is relatively well known. It acts as agonist by binding to nicotinic acetylcholine receptor in the insects nervous system. This leads to the accumulation of acetylcholine resulting in the paralysis and death of insects[7].

Because of wide and constantly growing areas of application, high water solubility (0.58 gL^{-1}) and water

Figure 1 : Structure of Imidacloprid
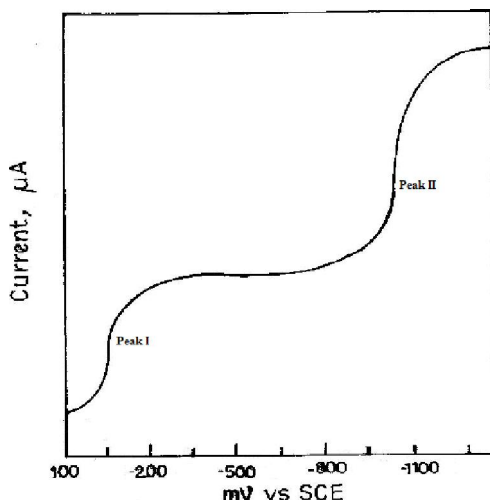
Current Research Paper

Figure 2 : Typical polarogram of Imidacloprid

stability of >30 days (at pH 5-7)[8], imidacloprid is increasingly present in environment. All above facts indicate the need for new analytical methods for the determination of this neonicotinoid, both in commercial formulations and real samples from the environment, using the possibly simple and low cost instrumental techniques.

Widely used analytical techniques for imidacloprid determination are high – performance liquid chromatography (HPLC) with diode array[9-11], mass – spectrometric[12,13], thermal lens spectrometric[14] or amperometric detection[15]. Some alternative techniques like an enzyme – linked immunosorbent assay[16,17], fluorimetry[18] and Fourier transform infrared spectroscopy[19] have also been employed for rapid, selective analysis of different samples containing imidacloprid. Several electroanalytical methods such as differential – pulse polarography[20] or square – wave adsorptive stripping voltammetry on a hanging mercury drop electrode[21] have also been described for the determination of imidacloprid in commercial formulations and spiked river water samples. The applicability of bismuth- film modified glassy carbon electrode for the monitoring of photocatalytic degradation of imidacloprid on TiO_2 catalyst was also described[22], widening thus the field of use of environment friendly bismuth – modified carbon – based electrodes[23,24]. On the other hand a recent publication[25] described, photochemical transformation of imidacloprid, allowing highly sensitive and selective, indirect determination of both parent compounds and their stable degradation products using HPLC with an electrochemical deter and electroana-

lytical determination of imidacloprid using carbon paste electrodes RE were also described. As for as we know, there are no publications yet that would deal with determination of imidacloprid by spectrophotometry using 2, 2 -BPL and Potassium ferricynide as reagents and d.c polarogaphic data of this compound in sodium acetate as supporting electrolyte.

In this present investigation d.c polarographic method for the determination of imidacloprid in commercial formulations and spiked water samples are reported and these results are compared with spectrophotometric studies.

EXPERIMENTAL

Reagents and solutions

All chemicals used were of analytical reagent grade. A 99% pure references standard imidacloprid is obtained from Hyderabad chemicals Ltd, Hyderabad, India. A Stock solution of 1.0×10^{-2} of imidacloprid is prepared by dissolving the required quantity of the substance in methanol and made up with methanol and diluted to get the desired concentration.

The 1M sodium acetate-supporting electrolyte was prepared by dissolving 34 gr of substance in 500 ml of double distilled water. 0.2 % of Triton X -100 was used as maximum suppressor in the present study.

Apparatus

The current-voltage curves are recorded using a D.C. polagraph, model CL-358 coupled with EPSON LX-300+ printer manufactured by Elico Pvt Limited (Hyderabad, India).

Shimazu UV- Visible double beam spectrophotometer (Model 2450) with 1 cm matched quartz cells were used for all the spectral measurements.

RESULTS AND DISCUSSION

D.C.polrographic results

Two well defined waves are observed in d.c.polarograpy in p^H range 5.0 to 10 which are attributed to the reduction of two nitro groups to diamine involving six electrons each. Typical polarogram of imidacloprid in sodium acetate supporting electrolyte is
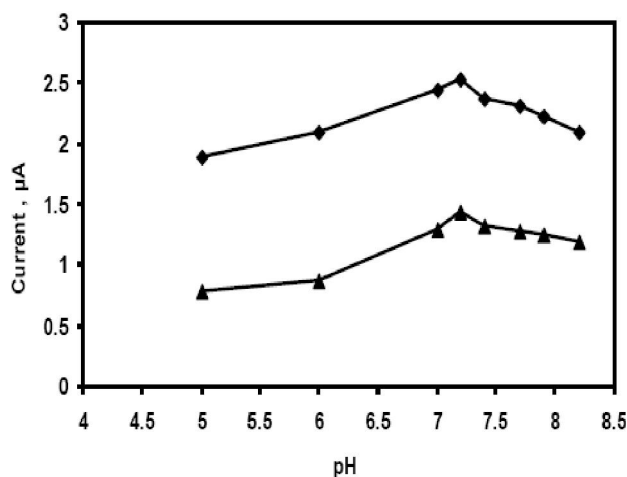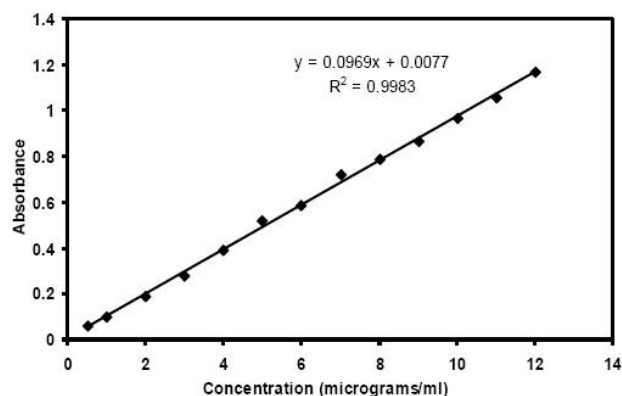
Figure 3 : Effect of P^H

Figure 4 : Calibration curve of Imidacloprid in 0.15 M sodium acetate, p^H: 7.2, methanol:10%

Figure 5 : Calibration plot of Imidacloprid with spectrophotometry (Method A)

Figure 6 : Calibration plot of Imidacloprid with spectrophotometry (Method B)

shown in figure 2. A detailed study of the various parameters involved in the reduction of imidacloprid is presented in acetate supporting electrolyte in the following lines.

Effect of p^H

In 0.15 M sodium acetate supporting electrolyte with $3.2×10^{-4}$ M imidacloprid two cathodic peaks are found. The p^H of the medium is changed step wise from 5.0 to 10.0. The half wave potential of both the waves shifted to negative values with increasing p^H from 5.0 to 10.0 indicating proton involvement in both the steps of electrode reduction process. The wave heights increased with increasing p^H upto 7.2 further decreased with increasing p^H. The waves are well defined in p^H 7.2. (Figure 3) So p^H 7.2 is selected for further studies.

Effect of variation of supporting electrolyte

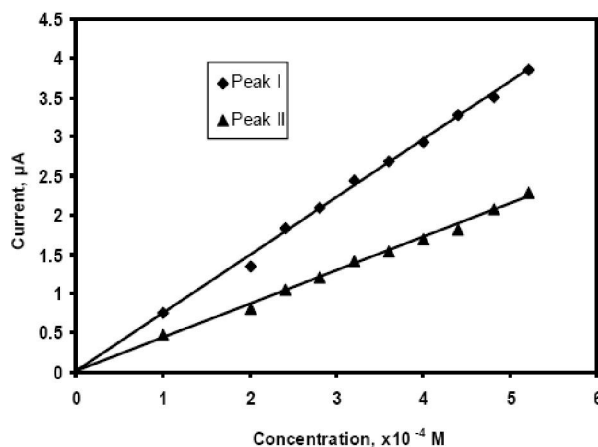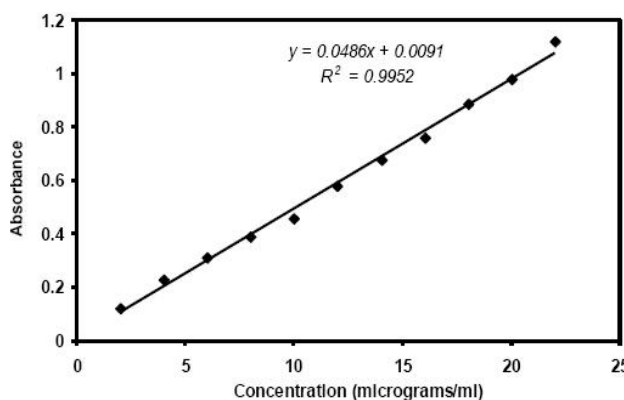Variation of supporting electrolyte concentration from 0.05 to 0.4 M shows a slight change in both the

wave heights of $3.2×10^{-4}$M Imidacloprid at p^H 7.2. The diffusion current increased with increase in concentration upto 0.15 M and then decreased thereafter. So, 0.15M supporting electrolyte is therefore, used in the present study.

Effect of concentration of imidacloprid

Imidacloprid is used from $1×10^{-4}$ to $5.2×10^{-4}$ M at p^H 7.2 in sodium acetate medium maintaining 10% Methanol. It is observed that both the wave heights, i_d (I) and i_d (II) increased proportionately indicating diffusion controlled nature of the electrode process .With increasing concentration, half – wave potentials of both the waves (I and II) shifted to more negative values pointing out irreversible nature of reduction of nitro group of imidacloprid. A calibration plot of i_d vs. C is shown in figure 4 and values are reported in TABLE 1.

Effect of height of the mercury pressure

The limiting currents of both the waves in 0.15 M

Current Research Paper

TABLE 1 : Effect of Concentration of Imidacloprid, Sodium acetate: 0.15 M, p^H: 7.2, methanol: 10%

S.No	Concentration, C $\times 10^{-4}$M	I_d(I) µA	I_d(II) µA
1	1.0	0.48	0.76
2	2.0	0.82	1.36
3	2.4	1.06	1.85
4	2.8	1.21	2.1
5	3.2	1.42	2.45
6	3.6	1.55	2.69
7	4.0	1.70	2.94
8	4.4	1.83	3.28
9	4.8	2.08	3.51
10	5.2	2.30	3.85

TABLE 2 : Effect of height of the mercury column, Sodium acetate: 0.15 M, p^H: 7.2, Imidacloprid : 3.2$\times10^{-4}$, methanol: 10%

S. No	Height of the mercury column, h cm	I_d(I) µA	I_d(I)/ $\sqrt{h}$	I_d(II) µA	I_d(II)/ $\sqrt{h}$
1	50	1.59	0.2248	2.55	0.3606
2	55	1.64	0.2211	2.68	0.3613
3	60	1.70	0.2194	2.79	0.3601
4	65	1.76	0.2183	2.90	0.3597

TABLE 3 : Effect maximum suppresser (TritonX-100)

S.No	Concentration of TritonX-100	Current I_d(I) (µA)	Current I_d(II) (µA)
1	0.000	1.40	2.13
2	0.002	1.36	2.10
3	0.004	1.32	2.05

TABLE 4 : Optical characteristics of proposed methods by spectrophotometry

Parameters	Method A	Method B
λmax nm	486	363
Beer's Law limit (µg ml^{-1})	0.5-12	2-22
Molar absorptivity (L. mol^{-1} cm^{-1})	2.43X10^4	1.33X10^4
Specific absorptivity	0.0095	0.0520
Sandell's sensitivity (µg.cm^{-2}/0.001 A.U)	0.1052	0.0192
Correlation coefficient (r^2)	0.998	0.995
Regression equation (Y = mX + C)		
Slope (m)	0.096	0.048
Intercept (C)	0.007	0.009
% Relative Standard deviation	0.5698	0.4731
Color	Orange red	Bluish green

sodium acetate medium increased with increasing mercury pressure at 3.2$\times10^{-4}$ M concentration of imidacloprid at p^H 7.2 and i$_d$/√h are found to be constant showing diffusion controlled nature of the waves

and the values are given in TABLE 2.

Effect of maximum suppressor

The effect of Triton X-100 was studied on polarogram of Imidacloprid keeping the concentration of Imidacloprid at 3.2$\times10^{-4}$M and sodium acetate at 0.15M and p^H at 7.2. It is found that TritonX-100 suppressed the peak by 15-20 % initially upto the concentration of 0.002% and the wave height remained constant from 0.004% on words. The observations are presented in TABLE 3.

Effect of temperature

Temperature variation from 20-50°C on 3.2$\times10^{-4}$M Imidacloprid in 0.15M sodium acetate at p^H 7.2 was studied and found that temperature variation has little effect on the shape of the polarogram .The limiting current is increased by 2% per degree rise of temperature indicating diffusion controlled nature of the process.

Spectrophotometric results

Preparation of standard pesticide solution

100 mg of the Imidacloprid (Pure or equivalent formulation) was accurately weighed and dissolved in 20 ml methanol, after the substance was dissolved completely, it was treated with 10 ml 5N HCl and 4g of Zinc dust. The solution was allowed to undergo reduction by allowing it to stand for one hour. After one hour the solution was slowly filtered through cotton wool and the residue was washed with about 10-15 ml of water. The solution was finally made upto the mark in a volumetric flask. The final concentration of imidacloprid was brought to 100 µg/ml with methanol. The stock is furthered diluted to required concentrations of working pesticide solutions for methods A and B.

In case of formulations, an amount equivalent to 100 mg of the imidacloprid was shaken with 25 ml of methanol for 5 min and the mixture was centrifuged. The supernatant solution was filtered by decantation .The residue was extracted four times with 10 ml portions of methanol. The filtrate and extracts were combined and diluted to 100 ml with methanol and the dilution was carried out in the same manner as described for standard solution.

Method A

Aliquots of standard pesticide solution of Imidaclo-

Current Research Paper

TABLE 5 : Determination of Imidacloprid in spiked water samples (Tap water)

S. No.	Amount taken, ppm	D.C. polarography			Spectrophtometry		
		Amount found*ppm	Recovery %	Standard deviation	Amount found* ppm	Recovery %	Standard deviation
1	1.5	1.477	98.51	0.38	1.482	98.8	0.11
2	2.0	1.975	98.78	0.23	1.973	98.66	0.40
3	2.5	2.484	99.38	0.22	2.486	99.44	0.20
4	3.0	2.971	99.04	0.11	2.973	99.12	0.17

*Each value is an average of three determinations

TABLE 6 : Determination of Imidacloprid in formulations

Name of the formulation	Labeled amount ppm	D.C.polarograpy			Spectrophotometry		
		Amount found* ppm	Recovery (%)	Standard deviation	Amount found*ppm	Recovery (%)	Standard deviation
Confidar	4.0	3.87	96.83	1.42	3.86	96.5	1.32
	6.0	5.93	98.83	1.25	5.92	98.77	0.85
Gaucho	4.0	3.86	96.58	1.42	3.88	97.08	0.62
	6.0	5.78	96.44	1.66	5.78	96.33	1.62

*Each value is an average of three determinations

prid ranging from 0.1 to 1.2ml (1-12 μg/ml) were transferred to a series of 10 ml graduated tubes. To each tube 1 ml of 2, 2- bipyridyl solution was added followed by 1ml of ferric Chloride solution and the resulting solution was heated for 15 min at 100°C and cooled, finally 2 ml of orthophosphoric acid was added. The volume was made upto 10 ml with distilled water and the absorbance of the orange colored product was measured at 486 nm against the corresponding reagent blank. The amount of Imidacloprid was computed from the Beer- Lambert's plot.

The results obtained in this method were based on reduction of Fe^{+3} to Fe^{+2} followed by complex formation to form orange colored product that exhibited maximum absorption at 486 nm against the corresponding reagent blank.

Method B

Aliquots of standard pesticide solution of Imidacloprid ranging from 0.2 to 2.2 ml (2-22 μg/ml) were transferred to a series of 10 ml graduated tubes. To each tube ferric chloride (0.5% 1 ml), potassium ferricyanide (0.2%, 2 ml) were added and kept aside for 10 min. To these tubes conc. HCl (1N, 1 ml) was added and the absorbance of bluish green colored product was measured at 363 nm against the corresponding reagent blank. The amount of Imidacloprid was com-

puted from the Beer –Lambert's plot.

The results obtained in this method were due to redox reaction followed by complex formation between the pesticide, potassium ferricynide and ferric chloride to form a bluish green colored solution that exhibited maximum absorption at 363 nm against the corresponding reagent blank.

In order to ascertain the optimum wavelength the absorption spectra were scanned in the wave length region of 250-700 nm against a corresponding reagent blank. The reagent blank absorption spectrum of each method was recorded against distilled water. The concentration vs. absorbance plots of the systems are illustrated in figure 5 and 6.

For each method the optical characteristics such as absorption maximum, Beers law limits, molar absorptivity and Sandell's sensitivity for these methods are presented in TABLE 4.

Analysis of imidacloprid in spiked water samples and its formulations

100 ml of water sample is spiked with known concentration of the pesticide dissolved in methanol .The sample is extracted with trichloromethane and washed with 0.1M potassium carbonate solution and dried over anhydrous sodium sulphate. The organic phase was evaporated and the residue is dissolved in methanol in 50 ml flask. Known aliquot of the solution is taken and analyzed maintaining optimum condition. The amount of pesticide is determined from calibration graph and the results are shown in TABLE 5.

The above developed procedure was successfully employed for the determination of Imidacloprid in their formulations. The required quantity of Imidacloprid formulations (Confidar, Gaucho) corresponding to stock solution concentration of 1×10^{-2} M was accurately measured and transferred into a 100 ml flask and made up with methanol The assay results of Imidacloprid formulations are given in TABLE 6.

CONCLUSIONS

Imidacloprid, a neonicotinoid class of insecticide, and acts on the nicotine acetylcholine receptor and, therefore have specific activity against the insect nervous system. Imidacloprid exhibited two well –defined

Current Research Paper

diffusion controlled reduction waves in simple experimental conditions of 0.15M sodium acetate in 10% methanol at p^H 7.2. The irreversible nature of the d.c.polarographic reduction is identified by log plot graphs.

These results obtained are compared with spectrophotometric methods. Good recoveries and low relative standard deviations reflect the high accuracy and precision of the proposed method. Moreover, the method is simple, easy and inexpensive, thus making of an excellent tool for the determination of imidacloprid in pesticide formulations and spiked water samples.

REFERENCES

[1] C.Tomilin; 'The Pesticide Manual: A World Compendium', 12th Edition, British Crop.Protection Council, Farnha, United Kingdom, 591, 592, 959, 960 **(2000)**.

[2] H.J.Kim, S.Liu, Y.S.Keum, Q.X.Li; J.Agric. Food.Chem., **51**, 1823 **(2003)**.

[3] G.W.Ware; An Introduction to Insecticides, 3rd Edition, online http://impworld.umn.edu/chp-ters/ware.htm.

[4] D.Drobne, M.Blazic, C.A.M.Van Gestel, V.Leser, P.Zidar, A.Jemec, P.Trebse; Toxicity of Imidacloprid to the Terrestrial Isopod Porcellio Scaber (Isopoda, Crustacea), Chemosphere, **71**, 1326 **(2008)**.

[5] C.Cox; J.Pest.Ref., **21**, 15 **(2001)**.

[6] G.W.Ware, D.M.Whitacre; 'An Introduction to Insecticides', Meisterpro Information Resources, A Division of Meister Media Worldwide, 4th Edn., Willoughby, Ohio, USA, **(2004)**.

[7] T.Iwasa, N.Motoyama, J.T.Ambrose, M.R.Roe; Apis Mellifera.Crop., **23**, 371 **(2004)**.

[8] P.Jeschke, R.Nauen; 'Neonicotinoid Insecticides', In: L.Gilbert, K.Iatrou, S.S.Gill (Eds.); Comprehensive Molecular Insect Science, Elsevier, Amsterdam, **5**, 53-105 **(2005)**.

[9] H.Obana, M.Okihashi, K.Akustu, Y.Kitagawa, S.Hori; J.Agri.Food Chem., **50**, 4464 **(2002)**.

[10] A.Mandic, S.Lazic, Sz.Okresz, F.J.Gaal; Anal. Chem., **12**, 1134 **(2005)**.

[11] S.Seccia, P.Fidente, D.Montesano, P.Morrica; J.Chromatogr A, **115**, 1214 **(2008)**.

[12] H.Obana, M.Okihashi, K.Akutsu, Y.Kitagawa, S.Hori; J.Agri.Food Chem., **51**, 2501 **(2003)**.

[13] S.Seccia, P.Fidente, D.Barbini Attard, P.Morrica; Anal.Chim.Acta, **21**, 553 **(2005)**.

[14] V.Guzsvany, A.Madzgalj, P.Trebse, F.Gaal, M.Franko; Environ.Chem.Lett., **5**, 203 **(2007)**.

[15] N.R.De Erenchum, Z.G.De Balugera, M.A.Goicolea, R.J.Barrio; Anal.Chim.Acta, **349**, **(1999)**.

[16] E.Watanable, H.Eun, K.Baba, T.Arao, Y.Ishii, S.Endo, M.Ueji; J.Agri.Food Chem., **52**, 2756 **(2004)**.

[17] E.Watanable, H.Eun, K.Baba, T.Arao, Y.Ishii, S.Endo, M.Ueji; Anal.Chim.Acta, **45**, 521 **(2004)**.

[18] J.L.Vichez, M.C.Valencia, A.Navalon, B.Molinero-Morales, L.F.Cpitan-Vallvey; Anal.Chim.Acta, **439**, 299 **(2001)**.

[19] G.Quintas, S.Armenta, S.Garrigues, M.de la Guardia; J.Braz.Chem.Soc., **15**, 307 **(2004)**.

[20] A.Navalon, R.El- Khattabi, A.Gonzalez- Casado, J.L.Vilchez; Microchim.Acta, **130**, **(1999)**.

[21] A.Guiberteau, T.Galeano, N.Mora, P.Parrilla, F.Salinas; Talanta, **53**, 943 **(2001)**.

[22] V.Guzsvany, M.Kadar, Z.Papp, L.Bjelica, F.Gaal, K.Toth; Electroanalysis, **20**, 291 **(2008)**.

[23] A.Economou; Trends Anal.Chem., **24**, 344 **(2005)**.

[24] B.Claux, O.Vittori; Electroanalysis, **19**, 2243 **(2007)**.

[25] M.Rancan, G.A.Sabatini, G.Achilli, C.G.Galletti; Anal.Chim.Acta, **555**, 20 **(2006)**.