

Spectrophotometric Method for the Joint Determination of Micro Quantities of DDT and DDE

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A spectrophotometric method has been developed which permits the simultaneous determination of micro quantities of DDT and its degradation product, DDE. Results shown have been obtained by

applying the proposed method to solutions of cyclohexane containing known quantities of DDT and DDE. Satisfactory results have been obtained in the range between 0.5 and 20.0 p.p.m.

In the bibliography consulted were found a great number of methods for the determination of micro quantities of DDT. With the exception of gas chromatography (Henly *et al.*, 1966), there are few existing quantitative analytical methods which permit an easy and suitable determination of mixtures of DDT [1,1,1-chlorine-2,2,-bis(*p*-chlorophenyl) ethane] and of DDE [1,1-chlorine-2,2-bis(*p*-chlorophenyl) ethylene].

On studying the diffusion process of DDT on homoionic clay minerals, the authors developed a rapid and suitable analytical method which permitted the joint determination of DDT and DDE, as DDE is the principal decomposition product of DDT in the decomposition process of the latter on homoionic clay minerals (López-González and Valenzuela-Calahorro, 1968a, 1968b, and 1968c).

In view of the data existing in the bibliography on the absorption of UV radiation by DDT (Neal *et al.*, 1944) and by DDE (World Health Organization, 1961), the authors undertook to determine mixtures of micro quantities of these two substances analytically.

MATERIALS AND METHODS

The object of this work was the development of a rapid spectrophotometric method which would permit the determination of micro quantities of DDT retained in homoionic clay minerals. This problem is complicated by the fact that a part of the DDT retained in these minerals is partially degraded into DDE, the percentage of degradation depending on different factors. The quantitative separation of both compounds, when they are found in micro quantities, is practically impossible.

After preliminary tests, in which the pesticide retained by the clay was extracted with different organic solvents, spectroscopically pure cyclohexane was selected as the most suitable solvent for extraction.

Spectrophotometric investigations revealed that the spectral curves of DDT and of DDE show maximum absorption at

different wavelengths (Figure 1). These curves were obtained with a DU2 Beckman spectrophotometer using cells of 1-cm. path length. Maximum absorption of DDT occurs at 200, 225, and 238 $m\mu$; and that of DDE at 203 and 247 $m\mu$.

The DDT used, m.p. 110.0–110.5° C, was purified from a commercial insecticide (López-González and Valenzuela-Calahorro 1968a) and the DDE, m.p. 90.0–90.5° C, was obtained from DDT (López-González and Valenzuela-Calahorro, 1968a) which had previously been purified.

The application of the method of Knudson (Knudson *et al.*, 1940) to systems of two components which absorb radiations in the UV zone of the spectrum permits these systems to be classified in two groups. The first of them includes the systems of two components whose absorption bands do not interfere at all, or that such interference does not occur for the wavelengths (λ_α and λ_β) of maximum absorption of the components α and β .

In this case, supposing that α and β obey Beer's Law at

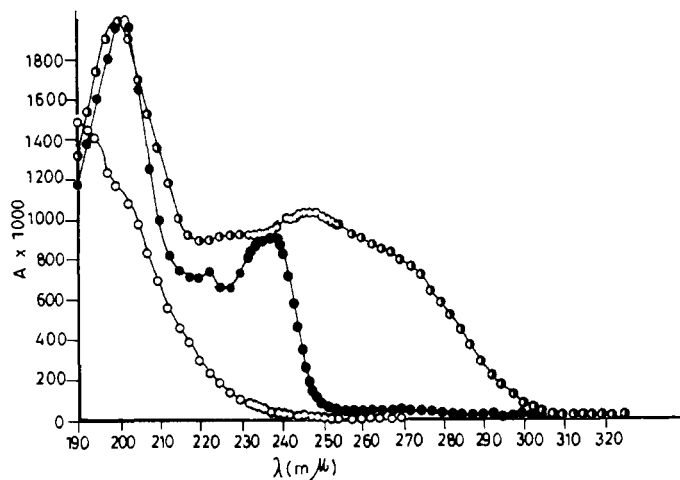


Figure 1. Absorption spectra

- C_6H_{12} (R.E.) Blank = distilled water
- p-p'-DDT (C = 16 p.p.m.) blank, C_6H_{12} (R.S.)
- p-p'-DDE (C = 16 p.p.m.) blank, C_6H_{12} (R.S.)

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Table I. Data for Standard Solutions

Conc; P.P.M.	A × 1000			
	DDT		DDE	
	λ = 238 mμ	λ = 247 mμ	λ = 238 mμ	λ = 247 mμ
0.1	13	8	0	0
0.2	22	7	14	18
0.4	23	6	24	27
0.6	33	8	35	39
0.8	45	19	46	62
1.0	55	22	58	65
2.0	125	33	120	130
4.0	225	42	230	252
6.0	345	75	356	390
8.0	451	85	465	510
10.0	552	112	579	634
12.0	660	144	710	780
14.0	762	172	810	884
16.0	910	185	940	1053
18.0	980	216	1022	1123
20.0	1108	226	1170	1272

λ_α and λ_β , respectively, the system can be determined by measuring the absorbance (A) at λ_α and λ_β and afterwards operating as if there were two independent solutions, one containing only α and the other only β .

The second group includes the systems of two components, α and β , such that α , whose maximum absorbance occurs at λ_α , absorbs also at λ_β , and vice versa.

To measure these systems, it is necessary that both α and β obey Beer's Law simultaneously at λ_α and λ_β and in that case.

$$A_{\lambda_\alpha} = K_{\lambda_\alpha}^\alpha C^\alpha + K_{\lambda_\alpha}^\beta C^\beta \quad (1)$$

$$A_{\lambda_\beta} = K_{\lambda_\beta}^\alpha C^\alpha + K_{\lambda_\beta}^\beta C^\beta \quad (2)$$

where A_{λ_α} and A_{λ_β} are the total absorbancies of the system at λ_α and λ_β , respectively. $K_{\lambda_\alpha}^\alpha$ and $K_{\lambda_\alpha}^\beta$ are the coefficients of extinction of α and β at λ_α ; $K_{\lambda_\beta}^\alpha$ and $K_{\lambda_\beta}^\beta$ are the coefficients of extinction of α and β at λ_β .

C^α and C^β are the concentrations of α and β in the solution which it is desired to determine.

As $K_{\lambda_\alpha}^\alpha$, $K_{\lambda_\beta}^\alpha$, $K_{\lambda_\alpha}^\beta$, and $K_{\lambda_\beta}^\beta$ can be previously determined, on substituting the average values of A_{λ_α} and A_{λ_β} in Equations 1 and 2, and determining the system formed by them, it is possible to determine C^α and C^β :

$$C^\beta = \frac{A_{\lambda_\alpha} \cdot K_{\lambda_\beta}^\alpha - A_{\lambda_\beta} \cdot K_{\lambda_\alpha}^\alpha}{K_{\lambda_\beta}^\alpha \cdot K_{\lambda_\alpha}^\beta - K_{\lambda_\alpha}^\alpha \cdot K_{\lambda_\beta}^\beta} \quad (3)$$

$$C^\alpha = \frac{K_{\lambda_\beta}^\beta \cdot A_{\lambda_\alpha} - K_{\lambda_\alpha}^\beta \cdot A_{\lambda_\beta}}{K_{\lambda_\beta}^\beta \cdot K_{\lambda_\alpha}^\alpha - K_{\lambda_\alpha}^\beta \cdot K_{\lambda_\beta}^\alpha} \quad (4)$$

RESULTS AND DISCUSSION

To determine whether DDT and DDE obey Beer's Law satisfactorily at $\lambda = 238$ mμ and at $\lambda = 247$ mμ, respectively, solutions of pure DDT and DDE in C_6H_{12} were prepared, whose concentrations vary between 0.1 and 20 p.p.m. The results obtained are shown in Table I.

The data in Table I show that both DDT and DDE solutions obey Beer's Law within a wide range of concentrations, that is, from approximately 0.5 p.p.m. up to concentrations higher than 20.0 p.p.m. (except in the case of DDE at $\lambda = 238$ mμ, in which case it does not obey this law above 16 p.p.m.).

In all cases, the determination of the coefficients of extinction of DDT and of DDE, both at 238 and at 247 mμ, was made following the method of the mean squares and using

Table II. Results on Synthetic Samples

Sample No.	Amts. Present, P.P.M.		A × 1000		Amts. Found, P.P.M.	
	DDT	DDE	λ = 238 λ = 247		DDT	DDE
			mμ	mμ		
1	5.0	0	277	63	4.9	0.1
2	4.5	0.5	278	85	4.5	0.5
3	4.0	1.0	280	112	4.0	1.0
4	3.5	1.5	281	138	3.5	1.5
5	3.0	2.0	282	164	3.0	2.0
6	2.5	2.5	283	185	2.6	2.4
7	2.0	3.0	285	217	2.0	3.0
8	1.5	3.5	286	244	1.5	3.5
9	1.0	4.0	288	280	0.8	4.2
10	0.5	4.5	290	297	0.5	4.5
11	0	5.0	291	318	0.1	4.9
12	14.0	0	775	164	14.0	0
13	12.6	1.4	779	239	12.6	1.4
14	11.2	2.8	783	312	11.2	2.8
15	9.8	4.2	787	387	9.8	4.2
16	8.4	5.6	790	460	8.4	5.6
17	7.0	7.0	795	535	7.0	7.0
18	5.6	8.4	798	609	5.6	8.4
19	4.2	9.8	803	683	4.2	9.8
20	2.8	11.2	806	757	2.8	11.2
21	1.4	12.6	810	831	1.4	12.6
22	0	14.0	814	905	0	14.0

only those data which obey Beer's Law. These coefficients were:

DDT, $K_{238} = 5.539 \times 10^{-2} A$ per μgram; $K_{247} = 1.171 \times 10^{-2} A$ per μgram.

DDE, $K_{238} = 5.812 \times 10^{-2} A$ per μgram; $K_{247} = 6.466 \times 10^{-2} A$ per μgram.

The substitution of these values in Equations 3 and 4 gives the following equations:

$$\text{DDT: } C = 20.036 (1.113 A_{238} - A_{247})$$

$$\text{DDE: } C = 4.036 (4.731 A_{247} - A_{238})$$

which give the concentrations of DDT and of DDE in a mixture of both, by only measuring the absorbancies.

From Table II, the proposed method apparently gives, in general, satisfactory results.

Of the 22 samples of known concentration in which the proposed method has been tested, only in four of them do differences of some ± 0.1 p.p.m., appear between the concentrations present in the solutions and those determined experimentally.

The data of Table II lead us to consider the method proposed as being satisfactory for the joint determination of microquantities of DDT and DDE.

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