PHOTOMETRIC DETERMINATION OF INDOLE COMPOUNDS IN THE FORM OF CHARGE TRANSFER COMPLEX

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A photometric method is developed for the quantitative analysis of indole nucleus compounds with 2,6-dichloroquinone-4-chlorimide in the form of charge transfer complex (CTC). The method is simple and suited for routine quantitative analysis of indole compounds. Each determination can be performed approximately in 60 min.

INTRODUCTION

The high capacity of indoles to form charge transfer complexes with various electron acceptors are well established [1–5]. Indoles form coloured solution with good acceptors. The colour formed with indoles is undoubtedly due to complex formation [6]. Coloured reaction [7,8] is available for analysis and identification of indole compounds. But the charge transfer complexes of indole compounds are not used in quantitative determination through photometric method. The development of photometric procedure seems to be a prospective method to determine indole compounds especially in the form of charge transfer complexes. Indole compounds being good electron donor [9] can easily interact with strong acceptor like 2,6-dichloroquinone-4-chlorimide to form charge transfer complex. The mentioned six indole compounds have not been photometrically determined in the form of CTC before. Complex composition is also studied and is found to be in the ratio of 1:1, which is useful for analytical purpose. The indole compounds can be quantitatively determined in the presence of other indole compounds which do not form coloured complexes. This simple method is suitable for routine analysis because it does not involve lengthy process and harsh technique. The method is simple and less time-consuming.

EXPERIMENTAL

Material. Freshly prepared (i) 2,4-dichloroquinone-4-chlorimide solution (4.2 g/l in isopropanol, $10^{-3}M/l$). (ii) Indole compounds were taken either directly from industry or synthesized in the laboratory (purity was tested by taking m.p. and TLC). Table 1 shows the condition for the

Table 1. Condition for the formation of indole complexes with 2,6-dichloroquinone-4-chlorimide.

Indole compound	Wt. of the substance (mg)	Access of reagent (M)	Concn of the substances $(10^3 M/l)$
Indole	117.0	2	2.00
2-Methylindole	65.5	4	1.00
2,3-Dimethylindole	100.0	3	1.38
2,3,6-Trimethylindole	58.0	7	0.37
2,3-Dimethyl-5-methoxyindole	70.0	4	0.80
2,3-Dimethyl-6-methoxyindole	70.0	5	0.80
2,3-Dimethyl-7-methoxyindole	70.0	4	0.80

formation of coloured compound (CTC).

Method of Analysis. Dissolve X mg of the indole nucleus compound in ethanol or isopropanol as the case may be in 50 ml measuring flask (flask No. 1). Pipette out 1–6 ml of the indole compound solution from flask No.1 into 10-ml volumetric measuring flask saparately. Add 4.00 ml reagent solution in each flask. Shake well each flask for the formation of coloured solution. Keep the solution for a few minutes at room temperature (for stable coloured solution) and then make up the volume with ethanol or isopropanol as the case may be. Measure optical density of the solution with photoelectric colorimeter FEK-56-2 with coloured filter No. 5 (λ_{max} 490 nm), 3 (λ_{max} 400 nm), 6 (λ_{max} 540 nm) in a cuvett 2-cm,1 and 7 (λ_{max} 582 nm). For comparison the reagent solution was used. Calibration curves were determined individually for each indole com-

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pounds solution. Absorbance spectra of each coloured solution was measured with spectrophotometer CEK-10 and molar extinction coefficient (ϵ) was also found as follows:

$$\epsilon = A/C.l$$

where ϵ, molar extinction coefficient; A, optical density; C, concentration of the solution, mole/l, l, length of the absorbing solution (the cuvett layer thickness), cm.

Statistical Treatment of the Result. A fixed quantity of each solution (in ml) was taken in six different 10-ml volumetric microflask and optical density was determined as mentioned earlier with the different values of optical density A_1, A_2, A_3, ----- A_6 in the calibration curve, the concentration of the solution was calcualted.

Calculation

n = No. of variant

$$\overline{X} = \frac{1}{n} \Sigma X_i \quad - \quad \text{Average variant}$$

Table 2. Determination of complex composition by isomolecular series.

Molecular ratio Substance/Reagent	1:9	3:7	5:5	7:3	9:1
Optical density					
Indole *	0.14	0.30	0.37	0.33	0.14
2,3-Dimethylindole †	0.37	0.81	0.89	0.80	0.37

*Indole in isopropanol: $1 = 2$ cm, λ_{max} 490 nm.
†2,3-Dimethylindole in isopropanol: $1 = 2$ cm, λ_{max} 582 nm. Measurement time 3–10 min.

$$S = [\frac{1}{n-1} \Sigma (\overline{X} - X_i)^2]^{1/2} - \text{Standard deviation}$$

$$S_r = S/\overline{X} - \text{Relative standard deviation}$$

Determination of Complex Composition

Method of Isomolecular Series. With the help of isomolecular series [10] method the complex composition was determined with the reagent 2,6-dichloroquinone-4-chlorimide. Results of indole and 2,3-dimethylindole are given in the Table 2.

Determination of Indole Compounds in Presence of Mixture. 2,3-Dimethylindole compound was determined in presence of other indole compound which did not form coloured complexes with 2,6-dichloroquinone-4-chlorimide. 2,3-Dimethylindole can be quantitatively determined in presence of tryptaphane and 2-methyl-3,7-diphenylindole (Table 3).

RESULTS AND DISCUSSION

The purpose of study was to develop a new method of analysis of indole nucleus compounds in the form of charge transfer complexes (CTC). Photometric method was used to quantitative determination of the indole compounds having CH_3- and CH_3O- group attached in benzene ring or in pyrrole ring. Results show that the method is precise, accurate and simple. The method is suitable for all indole compound which form stable coloured complexes with a good acceptor like 2,6-dichloroquinone-4-chlorimide.

By the interaction of indole and its compound with 2,6-dichloroquinone-4-chlorimide form complex of different colour (Table 4).

Indole compounds and 2,6-dichloroquinone-4-chlori-

Table 3. Determination of 2,3-dimethylindole in presence of tryptaphane and 2–methyl-3,7-diphenylindole.

Concn of 2,3-dimethyl- indole ($10^{-4}M/l$)	Optical activity	Concn of 2,3-dimethyl- indole + tryptaphane ($10^{-4}M/l$)	Optical activity	Concn of 2,3-dimethyl- indole + 2-methyl-3,7- diphenylindole ($10^{-4}M/l$)	Optical activity
27.6	0.29	27.6+4.8	0.28	+6.8	0.29
34.5	0.34	34.5+3.0	0.33	+5.9	0.33
41.4	0.39	41.4+3.6	0.39	+5.1	0.37
48.3	0.45	48.3+4.2	0.44	+4.2	0.44

$1 = 2$ cm, λ_{max} 582 nm, reagent concentration (20×10^{-4} M/l).

Table 4. Characteristics of indole complexes with 2,6-dichloroquinone-4-chlorimide.

Indole compound	Colour produced	Appearance of colour (min)	Stability of colour (min)	ϵ
Indole	Pink	At once	30	20
2-Methylindole	Brownish yellow	,,	3–40	37
2,3-Dimethylindole	Dark greenish black	,,	3–30	45
2,3,6-Trimethylindole	Greenish	,,	5–30	83
2,3-Dimethyl-5-methoxyindole	Greenish with bluishtint	,,	3–30	71
2,3-Dimethyl-6-methoxyindole	Green with blue tint	,,	3–30	66
2,3-Dimethyl-7-methoxyindole	Blue with black tint	,,	5–30	61

mide were taken in the ratio of 1:1 in isopropanol or in ethanol. The coloured complex solution of indole compound was obtained as in Table 4. Optical activity of the coloured solution was measured in a cuvette 2-cm and the reagent 2,6-dichloroquinone-4-chlorimide was used for comparison. Results show that indole coloured complexes are stable (Table 4). The stability of the coloured complexes is not less than 25 min. (i.e. the optical density of the indole complex solution practically does not change with the variation of time). The 25-min stability of the complex solution is quite enough for analytical purpose.

Absorption spectra of the coloured indole complexes was taken from the spectrophotometer CEF-10 in the region of 400–750 nm. The maximum absorption spectra of indole itself was found near 490 nm. There is a slight change in the absorption spectra when CH_3-group introduced at position 2 in the indole nucleus, but marked increase (Fig. 1) in absorption spectra when CH_3– group introduced in position 2 and 3. The maximum absorption spectra

of 2,3-dimethylindole was 480–620 nm. Further introduction of CH_3–group within pyrrole nucleus or in benzene nucleus will more expand the absorption spectra towards long wavelength.

In methoxyindole complexes the characteristics of absorption spectra depend upon the position of CH_3O-group in the nucleus, which more likely indicate the structure of complex itself, as the absorption spectra of the observed compounds are very close to each other. In 5-methoxyindole complex one can observe very sharp increase in absorption intensity in the region of 480–620 nm. (Fig. 2) which is characteristic for charge transfer complex [4,11,12].

Isomolecular series method was used for the determination of complex composition of indole compound with 2,6-dichloroquinone-4-chlorimide and was found in the 1:1 ratio – the ratio is generally suitable for quantitative analysis work. So this ratio allowed for the first time, a complex quantitative of indole nucleus compound in the form
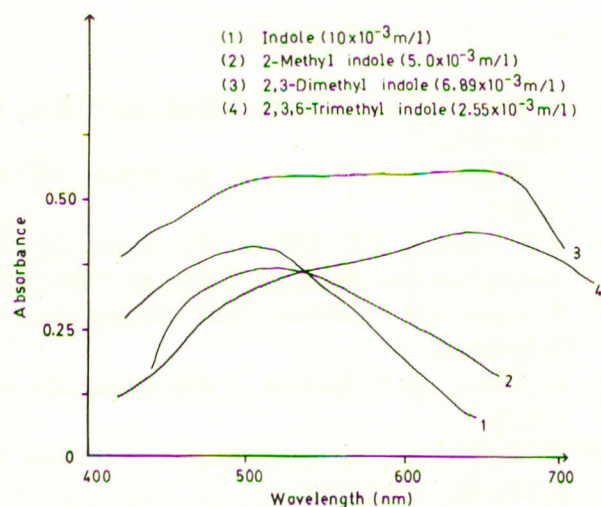
(1) Indole $(10 \times 10^{-3}$ m/1$)$
(2) 2-Methyl indole $(5.0 \times 10^{-3}$ m/1$)$
(3) 2,3-Dimethyl indole $(6.89 \times 10^{-3}$ m/1$)$
(4) 2,3,6-Trimethyl indole $(2.55 \times 10^{-3}$ m/1$)$

(5) 2,3-Dimethyl-5-methoxy indole $(4.0 \times 10^{-3}$ m/1$)$
(6) 2,3-Dimethyl-6-methoxy indole $(3.2 \times 10^{-3}$ m/1$)$
(7) 2,3-Dimethyl-7-methoxy indole $(4.0 \times 10^{-3}$ m/1$)$

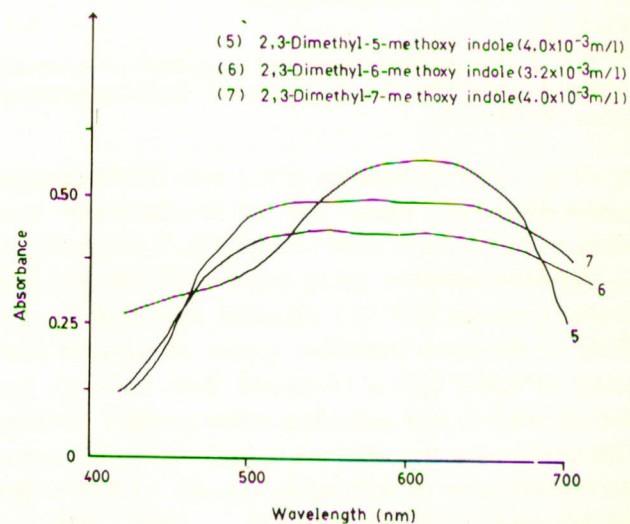Fig. 1. Determination of λ_{max} of various indoles compounds used in present investigation.

Fig. 2. Determination of λ_{max} of various indoles compounds used in present investigation.

Table 5. Determination of indole compound with 2,6-dichloroquinone-4-chlorimide.

Indole compound	Given $(10^{-4}M)$	Observed $(10^{-4}M)$	S	S_r
Indole	8.00	8.02	0.370	0.0460
2-Methylindole	3.00	3.10	0.031	0.0102
2,3-Dimethylindole	5.51	5.49	0.091	0.0167
2,3,6-Trimethylindole	1.82	1.78	0.035	0.0200
2,3-Dimethyl-5-methoxyindole	2.40	2.45	0.032	0.0133
2,3-Dimethyl-6-methoxyindole	2.40	2.55	0.122	0.0470
2,3-Dimethyl-7-methoxyindole	2.40	2.49	0.065	0.0262
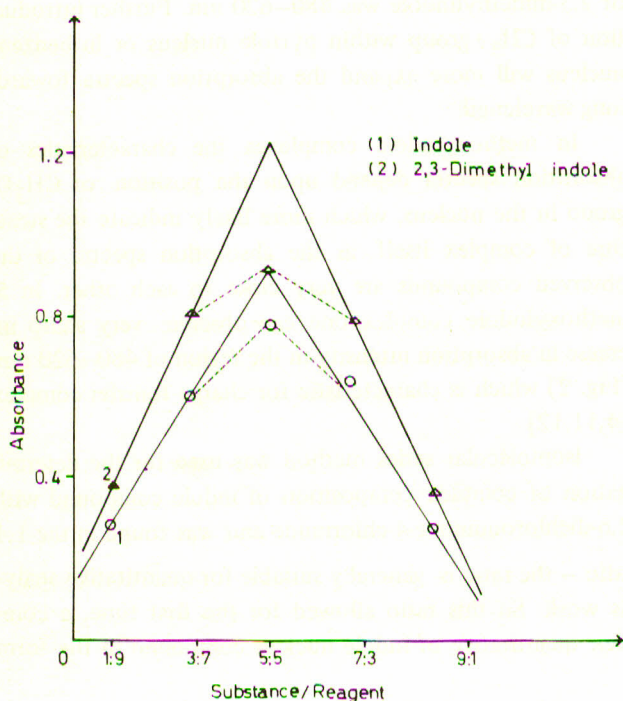
Fig. 3. Determination of complex composition of indole and 2,3-dimethylindol with 2,6-dichloroquinone-4-chlorimide by isomolecular series method.

of charge transfer complexes (CTC) with 2,6-dichloroquinone-4-chlorimide. Indole and 2,3-dimethylindole were taken as an example to show 1:1 ratio (Fig. 3) of complexes.

Spectrophotometer CF-10 (region 400–470 nm) and photocolorimeter FEK-56-2 (Russian) were used for the study of maximum absorption spectra of coloured complexes of indole nucleus compound. Beer—Lambert's law was observed in each individual indole complex solution. Calibration curve was observed in each case to determine the concentration of each indole complex solution under the following wavelength: indole (λ_{max} 490); 2-methylindole (λ_{max} 400 nm); 2,3-dimethylindole (λ_{max} 582 nm); 2,3,6-dimethylindole (λ_{max} 582 nm); 2,3-dimethyl-5-

methoxyindole (λ_{max} 582 nm); 2,3-dimethyl-6-methoxyindole (λ_{max} 582 nm); and 2,3-dimethyl-7- methoxyindole (λ_{max} 582 nm).

At the time of analyses each indole compound was characterised by its m.p. and tested individually by TLC. Results of the analysis of indole compounds are given in the Table 5.

Statistical values clearly prove that the result of analysis of indole compounds with 2,6-dichloroquinone-4-chlorimide in the form of charge transfer complexes are quite satisfactory. Therefore, the proposed method of analysis may be recommended for the quantitative determination of all indole compounds which form complexes with good acceptors like 2,6-dichloroquinone-4-chlorimide. The present method also had the advantage of determining the indole compound in presence of other indole compounds which did not form coloured complex with 2,6-dichloroquinone-4-chlorimde.

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