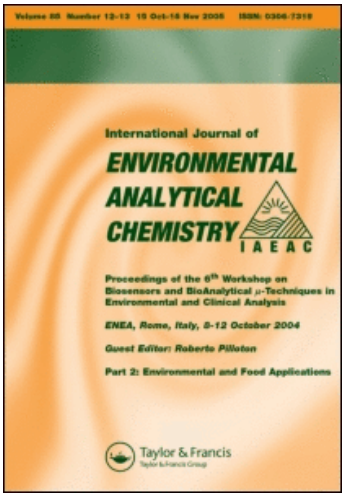

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Spectrophotometric Determination of Primaquine, Chloroquine, 8-Aminoquinoline and 4-Aminoquinalidine with Chloranil

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Spectrophotometric Determination of Primaquine, Chloroquine, 8-Aminoquinoline and 4-Aminoquinalidine with Chloranil

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Primaquine, Chloroquine, 8-aminoquinoline and 4-aminoquinalidine form molecular complexes with chloranil at pH 9. The composition and stability of these complexes have been studied spectrophotometrically. The results indicate that all complexes were of 1:1 type. The method of complexation was used to determine a ppm amount of the intended compounds in solution spectrophotometrically.

KEY WORDS: Primaquine, Chloroquine, 8-aminoquinoline, 4-aminoquinalidine, Chloranil, Charge-transfer complexes, spectrophotometry.

INTRODUCTION

In spite of the importance of primaquine diphosphate (PQ), chloroquine diphosphate (CQ), 8-aminoquinoquinoline (8AQ) and 4-aminoquinalidine (4AQ), especially PQ and CQ as antimalarial drugs, few methods[1,2,3] have been reported for their determination.

However, some of these methods are applicable to macro amounts only, whilst the others might be not applicable to all these compounds.

The formation of molecular (charge-transfer) complexes has been used for the spectrophotometric determination of nitrogen containing organic compounds, such as aliphatic and aromatic amines,[4,5] amino acids,[6,7] and isonicotinyl, nicotonoyl and piconoylhydrazines with chloranil.[8]

This paper describes the reaction of chloranil with PQ, CQ, 8AQ and 4AQ. The stability constants and composition of the complexes of chloranil with these species were determined and used for their quantitative determination. The results obtained are accurate and precise.

EXPERIMENTAL

Apparatus

All absorption measurements were carried out using SP 30 UV Spectrophotometer, using 1-cm silica cells. All pH measurements were made using Sargent Model NX pH-meter.

Reagents

All chemicals used were of A.R. grade quality, and all preparations were made in distilled water.

Standard solutions of primaquine diphosphate, chloroquine diphosphate, 8-aminoquinoline and 4-aminoquinalidine. Aqueous solutions of concentrations 1×10^{-3} M were prepared by dissolving 0.11385 g, 0.12898 g, 0.0365 g, or 0.03950 g of each compound in 250 ml distilled water. Less concentrated solutions were made by dilution.

Ethanolic chloranil solution (1×10^{-3} M), and borate buffer solution (5×10^{-2} M) of pH 9 were prepared.

Procedure

For calibration: To a series of 25 ml calibrated flasks, introduce a suitable volume of sample solution containing 0.4–40 ppm of PQ,

CQ, 8AQ or 4AQ. Add 5 ml of borate buffer solution (5×10^{-2} M) of pH 9, 5 ml of chloanil solution (1×10^{-3} M), and complete to the mark with water. Stopper the flasks and heat in a water bath at 65 ∓ 2°C for 20 min. Cool to room temperature and measure the absorbance against the blank solution at 305 nm (at 298 nm for chloroquine). Plot the absorbance versus the concentration of the studied species. From this plot the concentration of the unknown samples could be obtained. The blank solution was handled following the procedure but containing no analyte.

RESULTS AND DISCUSSION

The colour reactions of PQ, CQ, 8AQ and 4AQ with chloranil were carried out at pH 9, which has previously been found to be optimum for amines,[4] amino acids[6] and hydrazines.[8] The reaction of the studied compounds with choranil is slow at room temperature, but at 65°C, maximum absorbance is obtained within 20 min. The complexes gave a wavelength of maximum absorption at 305 nm (298 nm for chloroquine).

The composition of the chloranil-PQ, CQ, 8AQ or 4AQ complexes were established by the mole ratio method. The results indicate that all the complexes were of 1:1 type.

The effects of the reagent concentrations were also investigated, and it was found that 5 ml of pH 9 buffer solution and 5 ml of choranil were optimum. The order of addition of reagents was of no consequence.

The apparent stability constants[9] were determined by measuring the absorbance of a solution containing stoichiometric amounts of PQ, CQ, 8AQ or 4AQ and chloranil, to one containing a tenfold excess of chloranil, under the optimum reaction conditions e.g.: The stability constant of primaquine was calculated as follows: Sample I: contains 0.5 ml of 1×10^{-3} M primaquine, 5 ml of buffer solution and 0.5 ml of 1×10^{-3} M chloranil, then the sample was diluted with water to 25 ml in a calibrated flask. Sample II: was prepared as in Sample I, except that it contains 5 ml of 1×10^{-3} M chloranil.

The absorbance was recorded for each sample following the recommended procedure.

A_1 for sample $I = 0.096$, A_2 for sample II $= 0.409$

$\alpha = A_2 - A_1$ (A is absorbance)
$= 0.409 - 0.096$ (α is the degree of dissociation)
$= 0.313$

$1 - \alpha = 1 - 0.313$; $C = 0.02 \times 10^{-3}$ M concentration of primaquine
$= 0.687$

$$\text{Stability constant, } K = \frac{1-\alpha}{\alpha^2 C}$$

$$= \frac{0.687}{1.9594 \times 10^{-3} \times 0.02 \times 10^{-3}}$$

$$= 3.5 \times 10^{-5} \text{ liter mole}^{-1}$$

The rapid, initial colour development is $n-\pi$ charge-transfer complex formation followed by slow conversion to the Schiff's base.[5] The colour formation was found to stand for more than 24 hours.

Beer's law was obeyed over the ranges indicated in Table I. A slight positive intercepts on the absorbance axis were obtained on extrapolation to zero concentrations.

The wavelengths of PQ, CQ, 8AQ and 4AQ in a borate buffer solution of pH 9 but without chloranil were: 250, 226, 246 and 240 nm, respectively. It was found that the sensitivity of the determinands–chloranil complexes is about 20 times that of the pure compounds.

TABLE I
Wavelengths, stability constants and molar absorptivities of PQ-, CQ-, 8AQ- and 4AQ-chronanil complexes.

Compound	λ max (nm)	Stability constant (liter . mole^{-1})	E^a (liter mole^{-1} cm^{-1})
Primaquine diphosphate	305	3.5×10^5	20,000
Chloroquine diphosphate	298	3.9×10^8	11,538
8-Aminoquinoline	305	2.8×10^6	7,273
4-Aminoquinalidine	305	4.3×10^5	1,000

[a]Calculated from calibration graphs.

Experimental results showed that ethanol has no significant effect on the complex formation and stability constants, since its amount is fixed in all experiments.

Accuracy and Precision. The accuracy and precision of the method under the optimized conditions were checked. The results (5 replicates) are compiled in Table II, and indicate a reliable method.

TABLE II
Accuracy and precision of the method (5 replicates).

Compound	Amount taken ppm	Recovery, %	Coefficient variation, %	Correlation coefficient, *R*
Primaquine diphosphate	0.4	96.9	1.8	0.9981
	20.0	99.1	0.9	
	36.0	99.7	0.5	
Chloroquine diphosphate	1.0	97.2	2.9	0.9971
	20.6	98.8	1.3	
	41.0	100.0	0.7	
8-Aminoquinoline	1.1	97.9	3.2	0.9975
	10.4	100.1	1.9	
	29.0	99.5	0.8	
4-Aminoquinaldine	1.2	100.2	2.7	0.9991
	12.6	99.1	2.0	
	31.0	99.8	0.6	

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