The Solvent Extraction-Spectrophotometric Determination of Perchlorate Ions with Monoethynolog of Malachite Green[1)]

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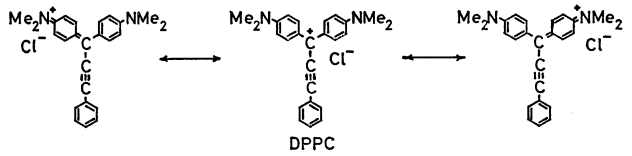
Synopsis. By the use of a new reagent, 1,1-bis(*p*-dimethylaminophenyl)-3-phenyl-2-propynylium chloride, *i.e.*, one of the ethynologs of Malachite Green, micro amounts of perchlorate ions could be extracted into chlorobenzene and determined spectrophotometrically. Beer's law holds over the range of 4×10^{-6}—2.5×10^{-5} M (M=1 mol dm^{-3}); $\varepsilon=4.0\times10^{4}$ dm^3 mol^{-1} cm^{-1} at 690 nm.

The study of the synthesis and the properties of the ethynologs of triphenylmethane dyes has been developed and has demonstrated that the introduction of an acetylenic bond into such a classical dye system causes a large bathochromic shift in the longest wavelength.[2)]



For the application of the effect to analytical chemistry, one of the monoethynologs of Malachite Green, *i.e.*, 1,1-bis(*p*-dimethylaminophenyl)-3-phenyl-2-propynylium chloride (DPPC), was newly prepared and examined in order to determine micro amounts of perchlorate ions by means of solvent-extraction spectrophotometry.[3)]

Experimental

Apparatus. The spectrophotometric measurements were made with Shimadzu UV-300 and UV-150 spectrophotometers.

Materials. *Synthesis of DPPC.* Dried hydrogen chloride was bubbled through a solution of 1,1-bis(dimethylaminophenyl)-3-phenyl-2-propyn-1-ol[2)] (0.500 g, 0.0014 M) in toluene (150 ml) for 15 min. The resulting dark green solution was concentrated *in vacuo* to give crude crystals, which were then recrystallized from the same solvent: deep green crystals,[4)] 0.439 g, 81%; mp 85 °C.

Found; C, 67.76; H, 6.72; N, 5.73%. Calcd for $C_{25}H_{25}N_2Cl\cdot3H_2O$; C, 67.80; H, 7.01; N, 6.33%. MS (*m/e*): 353 (M−Cl$^-$); UV λ (H_2O) 645 nm (ε=18500).

Buffer (Potassium Phosphate Solution). Various kinds of pH solutions were made by the use of potassium dihydrogenphosphate (1 M), sulfuric acid (0.1 M), and sodium hydroxide (1 M).

Solvents. Chlorobenzene was purified by distillation. All the other reagents were of an analytical grade and were used without further purification.

Procedure. Place an aliquot of the standard potassium perchlorate solution (1×10^{-5}—6.25×10^{-4} M) into a 25-ml calibrated flask. Add 5 ml of a potassium phosphate buffer (1 M, pH 3.5) and 2 ml of a DPPC aqueous solution (1×10^{-3} M). Dilute the solution to the mark with distilled water. Take 10 ml of the above solution, transfer it into a 100-ml separatory funnel, and shake with 10 ml of chlorobenzene for 3 min. Filter the organic layer after 15 min and measure the absorbance at 690 nm in a 1-cm cell against the reagent blank or chlorobenzene as a reference.

Results and Discussion

The absorption spectra of the chlorobenzene extract containing the ion pair obtained by the above procedure are shown in Fig. 1. The wavelength of the maximum absorption occurs at 690 nm.

The effect of the pH value on the absorbance was examined in the range of pH 0.5 to 10. As is shown in Fig. 2, constant absorbances were obtained in the pH region from 2 to 4, from which the buffer solution of pH 3.5 was used.

The concentration of DPPC to 1.6×10^{-5} M of perchlorate was confirmed by using 8×10^{-5} M for the determination.

The effect of the shaking time in the extraction was examined to give a constant absorbance from 2 to 10 min.

The absorbance of the extract of perchlorate did not change at all for 1 h.

Various organic solvents (chlorobenzene, benzene, nitrobenzene, toluene, chloroform, 1,2-dichloroethane, and carbon tetrachloride) were tested for the extrac-

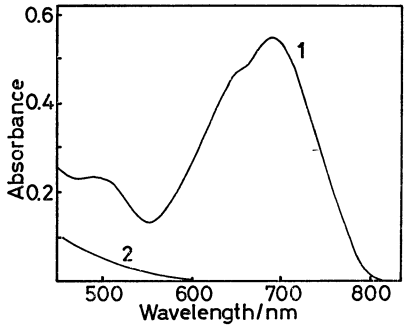


Fig. 1. Absorption spectra of 1,1-bis(*p*-dimethylaminophenyl)-3-phenyl-2-propynylium perchlorate (DPPP). 1: DPPP complex against chlorobenzene, 2: reagent blank against chlorobenzene, ClO_4^-: 1.4×10^{-5} M.

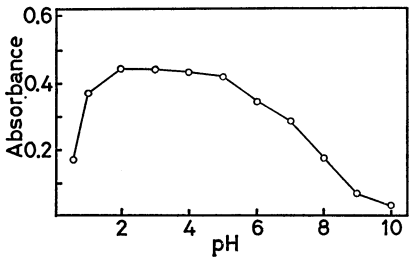


Fig. 2. Effect of pH. ClO_4^-: 1.2×10^{-5} M.

Table 1. Effects of diverse ions

Ion	Added as	Concentration/M	Absorbance
None	—	—	0.425
ClO_3^-	$KClO_3$	1.2×10^{-4}	0.422
BrO_3^-	$KBrO_3$	1.2×10^{-4}	0.434
IO_3^-	KIO_3	1.2×10^{-4}	0.457
IO_4^-	KIO_4	1.2×10^{-6}	0.418
Cl^-	KCl	1.2×10^{-3}	0.435
Br^-	KBr	1.2×10^{-3}	0.433
I^-	KI	1.2×10^{-6}	0.438
NO_3^-	$NaNO_3$	1.2×10^{-5}	0.420
SCN^-	KSCN	1.2×10^{-6}	0.423
SO_4^{2-}	Na_2SO_4	2.4×10^{-5}	0.427

ClO_4^- added: 1.2×10^{-5} M.

tion. Subsequently, chlorobenzene was chosen because it showed a small blank value and the largest absorbance difference at 690 nm between the ion pair and the blank.

On the basis of the above results, a standard procedure was evolved, by which the linear calibration graph was obtained in the range from 4×10^{-6} to 2.5×10^{-5} M of perchlorate. The practical absorptivity was 4.0×10^4 dm^3 mol^{-1} cm^{-1}. The coefficient of variation for the ten replicated experiments was satisfactory (2.20% for 1.6×10^{-5} M of perchlorate).

The interferences due to various ions were also examined, as is shown in Table 1. The periodate, iodide, and thiocyanate caused considerable errors. It is worth noting that the characteristic larger red shift (*ca.* 100 nm) due to the effect of an acetylenic bond larger than Crystal Violet[3] has been observed. The absorptivity was about one-half of that for Crystal Violet; however, the sensitivity and the reproducibility were quite good in this method. DPPC is useful enough as an analytical reagent for perchlorates.[5]

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References

1) Development and Application of Organic Analytical Reagents, Part II. Part I: S. Nakatsuji, R. Nakano, M. Kawano, K. Nakashima, and S. Akiyama, *Chem. Pharm. Bull.*, **30**, 2467 (1982).

2) S. Akiyama, K. Yoshida, M. Hayashida, K. Nakashima, S. Nakatsuji, and M. Iyoda, *Chem. Lett.*, **1981**, 311.

3) For the related works using cationic triphenylmethane dyes, see a) S. Uchikawa, *Bull. Chem. Soc. Jpn.*, **40**, 798 (1967); b) S. Motomizu, S. Fujiwara, and K. Tôei, *Anal. Chem. Acta*, **128**, 185 (1981).

4) The chloride was found to be very hygroscopic; this fact was also demonstrated with the elemental-analyses data.

5) Good recovery yields were obtained in the determination of perchlorates by using the above calibration graph: $NaClO_4$(recovery yield, 103.6%; standard deviation, 0.91; $n=5$), NH_4ClO_4(102.5%; 1.05; 5), and 60% $HClO_4$(98.6%; 1.34; 5).