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Azine Dyes as Iodometric Indicators

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Methods involving the use of five azine dyes, phenosafranine, methylenev iolet, amethyst violet, safranine (colour index Nos 50200, 50210, 50225 and 50240 respectively) and aposafranine in the direct and reverse titrations of iodine with thiosulphate, arsenic(III), ascorbic acid and hydrazine have been developed. The method has been applied for the determination of ascorbic acid in vitamin C tablets (Redoxon, Celin, Sukcee and Chewcee) and the results are in excellent agreement with those obtained by the official method.

A NUMBER of dyes have been used recently as indicators in the iodine-thiosulphate and iodine-arsenic(III) titrations[1-7]. Variamine Blue[1] 2-Oxyvariamine Blue[8], and 2,6-dichlorophenol-indophenol[9] have been proposed as indicators in the iodine-ascorbic acid titration. In the titration of hydrazine with iodine, Kolthoff[10] and Tolstikov *et al.*[11] state that starch cannot be used as indicator since the hydrazine-iodine reaction is inhibited by starch. From a survey of the literature, we find that till now no indicator has been proposed for the titration of hydrazine with iodine.

This note describes the use of azine dyes, phenosafranine, methylene violet, amethyst violet, safranine (colour index Nos 50200, 50210, 50225 and 50240 respectively) and aposafranine as indicators in the direct and reverse titrations of thiosulphate, arsenic(III), ascorbic acid and hydrazine with iodine. Apart from the advantages of easy availability, relative cheapness and stability of the aq. solutions, mention may be made of the fact that the reported methods[1,8,9] for the ascorbic acid- iodine titrations using variamine blue, 2-oxyvariamine blue and 2,6-dichlorophenol-indophenol employ 0·1*N* solutions, whereas the present method can be applied for titrations involving 0·01*N* solutions also. Moreover, the present method describes the use of these indicators in the iodometric titration of hydrazine or vice versa, for the first time.

All the chemicals used were of reagent grade. Approximately 0·1*N* solution of I_2 (in 2% KI) was prepared from resublimed I_2 (S. Merck grade) and standardized against As(III) solution. 0·1*N* solutions of sodium thiosulphate (BDH), ascorbic acid (S. Merck) and hydrazine sulphate (BDH) were prepared and standardized. The ascorbic acid solution was prepared in deionized water and EDTA added as stabilizer. 0·01*N* solutions were also prepared by suitably diluting the 0·1*N* solutions with deionized water as and when necessary. 0·1*N* solution of arsenic(III) was prepared from As_2O_3 (E.Merck, pro analysi).

TABLE 1 — IODOMETRIC DETERMINATION OF THIOSULPHATE, ARSENIC(III), ASCORBIC ACID AND HYDRAZINE

Amount of substance taken (mmoles)	Amount of substance found (mmoles) using				
	Phenosafranine	Methylene violet	Amethyst violet	Safranine	Aposafranine
THIOSULPHATE					
0·04100	0·04120	0·04100	0·04120	0·04120	0·04100
0·09225	0·09226	0·09225	0·09245	0·09237	0·09237
0·5125	0·5135	0·5125	0·5125	0·5115	0·5125
0·8200	0·8210	0·8220	0·8190	0·8200	0·8200
ARSENIC(III)					
0·0400	0·0396	0·0400	0·0404	0·0400	0·0404
0·0800	0·0798	0·0800	0·0802	0·0800	0·0802
0·5000	0·5020	0·4980	0·4980	0·4980	0·5020
0·9000	0·8980	0·9020	0·9000	0·8980	0·9020
ASCORBIC ACID					
0·03956	0·03950	0·03956	0·03968	0·03968	0·03950
0·06923	0·06939	0·06939	0·06939	0·06939	0·06918
0·4945	0·4965	0·4935	0·4945	0·4945	0·4943
0·7912	0·7925	0·7916	0·7925	0·7925	0·7910
HYDRAZINE					
0·04980	0·04982	0·04982	0·05000	0·05000	0·04982
0·06972	0·06985	0·06968	0·06985	0·06985	0·06985
0·5976	0·5960	0·5960	0·5980	0·5980	0·5980
0·7968	0·7960	0·7964	0·7966	0·7960	0·7960

The dyes phenosafranine (Fluka grade), methylene violet, amethyst violet, safranine and aposafranine (Gurr grade) were used without further purification. Their 0·01% solutions were prepared in doubly distilled water. The indicator action of these dyes was retained for 8-9 months.

General procedure — An aliquot of 0·1*N* iodine solution was taken in a 250 ml iodine flask, diluted to 50 ml, indicator solution (0·2-0·6 ml) added and the mixture titrated against 0·1*N* sodium thiosulphate. The colour changes at the end points are: pale orange-red to pink with phenosafranine, methylene violet, amethyst violet and aposafranine, and pale orange-red to pale pink with safranine. The results obatained are given in Table 1.

The titration can also be performed using arsenic (III), ascorbic acid, or hydrazine sulphate in place of sodium thiosulphate. But in titrations with arsenic(III) and hydrazine sulphate, 0·5-1·0 g of $NaHCO_3$ should be added to the titration mixture so as to maintain the *p*H of the solution between 5 and 9.

The sharpness of the end points and the values obtained with the indicators now proposed are not vitiated by the presence of 20% NaCl or 50% ethanol in the titration of sodium thiosulphate and arsenic-(III). But in the titration of hydrazine, NaCl does not interfere whereas ethanol interferes. While titrating ascorbic acid with iodine, both NaCl and ethanol do not interfere. However, in the presence of ethanol, a waiting of 15-20 sec is necessary towards the last stages of the titration.

The reverse titrations, i.e. titrations of sodium thiosulphate, arsenic(III), ascorbic acid and hydrazine with iodine, can be carried out using 0·1*N* and 0·01*N* solutions under the same conditions as in the direct titrations and the colour changes at the end points are just the reverse of those observed in the direct titrations. In the reverse titrations no blank correction is necessary in titrations of 0·1*N* solutions, but while titrating with 0·01*N* solutions, a blank correction of 0·04-0·06 ml 0·01*N* iodine has to be applied for 0·2 ml of 0·01% indicator solution added.

While titrating with 0·01*N* solutions, the amount of the indicator added should be 0·1-0·3 ml; when higher amounts of indicator solution are employed, the colour changes at the end points are not quite satisfactory.

With a view to applying the method now developed for the titrimetric determination of ascorbic acid in commercial vitamin C tablets, we have studied the interferences of some substances. The results indicate that citric, tartaric, oxalic, succinic, malic, maleic and mandelic acids, dextrose, lactose, mannitol, Ca^{2+}, Mn^{2+}, and Mg^{2+} do not interfere, whereas Fe^{2+}, Ba^{2+}, Li^{+}, and Pb^{2+} interfere.

The ascorbic acid content in the commercial vitamin C tablets was determined as follows: The tablet was dissolved in deionized water, and the solution filtered through a G4 sintered glass crucible. The filtrate was made up to 100 ml and an aliquot of this solution titrated aganist 0·1*N* iodine solution, using any one of the five dyes as indicator. A similar aliquot was titrated following the literature method. The results presented in Table 2 show that they are in excellent agreement with those obtained by the official method.

In their studies on the use of neutral red as indicator in the argentometric titration of bromide and iodide, Sierra and Asensi[12] stated that the colour change at the end point is due to the formation of a compound between iodine and neutral red. Since the dyes of the present investigation have almost similar structures as neutral red, we believe that a compound is formed between iodine and the dye, and at the end point, thiosulphate, arsenic (III), hydrazine and ascorbic acid react with the compound and regenerate the dye.

TABLE 2 — DETERMINATION OF ASCORBIC ACID IN COMMERCIAL VITAMIN C TABLETS

Trade name	Manufacturer	Amount of ascorbic acid found (mg)	
		BP method*	Present method
Redoxon	Roche	461·9±0·3	461·5±0·4
Celin	Glaxo	498·6±0·5	497·6±0·4
Sukcee	IDPL	502·3±0·4	501·9±0·3
Chewcee	Lederle	480·3±0·4	480·7±0·3

*British Pharmacopoeia, 1973, 36.

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Spectrophotometric Investigation of Os(VI)-Thiocyanate Complex

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A simple and rapid method for the spectrophotometric determination of 2·5-38·0 µg/ml of Os(VIII) using thiocyanate as the chromogenic reagent in 0·5-3·0*M* H_3PO_4 is described. The reaction involves reduction of Os(VIII) to Os(VI) which forms a 1:1 (metal-ligand) complex with thiocyanate as is evidenced from the spectral data. The interference of various cations has also been investigated.

APART from the importance of thiocyanate in thyroid and brain metabolism[1,2,3], it gained wide popularity as a chromogenic reagent for the spectrophotometric determination of transition metal ions[4,5]. Qureshi *et al.*[6] and Shlenskaya *et al.*[7] proposed spectrophotometric assay of Os(VIII) as osmium-thiocyanate complex without mentioning either the valency state of the metal ion or the stoichiometric composition of the product formed. Thus in view of the above and in continuation of our interest in the redox behaviour of thocyanate[8-10], we have now reinvestigated the nature of the species in aq. medium and successfully explored optimum conditions for the rapid spectrophotometric determination of Os(VIII) as Os(VI)-thocyanate complex in aq. H_3PO_4 medium at room temperature (25°).

A solution of Os(VIII) was prepared by dissolving OsO_4 (Johnson Matthey Co., London) in 0·5*M* Na-OH (ref. 11) and stanardized iodometrically[12]. Os(VI) solution was prepared by the addition of 0·1 ml of aq. ethanol (1:2) to 10 ml of 10^{-3}*M* alkaline