The Spectrophotometric Determination of Anions by Solvent Extraction with Metal Chelate Cations. XIII. A New Method for the Determination of Picric Acid

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Several procedures for the determination of picric acid have been published in the literature. In the well-known alkalimetric assay procedure, however, it is evident that a fictiously high value of the picric acid content is given because of the presence of lower-nitrated phenols as contaminates. Similarly, Bolliger's titration method,[1] based upon the principle that methylene blue picrate is extracted into chloroform, while methylene blue is not extractable, has been found by Baker[2] not to be universally applicable. Moreover, a titration method described by Johnson et al.,[3] in which the Koppeschaar method is applied to the procedure, is not desirable because of its experimental complexities.

Gravimetric methods using nitron[2,4,5] or 4-*n*-octyloxyphenylguanidine chloride[6] as a precipitant are too time-consuming and lack sensitivity.

Mites et al.[7] have studied the reduction of picric acid at a mercury cathode under a constant potential. Tur'yan et al.[8] have also investigated the polarographic behavior of picric acid, but their method requires the preliminary separation of some nitrophenols.

In an earlier work, Ruchhoft et al.[9] have described a spectrophotometric method of measuring the absorbance of ammonium picrate. Stöhr et al.[10] have reported that color is produced by heating picric acid with glucose in a weakly-alkaline medium.

Although it has been generally known that

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[1] A. Bolliger, *Analyst*, **64**, 416 (1939).

[2] P. R. W. Baker, ibid., **79**, 289 (1954).

[3] L. D. Johnson, W. M. McNabb and E. C. Wagner, *Anal. Chem.*, **27**, 1494 (1955).

[4] M. Bush and G. Blume, *Z. angew. Chem.*, **21**, 354 (1908).

[5] W. C. Cope and J. Barab, *J. Am. Chem. Soc.*, **39**, 504 (1917).

[6] C. Pasini and A. Vercellone, *Z. anal. Chem.*, **143**, 172 (1954).

[7] L. Meites and T. Meites, *Anal. Chem.*, **28**, 103 (1956).

[8] Ya. I. Tur'yan and P. M. Zaitsev, *Zhur. Anal. Khim.*, **17**, 231 (1962); *Chem. Abstr.*, **57**, 56 (1962).

[9] C. C. Ruchhoft and F. I. Norris, *Ind. Eng. Chem., Anal. Ed.*, **18**, 480 (1946).

[10] R. Stöhr and F. Scheibl, *Mikrochemie ver Mikrochim. Acta*, **36/37**, 362 (1951).

picric acid can be quite well extracted into organic solvents with cationic dyes, such as methylene blue[1] and crystal violet[11], little attention has been paid to employing such solvent extraction techniques for the spectrophotometric determination of picric acid.

On the other hand, it has been found by the present authors that the 2, 2′-dipyridyl iron(II) chelate is extracted into nitrobenzene from an aqueous solution in the presence of picric acid as well as of pentachlorophenol[12] and that the color intensity of the nitrobenzene extract is proportional to the amount of picric acid.

On the basis of these facts, this work was undertaken in order to establish a method for the determination of picric acid by solvent extraction, followed by the measurement of the absorbance of the extracted picrate of the 2, 2′-dipyridyl iron(II) chelate. The proposed method has the advantage of being simpler, and the extraction is adequate to remove the interference of moderate amounts of mono- and dinitrophenols.

Experimental

Apparatus and Reagents.—Unless otherwise stated, the apparatus and reagents were the same as those described in a preceding paper.[13]

Standard Picric Acid Solution.—A standard solution containing 1 mg. of picric acid per milliliter was prepared by dissolving purified picric acid (m. p. 120—121°C) in distilled water, as has been described by Meites et al.[7] This standard solution was then diluted to the concentration required for the experiments.

Other Nitrophenols.—All were purified until they had the proper constant melting points, *o*-nitrophenol by steam distillation and the others by recrystallization.

All other reagents of the analytical grade were used without further purification.

Procedure.—Mix a 2, 2′-dipyridyl solution (6×10^{-3} M), a ferrous ammonium sulfate solution (1.5×10^{-3} M), a sodium acetate solution (3 M) and a standard picric acid solution in the proper concentration. Adjust the pH of the solution to the required value and dilute it to 25 ml. with distilled water. To this, add 10.0 ml. of nitrobenzene and shake the solution for 5 min. After the solution has stood for 30 min., transfer the organic layer into a flask containing 1 g. of anhydrous sodium sulfate and shake it vigorously in order to make the solution transparent. Then transfer it through a folded filter paper into a 10 mm. cell. Measure the absorbance of the solution at 528 mμ, using a reagent blank solution or nitrobenzene as a reference. Measure the pH of the aqueous layer after the separation.

Results and Discussion

The Absorption Spectrum.—The spectral absorbance curves using nitrobenzene as a reference are shown in Fig. 1. Curve 1 is a spectrum of the extract when picric acid is absent, while curve 2 is that of the extract with picric acid. Curve 2 corresponds essentially to a spectrum of the 2, 2′-dipyridyl iron(II) chelate in an aqueous solution. The maximum absorbance is shifted from 522 mμ in an aqueous solution, and to 528 mμ in nitrobenzene. As Joshi and Bhargava[14] have shown that picric acid forms a 2 : 1 complex with $Cu(NH_3)_4^{2+}$, the extracted species is assumed to be a complex of 1 part 2, 2′-dipyridyl iron(II) chelate and 2 parts picric acid.

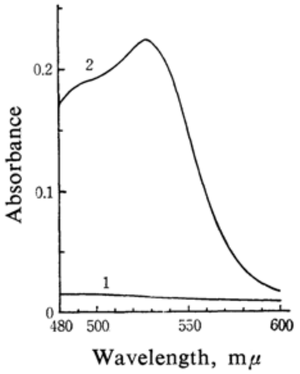

Fig 1. Absorption spectra.
Reference : Nitrobenzene, pH : 2.5
Curve 1 : Spectrum of organic phase extracted from the aqueous solution (25 ml.) contained Dip. 2.4×10^{-4} M, Fe(II) 6×10^{-5} M, NaAc 0.24 M but picric acid is absent.
Cueve 2 : Spectrum of organic phase extracted from the aqueous solution (25 ml.) containing 4 p. p. m. of picric acid in addition to the same component as that of curve 1.

The Effect of Reagents.—*The Effect of the 2, 2′-Dipyridyl Iron(II) Chelate Concentration.*—The formation of extractable species may be governed mainly by the concentration of the 2, 2′-dipyridyl iron(II) chelate cation.

Various amounts of ferrous ammonium sulfate and 2, 2′-dipyridyl were added to a solution containing a definite amount of picric acid, the mole ratio of dipyridyl to ferrous iron being kept at 4 to 1. In this case, because of the high stability of the chelate,[15]

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[11] M. Rebek and M. K. Semlitsch, *Monatsh. Chem.*, **92**, 254 (1961).

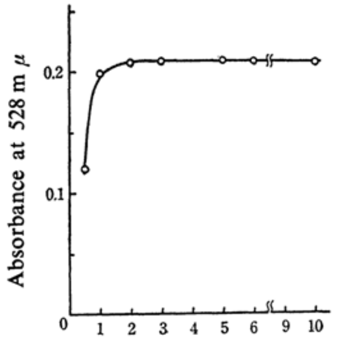
[12] Y. Yamamoto, K. Kotsuji and T. Sakurai, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **86**, 519 (1965).

[13] Y. Yamamoto and K. Kotsuji, This Bulletin, **37**, 785 (1964).

[14] D. P. Joshi and P. P. Bhargava, *J. Indian Chem. Soc.*, **40**, 19 (1963).

[15] K. B. Yatsimirskii and V. P. Vasilev, "Instability Constants of Complex Compounds," Pergamon Press, Oxford (1960), p. 139.

the molar concentration of the 2, 2′-dipyridyl iron(II) chelate was assumed to be equivalent to that of the ferrous iron added. The pH of the solutions was kept at 2.5, and the extraction was then carried out. As is shown in Fig. 2, an excess of the 2, 2′-dipyridyl iron(II) chelate is necessary to obtain a quantitative recovery; therefore, the concentration of ferrous ammonium sulfate was usually kept at 6×10^{-5} M in this work.



Concn. of ferrous iron, ($\times 1.2 \times 10^{-5}$ M)

Fig. 2. Effect of 2, 2′-dipyridyl iron(II) chelate concentration.
Concentration of picric acid, 4 p. p. m.
pH of aqueous layer, 2.5
Mole ratio of Dip. to iron(II), 4
Shaking time, 5 min.
Reference, Reagent blank

The Effect of the 2, 2′-Dipyridyl Concentration.—While the concentrations of ferrous iron, sodium acetate and picric acid in the final solutions were kept at 6×10^{-5} M, 0.24 M and 4 p. p. m. respectively, various amounts of 2, 2′-dipyridyl were added in which the mole ratio of dipyridyl to ferrous iron was varied from 3 to 5. The experiments were then carried out in a manner similar to that described above. The variation in the mole ratio did not effect any measurable change in the absorbance of the extracts. This mole ratio was always kept at 4 to 1 in this work.

The Effect of the Sodium Acetate Concentration.—When the concentration of sodium acetate was low in the solution, it took much time to separate the two layers because of the formation of an emulsion. When, however, the acetate concentration was kept between 0.2 to 0.3 M, the formation of an emulsion could be prevented. Thus, the concentration of the acetate was kept at 0.24 M in this work.

The Effect of the Shaking Time.—Although a good recovery could be obtaind with a one-minute shaking, the shaking time was fixed at 5 min. in this work.

The Effect of pH.—The effect of changes in the pH on the extraction is shown in Fig. 3 (curve 1). The absorbances of the extracts are at a maximum and are uniform over the pH range of the aqueous solution from 2.2 to 11.5. In addition, it was found that the extraction behavior of dinitrophenols was similar to that of picric acid in this system, while dinitrophenols were scarcely extracted into nitrobenzene from an aqueous solution at low pH values (pH 2—3). Thus, the pH of the solution to be extracted was adjusted to 2.5, because it appeared feasible that the interference of moderate amounts of dinitrophenols were avoided by the extraction procedure described above.

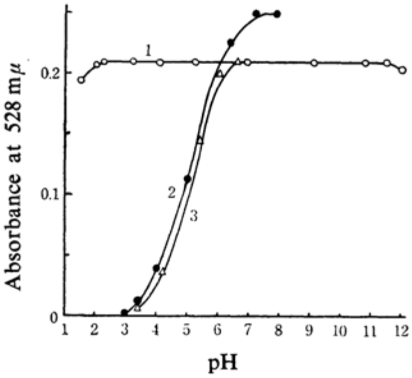


Fig. 3. Effect of pH.
The concentrations of dipyridyl, iron(II) and acetate in the final solutions were 2.4×10^{-4} M, 6×10^{-5} M and 0.24 M respectively.
Curve 1: Picric acid, 4 p. p. m.
Curve 2: 2, 4-Dinitrophenol, 5 p. p. m.
Curve 3: 2, 6-Dinitrophenol, 5 p. p. m.
Reference, Reagent Blank

The Stability of the Color.—The color intensity of the extract in the transmission cell with a stopper was stable, even after 24 hr.

The Choice of an Organic Solvent.—The extracting solvents, such as nitrobenzene, benzene, cyclohexanone, 1, 2-dichloroethane, chloroform, carbon tetrachloride, isoamylalcohol and methylisobutylketone, were tested; of these, nitrobenzene proved to give the highest net absorbance.

The effect of the times of extraction was examined in the following manner. An aqueous solution containing a definite amount of picric acid and an optimum amount of the reagents was prepared; the extraction was then carried out with successive portions of nitrobenzene. The absorbance at 528 mμ was measured for the nitrobenzene solution obtained by each extraction. As Fig. 4 shows, the second extract has an appreciable absorbance, but the absorbance of the third extract is

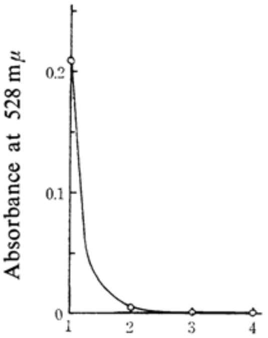


Fig. 4. Effect of times of extraction.
The concentrations of ferrous iron, dipyridyl, sodium acetate and picric acid in the aqueous solution before the first extraction were 6×10^{-5} M, 2.4×10^{-4} M, 0.24 M and 4 p. p. m. respectively, and the absorbance was measured for the nitrobenzene solution obtained by each extraction.
Reference, Reagent blank

almost negligible. Thus, a single extraction was used in this work.

Calibration Curve.—One milliliter of the 2, 2′-dipyridyl solution, 1 ml. of the ferrous ammonium sulfate solution, 2 ml. of the sodium acetate solution, and varying amounts (1—10 ml.) of the standard picric acid solution (20 p. p. m.) were mixed; the pH of this solution was then adjusted to 2.5 with a dilute sulfuric acid. The resulting solution was diluted to 25 ml. with distilled water. Then 10.0 ml. of nitrobenzene was added, and the mixture was treated by the preceding procedure. As can be seen from Fig. 5, up to 8 p. p. m. of picric acid obeys Beer's law.

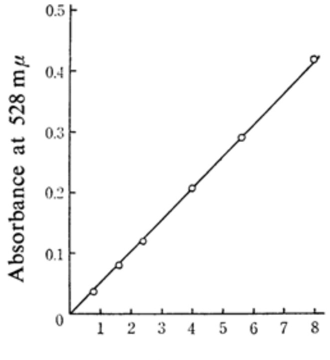


Fig. 5. Calibration curve.
Dip.: 2.4×10^{-4} M
Fe(II): 6×10^{-5} M
NaAc: 0.24 M
pH: 2.5
Reference, Reagent blank

TABLE I. EFFECT OF NITROPHENOLS ON EXTRACTION AND DETERMINATION OF PICRIC ACID
(4 p. p. m. of picric acid taken in each case)

Compound	Compound concn. p. p. m.	Absorbance at 528 mμ
None	—	0.209*
2, 4-Dinitrophenol	20	0.211
2, 4-Dinitrophenol	40	0.216
2, 5-Dinitrophenol	20	0.209
2, 5-Dinitrophenol	40	0.210
2, 6-Dinitrophenol	20	0.210
2, 6-Dinitrophenol	40	0.211
o-Nitrophenol	40	0.209
o-Nitrophenol	100	0.212
m-Nitrophenol	40	0.210
m-Nitrophenol	100	0.214
p-Nitrophenol	40	0.210
p-Nitrophenol	100	0.213
Phenol	40	0.209
Phenol	100	0.212

pH of aqueous layer: 2.5, other variables were the same as that of the calibration curve.
* The absorbance of 4 p. p. m. of picric acid without nitrophenols.

TABLE II. EFFECT OF DIVERSE IONS ON EXTRACTION AND DETERMINATION OF PICRIC ACID
(4 p. p. m. of picric acid taken in each case)

Ion	Ion concn. p. p. m.	Absorbance at 528 mμ
None	—	0.209*
SO_4^{2-}	3800	0.209
PO_4^{3-}	1900	0.209
NO_3^-	5	0.210
NO_3^-	12	0.216
Cl^-	700	0.210
Cl^-	1400	0.214
Br^-	64	0.209
Br^-	160	0.215

* The absorbance of 4 p. p. m. of picric acid without diverse ions.

Interferences.—A study was made of the effects of the appropriate substances which commonly occur in picric acid. Absorbance measurements were made for the nitrobenzene extracts from solutions containing various amounts of each substance with 4 p. p. m. of picric acid. The results are given in Table I. No interference was found in concentrations as high as 40 p. p. m. for nitrophenols, except with 2, 4-dinitrophenol. Although satisfactory results were obtained in the presence of large amounts of sulfate and phosphate, a small amount of nitrate produced a positive error.

Summary

The solvent extraction method has been applied to the spectrophotometric determination of minute amounts of picric acid with the 2, 2′-dipyridyl iron(II) chelate. The selectivity of the procedure is largely dependent on the pH of the solution. At pH 2.5 the extraction is selective for picric acid in the presence of nitrophenols.

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