tor using glass-modified calomel (1) electrodes.

0.1N Tributylethylammonium hy-droxide. Prepared from the iodide by the method of Cundiff and Markunas (1)

Adsorption alumina (Merck, No. 71707 or Fisher Scientific Co., No. A-540). The pH of a slurry of 10.0 grams in 90 ml. of distilled water was 10.2.

Diatomaceous earth (Johns-Manville Celite grade is satisfactory).

#### PROCEDURE

To 500 ml. of pyridine in a 1000-ml. iodine flask add 20 grams of alumina. Shake intermittently for 5 minutes and filter by suction through 9.0-cm. glass fiber filter paper (H. Reeve Angel & Co., No. 934AH) containing a layer (5.0 grams) of diatomaceous earth.

### RESULTS

A 100-ml. volume of commercial 2° pyridine was found to have a blank of 0.2 to 0.4 ml. of 0.1N tributylethylammonium hydroxide, probably due to carbon dioxide. The blank invariably increased for 5-gallon lots of pyridine as the pyridine was consumed. The purified pyridine (100 ml.) had a blank of less than 0.05 ml. of 0.1N tributylethylammonium hydroxide.

A 1000-ml. volume of commercial  $2^{\circ}$  pyridine was spiked with carbon dioxide. Before purification the blank on 100 ml. amounted to 0.6 ml. of 0.1Ntributylethylammonium hvdroxide. After purification, the blank on 100 ml. amounted to less than 0.05 ml. of 0.1Ntributylethylammonium hydroxide.

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In alkaline 2-methoxyethanol,

absorbed at 587 m $\mu$  and in neutral

# Spot Test Detection and Spectrophotometric Determination of Nitrite with p-Phenylazoaniline

SIR: Recently a procedure using p - phenylazoaniline and 1 - naphthylamine was introduced for the determination of the nitrite ion (2). Although this procedure probably has a greater potential sensitivity for the nitrite ion than any method in the literature, its main disadvantage is in the use of gaseous hydrogen chloride. However, the method should be capable of further improvement. Another recently introduced method uses pphenylazoaniline and benzaldehyde 2benzothiazolylhydrazone (3). The spectral data for some of these nitrite methods are compared in Table I. Although these methods for the nitrite ion are very sensitive, an alternative sensitive, simple method was desired in which the color would be formed in alkaline media. The present paper describes such a new method which is very sensitive and is simpler in the sense of using only one reagent which is both the substance diazotized and the coupling agent.

The mechanism of the present procedure as applied to the nitrite ion includes the following steps: reaction of the nitrite ion with p-phenylazoaniline to give the diazonium salt; combination of *p*-phenylazoaniline with the diazonium salt to form the triazene; and finally, formation of the blue anion in alkaline solution.

 $C_6H_5 \cdot N : N \cdot C_6H_4NH_2 \xrightarrow{HONO} \rightarrow$ 

 $C_6H_5 \cdot N : N \cdot C_6H_4N_2^+$ 

 $C_6H_5 \cdot N \cdot N \cdot C_6H_4NH_2 +$  $C_6H_5 \cdot N : N \cdot C_6H_4N_2^+ \rightarrow$  $C_6H_5 \cdot N : N \cdot C_6H_4N - \cdot N : N \cdot C_6H_4 \cdot$ 

 $N: N \cdot C_6H_5$ 

The triazene was synthesized in good yield by the analytical procedure. Yellow gold plates, m.p. 190-1° C., were obtained from methyl cyclohexane. Calculated for  $C_{24}H_{19}N_7$ : C, 71.1; H, 4.7; N, 24.2. Found: C, 70.8; H, 4.6; N, 24.6. In alkaline dimethylformamide the triazene gave a blue solution wavelength maximum 635 m $\mu$ ,  $\epsilon$  91,000. dimethylformamide at 435 m $\mu$ . The strong solvent effects shown in the spectra of this chromogen should prove of value in future studies of this analytical procedure. In the spectrophotometric determination of the nitrite ion, a wavelength maximum of  $595 \text{ m}\mu$ ,  $\epsilon$  67,000 (at 1.5 µg. of NO<sub>2</sub><sup>-</sup> per ml. of final solution) was obtained. However, this latter solution contains approximately 70% dimethylformamide. In the standard analytical procedure, dilution to 50 ml. with dimethylformamide instead of to 10 ml. gave a solution containing approximately 94% dimethylformamide and absorbing at  $622 \text{ m}\mu$ with an  $\epsilon$  of 75,000 (at 1.5  $\mu g.$  of NO2per ml. of final solution). The red spectral shift and intensity enhancement are mainly due to the increase in basicity of the solvent mixture (1).

#### EXPERIMENTAL

Reagent Solutions. p-Phenylazoaniline (Distillation Products Industries, Rochester, N. Y.) was recrystallized several times from pentane to give brilliant orange crystals, m.p. 150° C. For spectral work, a 1%solution of the dye in dimethylformamide containing 3% glacial acetic acid by volume was necessary.

Tetraethylammonium hydroxide, 29% solution in methanol, was obtained from Southeastern Analytical Chemists, Austin, Tex.

Equipment. A Cary Model 11 spectrophotometer with 1-cm. cells was used.

**Procedures.** Spectrophotometric. To 1 ml. of aqueous test solution is added 2 ml. of p-phenylazoaniline

# Table I. Comparison of Some Recent Methods for the Determination of Nitrite Ion

Reagents	Type of Ch <b>r</b> omogen	Maxi- mum Wave- length, mµ	$\epsilon \times 10^{-3}$	Absorp- tivity, µg. <sup>-1</sup> Ml. Cm. <sup>-1</sup>	Concn. Limit,ª P.P.M.
Sulfanilic acid $+$ N-1-naphthylethyl- enediamine	Azo dye cation	550	50	1.09	0.09
<i>p</i> -Phenylazoaniline + 1-naphthyl- amine	Bisazo dye dication	643	93	2.02	0.05
<i>p</i> -Phenylazoaniline + benzaldehyde 2-benzothiazolyl hydrazone	Formazan anion	590	58	1.26	0.08
p-Phenylazoaniline	Triazene anion	595	67*	$1.50^{b}$	0.12
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For absorbance = 0.10 in a 3-ml. cell with a light path of 1 cm. <sup>b</sup> For 1.5  $\mu$ g. NO<sub>2</sub><sup>-</sup> per ml. of final solution.

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reagent solution. The mixture is heated for 3 minutes in boiling water. After cooling, 2 ml. of the tetraethylammonium hydroxide solution is added. The solution is diluted to 10 ml. with dimethylformamide. Readings are then taken at  $595 \text{ m}\mu$ .

SPOT PLATE. One drop of the aqueous test solution is added to one drop of the p-phenylazoaniline solution. After a 5-minute wait, one drop of the alkali is added. In the presence of nitrite ion, blue to green colors are obtained. The identification limit is  $0.2 \ \mu g$ . of nitrite. The blank is yellow.

SPOT PAPER. One drop of the reagent is added followed by 1  $\lambda$  (0.001 ml.) of the aqueous test solution. The spot is heated for 1 minute on the metal part of a steam bath. One drop of alkali is then added. In the presence of nitrite ion, a blue to green color is obtained. The identification limit is  $0.02 \ \mu g$ , of nitrite. The blank is yellow.

Spot Test Procedures. The spot plate and spot paper tests reported in this paper for the nitrite ion are not quite as sensitive as the benzaldehyde 2-benzothiazolylhydrazone test (2). With amounts of nitrite ion greater than 25  $\mu$ g., a blue color is obtained; with lower amounts, a green color is obtained. The colors obtained in either the spot plate or spot paper methods are stable for at least 24 hours.

Spectrophotometric Procedure. The effect of variables on the standard procedure was investigated. In the diazotization step the relative proportions of water and dimethylformamide are critical. Optimum results were obtained with 1 ml. of test solution and 2 ml. of the reagent solution; a lower or higher volume of either test solution or the reagent solution gave lower intensities. Optimum intensities were obtained with 1.3 to 2.0% concentrations of *p*-phenylazoaniline; lower or higher concentrations gave lower intensities. However, a concentration of 1% was chosen in the procedure for, although the intensity was slightly lower, the blank was considerably improved. The amount of acetic acid in the reagent was not critical except that concentrations lower than 3% gave lower values. The optimum intensities were obtained with heating times of 2 to 5 minutes. From 1 to 5 ml. of alkali could be added with no effect on the color intensity. The final dilution could be made with dimethylformamide, acetone, methanol, or water. The effect of these various solvents on the wavelength maxima and molar absorptivity was as expected (1). The final chromogen absorbed at 595, 588, 575, and 575 m $\mu$  in dimethylformamide, acetone, methanol, and water, respectively. The molar absorptivity also decreased with the decreasing basicity of the solvents. Beer's law was not obeyed although a linear relationship was observed between the

absorbance and concentration from 0.2 to 1.5  $\mu$ g. of NO<sub>2</sub><sup>-</sup> per ml. of final solution.

The method is believed capable of further improvement, especially in respect to simplicity of operation and sensitivity.

Interferences. As in all diazotization methods, sulfite ion interfered. The following ions did not appreciably influence the results in the spectrophotometric procedure when present in the ratio of 30 to 1chloride, sulfate, cyanide, iedide, nitrate, calcium, magnesium, sodium, potassium, and lithium. Ferric chloride tended to give slightly higher values probably caused by the presence of nitrite ion in the salt.

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# Inaccuracy of Dumas Nitrogen Determinations of Certain 1,2,4-Triazoles

SIR: The inaccuracy of conventional nitrogen analyses of some azaheterocyclic compounds (1, 3, 4, 8, 10, 11), including 1,2,4-triazoles (2), has been often observed. In the case of 1,2,4triazoles, Potts suggests (9) that preparative rather than analytical difficulties account for low nitrogen values. If this were correct, a survey of a substantial body of analytical data would correlate errors of nitrogen analyses with those of carbon and hydrogen. Results of analyses [micro-Dumas method for nitrogen (7, 12) from Zimmermann] of 76 new 1,2,4-triazoles (5) are summarized in Table I.

The view of Potts is undoubtedly correct in group (a) (Table I), possibly correct in (b), but inapplicable to the triazoles in group (c); this lends further support to other findings on the interference of bromine with the determination of nitrogen in heterocyclic compounds (3, 8).

Triazoles free from bromine but containing nitrogroups or acyl hydrazine side chains may also give very low nitrogen analyses. In some cases the error can be avoided or minimized by slow purging, but when the absolute error

is of the order of 1%, the method of Spies and Harris (11) should be used (6) instead of the conventional Dumas method, as illustrated in the cases of 1 - p - nitrophenyl - 5 - phenyl - 1,2,4triazole - 3 - carboxylic acid hydrazide:

Table I.	Summary	of	Elemental	Analyses	of	Some	1,2,4	4-Triazoles
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Type of				Deviations				
1,2,4-Triazole	Element <sup>a</sup>	Found	Caled.	Absolute	Relative	Standard		
(a) N-Unsubstituted	${f C(18)\ H(18)\ N(20)}$	$56.06 \\ 5.05 \\ 24.91$	$\begin{array}{c} 56.24\\ 5.11\\ 24.72\end{array}$	$^{+0.18}_{-0.06}$	$^{+0.32}_{-1.19}_{-0.75}$	$\begin{array}{c} 0.45 \\ 0.02 \\ 0.53 \end{array}$		
(b) N-Aryl; No Br present	${f C(44)}\ {f H(44)}\ {f N(45)}$	$67.61 \\ 4.76 \\ 18.29$	$\begin{array}{r} 67.56\\ 4.85\\ 18.01 \end{array}$	-0.05 + 0.09 - 0.28	-0.07 +1.89 -1.5	$\begin{array}{c} 0.39 \\ 0.17 \\ 0.48 \end{array}$		
(c) N-Aryl; Br present	C(13) H(13) N(11)	$52.65 \\ 3.26 \\ 14.98$	$52.94 \\ 3.38 \\ 13.99$	$^{+0.29}_{+0.12}_{-0.99}$	+0.55 +3.68 -6.9	$\begin{array}{c} 0.21 \\ 0.18 \\ 1.08 \end{array}$		
		• .	•					

<sup>a</sup> Number of samples is given in parentheses.