RJC

RASĀYAN *J. Chem.*
Vol. 9 | No. 3 |340 - 347 | July - September | 2016
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

VISIBLE SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OFPHARMACEUTICALLY IMPORTANT AROMATIC PRIMARY AMINES BY USING p-N, N-DIMETHYLPHENYLENEDIAMINE AND SODIUM META PERIODATE

Srilatha Kornepati[1]and Elisha Divakar Tella[2]*
[1]Department of Chemistry, Govt. Polytechnic College, Repalli- 522265, (A.P) India
[2]Department of Chemistry, Noble College (Autonomous), Machilipatnam, (A.P), India.
*E-mail: divakartella@gmail.com

ABSTRACT

p-N,N-dimethylphenylenediamine is oxidized with sodium metaperiodate into p-N,N-dimethylbenzoquinonemonoimine which can form a purple–red charge–transfer complex with aromatic primaryamine at pH 3.0 The absorbance of the p-N,N-dimehylbenzoquinone monoimine–aromatic primary amine charge-transfer complex is measured at 530nm. This proposed method is simple, rapid and sensitive with reasonable precision and accuracy. The precision of the method was found by analyzing a set of eight solutions, each containing a final concentration value approximately in the middle of the Beer's law range. The percent relative standard deviation in this method is presented in table-1. The accuracy of the method was determined by taking different known amounts (with in Beer's law limits) of the drug and analyzing them by proposed method. The results are given in table-2. In the determination of aromatic primaryamine the excepients usually present in formulations did not interfere.

Keywords: Spectrophotometer, aromatic primary amine ,p-N,N-dimethylphenylenediamine , sodium metaperiodate, Buffer pH 3.0.

INTRODUCTION

The wide distribution of amines in nature, their importance in industry as raw materials, intermediates and finished products and their use in the laboratory causes continuous interest in the analytical problems connected with them. These are focused at two levels, functional level (nitrogen atom and its immediate vicinity) and the molecular level (the interactions between the amino group and the rest of the molecule). The primary aromatic amines are compounds having an amino group directly attached to aromatic nucleus .The substituted anilines fall into two main divisions: (A) those in which one or more hydrogen atoms attached to the aromatic nucleus are replaced by substituent (nucleo substituted anilines). (B) Those in which one or both of the hydrogen atoms of the amino group are replaced.

Many drugs such as shown in table 1 contain primary aromatic amino group. Few drugs attain primary aromatic amino group only after performing hydrolysis (e.g. N-acyl derivatives, cyclic compounds) or reduction (e.g. nitro derivatives). Most of the available methods for the assay of drugs (shown in table 1) in bulk samples, dosage forms and biological fluids (where the solutions are first deproteinised with trichloroacetic acid) are based on the characteristic reaction of primary aromatic amino group. Colorimetric methods constitute the main part of the literature on the subject , in books [1-5] and treatises on general analysis, as well as in original appears and reviews [6,7] .The author has summarized typical identification and assay procedures in the case of primary aromatic amines so-far reported basing on the colour development. Oxidations of amines usually yield degradation products , some of which provide indirect evidence for the presence of different types of amines [8,9].Korotkova and co-workers presented two methods ,which are based on the spectrophotometric determination of the quinine-imine formed from

aniline and amidopyrine by their simultaneous oxidation with hexacyanoferrate(III)[10] or iodine[11] .The condensation of primary amines with carbony1componds was first reported by schiff[12] and the condensation products are often referred to as Schiff bases (azomethines).The reaction was reviewed[13].

EXPERIMENTAL

Preparation of reagents

p-N,N-dimethylphenylenediamine Solution (0.05%)

It was freshly prepared by dissolving 50 mg of the Analytical grade substance in 100 ml of water.

Sodimmetaperiodate Solution (0.2%)

It was prepared by dissolving 200 mg of the analytical grade reagent in 100ml water.

Buffer solution (pH3.0)

It was prepared by mixing 50 ml potassium acid phthalate (0.2M) and 40.8 ml of hydrochloric acid (0.1M) and 109.2ml of water.

Primary aromatic aminesused were commercially available G.R., I.P, or B.P., grade. Their stock solutions were prepared in distilled water, the compounds insoluble in water being dissolved initially in the minimum amount of dilute hydrochloric acid or sodium hydroxide solution if necessary .Working solutions were prepared by appropriate dilution of the stock solutions after the neutralization of the excess acid or alkali. The pH of the final diluted solution was brought in the range of 3.0-5.0.

All the other chemical reagents were of analytical grade.

Instrumentation

Spectral and absorbance measurements were made on Shimadzu double beam spectrophotometer UV – 140 with 1 cm quartz cells pH measurements were carried out using Systronics pH meter 335.

Absorbance curve

The absorbance curve of aromatic primaryamine in the presence of appropriate reagents was scanned on a spectrophotometer in the range 400-700 nm against the reagent blank. However, the maximum characteristic absorption is obtained at 530nm. The results were graphically represented in Figures-2 to 4.

Optical characteristics - Adherence to Beer's law

In order to know the Beer's law limits of the proposed method, the absorbance of a series of solutions containing varying amounts of aromatic primaryamine and specified concentrations of the remaining as given in the procedure in a total volume of 25ml were measured at 530nm against a reagent blank. The linearity of plots between absorbance and the concentration of aromatic primaryamine shows that the system obeys Beer's Law (Figures-5 to 7).

The Beer's law limits, regression equation, correlation coefficient, molar absorptivity, Sandell's sensitivity,optimum photometric range were calculated and recorded in Table-3.

Procedure

General procedure compounds containing free primary aromatic amine)

To a 25 ml volumetric flask, these solutions were added in the following order: 15 ml of buffer solution (pH 3.0 ± 0.1), p-N,N-dimethylphenylenediamine, $NaIO_4$ and primary aromatic amine. The solution was then diluted to the mark. The absorbance was measured at (530 nm) after maximum colour development against the reagent blank prepared under similar conditions.

The aromatic amines concentration of the sample solution was deduced from the standard calibration curve.

Procedure for compounds which yield primary aryl amino group on reduction
About 10 mg of sample solution was accurately weighed and treated with 10 ml of 4 N hydrochloric acid and 0.25 g of zinc dust was added in positions after standing for 1hr. at room temperature, the solution was filtered through cotton wool, the residue was washed with **3 - 5** ml portions of water and excess HCl present in filtrate was removed under vacuum and the total volume was brought to 100 ml after bringing the pH between 5.0 and 7.0. The general procedure was then applied.

Procedure for compounds which yield primary aromatic amino group on hydrolysis
About 25 mg of sample was boiled under reflux with 20 ml of 4 N hydrochloric acid for 1 hr. under reflux, and the excess HCl was removed under vacuum .The residue was dissolved in 50 ml of water and diluted to 250 ml after keeping the pH between 5.0 – 7.0 .Then the general procedure was followed.

Procedure for the determination of amines in pharmaceutical preparations
for Tablets : 20 tablets were weighed and powered into a fine granules, The samples of powder equivalent to 100 mg of the primary aromatic amine was transferred to a centrifuge tube and extracted with 20 ml of alcohol . The solution was filteredand the residue was washed with alcohol. Filtrate and washings were diluted to 100 ml with distilled water.

Accuracy of the method
The accuracy of the method was determined by taking aliquots containing known quantities of each aromatic primary amine and estimated them by proposed method and the results were tabulated in Table-2.

Precision of the method
The precision of the method was found by analyzing set of eight solutions, each containing a final concentration value approximately in the middle of the Beer's law range. The %RSD and percent range of errors (for confidence limits p=005 and 0.01 levels) in method are presented in Table -3.

Recovery Experiments
To study the recovery and accuracy of the proposed method, statistical study was done. A fixed, amount of sample was accurately weighed in a series of 25 ml standard flasks and three different level of standard stock solution were added separately. Each level of the added drug was repeated seven times. The total amount drug was then determined by the proposed method. The percent recovery was calculated in the usual way. The results of accuracy testing experiments are presented in Table-4.Of the various reagents studied so far the author felt that p-N,N-dimethylphenylenediamine --$NaIO_4$ is the best chromogenic reagent in the spectrophotometric determination estimation of sulphacetamide was carried out of primary aromatic amines at pH 3.0 ± 0.1.

RESULTS AND DISCUSSION

The proposed method is simple, rapid and sensitive with reasonable precision and accuracy and it is useful for the determination of some typical and pharmaceutically important aromatic primary amines in bulk sample and pharmaceutical preparations. Though HPLC method is more accurate and rapid, it is expensive. Comparison of the results incorporated in Tables reveal that the proposed method is rapid, sensitive and simple with reasonable precision and accuracy. Sensitivity of the method is better than many of the methods.

Chemistry involved
Sodium metaperiodate can oxidize p-N,N-dimethylphenylenediamine into p-N-N-dimethylbenzoquinonemonoimine. Which can form a purple red p-N-N-dimethylbenzoquinonemonoimine - aromatic primary amines charge-transfer complex with aromatic primary amines at pH 3.0. Which can be measured at 530 nm.

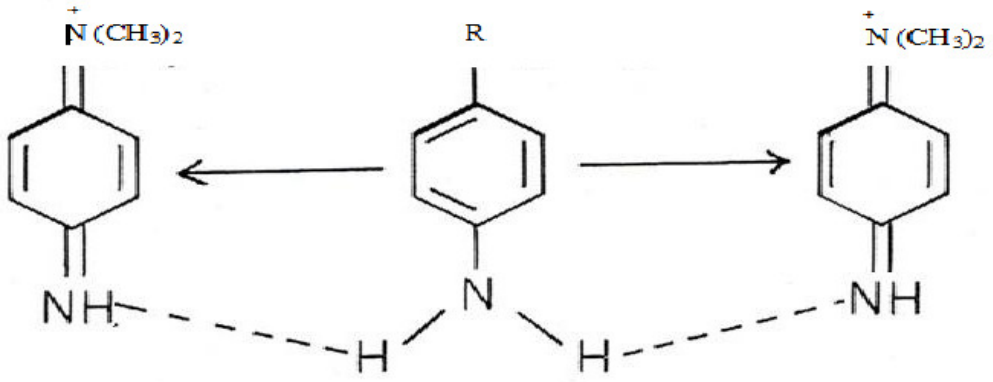


Figure-1

Table-1: Optical Characteristics

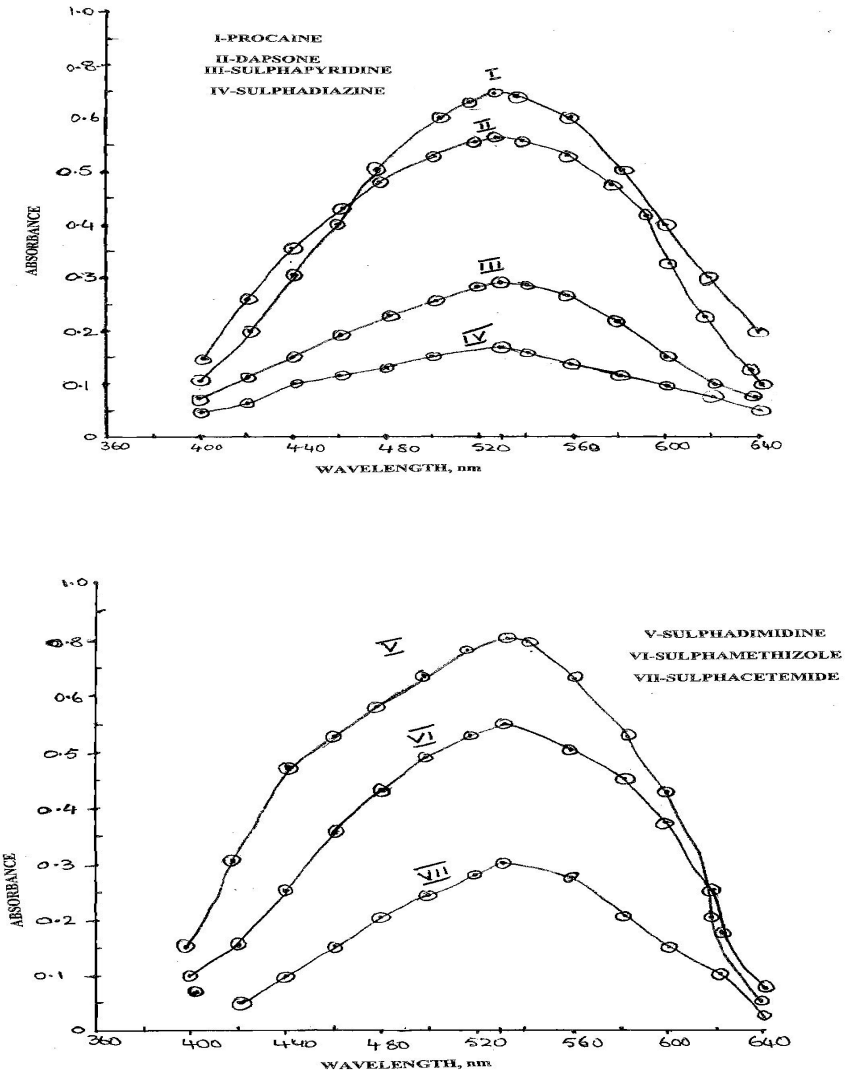
Compound	Beer's law limits µg/25 ml	Molar Absorptivity l. mol^{-1}. $cm^{-1}X10^{-3}$	Optimum Photometric Range µg/25 ml	Sandall's Sensitivity µg/cm^2 /0.001 absorbance unit
Procaine	50-375	6.09	100-400	0.038
Dapsone	25-350	13.54	100-300	0.018
Sulphanilamide	25-400	6.60	100-400	0.026
Sulphacetamide	50-450	6.40	150-400	0.040
Sulphapyridine	50-400	6.45	150-400	0.038
Sulphadiazine	50-500	7.00	150-400	0.042
Sulphamerazine	50-450	7.04	100-350	0.040
Sulphamethopyridiazine	50-500	7.00	150-400	0.040
Sulphadimidine	50-400	6.95	150-400	0.040
Sulphamethizole	50-300	6.75	150-325	0.040
Sulphasomidine	50-550	5.80	175-550	0.040
Sulphamoxole	50-350	6.67	100-350	0.040
Phthalyloulpha-thiazole	50-400	4.06	125-325	0.028
Chloramphenicol	100-400	4.03	200-450	0.080
Folic acid	100-400	5.88	125-400	0.075

Table-2: Accuracy of the Method

Compound	Amount Taken	(Mg) Found	% Error
Procaine	375	377	0.50
Dapsone	525	527	0.38
Sulphapyridine	500	497	-0.60
Sulphadiazine	225	224	-0.45
Sulphadimidine	150	149	-0.66
Sulphamethizole	150	151	0.66
Sulphacetemide	425	427	0.49
Sulphanilamide	425	421	0.98
Phthalyloulpha-hiazole	150	149	-0.66
Chloramphenicol	175	173	-1.10
Folic acid	175	176	0.58

Table-3: Precision of the Method

Compound	Standard Deviation	Probability limit, 95%	Probability limit, 99%
Procaine	0.014	0.5620.024	0.36±4.0056
Dapsone	0.016	0.58±0.018	0.38±0.029
Sulphapyridine	0.011	0.32±0.012	0.32±0.018
Sulphadiazine	0.007	0.37±0.007	0.37±0.011
Sulphadimidine	0.009	0.49±0.009	0.49±0.014
Sulphamethizole	0.015	0.46±0.016	0.46±0.025
Sulphacetemide	0.004	0.49±0.004	0.49±0.006
Sulphanilamide	0.005	0.36±0.005	0.36±0.008
Phthalyloulpha-thiazole	0.020	0.23±0.021	0.28±0.02
Chloramphenicol	0.020	0.30±0.021	0.30±0.033
Folic acid	0.018	0.22±0.018	0.22±0.029



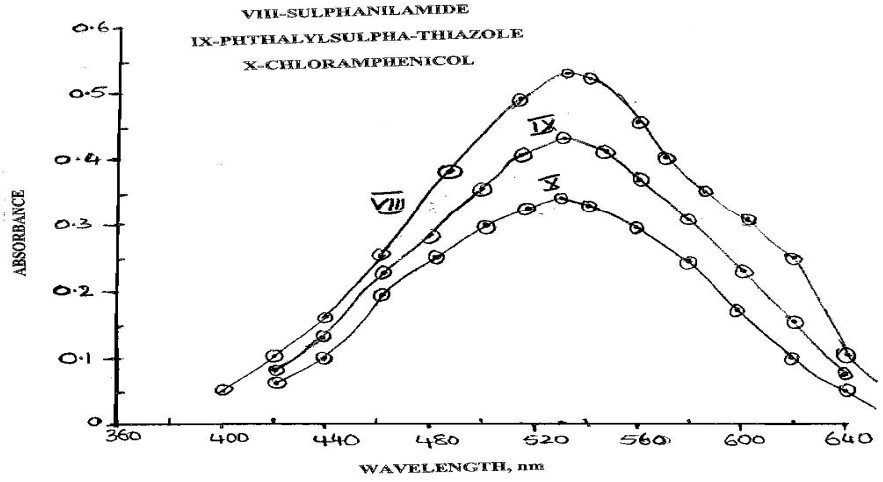


Fig. -2 to 4: Absorbance curves

Table-4: Percentage Recovery Data

Sample(mg)	Amount Found (mg)		Percentage Recovery (mg)
	Proposed	Reported	
Processing free aromatic amino group			
1. Dapsone a. Tablet(25) b. Tablet(25)	 24.41 24.10	 24.32 23.91	99.5
2. Sulphanilamide(5.33%)	5.20%	5.12%	99.1
3. SulphacetamideTablet (500)	496	497	99.4
4. Sulphapyridine Tablet (500)	488	491	99.6
5 .Sulphadiazine a. Tablet (500)	496.6	497	99.4
6 .Sulphadimidine a. Tablet (500)	496.8	498.8	99.7
7.Sulphamoxole a. Tablet (500)	499	495	99.7
8. Folic Acid a. Tablet (5) b. Folic acid (2) Vit.B_{12} (0.20)	 4.94 1.91	 4.91 1.93	99.3
Producing primary aryl emino group after hydrolysis			
9. Phthalyloulpha-thiazole- Sole (500)	493.5	494.3	98.8
Producing primary aromatic group after reduction			
10. chloramphenicol (Succinate (1 kg))	0.971g	0.964g	98.6

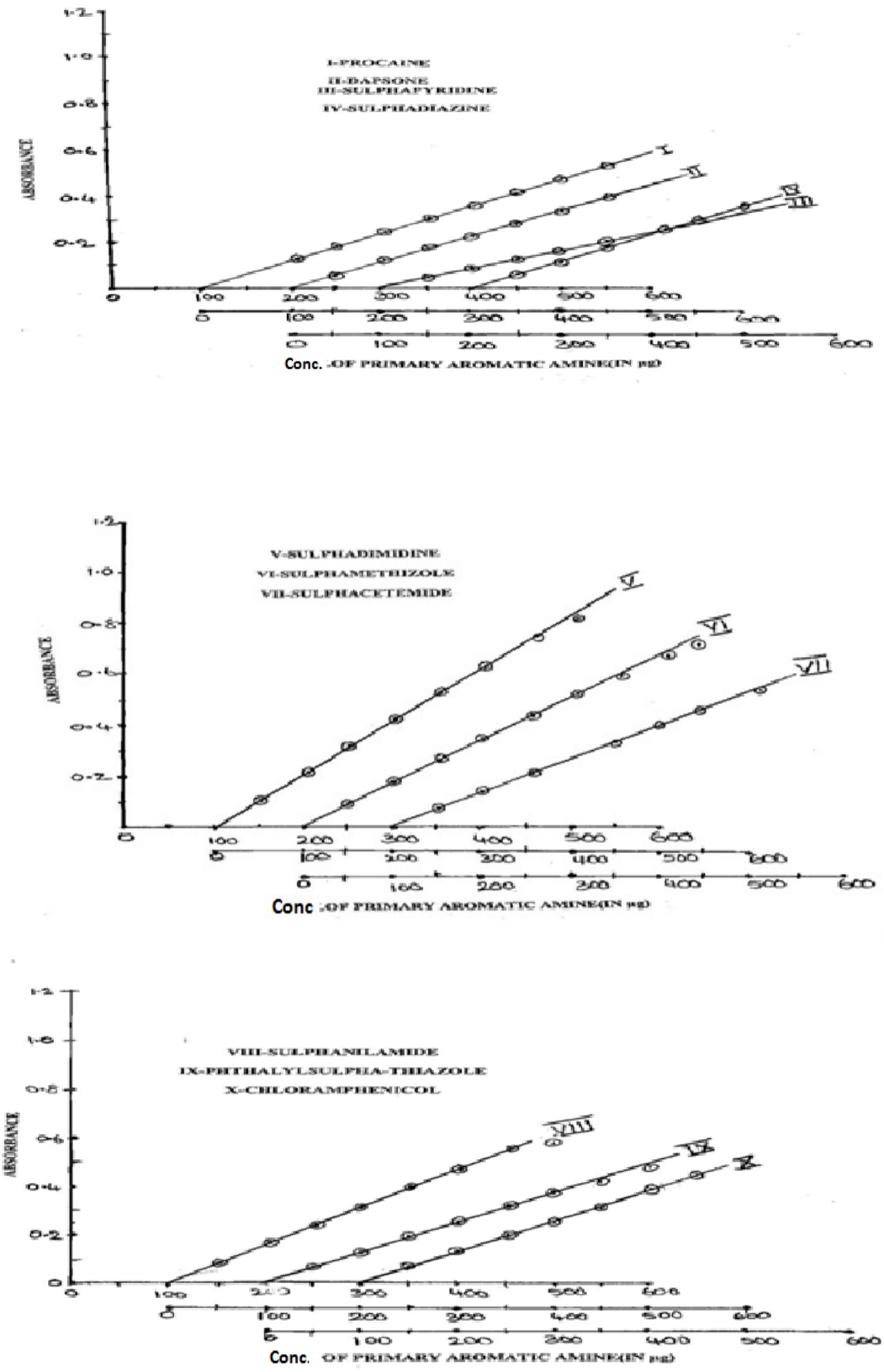


Fig.- 5 to 7 : Adherence to Beer's law

REFERENCES

1. N. D. Oheronis and T. S. Ma., *Organic Functional Group Analysis*, Inter Science. , New York, **1**, p. 229(1964).
2. F.D. Snell and C.T. Snell, *Colorimetric methods of Analysis*, Robert E. Krieger publishers, New York, **4**, p. 197(1964)
3. Idem and Ibid, *Princeton New Jersey*. D. Van Nostrand Company, **4A**, 369 (1967).
4. S. Patal, *The Chemistry of the Amino Group*, Inter-science, New York, **81**, p. 160 & p. 323 (1968).
5. (a) J.T. Woods and G.H. Schneller *Pharmaceutical analysis*, Editors T. Higuchi and E. Brochmenn-Hansien., Interscience, London, **1**, p. 137 (1961); (b) S. Siggia and H.J. Gordan., *Quantitative organic Analysis Via Functional Groups,* John Wiley and Sons , Interscience, New York, **4,** 83 (1979).
6. (a) R.K. Gilpin, L.A.Pachla and J.S. Renweller ,*Anal. Chem*., **53**,14R (1981); (b) W. T. Smith Jr. and J.M. Patterson, *Anal Chem*., **54**, 58R (1982).
7. I.T. Miller and H.D. Springall , *Shorter Sidgwick's Organic Chemistry of Nitrogen*, Clarendon press, Oxford , **1**, p. 76 (1969).
8. E.H. Rodd, C*hemistry of Carbon Componds, A Modern Comprehensive Treatise,* Elsevier Publishing Company, *New York*, **IIIA**, 158 (1954).
9. V.I. Korotkova and V.V Noskov, *ZhAnalit. Khin,* **27**, 580 (1972) and A.A. **25**, 941 (1973).
10. V.I. Korotkova ,V.V.Nosov and V.D. Chistota*wav lab*., **41**, 287 (1975) and A.A. **29**, 5049(1975).
11. (a) L.Vignoli , B. Cristau and J.P. Defretin*, Annais pharm*. *Fr*.,**23,**715 (1965); (b) C.T.H Ellcock and A.C. Fogg, *lab. Pract*., **23**, 555 (1974).
12. (a) H.Schiff, Ann*. Chem*., **131**, 118 (1864); (b) R.W. Layer, *Chem. Rev.*, **63**, 489 (1963).
13. (a) C. Menzie, *Anal*. *Chem*. **28,** 1321 (1956); (b) S.Patal, *The Chemistry of Double Bond,* Interscience, London, p.56 (1970); (c) K. Dey*, J .Sci. Ind Res*., **33**, 76 (1974).

[RJC-1408/2016]