RJC

RASĀYAN *J. Chem.*
Vol. 8 | No. 3 |373 - 379 | July - September | 2015
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

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

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ABSTRACT

p-N, N-dimethyl phenylene diamine (DMPD) is oxidized with sodium metaperiodate into p-N, N-dimehylbenzoquinonemonoimine which can form a purple –red charge –transfer complex with aromatic primary amine (APA) at pH 3.0. The absorbance of the p-N, N-dimehylbenzoquinonemonoimine – APA 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 APA the excipients usually present in formulations did not interfere.

Keywords: Spectrophotometer, APA, DMPD, sodium metaperiodate, Buffer pH 3.0.

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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:

i. Those in which one or more hydrogen atoms attached to the aromatic nucleus are replaced by substituents (nucleo substituted anilines).
ii. 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 color development. Oxidations of amines usually yield degradation products, some of which provide indirect evidence for the presence of different types of amines[4,8,9.] 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 [12,13].

EXPERIMENTAL

Preparation of reagents

DMPD Solution (0.05%)

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

Sodium meta periodate 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 amines used 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 APA 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 Fig-1.

Optical characteristics - Adherence to Beer's law

In order to know the Beer's law limits of the proposed method, the absorbances of a series of solutions containing varying amounts of APA 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 APA shows that the system obeys Beer's Law (Fig.-2). 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

To a 25 ml volumetric flask, these solutions were added in the following order: 15 ml of buffer solution (pH 3.0 ± 0.1), 2.0 ml DMPD, 1.0 ml of $NaIO_4$ and 1.0—6.0 ml of primary aromatic amine. The solution was then diluted to the mark. The absorbance was measured after 15 min at 530 nm against the reagent blank prepared under similar conditions. Concentration of the aromatic amines sample solution was deduced from the standard calibration curve.

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 filtered and 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 Tables-2. From the various reagents studied so far the author felt that DMPD--$NaIO_4$ is the best chromogenic reagent in the spectrophotometric determination of primary aromatic amines at pH 3.0 ± 0.1.

Table-1: Optical Characteristics

Compound	Beer's law limits µg/25 ml	Molar absorptivity $lmol^{-1}cm^{-1}X10^{-3}$	Optimum photometric Range µg/25 ml	Sandal's sensitivity $\mu g/cm^2$ /0.001 absorbance unit	Correlation coefficient
Aniline	100-350	1.65	150-450	0.057	0.9987
o-Toluidine	100-350	0.70	150-400	0.140	0.9996
p-Toluidine	150-300	0.70	150-400	0.150	0.9991
m-Anisidine	50-350	5.02	75—300	0.024	0.9994
p-Phenetidine	100-300	2.51	150-450	0.054	0.9988
m-Phenylenediamine	25-300	5.04	100-300	0.021	0.9993
p-Aminobenzoic acid	50-350	3.53	100-275	0.040	0.9997
m-Chloroaniline	50-300	5.30	75-300	0.024	0.9986
Sulphanilic acid	25-300	6.68	125-350	0.028	0.9992
Benzidine	25-300	8.28	100-300	0.022	0.9987

Table-2: Accuracy of the Method

Compound	Amount Taken(mg)	Amount Found(mg)	% Error
Aniline	200	198	-1.00
o-Toluidine	300	303	1.00
p-Toluidine	300	301	0.33
m-Anisidine	300	298	-0.66
p-Phenetidine	300	303	1.00
m-Phenylenediamine	300	296	-1.33
p-Aminobenzoic acid	350	352	0.57
m-Chloroaniline	250	248	-0.18
Sulphanilic acid	250	251	0.40
Benzidine	400	399	-0.25

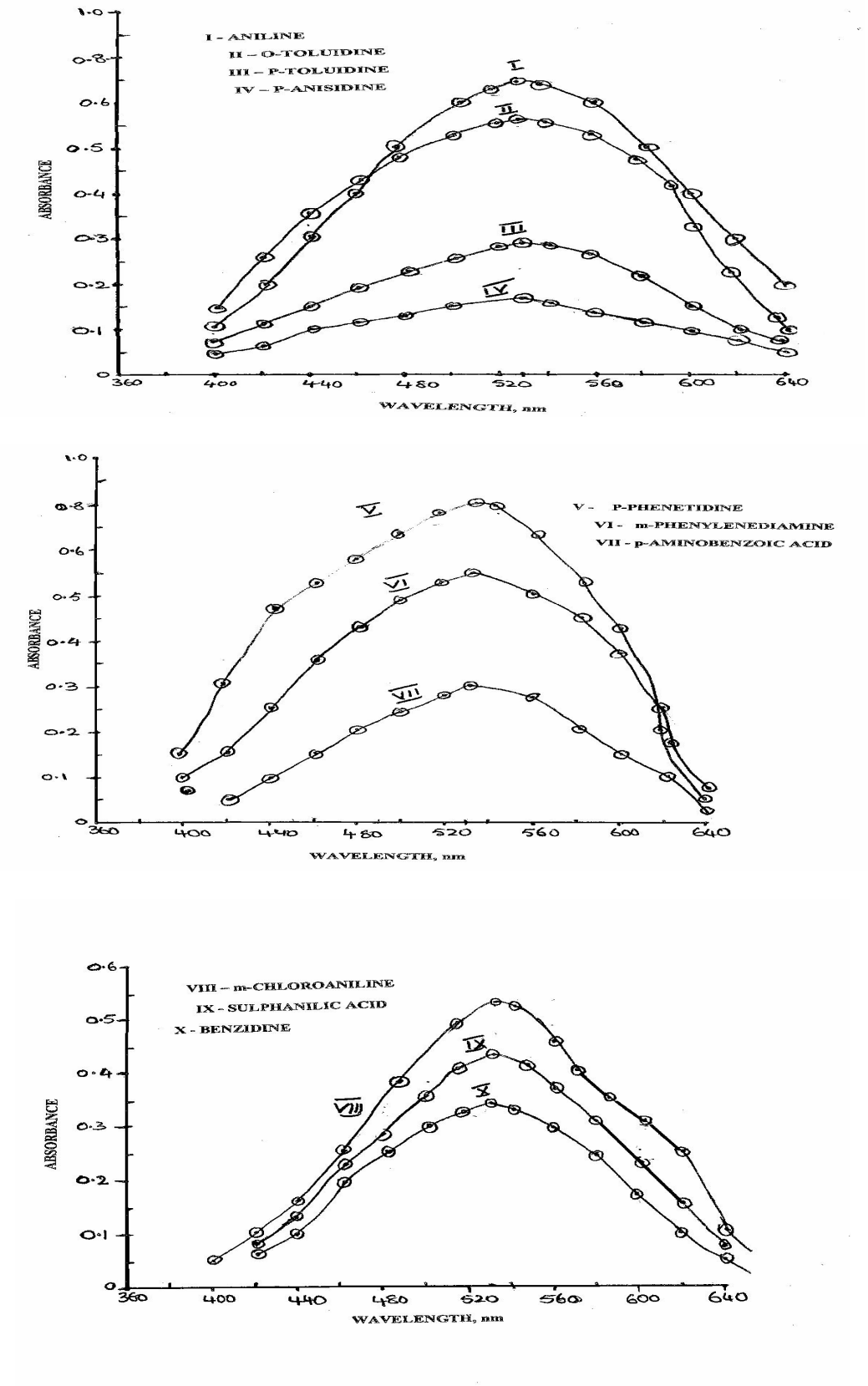


Fig.-1: absorbance curve of APA

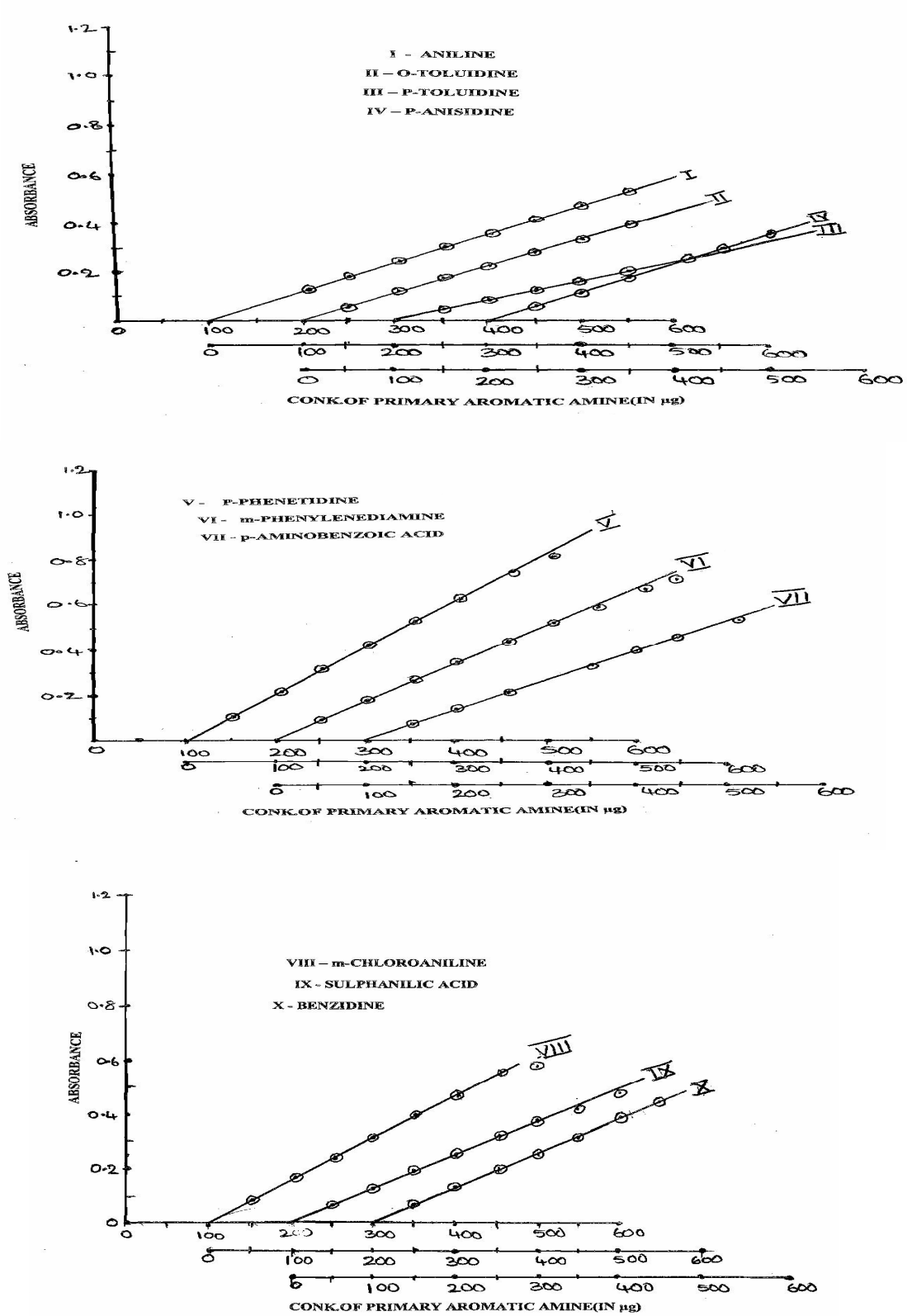


Fig.-2: The linearity of plots between absorbance and the concentration of APA shows that the system obeys Beer's Law

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.

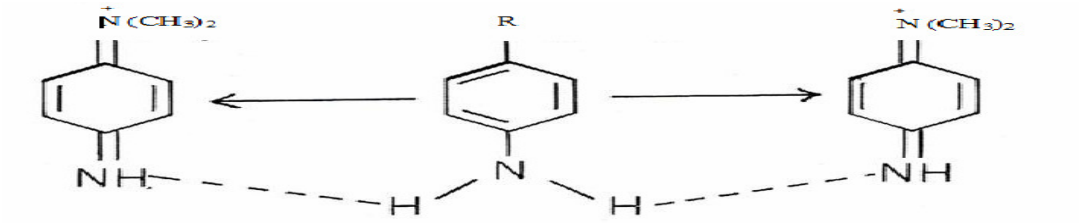
Comparison of the results incorporated in Tables reveal that the proposed method is rapid, sensitive and simple with reasonable precision and accuracy. Sensitivity of the method is better than many of the methods.

Table-3: Precision of the Method

Compound	Standard Deviation	Probability	Limits
		95%	99%
Aniline	0.009	0.14±0.024	0.14±0.014
o-Toluidine	0.022	0.20±0.023	0.20±0.036
p-Toluidine	0.012	0.21±0.013	0.21±0.020
m-Anisidine	0.018	0.60±0.018	0.60±0.029
p-Phenetidine	0.016	0.40±0.012	0.40±0.018
m-Phenylenediamine	0.015	0.58±0.016	0.58±0.025
p-Aminobenzoic acid	0.014	0.50±0.014	0.50±0.023
m-Chloroaniline	0.012	0.48±0.009	0.48±0.014
Sulphanilic acid	0.009	0.50±0.009	0.50±0.014
Benzidine	0.018	0.48±0.018	0..48±0.029

Chemistry involved

Sodium metaperiodate can oxidize DMPD into p-N-N-dimethylbenzoquinone monoimine. This can form a purple red p-N-N-dimethylbenzoquinone monoimine - aromatic primary amines charge-transfer complex with aromatic primary amines at pH 3.0. This can be measured at 530 nm.



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[RJC-1318/2015]