

Sensitive Method for Spectrophotometric Determination of Amines

J. P. Rawat and J. P. Singh

Department of Chemistry, Aligarh Muslim University, Aligarh, U.P., India

Amines are alkyl or aryl derivatives of ammonia and exhibit alkaline reactions in many solvents. Therefore, in the past years, amines have mainly been determined by acid base titrations in aqueous and nonaqueous solutions. Some colorimetric methods are available in the literature for the determination of amino compounds (1-4). Copper sulfate has been used for the determination of ethylenediamine (5). Colorimetric determination of small amounts of aromatic amines by diazotization was reported by Kuritsyn *et al.* (6). A photometric method for the determination of small amounts of aniline has also been reported (7). De-Atley reported a method for the determination of diphenylamine and its mono nitro derivatives by oxidation with iron(III) in sulfuric acid solution. All these spectrophotometric methods suffer from two limitations: they are less sensitive and cannot be applied for all types of amines. We have, therefore, decided to find a sensitive method for the determination of aliphatic as well as aromatic primary, secondary, and tertiary amines. Small amounts of the amino compounds react with acetyl chloride and ferric ion to produce a greenish violet colored complex. The use of this reaction for the determination of amines is described in this report.

EXPERIMENTAL

Apparatus. A Bausch & Lomb Spectronic-20 (U.S.A.) was used for the spectrophotometric work. Elico pH meter Model L1-10 (India) was employed for pH measurements.

Reagents. All the reagents were of analytical grade.

Solution of Amino Compounds. A 1% solution of the organic amino compound was prepared in conductivity water and those

compounds which were insoluble in water were dissolved in 1-propanol.

Solution of Ferric Nitrate. A 5% solution of ferric nitrate was prepared in conductivity water.

Solution of Acetyl Chloride. A 1% solution of acetyl chloride was prepared by taking 1 ml of acetyl chloride and diluting with conductivity water to a total volume of 100 ml.

Buffer solutions of pH 0-5.5 were prepared as reported (8).

Recommended Procedure. A small amount of amino compound (50 μ g-10 mg) was taken in a test tube; to this was added gelatin and 1 ml of 1% acetyl chloride solution and 2 ml of 5% ferric nitrate solution; after shaking 10 ml of pH 1.8 buffer solution was added; and after heating on water bath at 65 °C for 20 minutes, a greenish violet color was observed. Then the volume was made up to 25 ml with conductivity water and the absorbance was taken at the optimum wavelength (550 nm).

RESULTS

The absorbance of the violet colored complex formed by the action of acetyl chloride and ferric nitrate with amines was noted at varying wavelengths. The maximum absorbance (in the form of a plateau) was obtained at 550 nm. In order to get the optimum conditions for the determination of amines, the effect of possible variables was studied. The results are summarized as follows:

Effect of Temperature. One ml of 1% aniline (v/v) was taken in a boiling tube. To this was added 1 ml of 1% acetyl chloride and 1 ml of 5% ferric nitrate solution. The reaction mixture was kept at the specified temperature for 20 minutes in a temperature-controlled water bath. This was then transferred to a standard flask of 25-ml capacity and the volume was made up to the mark with water. The absorb-

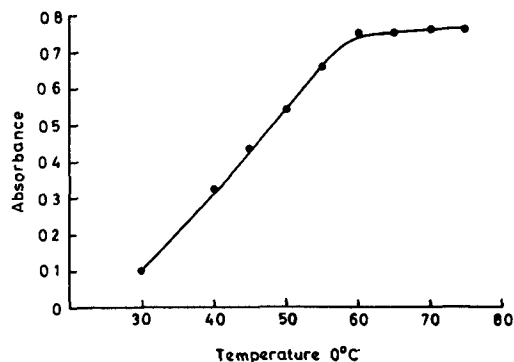


Figure 1. Variation of the absorbance of the greenish violet complex (at 550 nm) of aniline with temperature

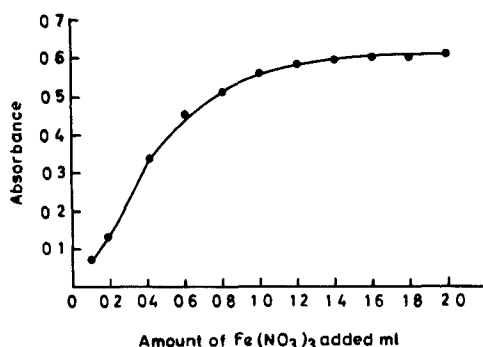


Figure 2. Effect of the amount of ferric nitrate on the formation of the colored complex of aniline

ance was recorded for each set with respect to a blank run under the same conditions. The results are given in Figure 1.

Effect of Ferric Nitrate Added. One ml of 1% aniline (v/v) was taken in a boiling tube. To this were added 0.1 ml of 1% acetyl chloride and varying amounts of 5% ferric nitrate solution with a small amount of gelatin. The reaction mixture was kept at 65 °C for 20 minutes in a temperature-controlled water bath. This was transferred to a standard flask to make the volume 10 ml with conductivity water, and it is clear from Figure 2 that complex formation depends upon the amount of ferric nitrate added and that by increasing the amount of ferric nitrate, absorbance increases and becomes constant; so 2.0 ml $\text{Fe}(\text{NO}_3)_3$ was added in every case.

Effect of the Amount of Acetyl Chloride Added. By applying the above procedure and varying the amount of acetyl chloride, it was observed that when the amount of acetyl chloride was increased, absorbance decreases and becomes constant, shown in Figure 3, and the best results were obtained by using 1 ml of 1% acetyl chloride (for aniline).

Effect of pH. To study the effect of pH, various buffer solutions were added to the reaction mixture. The maximum absorbance for aniline was obtained at pH 1.8 and, on addition of buffers of pH higher than 2.5, precipitation occurs. The results are shown in Figure 4.

Calibration Curves. Calibration curves were prepared applying the same procedure taking 20 μg –10 mg of amino compounds solution. The results are given in Table I.

Study of Precision. To test the reproducibility of the method, ten replicate determinations were made of aniline,

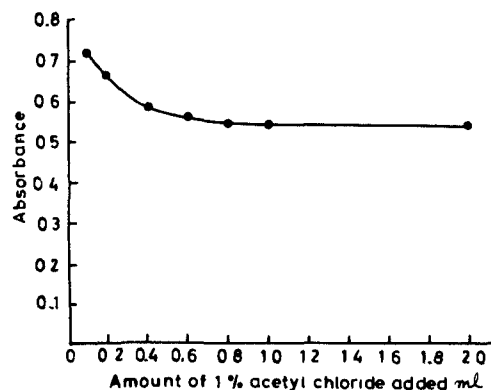


Figure 3. Effect of the amount of acetyl chloride on the formation of the colored complex with aniline

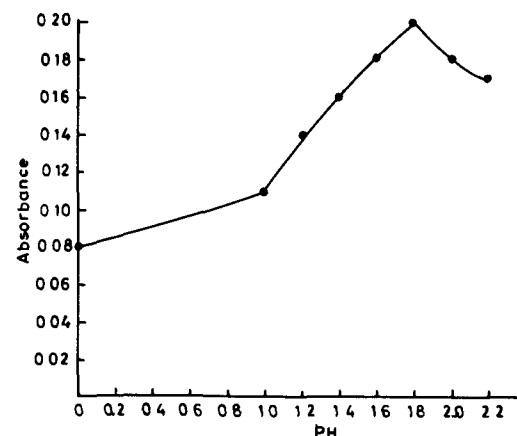


Figure 4. Effect of pH on the formation of the colored complex with aniline

and the standard deviation was calculated. The results are given in Table II.

Study of the Charge on the Complex. The sign of the complex was determined by adding the complexes formed by primary, secondary, and tertiary amines to two types of resin: (i) Dowex-1, an anion exchange resin, and (ii) Dowex-50, a cation exchange resin. The reaction mixture was shaken for 2–5 minutes and was repeatedly washed with demineralized water till the supernatant layer was colorless. The color on the resin beads was noted, and the results are summarized in Table III.

Interferences Certain organic compounds were added to aniline and it was found that nitrobenzene, acetic acid, bromobenzene, and benzaldehyde have no effect on the intensity of the color of the complex, whereas phenol, acetic anhydride, and benzamide interfere. The absorbance increases with phenol and benzamide while a decrease in absorbance was noted by the addition of acetic anhydride.

DISCUSSION

The results of this study reveal that this reaction can be used successfully for the determination of amino compounds. The formation of the greenish violet colored complex is dependent on the temperature (Figure 1), the amount of ferric nitrate (Figure 2), and the amount of acetyl chloride (Figure 3). The absorbance of the colored complex is highly dependent on pH (Figure 4) and, therefore, careful control of pH is required. This was done by adding a sufficient amount of buffer solution of pH 1.8. The opti-

Table I. Absorbance of the Complex Formed by Various Amines for Different Amounts

Amine, sol. no.	Aniline		Diphenylamine		Pyridine			
	Amount, μg	Absorbance	Amount, μg	Absorbance	Amount, μg	Absorbance		
1	102.3	0.13	20	0.15	490.5	0.09		
2	204.6	0.34	40	0.23	981.0	0.15		
3	306.9	0.55	60	0.32	1471.5	0.22		
4	409.2	0.77	80	0.41	1962.0	0.27		
5	511.5	0.99	100	0.49	2452.5	0.34		
	Diethylaniline		Phenylene diamine		p-Toluidine			
1	93.5	0.15	100	0.29	100	0.18		
2	187.0	0.20	200	0.51	200	0.58		
3	280.5	0.24	300	0.72	300	0.99		
4	374.0	0.29	400	0.95	400	1.41		
5	467.5	0.33	500	1.18	500			
	Methylamine		Ethylamine		Isopropylamine			
1	349.5	0.16	344.5	0.12	347	0.15		
2	699.0	0.21	689.0	0.19	694	0.26		
3	1048.5	0.27	1033.5	0.26	1041	0.38		
4	1398.0	0.33	1378.0	0.32	1388	0.49		
5	1747.5	0.40	1722.5	0.38	1735	0.60		
	Amylamine		1,3-Diaminopropane		Morpholine		Piperidine	
Amine sol. no.	Amount, μg	Absorbance	Amount, μg	Absorbance	Amount, μg	Absorbance	Amount, μg	Absorbance
1	383	0.08	89	0.08	499.5	0.13	430	0.06
2	766	0.18	178	0.15	999.0	0.17	860	0.16
3	1149	0.30	267	0.21	1498.5	0.21	1290	0.26
4	1532	0.40	356	0.27	1998.0	0.24	1720	0.36
5	1915	0.51	445	0.35	2497.5	0.28	2150	0.44

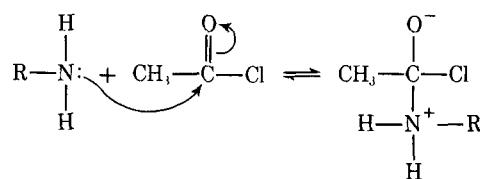
Table II. Reproducibility of Replicate Determinations of Aniline^a

Sol. no.	Amount taken, μg	Amount found, μg	Error, %
1	205	199	-3
2	205	205	0
3	205	210	+2.5
4	205	205	0
5	205	210	+2.5
6	205	205	0
7	205	199	-3
8	205	199	-3
9	205	205	0
10	205	210	+2.5

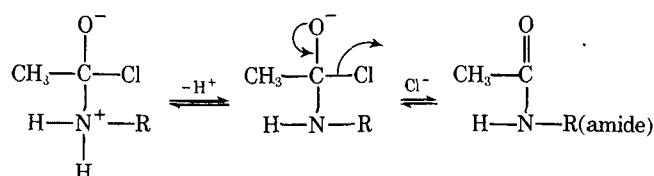
^a Standard deviation = 4.50 μg .

205 μg of aniline was 4.50 μg (Table II) and the maximum error was $\pm 3\%$ which is within the spectrophotometric error range. This method can also be applied to the determination of other amines.

The mechanism of the formation of the greenish violet colored complex may be represented as follows. The amines first react with acetyl chloride by a nucleophilic attack on the carbon atom of carbonyl group.

With Primary Amines.

This intermediate compound gives an amide by elimination of a proton and a chloride ion



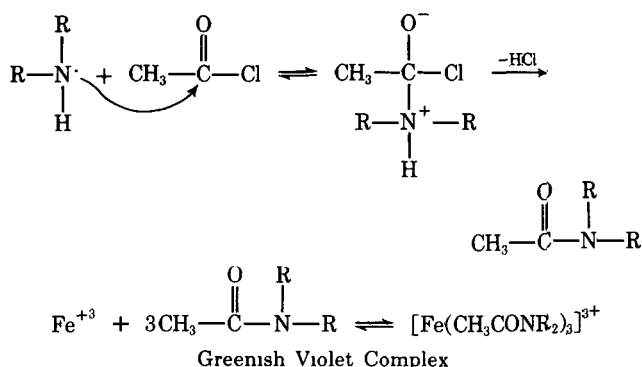
The amide then forms a positively charged colored complex with ferric ion.

Table III. Color of the Resin Beads on Treatment with the Colored Complex of Amines

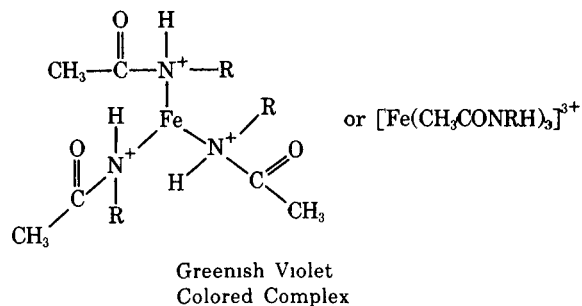
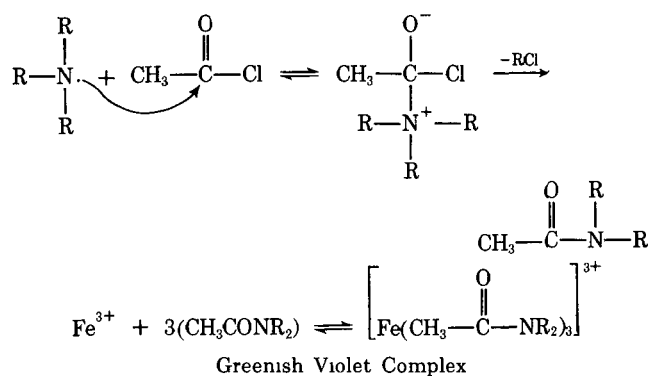
Sol. no.	Color of resin beads	Resin	Aniline	Diphenylamine	Diethylaniline
1	Very light yellow	Dowex-1	No change	No change	No change
2	Very light yellow	Dowex-50	Greenish violet	Greenish violet	Greenish violet

imum conditions are described in the recommended procedure. After these conditions were set, the calibration curves for various amines were found to be reproducible (Table I). The standard deviation for ten different measurements of

With Secondary Amines



With Tertiary Amines



The confirmation of this mechanism is obtained by the results of Table III; according to that, the complex formed is positively charged.

ACKNOWLEDGMENT

The authors are grateful to W. Rahman for providing research facilities.

LITERATURE CITED

- (1) R. A. Lanick, *Anal. Chem.* **35**, 1760 (1963)
- (2) P. H. Gore and B. B. Wheals, *Anal. Chim. Acta*, **30**, 34 (1964)
- (3) Vaughn Levin, B. W. Nippoldt, and R. L. Rebertus, *Anal. Chem.*, **39**, 581 (1967)
- (4) M. Pesez *et al.* "Partique de L'Analyse Organique Colormetrique," Messons Publishers, Paris, France
- (5) Ella Leizerovici and Cristian Oprescu, *Lucr. Conf. Nat. Chim. Anal.* **3rd**, 3, 369-74 (1971)
- (6) L. V. Kuritsyn and V. M. Kuritsyna, *Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Tekhnol.* **15**, 461-2 (1972)
- (7) V. V. Noskov and V. I. Kovotkova, *Sb. Nauch. Tr. Magnitogorsk. Gornom.-et. Inst.*, **87**, 30-34 (1971)
- (8) H. T. S. Britton, "Hydrogen Ions," Aberdeen University Press, Aberdeen, Scotland, 1932, p. 217

RECEIVED for review September 16, 1974. Accepted December 3, 1974. One of us (J. P. Singh) is also thankful to C.S.I.R., India for financial assistance.