MICRODETERMINATION OF SOME ORGANIC COMPOUNDS

"Microdetermination Of The Amino Function In Some Organic Compounds"

By

Mona Abd Elaziz Ahmed

(B. Sc.)

A Thesis

Submitted In Partial Fulfilment Of Requirement Of

Master Of Science Degree

Ain Shams University

University College For Women

Cairo

1973

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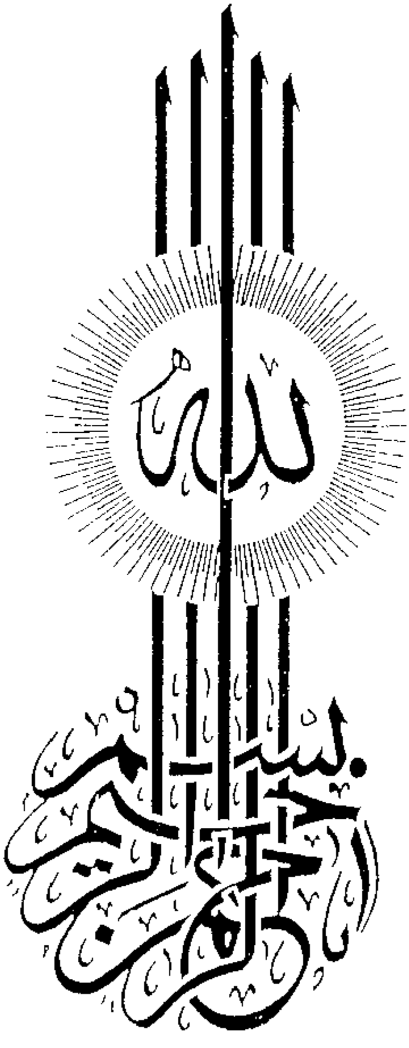
ORGANIC COMPOUNDS

"Microdetermination of The Amino Function
In Some Organic Compounds"

Thesis Advisor	Approved
Prof. W.I. Awad, D.Sc.	....
Dr. S.S.M. Hassan	....

Professor S.M. Abd-Elwahab

Head of Chemistry Department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NOTE

Besides the work carried out in this thesis, the condidate attended postgraduate courses in the following topics:

1) Organic Micro Analysis.
2) Electronic, Infrared, Nuclear Magnetic Resonance, Raman and Mass Spectroscopy of Organic Molecules.
3) Mechanisms of Organic Reactions.
4) Organic Reactions.
5) Chemistry of Heterocyclic Compounds.

She passed successfully an examination in these topics.

Prof. S.M. Abd-Elwahab

Head of Chemistry Department

PREFACE

All the work recorded in this thesis is original, unless otherwise stated by references. This work was carried out in the Department of Chemistry, University College for Women, Ain Shams University.

The author should like to express her deepest gratitude to Professor W.I. Awad, D.Sc., Professor of Organic Chemistry, University College for Women, Ain Shams University, and to Dr. Saad S.M. Hassan, Chemistry Department, Faculty of Science, Ain Shams University, not only for suggesting the subjects investigated but also for continuous advice and valuable criticism.

She wishes also to express her thanks to Dr. Marguerite A. Wassef, Lecturer, Chemistry Department, University College for Women, Ain Shams University, for her help during performing some experiments.

M.A. Ahmed

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SUMMARY

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. However, little work is known for the analysis of aromatic primary amines. The present investigation is undertaken to describe different micro-methods for the analysis of aromatic amines. Mercurimetric, electrometric, potentiometric and visual titrimetric procedures are presented and discussed in detail.

In Chapter I, procedures for mercurimetric and electrometric determination of the primary amino compounds are described. These are based on a reaction of the ethereal solutions of the amines with hydrogen chloride gas for 10 minutes and drying at 50° for 10 minutes to expell excess ether and hydrogen chloride. The chloride content of the hydrochloride salt is measured either by titration in 80 % ethanol with mercuric nitrate using diphenylcarbazone as indicator or by electrometric titration with silver nitrate using Ag/AgCl and quinhydrone electrode system. An average recovery of 99.7 % and 100.2 % is obtained using the mercurimetric and the electrometric procedures, respectively.

In Chapter II, procedures are described for titration of aromatic amines with perchloric acid in non-aqueous solvents. Amphiprotic solvents of low and high dielectric constant and aprotic solvents as alcohols, dioxan and benzene are used. Paramethyl red, Methyl red, and Methyl orange are recommended as suitable indicators for end point detection of many amine samples. An average recovery of 99.5 % is obtained.

In Chapter III, Potentiometric procedures are described for the analysis of aromatic amines by titration with perchloric acid in non-aqueous solvents using glass-calomel electrode system. Three factors are found to influence the shape of the titration curve, these are: (a) the basic strength of the amino compound; (b) the position of the substituent group in the aromatic nucleus, and (c) the nature of the solvent used as a medium in the titration. Sharp inflections in the titration curves at the equivalence point are observed on using dioxan as a solvent. An average recovery of 102.2 % is obtained with all the analysed compounds. It is observed also that there is a relation between the half neutralization potential values ($E_{\frac{1}{2}}$) of the amino compounds and their basic strength in methanol, isopropanol and dioxan.

METHODS OF DETERMINATION
OF AMINO GROUP
HISTORICAL INTRODUCTION

I- TITRIMETRIC METHODS

Amino group can be determined by a variety of titrimetric procedures involving acid-base, redox and diazotization reactions.

(A) Acid-Base Reactions:-

Amines are weak bases capable of reacting with acids. Several methods of detecting this reaction have been proposed. The low solubility of most amines in water is usually corrected by adding organic solvents. A rapid titration of the amino group with a standard solution of perchloric acid in acetic anhydride or acetic acid at low temperatures has been described[1]. Methyl violet, Malachite green, Neutral red, Safranine and Tropeolin OO have been recommended as indicators[2]. Acetonitrile and acetic anhydride may be used as solvents[3]. The analysis of aminopyrine and some primary aromatic amines by titration with perchloric acid shows an average error of ± 0.5 %. Titration in methyl alcohol, isopropyl-methyl alcohol mixture or dimethyl formamide-methanol solutions with hydrochloric acid solution in methanol has been reported by Khachapuridze[4], the error being ± 5 %.

Mixtures of primary, secondary and tertiary amines are determined for each component in the presence of the other. Total amines are determined by titration with hydrochloric acid in ethylene glycol-isopropyl alcohol mixture and to another sample salicyldehyde is added to trap[5] the primary amine as Schiff's base and total secondary and tertiary ones are then titrated. Lewis acids may be used in analyses of amines. Boron trifluoride and titanium tetrachloride[6] are used to titrate heterocyclic bases in aprotic solvents.

Determination of amines is also done by indirect acid-base reaction. Fedorov[7] analysed some aromatic amines by reaction with hydrochloric acid and the reaction mixture was dried. The hydrochloride salt obtained was then dissolved in water and titrated with sodium hydroxide using phenolphthalein as indicator. However, this method is not applicable to amino compounds containing acids function (e.g., COOH, SO_3H, OH). Furthermore, incomplete formation of the hydrochloride salt was usually observed with some amino compounds on the macroscale.

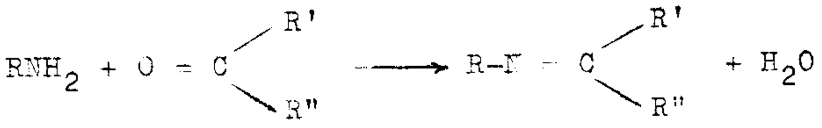
Sulphur trioxide in dioxan is employed for determination of the amino group in aromatic compounds, except for those containing negative substituents[8].

$$ArNH_2 + SO_3 \longrightarrow ArNHSO_3H$$

The dioxan - SO_3 solution is added to the sample and allowed to react for 3-5 minutes. Then water is added to destroy the excess reagent and the sulphuric acid produced is rapidly titrated with sodium carbonate solution using Congo red or Bromophenol blue as indicator.

Aliphatic amines in air[9] are determined by passing air through an absorber containing 0.001 N sulphuric acid and the excess acid is titrated with sodium hydroxide solution using Methyl red as indicator.

The condensation reaction of amines when carried out with certain reagents and under controlled conditions, provides good methods for determining primary amines, although some amines of other types may interfere.



$$RNH_2 + O = C\begin{matrix} R' \\ R'' \end{matrix} \longrightarrow R-N = C\begin{matrix} R' \\ R'' \end{matrix} + H_2O$$

Primary aliphatic and aromatic amines can be determined with benzaldehyde in non-aqueous solutions. Excess of this reagent is used and destroyed afterwards with hydrogen cyanide[10], and the water produced is measured by the Karl Fischer method[11].

$$C_6H_5CHO + HCN \longrightarrow C_6H_5CH(CN)OH$$

Aliphatic amines have been also determined by their reaction with 2,4-pentanedione[12], in which imines are formed. Condensation with formaldehyde has been also advocated[13]. The excess reagent is titrated with sodium methoxide in pyridine, using Phenolphthalein or Thymolphthalein indicator.

Acylation with acetic anhydride in anhydrous pyridine can be used for the determination of primary and secondary amines:

$$R{-}NH_2 + (CH_3CO)_2O \longrightarrow RNHCOCH_3 + CH_3COOH$$

$$R_2{-}NH + (CH_3CO)_2O \longrightarrow R_2NCOCH_3 + CH_3COOH$$

The amount of the amine is determined by titration of the liberated acid[14] or by the amount of water necessary for hydrolysing the excess acetic anhydride[15]. Similar determinations based on the use of acetyl chloride are proposed[16,17], but the anhydride methods seems to be more advantageous[18]. Phthalic anhydride[19] and pyromellitic anhydride[20,21], are used as reagents for the determination of primary and secondary amines.

Primary and secondary amines yield dithiocarbamic acids with carbon disulphide:

$$R\text{-}NH_2 + CS_2 \longrightarrow RNHCS_2H$$

$$R_2\text{-}NH + CS_2 \longrightarrow R_2NCS_2H$$

After discarding the excess reagent, the reaction can be followed by direct titration of the dithiocarbamic acid with alkali[22,23].

(B) Redox Reactions:-

Oxidation of amines usually yield degradation products, some of which provide indirect evidence for the presence of different types of amines. However, determination of the amino group by methods involving redox reactions has been described but little oxidants were tried.

Iodine solution in the presence of an excess of hydroxy methane sulphonic acid is used as a titrant[24]. This iodimetric method makes it possible to determine amines in mixtures containing components which do not react with it. Aromatic amines can be determined iodometrically[25] by dissolving the sample in water or alcohol, then iodized with hydrochloric acid solution of iodine trichloride. The iodine liberated after addition of potassium iodide is titrated with sodium thiosulphate. Amines after diazotization may be determined