ANALYSIS OF SOME ORGANIC FUNCTIONAL GROUPS USING ELECTROCHEMICAL AND SPECTRAL METHODS.

THESIS

SUBMITTED FOR THE DEGREE OF
M.Sc. IN CHEMISTRY

BY

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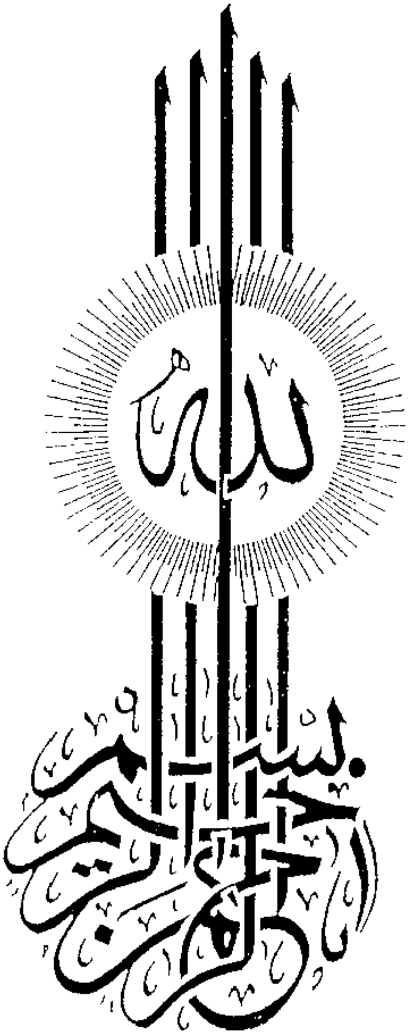
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NOTE

Beside the work carried out in this thesis, the candidate has attended post-graduate courses for one year in organic chemistry including the following topics :

1. Physical organic chemistry.
2. Chemical spectroscopy.
3. Advanced Heterocyclic chemistry.
4. Quantum chemistry.
5. Polymer science.
6. Organic reactions.
7. Instrumental Analysis.

He has successfully passed an examination in these topics.

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CONTENTS

CHAPTER III

Potentiometric Determination of Some Tertiary Amines and Alkaloids using Silver/Sulfide Ion-Selective Electrode.

SUMMARY

In the present investigation, new methods are described for the microdetermination of some quinones, in addition to primary, secondary and the tertiary amines.

New selective and sensitive spectrophotometric methods for quinone determination were developed. Quinone samples were treated with either methanolic solution of rhodanine or fluorene in ammoniacal media. Moreover, aqueous semicarbazide hydrochloride was also used as reagent. Semicarbazide was the most sensitive reagent for the determination of 1,4-benzoquinone, 1,4-naphthoquinone and 2-methyl-1,4-naphthoquinone. Quinones substituted with electron withdrawing groups such as tetrachloro-1,4-benzoquinone, tetrabromo-1,4-benzoquinone and 1,2-naphthoquinone-4-sulphonic acid were better determined using rhodanine. The average recovery was 99.1%, 98.7% and 99.2% using rhodanine, fluorene and semicarbazide hydrochloride as reagents, respectively. The sample standard deviation for the analyzed quinones was 0.34%, 0.42% and .60% using the former reagents, respectively.

Aliphatic primary and secondary amines were determined utilizing their reaction with carbon

disulphide. Potentiometric titration of the formed dithiocarbamates with standard silver nitrate solution using silver/sulfide ion-selective electrode was carried out. The effect of solvent, base, temperature and reaction time were investigated. The optimum conditions for the quantitative formation of dithiocarbamates require a minimal amount of 1,4-dioxane as solvent, 2 drops of 0.2% sodium hydroxide solution as base and excess carbon disulphide to stand for 15 minutes at room temperature. The titration requires prior evaporation of the unreacted carbon disulphide at 47 ± 1°C Sharp inflection breaks were obtained at the end points ranging from 150 mV for ethylamine to 480 mV for dibutylamine. An average recovery of 98.4% and 98.4% with 0.72% and 0.50% standard deviation were obtained for the analyzed primary and secondary amines, respectively.

Some tertiary amines and alkaloides were determined by reaction with methyl iodide at 44 ± 1°C The produced quaternary ammonium iodide salts were potentiometrically titrated with silver nitrate solution using either the iodide or silver/sulfide ion-selective electrode. The effect of solvent, temperature and time of reaction were examined. In the titration of the reaction product of triethylamine and methyl iodide with silver nitrate, the potential breaks at the end point were 140-160 mV for silver/sulfide electrode and 280-300 mV for the iodide electrode. An average recovery of 99.0% and 98.8% with standard deviation of 0.75% and 0.51% were obtained for the studied amines and alkaloides, respectively.

CHAPTER 1

Spectrophotometric Determination of Some Quinones using Rhodanine, Semicarbazide Hydrochloride and Fluorene as Reagents.

INTRODUCTION

The quinone function group widely occures in both nature and mankind manufactured materials. Over a 150 quinones, including K-vitamins, naturally exist. Moreover, the quinone function is present in an important class of synthetic dyes known as quinone dyes. In addition, it is present in pharmaceuticals, fungicides and leather tanning compounds.

Since quinones are highly conjugated, they are rather closely balanced, energetically, against the corresponding hydroquinones. The ready interconversion provides a convenient oxidation-reduction system. In many cases, quinones seem to take part in oxidation-reduction cycles essential for living organism.

Most of the reported methods for quinone determination using gasometric, titrimetric and polarographic techniques are of the oxidation-reduction type. Moreover, quinones behave as α, B-unsaturated ketones which undergo condensation or addition reactions. This is normally the basis of the described spectrophotometric methods of analysis for such compounds.

1. Gasometric Methods :

Willstätter and Cramer (1) described a macro gasometric method for quinone determination based on reduction with phenylhydrazine. The liberated nitrogen gas was collected in an azotometer and measured. However, the method was unsuccessful on the micro-scale, due to the partial decomposition of the reagent by heating (2). Hassan and Zaki utilized hydroxylamine, hydrazine sulphate and phenylhydrazine hydrochloride for the microgasometric determination of quinones. One mole of nitrogen gas evolved per mole of quinone in the reaction with hydroxylamine. However, the other two reagents produced one mole of nitrogen per two moles of quinone.

Sodium borohydride was applied as reagent for the microgasometric determination of quinones (3). The residual reagent, after reaction completion, was decomposed by sulphuric acid and the liberated hydrogen gas was measured.

This method was used for quinone determination on carbon black surface (4).

2. Titrimetric Methods :

a) Reaction with titanium (III)

Titanium (III) chloride was used to determine the quinone structure in the macro method of Hibbert and Suida (5). The sample was dissolved in acetic acid and 30 ml of 0.2 N titanium (III) chloride was added, boiled for two minutes, cooled, and the excess of titanium (III) was back-titrated with 0.2 N iron (III) sulphate.

A micro procedure has been developed by dissolving the sample in acetone and buffering the solution with sodium acetate before the addition of 0.02 N titanium (III) chloride. After the reaction was completed, the solution was acidified with sulphuric acid and the residual titanium (III) ions were determined by titration with 0.02N iron (III) ammonium sulphate using neutral red-ammoniumthiocyanate as indicator (6).

Veibel (7) stated that the reduction of quinone may be carried out in acid solution at room temperature without keeping the reaction mixture under an inert atmosphere.

b) Reaction with vanadium(II)

Vanadium (II) sulphate was used for the semimicro determination of quinones (8). The quinone sample was treated with excess vanadium (II) solution in acetate buffer media. The unreacted reagent was back titrated with iron (III) solution using safranine-T, phenosafranine or neutral red indicator. The method was successfully used for the analysis of benzoquinone and naphthoquinone derivatives.

Potential measurements were also used for the end point detection. Matrka and Zdenck (9) used vanadium (II) sulphate for direct potentiometric titration of anthraquinone.

c) Reaction with chromium (II)

The reaction of quinones with chromium(II) proceeded fairly fast at room temperature. It was carried out in inert gas atmosphere to prevent the reagent oxidation with oxygen. Iron (III) was generally used as an oxidizing agent for the determination of unreacted chromium (II) ions.

Bohei and Furman (10) used excess reagent in hydrochloric acid medium for quinone reduction. Thiocyanate was used as indicator to detect the end point for the titration unreacted reagent with iron (III) alum.

Tandon (11) recommended the same procedure on the microscale using tartrate buffer. Direct titration of quinones with chromium (II) using neutral red as indicator was also described (12).

d) Iodometric Methods :

Treatment of quinones with iodide ion in acidic media (hydriodic acid) produces the