# ;Spectrophotometric determination of [2-amino-(1-butanol, 1-pentanol, 1-hexanol$_{(DL)}$)] by oxidation with periodate via Malaprade reaction.

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## Abstrast

The research has involved of the development of the spectrophotometric methods to estimate micrograms amounts of amino alcohols (2-amino-1-butanol, 2-amino -1-pentanol $_{(DL)}$ and 2-amino -1-hexanol $_{(DL)}$),by oxidation with periodate via Malaprade reaction at 45° ,in determination the concentrations of these compounds at aqueous solution depending basically upon the standard calibration curve of iodate.

these methods characterized with hyper sensitivity, where as appeared through molar absorbability values , and study of many organic compounds interferences.

## الخلاصة

يتضمن البحث تطوير طريقة طيفية لتقدير كميات متناهية في الضغر من الكحولات الامينية (2-أمينو-1-بيوتانول $_{(DL)}$ و [2-أمينو-1- بنتانول $_{(DL)}$ وكذلك (2-أمينو-1-هكسانول $_{(DL)}$)] بأكسدتها بواسطة البيرودات بإستخدام تفاعل ملابراد وعند درجة حرارة 45م° وإجاد تراكيز هذه المركبات في محلولها المائي بالإعتماد على المنحني القياسي

لليودات . تمتاز الطرق بحساسية عالية حيث ظهرت من خلال قيم الامتصاصية المولارية للمركبات المدروسة ودراسة تداخلات لعدد من المركبات العضوية.

## Introduction

The alkanolamines are compounds which posses the properties of both amines and alcohols .

These compounds are highly useful materials for a wide Varity of applications (1) malfunctional additives for latex pains, dispersants for mineral slurries, sources of alkalinity corrosion, protection and emulsion stability for metalworking fluids(2), neutralizing amines for water treatment, biological buffers and as neutralization and buffering chemicals for personal care and household products. (ie): secondary amine and their derivatives content of raw materials used in the manufacture of cosmetic and personal care products(3).

We have found paucity or lacks of the spectrophotometric researches to determine those compounds and their derivations, let alone or exclusively the pharmaceutical researches which have been concentrated on medical medicaments or medical purposes (4) .

Some of the researches depend on potentiometric titration of these compounds and their derivatives with hydrochloric acid in water and perchloric acid in acetic acid which needed standardizations of elecrodes by using P-sulfo-o-methoxybenzeneazodimethyl-1-naphthylamine as indicator (5).

The second method involves tedious extractions steps which require carefull control of pH, often these are not usually readily available(6) .

Whereas these compounds constitute an imininm intermediate that's to say the N-substituted amino alcohols which consider unstable in aqueous solutions(7).

The last approach but on rely on the reaction of these compounds with phenylbenzimidazole sulfonic acid which form a lower level of product(8).

The latter method depends on the usage of multivariate

data analyses which has given an unexpected result by the significant increase in the screening and optimisation of the catalytic reactions (9)., and there are some methods which depend upon the oxidation with periodate . (10,11,12)

The present work describes a development of the spectrophotometer methods to estimate microgram amounts of some amino alcohol compounds, these methods it rely oxidation of these compounds by using periodate thought the Malaprade reaction

**Apparatus and Experimental arrangement:**

Absorption measurement were carried out using Philips PU 8800 uv/vis computerized recording double beam spectrophotometer and matched 1-cm optical bath quartz cells. All measurement were carried out using Model PW 9420 pH meter supplied with an electrode type CE 10-12 pH. weighing were carried out on balance type Mettler $H_{54}$AR. Heating of solutions were carried out on a water bath frost instruments LTD.

## Reagents

All reagents were of analytical reagents grade.

1. Periodate ($1.2\times10^{-3}$ M) solution: prepared by dissolving (0.069)g of potassium periodate in distilled water in 250 ml volumetric flask, and daily prepared and kept in an opaque bottle.
2. Buffer (0.5 M) solution: sodium chloroacetate buffer solution of pH 8 prepared in an aqueous solution and mixing this solution with dilute hydrochloric acid which is adjusted by pH meter.
3. Ammonium molybdate (0.072 M) solution: prepared by dissolving 8.830 gm of ammonium molybdate in 100 ml distilled water, and heating is necessary at about 50 $^{o}$C. The solution was to be standed for an overnight, then filtered and diluted with distilled

water to 100 ml and stored in a polyethylene container.

4. Potassium iodate ($10^{-4}$ M) solution: This solution was prepared by dissolving 0.00214 g of potassium iodate and diluting to 100 ml with distilled water.
5. Potassium iodide (0.5 M) solution: This solution was prepared by dissolving 8.250 g of potassium iodate and diluting to 100 ml with distilled water, This solution was prepared daily.
6. Amino alcohols compounds standard solutions: Aqueous solution of 10ppm was prepared for each compound of 2-amino-1-butanol $_{(DL)}$, 2-amino-1-pentanol $_{(DL)}$ and 2-amino-1-hexanol.

## Methods

All parameter affected the Malaprade reaction have been studied and the optimum condition have been used, and all operations are carried out in the dark at room temperature:

- **The calibration graph:**

Increasing volumes (0.5-2.5) ml of $1\times10^{-4}$ iodate solution were transferred to a series of 25 ml volumetric flasks followed by the addition of 4ml of potassium periodate, 6ml of ammonium molybdate, then 5ml of pH 8 and 3 ml iodide solutions added the solutions were diluted to the mark with distilled water and the absorbances were measured at 350 nm after 40 min . Beers law was obyed over the range of $0.8\times10^{-6}$ M to $10\times10^{-6}$ M iodate, It is noticeable in this respect that the calibration graph for iodate in the presence of periodate coincided with the calibration graph for iodate constructed in the absence of periodate (Fig 1).

**Spectrophotometric method of 2-amino-1-butanol$_{(DL)}$ via measurement of tri-iodide:**

In a 25 ml volumetric flask, place 4-22 µg of 2-amino-1-butanol$_{(DL)}$ followed by addition of 4 ml of $1.2\times10^{-3}$ M potassium periodate solution, heat on a water-bath at 45°C for 5 minutes, cool, allow the solution to stand at room temperature for 40 minutes to complete the oxidation then added 7 ml of ammonium molybdate solution followed by the addition of 5 ml of buffer solution of pH 8 and 3 ml of potassium iodide solution and dilute with distilled water to the mark allow to stand for 40 minutes at room temperature, measure the absorbance of tri-iodide at 360 nm against reagent blank prepared in the same way but containing no 2-amino-1-butanol $_{(DL)}$. A straight line passing through the origin was obtained.

The apparent molar absorptivity in the region of the least photometric error was $0.027\times10^{6}$ $1.mol^{-1}.cm^{-1}$

- **Spectrophotometric method of 2-amino-1-pentanol$_{(DL)}$ via measurment of tri-iodide.**

In a 25 ml volumetric flask, place 5-25 µg of 2-amino-1- pentanol $_{(DL)}$ followed by addition of 5 ml of $1.2\times10^{-3}$

M potassium periodate solution, heat on a water-bath at 40 °C for 10 minutes, cool, allow the solution to stand at room temperature for 65 minutes to complete the oxidation then added 6 ml of ammonium molybdate solution followed by the addition of 5 ml of buffer solution of pH 8 and 5 ml of potassium iodide solution and dilute with distilled water to the mark allow to stand for 40 minutes at room temperature and measure the absorbance of tri-iodide at 350 nm against reagent blank prepared in the same way but containing no 2-amino-1- pentanol $_{(DL)}$. A straight line passing through the origin was obtained. The apparent molar absorptivity with reference to the compound in the region of the least photometric error was found to be $0.020\times10^6$ $1.mol^{-1}.cm^{-1}$

### .Spectrophotometric method of 2-amino-1-hexanol$_{(DL)}$via measurement of tri-iodide.

In a 25 ml volumetric flask, place 5-29 µg of 2-amino-1- hexanol$_{(DL)}$ followed by addition of 6 ml of $1.2\times10^{-3}$ M potassium periodate solution, heat on a water-bath at 45°C for 15 minutes, cool, allow the solution to stand at room temperature for 75 minutes to complete the oxidation then added 7 ml of ammonium molybdate solution followed by the addition of 5 ml of buffer solution of pH 8 and 4 ml of potassium iodide solution and dilute with distilled water to the mark Allow to stand for 40 minutes at room temperature and measure the absorbance of tri-iodide at 350 nm against reagent blank prepared in the same way but containing no 2-amino-1- hexanol $_{(DL)}$.

A straight line passing through the origin was obtained. The apparent molar absorptivity with reference to compound in the region of the least photometric error was found to be $0.016\times10^6$ $1.mol^{-1}.cm^{-1}$ .

## Experimental Results and Disussion

1. Method was proposed for the spectrophotometric determination of 2-amino-1-butanol $_{(DL)}$, 2-amino-1-pentanol $_{(DL)}$, and 2-amino-1-hexanol $_{(DL)}$ based on the oxidation of these compounds with periodate at 45c° followed by spectrophotometric determination of iodate as tri-iodide after reaction with iodide. The excess of periodate was is masked with molybdate and the tri-iodid formed was measured at 350 nm to complete the oxidation of these compounds one mole of iodate was produced per mole of each compounds at (40, 65, 75) min respectively in the presence of a large excess of periodate with 40min, respectively and no further oxidation occurs at this temperature.

The periodate reacts quantitatively with these compounds to split the carbon-carbon bonds, one molecule of periodate was reduced to iodide for each (C-C) bond broken according to the Malaprade reaction.

The order of addition of the compounds showed significant importance, the obtained result sustained that the approaches which have been used were simple because the evaluation of the concentration of these compounds is relied on the calibration graph of iodate (Fig. 1). The method is selective as in the case of tri-iodide because the molar absortivity of these methods is $0.027\times10^{6}$ 1.mol$^{-1}$. cm$^{-1}$, $0.020\times10^{6}$ 1.mol$^{-1}$.cm$^{-1}$ and $0.016\times10^{6}$ 1.mol$^{-1}$.cm-$^{1}$ respectively of 2-amino-1-butanol $_{(DL)}$, 2-amino-1- pentanol $_{(DL)}$ and 2-amino-1-hexanol $_{(DL)}$.

The stochiometry of chemical reaction shows that the rate falls off after one mole of iodate has been produced per one mole of 2-amino-1-butanol $_{(DL)}$, 2-amino-1- pentanol $_{(DL)}$ and 2-amino-1-hexanol $_{(DL)}$. The required time for the reaction with periodate to each compound depends on the connected length of alkaline sery of each compound also which increase by the enhancement of the length of the sery according to Malaprade reaction. (Table 1,2,3). The accuracy and precision of these methods were checked under the optimized conditions, the results (six replicates) are given in (Table 4).

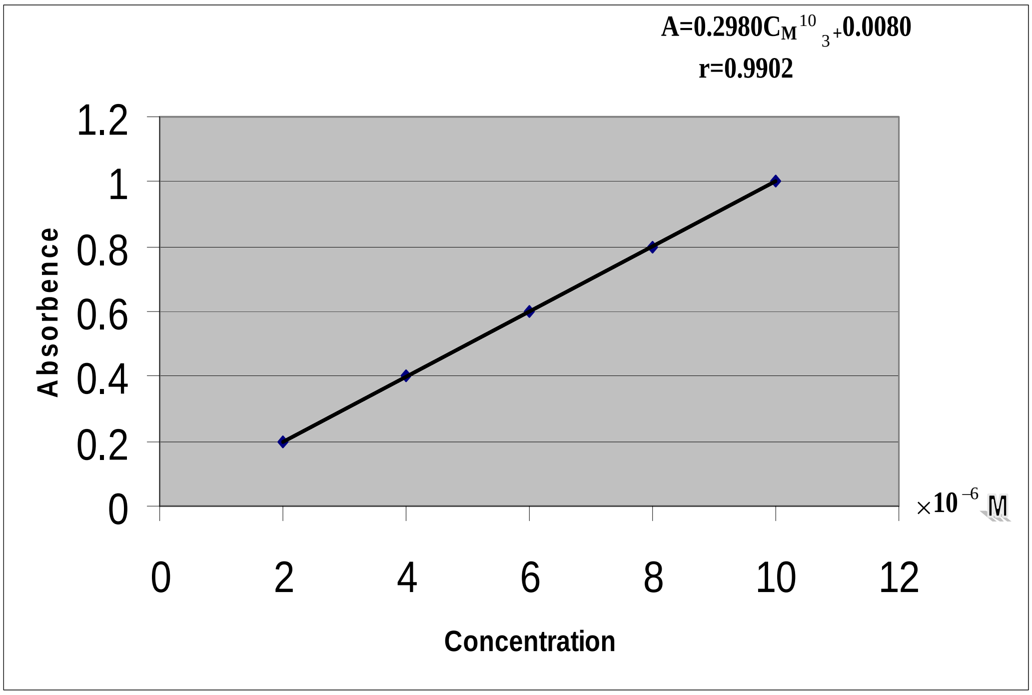

**Fig.(1) Calibration curves for the determination of iodate(0) and iodate in the presence of periodate (*) .**

## nterferences:

The effect of some foreign organic compounds in binary mixtures of 2-amino-1-butanol $_{(DL)}$, 2-amino-1- pentanol $_{(DL)}$ and 2-amino-1-hexanol $_{(DL)}$ studied by using 5-fold excess, 10-fold excess and 15-fold excess respectively of various compounds showed that the presence of 5-fold excess, 10-fold excess and 15-fold excess respectively of various compounds with 2-amino-1-butanol $_{(DL)}$, 2-amino-1- pentanol $_{(DL)}$ and 2-amino-1-hexanol $_{(DL)}$ respectively does not cause serious interfering effect on the determination of 13.36 µg of 2-amino-1-butanol $_{(DL)}$, 15.47 µg of 2-amino-1- pentanol $_{(DL)}$ and 17.57 µg of 2-amino-1-hexanol $_{(DL)}$ . The results are shown in (Table 5,6,7).

**Table (1): The rate of reduction of 2-amino-1-butanol $_{(DL)}$ with periodate**

| 2-amino-1-butanol $_{(DL)}$ X M | Moles of iodate produced* per mole of 2-amino-1-butanol $_{(DL)}$ after | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 5 min | 10 min | 15 min | 20 min | 25 min | 30 min | 35 min | 40 min |
| $2\times10^{-6}$ | 0.87 | 0.88 | 0.92 | 0.95 | 0.98 | 0.98 | 0.99 | 1.0 |
| $4\times10^{-6}$ | 0.95 | 0.89 | 0.91 | 0.93 | 0.97 | 0.99 | 0.99 | 1.0 |
| $6\times10^{-6}$ | 1.0 | 0.98 | 0.99 | 0.10 | 0.97 | 0.98 | 0.98 | 1.0 |
| $8\times10^{-6}$ | 1.0 | 0.91 | 0.93 | 0.95 | 1.01 | 0.99 | 1.0 | 1.0 |

**Table (2): The rate of reduction of 2-amino-1-pentanol$_{(DL)}$ with periodate**

| 2-amino-1-butanol $_{(DL)}$ X M | Moles of iodate produced* per mole of 2-amino-1-butanol $_{(DL)}$ after | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 10min | 20 min | 30 min | 35 min | 40 min | 50 min | 60 min | 65 min |
| $2\times10^{-6}$ | 0.90 | 0.96 | 0.95 | 0.98 | 0.99 | 1.01 | 0.95 | 1.0 |
| $4\times10^{-6}$ | 0.89 | 0.90 | 0.92 | 0.94 | 0.96 | 0.96 | 0.97 | 1.0 |
| $6\times10^{-6}$ | 0.93 | 0.95 | 1.0 | 0.98 | 0.97 | 1.0 | 1.0 | 1.0 |
| $8\times10^{-6}$ | 1.0 | 0.97 | 0.94 | 1.0 | 0.98 | 1.0 | 0.99 | 1.0 |

**Table (3): The rate of reduction of 2-amino-1-hexanol $_{(DL)}$ with periodate**

| 2-amino-1-butanol $_{(DL)}$ X M | Moles of iodate produced* per mole of 2-amino-1-butanol $_{(DL)}$ after | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 20min | 30 min | 40 min | 50 min | 60 min | 65 min | 70 min | 75 min |
| $2\times10^{-6}$ | 0.88 | 0.92 | 0.95 | 0.98 | 0.98 | 0.99 | 0.99 | 1.0 |
| $4\times10^{-6}$ | 0.95 | 0.95 | 0.97 | 0.99 | 1.0 | 1.0 | 0.98 | 1.0 |
| $6\times10^{-6}$ | 0.98 | 0.98 | 0.98 | 0.97 | 0.99 | 0.97 | 0.99 | 1.0 |
| $8\times10^{-6}$ | 0.98 | 0.96 | 0.97 | 0.99 | 1.0 | 0.98 | 0.98 | 1.0 |

* Determined by using the calibration graph of iodate

**Table (4): Accuracy and precision of the methods via measurement of tri-iodide**

| 2-amino-1-butanol $_{(DL)}$ | | | 2-amino-1- pentanol $_{(DL)}$ | | | 2-amino-1-hexanol $_{(DL)}$ | | |
|---|---|---|---|---|---|---|---|---|
| Amount taken (μg) | Recovery * (%) | R. S. D* | Amount taken (μg) | Recovery* (%) | R.S.D.* | Amount taken (μg) | Recovery * (%) | R.S.D.* |
| 10 | 99.25 | 0.940 | 10 | 97.40 | 0.995 | 10 | 97.12 | 1.250 |
| 15 | 98.90 | 1.510 | 15 | 97.16 | 1.740 | 15 | 98.16 | 1.936 |
| 20 | 98.15 | 1.902 | 20 | 98.38 | 1.916 | 20 | 97.10 | 2.018 |

**Table (5): Effect of 5–fold excess of some foreign organic compounds on determination of 13.36 $\mu$g of 2-amino-1-butanol $_{(DL)}$ via measurements of tri-iodide**

| Organic Compounds | Recovery (%) |
|---|---|
| Suceinic acid | 98.2 |
| Aspartic acid | 97.6 |
| 4-Amino butyric acid | 96.8 |
| Glutamic acid | 97.7 |
| sec-Butyl alcohol | 98.4 |

**Table (6): Effect of 10–fold excess of some foreign organic compounds on determination of 15.47 $\mu$g of 2-amino-1-pentanol $_{(DL)}$ via measurements of tri-iodide**

| Organic Compounds | Recovery (%) |
|---|---|
| Suceinic acid | 97.5 |
| Aspartic acid | 97.6 |
| 4-Amino butyric acid | 96.3 |
| Glutamic acid | 98.2 |
| sec-Butyl alcohol | 97.7 |

**Table (7): Effect of –fold excess of some foreign organic compounds on determination of 17.57 $\mu$g of 2-amino-1- hexanol $_{(DL)}$ via measurements of tri-iodide**

| Organic Compounds | Recovery (%) |
|---|---|
| Suceinic acid | 96.9 |
| Aspartic acid | 97.1 |
| 4-Amino butyric acid | 96.7 |
| Glutamic acid | 98.5 |
| sec-Butyl alcohol | 97.3 |

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