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Volume 12

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## The Air Quality as a Factor Affecting Food Hygiene

By Melánia Feszterová & Klaudia Jomová

*Constantine the Philosopher University in Nitra*

**Abstract** - Various economical and ecological consequences of the air pollution affect animals, plants, food hygiene and human health. One of the most endangered components of the environment is the air. Elevated anthropogenic SO<sub>2</sub> emissions can also have negative influences upon the human health, environmental conditions, and ecosystems. Monitoring of the air pollution is thus extremely important. The most emissions come from industry, heavy traffic, emissions and population density. Submitted work includes the summary of the sulphur dioxide pollution and its impact on the environment in the area of chemical factory Duslo Šaľa, Inc. Monitoring anthropic impacts helps us to predict what requirements on space particular industry requires and how they act in the area. The basis of our evaluation was observing diversity monitoring and types of negative anthropogenic features in monitored area: concentrations of SO<sub>2</sub> in air, real sources of air pollution from the vehicles and other mechanisms and real sources of air pollution from local town residential area sources.

**Keywords** : *Hygiene, Food, Health, Air pollutant, Model, Sulphur dioxide.*

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# The Air Quality as a Factor Affecting Food Hygiene

Melánia Feszterová <sup>α</sup> & Klaudia Jomová <sup>σ</sup>

**Abstract** - Various economical and ecological consequences of the air pollution affect animals, plants, food hygiene and human health. One of the most endangered components of the environment is the air. Elevated anthropogenic SO<sub>2</sub> emissions can also have negative influences upon the human health, environmental conditions, and ecosystems. Monitoring of the air pollution is thus extremely important. The most emissions come from industry, heavy traffic, emissions and population density.

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**Keywords** : Hygiene, Food, Health, Air pollutant, Model, Sulphur dioxide.

## I. INTRODUCTION

The Slovak Republic has been monitoring and evaluating emissions for years. It is important mainly in the areas which are damaged by anthropic influence, where energetics, traffic, industry and agriculture have been dominant and pollutants escape into the air [15, 16]. The global emission sources of air pollutants caused by the human activity differ in the type of pollutant [13]. Possible sources of contamination are soil, faeces, water, ice, animals, handling of the products, harvesting and processing equipment and transport [9, 20, 27].

It is obvious that the worse air quality is caused by gases as sulphur dioxide [1, 22], nitrogen oxides [3, 23]. The anthropogenic sources of emissions include industrial processes, agriculture, traffic, mining, energetics and others [3, 8, 21, 28]. High consumption of the energy in industry as well as high consumption of energy per inhabitant, which exceeds the average numbers of other developed EC countries, is remarkable in high production of sulphur oxides and nitrogen oxides [6]. Particular substances have emission limits and long-term protection plans not only for human health

protection [25] but also for the ecosystem and vegetation protection. According to this fact, evaluation of pollution contents and monitoring of their diffusion into the country is very important [2, 17, 19, 33].

Harmfulness of the pollutants is considered from the hygienic and global point of view, mainly concerning influence upon climatic conditions and life on the Earth [7, 24, 30, 31]. Sulphur oxides (SO<sub>x</sub>) form complex compound of polluting substances. The most important are sulphur dioxide (SO<sub>2</sub>) and sulphur trioxide (SO<sub>3</sub>). Sulphur dioxide (SO<sub>2</sub>) is formed by the burning of sulphur containing fossil fuels, by melting mineral raw materials and other processes. Sulphur dioxide rank among the principal pollutants contaminating the urban atmosphere. Another source of SO<sub>2</sub> pollution is heating the houses. However, the amounts of emissions have decreased within recent years as a consequence of changing the fuel type and its quantity and using of separatory technologies, as it is mentioned in the documents of the Regional Environmental Office in Nitra *Information about air quality and particular sources sharing on its pollution* (2006) [4]. Furthermore, the character of emission sources have changed when small sources has been replaced by big particular sources which diffuse pollutants high above so that the concentration of sulphur dioxide has been lowered in big towns which had been polluted before. Presence of sulphur dioxide goes together with increased concentration of nitrogen oxides.

## II. MATERIAL AND METHODS

Submitted work includes the summary of the sulphur dioxide pollution and its impact on the environment in the area of Duslo Šaľa, Inc. – the biggest chemical factory in Nitra region. The basis of the work consists of the sources (industrial, transport, urban development) that take part in the increase of pollutants and at the same time reflects chemical industry development in the region. The aim of the work is, on the basis of real load of the countryside with SO<sub>2</sub> pollution, in delimitation of the countryside to present the importance and exploitation of the Czekanowsky method of inside homogeneous entities. The monitoring of pollutant indicators and their transport supplies information and dates to consider the emission conditions. According to the threat territory pollution with SO<sub>2</sub> on the basis of our analyses, we can predict what requirements on space particular industry requires and

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how they act in the area (integration of imissions in selected period with the intensity of transport element group and the intensity of urban development element group). The predicted and our research supported emission concentrations occur in urbanized areas where they impact the urban environment as well as working environment.

Monitoring anthropic impacts we monitored in following steps:

- concentrations of  $SO_2$  in air – on monitoring places affected by emissions released from chemical factory Duslo Šaľa, Inc.,
- the matrix of area cartographic procession and formation,
- diffusion study process,
- comparison of measured and counted concentrations in model situations,
- the method of differences and similitude,
- the analysis of air pollution in monitoring of anthropic impacts in landscape ecological evaluation of the area.

#### a) The concentration of $SO_2$ in the air

The  $SO_2$  concentration from chemical factory Duslo Šaľa, Inc. was monitored in two phases:

- 1<sup>st</sup> phase – the analysis of chosen air samples in laboratory conditions in years 1999-2003. In the first phase the samples taking was realized in three testing points (Duslo Šaľa, Inc., Trnovec nad Váhom, Šaľa – Veča). Sulphur dioxide was defined with colorimetric method according to STN 03 8211 (1987) [29].
- 2<sup>nd</sup> phase – since 2003 the imission concentration has been measuring with chemiluminescence's method obtained from stationary background measuring point for suburb of Trnovec nad Váhom.

#### b) The analyses of air samples results ( $SO_2$ ) in landscape ecology evaluation of tested area

The area is situated in four maps in the scale 1: 10 000 (maps sheet numbers: 1145-12-24, 1145-12-25, 1145-14-04, 1145-14-05) and includes 7140 ha. They were transformed to make coherent whole. All area of interest was divided into squares 200 x 200 m forming raster with 1776 squares ( $37 \times 48 = 1776$ ). The matrix serves for the whole area characterization according to chosen categories. From the cartographic base there have been printed four types of thematic maps (Map 1. The Occurrence of Element Group of Transport, Map 2. The Occurrence of Residential Elements, Map 3. Anthropic Impacts on the Elements of Secondary Landscape Structure, Map 4. The Threat of Secondary Landscape Structure by Imissions). The basis in map legend making is optical scale of Czekanowsky method. Internally homogeneous elements details (The method of difference and similitude) perform summary of values.

The ranges expressed the intensity of features monitored in chosen categories. We made ranges dependent on the indicators choice. Isolines of maximal short term concentration of  $SO_2$  were transformed into digitalized map. The isolines were used for areal elements including the area between particular isolines that were later used for other evaluation of environment threat. New evaluation matrix was made to analyse the cooperation of relations between the transport elements and residential elements. The secondary landscape structure with landscape elements (transport, water wood vegetation elements, grass vegetation, agricultural cultures, residential and technical elements) isolines of maximal short term concentration  $SO_2$  and evaluating matrix was the basis for evaluation of tested area.

### III. RESULTS AND DISCUSSION

The diffusion study has been figured out on the basis of selected emissions development in the monitored period from the chemical factory Duslo, Inc. Šaľa. (Fig. 1) The amount of emissions from chemical factory Duslo Šaľa, Inc. has depended on the amount and quality of used fuels and production needs. The largest amount of emission was in 2001 ( $SO_2=1506.10^3$  kg). The year 2007 was the year with the lowest value of emissions from Duslo Šaľa, Inc. ( $SO_2 = 6.10^3$  kg).

The concentrations of pollutants were counted with the help of Gaussian air pollution model [10, 11]. The counted results of pollutants concentration were compared with measured results. Comparing short term counted and measured  $SO_2$  concentrations in 1999 – 2003 we may add that none of the monitored point (Trnovec nad Váhom, Duslo Šaľa, Inc., Šaľa – Veča) had exceeded value of imission limit of  $SO_2$  ( $IH_{k(SO_2)} = 500 \mu\text{g}\cdot\text{m}^{-3}$ ).

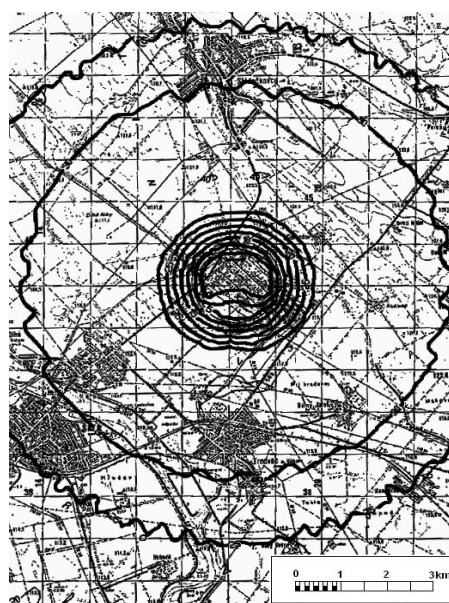


Figure 1 : Distribution of the maximum short - term  $SO_2$  concentrations in 2000 [ $\mu\text{g}\cdot\text{m}^{-3}$ ]

In the areas with a flat terrain the agreement between counted and measured values of pollutant is good [11]. During monitored years (1999 - 2003) the pollutant did not exceed the limits of average concentration ( $IHr_{(SO_2)} = 60 \mu g.m^{-3}$ ) [5]. The average values of measured maximum annual concentrations are below the border of imission limits.

a) *Imissions*

The differences between the monitored concentrations of sulphur dioxide in the monitored period were noted in particular years as well as between measuring points. (Table 1)

Table 1 : The average annual concentrations of air pollutant.

SO <sub>2</sub> [ $\mu g.m^{-3}$ ]					
Measuring points	1999	2000	2001	2002	2003
Trnovec nad Váhom	1.13	6.17	12.62	7.83	12.70
Duslo Šaľa, Inc.	1.52	5.27	5.60	3.33	-
Measuring point	2004	2005	2006	2007	2008
Trnovec nad Váhom	6.50	10.02	6.54*	7.18*	5.91*

Source: \*Duslo Šaľa, Inc. 2009

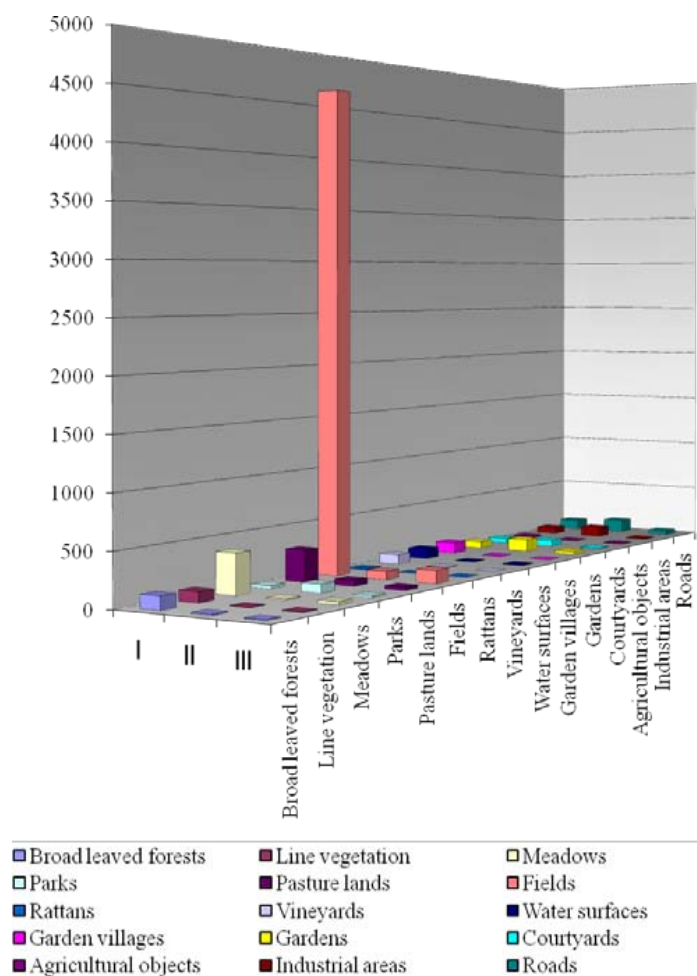


Figure 2 : Percentage evaluation of endangered landscape features.

b) *The air quality analysis in monitoring of anthropic elements in landscape ecology evaluation of the area*

The basis of our evaluation consist of diversity monitoring and types of negative anthropogenic features in monitored area. This part is synthetic and compares the expected imissions and real imissions as well in connection with secondary landscape structure. The synthesis expect following steps:

1. The choice of the sources influencing imissions rate as well as reflecting the chemistry development in the tested area. We considered various factors to choose: availability of material, process form and the aim. The chosen indicators were obtained by monitoring air pollution analysis in the factory Duslo Šaľa, Inc. statistic process and processing of existing materials. The result of this part is the set of cartographic materials showing the development indicators connected with particular branches in the area. This cartographic material shows indicators connected with existing branches causing increasing concentrations pollutants in the country.
2. The secondary landscape setup is the function of two definitive integrating processes – natural and anthropic [18]. Map 1. and Map 2. deal with first sectional synthesis of transport and residential elements. It results in Map 3. with marked isoline of maximal short – term concentration SO<sub>2</sub>. The most loaded area is that of Duslo Šaľa, Inc. And the least are suburb areas as the town Šaľa, Riegler, Kenderes.

3. The land ecology synthesis – threatening of secondary landscape structure with chosen contaminants. The secondary landscape structure reflects not only changes made by the men in the primary landscape structure but also socioeconomic aspect, the usage of the soil in tested area [14, 26]. According to the tested area there were selected four landscape elements as units of secondary landscape structure: water (water surface, water courses, canals), the elements of wood vegetation (broad leaved forests, linear vegetation), persistent grass vegetation (pasture lands, meadows), agricultural cultures (fields, vineyards, fruit groves, gardens), residential elements (buildings, parks, courtyards), technical elements (industrial areas, agricultural objects), transport (main roads, minor roads, bridges and footbridges, functional metalled roads, unmetalled roads, important paths). In the ecological point of view we differentiated stability elements (ecological and biotic important places – biocentres, biocorridors and conservation areas).

c) *Relation of imissions and secondary landscape structure*

Intersection of imission models and the secondary landscape structure enables the interpretation of endangered and endangering features. We will consider the features resulting from imission to be the endangering features and biotic elements to be endangered features [32]. There are several categories of endangering features. Water surfaces, water courses, canals, broad leaved forests, linear vegetation, pasture lands, meadows fields, vineyards, fruit groves, gardens, courtyards, main roads, minor roads, bridges and footbridges, functional metalled roads, unmetalled

roads, important paths, biocentres, biocorridors, protected territories are considered to be endangered landscape elements. The landscape elements mentioned are divided into three categories: natural sources, the part of ecological stability system, environment. Fields occupy the largest area. (Fig. 2)

#### IV. CONCLUSION

It is difficult to evaluate the qualitative changes on the secondary landscape structure caused by anthropogenic effects exactly. The basis of our evaluation was observing the diversity of anthropic effects; the more types of negative anthropogenic effects occur on a particular place, the bigger is their effect on the place. The syntheses presumed following steps: evaluation of imissions in the area, interpretation of secondary landscape structure, threat of secondary landscape structure with chosen contaminants. Selected indicators have been reached by monitoring and analysis of the air quality in the area of Duslo Šaľa, Inc. together with statistic dates and existing documents. We have compared imissions  $SO_2$ , presumed and real with secondary landscape structure. We have expressed it in the system of endangered and endangering effects. Used parametric analysis has analyzed interactivity among relations and was transformed into four maps. The space relation expressing interactive impacts of transport and residential elements, real and expected imissions show space collisions of secondary landscape danger. (Fig. 3) The concussing synthesis aims at possible danger of landscape features which enables to predict the danger. The analyses and evaluation of various anthropic impacts in the land are help to form the classification of environment.

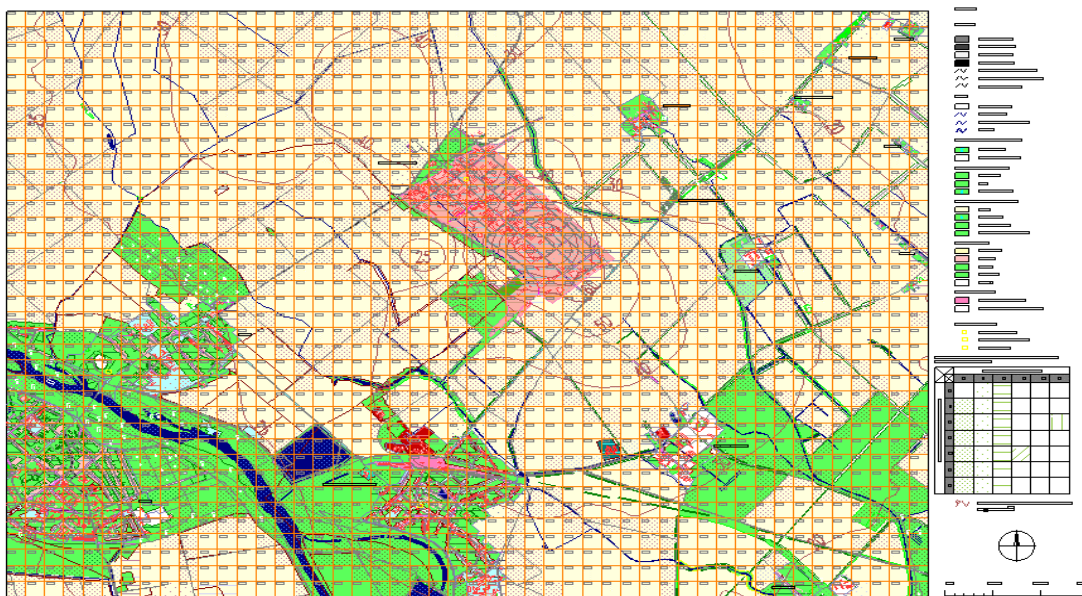


Figure 3 : Anthropic Impacts on the Elements of Secondary Landscape Structure.

The results taken from the interpretation of secondary landscape structure and space relation can be used in ecological systems of urban development stability planning, in environmental predictions and in environmental health solving. This belongs to current problems deserving strong attention of all parties included. The food hygiene is the first step which starts the whole process of healthy style of living. Air quality affects the soil hygiene and subsequently the plant production and that affects human health.

## V. ACKNOWLEDGMENT

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# Synthesis and Antimicrobial Activity of Some New Nitrogen Heterocyclic Systems Bearing 1, 2, 4-Tiazine Moiety

By Wafaa R. Abdel-Monem

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**Abstract** - Synthesis and antimicrobial activity of some new heterocycles such as pyrimidines, 1,2,4-triazoles, 1,2,4-triazines, 1,3-thiazoles and related compounds (2-26) bearing 1,2,4-triazine moiety have been prepared from the reaction of the 3-amino-5,6-diphenyl-1,2,4-triazine (1) with different organic reagents under different reaction conditions. Structures of the new synthesized compounds were confirmed by elemental analyses and spectral data. Some of the synthesized products were tested and evaluated as antimicrobial agents.

**Keywords** : 1,2,4-triazines, nitrogen heterocycles, antimicrobial activity.

**GJSFR-B Classification** : FOR Code: 030503



SYNTHESIS AND ANTIMICROBIAL ACTIVITY OF SOME NEW NITROGEN HETEROCYCLIC SYSTEMS BEARING 1, 2, 4-TIAZINE MOIETY

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Wafaa R. Abdel-Monem

**Abstract** - Synthesis and antimicrobial activity of some new heterocycles such as pyrimidines, 1,2,4-triazoles, 1,2,4-triazines, 1,3-thiazoles and related compounds (2-26) bearing 1,2,4-triazine moiety have been prepared from the reaction of the 3-amino-5,6-diphenyl-1,2,4-triazine (1) with different organic reagents under different reaction conditions. Structures of the new synthesized compounds were confirmed by elemental analyses and spectral data. Some of the synthesized products were tested and evaluated as antimicrobial agents.

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## I. INTRODUCTION

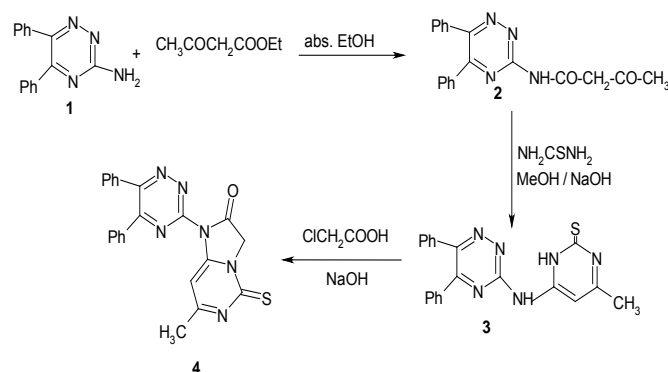
Substituted 1,2,4-triazines represent an important class of nitrogen containing heterocyclic systems. The 1,2,4-triazine nucleus has been considered as a source of great interest to organic, medicinal and materials scientists over many years, which is present in a number of biologically active organic compounds which exhibit, antibacterial<sup>1</sup>, anticancer<sup>2</sup>, antimicrobial<sup>3</sup>, antifungal<sup>4, 5</sup>, anti-inflammatory<sup>6</sup>, antibiotic<sup>7</sup>, anti HIV<sup>8</sup> activities. Various condensed 1,2,4-triazines found applications as pharmaceuticals, herbicides<sup>9</sup>, pesticides<sup>10</sup>, and dyes<sup>11</sup>.

Nitrogen heterocycles such as pyrimidines, 1,2,4-triazoles, 1,2,4-triazines, 1,3-thiazoles are found to be endowed with potential therapeutic activities such as antitumor<sup>12</sup>, antiviral<sup>13</sup>, antimycobacterial<sup>14</sup>, anticancer<sup>15</sup>, and analgesic<sup>16, 17</sup>, antimicrobial<sup>18</sup>, antiproliferate<sup>19</sup>, antihistaminic<sup>20</sup> activities.

The systematic propagation of heterocyclic rings in 1,2,4 triazines precursors with the installation of biologically active heterocyclic units such as pyrimidines, 1,2,4-triazoles, 1,2,4-triazines, 1,3-thiazoles is the major focal point of the present investigation which would be expected to afford interesting biologically active series of compounds.

The synthetic routes followed for the preparation of compounds are outlined in schemes 1-4. The starting compound 3-amino-5,6-diphenyl-1,2,4-triazine (1)<sup>21</sup> reacted with ethyl acetoacetate to afford the *N*-triazinyloxobutamide 2, which underwent

cyclocondensation on treatment with thiourea in MeOH/NaOH to afford the substituted triazinylpyrimidinethione derivative 3 (Scheme1). Structure of compound 3 was established based on analytical and spectral data. The <sup>1</sup>H NMR spectrum revealed the appearance of two singlets at  $\delta$  8.32 and 9.55 ppm corresponding to NH protons, and two singlets at  $\delta$  3.23 and 6.18 ppm attributed to methyl protons and the C<sub>5</sub>-H<sub>pyrimidinethione</sub>, respectively. Treatment of compound 3 with chloroacetic acid in NaOH solution afforded the 1-(5,6-diphenyl-1,2,4-triazin-3-yl)-7-methyl-2-oxo-3*H*imidazo [3,2-*c*] pyrimidine-5-thione (4) (Scheme 1). The IR spectrum of compound 4 confirmed disappearance absorption bands of NH groups in compound 3. Its <sup>1</sup>H NMR spectrum revealed the appearance of three singlets at  $\delta$  2.53, 2.79 and 6.43 ppm assigned to methyl, COCH<sub>2</sub> and the C<sub>5</sub>-H<sub>pyrimidinethione</sub> protons, respectively.



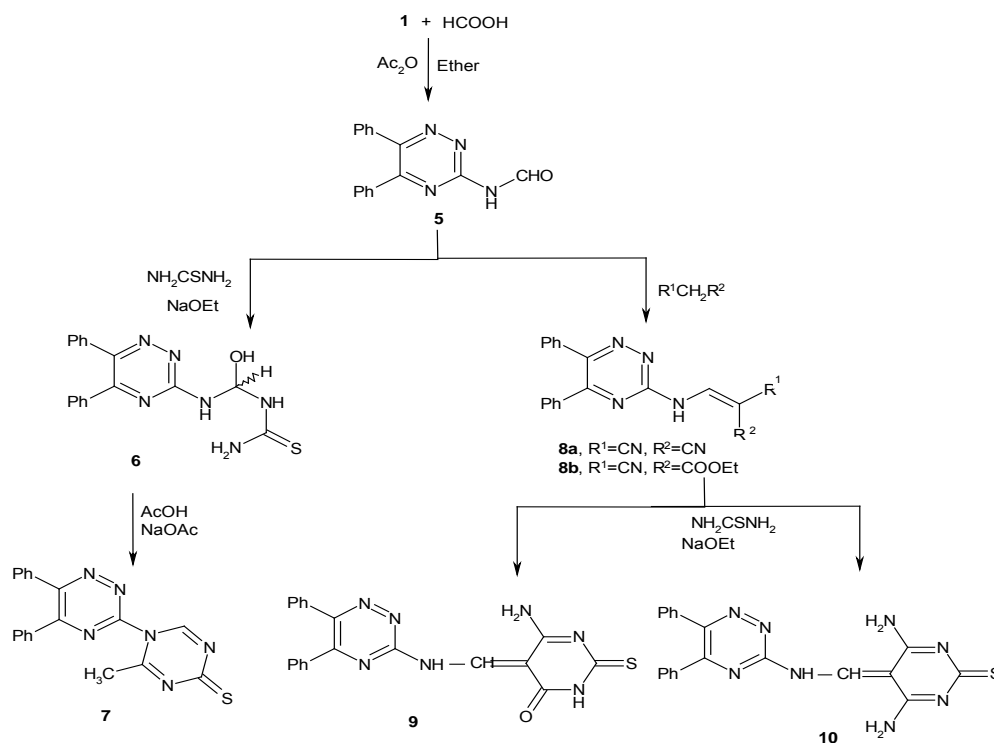
**Scheme 1** : Synthetic pathway for the preparation of compounds 1 – 4.

On the other hand, the important synthon *N*-(5,6-diphenyl -1,2,4-triazin-3-yl)formamide (5) was obtained from formylation of 3-amino-5,6-diphenyl-1,2,4-triazine (1) with Ac<sub>2</sub>O/HCO<sub>2</sub>H.<sup>22</sup> The reaction of compound 5 with thiourea in the presence of sodium ethoxide, via addition reaction gave 1-[(5,6-diphenyl-1,2,4-triazin-3-yl)amino] hydroxy methyl }thiourea (6) (Scheme 2). Cyclocondensation reaction of 6 by boiling in glacial acetic acid /fused sodium acetate gave 5-(5,6-diphenyl -1,2,4-triazin-3-yl) -4-methyl-1,3,5-triazine-2-thione (7) (Scheme 2). The analytical and spectral data

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are in agreement with proposed structure. Thus, its  $^1\text{H}$  NMR spectrum showed signals at  $\delta$  1.96 ppm due to  $\text{CH}_3$  protons, 7.25–7.59 ppm corresponding to aromatic protons. Also, condensation of compound 5 with active methylene compounds such as malononitrile and ethyl cyanoacetate in refluxing ethanolic sodium ethoxide afforded 8a and 8b, respectively. Cyclocondensation of 8a,b with thiourea on boiling with sodium ethoxide furnished the methylenaminopyrimidinethiones 9 and 10, respectively (Scheme 2). The IR spectrum of compound 9 showed three characteristic absorption

bands at 3479, 3365 and 3228  $\text{cm}^{-1}$  due to two  $\text{NH}_2$  functions and NH groups. Its  $^1\text{H}$  NMR spectrum showed three characteristic signals at  $\delta$  4.59, 5.19 and 8.87 ppm assigned to two  $\text{NH}_2$  and NH protons. Also, its mass spectrum showed the molecular ion peak at  $m/z$  340  $[\text{M}+1]$  and the base peak at  $m/z$  178. Also, the IR spectrum of compound 10 showed two characteristic absorption bands at 1668 and 1274  $\text{cm}^{-1}$  due to  $\text{C}=\text{O}$  and  $\text{C}=\text{S}$  groups. Its  $^1\text{H}$  NMR spectrum showed two characteristic signals at  $\delta$  5.19, 9.17 ppm assigned to  $\text{NH}_2$  and NH protons.



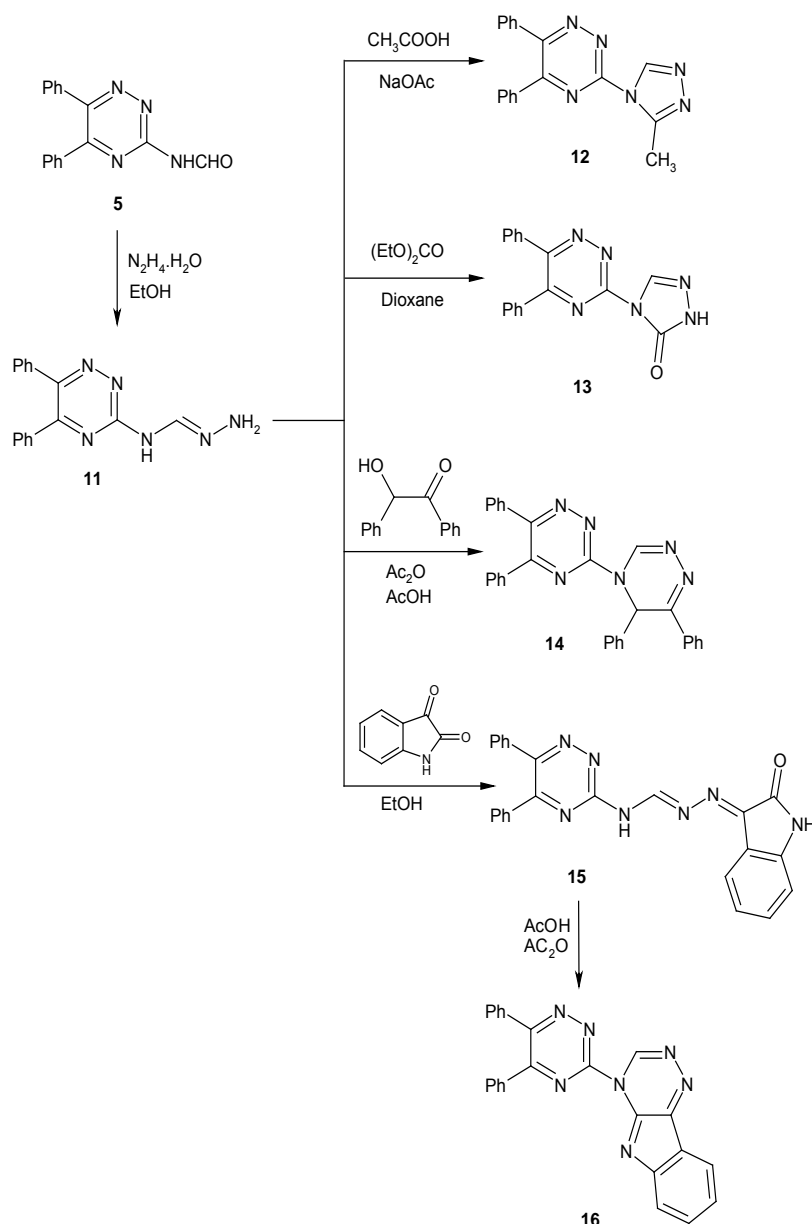
**Scheme 2 :** Synthetic pathway for the preparation of compounds 5 – 10

Derivatives of 1, 2, 4-triazole and 1, 2, 4-triazine have been found to possess wide spectrum of pharmacological, medicinal and biological activities.<sup>23, 24</sup> Thus, condensation of compound 5 with hydrazine hydrate in absolute ethanol produced the amidrazone 11 which upon heterocyclization by refluxing with glacial acetic acid in the presence of fused sodium acetate and/or diethyl carbonate in dry dioxin<sup>25</sup> afforded 3-(3-methyl-1,2,4-triazol-4-yl)-5,6-diphenyl-1,2,4-triazine (12) and 3-[3-oxo-1H-1,2,4-triazol-3-yl]5,6-diphenyl-1,2,4-triazine 13, respectively (Scheme 3). Structures of compounds 11–13 were established on the basis of analytical and spectral data. Thus, the IR spectrum of compound 11 showed absorption bands at 3300, 3220 and 3150  $\text{cm}^{-1}$  due to  $\text{NH}_2$  and NH groups, which were disappeared in compound 12, in addition compound 13 revealed the absorption bands at 3050 and 1680  $\text{cm}^{-1}$  due to cyclic NH and  $\text{C}=\text{O}$  groups. On the other hand,

the  $^1\text{H}$  NMR spectrum of 11 showed signals at  $\delta$  2.92, 7.64, 7.76–7.97 and 9.85 ppm due to  $\text{NH}_2$ ,  $\text{CH}=\text{N}$ , aromatic and NH while that of 12 showed the presence of two signals due to  $\text{CH}_3$  and the  $\text{C}_3\text{-H}_{\text{triazole}}$  at  $\delta$  3.45 and 7.32 ppm. Some new 1,2,4-triazine derivatives bearing other 1,2,4-triazine moieties have been deduced from cyclization of amidrazone 11 with 1,2-bioxo-compounds. Thus, triazinyltriazine 14 was prepared from cyclocondensation of amidrazone 11 with benzoin in the presence of glacial acetic acid and fused sodium acetate. The structure of compound 14 was established on the basis of analytical and spectral data. The IR spectrum showed the disappearance of  $\text{NH}_2$  and NH groups. While condensation of compound 11 with isatin in methanol yielded the isatin-3-hydrazone 15, which on refluxing in glacial acetic acid and fused sodium acetate furnished 4-(5,6-diphenyl-1,2,4-triazin-3-yl)-4H-[1,2,4]triazino[5,6-b]indole 16. The structure of compound 16

was established on the basis of analytical and spectral data. Its IR spectrum showed the disappearance of the NH, OH and C=O groups. Also, the mass spectrum

showed the molecular ion peak at  $m/z$  401 which agreed with its molecular formula.



*Scheme 3* : Synthetic pathway for the preparation of compounds 11 – 16.

Isoxazoles are widely investigated for therapeutic uses, especially as tranquillizing agent and central nervous systems (CNS) regulation and are reported to have bactericidal and fungicidal activities.<sup>26</sup> Pyrazoles display a number of antimicrobial activities like antitumor<sup>27</sup>, immunosuppressive<sup>28</sup>, antibacterial<sup>29</sup>, anticancer<sup>30</sup>, antidiabetic and antidepressants.<sup>31</sup> The imidazolinone moiety is a useful functionality for development of biologically interesting molecules such as hypertensive<sup>32</sup>, antimalarial<sup>33</sup>, antihypnotic<sup>34</sup> and antihypertensive<sup>35</sup> activities.

In view of continuous and widespread interest in the design of a new heterocyclic derivatives containing

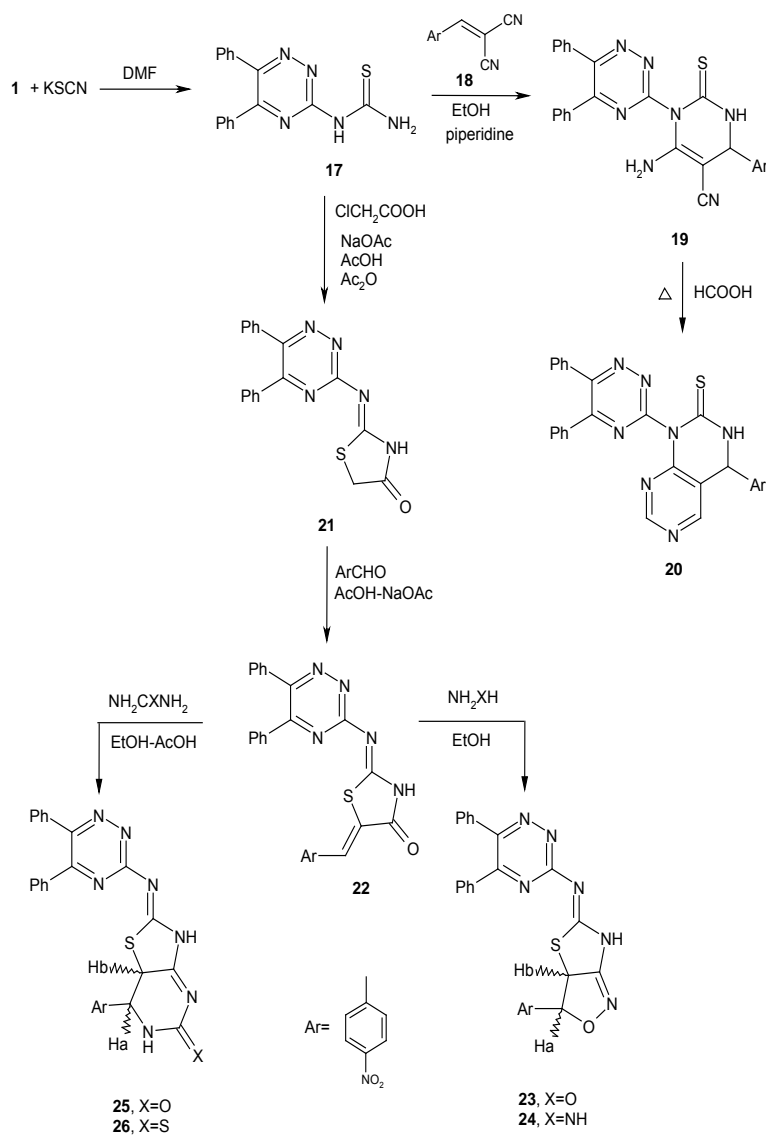
1, 2, 4-triazine moiety, particularly on account of fused 1,2,4-triazine aryl derivatives containing isoxazole, pyrimidine and pyrazole derivatives. Thiourea plays a vital role in many biological processes and is used as intermediates for the synthesis of drugs<sup>36</sup>. Thus, the reaction of 1 with potassium thiocyanate in DMF afforded 1-(5,6-diphenyl-1,2,4-triazin-3-yl)thiourea 17, which upon heterocyclization by refluxing with arylidene malononitrile 18 in boiling absolute ethanol containing a catalytic amount of piperidine, afforded 6-amino-1-(5,6-diphenyl-1,2,4-triazin-3-yl)-4-(4-nitrophenyl)-2-thioxo 1,2,3,4-tetrahydropyrimidine-5-carbonitrile (19) (Scheme 4). Compound 19 underwent treatment with formic acid to

yield 8-(5,6-diphenyl-1,2,4-triazin-3-yl)-5-(4-nitrophenyl)-7-thioxo-5,6,7,8-trihydropyrimido[4,5-*d*]pyrimidin-2(1*H*)-one (20) (Scheme 4). The  $^1\text{H}$  NMR spectrum of 19 showed two characteristic signals at  $\delta$  6.15, 8.93 ppm assigned to  $\text{NH}_2$  and NH protons. While the  $^1\text{H}$  NMR spectrum of 20 showed characteristic signals at  $\delta$  9.25 ppm assigned to NH proton.

The reaction between key intermediate 17 with chloroacetic acid and sodium acetate in acetic anhydride afforded 1,3-thiazolidinones 21. The  $^1\text{H}$  NMR of 21 showed a sharp singlet at  $\delta$  3.45 due to two protons of the  $\text{CH}_2\text{S}$  group. Its IR spectra showed the disappearance of the coupled vibrations and appearance of bands for  $\text{C}=\text{O}$  and NH at around  $1730$  and  $3350\text{ cm}^{-1}$ , respectively (Scheme 4). The thiazolidinone 21 undergoes condensation with aromatic aldehyde like 3-nitrobenzaldehyde to give the cyclic

chalcone 22 (Scheme 4). The formation of compound 22 was confirmed by the absence of  $\text{CH}_2$  protons in its  $^1\text{H}$  NMR spectrum.

Treatment of 22 with various *bi*-nucleophiles such as hydroxylamine, hydrazine hydrate, urea and thiourea afforded their respective *in situ* oxidized products 23, 24, 25 and 26 (Scheme 4). The driving force for this *in situ* oxidation is the formation of new heterocyclic rings. The disappearance of the carbonyl frequency in IR spectrum for 23 and 24 confirms the installation of isoxazole and pyrazole moieties. In case of 25 the band at around  $1725\text{ cm}^{-1}$  was assigned to the new amidic  $\text{C}=\text{O}$  group. However, the  $^1\text{H}$  NMR spectrum of 24 showed additional signal at  $\delta$  5.56 and 6.48 ppm for two NH, similarly in the  $^1\text{H}$  NMR of compound 26 the amidic NH proton at  $\delta$  8.49 ppm.



Scheme 4 : Synthetic pathway for the preparation of compounds 17 – 26.

## II. ANTIMICROBIAL ACTIVITY

Some new synthesized compounds were screened for their antimicrobial activities against two species of bacteria *Bacillus subtilis* and *Escherichia coli* and two species of fungi *Alternaria alternata* and *Aspergillus niger* using the disc diffusion method<sup>37-39</sup>, spore suspension 0.5 ml ( $10^6$ – $10^7$  spore/ml) of each of the investigated microorganisms was added to a sterile agar medium just before solidification then poured into sterile Petri dishes (9 cm in diameter) and left to solidify. By using sterile cork borer (6 mm in diameter), three holes (wells) were made in each dish, then 0.1 ml of the tested compounds dissolved in DMF (100 µg/ml) were poured into these holes. Finally the dishes were incubated at 37°C for 48 hr (for bacteria) and at 30°C for 72 hr (for fungi), where clear or inhibition zones were detected around each hole. 0.1 ml of DMF alone was used as a control under the same conditions for each microorganism and by subtracting the diameter of

inhibition zone resulting with DMF alone from that obtained from that obtained in each case, both antibacterial and antifungal activities can be calculated as a mean of three replicates. Terbinafin used as a standard agent (antifungal) and chloramphenicol used as a standard agent (antibacterial) (Table 1). The results for antibacterial activities depicted in Table 1 revealed that most of the synthesized compounds were found to possess various antimicrobial activities towards all the microorganisms tested.

## III. CONCLUSION

In this report easy, a simple and convenient route for the synthesis of biologically active 1,2,4-triazine aryl derivatives containing pyrimidines, 1,2,4-triazoles, 1,2,4-triazines, 1,3-thiazoles and related compounds. The microbial evaluation of these compounds indicated that they are good potent antimicrobial agents in comparison with the standard drug.

Table 1 : Antimicrobial activity of some of the prepared compounds.

Compound No	Bacteria		Fungi	
	Gram +ve	Gram -ve	<i>Alternaria alternata</i>	<i>Aspergillus niger</i>
	<i>Bacillus subtilis</i>	<i>Escherichia coli</i>		
1	+	++	+	+
2	+	+	+	++
4	+	++	+	++
5	++	++	++	++
7	++	+	++	++
9	++	++	++	++
10	+	+	++	+
11	+	+	+	+
12	+++	++	+++	++
13	++	++	++	++
14	+++	++	++	++
16	++	+++	+	++
20	+	++	+	++
21	+++	++	++	++
22	+	++	+	++
23	+	++	+	++
24	+	+	+	+
25	++	+	++	+
26	+++	+++	++	++
Terbinafin	-	-	+++	++
Chloramphenicol	+++	+++	-	-

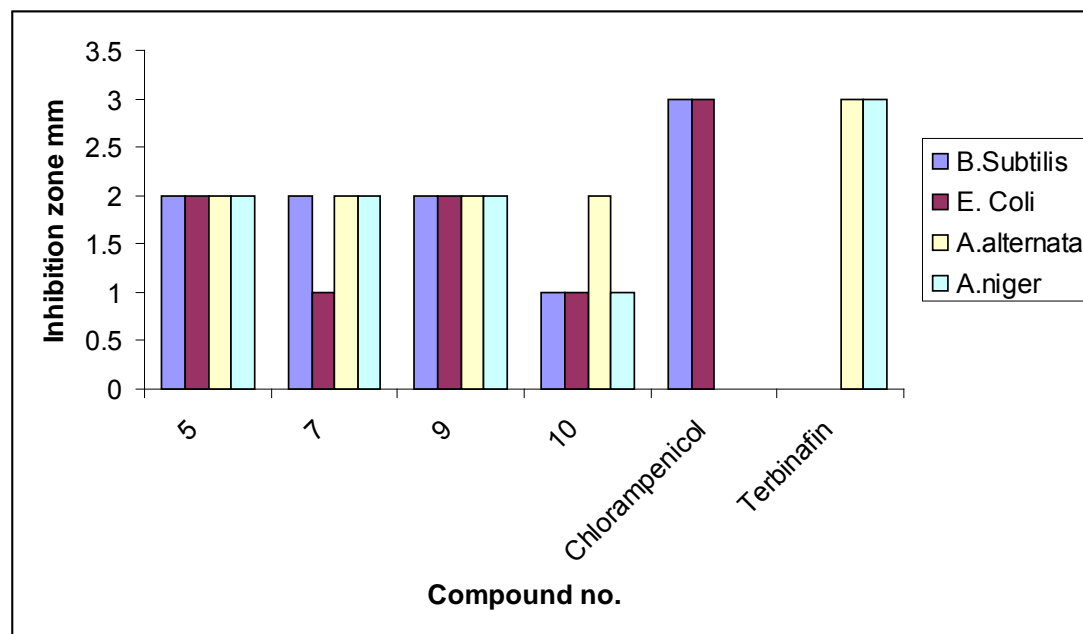
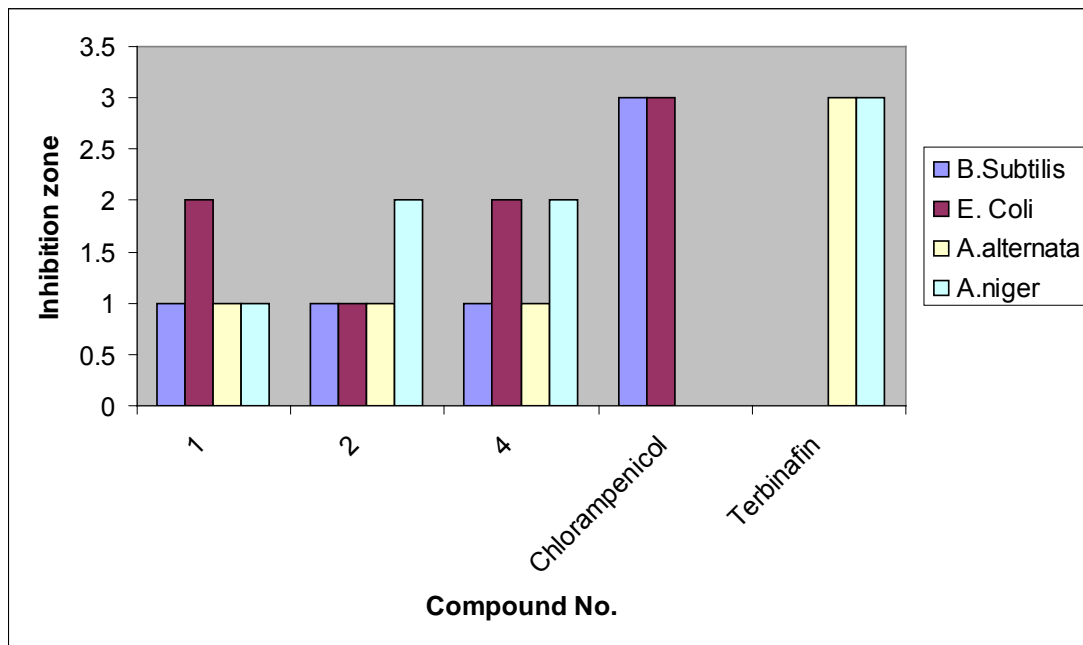
The test done using the diffusion agar technique

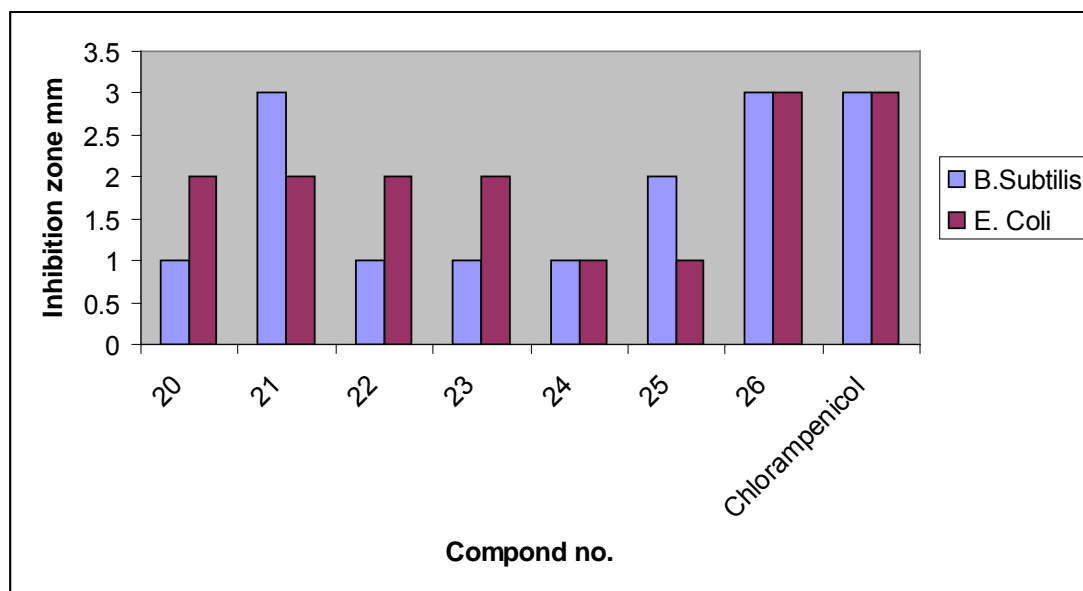
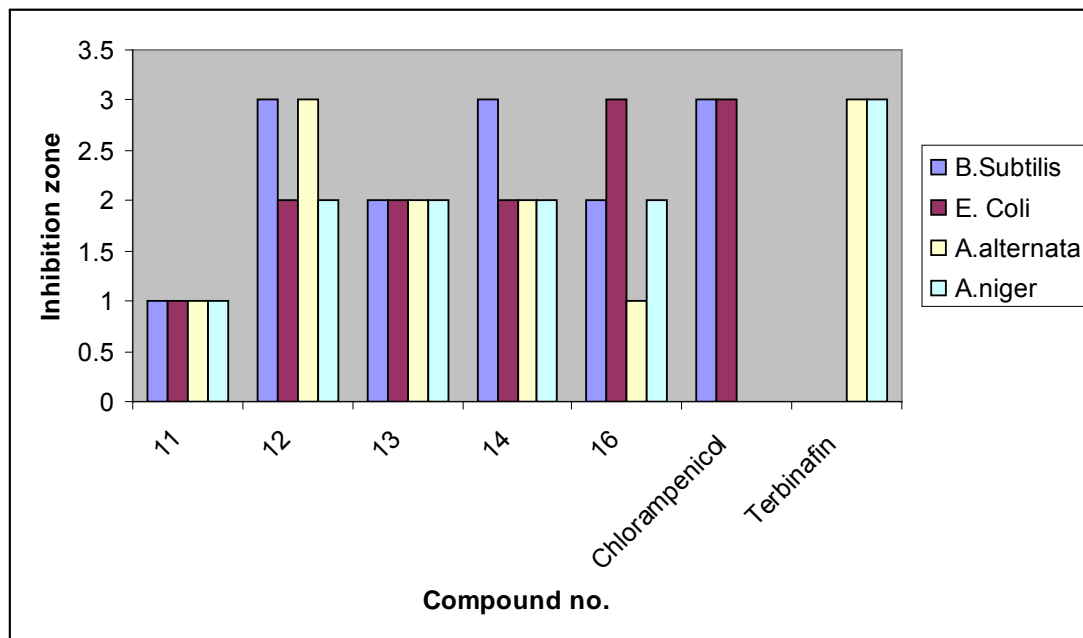
Well diameter = 0.06 cm

Inhibition values = 0.1 – 0.5 cm beyond control = + (less active)

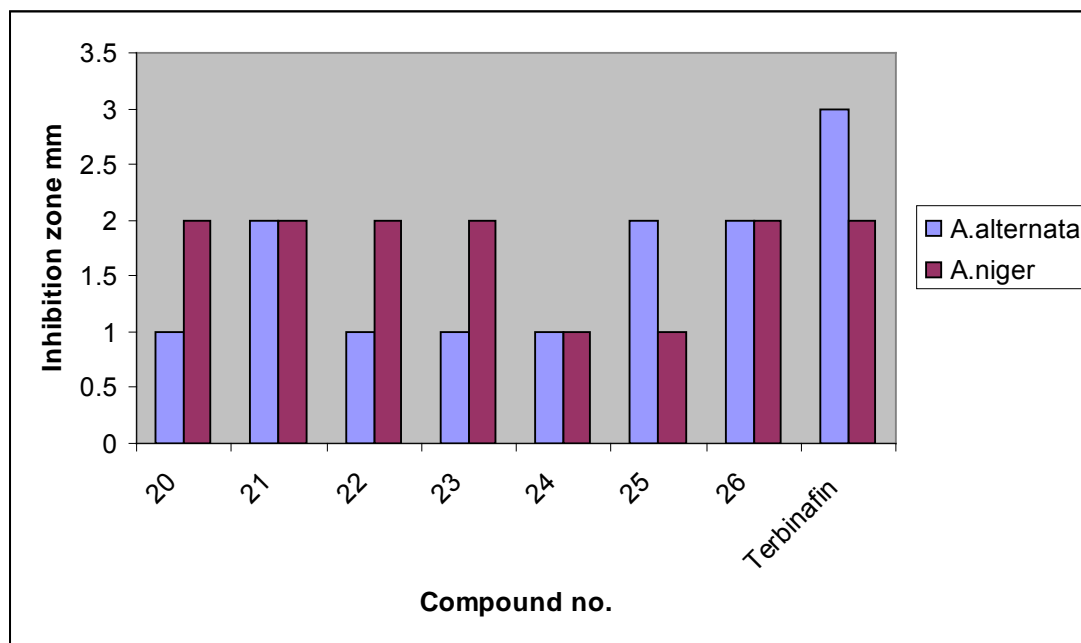
Inhibition values = 0.6 – 1.0 cm beyond control = ++ (moderate active)

Inhibition values = 1.1 – 1.5 cm beyond control = +++ (highly active)









#### IV. EXPERIMENTAL SECTION

Melting points were recorded on a digital Stuart SMP-3 apparatus. Infrared spectra were recorded on FT-IR Bruker Vector 22 spectrophotometer using KBr wafer technique.  $^1\text{H}$  NMR spectra were measured on Gemini spectrometer 200 MHz using  $\text{DMSO-d}_6$  as solvent and TMS (Chemical shift in  $\delta$  ppm) as an internal standard. Mass spectra were obtained using as chromatography GCMS qp 1000 ex Shimadzu instrument mass spectrometer (70 eV). Elemental microanalyses were performed at the Cairo University Microanalytical Center and were in the range of  $\pm 0.4\%$  for each element analyzed (C, H, N, S). The purity of compounds was checked by thin layer chromatography on silica gel (silica gel, aluminum sheets 60 F254, Merck). 3-Amino-5,6-diphenyl-1,2,4-triazin(1) was prepared according to the previously procedure<sup>21</sup>.

##### *N*-(5,6-Diphenyl -1,2,4-triazin-3-yl)-3-oxobutanamide (2)

A mixture of compound 1 (0.01 mol) and ethyl acetoacetate (0.01 mol) in absolute ethanol (15  $\text{cm}^3$ ) containing a few drops of piperidine (3 drop) was refluxed for 6 h. The reaction mixture was cooled and the solid so obtained was filtered off and recrystallized from ethanol. Yield 86%. M.p.: 194–196 °C. FT-IR,  $\nu$  ( $\text{cm}^{-1}$ ): 3295 (NH), 1716, 1662 (2 C=O).  $^1\text{H}$  NMR (200 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 2.48 (s, 3H,  $\text{CH}_3$ ), 2.79 (s, 2H,  $\text{CH}_2$ ) 7.24 – 8.43 (m, 10H, Ar-H), 9.23 (s, 1H, NH). Anal. Calcd. for  $\text{C}_{19}\text{H}_{16}\text{N}_4\text{O}_2$  (332): C, 68.67; H, 4.81; N, 16.86. Found: C, 68.27; H, 4.49; N, 16.51 %.

##### *3*-[4-Methyl-2-thioxo-1H-pyrimidinylamino] 5,6-diphenyl-1,2,4-triazine- (3)

To a solution of compound 2 (0.01 mol) in methanolic NaOH (10%, 20  $\text{cm}^3$ ), thiourea (0.01 mol) was added and the reaction mixture was heated under

reflux for 4 h, and then allowed to cool. The precipitate that formed was filtered off, dried and recrystallized from ethanol. Yield 90 %. M.p.: 203–205 °C. FT-IR,  $\nu$  ( $\text{cm}^{-1}$ ): 3200 (NH), 3100 (NH), 1565 (C=N), 1532 (C=N), 1239 (C=S).  $^1\text{H}$  NMR (200 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 3.23 (s, 3H,  $\text{CH}_3$ ), 6.18 ( $\text{CH}_{\text{pyrimidine}}$ ), 7.16–7.96 (m, 11H, Ar-H), 8.92 (s, 1H, NH), 9.25 (s, 1H, NH). Anal. Calcd. for  $\text{C}_{20}\text{H}_{16}\text{N}_6\text{S}$  (372): C, 64.51; H, 4.30; N, 22.58; S, 8.60. Found: C, 64.83; H, 4.73; N, 22.94; S, 8.24 %.

##### *1*-[5,6-Diphenyl-1,2,4-triazin-3-yl]-7-methyl-2-oxo-3H-imidazo[3,2-c]pyrimidine-5-thione (4)

A mixture of compound 3 (0.01 mol) and chloroacetic acid (0.01 mol) in NaOH (5%, 20  $\text{cm}^3$ ) was refluxed for 6 h. The precipitate obtained was filtered off dried and recrystallized from a mixture of ethanol and DMF (1: 1). Yield 75 %. M.p. 196–198 °C. FT-IR,  $\nu$  ( $\text{cm}^{-1}$ ): 1527, 1538 (2 C=N), 1470 (def.  $\text{CH}_3$ ) 1720 (C=O).  $^1\text{H}$  NMR (200 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 2.53 (s, 3H,  $\text{CH}_3$ ), 2.79 (s, 2H,  $\text{CH}_2$ ), 6.43 ( $\text{CH}_{\text{pyrimidine}}$ ), 7.35–7.29 (m, 11H, Ar-H). Ms (m/z, I %): 412 (M, 2%), 314 (13), 178 (100), 167 (8), 152 (4), 126 (2), 110 (4). Anal. Calcd. for  $\text{C}_{22}\text{H}_{16}\text{N}_6\text{OS}$  (412): C, 64.07; H, 3.88; N, 20.38; S, 7.76. Found: C, 63.78; H, 4.11; N, 20.03; S, 7.42 %.

##### *N*-(5,6-Diphenyl -1,2,4-triazin-3-yl)formamide (5)

A mixture of formic acid (3.4  $\text{cm}^3$ ) and acetic anhydride (8.2  $\text{cm}^3$ ) was refluxed for 2h. The mixture was added drop wise to a solution of compound 1 (0.01mol) in diethyl ether (50  $\text{cm}^3$ ), the formed solid product was filtered off, dried and recrystallized from ethanol. Yield 55%. M.p.: 182–184 °C. FT-IR,  $\nu$  ( $\text{cm}^{-1}$ ): 3189 (NH), 1708 (C=O), 1528 (C=N), 1631 (C=C).  $^1\text{H}$  NMR (200 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 2.25 (s, 3H,  $\text{CH}_3$ ), 7.45 – 7.98 (m, 10H, Ar-H), 8.62 (s, 1H, NH), 9.95 (s, 1H, CHO). Ms (m/z, I%): 277 ( $\text{M}^+ + 3$ , 5%), 276 ( $\text{M} + 2$ , 7%), 195 (11),

156 (6) , 140 (8) , 178 (100) , 115 (13) , 112 (9) , 101 (7) , 70 (8). Anal. Calcd. for  $C_{16}H_{12}N_4O$  (274): C, 70.07; H, 3.97; N, 20.43. Found: C, 69.73; H, 4.49; N, 20.08 %.

*1-[(5,6-Diphenyl-1,2,4-triazin-3-yl)amino]hydroxylmethyl} thiourea(6)*

A mixture of compound 5 (0.01 mol) and thiourea (0.01 mol) in sodium ethoxide (0.23g sodium in 100 cm<sup>3</sup> absolute ethanol) was stirred for 2h at room temperature then neutralized with diluted acetic acid. The formed solid product was collected by filtration, dried and recrystallized from diluted methanol. Yield 65%. M.p.: 159–161 °C. FT-IR,  $\nu$  (cm<sup>-1</sup>): 3475 (OH), 3398, 3290 (NH<sub>2</sub>), 3228, 3289 (2NH), 1620 (def. NH<sub>2</sub>). 1560 (C=N), 1237 (C=S), 878, 806 (2-phenyl groups). <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 6.26 (brs, 2H, NH<sub>2</sub>) 7.25 – 7.92 (m, 12H, Ar-H), 8.95 (s, 1H, NH), 9.53 (s, 1H, NH), 10.21 (s, 1H, OH). Ms (m/z, I %): 354 (M+2, 3%), 324(7), 178(12), 174(3), 160(4), 142(6), 141(100), 115(6), 77(4), 65(8). Anal. Calcd. For  $C_{17}H_{16}N_6OS$  (352): C, 57.95; H, 4.54; N, 23.86; S, 9.09. Found: C, 57.66; H, 4.31; N, 23.46; S, 8.73 %.

*5-(5,6-Diphenyl-1,2,4-triazin-3-yl)-4-methyl-1,3,5-triazine-2-thione (7)*

A mixture of 6 (0.01 mol) and glacial acetic acid (30 cm<sup>3</sup>) with fused sodium acetate (3 gm) was refluxed for 6 h and then allowed to cool. The precipitate that formed was filtered off, dried and recrystallized from pet. ether (80%). Yield 50%. M.p.: 206–208 °C. FT-IR,  $\nu$  (cm<sup>-1</sup>): 1545, 1579 (2 C=N), 1237 (C=S). <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 1.96 (s, 3H, CH<sub>3</sub>), 7.25 – 7.59 (m, 11H, Ar-H), Ms (m/z, I %): 359 (M + 1, 1.08%), 512 (3), 343 (5.68), 327 (14), 301 (8), 259 (11), 178 (100), 112 (10), 54 (5). Anal. Calcd. for  $C_{19}H_{14}N_6S$  (358): C, 64.77; H, 3.97; N, 23.46; S, 8.93. Found: C, 64.54; H, 3.61; N, 23.17; S, 8.69 %.

*2-Cyano-3-[(5,6-diphenyl-1,2,4-triazin-3yl)amino] acrylonitrile (8 a) and ethyl 2-cyano-3-[(5,6-diphenyl-1,2,4-triazin-3-yl) amino] acrylate(8b)*

A mixture of compound 5 (0.01 mol) and active methylene compounds namely, malononitrile, ethyl cyanoacetate (0.01 mol) in sodium ethoxide (0.23g sodium in 100 cm<sup>3</sup> absolute ethanol) was refluxed for 4h. The reaction mixture was cooled and then poured into a beaker containing ice/water mixture containing few drops of HCl for neutralization. The solid so obtained was filtered off and recrystallized to give compounds 8a, b, respectively.

For compound 8a recrystallized from MeOH. Yield 50%. M.p.: 110–112 °C. FT-IR,  $\nu$  (cm<sup>-1</sup>): 3192 (NH), 2219 (C≡N), 2226 (C≡N), 1597 (C=N). Anal. Calcd. for  $C_{19}H_{12}N_6$  (324): C, 70.37; H, 3.70; N, 25.92. Found: C, 70.12; H, 3.42; N, 25.61%.

For compound 8b recrystallized from isopropanol. Yield 62 %. M.p.: 132– 134 °C. FT-IR,  $\nu$  (cm<sup>-1</sup>): 3245 (NH), 2230 (C≡N), 1675 (C=O), 1578 (C=N). <sup>1</sup>H

NMR (200 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 2.79 (t, 3H, CH<sub>3</sub>), 4.15 (q, 2H, CH<sub>2</sub>), 7.15 – 7.98 (m, 11H, Ar-H), 9.16 (s, 1H, NH). Anal. Calcd. for  $C_{21}H_{17}N_5O_2$  (371): C, 67.92; H, 4.58; N, 18.86. Found: C, 67.57; H, 4.23; N, 18.51 %.

*4,6-Diamino-5-[(5,6-diphenyl-1,2,4-triazin-3yl)methylideneamino] }pyrimidine-2-thione (9)*

A mixture of compound 8a (0.01 mol) and thiourea (0.01 mol) and sodium ethoxide (0.02 mol Na in 100 cm<sup>3</sup> absolute ethanol) was refluxed for 4 h, cooled and then poured into ice /water mixture containing few drops of CH<sub>3</sub>CO<sub>2</sub>H to neutralization. The formed solid product was collected by filtration, dried and recrystallized from DMF. Yield 54 %. M.p.: 236–238 °C. FT-IR,  $\nu$  (cm<sup>-1</sup>): 3479, 3365 (2NH<sub>2</sub>), 3228 (NH), 1557 (C=N). <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 4.59 (brs, 2H, NH<sub>2</sub>), 5.19 (brs, 2H, NH<sub>2</sub>), 6.95 (s, 1H, =CH), 7.26 – 7.98 (m, 10H, Ar-H), 8.87 (s, 1H, NH). Ms (m/z, I %): 343 (M + 2, 12 %), 397 (M - 4, 3%), 261(4), 222 (5), 178 (100), 141 (3), 120 (5), 102 (9), 94 (2), 80 (7). Anal. Calcd. for  $C_{20}H_{15}N_7OS$  (401): C, 59.85; H, 3.74; N, 24.43; S, 7.98. Found: C, 59.51; H, 3.49; N, 24.07; S, 7.62 %.

*6-Amino-5-[(5,6-diphenyl-1,2,4-triazin-3-yl)methylideneamino]}-2-thioxo-2,5-dihydropyrimidin-4-one (10)*

A mixture of compound 8b (0.01 mol) and thiourea (0.01 mol) and sodium ethoxide (0.02 mol Na in 100 cm<sup>3</sup> absolute ethanol) was refluxed for 4 h, cooled and then poured into ice-water mixture containing few drops of acetic acid to neutralization. The formed solid product was collected by filtration, dried and recrystallized from DMF. Yield 55 %. M.p.: 222–224 °C. IR FT-IR,  $\nu$  (cm<sup>-1</sup>): 3378, 3223(NH<sub>2</sub>), 3192, 3050 (2NH), 1668 (C=O), 1274 (C=S), 1588 (C=N). <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 5.19 (brs, 2H, NH<sub>2</sub>), 7.21–7.87 (m, 11H, Ar-H), 9.17 (s, 1H, NH). Ms (m/z, I %): 403 (M + 3, 11%), 248 (3), 197 (2), 178 (100 %), 151 (3), 138 (5), 104 (11), 76 (2). Anal. Calcd. for  $C_{20}H_{16}N_8S$  (400): C, 60.00; H, 4.00; N, 28.00; S, 8.00. Found: C, 59.66; H, 3.76; N, 27.73; S, 7.63 %.

*N-(5,6-Diphenyl-1,2,4-triazin-3-yl) hydrazonoformamide (11)*

A mixture of 5 (0.01 mol) and hydrazine hydrate (98 %, 0.15 mol) in absolute ethanol (20 cm<sup>3</sup>) was refluxed for 30 min., and then allowed to cool. The precipitate that formed was filtered off and recrystallized from EtOH. Yield 72 %. M.p.: 220–222 °C. FT-IR,  $\nu$  (cm<sup>-1</sup>): 3391, 3250 (NH<sub>2</sub>) 3203 (NH), 1516 (C=N). <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 2.92 (brs, 2H, NH<sub>2</sub>), 7.64 (s, 1H, CH=N), 7.76 – 7.97(m, 10H, Ar-H), 9.85 (s, 1H, NH). Anal. Calcd. for  $C_{16}H_{14}N_6$  (290): C, 66.20; H, 4.82; N, 28.96. Found: C, 65.86; H, 4.46; N, 28.67 %.

*3-(3-Methyl-1,2,4-triazol-4-yl)-5,6-diphenyl-1,2,4-triazine (12)*

A mixture of 11 (0.01 mol) and glacial acetic

acid (30 cm<sup>3</sup>) with fused sodium acetate (3 g) was refluxed for 4 h, cooled and poured onto ice. The solid obtained was filtered off, and recrystallized from benzene. Yield 78 %. M.p.: 190–192°C. FT-IR,  $\nu$  (cm<sup>-1</sup>): 3391 (NH<sub>2</sub>), 3203 (NH), 1556 (C=N). <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 3.45 (s, 3H, CH<sub>3</sub>), 7.21 (s, 1H, CH=N), 7.43–7.89 (m, 11H, Ar-H and C<sub>5</sub>-H triazole). Anal. Calcd. for C<sub>18</sub>H<sub>14</sub>N<sub>6</sub> (314): C, 68.78; H, 4.45; N, 26.75. Found: C, 68.44; H, 4.20; N, 26.40 %.

*3-[3-Oxo-2H-1,2,4-triazol-4-yl] 5,6-diphenyl-1,2,4- (13)*

A mixture of 11 (0.01 mol) and an equimolar amount of diethyl carbonate in dioxan (50 cm<sup>3</sup>) was refluxed for 6 h, then concentrated and the separated solid was filtered off, dried and recrystallized from benzene. Yield 59 %. M.p.: 241–243°C. FT-IR,  $\nu$  (cm<sup>-1</sup>): 3137 (NH), 1670 (C=O), 1532 (C=N). <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 7.15–7.98 (m, 11H, Ar-H and C<sub>2</sub>-H pyrazole), 8.97 (s, 1H, NH). Anal. Calcd. for C<sub>17</sub>H<sub>12</sub>N<sub>6</sub>O (316): C, 64.55; H, 3.79; N, 26.58. Found: C, 64.21; H, 3.43; N, 26.21 %.

*5,5[,6,6]-Tetraphenyl -3,4]-bi-1,2,4-triazine (14)*

A mixture of 11 (0.01 mol) and benzoin (0.01 mol) in absolute ethanol (20 cm<sup>3</sup>) was refluxed for 12 h, cooled and then the reaction mixture was poured into crushed ice, and the separated solid was filtered off, dried and recrystallized from MeOH. Yield 57 %. M.p.: 189–199 °C. FT-IR,  $\nu$  (cm<sup>-1</sup>): 561 (C=N). Ms (m/z, I %): 467 (M +2, 21%), 465 (M, 12%), 205 (12), 178 (8), 105(100), 103 (13), 79 (7), 54 (3). Anal. Calcd. for C<sub>30</sub>H<sub>21</sub>N<sub>6</sub> (465): C, 77.41; H, 4.51; N, 18.06. Found: C, 77.05; H, 4.14; N, 17.71 %.

*N-(5,6-Diphenyl-1,2,4-triazin-3-yl)-N-[2-oxo-1,2-dihydro-indol-3-ylidene]hydrazonoformamide (15)*

A mixture of 11 (0.01 mol) and isatin (0.01 mol) in absolute ethanol (30 cm<sup>3</sup>) was refluxed for 1h. The reaction mixture was cooled and the solid so obtained was filtered off and recrystallized from MeOH. Yield 75 %. M.p.: 197–198 °C. IR FT-IR,  $\nu$  (cm<sup>-1</sup>): 3216, 3174 (2 NH), 3091 (CH aryl), 1725 (C=O), 1549 (C=N). <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 7.15 – 7.97 (m, 15H, Ar-H and =CH), 8.92 (s, 1H, NH), 9.62 (s, 1H, NH). Anal. Calcd. for C<sub>24</sub>H<sub>17</sub>N<sub>7</sub>O (419): C, 68.73; H, 4.05; N, 23.38. Found: C, 68.39; H, 3.69; N, 23.02%.

*4-(5,6-Diphenyl-1,2,4-triazin-3-yl)-[1,2,4]triazino[5,6-b] indole(16)*

A mixture of 15 (1g) and glacial acetic acid (20 cm<sup>3</sup>) with fused NaOAc (5g) was refluxed for 4h and then allowed to cool. The precipitate that formed was filtered off, dried and recrystallized from CHCl<sub>3</sub>. Yield 72 %. M.p.: 272–274 °C. FT-IR,  $\nu$  (cm<sup>-1</sup>): 1590 (C=N), 1522 (C=N). <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 7.25 – 8.2 (m, 15H, Ar-H). Ms (m/z, I %): (M, 401, 12%), 223 (14), 169 (8), 141 (100), 128 (12), 54(8). Anal. Calcd. for C<sub>24</sub>H<sub>15</sub>N<sub>7</sub>

(401): C, 71.82; H, 3.74; N, 24.43. Found: C, 71.44; H, 3.38; N, 24.05 %.

*1-(5,6-Diphenyl-1,2,4-triazin-3-yl)thiourea (17)*

A mixture of 1 (0.01 mol) and potassium thiocyanate (0.01 mol) in DMF (20 cm<sup>3</sup>) and dil. HCl (20%, 2 cm<sup>3</sup> in 10 ml of water) was refluxed for 6h, then the reaction mixture was poured into crushed ice, and the separated solid was filtered off, dried well and recrystallized from ethanol. Yield 73 %. M.p.: 184 – 186 °C. FT-IR,  $\nu$  (cm<sup>-1</sup>): 3452, 3340 (NH<sub>2</sub>), 3269 (NH), 1529 (C=N), 1228 (C=S), 853, 820 (2-phenyl groups), <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 4.33 (s, 1H, NH), 5.92 (brs, 2H, NH<sub>2</sub>), 7.15– 8.23 (m, 10H, Ar-H). Anal. Calcd. for C<sub>16</sub>H<sub>13</sub>N<sub>5</sub>S (307): C, 62.54; H, 4.23; N, 22.80; S, 10.42. Found: C, 62.16; H, 3.88; N, 22.43; S, 10.04 %.

*6-Amino-1-(5,6-diphenyl-1,2,4-triazin-3-yl)-4-(4-nitrophenyl)-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carbonitrile (19)*

A mixture of 17 (0.01 mol) and 3-nitrobenzyliden malononitrile (18) (0.01 mol) in absolute ethanol (20 cm<sup>3</sup>) containing piperidine (0.5 cm<sup>3</sup>). The reaction mixture was heated under reflux for 4 h and allowed to cool. The precipitate that formed was filtered off, dried and recrystallized from ethanol. Yield 87 %. M.p.: 190–192 °C. IR FT-IR,  $\nu$  (cm<sup>-1</sup>): 3423, 3310(NH<sub>2</sub>), 3212 (NH), 2218 (CN), 1587 (C=N), 1235 (C=S). <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 6.15 (brs, 2H, NH<sub>2</sub>), 7.12–8.15 (m, 15H, Ar-H and C<sub>4</sub>-H pyrimidine), 8.93 (s, 1H, NH). Anal. Calcd. for C<sub>26</sub>H<sub>17</sub>N<sub>8</sub>O<sub>2</sub>S (505): C, 61.78; H, 3.02; N, 22.17; S, 6.33. Found: C, 61.42; H, 3.36; N, 21.79; S, 5.99 %.

*8-(5,6-Diphenyl-1,2,4-triazin-3-yl)-5-(4-nitrophenyl)-7-thioxo-5,6,7- trihydropyrimido[4,5-d]pyrimidin-4-one(20)*

A mixture of 17 (0.01 mol) and formic acid (10 cm<sup>3</sup>) was refluxed for 24 h. The formed solid product was filtered off, dried and recrystallized from ethanol. Yield 56%. M.p.: 201– 203 °C. FT-IR,  $\nu$ (cm<sup>-1</sup>): 3245 (NH), 1579 (C=N), 1215 (C=S). <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 7.15 – 7.98 (m, 16H, Ar-H), 9.25 (s, 1H, NH). Ms (m/z, I %): 493 (12), 315 (4), 263 (2), 197 (13), 178 (100), 111 (3). Anal. Calcd. for C<sub>27</sub>H<sub>17</sub>N<sub>8</sub>O<sub>2</sub>S (517): C, 62.66; H, 3.28; N, 21.66; S, 6.18. Found: C, 62.29; H, 2.90; N, 21.28; S, 5.82 %.

*2-[(5,6-Diphenyl-1,2,4-triazin-3-yl)imino]-1,3-thiazolididin-4-one(21)*

A mixture of 17 (0.01 mol) and chloroacetic acid (0.01 mol) and anhydrous sodium acetate (0.01 mol) in glacial acetic acid (15 cm<sup>3</sup>) with a trace of acetic anhydride (0.5 cm<sup>3</sup>) was refluxed for 8 h. The reaction mixture was cooled and poured into ice-cold water. The solid that separated out was filtered off and purified by recrystallization from glacial acetic acid. Yield 60 %. M.p.: 191– 93 °C. FT-IR,  $\nu$  (cm<sup>-1</sup>): 3292 (NH), 1660 (C=O),

1609, 1575(2 C=N).  $^1\text{H}$  NMR (200 MHz, DMSO- $d_6$ )  $\delta$ : 3.35(s, 2H,  $\text{CH}_2$ ), 5.67 (s, 1H, NH), 7.15–7.98 (m, 10H, Ar-H). Anal. Calcd. for  $\text{C}_{18}\text{H}_{13}\text{N}_5\text{OS}$  (347): C, 62.24; H, 3.74; N, 20.17; S, 9.22. Found: C, 61.97; H, 3.36; N, 19.83; S, 8.85 %.

*2-[(5,6-Diphenyl-1,2,4-triazin-3-yl)imino]-5-(4-nitrobenzylidene)-1,3-thiazolidin-4-one(22)*

A mixture of 21 (0.01 mol), the 3-nitrobenzaldehyde (0.01 mol) and anhydrous sodium acetate (0.02 mol) in glacial acetic acid (20  $\text{cm}^3$ ) was refluxed for 5 h. The reaction mixture was allowed to at room temperature and treated with cold water. The solid thus separated was filtered off, washed with water and recrystallized from glacial acetic acid. Yield 82 %. M.p.: 186–188 °C. FT-IR,  $\nu$  ( $\text{cm}^{-1}$ ): 3293 (NH), 1608 (C=C), 1673 (C=O), 1563 (C=N).  $^1\text{H}$  NMR (200 MHz, DMSO- $d_6$ )  $\delta$ : 5.67 (s, 1H, NH), 6.58 (s, 1H, CH), 7.16–7.96 (m, 14H, Ar-H). Anal. Calcd. for  $\text{C}_{25}\text{H}_{16}\text{N}_6\text{O}_3\text{S}$  (480): C, 62.50; H, 3.33; N, 17.50; S, 6.66. Found: C, 62.13; H, 2.98; N, 17.13; S, 6.30 %.

*2-[5,6-Diphenyl-1,2,4-triazin-3-ylimino]-6-(3-nitrophenyl)-3,6,7-trihydro-1,3-thiazolo[4,5-c]isoxazole (23)*

A mixture of 22 (0.01 mol) and hydroxylamine hydrochloride (0.01 mol) was taken in absolute ethanol (20  $\text{cm}^3$ ) and two drops of KOH (2 %) were added slowly to the solution. It was refluxed for 12 h. The reaction mixture was kept overnight and then the solution was poured into water. The resulting solid was filtered off, dried and recrystallized from EtOH. Yield 53 %. M.p.: 213–215 °C. FT-IR,  $\nu$  ( $\text{cm}^{-1}$ ): 3301 (NH), 1617, 1591 (2, C=N), 1075 (C–O), 900 (N–O), 770 (C–Cl).  $^1\text{H}$  NMR (200 MHz, DMSO- $d_6$ )  $\delta$ : 3.30 (d, 1H,  $\text{CH}_b$ ), 4.36 (d, 1H,  $\text{CH}_a$ ), 6.51 (s, 1H, NH), 7.16–8.25 (m, 14H, Ar-H). Ms (m/z, I %): 495(M, 11%), 318 (16), 317 (7.), 303 (5.), 203 (13), 191(6), 192 (5), 178 (100). Anal. Calcd. for  $\text{C}_{25}\text{H}_{17}\text{N}_7\text{O}_3\text{S}$  (495): C, 60.60; H, 3.43; N, 19.79; S, 6.46. Found: C, 60.31; H, 3.06; N, 19.42; S, 6.09 %.

*2-[5,6-Diphenyl-1,2,4-triazin-3-ylimino]-6-(3-nitrophenyl)-3,5,6,7-tetrahydro-1,3-thiazolo[4,5-c]pyrazole (24)*

A mixture of 22 (0.01 mol) and hydrazine hydrate (0.01 mol) were dissolved in ethanol (20  $\text{cm}^3$ ). After the addition of two drops of pyridine, the reaction mixture was refluxed for 16 h. After evaporating the excess solvent, it was cooled and poured into ice-cold water. The solid obtained was filtered off, dried and recrystallized from EtOH. Yield 64 %. M.p.: 191–193 °C. FT-IR,  $\nu$  ( $\text{cm}^{-1}$ ): 3320, 3293 (2NH), 1626, 1568 (2C=N), 770 (C–Cl), 712(C–S–C).  $^1\text{H}$  NMR (200 MHz, DMSO- $d_6$ )  $\delta$ : 3.45 (d, 1H,  $\text{CH}_b$ ), 4.67 (d, 1H,  $\text{CH}_a$ ), 5.56 (s, 1H, NH), 6.48 (s, 1H, NH), 7.22–8.25 (m, 14H, Ar-H), Ms (m/z, I %): 495 (M + 1, 12%), 392 (21), 330 (7), 316 (22), 269

(21), 254 (2), 178 (100), 115 (7). Anal. Calcd. For  $\text{C}_{25}\text{H}_{18}\text{N}_9\text{O}_2\text{S}$  (494): C, 60.72; H, 3.25; N, 22.67; S, 6.47. Found: C, 60.34; H, 3.64; N, 22.37; S, 6.20 %.

*2-[(5,6-Diphenyl-1,2,4-triazin-3-ylimino)-7-(3-nitrophenyl)-6,7,8-trihydro-1,3-thiazolo[4,5-d]pyrimidine-5-(6H) one (25)*

A mixture of 2 (0.01 mol) and urea (0.01 mol) in ethanol (20  $\text{cm}^3$ ) with a trace of acetic acid (0.5 ml) was refluxed for 17 h. After cooling the reaction mixture was neutralized with 5% NaOH solution. The solid that separated out was filtered off, washed several times with water and recrystallized from acetic acid. Yield 63 %. M.p.: 204–206 °C. FT-IR,  $\nu$  ( $\text{cm}^{-1}$ ): 3293, 3183 (2, NH), 1667 (C=O), 1556 (2C=N), 747 (C–Cl), 710 (C–S–C).  $^1\text{H}$  NMR (200 MHz, DMSO- $d_6$ )  $\delta$ : 3.50 (d, 1H,  $\text{CH}_b$ ), 4.56 (d, 1H,  $\text{CH}_a$ ), 5.98 (s, 1H, NH), 6.45 (s, 1H, =CH), 7.15–7.98 (m, 14H, Ar-H), 9.32 (s, 1H, CONH), Ms (m/z, I %): 522 (M, 11%), 344 (23), 330 (5), 298 (19), 178 (100), 176 (8), 144 (6), 141 (3). Anal. Calcd. for  $\text{C}_{26}\text{H}_{18}\text{N}_8\text{O}_3\text{S}$  (522): C, 59.77; H, 3.44; N, 21.45; S, 6.13. Found: C, 59.40; H, 3.17; N, 21.17; S, 5.86 %.

*2-[(5,6-Diphenyl-1,2,4-triazin-3-ylimino)-7-(3-nitrophenyl)-6,7,8-trihydro[1,3]thiazolo[4,5-d]pyrimidine-5-(6H) thione (26)*

A mixture of 22 (0.01 mol) and thiourea (0.01 mol) in ethanol (20  $\text{cm}^3$ ) with a trace of acetic acid (0.5 ml) was refluxed for 17 h. The solid that separated out was filtered off, washed several times with water and recrystallized from acetic acid. Yield 63 %. M.p.: 215–217 °C. FT-IR,  $\nu$  ( $\text{cm}^{-1}$ ): 3330, 3212 (2NH), 1617, 1589 (2C=N), 1235 (C=S), 762 (C–Cl).  $^1\text{H}$  NMR (200 MHz, DMSO- $d_6$ )  $\delta$ : 3.4 (d, 1H,  $\text{CH}_b$ ), 4.50 (d, 1H,  $\text{CH}_a$ ), 5.96 (s, 1H, NH), 6.98–7.89 (m, 14H, Ar-H), 8.49 (s, 1H, NH). Ms (m/z, I %): 539 (M + 1, 11%), 384 (3), 370 (4), 350 (8), 347 (3), 335 (5), 178 (100), 143(5). Anal. Calcd. for  $\text{C}_{26}\text{H}_{18}\text{N}_8\text{O}_2\text{S}_2$  (538): C, 57.99; H, 3.34; N, 20.81; S, 5.94. Found: C, 57.75; H, 2.97; N, 20.44; S, 5.70 %.

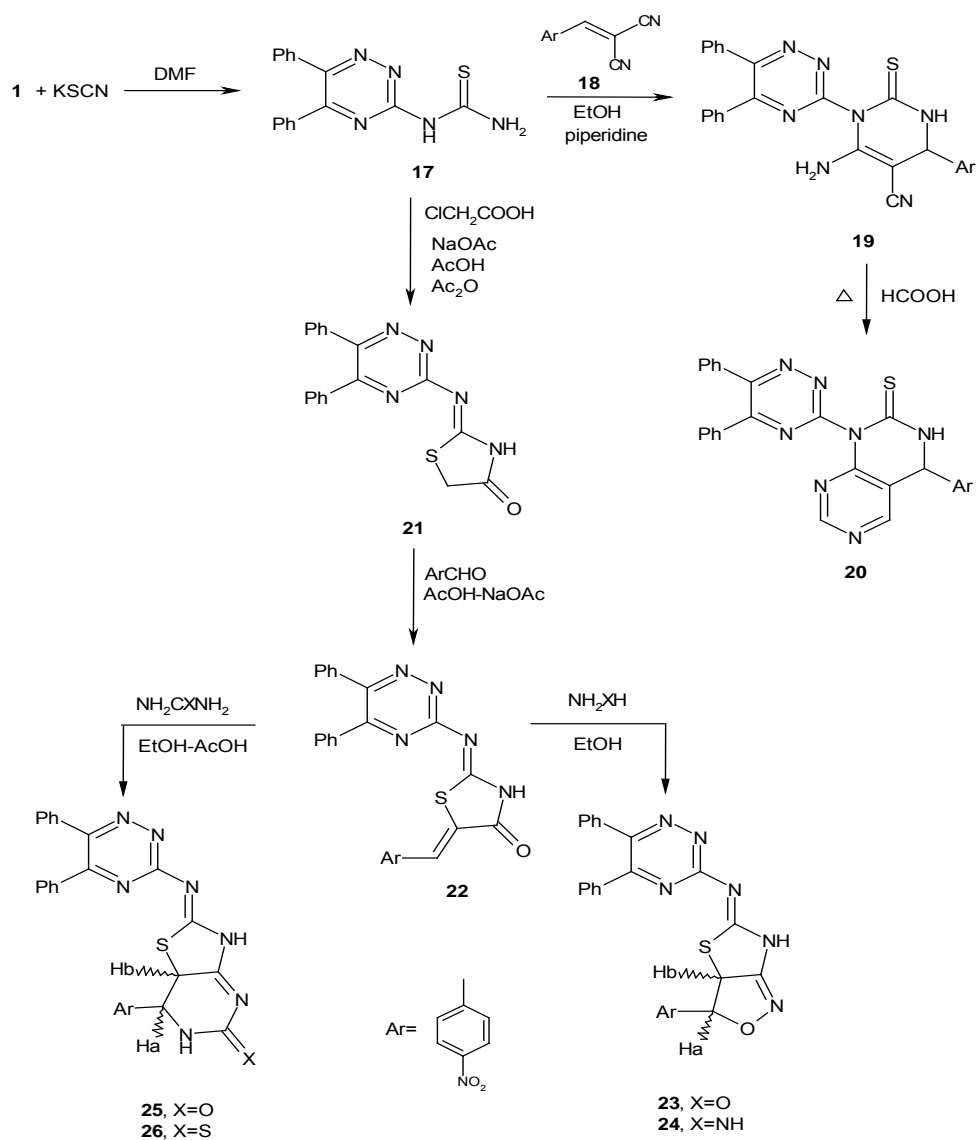
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### GRAPHICAL ABSTRACT

A series of some new 1,2,4-triazines aryl derivatives containing isoxazoles, pyrimidines, pyrazoles and imidazoles moieties was synthesized and screened for their antimicrobial activity against bacterial and fungal strain. The results suggest that some of these compound to be potent antimicrobial agents.





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## Seasonal Variations of Tropospheric Ozone Concentrations

By Nnnesi A. Kgabi & Ramotsamai M. Sehloho

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**Abstract** - This study shows strong seasonality of ground level ozone concentrations with spring (September and October) maximum and winter (May and June) minimum levels. The levels were observed in decreasing order per season as: spring>summer>autumn>winter. The Johannesburg ozone levels were much lower than Botsalano and Marikana levels. The monthly levels for the 2007 to 2008 period were determined in order of decreasing abundance as Marikana (21.07 – 50.02 ppb), Botsalano (28.17 – 37.94 ppb), Buccleuch (2.03 – 23.42 ppb), Delta (5.76 – 17.32 ppb) and Newtown (1.73 – 17.19 ppb). The precursors of ozone ( $\text{NO}_x$ ,  $\text{NO}_2$ , and NO) also showed peaks in winter (May-June). Anti- correlation of ozone and its precursors ( $\text{NO}_x$ ,  $\text{NO}_2$ , and NO) were also observed. The authors also conclude that the formation of ozone in Johannesburg occurs under the VOC-sensitive regime, and that the possible sources of ozone in the city are vehicular and industrial and businesses.

**Keywords** : Tropospheric ozone, oxides of nitrogen, seasonal variations.

**GJSFR-B Classification** : FOR Code: 039901



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**Abstract** - This study shows strong seasonality of ground level ozone concentrations with spring (September and October) maximum and winter (May and June) minimum levels. The levels were observed in decreasing order per season as: spring>summer>autumn>winter. The Johannesburg ozone levels were much lower than Botsalano and Marikana levels. The monthly levels for the 2007 to 2008 period were determined in order of decreasing abundance as Marikana (21.07 – 50.02 ppb), Botsalano (28.17 – 37.94 ppb), Buccleuch (2.03 – 23.42 ppb), Delta (5.76 – 17.32 ppb) and Newtown (1.73 – 17.19 ppb). The precursors of ozone (NO<sub>x</sub>, NO<sub>2</sub>, and NO) also showed peaks in winter (May-June). Anti-correlation of ozone and its precursors (NO<sub>x</sub>, NO<sub>2</sub>, and NO) were also observed. The authors also conclude that the formation of ozone in Johannesburg occurs under the VOC-sensitive regime, and that the possible sources of ozone in the city are vehicular and industrial and businesses.

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## 1. INTRODUCTION

Ozone is considered as a pollutant at ground level and the overall effect of its exposure leads to decrease of lung capability to perform normal function. The reduction of surface ozone which is harmful to human health, animals, and plants, is an important objective of air quality policy for many governments (Reddy et al, 2011).

Ground level ozone (O<sub>3</sub>) is a major component of smog, produced in the troposphere by the catalytic reactions of nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>) with carbon monoxide (CO), methane (CH<sub>4</sub>), and non-methane volatile organic compounds (NMVOCs) in the presence of sunlight (Avnery et al, 2011). Exposure to elevated concentrations of surface ozone (O<sub>3</sub>) causes substantial reductions in the agricultural yields of many crops. As emissions of O<sub>3</sub> precursors rise in many parts of the world over the next few decades, yield reductions from O<sub>3</sub> exposure appear likely to increase the challenges of feeding a global population projected to grow from 6 to 9 billion between 2000 and 2050 (Avnery et al, 2011). Through the absorption of infrared radiation at 9.6 mm, ozone also acts as a greenhouse gas, which has implications for the global climate. Even though the

warming effect of ozone is small compared to gases such as CO<sub>2</sub>, methane, and water vapor, at ~0.35 W m<sup>-2</sup>, it is still significant (Intergovernmental Panel on Climate Change, 2007).

About 50% of all large biomass fires on earth occur in Africa (Hao et al., 1991) where burning emissions are strongest in the dry season mainly south of the equator between July and October. Of these fires, 50% is attributed to savanna burning, 24% to shifting cultivation, 10% deforestation, 11% domestic burning and 5% agricultural waste burning (Hao and Liu, 1994). These biomass sources make a 35% contribution to global photochemical ozone formation (Marufu, 1999). According to Zunckel et al. (2004), mean surface ozone concentrations exhibit strong seasonal and diurnal variations over Southern Africa. The major anthropogenic source regions of atmospheric pollutants in southern Africa are the mining and smelting activities on the Copperbelt in northern Zambia and emissions from coal in the South African Highveld (Fleming and van der Merwe, (2002).

Levine et al. (1996) indicated that biomass burning is a major source of gases and aerosols in the Southern African atmosphere. Biomass burning is seasonal and occurs almost exclusively during winter and spring, July to September. Biomass burning of the African savannas is known to produce large amounts of photochemically active aerosols and trace gases that are necessary precursors of tropospheric ozone (Crutzen and Andreae, 1990).

Biomass burning, fossil fuel combustion, and other anthropogenic activities generate CO, CH<sub>4</sub>, VOCs, etc., which are oxidized to ozone in a NO<sub>x</sub>-rich environment. The main sources of NO<sub>x</sub> are fossil fuel combustion, biomass burning, soil microbial activity, and lightning. NO plays a critical role in ozone production, even in rural regions, where NO concentration is higher than 10 parts per trillion (ppt) (Lin et al., 1988). Emissions of NO<sub>x</sub> are produced primarily when fossil fuels are burned in motor vehicle engines, power plants, and industrial boilers. Mobile sources (including on-road and others) of NO<sub>x</sub> include emissions from aircraft, trains, ships, recreational boats, industrial and construction equipment, farm equipment, off-road recreational vehicles, and other equipment. Stationary sources include both internal and external combustion processes in industries such as manufacturing, food processing, electric utilities, and

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petroleum refining. Area-wide sources include residential fuel combustion, waste burning, and fires (Drechsler et al., 2006).

Besides the photochemical reactions affected by solar radiation and variations in anthropogenic emissions, boundary layer processes and meteorological parameters also play important roles in the process of diurnal variations in  $O_3$  and its precursors. Ozone concentrations depend sensitively upon meteorological parameters such as temperature, sunlight, wind speeds and the mixed layer depth. Therefore, changes in these meteorological parameters due to climate change will necessarily impact surface ozone concentrations (Reddy et al, 2011). Meteorology also plays a crucial role in the formation, dispersion, transport, and dilution of ozone in the atmosphere (Elminir, 2005; Tu et al., 2007).

In this study, monthly ground level ozone concentrations were measured at Botsalano Game Reserve and Marikana in the North West province (which depends mostly on agriculture and mining activities); and Buccleuch, Delta, and Newtown in Johannesburg - Gauteng province (which is highly industrialized and is mostly urban); and the relation between ozone and  $NO_x$ ,  $NO_2$ , and  $NO$  was also determined. The significance of this study is on provision of knowledge of the interactions between  $O_3$  and its precursors, which according to Mioduszewski et al, (2011) is also crucial to understanding their atmospheric concentrations and lifetimes and the environmental impacts that can be expected with modifications to their sources and sinks. The study presents observations and analysis of the seasonal variations in tropospheric ozone ( $O_3$ ) in association with its precursors, nitrogen oxides ( $NO_x = NO + NO_2$ ), and the meteorological conditions; thus giving a better understanding of the relationship between ozone precursors and formation of ozone in industrialized and non-industrialized environments, which is also a critical pre-requisite for development of effective  $O_3$  control strategies.

## II. MATERIAL AND METHODS

Environment SA 41 m UV photometric ozone analyzer was used to measure ozone concentrations in Botsalano and Marikana during the period 2007 to 2008. The ozone analyzer operates on a full scale of 0 – 500 ppb, at a temperature range of 10°C to 35°C, with response time setting of 11 (Automatic response time), and with or without any of the internal ozone generator, and span external control (zero/span solenoid valve) ([www.epa.gov/ttn/amtic/criteria.html](http://www.epa.gov/ttn/amtic/criteria.html)). The UV photometric method is not subject to interference from any of the common gaseous pollutants.

The ozone analyzer has three major systems: the optical system, the pneumatic system, and the

processing electronic system. Pneumatic system consists of sample probe, sample inlet line, particulate filter which eliminates the dust particles contained in the sample to be analyzed, solenoid valves, and scrubber, internal tubing, flow meter which maintains the necessary flow in the measurement system, and pump, all used to bring ambient air samples to the analyzer inlet (McElroy and Nees, 1997).

The ozone concentrations were measured continuously and air sampled 24 hours a day by a pump which passed first through exchangeable Teflon filter. The filter was changed after every two weeks. A detector measured the light intensity in the absence of ozone and the Beer-Lambert equation was used to calculate the concentration of ozone from ratio of the light intensity (US EPA, 1996). The data logger was connected to the instruments to log the data to the computer. The data for temperature, relative humidity, rain, and wind speed and wind direction were also recorded and stored daily.

Calibration of the ozone analyzer is carried out until the preset values of reading in the analyzer match the current applied to the UV lamp. The  $O_3$  determination is based on a commercial instrument using UV mercury absorption of 253.7 nm radiation. The  $O_3$  analyzer is so designed that it absorbs ozone at 253.7 nm, and the UV mercury lamp used in the instrument also emits light of the same wavelength. The calibration factor is not be required in this process. The detector is employed before and after the absorption takes place in the fixed length flow path. So the variations in the intensity of the light are balanced. In order to check the zero reading of the analyzer zero air has to be admitted which is free of ozone. If the analyzer is reading a higher value for zero air, then the ozone scrubber in the analyzer needs to be changed; for which the analyzer scrubbers continually check the zero every 10 s and goes to the sample line (Reddy et al, 2008).

Temperature and relative humidity were measured using Rotronic MP 101A (Vaisala HMP50), rain intensity was measured using Thies 5.4103.20.041 Adolf Thies GmbH Co.KG, and wind direction and wind speed were measured using Vector A101ML (Vector W200P). Data on three monitoring stations (Buccleuch, Delta, and Newtown) in Johannesburg were supplied by the Johannesburg City and the South African weather Services.

Figure 1 shows the location of study sites within Gauteng (Buccleuch, Delta, and Newtown) and North West Province (Botsalano and Marikana). The Botsalano game reserve is situated 18 km east of Ramatlabama (Botswana – South Africa) border post, and 65 km north of Mafikeng. The Game Reserve is situated between longitude 25degrees 32' 30.4" south and latitude 25degrees 45' 17.8" east and is far from the central business districts and mining industries. Ozone concentrations and meteorological parameters were

also measured at Marikana municipal offices, with a community health clinic, community hall and library buildings in the same location. Marikana is a township situated between longitude 27°21'53.61" south and latitude 27°28'36.58" east, located to the east of Rustenburg, a pollution hotspot in the North West Province.

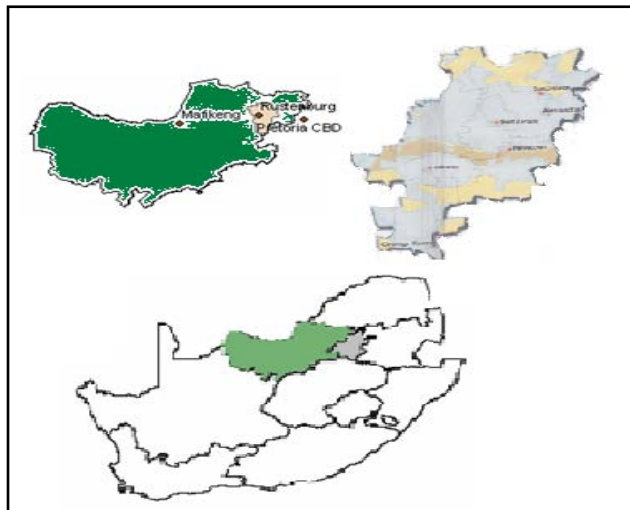


Figure 1 : Location of the study sites within North West (green shading) and Gauteng Province (grey shading) of South Africa.

The Newtown station (Latitude: -26.2052; Longitude: 28.0321) located within Johannesburg Central Business District measures urban, commercial and industrial emissions; the Buccleuch station is located at the intersection of the N1 and M<sub>1</sub> highways (Latitude: -28.0453; Longitude: 28.0991) within the City of Johannesburg to measure vehicle emissions; and the Delta Park (Latitude: -26.125; Longitude: 28.0086) is located with the Delta Park Environmental Centre. This station is not exposed to any direct emissions from air pollution sources. However, measured concentrations at this station compare well with the rest of the stations and it is therefore not representative of background concentrations.

### III. RESULTS AND DISCUSSION

#### a) Monthly Ozone Concentrations and Meteorology

##### i. Monthly ozone concentrations for Botsalano Game Reserve and Johannesburg during 2007

Ozone formation is high during summer, long hours of sunlight and high temperatures speed up the ozone forming photochemical reactions. Low wind leads to the build-up of high local pollutants concentrations and high wind speed promotes the dispersion of ozone precursors and wind direction turn to direct the precursors for the source point to the area without large sources (Goddish, 1991). An increase in relative humidity leads to the decrease in ozone levels (Li et al., 2007).

Figure 2 shows that highest monthly mean ozone concentration was observed in October (37.94 ppb), and the lowest concentration was observed in July (28.17 ppb). The results also show seasonal variations, with the maximum occurring in spring to early summer, and minimum during the autumn to winter period.

The low ozone concentrations were observed in July when temperature and wind speed were also low, and there was no precipitation. The low ozone concentration in winter months is associated with low ambient temperatures (Altshuler, 1975).

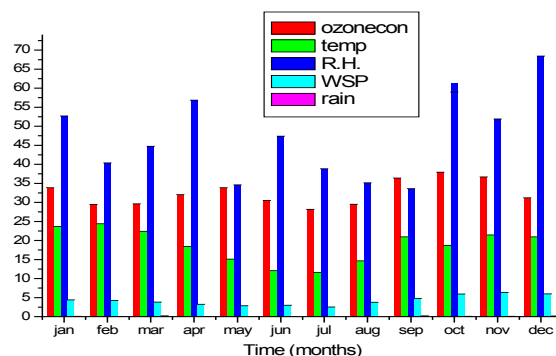


Figure 2 : Monthly mean ozone concentrations and meteorology at Botsalano in 2007.

The monthly maximum observed in October occurred at monthly average temperature of 18.66 °C and relative humidity of 61.19%. A positive correlation of ozone with temperature and wind speed was obtained as 0.30 and 0.62 respectively. A spring maximum and winter minimum was also observed from monthly concentrations at Etosha, Namibia during the period June 2000 to May 2002, were a maximum (30 ppb) was measured in October 2000 and a minimum of about 11 ppb in March 2001 (Zunckel et al, 2004).

Similar trends in ozone concentrations were also observed in the same year (2007) at three monitoring sites (Figure 3) within the heavily industrialized city of Johannesburg. The minimum levels were measured in winter (June and July) and a maximum in September.

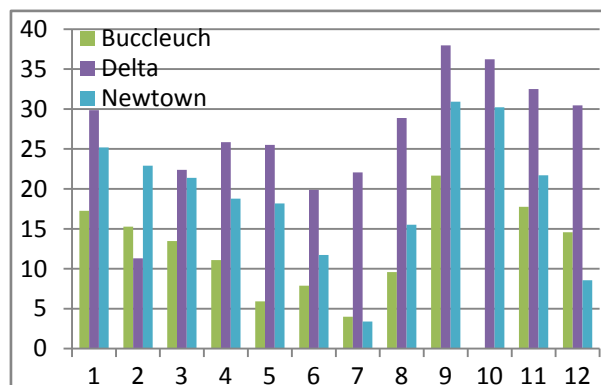


Figure 3 : Monthly mean ozone concentrations at the city of Johannesburg in 2007.

The monthly levels ranged from 3.98 to 21.66  $\mu\text{g}/\text{m}^3$  (2.03 to 11.03 ppb) for Buccleuch, from 11.31 to 37.97  $\mu\text{g}/\text{m}^3$  (5.76 to 19.33 ppb) for Delta; and 3.39 to 30.92  $\mu\text{g}/\text{m}^3$  (1.73 to 15.74 ppb) for Newtown. The levels observed in the three sites were however lower than the Marikana levels for the same year.

ii. *Monthly ozone concentrations for Marikana and Johannesburg during 2008*

Minimum levels (21.07 ppb) were observed at Marikana in April 2008 and a maximum in October (50.02 ppb) as shown in Figure 4. A positive correlation between ozone and temperature, and ozone and wind speed, with correlation coefficients of 0.38 and 0.29 respectively was also observed. The observed high concentrations during spring can be attributed to the higher temperatures which promote photochemical generation of ozone. The concentration of ozone increases with the increase in the temperature (Garcia et al., 2005). Clear skies, warm temperatures have a great influence on ozone concentrations (Vecchi and Valli, 1999). Ozone concentrations increased with temperature at this site, and relative humidity was high when both temperature and ozone concentrations were low, with a moderate wind speed.

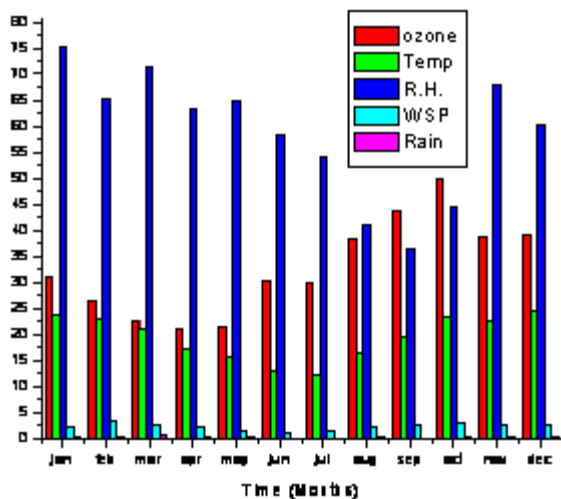


Figure 4 : Monthly average ozone and meteorology 2008.

Zunckel et al (2004) found that the seasonal maximum surface ozone in the Southern African regions generally occur in the spring months to early summer, that is from August to November. The solar radiation becomes intense in spring, causing photochemical reactions of ozone precursors that were accumulated during winter and this contribute to high ozone concentration to be observed during spring. The long lifetime of ozone in winter, which is about 200 days, also allows the anthropogenically formed ozone to accumulate in the inversion layer and then contributes to

the high spring ozone concentrations (Monks, 2000). Three monitoring sites (Figure 5) within the heavily industrialized city of Johannesburg showed minimum levels from autumn to winter (April to July) and high levels from spring to early summer (September to November), with a maximum in October.

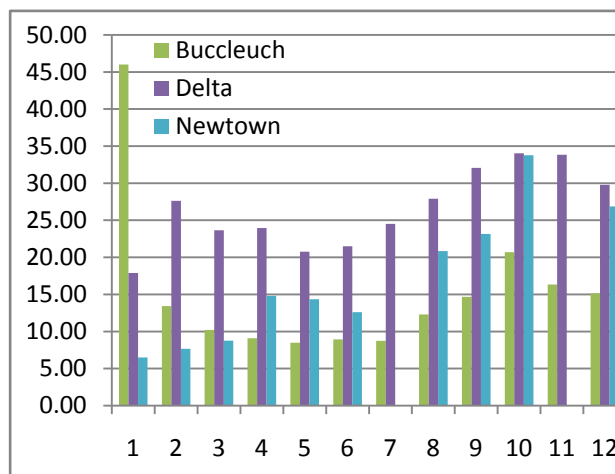


Figure 5 : Monthly mean ozone concentrations at the city of Johannesburg in 2008.

The ozone concentrations for Johannesburg sites were measured in the range of 8.48 - 46.01  $\mu\text{g}/\text{m}^3$  (4.32 - 23.42 ppb), 17.89 - 34.03  $\mu\text{g}/\text{m}^3$  (9.11 - 17.32 ppb), and 6.50 - 33.78  $\mu\text{g}/\text{m}^3$  (3.31 - 17.19 ppb), for Buccleuch, Delta, and Newtown respectively.

The City of Johannesburg has a temperate climate, experiencing over eight hours of sunlight per day in both winter and summer. Temperatures are mild with average maximum day-time temperatures of 26 °C in January, dropping to 16 °C in June. Rainfall averages about 710 mm per annum although significant inter-annual variation in total rainfall is experienced. Rainfall occurs predominantly during the summer months in late afternoon electrical storms.

Significant positive correlation coefficients were also found between  $\text{O}_3$  and temperature by Khoder (2010) in two seasons and between  $\text{O}_3$  and relative humidity in the summer season, indicating that high temperature and high relative humidity besides the intense solar radiation (in summer) are responsible for the formation of high  $\text{O}_3$  concentrations.

The low levels observed in autumn can be due to the non-availability of enough solar radiation due to the cloudy skies that reflect back the solar radiation from reaching the surface, and also the washouts of air pollutants from the atmosphere by precipitation. The highest ozone concentrations occurred in Botswana and Mpumalanga, in both regions the spring time maximum was between 40 and 69 ppb, but reached an average of more than 90 ppb on October 2000. Zunckel et al. (2004) found that minimum average monthly ozone concentration occurred in December and January.

For the 2007 and 2008 period, similar seasonal variations of ozone concentrations were observed at two different environments. A general representation of the variations of ozone can be given in order of decreasing concentrations as follows: spring, summer, autumn, and winter for all the study sites. The levels were also similar to those reported by Lacaux et al. (1993) (between 30 and 40 ppb) in central Africa during 1983 and 1988. Combrink et al. (1995) also obtained surface ozone concentrations in the range between 25 and 50 ppb at two stations in South Africa.

b) *Ozone and the Oxides of Nitrogen*

i. *Monthly Ozone and the Oxides of Nitrogen*

Photochemical production of ozone associated with emissions of CO, hydrocarbons and NO<sub>x</sub> from biomass burning may contribute significantly to high values of ozone, Logan and Kirchoff (1986). The figures 6, 7 and 8 below show the monthly levels of NO<sub>x</sub>, NO<sub>2</sub>, and NO measured from January to December 2007 at the Buccleuch, Delta, and Newtown monitoring stations within Johannesburg. The occurrence of high NO<sub>x</sub> concentrations in all the three stations is resultant of the sum of NO<sub>2</sub> and NO, and may also be caused by anthropogenic sources of NO<sub>x</sub> that occur throughout the southern African region (Fleming and van der Merwe, 2002) and soil emissions (Levine et al., 1996).

High ozone concentrations might be registered within a city or at a distance downwind because of the high emissions of precursors in urban areas. These precursors may also be transported over long distances, resulting in ozone formation far from the sources under the influence of meteorological conditions (Hastie et al., 1999). Thus, the potential for high ozone concentrations in an area that has small amounts of local nitrogen oxides and non-methane hydrocarbons is created, as reported by Cheng (2001). A similar observation was made at the Delta station (Figure 6) throughout the 2007 monitoring period, where ozone concentrations (11.31–37.97 μg/m<sup>3</sup>) were higher than the NO (1.96 – 17.98 μg/m<sup>3</sup>) and NO<sub>2</sub> (8.76 – 22.28 μg/m<sup>3</sup>), and lower than NO<sub>x</sub> (13.49 – 45.23 μg/m<sup>3</sup>) levels.

High levels of NO<sub>x</sub>, NO<sub>2</sub> and NO were observed in winter (May to July), and O<sub>3</sub> in spring (September–October).

The oxides of nitrogen, (NO<sub>x</sub> (NO+NO<sub>2</sub>)) mainly emitted into the atmosphere as NO, which is subsequently transformed into NO<sub>2</sub> and other nitrogenous species play important roles in controlling the oxidative chemistry of the lower atmosphere, including regulation of the photochemical production of ozone, nitric acid and organic nitrates (Adon et al, 2010).

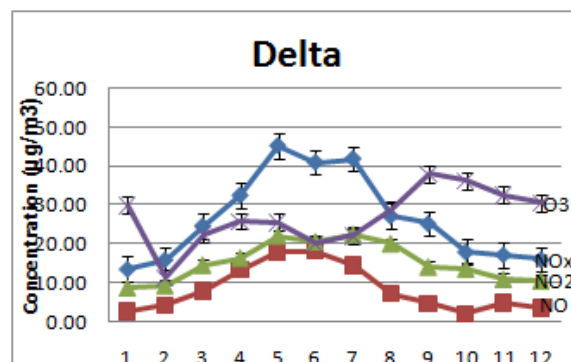


Figure 6 : Concentrations of ozone, NO<sub>x</sub>, NO<sub>2</sub>, and NO at the Delta station.

The Buccleuch station (Figure 7) however, reported low ozone levels (3.98 – 21.66 μg/m<sup>3</sup>) with high NO<sub>x</sub> (85.98 – 232.54 μg/m<sup>3</sup>), NO<sub>2</sub> (17.06 – 73.56 μg/m<sup>3</sup>), and NO (69.66 – 197.17 μg/m<sup>3</sup>) concentrations for the same period (January to December 2007).

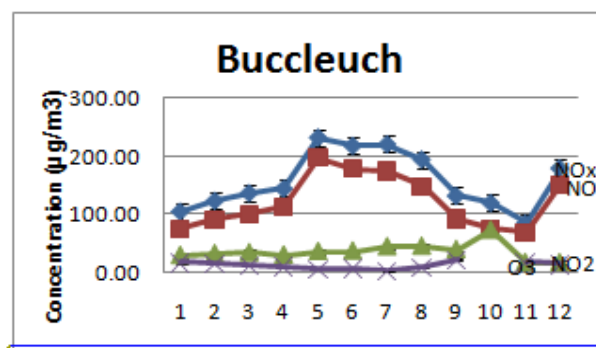


Figure 7 : Concentrations of ozone, NO<sub>x</sub>, NO<sub>2</sub>, and NO at the Buccleuch station.

Figure 8 shows the levels for Newtown as follows: ozone (3.39 – 30.92 μg/m<sup>3</sup>), NO<sub>x</sub> (33.93 – 104.44 μg/m<sup>3</sup>), NO<sub>2</sub> (18.80 – 36.15 μg/m<sup>3</sup>), and NO (16.53 – 96.09 μg/m<sup>3</sup>), indicating the low ozone high NO<sub>x</sub>, NO<sub>2</sub>, and NO relation. The high levels of NO<sub>x</sub> and NO were observed in winter (May to July), for NO<sub>2</sub> in spring (October), and O<sub>3</sub> in spring (September). An inverse relation between ozone and the oxides of nitrogen is evident in this site/station.

Favorable conditions for photochemical O<sub>3</sub> production are high temperature, high intensity of solar radiation, and sufficiently high concentrations of NO (Naja and Lal 2002).

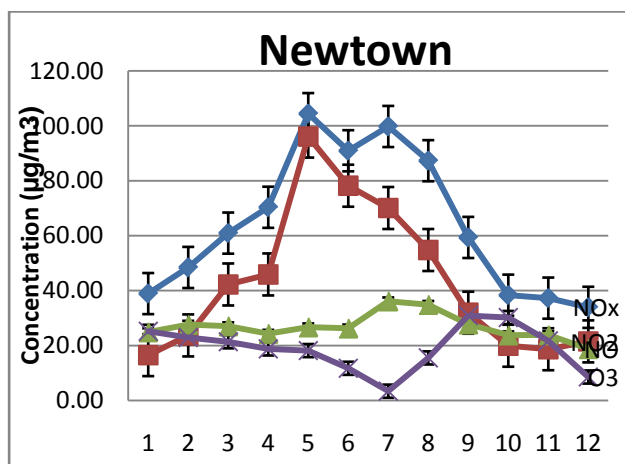


Figure 8: Concentrations of ozone, NO<sub>x</sub>, NO<sub>2</sub>, and NO at the Newtown station.

Elevated NO<sub>2</sub> concentrations in the Newtown station are associated with the City's highways (N3, N1, M<sub>2</sub> and M<sub>1</sub>) and the Central Business District (CBD) due to vehicle tailpipe emissions. Although elevated O<sub>3</sub> concentrations were anticipated to occur across the City, the main impact areas associated with the emission of O<sub>3</sub> precursors from sources within the City occur within areas to the south and south-east of the City due to the prevailing airflow patterns (ICF International, 2009).

An increase in ozone levels as NO<sub>x</sub>, NO<sub>2</sub>, and NO decreases is evident for the Buccleuch and Newtown sites within Johannesburg. High levels of NO<sub>x</sub>, NO<sub>2</sub> were observed in winter (May and June) and for O<sub>3</sub> in spring (September and October). The seasonal behavior of NO<sub>x</sub> and NO<sub>2</sub> (peaks in winter) observed for the three sites may suggest fuel/biomass burning as one of the sources of ozone precursors. Excessive NO<sub>x</sub> in urban areas is unbeneficial for the accumulation of ground-level ozone. O<sub>3</sub> shows a well-defined seasonal variation at these sites. The low values appear in winter, while the high values appear in early summer. This is attributed to the higher NO<sub>x</sub> concentration from vehicular emission and also due to the fast titration of O<sub>3</sub>. This feature of ozone variations distinguishes the urban and rural sites (Reddy et al, 2011).

Percentage contribution to the total NO<sub>x</sub> measured in Johannesburg was determined by ICF International, (2009) as 86.9 for area sources, vehicular sources (7.9), industrial sources (5.2). The main area sources were identified as domestic cooking fuel use and emissions from small industrial facilities and businesses.

#### ii. Correlation of O<sub>3</sub> to NO<sub>x</sub>, NO<sub>2</sub>, NO

Anti-correlation between O<sub>3</sub> and NO<sub>x</sub>, NO<sub>2</sub>, and NO is evident for the three study sites as shown in Table 1. NO and NO<sub>2</sub> shown a negative correlation at Buccleuch, strong positive correlation at Delta, and

weak positive correlation at Newtown. The NO concentrations were highly correlated to NO<sub>x</sub> for the three sites. NO<sub>2</sub> levels showed high correlation to NO<sub>x</sub> for Delta and Newtown, and a weak positive one for Buccleuch.

Table 1: Correlation matrix for the Johannesburg study sites.

	O <sub>3</sub>	NO	NO <sub>2</sub>
Delta			
NO	-0.43		
NO <sub>2</sub>	-0.16	0.84	
NO <sub>x</sub>	-0.28	0.96	0.94
Buccleuch			
NO	-0.78		
NO <sub>2</sub>	-0.46	-0.02	
NO <sub>x</sub>	-0.85	0.98	0.12
Newtown			
NO	-0.51		
NO <sub>2</sub>	-0.29	0.47	
NO <sub>x</sub>	-0.51	0.96	0.68

The observed nonlinearities may be due to the fact that ozone production potential per unit NO<sub>x</sub> increases as NO<sub>x</sub> concentrations decrease (Atherton et al. 1996).

The most important biogenic emission for tropospheric ozone production is the direct emission of nitric oxide (NO) from recently wetted-soils (Williams et al, 2009). For instance, Jaegle et al. (2004) investigated the spatial and seasonal variation of the release of NO from soils, and concluded that such soil emissions account for approximately 40% of surface NO<sub>x</sub> in Africa, affecting 3X10<sup>6</sup> km<sup>2</sup> of sub-Saharan Africa during the wet season. Once emitted, NO is oxidized to NO<sub>2</sub> via the reaction with HO<sub>2</sub>, CH<sub>3</sub>O<sub>2</sub> or O<sub>3</sub>. This additional NO<sub>2</sub> can then be either rapidly photolysed (producing O<sub>3</sub>) or react with reactive free-radical species such as OH, HO<sub>2</sub> or CH<sub>3</sub>C(O)O<sub>2</sub> to form more stable reservoir species for reactive nitrogen, namely HNO<sub>3</sub>, HNO<sub>4</sub> or PAN.

The reason for the winter anomaly is biological activity in the ground related to the availability of the water during the humid season, which increases NO emissions (Otter et al., 1999).

It may not be possible to calculate and draw conclusions on ozone formation budgets without measuring the levels of VOC's since the two (oxides of nitrogen and VOC's) play an important role in ozone formation. The anti-correlation observed between NO<sub>x</sub> and O<sub>3</sub> in the three sites however, suggests that formation of ozone in Johannesburg occurs under the VOC-sensitive regime, which according to (Geng et al,

2009), is associated with a decrease in  $O_3$  concentrations with enhancement of  $NO_x$  concentrations.

### iii. Annual Ozone and the Oxides of Nitrogen

Annual levels for the three Johannesburg stations in Table 2 show a general decrease in annual  $O_3$ ,  $NO_x$ ,  $NO_2$ , and  $NO$  levels from 2007 to 2009 for the Delta study site. Annual average ozone levels also decreased during the 1984-1986 period from 0.037 ppm to 0.016 ppm, then steadily increased to 0.033 ppm in 1990, and has since decreased and leveled out around 0.028 ppm. Annual average  $NO_2$  levels at South Hills dropped from 0.1 ppm in 1984 to 0.02 ppm in 1985, and have since mainly fluctuated around this level (GJMC, 2000).

The ozone levels at Buccleuch showed no specific trend whilst a decrease in  $NO_x$ ,  $NO_2$ , and  $NO$  levels from 2007 to 2009 was observed.

**Table 2:** Annual levels of  $O_3$ ,  $NO_x$ ,  $NO_2$  and  $NO$ .

		2007	2008	2009
		( $\mu\text{g}/\text{m}^3$ )	( $\mu\text{g}/\text{m}^3$ )	( $\mu\text{g}/\text{m}^3$ )
$O_3$	Buccleuch	12.62	17.04	11.71
	Delta	26.59	26.39	23.92
	Newtown	18.77	17.47	19.54
$NO_x$	Buccleuch	158.37	-	122.32
	Delta	26.91	20.15	16.17
	Newtown	64.89	52.99	59.81
$NO_2$	Buccleuch	37.82	-	28.08
	Delta	15.27	12.91	13.41
	Newtown	26.94	26.90	26.61
$NO$	Buccleuch	123.92	-	94.23
	Delta	8.51	6.65	6.83
	Newtown	45.16	34.34	37.34

No specific trends were observed for Newtown except for a decrease in  $NO_2$  levels from 2007 to 2009. A decrease in  $NO_x$ ,  $NO_2$  and  $NO$  annual averages were observed from 1995-1996 for Newtown (GJMC Photochemical Smog Monitoring Program, 1996). The Newtown station covering the central business district (CBD) showed an increase in average annual ozone levels from 0.012 to 0.013 ppm, as well as  $CO$  levels from 2.33 to 2.51 ppm during 1995/1996. A rise in ozone levels of 2-3 ppb per annum was thus estimated in the inner city by the state of the environment report (GJMC State of Air Pollution Report, 2000).

In general, annual levels for the three sites show anti-correlation of  $O_3$  to  $NO_x$ ,  $NO_2$ , and  $NO$ , which agrees with the Northern Works (sub-rural) monitoring station at the Northern sewage works within Johannesburg, where a slight increase in annual levels of  $NO_x$  (0.015-0.024 ppm),  $NO_2$  (0.008-0.013 ppm) (15.05 – 24.45  $\mu\text{g}/\text{m}^3$ ) and  $NO$  (0.002-0.012 ppm) (2.45 – 14.7  $\mu\text{g}/\text{m}^3$ ) from 1985-1989, and a decrease in ozone

(0.033-0.015 ppm) (64.78 – 29.45  $\mu\text{g}/\text{m}^3$ ) and hydrocarbons (0.329-0.283 ppm) was observed (GJMC Photochemical Smog Monitoring Program, 1996).

## IV. CONCLUSION

The study has shown that ground level ozone concentrations exhibit strong seasonality, with a seasonal maximum occurring during spring (September and October) and minimum levels in winter (May and June) for all the sites studied. This implies that high temperature and relative humidity besides the intense solar radiation in summer are responsible for the formation of high  $O_3$  concentrations. The levels of ozone were observed in order of decreasing abundance as follows: spring, summer, autumn, and winter. Though a similar seasonal behavior was observed for Botsalano, Marikana, and Johannesburg study sites, the Johannesburg ozone levels were much lower than Botsalano and Marikana levels throughout the study. The monthly levels of ozone for the 2007 to 2008 period can be given in order of decreasing abundance as Marikana (21.07 – 50.02 ppb), Botsalano (28.17 – 37.94 ppb), Buccleuch (2.03 – 23.42 ppb), Delta (5.76 – 17.32 ppb) and Newtown (1.73 – 17.19 ppb).

The precursors of ozone ( $NO_x$ ,  $NO_2$ , and  $NO$ ) also showed a general seasonality throughout the study period with peaks in winter (May-June). Elevated  $NO_2$  concentrations were observed in the Newtown station, suggesting traffic and other industrial sources.

Delta station levels were recorded as 1.96 – 17.98  $\mu\text{g}/\text{m}^3$ , 8.76 – 22.28  $\mu\text{g}/\text{m}^3$ , and 13.49 – 45.23  $\mu\text{g}/\text{m}^3$  for  $NO$ ,  $NO_2$  and  $NO_x$  levels respectively while the levels for Buccleuch and Newtown were recorded as  $NO_x$  (85.98 – 232.54  $\mu\text{g}/\text{m}^3$ ),  $NO_2$  (17.06 – 73.56  $\mu\text{g}/\text{m}^3$ ), and  $NO$  (69.66 – 197.17  $\mu\text{g}/\text{m}^3$ ); and  $NO_x$  (33.93 – 104.44  $\mu\text{g}/\text{m}^3$ ),  $NO_2$  (18.80 – 36.15  $\mu\text{g}/\text{m}^3$ ), and  $NO$  (16.53 – 96.09  $\mu\text{g}/\text{m}^3$ ) respectively.

The anti-correlation of ozone and its precursors ( $NO_x$ ,  $NO_2$ , and  $NO$ ) was also observed, thus suggesting that the formation of ozone in Johannesburg occurs under the VOC-sensitive regime.

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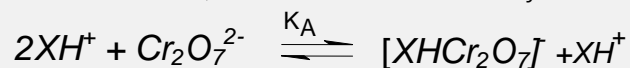
# Conductance and Solvation Behavior of Some Onium Dichromates in Aqueous-Ethanol Mixtures

By V Radhika, M. Narsimha Reddy & P Manikyamba

*Kakatiya University, Warangal*

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(  $XH^+$  = onium ion ( $XNH^+$ ) )

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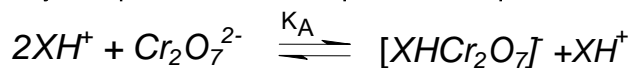


# Conductance and Solvation Behavior of Some Onium Dichromates in Aqueous-Ethanol Mixtures

V Radhika <sup>α</sup>, M. Narsimha Reddy <sup>σ</sup> & P Manikyamba <sup>ρ</sup>

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## I. INTRODUCTION

Quinolinium dichromate is a stable oxidant which was prepared and analyzed by Balasubramanian and coworkers [1]. This was used as an oxidant in the kinetic studies of oxidation of different functional groups [2-4]. Solvation behavior of this oxidant in Aq-DMF was presented in our earlier paper [5]. Pyridinium dichromate is a stable oxidant which was prepared and analyzed by Corey E J and Schmidt G[6], It is a very useful and versatile oxidant which can be used in many applications [7-9]. Nicotinium dichromate is a stable oxidant [10], which was prepared and analyzed by Lopez C and coworkers [11]. Though a large body of literature is available on kinetic aspects of these three oxidants, no information on the conductance behavior of these dichromates is available. Density, viscosity and dielectric constant of the medium, ion-solvent and

dielectric constant of the medium, ion-solvent and solvent-solvent interactions influence the conductance behaviour of electrolytes in binary solvent mixtures. Ion-solvent interactions stabilize the ion by solvating it which is substantiated through vast information [12-21]. The present paper details the observations on conductance behaviour of Quinolinium, Pyridinium and Nicotinium dichromates in binary solvent mixtures of aqueous-ethanol.

## II. EXPERIMENTAL SECTIONS

### a) Chemicals Used

Quinolinium, Pyridinium and Nicotinium dichromates are prepared on the lines of the literature methods [1,6,11]. A stock solution of the reagent is prepared by dissolving a known weight of the sample in water and is standardized by iodometric method. A conductivity bridge (ELICO model-180) equipped with a glass conductivity cell of cell constant  $1.103 \text{ cm}^{-1}$  is used to measure the conductance of the solution. Conductivity cell is calibrated using 0.1M KCl solution. Deionised water is distilled and used for the preparation of the solution. The precision of the conductivity bridge used is  $\pm 0.05 \text{ mS}$ . Temperature is kept constant during the experiment using a thermostat with an accuracy of  $\pm 0.1^\circ \text{C}$ . To maintain the temperature below room temperature an ice bath equipped with a mechanical stirrer is used. Spectroscopic grade sample of acetone is procured from Sd-fine Chemicals Ltd., Bombay, India.

## III. THEORY/CALCULATION

The solutions of Quinolinium, Pyridinium and Nicotinium dichromates are diluted to different concentrations in the range 0.1M to  $5.0 \times 10^{-3} \text{ M}$  using different volumes of solvent / solvent mixture and their conductance is measured at 283-313K. The solvent systems used in this study have conductance values between 0.029 - 0.0315mS. The conductance values are found to be reproducible with  $\pm 0.1\%$  error. The solvent conductance values are deducted from the conductance of the solution to get the conductance of the solute. The molar conductance is calculated using the relation  $\Lambda = 1000 \times \mathbf{K}/\mathbf{C}$  where  $\mathbf{K}$  is the specific conductance and  $\mathbf{C}$  is the molarity of the solute in the solution. The same procedure is followed at different

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compositions of solvent mixtures and at different temperatures.

To find out the limiting molar conductance of Pyridinium dichromate two models, Kraus- Bray model [22], and Shedlovsky model [23] have been used. Kraus-Bray equation, Eq. 1, takes into consideration the dissociation constant ( $K_C$ ) of the partially dissociated electrolyte and correlates molar conductance ( $\Lambda_m$ ) and the limiting molar conductance ( $\Lambda^0$ ) as

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda^0} + \frac{1}{K_C \Lambda^{0^2}} (\Lambda_m C) \quad (1)$$

Shedlovsky equation, Eq. 2, considers the association constant of the ion-pair formed from the dissociated electrolyte into consideration and correlates the molar and limiting molar conductance values according to the equation

$$\frac{1}{S \Lambda_m} = \frac{1}{\Lambda^0} + \frac{K_A}{\Lambda^{0^2}} (S f_{\pm}^2 \Lambda_m C) \quad (2)$$

where  $\Lambda_m$  is molar conductance of the solute in the solution at concentration C,

$\Lambda_0$  is the limiting molar conductance

$K_A$  is the association constant of the ion- pair,

$K_C$  is the dissociation constant,

$f_{\pm}$  is the mean ionic activity coefficient,

S is a factor given by

$$S = \left[ \frac{\beta \sqrt{C \Lambda}}{4 \Lambda^{0^3/2}} + \sqrt{1 + \frac{\beta^2 C \Lambda}{4 \Lambda^{0^3}}} \right]^2 \quad (3)$$

$$\log f_{\pm} = \left[ \frac{-1.8246 \times 10^6 (C \alpha)^{1/2} / (\epsilon T)^{3/2}}{1 + 50.24 \times 10^8 q (C \alpha)^{1/2} (\epsilon T)^{1/2}} \right]^2 \quad (4)$$

$$\alpha = \frac{S \Lambda}{\Lambda^0} \quad (5)$$

$$\beta = \frac{8.20 \times 10^5 \Lambda^0}{(\epsilon T)^{3/2}} + \frac{82.5}{\eta (\epsilon T)^{1/2}} \quad (6)$$

Where q is Bjerrum's critical distance q given by

$$q = \frac{e^2}{2 \epsilon k T} = \frac{Z_+ Z_- e^2}{2 \epsilon k T} \quad (7)$$

$\epsilon$  is dielectric constant of the medium and  $\eta$  is viscosity of the solvent,  $Z_+ e$  and  $Z_- e$  are the charges on the ions. k is Boltzmann's constant, T is the temperature in degrees Kelvin. S is calculated using  $\Lambda^0$  obtained from the Onsager model using the plot of  $\Lambda_m$  against  $\sqrt{C}$ . The least square analysis of the data ( $\Lambda_m$  and C)

using the above two eqs. 1, 2 is satisfactory with linear correlation coefficients in the range 0.95-0.97.

## IV. RESULTS AND DISCUSSION

### a) Limiting molar conductance

The limiting molar conductance values  $\Lambda^0$  thus obtained with the two equations (eq. 1 and eq. 2) are presented in Table 1. These values increase with increase in the temperature as expected. This is attributed to increase in the mobility of the ions due to increase in the temperature. The  $\Lambda^0$  values also depend on the composition of the binary solvent mixture. Addition of ethanol to water decreases  $\Lambda_0$  value. This may be due to decrease in the dielectric constant of the medium.

It is observed that the conductivity of the solution in each solvent system is increased with increase in the temperature. It is supposed that this variation has to follow Arrhenius relation like rate process. So the energy of activation of the conducting process is obtained from the Arrhenius relationship

$$\text{i.e.,} \quad \Lambda^0 = A e^{-E_a/RT} \quad (8)$$

Where A is a constant

$E_a$  is activation energy of the conducting process

R is gas constant

T is the temperature

$E_a$  values are obtained by correlating  $\log \Lambda^0$  values with  $1/T$  by means of linear least square analysis. These values are presented in Table 2. These values indicate that they are highly dependent on the proportion of organic solvent in the medium. These values are maximum in 60% ethanol for Quinolinium dichromate and in 20% ethanol for Pyridinium dichromate. For Nicotinium dichromate the maximum  $E_a$  is observed in pure water.

### b) Radii of solvated ions

The effective ionic radii ( $r_i$ ) of the cation and anion in each solvent system used are calculated by using Stoke's radius equation modified by Gill [24]

$$r_i = \frac{0.820 |Z|}{\Lambda_+ \eta_o} + 0.0103 \epsilon + r_y \quad (9)$$

Where  $r_y$  is a parameter equal to  $0.85 \text{ \AA}^0$  for non associated solvents and  $1.13 \text{ \AA}^0$  for associated solvents. These values are tabulated in Table 3. These values which are radii of solvated ions vary with the solvent composition suggesting the operation of ion-solvent interactions.

### c) Solvation Number

$S_n$ , the solvation number, which is the number of solvent molecules in the solvent cover around the

species, is calculated from the effect of dielectric constant ( $\epsilon$ ) on  $\Lambda^0$ . This is based on the equation

$$\log \Lambda^0 = \log \Lambda^{01} - \frac{Z_A Z_B e^2}{\epsilon d_{AB} k_B T} \quad (10)$$

Where,  $\Lambda^{01}$  is the limiting molar conductance in a solvent of infinite dielectric constant

$Z_A e$ ,  $Z_B e$  are the ionic charges

$k_B$  is Boltzmann constant

$T$  is the temperature

$d_{AB}$  is the distance between the centers of the two ions.

The plot of  $\log \Lambda^0$  against  $1/\epsilon$  is linear with negative slope from which,  $d_{AB}$  is calculated.  $S_n$  is computed using the relation.

$$S_n = \frac{d_{AB} - r_i}{r_{solvent}} \quad (11)$$

Where  $r_i$  is the Stokes radius of the ion calculated using Stoke's equation [25]

$$r_i = \frac{0.820|Z|}{\Lambda_o \eta_o} + 0.0103\epsilon + r_y \quad (12)$$

Where  $r_y = 0.85 \text{ \AA}$  for dipolar unassociated solvents and  $1.13 \text{ \AA}$  for protic and associated solvents. These  $r_i$  values are tabulated in Table 3.

In order to understand the extent molecular interactions occurring in the solutions, solvation number was calculated.

Solvation numbers thus determined at 293K - 303K are presented in Table 4.

The variable solvation number indicates that the ion-pair is solvated to different extents depending on the composition of the solvent which reflects variable ion-solvent interactions.

#### d) Ionic conductances and Ion-solvation

As suggested by Hammamy [26] the ionic conductances  $\Lambda_+^0$  and  $\Lambda_-^0$  of the onium ion and the dichromate ion are computed in all the solvent systems used and presented in Table 3.  $\Lambda_+^0$  is maximum in 100% water and decreases due to the addition of ethanol attaining a slight higher value in 100% ethanol. The ionic conductance of the anion slightly increases due to the initial addition of ethanol and gradually decreases attaining a minimum value in 100% ethanol. This variation in the ionic conductance suggests that the specific solvation of the anion is by water while ethanol from the solvent mixture selectively solvates the cation. The solvation behavior of the ions in mixed solvent systems can be better understood in terms of the ionic

Walden products,  $\eta \Lambda_{\pm}^0$ , of the electrolytes. The calculated values of these ionic Walden products are presented in fig. 1(A,B). These values are maximum in water and decrease gradually due to the addition of organic component in each system. According to Morinaga and coworkers [27] the ratio (R),

$$R = \frac{\eta \Lambda_{\pm}^0(\text{solvent})}{\eta \Lambda_{\pm}^0(\text{water})}$$

can be used to obtain information on the nature of solvation of an electrolyte and its constituent ions in aqueous solvent mixtures. The calculated values of these factors for both the ions are shown in Table 3. This ratio for the cation is less than one and decreases sharply with the increase in the proportion of organic component. According to Morinaga [27] this is a strong indication of selective solvation of the ion by the ethanol. Thus it may be concluded that the cation is more solvated by acetone from the solvent system. The 'R' factor of the dichromate ion increases up to 80% (v/v), indicating that the anion is selectively hydrated from the aqueous solvent mixture. The addition of organic solvent breaks the structure of water and makes the water molecules available for hydration of the anion. This type of behavior is observed by Morinaga [27] for alkali metal ions in water rich regions of water-acetonitrile and water-DMSO mixtures.

## V. CONCLUSIONS

Among the three dichromates studied higher solvation number is observed for Pyridinium ion compared to Quinolinium and Nicotinium ions. This may be attributed to smaller size of the Pyridinium ion which increases the charge density.

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Table 1 : Limiting molar conductance ( $\Lambda^\circ$ ) values in S cm<sup>2</sup> mol<sup>-1</sup> of Quinolinium , Pyridinium and Nicotinium dichromates in aqueous mixtures of ethanol at different temperatures.

Quinolinium dichromate

T (K)	0% Ethanol		20% Ethanol		40% Ethanol		60% Ethanol		80% Ethanol		100% Ethanol	
	1	2	1	2	1	2	1	2	1	2	1	2
283	121.66	122.27	101.03	10.614	80.45	80.24	64.19	64.17	76.91	77.32	45.73	44.53
293	143.89	138.02	128.21	126.94	109.15	108.83	98.06	98.31	92.66	93.07	46.96	48.74
303	154.66	154.93	146.91	139.55	125.52	139.30	115.94	116.93	98.54	98.62	49.49	49.33
313	196.67	196.40	159.95	160.66	167.67	154.71	156.67	147.51	124.84	123.57	55.38	55.04

## Pyridinium dichromate

T(K)	0% Ethanol		20% Ethanol		40% Ethanol		60% Ethanol		80% Ethanol		100% Ethanol	
	1	2	1	2	1	2	1	2	1	2	1	2
283	205.55	205.67	126.06	132.50	108.5	108.41	95.50	95.35	75.05	78.58	69.61	69.85
293	221.58	222.80	176.98	175.56	140.35	137.35	112.05	112.25	95.80	90.65	72.08	71.73
303	253.42	259.61	225.41	226.76	159.62	158.32	122.84	123.24	104.34	98.09	76.24	76.61
313	303.43	307.27	252.61	254.71	219.88	219.19	158.29	159.57	128.85	121.30	85.42	84.81

## Nicotinium dichromate

T(K)	0% Ethanol		20% Ethanol		40% Ethanol		60% Ethanol		80% Ethanol		100% Ethanol	
	1	2	1	2	1	2	1	2	1	2	1	2
283	127.77	127.27	115.03	113.14	98.45	97.24	84.19	84.17	79.91	79.32	48.31	47.86
293	154.66	154.93	138.21	136.94	119.15	118.83	108.06	108.31	99.66	97.07	55.56	55.75
303	173.71	179.40	156.76	155.53	145.52	139.30	123.94	123.93	104.76	104.56	60.24	60.25
313	199.66	198.50	169.49	169.57	158.67	158.51	151.51	154.84	124.42	132.56	67.11	67.24

1 = Kraus-Bray Model

2 = Shedlovsky model

**Table 2:**  $K_A$  and  $K_C$  values of Quinolinium, pyridinium and Nicotinium dichromates in aqueous-ethanol mixtures

## Quinolinium dichromate

T (K)	0% Ethanol		20% Ethanol		40% Ethanol		60% Ethanol		80% Ethanol		100% Ethanol	
	$K_A$	$K_C$	$K_A$	$K_C$	$K_A$	$K_C$	$K_A$	$K_C$	$K_A$	$K_C$	$K_A$	$K_C$
283	54.67	0.02	31.60	0.03	21.12	0.05	35.33	0.04	35.57	0.03	61.65	0.02
293	70.07	0.01	22.03	0.06	20.55	0.04	21.39	0.09	29.69	0.03	54.90	0.02
303	28.24	0.02	13.56	0.04	19.90	0.05	16.20	0.13	29.86	0.05	45.61	0.02
313	21.89	0.05	45.14	0.23	19.41	0.05	18.70	0.16	29.10	0.04	44.91	0.02

## Pyridinium dichromate

T (K)	0% Ethanol		20% Ethanol		40% Ethanol		60% Ethanol		80% Ethanol		100% Ethanol	
	$K_A$	$K_C$	$K_A$	$K_C$	$K_A$	$K_C$	$K_A$	$K_C$	$K_A$	$K_C$	$K_A$	$K_C$
283	7.58	0.13	4.07	0.21	19.10	0.05	7.00	0.14	8.76	0.13	13.89	0.03
293	15.20	0.11	6.73	0.15	19.88	0.05	6.59	0.16	10.29	0.12	7.73	0.03
303	37.65	0.28	8.91	0.11	12.66	0.08	38.09	0.26	8.40	0.15	31.08	0.03
313	38.61	0.27	4.77	0.21	19.23	0.08	50.00	0.19	10.64	0.12	36.11	0.03

## Nicotinium dichromate

T (K)	0% Ethanol		20% Ethanol		40% Ethanol		60% Ethanol		80% Ethanol		100% Ethanol	
	$K_A$	$K_C$	$K_A$	$K_C$	$K_A$	$K_C$	$K_A$	$K_C$	$K_A$	$K_C$	$K_A$	$K_C$
283	11.95	0.059	10.98	0.091	11.33	0.077	9.09	0.11	10.98	0.092	17.30	0.057
293	10.78	0.091	11.24	0.081	12.00	0.088	8.89	0.12	15.87	0.082	32.80	0.031
303	12.77	0.077	12.55	0.079	8.75	0.113	15.43	0.066	12.5	0.07	30.1	0.033
313	5.76	0.174	6.34	0.1	12.01	0.084	11.33	0.088	13.16	0.075	33.82	0.030

 $K_A$  = Association constant from Shedlovsky equation.

 $K_C$  = Dissociation constant from Kraus-Bray equation.



Table 3 : Computed Values of  $E_a$  for Quinolinium, pyridinium and Nicotinium dichromates at different compositions (v/v) of aqueous-ethanol mixtures.

Quinolinium dichromate

	0% Ethanol	20% Ethanol	40% Ethanol	60% Ethanol	80% Ethanol	100% Ethanol
$E_a$	9.12	11.06	17.68	19.74	10.75	4.77

Pyridinium dichromate

	0% Ethanol	20% Ethanol	40% Ethanol	60% Ethanol	80% Ethanol	100% Ethanol
$E_a$	9.12	17.06	16.12	11.83	10.08	4.88

Nicotinium dichromate

	0% Ethanol	20% Ethanol	40% Ethanol	60% Ethanol	80% Ethanol	100% Ethanol
$E_a$	9.12	14.03	15.44	17.01	12.37	8.45

Table 4 : Computed change in free energy ( $\Delta G_a$ ) and transfer ( $\Delta G_t$ ) Quinolinium, Pyridinium and Nicotinium dichromate in aqueous mixtures of ethanol at different temperatures in  $\text{kJ mol}^{-1}$ .

Quinolinium dichromate

T (K)	0% Ethanol		20% Ethanol		40% Ethanol		60% Ethanol		80% Ethanol		100% Ethanol	
	$\Delta G_a$	$\Delta G_t$	$\Delta G_a$	$\Delta G_t$	$\Delta G_a$	$\Delta G_t$	$\Delta G_a$	$\Delta G_t$	$\Delta G_a$	$\Delta G_t$	$\Delta G_a$	$\Delta G_t$
283	-4.76	-	-3.89	0.87	-5.73	-0.18	-4.92	-0.030	-4.51	0.05	-5.34	0.58
293	-4.03	-	-5.15	1.47	-10.08	0.09	-5.21	0.25	-4.73	0.34	-5.69	-0.17
303	-9.15	-	-5.39	3.76	-6.54	2.61	-5.68	0.60	-5.21	0.68	-5.44	0.64
313	-9.51	-	-5.92	3.59	-6.89	2.62	-5.89	0.61	-5.86	0.61	-6.38	0.52

Pyridinium dichromate

T (K)	0% Ethanol		20% Ethanol		40% Ethanol		60% Ethanol		80% Ethanol		100% Ethanol	
	$\Delta G_a$	$\Delta G_t$	$\Delta G_a$	$\Delta G_t$	$\Delta G_a$	$\Delta G_t$	$\Delta G_a$	$\Delta G_t$	$\Delta G_a$	$\Delta G_t$	$\Delta G_a$	$\Delta G_t$
283	-4.94	-	-8.03	-0.16	-8.05	-3.02	-8.46	-2.69	-13.05	9.27	-9.41	-1.94
293	-8.07	-	-7.74	-3.86	-8.06	2.30	-6.94	-2.69	-8.95	-1.41	-8.68	-1.68
303	-7.99	-	-7.48	-2.01	-7.18	-1.22	-7.37	-1.03	-7.51	-0.89	-7.18	-1.22
313	-8.74	-	-7.24	-2.60	-5.77	-2.24	-7.07	-2.14	-7.90	-0.12	-10.23	2.21

Nicotinium dichromate

T (K)	0% Ethanol		20% Ethanol		40% Ethanol		60% Ethanol		80% Ethanol		100% Ethanol	
	$\Delta G_a$	$\Delta G_t$	$\Delta G_a$	$\Delta G_t$	$\Delta G_a$	$\Delta G_t$	$\Delta G_a$	$\Delta G_t$	$\Delta G_a$	$\Delta G_t$	$\Delta G_a$	$\Delta G_t$
283	-4.760	-	-5.52	-0.758	-8.17	-2.65	-8.24	-2.54	-8.24	-3.48	-5.57	-0.81
293	-4.032	-	-9.13	-5.10	-8.59	-4.56	-8.51	-3.27	-8.51	-4.48	-5.88	-1.85
303	-9.151	-	-10.25	-1.10	-8.57	+0.58	-9.33	-0.18	-9.90	-0.75	-5.91	+3.24
313	-9.513	-	-9.63	-0.12	-6.70	+2.81	-9.21	+0.30	-8.91	+0.60	-8.91	+0.60

Table 5 : Ionic conductances and radii of solvated ions of Quinolinium, pyridinium and Nicotinium dichromate in aqueous-ethanol mixtures.

Quinolinium dichromate

T = 293K

Composition (v/v) ethanol	$\Lambda_+^0$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$\Lambda_-^0$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$r_+(A^0)$	$r_-(A^0)$	$r_+ + r_-(A^0)$
0%	48.98	94.94	3.11	2.71	5.82
20%	44.87	82.07	3.83	2.36	6.19
40%	32.43	76.72	3.67	2.57	6.24
60%	31.32	66.74	3.99	1.42	5.41
80%	29.72	62.94	5.27	1.38	6.65
100%	10.63	36.32	2.07	0.95	3.02

T = 303K

Composition (v/v) ethanol	$\Lambda_+^0$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$\Lambda_-^0$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$r_+(A^0)$	$r_-(A^0)$	$r_+ + r_-(A^0)$
0%	59.74	94.92	3.09	2.82	5.83
20%	50.60	88.17	2.99	2.52	6.23
40%	37.52	87.99	3.62	2.24	5.86
60%	33.33	82.65	3.38	2.24	7.07
80%	33.78	64.76	5.06	3.20	5.87
100%	3.91	45.59	7.31	2.95	10.36

Pyridinium dichromate

T = 293K

Composition (v/v) ethanol	$\Lambda_+^0$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$\Lambda_-^0$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$r_+(A^0)$	$r_-(A^0)$	$r_+ + r_-(A^0)$
0%	126.64	94.94	2.52	2.71	5.23
20%	94.91	82.07	2.53	2.36	6.33
40%	60.63	76.72	2.61	2.57	4.89
60%	45.51	66.74	3.15	1.42	4.57
80%	27.71	62.94	1.65	1.38	3.03
100%	35.41	36.32	1.85	0.95	3.68

T = 303K

Composition (v/v) ethanol	$\Lambda_+^0$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$\Lambda_-^0$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$r_+(A^0)$	$r_-(A^0)$	$r_+ + r_-(A^0)$
0%	164.69	94.92	2.14	2.82	4.96
20%	137.24	88.17	2.07	2.52	4.59
40%	60.32	87.99	2.62	2.24	4.86
60%	33.59	82.65	3.08	2.24	5.32
80%	33.33	64.76	1.57	3.20	4.77
100%	30.65	45.59	1.96	2.95	4.91

Nicotinium dichromate

T = 293K

Composition (v/v) ethanol	$\Lambda_+^0$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$\Lambda_-^0$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$r_+(A^0)$	$r_-(A^0)$	$r_+ + r_-(A^0)$
0%	59.72	94.94	1.02	2.71	3.73
20%	54.14	82.07	1.23	2.36	3.59
40%	42.43	76.72	1.32	2.57	3.89
60%	52.09	66.74	1.66	1.42	3.08
80%	45.12	62.94	1.69	1.38	3.07
100%	19.24	36.32	2.02	0.95	2.97

T = 303K

Composition (v/v) ethanol	$\Lambda_+^0$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$\Lambda_-^0$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$r_+(A^0)$	$r_-(A^0)$	$r_+ + r_-(A^0)$
0%	78.79	94.92	2.03	2.82	4.85
20%	68.59	88.17	1.64	2.52	4.16
40%	57.53	87.99	1.61	2.24	3.85
60%	41.29	82.65	1.55	2.24	3.79
80%	40.00	64.76	1.17	3.20	4.37
100%	14.65	45.59	1.05	2.95	4.00

Table 6 : Solvation number values of Quinolinium, Pyridinium and Nicotinium dichromates in aqueous-ethanol mixtures at 293 and 303K.

Quinolinium dichromate

T(K)	0% Ethanol	20% Ethanol	40% Ethanol	60% Ethanol	80% Ethanol	100% Ethanol
293	5.02	4.78	4.48	4.38	4.34	3.19
303	5.93	5.83	5.31	4.70	4.63	2.59

Pyridinium dichromate

T(K)	0% Ethanol	20% Ethanol	40% Ethanol	60% Ethanol	80% Ethanol	100% Ethanol
293	6.34	5.86	5.44	5.36	4.52	3.63
303	6.15	5.84	5.62	4.65	4.42	3.72

Nicotinium dichromate

T(K)	0% Ethanol	20% Ethanol	40% Ethanol	60% Ethanol	80% Ethanol	100% Ethanol
293	0.79	1.06	1.01	1.49	1.23	1.02
303	1.64	1.39	1.90	1.78	1.37	1.32

*Table 7:* Computed change in free energy of solvation ( $\Delta G_{i-s}^+$ ) and ( $\Delta G_{i-s}^-$ ) for Quinolinium, P yridinium and Nicotinium dichromate in aqueous-ethanol mixtures at 293,303K in  $\text{kJ mol}^{-1}$ .

T (K)	0% Ethanol		20% Ethanol		40% Ethanol		60% Ethanol		80% Ethanol		100% Ethanol	
	$\Delta G_{i-s}^+$	$\Delta G_{i-s}^-$	$\Delta G_{i-s}^+$	$\Delta G_{i-s}^-$	$\Delta G_{i-s}^+$	$\Delta G_{i-s}^-$	$\Delta G_{i-s}^+$	$\Delta G_{i-s}^-$	$\Delta G_{i-s}^+$	$\Delta G_{i-s}^-$	$\Delta G_{i-s}^+$	$\Delta G_{i-s}^-$
293	3.1	3.2	2.6	4.3	3.3	4.7	3.9	10.8	3.9	14.8	30.8	18.0
303	3.0	3.0	3.7	3.9	3.6	4.3	4.8	5.9	4.4	7.3	4.7	16.4

T (K)	0% Ethanol		20% Ethanol		40% Ethanol		60% Ethanol		80% Ethanol		100% Ethanol	
	$\Delta G_{i-s}^+$	$\Delta G_{i-s}^-$	$\Delta G_{i-s}^+$	$\Delta G_{i-s}^-$	$\Delta G_{i-s}^+$	$\Delta G_{i-s}^-$	$\Delta G_{i-s}^+$	$\Delta G_{i-s}^-$	$\Delta G_{i-s}^+$	$\Delta G_{i-s}^-$	$\Delta G_{i-s}^+$	$\Delta G_{i-s}^-$
293	3.4	3.2	4.0	4.3	4.7	4.7	4.9	10.8	6.9	14.8	17.8	18.0
303	4.2	3.2	5.2	4.3	5.0	4.7	5.3	10.9	14.0	14.8	17.6	18.0

T (K)	0% Ethanol		20% Ethanol		40% Ethanol		60% Ethanol		80% Ethanol		100% Ethanol	
	$\Delta G_{i-s}^+$	$\Delta G_{i-s}^-$	$\Delta G_{i-s}^+$	$\Delta G_{i-s}^-$	$\Delta G_{i-s}^+$	$\Delta G_{i-s}^-$	$\Delta G_{i-s}^+$	$\Delta G_{i-s}^-$	$\Delta G_{i-s}^+$	$\Delta G_{i-s}^-$	$\Delta G_{i-s}^+$	$\Delta G_{i-s}^-$
293	4.1	3.20	5.95	4.30	7.30	4.74	11.67	10.80	20.03	14.80	32.42	17.98
303	4.4	3.89	6.64	4.27	8.04	5.79	10.50	7.30	18.75	16.40	33.00	11.71

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# Synthesis and Spectral Characterization of Thorium(IV) Complexes with 3-Substituted-4-Amino-5-Mercapto-1,2,4-Triazole Schiff Bases

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**Abstract** - Thorium(IV) complexes have been synthesized by reacting Th(IV) nitrate with Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole and glyoxal/ biacetyl/ benzyl in ethanol. These complexes have been characterized on the basis of elemental analysis, molar conductance and spectral studies. Analytical and spectral data suggest structures in which Th(IV) is six coordinated. All these complexes are light yellow in colour and are insoluble in DMF and DMSO. The elemental analysis show that, the complexes analysed for 1:1 stoichiometry of the type,  $\text{Th.LH}_2(\text{NO}_3)_4$ . Conductance measurement in DMF are too low to account for any dissociation of these complexes in DMF at the concentration of the  $10^{-3}\text{M}$ .

**Keywords** : *Synthesis, Elemental analysis, Th(IV) complexes.*

**GJSFR-B Classification** : *FOR Code: 030699, 030505*



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# Synthesis and Spectral Characterization of Thorium(IV) Complexes with 3-Substituted-4-Amino-5-Mercapto-1,2,4-Triazole Schiff Bases

Mallikarjun S Yadawe <sup>α</sup> & Sangamesh A Patil <sup>σ</sup>

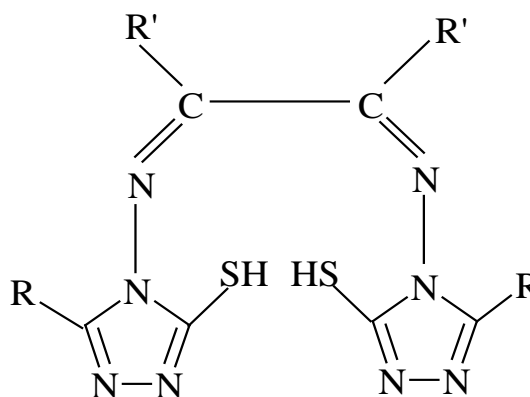
**Abstract** - Thorium(IV) complexes have been synthesized by reacting Th(IV) nitrate with Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole and glyoxal/biacetyl/ benzyl in ethanol. These complexes have been characterized on the basis of elemental analysis, molar conductance and spectral studies. Analytical and spectral data suggest structures in which Th(IV) is six coordinated. All these complexes are light yellow in colour and are insoluble in DMF and DMSO. The elemental analysis show that, the complexes analysed for 1:1 stoichiometry of the type, Th.LH<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>. Conductance measurement in DMF are too low to account for any dissociation of these complexes in DMF at the concentration of the 10<sup>-3</sup>M.

**Keywords** : Synthesis, Elemental analysis, Th(IV) complexes.

## I. INTRODUCTION

In continuation of our earlier work on complexes with Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole<sup>1-5</sup>, we report Th(IV) complexes of Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole and glyoxal/biacetyl/benzyl. The metal complexes 1,2,4-triazole derivatives have been extensively investigated in previous reports<sup>6,7</sup>. Substituted triazoles are well known as bactericides<sup>8</sup>, pesticides<sup>9</sup>, insecticides<sup>10</sup> and potential fungicides<sup>11</sup>. In continuation of our work on metal complexes of triazoles and in our pursuit of a new ligand for metal complexes, we have synthesized 3-substituted-4-amino-5-mercapto-1,2,4-triazole and glyoxal/biacetyl/benzyl, as there is scant information on these complexes of the ligands. Therefore, it was thought worthwhile to study the synthesis and characterization of Th(IV) complexes with the following Schiff bases (fig.1).

Figure 1 : Structure of Schiff bases



Schiff base	R'	R
I	H	H
II	H	CH <sub>3</sub>
III	H	C <sub>2</sub> H <sub>5</sub>
IV	H	C <sub>3</sub> H <sub>7</sub>
V	CH <sub>3</sub>	H
VI	CH <sub>3</sub>	CH <sub>3</sub>
VII	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>
VIII	CH <sub>3</sub>	C <sub>3</sub> H <sub>7</sub>
IX	C <sub>6</sub> H <sub>5</sub>	H
X	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>
XI	C <sub>6</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>
XII	C <sub>6</sub> H <sub>5</sub>	C <sub>3</sub> H <sub>7</sub>

## II. EXPERIMENTAL

All the chemicals used were of reagent grade. 3-substituted-4-amino-5-mercapto-1,2,4-triazoles were prepared by the reported methods<sup>12,13</sup>.

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### III. SYNTHESIS OF 3-SUBSTITUTED-4-AMINO-5-MERCAPTO-1,2,4-TRIAZOLES

A mixture of 3-substituted-4-amino-5-mercapto-1,2,4-triazole and lyoxal/biacetyl/benzyl in 1:1 molar proportions in EtOH was boiled under reflux for 4-5 h on a water bath. The reaction mixture was cooled at room temperature, within an hour the compound separated from the clear solution. It was filtered, washed and recrystallised from EtOH.

### IV. SYNTHESIS OF Th(IV) COMPLEX

Thorium(IV) nitrate (0.01 mol) was boiled under reflux with the ligand (0.01 mol) in alcohol for 3h. The

complex was ppted by adding distilled water containing liquor ammonia. The precipitated complex was filtered, washed thoroughly with distilled water, alcohol and dried under reduced pressure over fused  $\text{CaCl}_2$ .

### V. ANALYSIS

The thorium in the complex was determined by gravimetric method. Nitrogen was determined by Dumas method and sulphur was determined gravimetrically as  $\text{BaSO}_4$ <sup>14</sup>. The results of elemental analysis and molar conductance values are listed in the Table.1

**Table 1 :** Elemental Analysis and molar conductance (in DMF) of Thorium(IV) complexes of 3-substituted-4-amino-5-mercapto-1,2,4-triazole Schiff bases.

Complex NO	Empirical formula	M%		N%		S%		Molar conductance $\text{Ohm}^{-1}\text{cm}^2\text{mole}^{-1}$
		Cald	Obtd	Cald	Obtd	Cald	Obtd	
1	$(\text{C}_6\text{H}_6\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	31.61	31.63	22.88	22.90	8.71	8.75	10.66
2	$(\text{C}_8\text{H}_{10}\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	30.45	30.54	22.04	22.05	8.39	8.42	12.68
3	$(\text{C}_{10}\text{H}_{14}\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	29.38	29.32	21.32	21.30	8.14	8.12	10.73
4	$(\text{C}_{12}\text{H}_{18}\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	28.36	28.30	20.55	20.65	7.93	7.92	13.40
5	$(\text{C}_8\text{H}_{10}\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	30.45	30.48	22.04	22.10	8.39	8.35	18.71
6	$(\text{C}_{10}\text{H}_{14}\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	29.48	29.45	21.21	21.31	8.06	8.00	15.05
7	$(\text{C}_{12}\text{H}_{18}\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	28.38	28.30	20.53	20.55	7.80	7.85	18.78
8	$(\text{C}_{14}\text{H}_{22}\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	27.42	27.42	19.85	19.90	7.56	7.53	16.34
9	$(\text{C}_{18}\text{H}_{14}\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	26.28	26.23	18.94	18.99	7.23	7.25	14.42
10	$(\text{C}_{20}\text{H}_{18}\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	25.42	25.40	18.38	18.35	7.03	7.08	15.30
11	$(\text{C}_{22}\text{H}_{22}\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	24.64	24.63	17.86	17.83	6.81	6.79	13.87
12	$(\text{C}_{24}\text{H}_{26}\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	23.95	23.96	17.38	17.35	6.61	6.59	12.84

### VI. RESULTS AND DISCUSSION

The thorium(IV) complexes 1-8 are light yellow in colour, whereas 9-12 are orange in colour. All the complexes are insoluble in common organic solvents. However, they are sparingly soluble in DMF and DMSO. The elemental analysis shown in Table.1 indicates that the complexes analysed for 1:1 stoichiometry of the type,  $\text{Th.LH}_2(\text{NO}_3)_4$ . Conductance measurements in DMF are too low to account for dissociation of these complexes in DMF at the concentration of the  $10^{-3}\text{M}$ . Hence the complexes may be regarded as nonelectrolytes. The molecular weight of the complexes could not be determined because of their insolubility in nitrobenzene.

### VII. INFRARED SPECTRA

The important IR frequencies which characterize the Schiff bases are discussed in the following texts (Table.2).



**Table 2 :** Important Infrared frequencies (in  $\text{cm}^{-1}$ ) of Thorium(IV) Complexes of 3-substituted-4-amino-5-mercapto-1,2,4-triazole and glyoxal/biacetyl/benzyl Schiff bases along with their Assignments.

Complex.No	(NH)	$\nu$ (SH)	$\nu$ (C=N)	$\nu$ (CS)	$\nu$ (M-N)
1	3275m	2400w	1620m	740m	540m
2	3260m	2385w	1615m	745m	450m
3	3255m	2390w	1620m	730m	460m
4	3240m	2405w	1615m	735m	480m
5	3265m	2410w	1620m	750m	495m
6	3180m	2400w	1615m	730m	535m
7	3200m	2385brw	1615m	740m	540m
8	3205m	2395brw	1620m	745m	530m
9	3245m	2405w	1615m	740m	490m
10	3255m	2410w	1615m	730m	465m
11	3100m	2405w	1615m	735m	470m
12	3255m	2400w	1620m	745m	495m

The present free ligands exist both in tautomeric thiol and thione forms. These ligands show a broad medium band in the region  $3280\text{-}3130\text{cm}^{-1}$  followed by a weak band around  $2400\text{cm}^{-1}$  due to  $\nu(\text{NH})$  and  $\nu(\text{SH})$  vibrations. Thus these ligands exhibit thiol thione tautomerism. The high intensity bands around  $1635 \pm 5\text{cm}^{-1}$  are assigned to  $\nu(\text{CN})$  in view of the previous assignments<sup>15</sup>. This observation renders proof for the presence of glyoxal, biacetyl and benzyl residue. These ligands also exhibit a medium intensity band around  $740\text{cm}^{-1}$  has been attributed to  $\nu(\text{C}=\text{S})$ <sup>16</sup>. These thorium(IV) complexes exhibit medium intensity bands in the region  $3275\text{-}3100\text{cm}^{-1}$  followed by weak band around  $2400\text{cm}^{-1}$  are attributed to  $\nu(\text{NH})$  and  $\nu(\text{SH})$  vibrations respectively. This indicates that, the ligands exhibit thiol thione tautomerism in the complexes. This supports the noninvolvement of the sulphur atom of the mercapto group in the coordination to the metal ion. Further, this is confirmed by the band due to  $\nu(\text{C}=\text{S})$  vibration appear around  $740\text{cm}^{-1}$ . The absence of shift in the  $\nu(\text{C}=\text{S})$  is suggestive of non-coordination of sulphur to the metal ion. Remarkable changes have occurred in the azomethine group of the ligands. The high intensity band around  $1640\text{cm}^{-1}$  due to  $\nu(\text{C}=\text{N})$  of the ligands appears in the region  $1620\text{-}1615\text{cm}^{-1}$  in the complexes. The low frequency shift of the band relative to that of ligand provides support for the coordination of  $\text{C}=\text{N}$  groups to the metal ion through nitrogen.

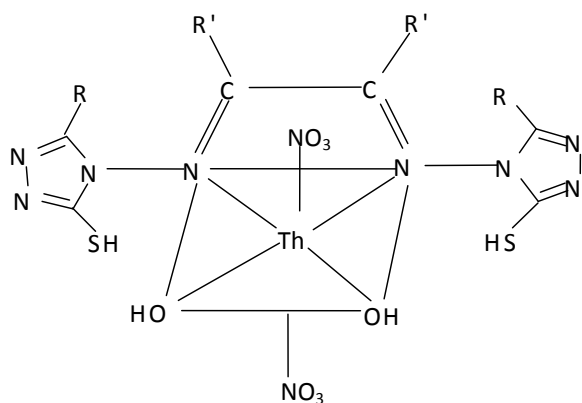
A strong band appeared in the region  $1260\text{-}1235\text{cm}^{-1}$  attributed to coordinated nitrate group. The assignments of the lower region are combroused as various skeletal vibrations of the ligands appear as high intensity bands and sometimes they are associated with metal in regard of these complexes are purely tentative and are founded on the previous reports. In these thorium(IV) complexes the  $\nu$  (M-N) bands have been assigned in the region  $540\text{-}450\text{cm}^{-1}$  in view of previous assignments<sup>18</sup>.

## VIII. PMR SPECTRUM

The PMR spectrum has been studied for only one representative complex viz., complex No.1. The PMR spectrum of corresponding ligand NO.1 exhibit resonance due to NH proton of 13.6ppm which is unaffected in the case of thorium(IV) comp. (around 13.6ppm). This suggests that, sulphur atom of SH group has not taken part in coordination as the ligand exists in thione form which is indicated by the signal appeared at 13.6 ppm in the present complex. There is a remarkable change in the position of resonance due to azomethine proton which is appeared at 9.14ppm in the thorium(IV) complex in relative to the corresponding ligand (8.2ppm). This downfield shift indicates the coordination of azomethine group to the metal ion through nitrogen. Another resonance due to proton of  $\text{CH}=\text{N}$  group of the triazole moiety appeared at 9.43 ppm. All these observations support IR inferences.

## IX. CONCLUSION

Analytical data indicates 1:1 stoichiometry for these complexes. IR and PMR spectral studies suggest the involvement of both  $\text{C}=\text{N}$  groups in the complex formation by keeping SH groups away from the coordination, considering all these observations, we propose the following structure, in which thorium exhibits coordination number of six.



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## Synthesis and Characterization of 2-Substituted Derivatives of 1, 3-Indandione

By N.D. Zargar & K.Z Khan  
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**Abstract** - Dimethyl sulphoxide –acetic anhydride reagent brings about an easy conversion of 1,3-indandione to its corresponding derivatives. At room temperature this reagent converts 1,3-indandione to ylide(2), an unusual dimer(3) and a novel dimeric condensation product(6). However, at waterbath temperature it affords a spiran(8) along with (2) &(6)..

**Keywords** : DMSO, acetic anhydride, 1,3-indandione, spiran, ylide, Dimer.

**GJSFR-B Classification** : FOR Code: 030503



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## I. INTRODUCTION

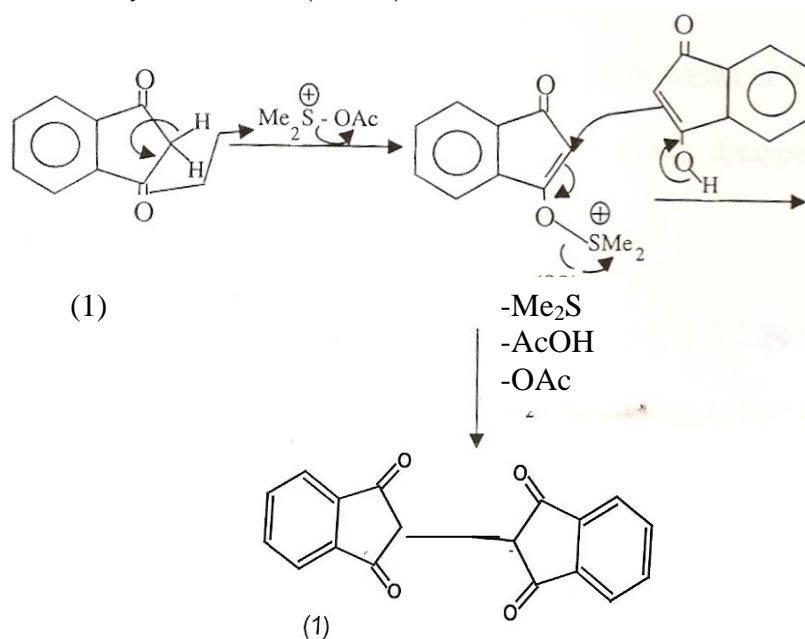
The present study was prompted by our earlier observation<sup>1,2</sup> that DMSO-acetic anhydride reagent upon interaction with 4-hydroxycoumarin, dicoumarol and 3-substituted 4-hydroxycoumarins furnishes, under varying conditions, a variety of products of both mechanistic and pharmacological interest.

1,3-indandione (1) an important member of the class of 1,3-dicarbonyl compounds yields a wide range of compounds of chemical and pharmaceutical interest with different substrates<sup>3-11</sup>. Its reactions with DMSO-acetic anhydride has been found to yield the corresponding ylide (2) in minimal amounts<sup>12</sup>.

## II. RESULTS AND DISCUSSION

Interaction of 1,3-indandione with freshly prepared DMSO –acetic anhydride mixture (2:1;V/V) for

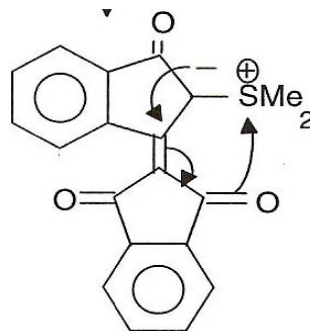
three days and work up through removal of the reagent under reduced pressure and chromatography of the residue over silica gel afforded two compounds. The major, water-soluble, constituent with improved yield (50%) was readily identified as the ylide. (2) on the basis of its m.p. and spectral data which were in full agreement with those reported for this compound<sup>12</sup>. The minor constituent, m.p. 280°C was devoid of sulphur and insoluble in all solvents except methanol. Its mass spectrum showing molecular ion peak at m/z 290 indicated involvement of two indandione units. With this molecular weight the only plausible structure for this compound could be the much awaited dimer (3). The infrared spectrum showing strong carbonyl band at 1710 cm<sup>-1</sup> is at the right value for the carbonyls in indandione residues substituted at C-2. The mechanism for the formation of ylide from 1,3-diketones is well known. A slightly different origin is proposed for the dimer (3). The activated DMSO can convert 1,3-indandione into enol Sulphonium salt (4) which can interact with another enol moiety of 1,3-Indandione to give dimer as depicted below (Scheme I).



Though this mechanism appears to be theoretically sound and logical, the literature records no reference of such dimerisation involving 1,3-diketones and activated DMSO.

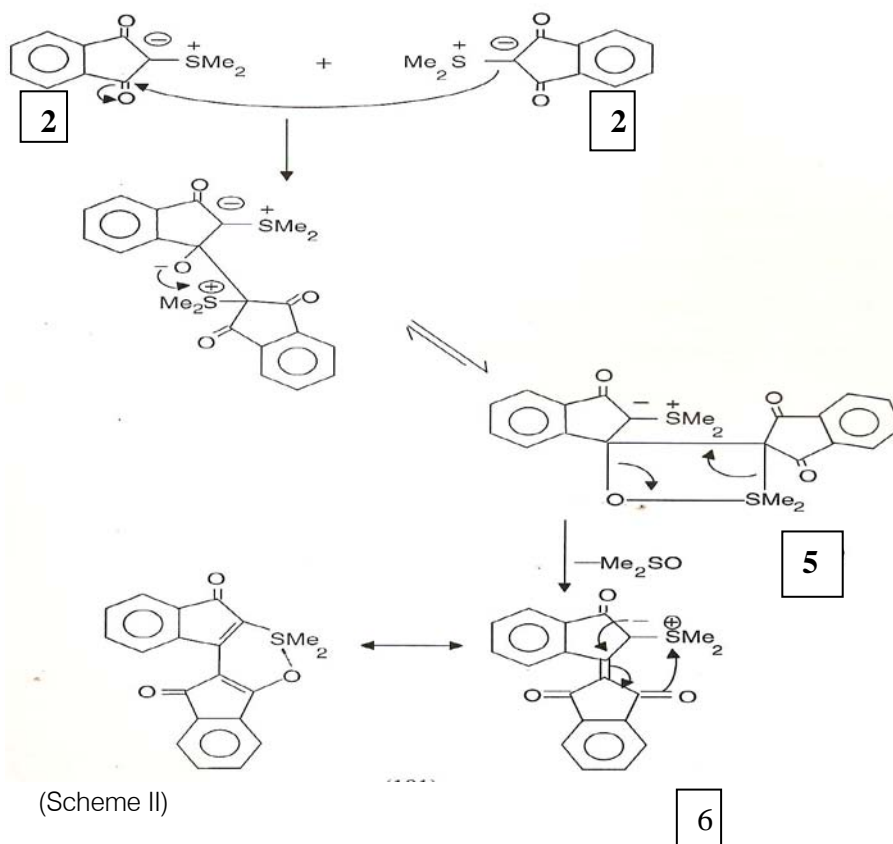
In a recent attempt when the same reaction was carried out but worked up differently i.e. through addition of excess of water and allowing it to stand as such for 24 hours, yields a colored solid which upon crystallization from chloroform pet-ether afforded a pure compound, m.p.220°C, responded positively when tested for the presence of sulphur. It was shown to have the molecular formula  $C_{20}H_{14}O_3S$  on the basis of its mass spectrum showing molecular ion peak at  $m/z$  334 and characteristic  $M+1$  and  $M+2$  peaks confirming presence of sulphur. It clearly indicated presence of two indandione residues. The infrared spectrum of the compound shows carbonyl bands at 1653 and 1629  $cm^{-1}$ , indicating presence of 2-substituted indandione residues in which the carbonyls must also be  $\alpha,\beta$ -unsaturated. It is pertinent to mention here that the infrared spectrum of 1,3-indandione shows two carbonyl absorption bands at 1740 and 1700  $cm^{-1}$  and substitution at C-2 invariably shows disappearance of the carbonyl band at higher frequency. The singlet,

equivalent to six protons at  $\delta$  3.249 in its PMR spectrum can be assigned to the two methyl groups present on sulphur. The spectrum is devoid of any other signal except for the multiplets equivalent to eight aromatic protons in the region of  $\delta$  7.269-8.420. This justifies our assumption that the compound must have resulted through condensation of two indandione moieties.



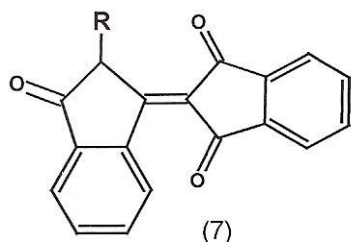
(6)

Mechanistically the carbanion of ylide (2) under the conditions attacks the carbonyl of the other moiety and the resulting four membered cyclic intermediate (5) being unstable collapses through elimination of DMSO to give a compound (6). (Scheme II)



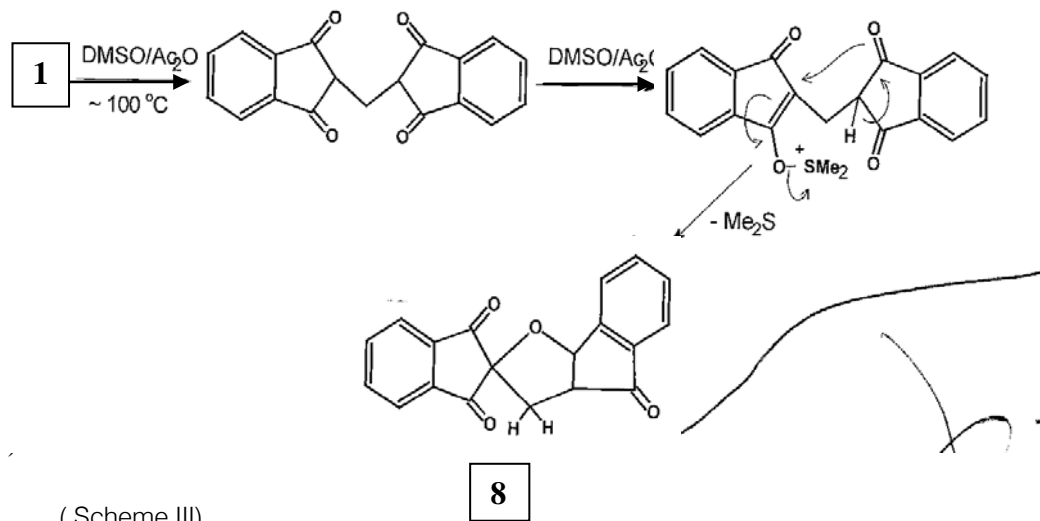
A different route for the formation of this compound can also be envisaged on the analogy of compound (7), which arises through condensation

between two indandione moieties under mild basic condition<sup>13</sup>.



The reaction between 1,3-indandione and DMSO-acetic anhydride reagent when carried out at

water bath temperature, reaches completion in 12 hours. Work up through removal of the reagent under vacuum followed by chromatography afforded compounds (2) and (6). The minor product, m.p. 255°C isolated from this reaction was characterized as the spiran (8). Its pmr and ir spectra showing a singlet equivalent to two protons at  $\delta$  3.01, apart from eight protons in the aromatic region and carbonyl bands at 1750 (shoulder), 1722 and 1700  $\text{cm}^{-1}$ , are in full agreement with this structure. The mass spectrum showing  $M^+$  at  $m/z$  302 (base peak) and other expected fragments, confirms this. (Scheme III)



(Scheme III)

### III. SPECTRAL DATA

(2) $^1\text{H NMR}(\delta)$ ( $\text{CDCl}_3$ )	3.024 (6H,s, S- (CH <sub>3</sub> ) <sub>2</sub> ), 7.760 – 7.946 (4H,m, Ar – H).
$V_{\text{max}}$ (KBr)	1635 and 1595 $\text{cm}^{-1}$
(3) $V_{\text{max}}$ (KBr)	3400, 1710, 1645 (weak) , 1545-1600 (broad multiplet), 1400 and 1260 $\text{cm}^{-1}$
Mass	$m/z$ 290 ( $M^+$ ), 148, 105, 104 (base peak) and 76.
(6) $^1\text{HNMR}(\delta)$ ( $\text{CDCl}_3$ )	3.249 (6H, s, S - (CH <sub>3</sub> ) <sub>2</sub> ), 7.269 – 7.740 (8H,m, Ar-H)
$V_{\text{max}}$ (KBr),	1653 and 1629 $\text{cm}^{-1}$
Mass. $M/z$	334 ( $M^+$ ), 319, 309, 272 (base peak) 202, 189, 144, 132, 104 and 76.
(8) $^1\text{H NMR}(\delta)$ ( $\text{CDCl}_3$ )	3.01 (2H,s,-CH <sub>2</sub> ), 6.90 – 8.75 (8H,m, Ar – H)
$V_{\text{max}}$ (KBr),	1722 (broad), 1700, 1750 (shoulders) $\text{cm}^{-1}$
Mass $m/z$ ,	302 ( $M^+$ base peak), 274, 273, 246, 218, 158, 104, 94 and 76.

### IV. EXPERIMENTAL

A mixture of 1,3 indandione (1.5gms), DMSO (12ml) and acetic anhydride was kept at room temperature for three days. Workup through removal of reagent under reduced pressure afforded a solid which upon column chromatography over silica gel using benzene – ethyl acetate as eluent yielded (2) and (3). The compound (2), m.p. 165°C was found to be soluble in chloroform and responded positively when tested for the presence of sulphur and identified as ylide. The second compound (3) obtained in minimal amounts

melts at 280° dissolves only in methanol and contains no sulphur.

An identical mixture of 1,3 indandione and DMSO acetic anhydride was also kept at room temperature for 3 days but worked up in a different manner, i.e, through addition of excess of water. On standing for about 24 hours a red coloured solid separated out which was washed and dried. Crystallisation from chloroform – pet-ether afforded (6), m.p 220°C and is freely soluble in chloroform.

However, when a mixture of 1,3 indandione (2gms), DMSO (16ml) and acetic anhydride (8ml) was

maintained at water bath temperature for 12 hours and work up through removal of solvent under reduced pressure afforded red coloured solid residue. Chromatography of which over silicagel using benzene – ethyl acetate (70:30) as eluent afforded again the ylide (2), a spiran (8) in minimal amounts and (6).

## V. GENERAL INFORMATION

DMSO was carefully dried according to the standard procedure. Melting points taken are uncorrected and spectral data of the compounds was recorded in RSIC Punjab University Chandigarh.

## VI. CONCLUSION

In conclusion it is found that interaction of DMSO/Ac<sub>2</sub>O reagent with 1,3-indandione leads to the synthesis of different substituted products with better yields by conventional methods. Silica gel acts as a good adsorbent. Accurate spectral data coupled with proposed mechanisms confirmed the assigned structures of different compounds.

## VII. ACKNOWLEDGEMENT

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## Evaluation of Some Synthesized Compounds as Corrosion Inhibitors in Oil Fields

By B. A. Salah , M. G. Abd-El-Nasser & A. T. Kandil

*Faculty of Science Helwan University, Cairo*

**Abstract** - The inhibition efficiency of previously prepared compounds namely, phthalimide derivatives on the corrosion of C-steel in 1 M HCl solutions has been studied using weight loss and electrochemical polarization methods. The results showed that the inhibition efficiency of the investigated compounds was found to depend on the concentration and the nature of the inhibitor. The effect of temperature on the corrosion behavior of C-steel in 1 M HCl without and with the inhibitors was studied in the temperature range from 303 to 333K. The activation and thermodynamic parameters for dissolution  $\Delta E_a^*$ ,  $\Delta H^*$  and  $\Delta S^*$  were calculated. The inhibitors were adsorbed on the C-steel surface according to Langmuir adsorption isotherm.

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**Abstract** - The inhibition efficiency of previously prepared compounds namely, phthalimide derivatives on the corrosion of C-steel in 1 M HCl solutions has been studied using weight loss and electrochemical polarization methods. The results showed that the inhibition efficiency of the investigated compounds was found to depend on the concentration and the nature of the inhibitor. The effect of temperature on the corrosion behavior of C-steel in 1 M HCl without and with the inhibitors was studied in the temperature range from 303 to 333K. The activation and thermodynamic parameters for dissolution  $\Delta E_a^*$ ,  $\Delta H^*$  and  $\Delta S^*$  were calculated. The inhibitors were adsorbed on the C-steel surface according to Langmuir adsorption isotherm.

## I. INTRODUCTION

Even with advanced corrosion resistant materials available, carbon steel has been widely employed as construction materials for pipe work in the oil and gas production such as down hole tubulars, flow lines and transmission pipelines [1]. Also, in oil fields hydrochloric acid solution is recommended as the cheapest way to dissolve calcium carbonate,  $\text{CaCO}_3$ , scale inside the pipelines under most conditions. Accordingly, corrosion inhibitors (usually surfactants) must be injected with the hydrochloric acid solution to avoid the destructive effect of acid on the surface of the pipe lines [2]. Corrosion inhibitors may be divided into three broad classes, namely oxidizing, precipitation and adsorption inhibitors.

Compounds containing nitrogen, oxygen, sulphur and phosphorus like hydroxy ethyl, amino ethyl and amido ethyl imidazoline in the conjugated system have particularly been reported as efficient corrosion inhibitors. These compounds can adsorb on the metal surface by blocking the active sites and thereby

decreasing the corrosion rate. The choice of inhibitors was based on the fact that these compounds contain  $\pi$ -electrons and heteroatom such as N, O and S which involve greater adsorption of the inhibitor molecules onto the surface of steel [3,4].

The aim of the present work is to study the inhibition of C-steel in 1 M HCl by some derivatives of phthalimide by two techniques (weight loss and electrochemical techniques). Weight loss measurements were used at different temperatures (303-333K) and the electrochemical technique is used at 303K.

## II. EXPERIMENTAL WORK

### a) Materials

#### i. Composition of material sample

The experiments were performed on samples of C-steel whose chemical composition (weight %) is as follows:  $C = 0.17\%$ ,  $Mn = 1.18\%$ ,  $P = 0.008\%$ ,  $Si = 0.27\%$ ,  $S = 0.008\%$ ,  $Cr = 0.27\%$ ,  $Mo = 0.04\%$ ,  $Fe = 98.05\%$ .

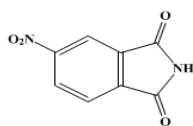
Specimens were mechanically polished with fine grade emery paper in order to obtain a smooth surface, followed by ultra sonically degreasing in acetone and then rinsed with distilled water, dried and weighed.

#### ii. Hydrochloric acid (BDH)

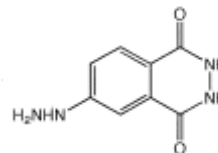
A stock solution of hydrochloric acid (8 M) was prepared using bidistilled water. The acid solution was prepared by diluting the appropriate volume of the concentrated chemically pure grade acid with bidistilled water. The concentration of the acid was checked by titration of an appropriately diluted portion with standard solution of analar sodium carbonate. 1 M HCl solutions were prepared by dilution using bidistilled water.

#### iii. Inhibitors

The organic inhibitors were prepared as before [5, 6 and 7].



4-nitrophthalimide  
(Compound A)



6-Hydrazinophthalazine-1, 4(2H,3H)-dione  
(Compound B)

#### iv. Inhibitor solutions

Five different concentrations viz, 50, 100, 150, 200 and 250 ppm from compounds A & B were used.

#### b) Methods

##### i. Weight loss method

Test pieces of C-steel (7 x 2 x 0.2 cm) were suspended by suitable glass hooks at the edge of the basin. The test specimen of C-steel was treated as described before and it had an average weight = 37.5 gm. It was dipped in 100 ml of test solution at 303K. This was conducted in a covered beaker to prevent contact with air and allow the escape of evolving gases. After the required immersion time, the test specimen was removed, washed with double distilled water, dried as before and finally weighed. The average weight loss at a certain time for the tested samples was taken in mg cm<sup>-2</sup>. The change in weight was recorded to the nearest 0.0001 g which is the sensitivity of the used analytical balance. Precautions were always made to avoid scratching the specimen during washing after exposure. Therefore, the weight losses/cm<sup>2</sup> are given from the equation:

$$\Delta W = (W_1 - W_2)/a \quad (1)$$

Where  $W_1$  and  $W_2$  are the weights of specimen before and after reaction, respectively and  $a$  is the surface area in cm<sup>2</sup>. The inhibition or acceleration efficiency  $\eta$  % was computed from the equation:

$$\theta = \frac{\Delta W - \Delta W_i}{\Delta W} \quad (2)$$

Where:  $\theta$  is the degree of surface coverage.

$$\eta \% = \frac{\Delta W - \Delta W_i}{\Delta W} \times 100 \quad (3)$$

Where,  $\Delta W$  and  $\Delta W_i$  are the weight loss per unit area in absence and presence of additive.

##### ii. Electrochemical method

Electrochemical measurements were carried out in a standard three-electrode cell. The counter electrode was a mesh of platinum of high purity (99.9%) and the reference electrode consisted of a saturated calomel electrode (SCE). The third electrode was the working electrode which was prepared from a round bar of carbon steel embedded in a cylindrical rod made out of Teflon. The cross-section area in contact with the solution was 1 cm<sup>2</sup>. All tests were performed in open air at room temperature of 303K. Electrochemical testing was performed using VOLTMASTER 4 version 4 through the galvanostatic polarization circuit at range from -1mV to 1mV for 20 min. The working electrode (WE) was polished mechanically. After polishing, the electrode was washed with acetone, rinsed several times with distilled water and dried. The freshly polished electrode was pretreated further before each experiment by holding the potential at -1 V vs. a saturated calomel electrode for 1min to reduce the oxide surface layer, and then open circuit potential ( $E_{ocp}$ ) was allowed to stabilize for 10 min.

### III. RESULTS AND DISCUSSION

#### a) Weight loss measurements

Weight loss in mg cm<sup>-2</sup> of the surface area for C-steel was determined in the absence and presence of the additives. Fig.1 shows the calculated weight loss/cm<sup>2</sup> for C-steel which was exposed to 1 M HCl at 303K in the absence and presence of 250 ppm from compounds A & B. The figure shows that weight loss for both compounds is lower than that for blank

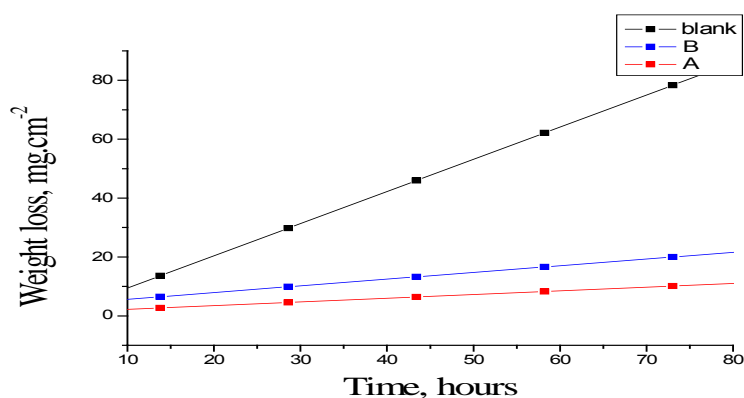


Figure 1: Weight loss-time curves for C-steel corrosion in the absence and presence of 250 ppm of A & B at 303K.

Rate of corrosion in mg.cm<sup>-2</sup> of the surface area for C-steel was determined in the absence and presence of the additives. It's obvious that the rate of corrosion of carbon steel in presence of inhibitors is much lower than that obtained in blank solution. Inspection of Table-1 reveals that, the inhibition

efficiency increase with an increase in inhibitor concentration. This behavior could be attributed to the increase of the number of adsorbed molecules at the metal surface. At one and the same inhibitors concentration the percentage of inhibition efficiency decreases in the following order: A > B. This increase

until 250 ppm after that there is no obvious increasing. Thus, at low concentrations (Sketch 1) a mono disordered layer may be formed while at high concentration, un-complete packing layer of the inhibitor molecules should be formed as shown in (Sketch 2). Meanwhile at maximum inhibition efficiency obtained,

the inter space area between the adsorbed inhibitor molecules on the surface may be lesser than the area of the inhibitor molecules. So that, the inhibitor molecules turn out to form the double layer adsorption as shown in (Sketch 3) [8].

**Table 1:** Corrosion Rate Dependence of Carbon Steel, the Degree of Surface Coverage ( $\theta$ ) at Different Concentrations of A and B in 1M HCl Solution at 303 K.

Concentration (ppm)	Rate of Corrosion (mg/cm <sup>2</sup> )		$(\theta)$		Efficiency $\eta$ (%)	
	A	B	A	B	A	B
Blank	8.48734	8.487339	/		/	
50	4.028088	4.073065	0.5254	0.5201	52.54	52.01
100	3.556181	3.836265	0.5810	0.5480	58.10	54.80
150	2.356929	3.254041	0.7223	0.6166	72.23	61.66
200	1.120319	2.580137	0.8680	0.6960	86.80	69.60
250	0.662851	2.534314	0.9219	0.7014	92.19	70.14



Sketch 1 : The adsorption of inhibitor on the surface at low concentration.



Sketch 2 : The adsorption of inhibitor on the surface at high concentration.



Sketch 3 : The adsorption of inhibitor on the surface at the maximum inhibition efficiency obtained (over dose concentration).

#### i. Effect of temperature

The effect of temperature on the rate of dissolution of carbon steel in 1M HCl containing 250 ppm of the inhibitors was studied by weight loss measurement over a temperature range from 303 to 333K.

Table-2 shows the effect of increasing temperature, as the temperature increases, the rate of

corrosion increases and hence the inhibition efficiency decreases. This is due to the adsorption is decreased by increasing the temperature. This behavior proves that the adsorption of inhibitors on C-steel surface occurs through physical adsorption.

**Table 2:** Corrosion Rate Dependence of Carbon Steel, the Degree of Surface Coverage ( $\theta$ ), the Percentage Inhibition ( $\eta$  %) in absence and presence of 250 ppm of A& B at Different Temperatures in 1M HCl Solution.

Temp. (K)	Corrosion Rate (k) (mg/cm <sup>2</sup> )			$(\theta)$		Efficiency $\eta$ (%)	
	Blank	A	B	A	B	A	B
303	8.4873	0.6628	2.5343	0.9219	0.7014	92.19	70.14
313	17.9303	2.6160	6.6216	0.8541	0.6307	85.41	63.07
323	42.4930	10.8867	17.2394	0.7438	0.5943	74.38	59.43
333	57.9389	16.7848	25.3714	0.7103	0.5621	71.03	56.21

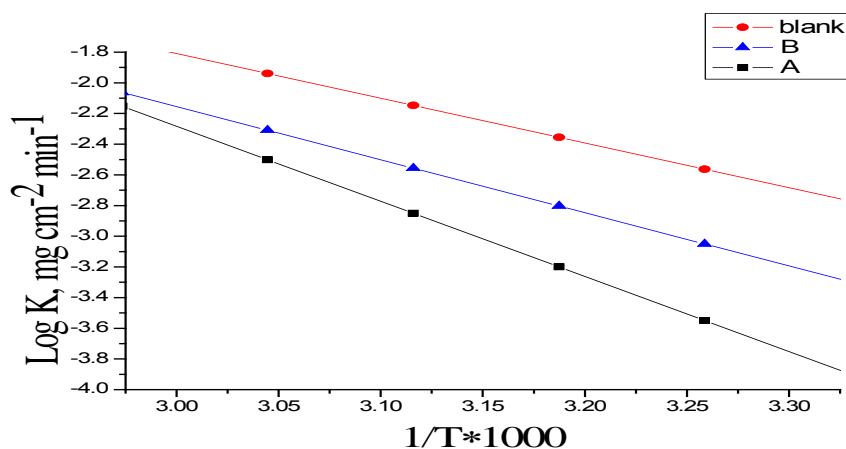


Figure 2 : a relation between Log K and 1/T for blank, A and B.

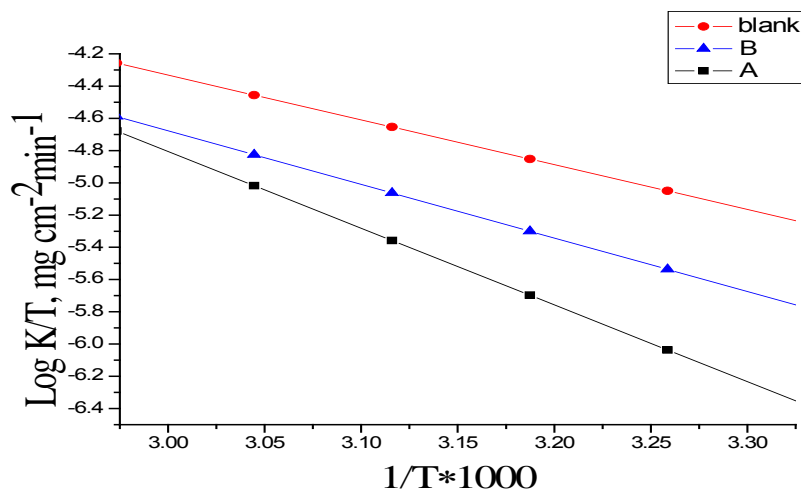


Figure 3 : a relation between Log K/T and 1/T for blank, A and B.

#### b) Activation parameters for dissolution

The apparent activation energy  $E_a^*$ , the enthalpy of activation  $\Delta H^*$ , the entropy of activation  $\Delta S^*$  and Gibbs free energy  $\Delta G^*$  for the corrosion of C-steel samples in 1 M HCl solutions in the absence and presence of different concentrations of inhibitors at 303–333K were calculated from Arrhenius equations:

$$K = A \exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

$$K = \frac{RT}{Nh} \exp\left(\frac{\Delta S^\circ}{R}\right) \exp\left(\frac{-\Delta H^\circ}{RT}\right) \quad (5)$$

$$\Delta S^* = (\Delta H^* - \Delta G^*)/T \quad (6)$$

Where  $k$  is the corrosion rate,  $A$  is the frequency factor,  $h$  is the Plank constant,  $N$  is Avogadro's number and  $R$  is the universal gas constant. A plot of  $\log k$  vs.  $1/T$  and  $\log (k/T)$  vs.  $1/T$  give straight lines with slope of  $-E_a^*/2.303 R$  and  $-\Delta H^*/2.303 R$ , respectively. The

intercepts which are calculated will be  $A$  and  $\log R/Nh + \Delta S^*/2.303 R$  for Arrhenius and transition state equations, respectively.

Figs. 2-3 represent the plot of  $\log k$  vs.  $1/T$  and the plot of  $\log (k/T)$  vs.  $1/T$  data respectively in the absence and presence of 250 ppm of the investigated compounds. The calculated values of the apparent activation energy,  $E_a^*$ , activation entropies,  $\Delta S^*$  and activation enthalpies,  $\Delta H^*$  are given in Table 3. It is clear that the presence of tested compounds increased the activation values and consequently decreased the corrosion rate of C-steel. Also, the activation energy values increased by increasing the concentration of the inhibitors.

These results indicate that these tested compounds acted as inhibitors through increasing the activation energy of C-steel dissolution by making a barrier to mass and charge transfer by their adsorption on the C-steel surface. The values of  $\Delta H^*$  reflected the strong adsorption of these compounds on the C-steel surface. The values of  $\Delta S^*$  in the absence and presence of the tested compounds were negative; this indicates that the activated complex in the rate determining step

represents an association rather than dissociation step [9]. The values of  $\Delta G^*$  are all positive reflecting the high energy barrier for the corrosion process [10]. On the other hand,  $\Delta G^*$  values in presence of the inhibitors are higher than that obtained from 1M HCl (blank), and hence, the process is activation controlled. This means

that the activated molecules were in a higher order state than that at the initial state. The order of the inhibition efficiency of the investigated compounds as gathered from the increase in  $Ea^*$ ,  $\Delta H^*$  and the decrease in  $\Delta S^*$  values remains unchanged and follows the order  $A > B >$ .

Table 3: Thermodynamic Functions of Activation of the prepared inhibitors.

Inhibitor code	$\Delta E_a^*$ K.J.mol <sup>-1</sup>	$\Delta G^*$ K.J.mol <sup>-1</sup>	$\Delta H^*$ K.J.mol <sup>-1</sup>	$-\Delta S^*$ J.mol <sup>-1</sup> .K <sup>-1</sup>
Blank	55.83	77.80	58.42	60.95
A	93.81	149.09	96.38	165.76
B	66.33	96.19	68.91	85.81

c) adsorption isotherm

The Langumire adsorption was calculated by.

$$C_i / \theta = 1 / K_{ad} + C_i \quad (7)$$

Where:  $C_i$  is the inhibitor concentration (in ppm).

$K_{ad}$  is the adsorption equilibrium constant.

Applying Langmuir adsorption equation (8) for the inhibitors, plots of  $C_i / \theta$  versus  $C_i$  are shown in Fig.4

Inspecting Langmuir plots for A and B, it is found that, all the investigated inhibitors showed linear plots. This behavior suggests that these inhibitors obey Langmuir adsorption. There is no interaction between the molecules adsorbed at the metal surface.

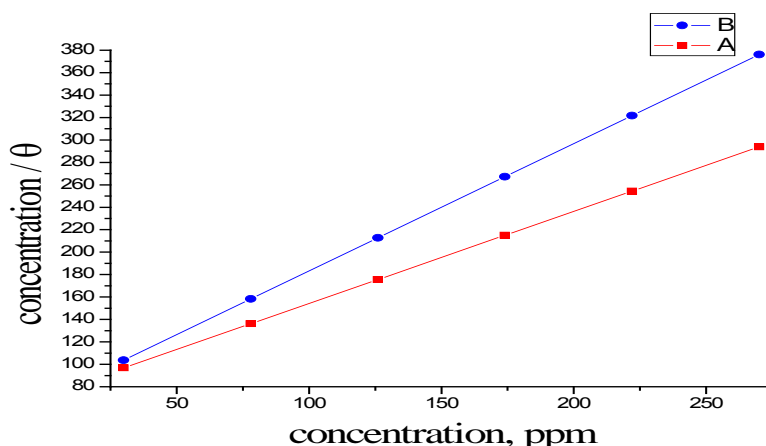
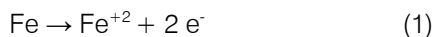


Figure 4: Langmuir adsorption isotherm for the inhibitor A& B on the carbon steel in 1M HCl at 298 K.

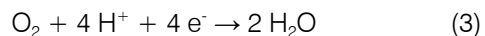
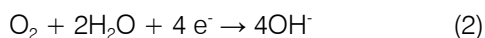
d) Potentiodynamic polarization measurements

i. Corrosion mechanism

A typical anodic oxidation that produces dissolved ionic products, for example for iron metal is:



Examples of cathodic reduction involved in corrosion process are:

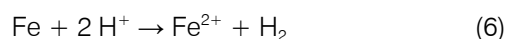


The cathodic reaction represented by equation (2) exemplifies corrosion in natural environments which

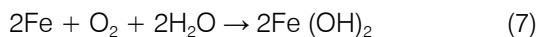
occurs at nearly neutral pH values. Equations (3) and (4) represent corrosion processes taking place in the acidic environments encountered in industrial processes where the pH can reach acidic values because of hydrolysis reactions such as:



This reaction produces  $H^+$  ions, the concentration of which can, under certain conditions, become large if the  $H^+$  ions cannot readily move out from a confined volume. The overall corrosion reaction is, of course, For example,



Or, for a reaction producing hydroxide (sum of reactions 3 and 5):



ii. *Polarization measurements*

The efficiency was calculated from Potentiodynamic data according to equation 8 and 9.

$$\eta \% = 1 - (I_{\text{corr}} / I_{\text{corr}}^0) \cdot 100 \quad (8)$$

$$\theta = (I_{\text{corr}}^0 - I_{\text{corr}}) / I_{\text{corr}}^0 \quad (9)$$

$$R_p = \frac{B}{I_{\text{corr}}} = \frac{(\Delta E)}{(\Delta I)} \quad (10)$$

Where  $I_{\text{corr}}$  Is the current density in presence of inhibitors.

$I_{\text{corr}}^0$  Is the current density in absence of inhibitors.

$\theta$ : Is the degree of surface coverage.

$R_p$ : Is the polarization resistance.

$B$ : Is constant =  $b_a \cdot b_c / 2.303 (b_a + b_c)$ .

$\Delta E$ : Is the potential difference.

$\Delta I$ : Is the current density difference.

The extrapolation of anodic and/or cathodic Tafel lines of charge transfer controlled corrosion reaction giving the corrosion current density,  $i_{\text{corr}}$ , at the corrosion potential,  $E_{\text{corr}}$ . This method is based on the electrochemical theory of corrosion processes developed by Wagner and Traud [11-14]. Anodic and cathodic polarization was carried out Potentiodynamically in unstirred 1 M HCl in the presence and absence of various concentrations of the compounds A&B at 303K. At all current densities, during

polarization, the overpotentials were slightly shifted with time and then attained steady values. These steady overpotentials values were used for the construction of anodic and cathodic Tafel plots. Figs.5-6 represent the Potentiodynamic polarization curves for the dissolution of C-steel in 1 M HCl in the presence and absence of different concentrations of the compounds at 303K. The numerical values of the variation of the corrosion current density ( $i_{\text{corr}}$ ), the corrosion potential ( $E_{\text{corr}}$ ), degree of surface coverage ( $\theta$ ) and the inhibition efficiency ( $I$  %) with the concentrations of different inhibitors are given in Tables 4-5. From the results in Figs. 5-6 and Tables 4-5 it was found that:

1. The cathodic and anodic curves which were obtained exhibited Tafel type behavior and the addition of the inhibitors increased both the cathodic and anodic overvoltages which caused mainly parallel displacement to the more negative and positive values respectively, i.e. the presence of inhibitors in solution inhibits both of hydrogen evolution and the anodic dissolution processes.
2. The corrosion current density ( $i_{\text{corr}}$ ) decreased with increasing the concentration of the inhibitors which indicated that these compounds acted as inhibitors, and the degree of inhibition depended on the concentration and type of the inhibitors present.
3. The values of polarization resistance of the inhibitors higher than the blank and its value increase with increasing the concentration of inhibitors.
4. The order of the inhibition efficiency of the inhibitors at different concentrations as given by polarization measurements is listed in Tables 4-5, where the arrangement of the compounds is ordered as in weight loss measurements as follows:  $A > B$

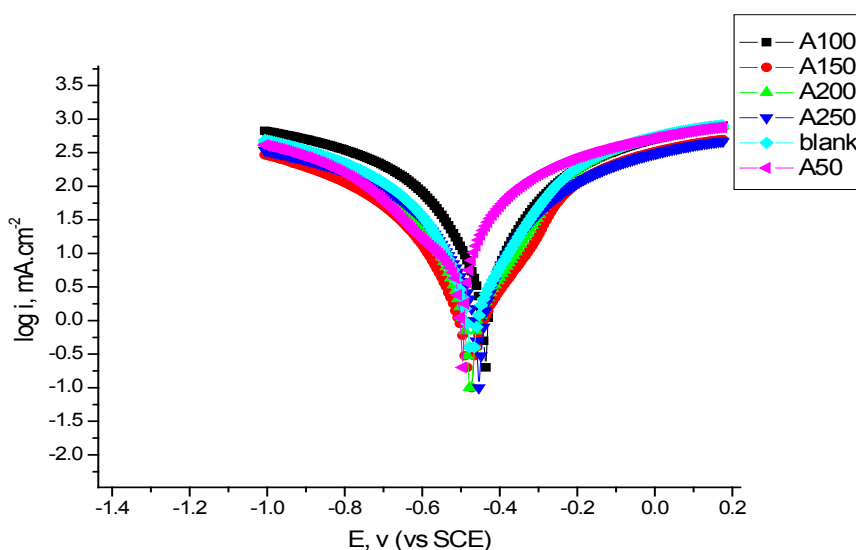


Figure 5 : Potentiodynamic polarization curves (E against log i) of carbon steel in 1M HCl in absence and presence of different concentrations of inhibitor A at 298 K.

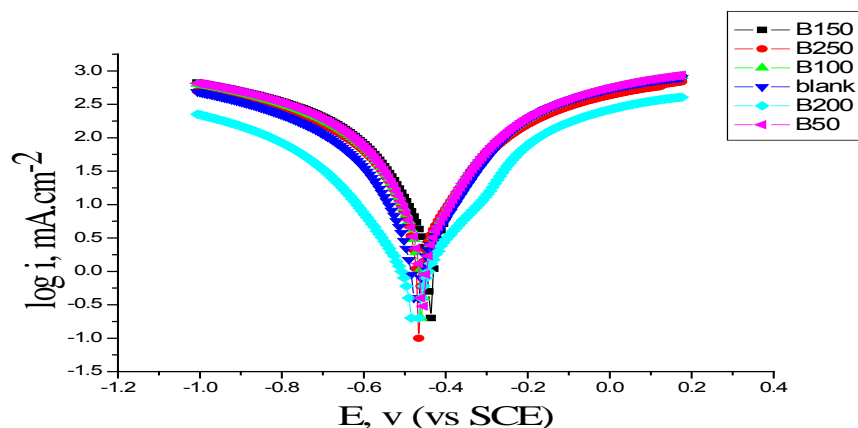


Figure 6 : Potentiodynamic polarization curves (E against log i) of carbon steel in 1M HCl in absence and presence of different concentrations of inhibitor A at 298 K.

Table 4 : Data from Potentiodynamic Polarization of Carbon Steel in 1 M HCl Containing Various Concentrations of Inhibitor A at 298 K.

Concentration, (ppm)	-E <sub>corr</sub> mV,	I <sub>corr.</sub> mA/cm <sup>2</sup>	R <sub>p</sub> , m(Ohm).cm <sup>-2</sup>	(θ)	η (%)
Blank	460	<b>0.39</b>	1.1	/	/
50	485	0.2	2.4	0.48	48.71
100	476	0.11	4.3	0.71	71.79
150	480	0.10	4.8	0.74	74.35
200	485	0.09	5.3	0.76	76.92
250	490	0.07	7.0	0.82	82.05

Table 5 : Data from Potentiodynamic Polarization of Carbon Steel in 1 M HCl Containing Various Concentrations of Inhibitor B at 298 K.

Coccentration, (ppm)	-E <sub>corr</sub> mV,	I <sub>corr.</sub> mA/cm <sup>2</sup>	R <sub>p</sub> , m(Ohm).cm <sup>-2</sup>	(θ)	η (%)
Blank	460	0.39	<b>1.1</b>	/	/
50	467	<b>0.28</b>	1.6	0.28	28.20
100	470	0.2	2.3	0.48	48.71
150	481	0.17	2.8	0.56	56.41
200	480	0.14	3.4	0.64	64.10
250	485	0.09	5.3	0.76	76.92

#### IV. CONCLUSION

1. The inhibition efficiency of the studied inhibitors increases in the following order: 4-nitrophthalimide > 6-Hydrazinophthalazine-1,4(2H,3H)-dione
2. The inhibition efficiency of all studied inhibitors increases with increasing the concentration.
3. The maximum recommended dose is 250 ppm.
4. The values of activation energy (E<sub>a</sub><sup>\*</sup>) increases in the same order of increasing the inhibition efficiency of the inhibitor.

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## Effect of Inorganic Chromium Supplementation on the Intestinal Mucosa Development of Heat-Stressed Broilers

By Makanjuola, B. A. & Adebisi, O.A

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**Abstract** - Ninety (90) 7 day-old broilers under conditions of heat stress were randomly assigned to 3 dietary treatments of 3 replicates each. There were 10 birds in each replicate. The 3 diets were: Diet 1 – Control diet (without Chromium supplementation); Diet 2 - 0.15mg/kg Chromium supplementation and Diet 3 - 0.25mg/kg Chromium supplementation. The inorganic Chromium source was Chromium chloride. The aim of the study was to evaluate the effect(s) of heat stress on the intestinal mucosa of broilers. The study lasted 7 weeks and data on performance (feed intake, weight gain and feed conversion ratio) and intestinal morphology (villus height and crypt depth) were taken. Data taken were subjected to statistical analysis of variance (ANOVA) procedure of SAS 2010. Significant differences were observed in the weight gain with the birds fed diet 3 having the highest mean value of 45.00g/day and the least value of 40.00g/bird for birds the on control diet. However, birds fed diet 3 (0.25mg/kg) had the least significant feed conversion ratio 2.00 when compared with birds on control diet (2.25) and diet 2 (2.14). The villus height in the ileum of birds on Diet 3 was significantly ( $p < 0.05$ ) taller than that of birds on the other diets while the villus height in the jejunum of birds on Diet 1 was significantly ( $p < 0.05$ ) taller than that of birds on the other diets.

**Keywords** : *Broiler, Chromium chloride, heat-stress, villus height, crypt depth.*

**GJSFR-B Classification** : *FOR Code: 030699*



EFFECT OF INORGANIC CHROMIUM SUPPLEMENTATION ON THE INTESTINAL MUCOSA DEVELOPMENT OF HEAT-STRESSED BROILERS

*Strictly as per the compliance and regulations of :*



RESEARCH | DIVERSITY | ETHICS

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# Effect of Inorganic Chromium Supplementation on the Intestinal Mucosa Development of Heat-Stressed Broilers

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**Keywords** : Broiler, Chromium chloride, heat-stress, villus height, crypt depth.

## I. INTRODUCTION

High ambient temperatures coupled with high humidity levels as experienced in the tropics can be devastating to commercial broilers. It has been shown that heat stress has detrimental effects on the performance of broilers reducing the growth rate and feed intake and also affecting the feed efficiency, carcass quality and health of the birds (Temim *et al.*, 2000; Har *et al.*, 2000). Chronic heat stress increases the time to reach market weight and also increases

mortality rate. Chromium supplementation has been observed to alleviate the adverse effects of heat stress in broilers. Although Chromium is not currently considered an essential trace mineral for poultry, research data provide evidence that suggests a nutritional and physiological role for this micronutrient (Mertz, 1967). The National Research Council has recommended Chromium at 300 $\mu$ g/kg in diets of lab animals (NRC, 1995), however currently there are no NRC recommendations for Chromium in poultry diets (NRC 1994).

Toghyani *et al.* (2006) reported an increase in body weight gain and feed intake of broilers under heat stress conditions when supplemented with Chromium. The authors also observed an increase in carcass yield and decrease in abdominal fat contents. Sahin *et al.* (2002a) reported an increase in feed intake, feed efficiency and body weight of broilers under heat stress with supplementation of Chromium. Increase in carcass yield and decrease in abdominal fat content in broilers was observed when supplemented with Chromium picolinate or high Chromium yeast (Debski *et al.*, 2004). Zhang *et al.* (2002) reported that Chromium supplementation improved FCR in broilers by 6.2%. Rosebrough and Steele (1981) observed that turkeys fed a diet supplemented with Chromium had greater liver glycogen levels as a result of the increased activity of the enzyme glycogen synthetase and also that Chromium increased glucose transport by increasing insulin activity. Kim *et al.* (1995) reported increased HDL cholesterol and decreased total cholesterol in Chromium-supplemented broilers. Anandhi *et al.* (2006) observed a significant reduction in breast and thigh muscle cholesterol levels and an increase in breast and thigh muscle protein levels in broilers supplemented with organic Chromium. There is a however a dearth of research data on the effect(s) of Chromium on the intestinal mucosa morphology development of broilers therefore the aim of this study was to investigate the effect of 2 levels of Chromium supplementation on the intestinal mucosa development in broilers.

## II. MATERIALS AND METHODS

Ninety (90) day old broilers were brooded for one week after which they were randomly allotted to 3

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dietary treatments of 3 replicates with 10 birds per replicate. The experimental design was Completely Randomized Design. The temperature of the house during the experiment was  $32.3 \pm 3^{\circ}\text{C}$ . The treatments were 1 – control diet without Chromium chloride, 2 – diet with 0.15mg/kg Chromium chloride and 3 – diet with 0.25mg/kg Chromium chloride. The experiment lasted 7 weeks. Feed was offered to the birds ad libitum and data on feed intake and weight gain were taken on a weekly basis. At the end of the period, three birds per replicate was slaughtered after a period of fasting (12 hours) and samples of the ileum and jejunum were taken from each bird. The specimens were fixed in 10% formalin after which they were dehydrated in 100%

ethanol. The specimens were then cleared with xylene and embedded in paraffin. A microtome was used to make  $4\mu\text{m}$  cuts that were mounted on glass slides and stained using the H and E (Haematoxyline and Eosin) method. Five readings each of villus height and crypt depth were taken per specimen. This was done with a light microscope (Olympus). Villus height was measured from the apical to the basal region which corresponded to the superior portion of the crypts. Crypts were measured from the basis until the region of transition between the crypt and the villus. All data were subjected to analysis of variance (ANOVA) procedure of SAS, 2010.

**Table 1 :** Gross Composition of broiler diets Supplemented With Different Levels Of Chromium Chloride.

Ingredients (kg)	Diet 1 Control	Diet 2 (0.15mg/kg)	Diet 3 (0.25mg/kg)
Maize	58.00	58.00	58.00
Groundnut Cake	21.00	21.00	21.00
Palm kernel cake	1.00	1.00	1.00
Fish meal	2.00	2.00	2.00
Soyabean meal	14.60	14.60	14.60
Bone meal	2.40	2.40	2.40
Premix(Broiler starter)	0.30	0.30	0.30
Salt	0.30	0.30	0.30
Lysine	0.30	0.30	0.30
Methionine	0.20	0.20	0.20
Chromium Chloride (mg/kg)	0.00	0.15	0.25
<b>Total</b>	<b>100.00</b>	<b>100.00</b>	<b>100.00</b>
<b>Calculated Nutrient</b>			
Crude Protein (%)	23.00	23.00	23.00
Metabolisable Energy (kcal/kg ME)	3,019.27	3,019.27	3,019.27
Crude fibre (%)	3.30	3.30	3.30

### III. RESULTS

The gross compositions of the experimental diets are shown in Table 1. The diets were formulated to meet the nutritional requirements of broilers as recommended by NRC, 1994. Table 2 shows the performance characteristics of the birds. Final weight, weight gain and feed conversion ratio differed significantly among birds on the different dietary treatments with birds on diet 3 having the highest values. Feed intake however did not differ significantly. Table 3 shows the results of the morphology of the

intestinal mucosa of the birds on the different dietary treatments. The morphological indices evaluated were the villus height and crypt depth in the ileum and jejunum. Ileal villus height ( $545.35\mu\text{m}$ ) of birds on Diet 3 was significantly ( $p < 0.05$ ) taller than that of birds on the other diets. The jejunal villus height ( $519.65\mu\text{m}$ ) of birds on Diet 1 was significantly ( $p < 0.05$ ) taller than that of birds on the other diets. Birds on Diet 1 had significantly ( $p < 0.05$ ) deeper ileal crypts ( $84.13\mu\text{m}$ ) than birds on the other diets. The crypt depth in the jejunum of the birds were however not significantly affected by the dietary treatments.

**Table 2 :** Performance Characteristics Of Broiler Birds Fed Diets Supplemented With Different Levels Of Chromium Chloride

Parameters	Diet 1 Control	Diet 2 (0.15mg/kg)	Diet 3 (0.25mg/kg)	SEM
Final weight (g)	2006.00 <sup>c</sup>	2020.00 <sup>b</sup>	2056.00 <sup>a</sup>	12.34
Weight gain (g/day)	40.00 <sup>c</sup>	42.14 <sup>b</sup>	45.00 <sup>a</sup>	3.68

Feed Intake (g/day)	90.00	90.00	90.00	3.54
Feed Conversion Ratio	2.25 <sup>c</sup>	2.14 <sup>b</sup>	2.00 <sup>a</sup>	0.21

<sup>ab</sup> Means within the same row without common superscripts differ significantly ( $p < 0.05$ )

**Table 3 :** Intestinal mucosa morphology of broilers fed diets supplemented with different levels of Chromium Chloride.

Parameter	Diet 1 (Control)	Diet 2 (0.15mg/kg)	Diet 3 (0.25mg/kg)	SEM
Villus height (Ileum)	367.21 <sup>b</sup>	529.15 <sup>a</sup>	545.35 <sup>a</sup>	8.97
Villus height (Jejunum)	519.65 <sup>a</sup>	457.18 <sup>b</sup>	460.24 <sup>b</sup>	10.56
Crypt depth (Ileum)	84.13 <sup>a</sup>	58.47 <sup>b</sup>	60.22 <sup>b</sup>	5.32
Crypt depth (Jejunum)	78.93	74.48	80.69	4.43

<sup>abc</sup> Means within the same row with different superscripts differ significantly ( $p < 0.05$ )

#### IV. DISCUSSION

This study showed that Chromium supplementation particularly at 0.25mg/kg improved the performance of the broilers in terms of the final weight, weight gain and feed conversion ratio. This is in line with the reports of Sands and Smith (1999). The authors reported that chromium supplementation has been found to improve the body weight gain and feed efficiency in broilers under heat stress. The better performance observed in birds on Diet 3 may be attributed to better metabolism of nutrients by Cr supplementation as dietary Chromium supplementation has been shown to positively affect growth rate and feed efficiency in growing poultry (Kheiri and Toghyani, 2009).

With regard to the intestinal mucosa development, the study showed that birds on Chromium-supplemented diets had significantly ( $p < 0.05$ ) taller villi in the ileum than birds on the control diet. This is in line with the report of Sandikci et al. (2004). The authors reported that environmental conditions like heat stress could significantly modify intestinal histological parameters; they observed a significant reduction of the villus height in the duodenum, jejunum and ileum from quails exposed to heat stress. This explains why birds on the control diet had the shortest ileal villus height while those on Chromium-supplemented diets had higher ileal villus height. This also explains why the Chromium-supplemented birds especially those on diet 3 (25mg/kg) had higher mean values of final weight and weight gain than birds on the control diet as failure to preserve the morphometric integrity of the digestive system in stressed birds compromise the absorption of nutrients (Noy and Sklan, 1999) therefore altering the growth, development and performance of birds.

The jejunal villus height and ileal crypt depth were not affected by the heat stress as it was observed that birds on the control diet had taller jejunal villus height and deeper ileal crypts than birds on the Chromium-supplemented diets. The jejunal crypt depth values too showed no significant differences. It could be that the Chromium levels were not high enough to alleviate the effect of heat stress on the parameters in question. This however corroborates the findings of Marchini *et al.* (2011). The authors investigated the effects of heat stress on the body weight, intestinal length, mucous area, crypt depth, villus height and percentage of cells in proliferation activity in male broiler chickens and found out that heat stress did not influence the of PCNA positive cells, the area of the mucosa, crypt depth and villus height in the jejunum and ileum.

#### V. CONCLUSION

In conclusion, Chromium supplementation of broiler diets exerted some benefits on the performance characteristics. Further studies are however required to investigate the optimum inclusion levels of Chromium in broiler diets and its influence on the intestinal mucosa development.

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**3. Think Like Evaluators:** If you are in a confusion or getting demotivated that your paper will be accepted by evaluators or not, then think and try to evaluate your paper like an Evaluator. Try to understand that what an evaluator wants in your research paper and automatically you will have your answer.

**4. Make blueprints of paper:** The outline is the plan or framework that will help you to arrange your thoughts. It will make your paper logical. But remember that all points of your outline must be related to the topic you have chosen.

**5. Ask your Guides:** If you are having any difficulty in your research, then do not hesitate to share your difficulty to your guide (if you have any). They will surely help you out and resolve your doubts. If you can't clarify what exactly you require for your work then ask the supervisor to help you with the alternative. He might also provide you the list of essential readings.

**6. Use of computer is recommended:** As you are doing research in the field of Computer Science, then this point is quite obvious.

**7. Use right software:** Always use good quality software packages. If you are not capable to judge good software then you can lose quality of your paper unknowingly. There are various software programs available to help you, which you can get through Internet.

**8. Use the Internet for help:** An excellent start for your paper can be by using the Google. It is an excellent search engine, where you can have your doubts resolved. You may also read some answers for the frequent question how to write my research paper or find model research paper. From the internet library you can download books. If you have all required books make important reading selecting and analyzing the specified information. Then put together research paper sketch out.

**9. Use and get big pictures:** Always use encyclopedias, Wikipedia to get pictures so that you can go into the depth.

**10. Bookmarks are useful:** When you read any book or magazine, you generally use bookmarks, right! It is a good habit, which helps to not to lose your continuity. You should always use bookmarks while searching on Internet also, which will make your search easier.

**11. Revise what you wrote:** When you write anything, always read it, summarize it and then finalize it.

**12. Make all efforts:** Make all efforts to mention what you are going to write in your paper. That means always have a good start. Try to mention everything in introduction, that what is the need of a particular research paper. Polish your work by good skill of writing and always give an evaluator, what he wants.

**13. Have backups:** When you are going to do any important thing like making research paper, you should always have backup copies of it either in your computer or in paper. This will help you to not to lose any of your important.

**14. Produce good diagrams of your own:** Always try to include good charts or diagrams in your paper to improve quality. Using several and unnecessary diagrams will degrade the quality of your paper by creating "hotchpotch." So always, try to make and include those diagrams, which are made by your own to improve readability and understandability of your paper.

**15. Use of direct quotes:** When you do research relevant to literature, history or current affairs then use of quotes become essential but if study is relevant to science then use of quotes is not preferable.



**16. Use proper verb tense:** Use proper verb tenses in your paper. Use past tense, to present those events that happened. Use present tense to indicate events that are going on. Use future tense to indicate future happening events. Use of improper and wrong tenses will confuse the evaluator. Avoid the sentences that are incomplete.

**17. Never use online paper:** If you are getting any paper on Internet, then never use it as your research paper because it might be possible that evaluator has already seen it or maybe it is outdated version.

**18. Pick a good study spot:** To do your research studies always try to pick a spot, which is quiet. Every spot is not for studies. Spot that suits you choose it and proceed further.

**19. Know what you know:** Always try to know, what you know by making objectives. Else, you will be confused and cannot achieve your target.

**20. Use good quality grammar:** Always use a good quality grammar and use words that will throw positive impact on evaluator. Use of good quality grammar does not mean to use tough words, that for each word the evaluator has to go through dictionary. Do not start sentence with a conjunction. Do not fragment sentences. Eliminate one-word sentences. Ignore passive voice. Do not ever use a big word when a diminutive one would suffice. Verbs have to be in agreement with their subjects. Prepositions are not expressions to finish sentences with. It is incorrect to ever divide an infinitive. Avoid clichés like the disease. Also, always shun irritating alliteration. Use language that is simple and straight forward. put together a neat summary.

**21. Arrangement of information:** Each section of the main body should start with an opening sentence and there should be a changeover at the end of the section. Give only valid and powerful arguments to your topic. You may also maintain your arguments with records.

**22. Never start in last minute:** Always start at right time and give enough time to research work. Leaving everything to the last minute will degrade your paper and spoil your work.

**23. Multitasking in research is not good:** Doing several things at the same time proves bad habit in case of research activity. Research is an area, where everything has a particular time slot. Divide your research work in parts and do particular part in particular time slot.

**24. Never copy others' work:** Never copy others' work and give it your name because if evaluator has seen it anywhere you will be in trouble.

**25. Take proper rest and food:** No matter how many hours you spend for your research activity, if you are not taking care of your health then all your efforts will be in vain. For a quality research, study is must, and this can be done by taking proper rest and food.

**26. Go for seminars:** Attend seminars if the topic is relevant to your research area. Utilize all your resources.

**27. Refresh your mind after intervals:** Try to give rest to your mind by listening to soft music or by sleeping in intervals. This will also improve your memory.

**28. Make colleagues:** Always try to make colleagues. No matter how sharper or intelligent you are, if you make colleagues you can have several ideas, which will be helpful for your research.

**29. Think technically:** Always think technically. If anything happens, then search its reasons, its benefits, and demerits.

**30. Think and then print:** When you will go to print your paper, notice that tables are not be split, headings are not detached from their descriptions, and page sequence is maintained.

**31. Adding unnecessary information:** Do not add unnecessary information, like, I have used MS Excel to draw graph. Do not add irrelevant and inappropriate material. These all will create superfluous. Foreign terminology and phrases are not apropos. One should NEVER take a broad view. Analogy in script is like feathers on a snake. Not at all use a large word when a very small one would be



sufficient. Use words properly, regardless of how others use them. Remove quotations. Puns are for kids, not grunt readers. Amplification is a billion times of inferior quality than sarcasm.

**32. Never oversimplify everything:** To add material in your research paper, never go for oversimplification. This will definitely irritate the evaluator. Be more or less specific. Also too, by no means, ever use rhythmic redundancies. Contractions aren't essential and shouldn't be there used. Comparisons are as terrible as clichés. Give up ampersands and abbreviations, and so on. Remove commas, that are, not necessary. Parenthetical words however should be together with this in commas. Understatement is all the time the complete best way to put onward earth-shaking thoughts. Give a detailed literary review.

**33. Report concluded results:** Use concluded results. From raw data, filter the results and then conclude your studies based on measurements and observations taken. Significant figures and appropriate number of decimal places should be used. Parenthetical remarks are prohibitive. Proofread carefully at final stage. In the end give outline to your arguments. Spot out perspectives of further study of this subject. Justify your conclusion by at the bottom of them with sufficient justifications and examples.

**34. After conclusion:** Once you have concluded your research, the next most important step is to present your findings. Presentation is extremely important as it is the definite medium through which your research is going to be in print to the rest of the crowd. Care should be taken to categorize your thoughts well and present them in a logical and neat manner. A good quality research paper format is essential because it serves to highlight your research paper and bring to light all necessary aspects in your research.

## INFORMAL GUIDELINES OF RESEARCH PAPER WRITING

### Key points to remember:

- Submit all work in its final form.
- Write your paper in the form, which is presented in the guidelines using the template.
- Please note the criterion for grading the final paper by peer-reviewers.

### Final Points:

A purpose of organizing a research paper is to let people to interpret your effort selectively. The journal requires the following sections, submitted in the order listed, each section to start on a new page.

The introduction will be compiled from reference matter and will reflect the design processes or outline of basis that direct you to make study. As you will carry out the process of study, the method and process section will be constructed as like that. The result segment will show related statistics in nearly sequential order and will direct the reviewers next to the similar intellectual paths throughout the data that you took to carry out your study. The discussion section will provide understanding of the data and projections as to the implication of the results. The use of good quality references all through the paper will give the effort trustworthiness by representing an alertness of prior workings.

Writing a research paper is not an easy job no matter how trouble-free the actual research or concept. Practice, excellent preparation, and controlled record keeping are the only means to make straightforward the progression.

### General style:

Specific editorial column necessities for compliance of a manuscript will always take over from directions in these general guidelines.

To make a paper clear

· Adhere to recommended page limits

Mistakes to evade

Insertion a title at the foot of a page with the subsequent text on the next page

•



- Separating a table/chart or figure - impound each figure/table to a single page
- Submitting a manuscript with pages out of sequence

In every sections of your document

- Use standard writing style including articles ("a", "the," etc.)
- Keep on paying attention on the research topic of the paper
- Use paragraphs to split each significant point (excluding for the abstract)
- Align the primary line of each section
- Present your points in sound order
- Use present tense to report well accepted
- Use past tense to describe specific results
- Shun familiar wording, don't address the reviewer directly, and don't use slang, slang language, or superlatives
- Shun use of extra pictures - include only those figures essential to presenting results

#### **Title Page:**

Choose a revealing title. It should be short. It should not have non-standard acronyms or abbreviations. It should not exceed two printed lines. It should include the name(s) and address (es) of all authors.

#### **Abstract:**

The summary should be two hundred words or less. It should briefly and clearly explain the key findings reported in the manuscript-- must have precise statistics. It should not have abnormal acronyms or abbreviations. It should be logical in itself. Shun citing references at this point.

An abstract is a brief distinct paragraph summary of finished work or work in development. In a minute or less a reviewer can be taught the foundation behind the study, common approach to the problem, relevant results, and significant conclusions or new questions.

Write your summary when your paper is completed because how can you write the summary of anything which is not yet written? Wealth of terminology is very essential in abstract. Yet, use comprehensive sentences and do not let go readability for briefness. You can maintain it succinct by phrasing sentences so that they provide more than lone rationale. The author can at this moment go straight to



shortening the outcome. Sum up the study, with the subsequent elements in any summary. Try to maintain the initial two items to no more than one ruling each.

- Reason of the study - theory, overall issue, purpose
- Fundamental goal
- To the point depiction of the research
- Consequences, including definite statistics - if the consequences are quantitative in nature, account quantitative data; results of any numerical analysis should be reported
- Significant conclusions or questions that track from the research(es)

Approach:

- Single section, and succinct
- As a outline of job done, it is always written in past tense
- A conceptual should situate on its own, and not submit to any other part of the paper such as a form or table
- Center on shortening results - bound background information to a verdict or two, if completely necessary
- What you account in an conceptual must be regular with what you reported in the manuscript
- Exact spelling, clearness of sentences and phrases, and appropriate reporting of quantities (proper units, important statistics) are just as significant in an abstract as they are anywhere else

**Introduction:**

The **Introduction** should "introduce" the manuscript. The reviewer should be presented with sufficient background information to be capable to comprehend and calculate the purpose of your study without having to submit to other works. The basis for the study should be offered. Give most important references but shun difficult to make a comprehensive appraisal of the topic. In the introduction, describe the problem visibly. If the problem is not acknowledged in a logical, reasonable way, the reviewer will have no attention in your result. Speak in common terms about techniques used to explain the problem, if needed, but do not present any particulars about the protocols here. Following approach can create a valuable beginning:

- Explain the value (significance) of the study
- Shield the model - why did you employ this particular system or method? What is its compensation? You strength remark on its appropriateness from a abstract point of vision as well as point out sensible reasons for using it.
- Present a justification. Status your particular theory (es) or aim(s), and describe the logic that led you to choose them.
- Very for a short time explain the tentative propose and how it skilled the declared objectives.

Approach:

- Use past tense except for when referring to recognized facts. After all, the manuscript will be submitted after the entire job is done.
- Sort out your thoughts; manufacture one key point with every section. If you make the four points listed above, you will need a least of four paragraphs.
- Present surroundings information only as desirable in order hold up a situation. The reviewer does not desire to read the whole thing you know about a topic.
- Shape the theory/purpose specifically - do not take a broad view.
- As always, give awareness to spelling, simplicity and correctness of sentences and phrases.

**Procedures (Methods and Materials):**

This part is supposed to be the easiest to carve if you have good skills. A sound written Procedures segment allows a capable scientist to replacement your results. Present precise information about your supplies. The suppliers and clarity of reagents can be helpful bits of information. Present methods in sequential order but linked methodologies can be grouped as a segment. Be concise when relating the protocols. Attempt for the least amount of information that would permit another capable scientist to spare your outcome but be cautious that vital information is integrated. The use of subheadings is suggested and ought to be synchronized with the results section. When a technique is used that has been well described in another object, mention the specific item describing a way but draw the basic



principle while stating the situation. The purpose is to text all particular resources and broad procedures, so that another person may use some or all of the methods in one more study or referee the scientific value of your work. It is not to be a step by step report of the whole thing you did, nor is a methods section a set of orders.

#### Materials:

- Explain materials individually only if the study is so complex that it saves liberty this way.
- Embrace particular materials, and any tools or provisions that are not frequently found in laboratories.
- Do not take in frequently found.
- If use of a definite type of tools.
- Materials may be reported in a part section or else they may be recognized along with your measures.

#### Methods:

- Report the method (not particulars of each process that engaged the same methodology)
- Describe the method entirely
- To be succinct, present methods under headings dedicated to specific dealings or groups of measures
- Simplify - details how procedures were completed not how they were exclusively performed on a particular day.
- If well known procedures were used, account the procedure by name, possibly with reference, and that's all.

#### Approach:

- It is embarrassed or not possible to use vigorous voice when documenting methods with no using first person, which would focus the reviewer's interest on the researcher rather than the job. As a result when script up the methods most authors use third person passive voice.
- Use standard style in this and in every other part of the paper - avoid familiar lists, and use full sentences.

#### What to keep away from

- Resources and methods are not a set of information.
- Skip all descriptive information and surroundings - save it for the argument.
- Leave out information that is immaterial to a third party.

#### Results:

The principle of a results segment is to present and demonstrate your conclusion. Create this part a entirely objective details of the outcome, and save all understanding for the discussion.

The page length of this segment is set by the sum and types of data to be reported. Carry on to be to the point, by means of statistics and tables, if suitable, to present consequences most efficiently. You must obviously differentiate material that would usually be incorporated in a study editorial from any unprocessed data or additional appendix matter that would not be available. In fact, such matter should not be submitted at all except requested by the instructor.

#### Content

- Sum up your conclusion in text and demonstrate them, if suitable, with figures and tables.
- In manuscript, explain each of your consequences, point the reader to remarks that are most appropriate.
- Present a background, such as by describing the question that was addressed by creation an exacting study.
- Explain results of control experiments and comprise remarks that are not accessible in a prescribed figure or table, if appropriate.
- Examine your data, then prepare the analyzed (transformed) data in the form of a figure (graph), table, or in manuscript form.

#### What to stay away from

- Do not discuss or infer your outcome, report surroundings information, or try to explain anything.
- Not at all, take in raw data or intermediate calculations in a research manuscript.

- Do not present the similar data more than once.
- Manuscript should complement any figures or tables, not duplicate the identical information.
- Never confuse figures with tables - there is a difference.

#### Approach

- As forever, use past tense when you submit to your results, and put the whole thing in a reasonable order.
- Put figures and tables, appropriately numbered, in order at the end of the report
- If you desire, you may place your figures and tables properly within the text of your results part.

#### Figures and tables

- If you put figures and tables at the end of the details, make certain that they are visibly distinguished from any attach appendix materials, such as raw facts
- Despite of position, each figure must be numbered one after the other and complete with subtitle
- In spite of position, each table must be titled, numbered one after the other and complete with heading
- All figure and table must be adequately complete that it could situate on its own, divide from text

#### Discussion:

The Discussion is expected the trickiest segment to write and describe. A lot of papers submitted for journal are discarded based on problems with the Discussion. There is no head of state for how long a argument should be. Position your understanding of the outcome visibly to lead the reviewer through your conclusions, and then finish the paper with a summing up of the implication of the study. The purpose here is to offer an understanding of your results and hold up for all of your conclusions, using facts from your research and generally accepted information, if suitable. The implication of result should be visibly described. Infer your data in the conversation in suitable depth. This means that when you clarify an observable fact you must explain mechanisms that may account for the observation. If your results vary from your prospect, make clear why that may have happened. If your results agree, then explain the theory that the proof supported. It is never suitable to just state that the data approved with prospect, and let it drop at that.

- Make a decision if each premise is supported, discarded, or if you cannot make a conclusion with assurance. Do not just dismiss a study or part of a study as "uncertain."
- Research papers are not acknowledged if the work is imperfect. Draw what conclusions you can based upon the results that you have, and take care of the study as a finished work
- You may propose future guidelines, such as how the experiment might be personalized to accomplish a new idea.
- Give details all of your remarks as much as possible, focus on mechanisms.
- Make a decision if the tentative design sufficiently addressed the theory, and whether or not it was correctly restricted.
- Try to present substitute explanations if sensible alternatives be present.
- One research will not counter an overall question, so maintain the large picture in mind, where do you go next? The best studies unlock new avenues of study. What questions remain?
- Recommendations for detailed papers will offer supplementary suggestions.

#### Approach:

- When you refer to information, differentiate data generated by your own studies from available information
- Submit to work done by specific persons (including you) in past tense.
- Submit to generally acknowledged facts and main beliefs in present tense.

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Topics	Grades		
	A-B	C-D	E-F
<i>Abstract</i>	Clear and concise with appropriate content, Correct format. 200 words or below	Unclear summary and no specific data, Incorrect form  Above 200 words	No specific data with ambiguous information  Above 250 words
<i>Introduction</i>	Containing all background details with clear goal and appropriate details, flow specification, no grammar and spelling mistake, well organized sentence and paragraph, reference cited	Unclear and confusing data, appropriate format, grammar and spelling errors with unorganized matter	Out of place depth and content, hazy format
<i>Methods and Procedures</i>	Clear and to the point with well arranged paragraph, precision and accuracy of facts and figures, well organized subheads	Difficult to comprehend with embarrassed text, too much explanation but completed	Incorrect and unorganized structure with hazy meaning
<i>Result</i>	Well organized, Clear and specific, Correct units with precision, correct data, well structuring of paragraph, no grammar and spelling mistake	Complete and embarrassed text, difficult to comprehend	Irregular format with wrong facts and figures
<i>Discussion</i>	Well organized, meaningful specification, sound conclusion, logical and concise explanation, highly structured paragraph reference cited	Wordy, unclear conclusion, spurious	Conclusion is not cited, unorganized, difficult to comprehend
<i>References</i>	Complete and correct format, well organized	Beside the point, Incomplete	Wrong format and structuring

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