

Spectrophotometric Determination of Chromium (III) Ion By 6-[(*E*)-(1,5-Dimethyl-3-Oxo-2-Phenyl-2,3-Dihydro-1*H*-Pyrazol-4-yl)Diazenyl]-1*H*-Indole-2,3-Dione

Eledalachi Evans Chinyere*, Oziri Pius Ukoha and Chukwudi Jude Okenwa

Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka, Enugu State, Nigeria

Abstract:- In the present paper, a new method is proposed for the spectrophotometric determination of chromium (III). The ligand; 6-[(*E*)-(1, 5-dimethyl-3-oxo-2-penyl-2, 3-dihydro-1*H*-pyrazol-4-yl)diazenyl]-1*H*-indole-2,3-dione was synthesized by coupling diazotized 1-phenyl-2,3-dimethyl-4-aminopyrazole-5-one and 1*H*-indole-2,3-dione. It formed coloured complex with Cr (III). The ligand and complex were characterized via UV, IR and NMR spectroscopy. The analytical data show that Cr(III) formed complex, with 2:1 metal-ligand stoichiometry when reacted with the ligand respectively. Cr(III) was determined spectrophotometrically by measuring the absorbance at 446.4 nm. Beer's law was valid between 0.15-1.18 ppm, with calibration and analytical sensitivities of 0.059 and 59.00 ppm respectively. Very few elements were found to interfere in the method. The method is quite simple and useful; its applicability has been tested by the analysis of solder, steel and brass.

Keywords: 4-aminoantipyrine; isatin; spectrophotometry; chromium (III); alloys

I. INTRODUCTION

Chromium, like tin and lead, belongs to those trace heavy metals that are of major interest in environmental protection, due to their toxicity¹. It is extremely important in the environmental, biological, agricultural, foods and industrial processes. Chromium occurs as a result of industrialization in manufacturing processes, causing significant contaminations in air, dust, soil, water, sediments, food, etc. The resultant pollution of chromium comes from many sources, such as coal burning power plants, refineries, run off from factories and industrial wastes. It also enters the environment from such sources as automobile exhausts, and water run-off from mining operations. The determination of chromium in environmental samples plays an important role in the monitoring of environmental pollution and the associated health hazards to both terrestrial and aquatic lives².

Most of the metal ion determinations require extraction using an organic solvent, surfactants or even fierce toxic cyanide as a masking agent to increase sensitivity or selectivity².

In this work, an azo chromogenic, reagent derived from isatin and 4-aminoantipyrine is used for the spectrophotometric determination of Cr(III). The choice of the

reagent; 6-[(*E*)-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)diazenyl]-1*H*-indole-2,3-dione, herein referred to as 'DPDD' is prompted by the growing importance of the 4-aminoantipyrine based reagents and their metal complexes in coordination and analytical chemistry³⁻⁸. Different classical and instrumental techniques have been used to determine chromium as a metal, but they are very expensive, readily unavailable and require high cost of maintenance. Secondly, instrumental method like atomic absorption spectrophotometry (AAS) is very sensitivity and highly selective in chromium determination, but does not give the needed information about chromium (III) as found in chromium (metal)^{9,10}. AAS does not take cognizance of complexation studies of metal ions, since the determination of the ions is based on the formation of light absorbing coloured complexes with an organic reagent (ligand).

There is therefore the need for a serious search as very few reagents have been reported for the determination of metal ions by a suitable method other than AAS¹¹⁻¹⁵.

We have examined the complexing-and ion discriminating ability of DPDD in the formation of metal complexes^{16,17}. It forms a very stable complex with chromium (III)^{18,19}. Although DPDD have been synthesized and used for the antimicrobial studies of some complexes^{20,21,22}, there is no report in the literature concerning the analytical application with chromium. In this present paper we report the viability of DPDD in spectrophotometric determination of chromium (III) in solder, steel and brass without any extraction procedure.

The optimum and fundamental conditions of Cr(III)-DPDD complex formation were established as precursor to the application in these samples. This method can be applied to several simple and complex samples. It is rapid, selective and sensitive.

II. EXPERIMENTAL

2.1 Apparatus and reagents

A UV visible spectrophotometer (model; Jenway 6305) with a quartz cuvette of 1.0 cm path length was used. Analytical grade reagents were used without further purification. A stock solution of chromium (III) was prepared

by dissolving 0.0700 g of chromium (III) nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) (99 %; British Drug House, England) in distilled water and made up to mark in a 50.0 cm^3 volumetric flask. It was found to contain 0.0036 M chromium (III).

2.2 Synthesis and spectral characteristics of DPDD

DPDD was synthesized according to reported methods²¹⁻³⁰. 0.1218 g of 4-aminoantipyrine (0.0006 M) was dissolved in 1.0 cm^3 of conc HCl (37 %) in 5.0 cm^3 of distilled water, and was diazotized with NaNO_3 solution (0.060 g) in 2.0 cm^3 of distilled water below 5.0°C. The resulting diazotized 4-aminoantipyrine was immediately poured into a mixture of 0.0882 g of isatin (0.0006 M) and 2.5000 g of sodium acetate (0.3050 M) in 30.0 cm^3 distilled water, using mechanical stirring at ice temperature. Full detail of the syntheses and spectral characteristics of DPDD and its Cr(III) complex is available elsewhere³⁶.

2.3 Preparation of the alloys (solder, steel brass)

1.0 g of a given alloy was taken to which 25-30 cm^3 of aqua regia was added and the mixture heated gently till the alloy decomposed completely. Then conc. HCl was added in installments of 4.0 cm^3 . The solution was evaporated to dryness. The residue was dissolved in 10 M HCl (20 cm^3) and diluted to 1 dm^3 for 1000 ppm of the alloy. Lower concentrations of the solution were obtained by serial dilution. Chromium concentration was determined in the solutions of the alloys using flame AAS method.

2.4 Generation procedure

An aliquot of a standard solution of Cr(III) was transferred into a 20 cm^3 test tube. The pH was adjusted to 5.0 with hydrogen phthalate/sodium hydroxide buffer. Distilled water was added, followed by the addition of the appropriate amount of DPDD to react under a given concentration in a total volume of 5.0 cm^3 for 45 minutes at 40 °C. The absorbance measurement was taken at 446.4 nm in a 1.0 cm quartz cuvette using mixture of the buffer and distilled water as blank.

III. RESULT AND DISCUSSION

3.1 Composition of Cr(III)-DPDD complex

As reported elsewhere³⁶, the absorption spectrum of the Cr(III) – DPDD complex against reagent blank in ethanol, under optimum conditions showed maximum absorption at 446.4 nm for the pale-red complex. Thus all measurements were made at this wavelength.

The stoichiometry of the Cr(III)-DPDD complex was investigated by the slope-ratio method. 7.20×10^{-4} M solution of Cr(III) was fixed (excess) in a reaction with varying amounts of the ligand, ranging from 7.20×10^{-5} to 5.04×10^{-4} M concentration. In a later experiment, a fixed (excess) concentration of the ligand reacted with varying amount of Cr(III). The ratio of the slopes of the absorbance (at 446.4 nm) values plotted against the corresponding concentrations for the

two sets of observations showed that Cr(III) to ligand (DPDD) mole ratio obtained is 2:1. The plots are shown in Figures 1 and 2 respectively.

3.2 Effect of Time on the formation of Cr (III)-DPDD complex

The variation of absorbance with time in the formation of Cr (III)-DPDD complex was investigated by measuring the absorbance at different intervals between 30 seconds and 60 minutes. The reaction between 7.20×10^{-4} M and 3.60×10^{-4} M of Cr(III) and DPDD respectively exhibited maximum absorbance of 0.478 after 45 minutes of the reaction. Therefore, 45 minutes was taken as the optimum time required for the reaction to take place under the prevailing conditions, and was used all through the determination of Cr(III). The plot is shown in Figure. 3

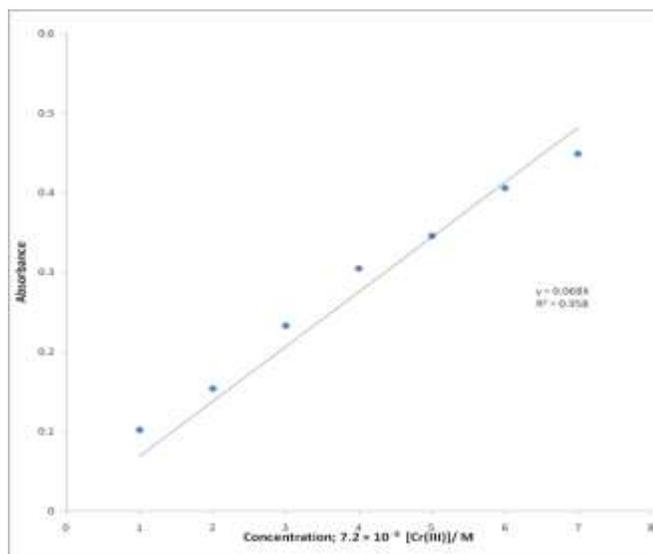


Fig: 1. Slope-Ratio Plot for Cr(III) Complex at Fixed Ligand concentration (7.2×10^{-4} M)

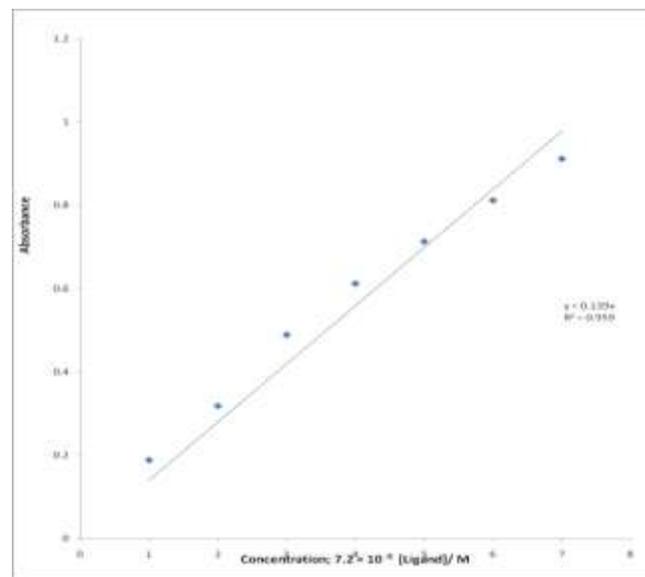


Fig: 2. Slope- Ratio Plot for Cr(III) Complex at fixed Metal concentration (7.2×10^{-4} M)

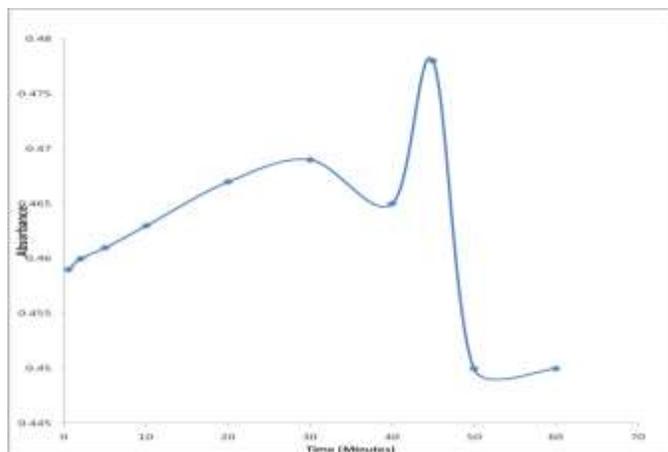


Fig. 3. Effect of Time on the Formation of Cr(III) Complex

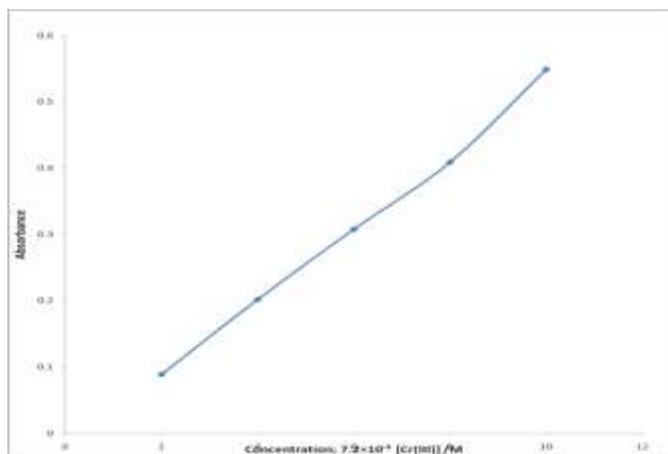


Fig. 4. Effect of the Concentration of the DPDD on the formation of Cr(III) Complex

3.3 Effect of the Concentration of DPDD on the formation of the Cr(III) complex.

Fig. 4 shows the effect of DPDD concentration on the formation of Cr(III)-DPDD complex. The influence of the DPDD concentration on the absorbance signal of the complex was studied with a fixed amount of Cr(III) (1.44×10^{-4} M) and DPDD from 1.44×10^{-4} to 7.20×10^{-4} M. The results show that absorbance increases with increasing amount of DPDD up to 7.20×10^{-4} M. This however suggests that the concentration of DPDD should be at least 5 times more than that of Cr(III). Thus 7.20×10^{-4} M DPDD concentration was decided upon as being the required amount necessary to obtain a Cr(III) complex.

3.4 Effect of Temperature on the formation of Cr(III)-DPDD complex

The effect of temperature on the absorbance of the complex was studied between 30° and 70 °C. 7.20×10^{-4} M DPDD was reacted with 1.44×10^{-3} M Cr(III) in a thermostated water bath for 45 minutes. The graph depicted in Fig. 5 shows that the absorbance is dependent on temperature. Maximum absorbance of 0.636 was obtained at 40 °C, and was

maintained all through the determination of Cr(III). The study on the variation of absorbance of Cr(III)-DPDD complex did not go beyond 70 °C, because above the temperature, certain physical conditions which are not within the framework of the study could rise up.

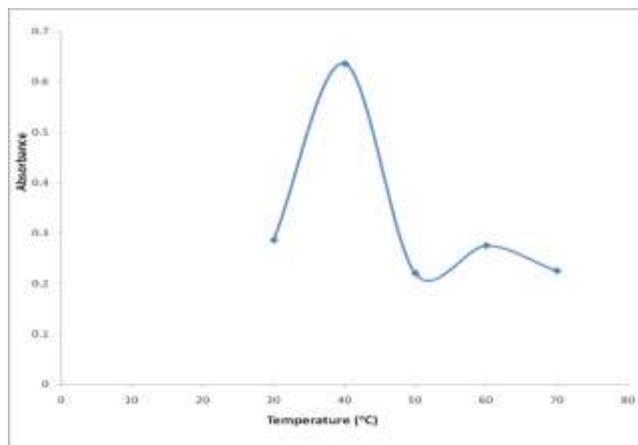


Fig. 5. Effect of Temperature on the Formation of Cr(III) Complex

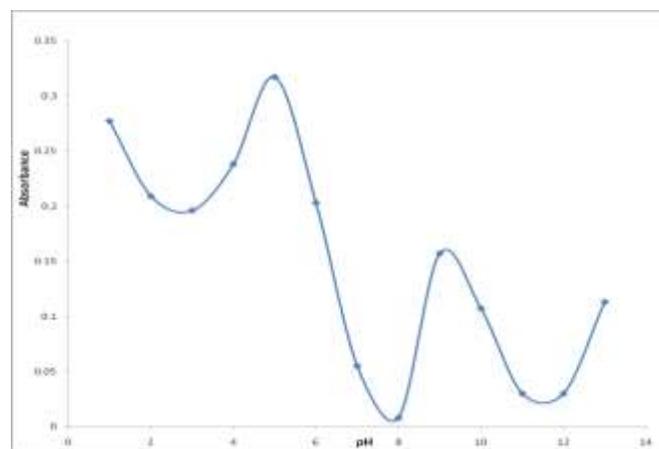


Fig. 6. Effect of pH on the Formation of Cr(III) Complex

3.5 Effect of pH on the formation of Cr(III)-DPDD complex

The effect of pH on the absorption of the complex was studied at 446.4 nm by measuring the absorbance of 1.44×10^{-3} M Cr(III) with 7.20×10^{-4} m solution of the ligand over the pH range of 1 - 13. A graph was plotted of absorbance values against pH (Fig.6), which show a maximum absorbance against pH (Fig.6), which show a maximum absorbance of 0.317 at pH 5.0. All through the studies, a potassium hydrogen phthalate/sodium hydroxide buffer of pH 5.0 was used. This result suggests that Cr(III)-DPDD complex could be acidic.

3.6 Effect of some interfering ions on the determination of Cr(III)

Under optimum conditions of the procedure, the selectivity of the proposed method was investigated by the determination of a fixed amount of Cr(III) (1.14 ppm) in the presence of a series of cations that could as well form similar

complex with DPDD. These ions were chosen due to their occurrence in alloys in which chromium III is also present. The absorbance was compared with the absorbance of the complex in the absence of foreign ion and percentage interference calculated. The limiting value of concentration of the foreign ion was taken as that which caused an error in the absorbance corresponding to twice the standard deviation of the absorbance of the Cr(III)-DPDD complex. The results are summarized in Table I.

In the determination of Cr(III)-DPDD complex, the mean absorbance obtained for six determinations was 0.051 ± 0.049 . The tolerance limit was set as the amount of foreign ion causing an error of $\pm 10\%$ in the absorbance of Cr(III)-DPDD complex. The main interferences observed were Mg(II); Fe(III) and Zn(II), Ca(II) and V(V), tolerable in the range of 0.18-0.36 ppm and 0.16-0.48 ppm respectively. The interference of these ions were checked by masking and/or pre-extraction (where applicable) in the direct determination of Cr(III) in various alloys. KCN was used to enhance selectivity and for the pre-extraction of Fe(III) in steel.

Table I. Effect of some interfering ions on Cr(III) Complex

Ion Added	Concentration (ppm)	Absorbance	Interference Level (%)
Mg ²⁺ added as MgO	0.78	0.089	+74.51
	0.90	0.096	+88.23
	1.02	0.077	+50.98
	1.14	0.110	+115.69
	1.28	0.103	+101.96
	1.38	0.109	+113.73
	1.50	0.060	+17.70
Ca ²⁺ added as CaSO ₄	0.18	0.047	-7.84
	0.36	0.047	-7.84
	0.72	0.052	+1.96
	1.10	0.035	-31.37
	1.44	0.080	+56.86
	1.80	0.042	-19.61
	2.16	0.080	+56.86
Fe ³⁺ added as FeCl ₃	0.24	0.009	-82.40
	0.48	0.030	-41.20
	0.72	0.074	+45.10
	0.96	0.117	+129.41
	1.20	0.166	+225.50
	1.44	0.218	+327.50
	1.68	0.158	+209.80
V ⁵⁺ added as NH ₄ VO ₃	0.16	0.056	+9.80
	0.48	0.057	+11.76
	0.80	0.184	+260.80
	1.12	0.328	+543.14
	1.44	0.393	+670.60
	1.76	0.495	+870.60
	2.08	0.577	+1031.40
Zn ²⁺ added as ZnO	0.12	0.090	+76.47
	0.36	0.079	+54.90
	0.60	0.092	+80.39
	0.84	0.036	-29.41
	1.08	0.068	-33.33
	1.32	0.047	-7.84
	1.56	0.007	-86.28
1.80	0.115	+125.50	

3.7 Analytical characteristics of the method

A calibration curve was prepared according to the general procedure described in the experimental, section 2.4. The Cr(III)-DPDD complex obeys Beer's law between the concentration ranges of 0.148-1184 ppm. The calibration curve which was constructed under the prevailing conditions is shown in Fig.8. The molar absorptivity of 7.20×10^{-4} M Cr(III)-DPDD complex in ethanol was 1.25×10^3 l mol⁻¹ cm⁻¹ at 446.4 nm.

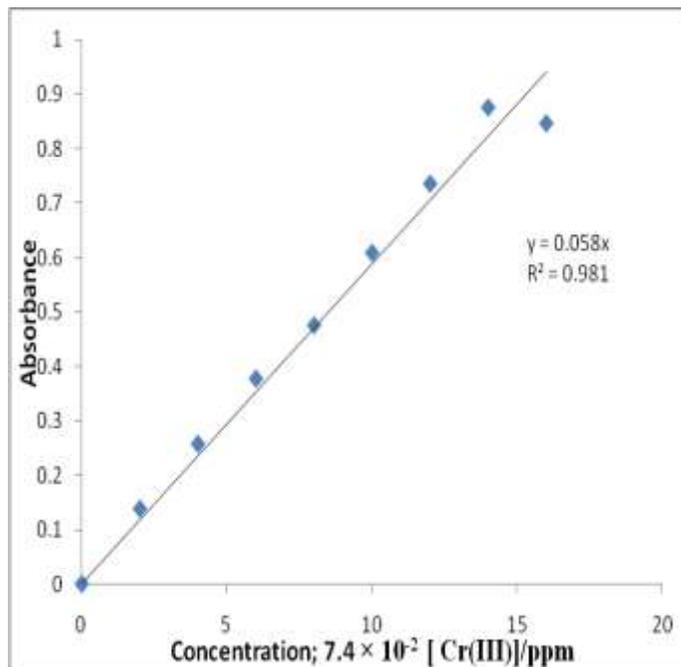


Fig: 8. Calibration Curve of Cr(III) Complex.

The analytical sensitivity, calibration sensitivity, limit of detection and limit of quantification as well as other analytical characteristics are summarized in Table II.

Table: II. Analytical characteristics of the procedures

Characteristic	Value of Cr(III) Complex
λ_{max} (nm)	446.4
Molar absorptivity (l mol ⁻¹ cm ⁻¹)	1250
Calibration sensitivity, m (ppm)	0.059
Analytical sensitivity: m/S _A (ppm)	59.00
Limit of detection, C _L ; 3S _A (ppm)	0.04
Limit of quantification, C _Q ; 10S _A (ppm)	0.13
Linear dynamic range, (ppm)	0.15 – 1.18
Coefficient of variation (%)	1.34

S_A = standard deviation of the blank;

3.8 Application to the analysis of alloys (solder, steel and brass)

An aliquot of the solutions of various alloys already analyzed by flame AAS was taken and the content of Cr(III)

in each case determined spectrophotometrically, under the prevailing conditions according to the general procedure. The concentration of the Cr(III) was extrapolated from the calibration curve. Table III summarizes the results obtained for the determination of Cr(III) in the various alloys with DPDD.

Table: III. Determination of Cr(III) in Solder, Steel and Brass with the Reagent

Sample	Amount added (ppm)	Amount found (ppm)	Recovery (%)	RSD (n=3)
Solder I	2.846	1.817	63.40	±6.00
Solder II	8.538	5.026	58.86	±1.00
Solder III	14.23	7.929	55.72	±1.00
Steel I	1.596	1.138	71.23	±4.00
Steel II	4.788	3.107	64.89	±2.00
Steel III	7.980	5.059	63.40	±1.00
Brass I	0.660	0.577	87.46	±3.00
Brass II	1.980	2.020	102.04	±1.00
Brass III	3.300	3.158	95.69	±1.00

The above results show that the direct determination of Cr(III) in Brass gave a very good recovery at concentrations above 0.660 ppm. It is evident that the nature of solder and steel could have effect on the selectivity of the method despite the stability of the Cr(III)-DPDD complex³¹. It appears that a prior separation of Cr(III) before determination in brass and steel is necessary. The ability of the method to determine small amounts of Cr(III) has been testified, and tells more about its sensitivity advantage over the flame atomic spectrophotometric method (which of course is not able to quantify the actual amount of various chromium ions present in the samples. Therefore, no firm quantitative comparison of the selectivity of the present method is possible with AAS due to differences in the methods used for their assessment³¹.

IV. CONCLUSION

DPDD and its Cr(III) complex have been successfully synthesized. Cr(III) was determined after establishing the required parameters, and adjusting the conditions of the sample. Interferences were masked with KCN, and absorbance measured at 446.4 nm under the optimum conditions already established for the Cr(III)-DPDD complex. The applicability of the proposed method has been evaluated by its application to the direct determination of Cr(III) in samples of solder, steel and brass previously analyzed by flame AAS. No extraction procedure was required in the study. The proposed method has proved to be promising in the analysis of simple and complex samples. It is rapid, selective and sensitive.

ACKNOWLEDGEMENT

The authors are grateful to the Best Analchem & Scientific Practices (Nig) Ltd, the Joint Development Authority of Nigeria and Sao-Tome & Principe and the Petroleum Technology Development Fund of Nigeria (PTDF) for the scholarships awarded to Eledalachi Evans Chinyere.

REFERENCES

- [1]. United State Environmental Protection Agency (2001). Toxic release inventory. www.epa.gov/lawsadregs/lead/pb.factsheet.pdf.
- [2]. Saba, S., Ali, H., Abdolhossein, P., Babak, G. and Sina, S. (2011). Determination of trace amounts of lead using the flotation-spectrophotometric method. *Analytical chemistry insight*. 6:15-20.
- [3]. Raman, N., Thalamuthu, S., Dhavedhuraja, J., Neclakandam, M.A. and Sharmila, B. (2008). DNA cleavage and antimicrobial activity studies on transition metal (II) complexes of 4-aminoantipyrine derivatives. *J. Chil.Com. Soc.* 53-1128-1133.
- [4]. Hitoshi, T., Tamao, N., Hideyuki, A., Manabu, F. and Takayuki, M. (1977). Preparation and characterization of novel cyclic tetranuclear manganese (III) complexes. *Polyhedron*. 16:3787-3792.
- [5]. Raman, N., Raja, J.J., Joseph, J. and Raja. J.D. (2009). Molecular designing, structural elucidation and comparison of the cleavage ability of oxovanadium (IV) Schiff basic complexes. *J. Chil. Chem. Soc.* 52:1099-1103.
- [6]. Vogel, A.I. (1997). A textbook of qualitative inorganic analysis. Longman, London. 605-629.
- [7]. Argarago, W.L.F., and Perin, D.D. (1942). Purification of laboratory chemicals. Butter worth. Hennaumaun.
- [8]. Suresh, M.S. and Prakash, V. (2010). Preparation and characterization of Cr(III), Mn(II), Co(III), Ni(III), Cu(II), Zn(II) and Co(II) chelates of Schiff base derived from vanillin and 4-aminoantipyrine. *Int. J. Phys. Sci.* 14:2203-2211.
- [9]. Skoog, D.A., Holler, F.J. and Crouch, S.R. (2008). Instrumental analysis. Cengage learning. India.
- [10]. Brian, S.F., Anthony, J.H., Peter, W.G.S. and Austin, R.T. (1989). Vogel's textbook of practical organic chemistry. Longman.
- [11]. Stoyanova, A.M. (2005). Catalytic-spectrophotometric determination of chromium. *Turkish. J. Chem.* 29:367-375.
- [12]. Barceloux, D.G. and Barceloux, D. (1999). Chromium, clinical toxicology and informal healthcare. *J. Toxicol. Clin. Toxicol.* 37: 173-194.
- [13]. Mertz, W. and Roginski, E.E. (1998). Essential of chromium for human nutrition and health. *J.Am. Coll. Nutri.* 17:544-547.
- [14]. Lee, J.A. (1996). Concise inorganic chemistry. Blackwell science. United kingdom. 5th edition.
- [15]. Johnson, E.I. and Polhill, R.D.A. (1955). The use of sodium hexametaphosphate in the determination of traces of lead in food. *Analyst*. 80:364-368.
- [16]. Sankhala, D.S., Mathur, R.C. and Mishra, S.N. (1980). Interaction of Schiff base derived from 4-aminoantipyrine. *India. J. chem.* 194:75-78.
- [17]. Akimov, V.K. and Busev, A.I. (1971). Complex compound of antipyrine and some of its derivatives. *zurnal analitiche Skoi Khimii*. 26:134-142.
- [18]. Shvenkheimer, M.G.A. (1996). The literature of heterocyclic chemistry Heterocyclic. *Compd.* 32:249-251.
- [19]. Jose, S.C., Garcia, T.M.S., Sanchez, A., Sordo, J. and Toueeda, A. (2007). Coordination modes of 5-pyrazolones-a solid state overview. *Coordination chemistry review*. 251:1561-1589.
- [20]. Agbo, J.N. (2010). Synthesis, characterization and preliminary antimicrobial activities of some azo ligands derived from 4-aminoantipyrine and their Co(II), Fe(III), and Os(VIII) complexes. M.Sc project report. University of Nigeria, Nsukka. 1-120.
- [21]. Agbo, N.J. and Ukoha, P.O. (2010). Synthesis, characterization and biological activities of some azo ligands and their metal complexes: 1:1,2-dihydroxy-1,5-dimethyl-4-[(E)-(2,3,4-trihydroxylphenyl)-3H-pyrazol-3-one (H₃L) and its Co(II), Fe(III) and Os(VIII) complexes. *Int.J. Chem.* 20: 217-225.
- [22]. Ukoha, P.O. and Agbo, N.J. (2012). Synthesis, characterization and biological activities of some azo ligands and their metal complexes III: 1,2-dihydro-4-[(E)-(3-hydroxy-4-phenyldiazonyl)-1-naphthalenyl]-1,5-dimethyl-2-phenyl-3H-pyrazol-3-one(HL) and its Co(II), Fe(III) and Os(VIII) complexes. *Int. J. Chem.* 22:281-289.
- [23]. Heinosuka Yasuda (1967). Infrared analysis of 2-pyrazol-in-5-one derivatives. *Applied spectroscopy*. 23:1969.

- [24]. Herzfeld, R. and Nagy, P. (1999). Organic compounds. Spectrosc. Lett. 32:57-71.
- [25]. Raman, N., Raja, S.J. and Sakthivel, A. (2009). Transition metal complexes with Schiff base ligands. J. Coord. Chem. 62:10, 691-709.
- [26]. Salman, S.R., Mahmoud, A.A.K. and Kamounah, F.S. (1998). Substitution and solvent effect of some substituted hydroxyl Schiff bases. Metals. 97:97-104.
- [27]. Neelamma, M. Rao, V.O. and Anuradha, G.H. (2011). Synthesis and structural studies on transition metal complexes derived from 4-hydroxy-4-methyl-2-pentanone-1H-benzimidazol-2-yl-hydrazone. E.J. Chem. 8:29-36.
- [28]. Robert, T.M. and Robert N.B. (1997). Organic chemistry. Prentice Hall. India 6th edition.
- [29]. Nasreen, R.J, Rana, S.A. and Yasmeen, A.A. (2011). Synthesis and spectral study of new azo-methane dyes and its copper (II) complexes derived from resorcinol-4-aminobenzoyl and 4-aminoantipyrine. J. Al. Nahrain. 14:50-56.
- [30]. El. Saied, F.A., Ayad, M.I., Issa, R.M. and Ally, S.A. (2001). Synthesis and characterization of Fe(III), Co(II), Ni(II), and Cu(II) complexes of 4-formylaxoaniline antipyrine. Polish. J. Chem. 75:774-775.
- [31]. Bahruddin Saad and Sala, M.S. (1995). Extraction-spectrophotometric determination of mercury(II) using thiocrown ethers and bromocresol green. Talanta. 42:1349-1354.
- [32]. Kanaev, N.A. (1963). The synthesis of the condensation products of certain aldehydes and antipyrine and their oxidation by tetravalent cerium salts. Zhurnal analiticheskoi Khimii. 18(5): 575-584.
- [33]. Johnson, E.I. and Polhill, R.D.A. (1955). The use of sodium hexametaphosphate in the determination of traces of lead in food. Analyst. 80:364-368.
- [34]. Chinyere, Evans .E. (2013). Spectrophotometric determination of chromium (III), tin(IV) and lead (IV) ions by 6-[(E)-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)diazenyl]-1H-indole-2,3-dione. M.Sc thesis. University of Nigeria, Nsukka. 1-122.
- [35]. Rao, A.L.J., Malik, A.K., Lata, P. and Mehta, S.K. (2005). Spectrophotometric determination of chromium (III) after extraction of its N-methylaniline carbodithioate complex into molten naphthalene. Electron. J. Environ. Agric. Food Chem. 4: 1005-1009.
- [36]. Chinyere, E.E., Ukoha, P.O., Agbo, J.N and Obasi, L.N(2018). Electrical conductivity, electronic absorption, IR and NMR studies on Cr(III), Sn(IV) and Pb(IV) complexes of an azo ligand derived from isatin and 4-aminoantipyrine. Nigerian journal of chemical research. 23(2):71-82.