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SYNTHESIS, CHARACTERIZATION AND EVALUATION OF GLUTARALDEHYDEPHENYL HYDRAZONE AS A CHROMOGENIC REAGENT FOR SPECTROPHOTOMETRIC DETERMINATION OF SELECTED TOXIC HEAVY METALS (PB, CR, CD AND AS) IN WATER, ENVIRONMENTAL AND BIOLOGICAL SAMPLES.

Echioda Samuel[1], Ekanem E.O[1a]., Chindo I.Y[1b]. and Kolo A. M[1c]

[1]*Department of Science Laboratory Technology, Federal College of Agricultural Produce Technology Kano, Nigeria.*
1abc *Chemistry Department, Abubakar Tafawa Balewa University Bauchi, Bauchi State.*

Corresponding author; samechioda@yahoo.com

ABSTRACT

The work involves the synthesis, characterization and evaluation of glutaralaldehydephenyl hydrazone as a chromogenic reagent in the UV/Vis spectrophotometric method for the determination of selected heavy metals in water, biological and environmental samples. The hydrazone was synthesized by single step condensation method. The product yield was 79.0% with melting points 129-131ºC, the nitrogen content yield was 18.91%. The infrared spectra data obtained from the measurement of glutaraldehydephenylhydrazone showed characterized absorptions bands in regions around 3492.5, 3451 due to –NHR groups. And stretches at 3085 and 1604 due to =CH and C=N respectively. The nuclear magnetic resonance (^{13}C-NMR) spectrum showed peaks around 111.0-141.0 due to aromatic carbon atom, 129.3 ppm due to cyano carbon atom and 40.0, 39.2 and 31.7ppm due to the three methylene carbons. The ^{1}HNMR spectrum revealed peaks at 1.64-1.69 ppm due to the multiplet –CH_2- protons, 2.214-2.386 ppm due to quartet –CH2- protons. 7.331-7.345 ppm due to =CH protons, 7.015 ppm due to –NH signal and 6.59-7.34 ppm due to aromatic protons. The Evaluation of the analytical properties of synthesized glutaraldehydephenylhydrazone (GPH) on the metals (Cd, As, Pb, and Cr), the reagent GPH revealed a wavelength range of between 360.0 (Cr) to 395.0 nm for (Pb and As) as maximum absorption at a working pH of 6.5 to 7.5 room temperature (37°C). The reagent had a molar absorptivities (L mol^{-1} cm^{-1}) ranging from 2.213 x 10^4 (Pb) to 2.460 x 10^4 (As), a mole ratio of metal to ligand of 2:1, a detection limit (µg/g) ranging from 0.3432 (As) to 0.5250 (Pb) and the metal-ligand complex was stable for 0-48 hours. The reagents had a Beer's law validity range (mgL^{-1}) of 0.001 to 100. The preliminary investigations of GPH as possible chelating reagents for the UV-Vis spectrophotometric determination of lead (Pb) on waste water and waste water soil from tannery was carried out, and the result were compared with results from Atomic absorption spectroscopy (AAS) methods. The results obtained were satisfactory with good precision for the GPH methods.

INTRODUCTION

The detection of metals and metal ions, especially transition metals both in solution and in solid materials is of increased concern as a result of increased environmental pollution worldwide. Metals play an important role for biological activities of all living organisms in a proper balance. Transition metals deficiency causes many clinical disorders and physiological abnormalities in the human body. Some metal ions may cause serious health problems and toxicity to humans, animals as well as to plants. Researchers were able to resolve many industrial and biological problems with the aid of complexation of metal ions (Ahmed and Chowdhury, 2014). The greatest use of spectrophotometry lies in its application to quantitative measurements. The reason for this stem from the ease with which most spectrophotometric measurements can be made, their sensitivity, precision, the relatively low cost of instrument purchase and operation. A molecule or an ion exhibits absorption in the visible or ultra-violet region when the radiation causes an electronic transition in molecules containing one or more chromophoric groups. The colour of a molecule may be identified by substituents called auxochromic groups, which displace the absorption maxima towards longer wavelength (bathochromic shift). The colour determining factors in many molecules is the introduction of conjugated double bonds by means of electrons donor and electron acceptor groups (Krishna and Devi 2012). Hydrazones have interesting analytical properties due to the presence of several potential coordination sites. Also hydrazones have attracted much attention as analytical reagents, their applications as photometric and fluorimetric analytical reagents for the determination of metal ions, have been reviewed. The formation of a highly fluorescent chelate through the combination of a metal ion and an organic ligand has often proved to be sensitive and specific method for the determination of metal ions particularly those which are difficult to measure by atomic absorption spectroscopy (Kaylentis, 1988).

Organic reagents containing the atomic arrangement namely hydrazones have been widely used for the spectrophotometric determination of metal ions because of their great complexing capability to form coloured complexes with transition metal ions. Compounds capable of behaving as tridentate chelating agents, considering the donor atoms involved and the steric restrictions imposed can be selective in their reactions with metals ions, such ligands show significant possibilities as analytical reagents. This work is aimed Synthesis, Characterization and Evaluation of Glutaraldehydephenyl hydrazone as a Chromogenic reagent for Spectrophotometric determination of selected toxic heavy metals (Pb, Cr, Cd and As) in Water, Environmental and Biological Samples

MATERIALS AND METHOD

All absorbance measurements were made on a U/V-Vis spectrophotometer matched with a 1cm quartz cell, (Model-1800) double beam Jenway (England, UK). An air-acetylene Atomic Absorption spectrophotometer (AAS) for comparing results. A pH meter (Hanna, U.S.A) with combination of electrodes, A Shimadzu (Model-prestige 21) FTIR spectrophotometer, range 7500-350 cm^{-1} to record FTIR spectrum, An Agilent-NMR-vnmrs 400.

Reagents: The following reagents were used: N,N-dimethylformamide, 1,4-Dioxane**,** Dimethyl sulfoxide **,** Potassium dichromate**,** Universal Buffer, Cadmium chloride**,** glutaraldehyde, Phenyl hydrazine, Lead nitrate, Arsenic trioxide.

Preparation of buffer solutions

Desired pH buffers were prepared by dissolving 1.0 M sodium acetate and 0.1M hydrochloric acid (pH 0.5 - 3.0), 0.2 M sodium acetate and 0.2 M acetic acid (pH 3.5 - 6.0), 1.0 M sodium acetate and 0.2 M acetic acid (pH 6.5 - 7.5), 2 M Ammonia and 2 M ammonium chloride (pH 8.0 - 12.0) buffer solutions were all prepared in distilled water. Equal volumes of these solutions were mixed to get the desired and adjusted pH (Deepa *el. at*., 2014). All metals shows maximum and constant colour development in basic phosphate buffer medium pH range 6.5 - 7.5

Determination of working pH range

In a series of 10.0 cm^3 volumetric flaks, 2.0 cm^3 solution (1.0×10^{-4} M), of the salt of metal of interest, 2.0 cm^3 of the hydrazone solution (1.0×10^{-4} M) and 4 cm^3 of the buffer of varying pH were added and made up to the mark with deionised water and the absorbance were measured against the ligand blank at a determined wavelength. A plot was then made between absorbance and pH in the UV-Vis range. The pH with the highest absorbance was determined as the working pH for each metal of interest (Nityananda *et al.*, 2015).

Determination of solubility of the ligands

The solubility of the glutaraldehydephenylhydrazone was tested in different organic and aqueous solvents. The organic solvent tested and yielded were N, N-dimethylformamide (DMF), demithyl sufoxide (DMSO) and 1, 4-dioxane.

Solutions for spectrophotometric determination

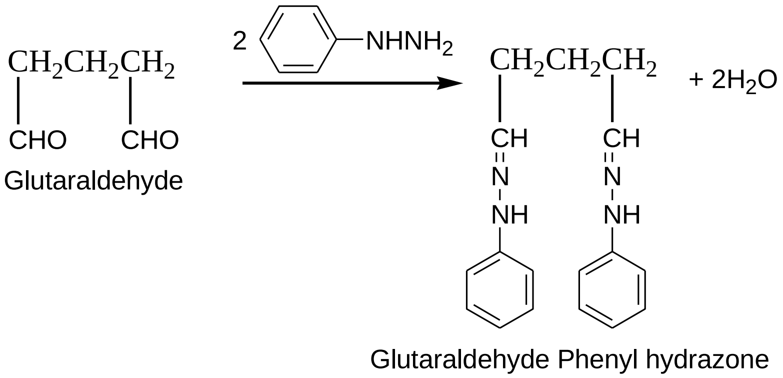
Standard stock solutions of the metals of interest (1000 ppm), of Pb, Cd, As, and Cr were prepared by dissolving requisite quantities of the salt of Lead nitrate, cadmium, and Arsenic oxide. The solutions were serially diluted to the required working standards of interest. The various chromogenic reagents in 1.0 x 10^{-4} M were prepared in each solvent (N, N-dimethylformamide, demithylsulphuroxide and 1, 4-dioxane) and diluting it to 100 cm^3 in volumetric flask (Okoye *et al*., 2013).

Working concentrations of the reagent solution

A known aliquot of metal ion solution was taken into set of 25.0 cm^3 volumetric flask containing 5.0 cm^3 of buffer solution of desired pH. Different known aliquots of the reagent solutions were added to these flask and the contents made up to the mark with distilled water. The absorbances of each solution were measured against the corresponding reagent blank solution. Based on the results, the required concentrations of the reagent for complete colour development were determined (Okoye *et al*, 2013).

Synthesis and characterization of the glutaraldehydephenylhydrazone

The reaction mixture containing glutaraldehyde (0.050mol, 4.7ml in 20ml ethanol) and phenyl hydrazine (0.1mol, 9.85g in methanol) dissolved in hot condition was taken into round bottom flask and reflux for 8hours. On cooling the reaction mixture gave a dark brown coloured product. It was collected by filtration. The compound was recrystallized twice with ethanol. The melting point was determined (^{0}C). The resultant compounds were characterized by FTIR and NMR spectral studies. The preliminary purity of the products obtained was confirmed by elemental analysis (E. Cristofol *et al* 1990).



Scheme 1: Synthesis of glutaraldehydephenylhydrazone

Nitrogen content of the synthesizes glutaraldehydephenylhydrazone

Preliminary investigation of the chemical and elemental constituents present in the product was carried out. The Nitrogen content of the product was carried out by Khjedal methods. About 0.2g of the sample was placed in Khjedal flask and digested with 4.0ml concentrated sulphuric acid. A tablet of khjedal was added to the mixture. The mixture was then heated in a fume cupboard until it became clear. The content was cooled and transferred quantitatively into a distillation apparatus, few anti-bombing granules were added. Calculated quantity of sodium hydroxide solution (40%) was added and the mixture was heated to boiling, the end of the condenser was dipped into a collection flask containing 100ml 0.1M hydrochloric acid. The distillation was continued until all the ammonia gas evolution ceased. The excess acid was titrated against standard 0.1M sodium hydroxide using phenolphthalein indicator (M. jamaluddin, 2012).

Evaluation of the analytical properties of the synthesized glutaraldehydephenylhydrazone

The following analytical parameters were analysed on the synthesized hydrazones to ascertain its analytical properties

Determination of the working wavelength

For the selection of the working wavelength, a number of solutions were made by mixing equal volume of the reagent concentration ($1.0x10^{-4}$ M) and ($1.0\ x10^{-4}$ M), of the salt of metal of interest in a 25.0 cm^3 volumetric flask and made to the mark with deionized water. The absorbance were scanned between 190-800 nm in a 1.0 cm^3 cuvette to determine the maximum wavelength of absorption (λ_{max}) using the UV-Visible spectrophotometer. The wavelength of maximum absorbance for each complex was noted (Omabaka and Gichobi, 2011).

Stability of the chromogenic reagent

To establish the maximum storage time of the chromogenic reagent solution without loss of reactivity, a study was performed to investigate the stability over time. About 1.0 cm^3 of 5 x 10^{-4} M of the various metals of interest was taken into 10.0 cm^3 volumetric flask. Then 5.0 cm^3 of $5.0\ x10^{-4}$ M of the hydrazones complex was added. The pH of these solutions was adjusted pH of 6.5 - 7.5 using acetate buffers. The solution was made to the mark with deionized water. The flask was stored at room temperature. The stability of these reagents was followed spectrophotometrically after 0, 3, 6, 9, 12, 24, 48, 72, 96 and 120 hours (Omabaka and Gichobi, 2011).

Determination of working wavelength of the metal-ligand complexes

About 1.0 cm^3 of 5.0 x 10^{-4} M of the various metals of interest was taken into 25 cm^3 volumetric flask. Then 5.0 cm^3 of 5.0 x 10^{-4} of the hydrazones complex was added. The pH of these solutions was adjusted pH of 6.5 - 7.5 using acetate buffers. The solution was made to the mark with deionized water. The absorbance were then determined in the entire UV-visible region against specific reagent blank. The spectra of the reagent were also measured in the same wavelength region against the organic solvent of interest. The plot of absorbance against wavelength was done on the same graph. The working wavelength was chosen where there was maximum difference between the absorbance due to complex and reagent (Ombaka and Gichumbi, 2011).

Applicability of Beer's law

The known aliquots of 10.0 cm^3 solutions, each containing constant volume of 4.0 cm^3 of buffer (desired pH), 3.0 cm^3 of 1.0 x 10^{-4} M of reagent hydrazone and 2.0 cm^3 of corresponding salt of metal of interest ranging from 0.1 x 10^{-4} to 1.0 x 10^{-4} M. The absorbances of these are measured at optimal wavelength for each metal of interest. A graph was plotted between the concentration of the metal and its absorbances. A straight line graph passing through the origin obeys Beer's. The correlation coefficient which indicates the linearity between the two variables, the molar absorptivity coefficient and Sandell's sensitivity of the ligand-metal complexes were obtained from the plot (Ombaka and Gichumbi, 2-011).

Composition and stability constants of the hydrazone-metal complexes

The molar ratio methods was performed to determine the composition of the complexes

Molar ratio method

To 25.0 cm^3 volumetric flask, 5.0 cm^3 of desired buffer was transferred into known volume of metal ion and varying volumes of the reagents solutions were added. The contents of each flask were made up to the mark with double distilled water. The absorbance of each solutions were measured at the selected wavelength against a blank containing 5.0 cm^3 buffer solution and required volume of reagent. From the plot between the absorbance and the volume of the reagent, the composition of the complex is computed (Humaira *et al.,* 2009) .

Sample collection and treatment

The samples (waste water, waste water soil) in triplicates were collected from Challawa industrial area of Kumbotso Local Government Area of Kano State Nigeria West Africa into polythene bags and transported to the laboratory of Federal College of Agricultural Produce Technology Kano for analysis.

The waste water collected (500.0 cm^3) were filtered using a filter paper (Whatman No.41) and then each filtered water sample was evaporated nearly to dryness with a mixture of 5.0 cm^3 of concentrated H_2SO_4 and 10.0 cm^3 concentrated HNO_3 in a fume cupboard and then cooled to room temperature. In order to dissolve the salts, the residue was then heated with 15.0 cm^3 of distilled water. After cooling the solution was neutralized with dilute NH_4OH solution and the obtained solution was filtered into 25.0 cm^3 standard flask and made up to the mark with distilled water (Adi *et. al*., 2012).

Before digestion of the soil samples, each was dried at 65°C for 48 hours. All samples were performed in triplicates. Five grams (5.0 g) of the samples in crucibles was placed in a preheated muffle furnace at 200-250 °C for 30 minutes, and the ashed for four hours at 500-550°C. Then, the sample was removed from the furnace and cooled down. 2.0 cm^3 of 5M of HNO_3 was added and evapourated to dryness on a sand bath. Next, the samples was placed in a furnace and heated to 400°C for 15 minutes. The samples were removed from the furnace, cooled and moistened with four drops of distilled water. Next, 2.0 cm^3 of concentrated HCl was added and the sample was evaporated to dryness, removed, and the 5.0 cm^3 2M HCl was again added and the tube was swirled. The solution was filtered through Whatman No. 42 filter paper and the transferred quantitatively to a 50 cm^3 flask by making it with distilled water (Zeng-Yei, 2004).

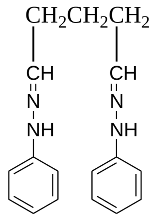
RESULTS AND DISCUSSION

Table 1: Physical properties of the synthesized glutaraldehydephenylhydrazone

Properties of synthesized hydrazone	Glutaraldehydephenylhydrazone
Yield (%)	84
Melting point (°C)	129-131
Colour	Dark brown
Nitrogen content (%)	19.01

The elemental analysis of the nitrogen content for glutaraldehydephenylhydrazone yielded 19.01 % (calculated value 19.15%). The data shows good agreement between experimental and calculated values as reported by Jamaluddin and Zanat, 2012. The Infrared spectrums of glutaraldehydephenylhydrazone recorded on FT-IR 4000-650 cm^{-1} spectrophotometer as shown in Figure 1. The infrared spectra of the synthesized hydrazones showed the presence of string bands and shoulders assigned to C=N, NH_2 and phenyl C=C. The NMR spectra showed peaks associated to cyano carbon atoms, aromatic carbon atoms and NH_2. From the results of the experimental, IR and NMR analysis, the structure shown for both hydrazones can be suggested to be their composition. The infrared spectrum of glutaraldehydephenylhydrazone (in Figure 1) showed peaks at 3492.5 $cm^{-1}$and 3451 associated to the amino (–NHR) groups. The spectrum also revealed a peak at 3085 cm^{-1} assignable to the =CH groups and 3034 cm^{-1}phenyl N-H groups and a peak at 1604.0 cm^{-1} assignable to the cyano group respectively as shown in figure 2 and 3, and tabulated in table 2.

Table 2: FT-IR and NMR properties of the synthesizes glutaraldehydephenylhydrazone

Structure	**FI-IR Analysis**		**^{13}C-NMR**		**^{1}HNMR**	
	Absorption (cm^{-1})	**Inference**	**δ (ppm)**	**Inference**	**δ (ppm)**	**Inference**
 Glutaraldehyde Phenyl hydrazone	3492.5, 3451	N-H stretch (due to the two –NHR groups)	111.0 to 141.0	Due to aromatic carbon atom	1.64–1.69(m)	Due to multiplet $–CH_2$- protons
	3085	=CH stretch	129.3	Due to Cyano carbon atom.	2.214-2.386(q)	Due to quartet $–CH_2$ protons
	3034	Phenyl N-H group	40.0, 39.2 and 31.7	Due to the three methylene carbon.	7.331-7.345	=C-H protons
	1604	C=N stretch (Cyano group)			7.015	Due to –NH signal
					6.59-7.34	Due to aromatic protons

The NMR spectra of Glutaraldehydephenylhydrazone (in DMSO) showed signals between 111-140 ppm associated to aromatic carbon atoms, while signal at 129.3 ppm is assignable to cyano carbon atom. The three methylene carbon atoms signals appeared at 40, 39 and 31ppm. The protons signals between 6.59-7.34 ppm are assignable aromatic protons, 1.64-2.38 ppm are for aliphatic protons, while N-H signal and olefinic proton were observed at 2.38 and 6.83ppm respectively. The ^{13}C-NMRand ^{1}H-NMR spectra of glutaraldehydephenylhydrazone (in DMSO) are revealed in figure 3 and 4 respectively. The ^{13}C-NMR spectrum showed signals between 111.0-141.0 ppm associated to aromatic the carbon atoms, while signal at 129.3 ppm is assignable to cyano carbon atom. The three methylene carbon atoms signals appeared at 40.0, 39.0 and 31.7ppm. The ^{1}H-NMR spectrum revealed signals between 1.64-1.69(m) ppm due to multiplet –CH2- protons. 2.214-2,386(q) ppm associated to quartet –CH_2-protons atoms. 7.331-7.345 ppm due to =C-H protons. Peak at 7.015 ppm was due to –NH atoms. 6.59-7.34 ppm is assignable aromatic protons as shown in figure 2 and 3.

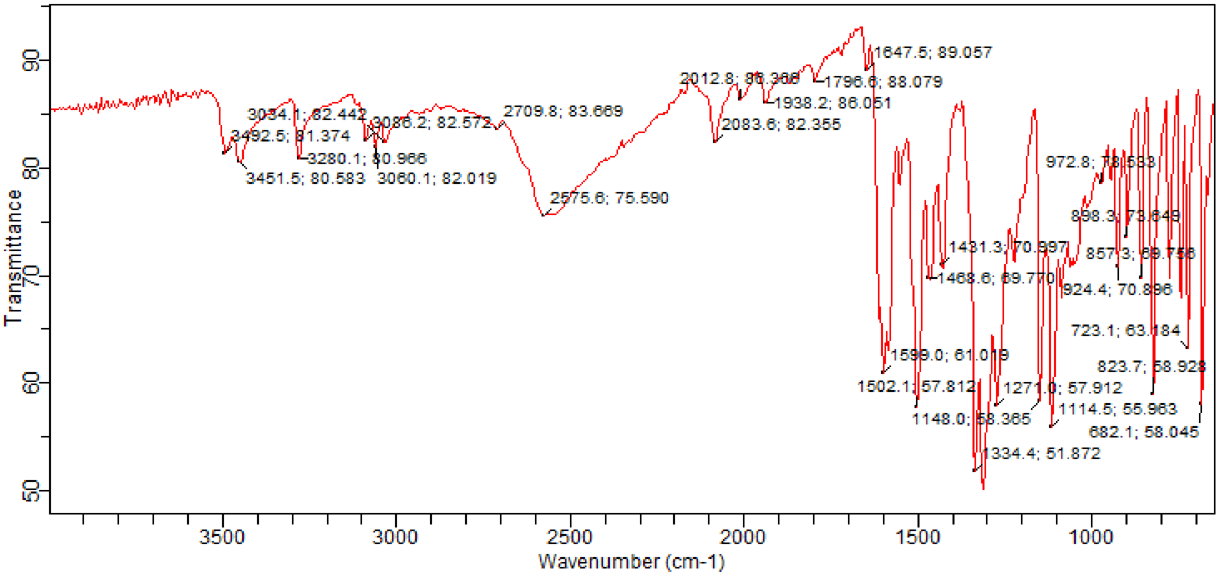


Figure 1: IR spectrum of glutaraldehydephenylhydrazone

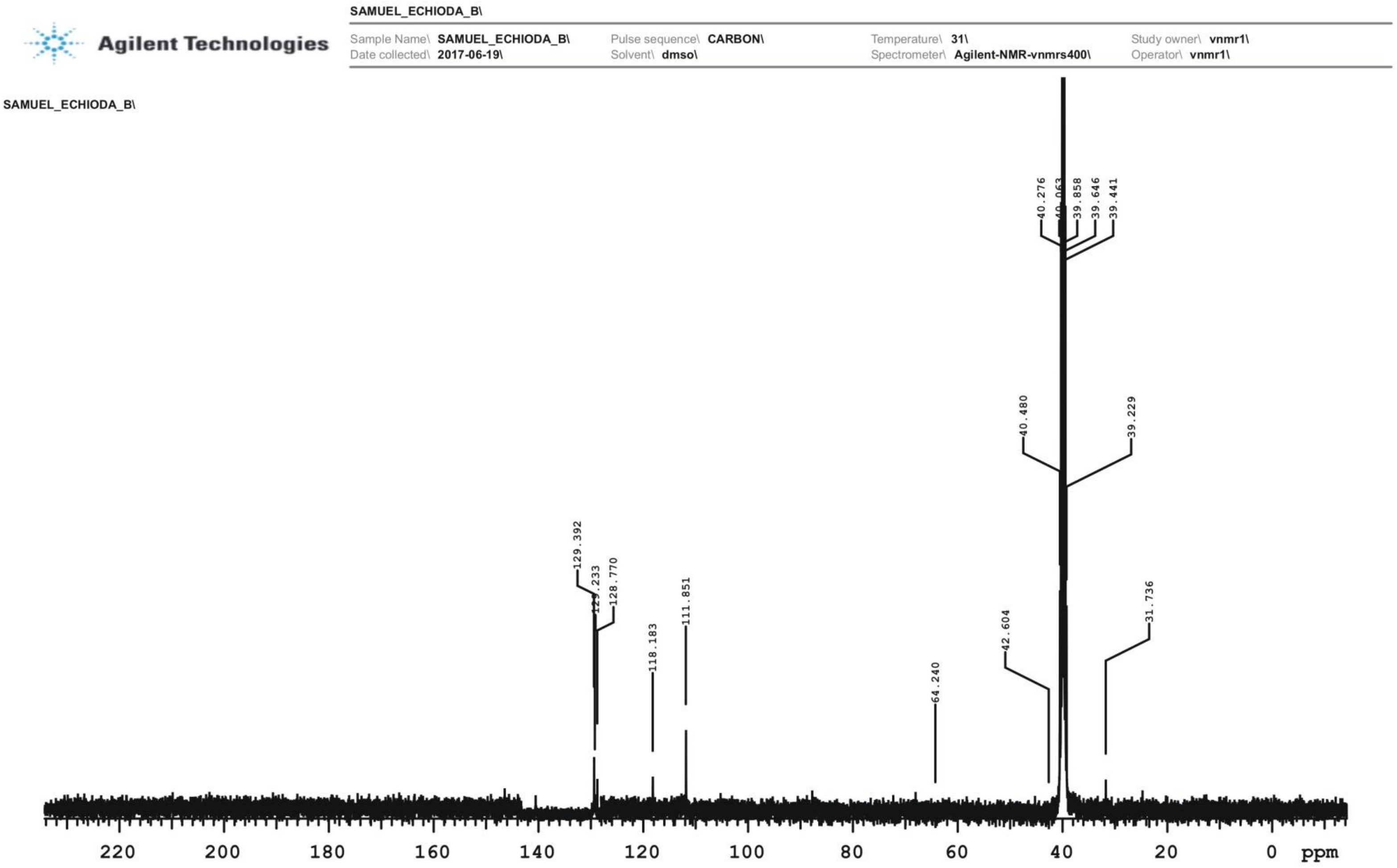


Figure 2: Carbon NMR Spectrum of glutaraldehydephenylhydrazone

Data file /home/vnmr1/vnmrsys/data/SAMUEL_ECHIODA_B_20170619_01/CARBON_01

Plot date 2017-07-26

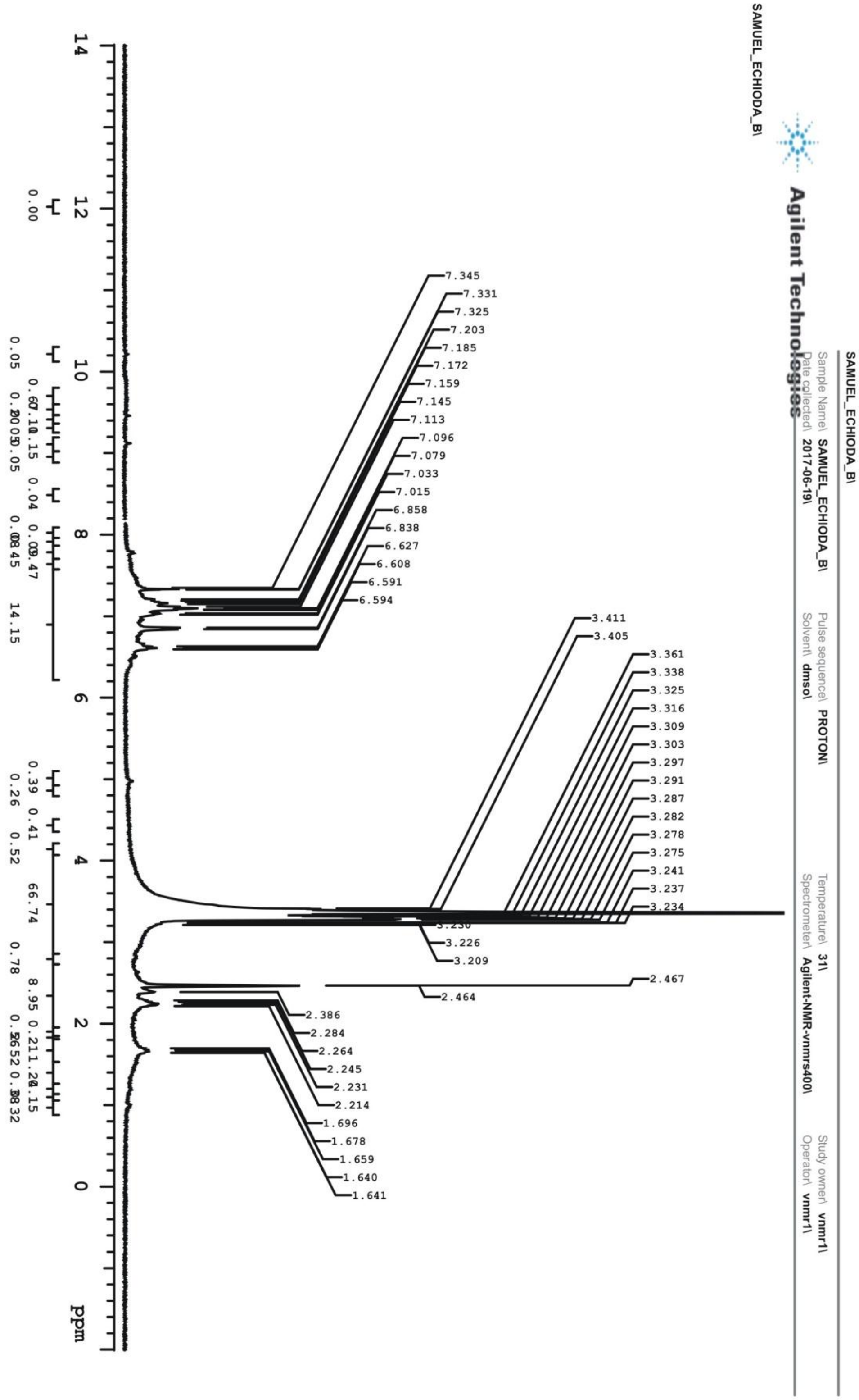


Figure 3: Proton NMR Spectrum of glutaraldehydephenylhydrazone

Table 4: Solubility of the synthesized hydrazone in various solvents

Solvent used	**Glutaraldehydephenylhydrazone (GPH)**
Water	Less soluble
Ethanol	Soluble
Dimethylformide	Soluble
Dimethysulfoxide	Soluble
1,4-dioxane	Soluble

Table 5: Absorbances of the synthesized hydrazone in various solvents

Solvent (50 % v/v)	**Absorbance of GPH**
Methanol	0.319
Chloroform	0.327
DMF	0.511
DMSO	0.487
Dioxane	0.352

Table 6: Analytical characteristic of selected metal complexes using glutaraldehydephenylhydrazone (metal-GPH)

characteristics	Cd-GPH	As-GPH	Pb-GPH	Cr-GPH
Selected wavelength (λ_{max}) nm	387.0	395.0	395.0	360.0
Selected pH	6.5-7.5	6.5-7.5	6.5-7.5	6.5-7.5
Working temperature (°C)	37±2	37±2	37±2	37±2
Molar absorptivity (Ɛ) (Lmol^{-1}cm^{-1})	2.261x10^4	2.460 x10^4	2.213 x10^4	2.274x10^4
Sandell's sensitivity (µg/cm^2)	0.00442	0.00406	0.00452	0.00440
Mole ratio (M:L)	2:1	2:1	2:1	2:1
Detection Limit (µg/g)	0.4933	0.3432	0.5250	0.3825
Quantification limit (µg/g)	1.4948	1.040	1.5909	1.1590
Complex Stability (h)	0-48	0-48	0-48	0-48
Beer's Law validity range/mgL^{-1}	0.001-100	0.001-100	0.001-100	0.001-100

Table 4: Result of concentrations of

Name of Sample	AAS method (ppm) *(ẋ ± SD)*	GPH method (ppm) *(ẋ ± SD)*
Waste water (ww)	0.878±0.0003	0.877±0.060
Waste water sand (wws)	1.173±0.0002	1.173±0.030

Note: ***ẋ is mean from the set of results***

SD is the standard deviation for the set of data with n = 3.

Organic compounds containing different functional groups have been used as chromogenic reagents in the trace metal analysis. The chromogenic reagent used in this study is glutaraldehydephenylhydrazone. The ligands generally is soluble and stable in dimethylformamide (DMF), dimethylsulfoxide (DMSO) and 1, 4-dioxane for between thirty six to fourty eight hours at room temperature without heating. The colour formation and development were instantly as shown in table 2. To avoid precipitation of the DMF, DMSO and 1, 4-dioxane content of the final solution, the solvents used must not be below 20% total volume as recommended by Cristofol *et al.,* 1991. Glutaraldehydephenylhydrazone tend to reduce the maximum wavelength of the absorptions of the metal complexes at the same working concentrations which tend to give better absorption for spectrophotometric determinations of metals in the UV-Vis regionwhich is in agreement with the report of Okoye *et. al.,*2013.

The working pH for the metal-reagent complex was selected based on the method reported by Nityananda *et al.,* 2015, could been seen that the metal-ligand complexes had higher absorbances at pH between 6.5-7.5 which was slightly acidic to almost neutral and was resolved to be the working pH for the study. The sensitivity of the spectrophotometric method is often described in terms of the molar absorptivity ($\mathcal{E}$, L $mol^{-1}cm^{-1}$) of the metal-ligand complex. The awareness of the sensitivity is very important in spectrophotometric determination of trace metals. Sanagi *et al.,* 2009 suggested a relation between sensitivity and molar absorptivity. They stated the following criteria for describing the sensitivity. Low sensitivity $\mathcal{E} < 2 \times 10^4$ L mol^{-1} cm^{-1}, Moderate sensitivity $\mathcal{E}= 2 - 6 \times 10^4$, L mol^{-1} cm^{-1} and High sensitivity $\mathcal{E} > 6 \times 10^4$, L $mol^{-1}cm^{-1}$. From the data generated the Molar absorptivity for GPH ranged 2.213×10^4 for Pb-GPH to 2.460×10^4 L mol^{-1} cm^{-1}. The values obtained indicated that they could be classified as moderately sensitive. The reactions and measurements could be made highly selective by using appropriate masking agents (Jamaluddin *et al.,* 2012, Humiara *et al.,* 2006. The values of the molar absorptivitives were higher than the values of Fahruddin *et. al.,* 2011, Jamaluddin and Tasnima 2012, and Srikanth and Chandra 2013, Saritha *et al*., 2014 and were improved by using appropriate masking agents. The mole ratio method was 2:1 (metal-ligand) for GPH respectively. The detection limit is the smallest concentration that can be detected with high degree of certainty (Guzar and Jin 2008). Based on the standard deviations of the reagent blank and the slope of the calibration curve of the analyte, the detection limit for glutaraldehydephenylhydrazone (GPH) ranged 0.3432 µg/g (As) - 0.5250 µg/g (Pb). The stability of the colour complex is influenced by experimental conditions like temperature and pH when the various concentrations have been maintained (Arain, 2009). The solutions formed were clear and free from precipitate as precipitates tend to scatter as well as absorb light. The reagent complex for metal-GPH for same metals studied (Cd, As, Pb, and Cr) were stable for 0-48 hours spectrophotometrically as tabulated in table 5. The preliminary investigations on GPH as possible chelating reagents for the spectrophotometric determination of lead (Pb) on waste water from tannery was carried out and the result compared with results from Atomic absorption spectroscopy (AAS) methods. The results obtained were satisfactory with good precision and accuracy as shown in table 6.

CONCLUSION; It’s a new and adopted approach that serves as an alternative for standard method in determining the concentrations of heavy metals. The present method was simple, inexpensive, sensitive, rapid and reasonably selective without the need for heating or extraction. The hydrazone was easy to synthesize and purify with available chemicals. The most favorable characteristic of these reagents is that it forms water soluble complexes which facilitate the determination of metals in biological, soil, water and waste water samples. The method offers a good procedure for speciation analysis of heavy metals. Although, many sophisticated techniques, such as pulse polarography, High performance chromatography, ICP-MS, AAS are available for the determination of Cadmium at trace levels in numerous complex materials factors such as low cost of the instrument, easy handling, portable, and almost no maintenance have caused spectrophotometry to remain popular technique particularly in laboratories of developing countries with limited budgets.

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