

# Synthesis, Characterization and Evaluation of acetylpyridine-2,4-dinitrophenyl hydrazone as a Chromogenic Reagent for Uv-Vis Spectrophotometric Determination of Selected Toxic Heavy Metals (Pb, Cr, Cd and As) in Water, Environmental and Biological Samples

Echioda Samuel, Ekanem E.O., Chindo I.Y., Kolo A. M

**Abstract**— This study involves the preparations, elemental analysis, characterization and evaluation of acetylpyridine-2,4-dinitrophenyl hydrazone as chromogenic reagents for UV/Vis spectrophotometric determination of heavy metals in environmental samples. The hydrazone was synthesized by single step condensation method. The yield of the product obtained was 84% with melting point of 211-214°C, the nitrogen content yielded 17.62 %. The infrared spectrum data obtained from the measurement of acetylpyridine-2,4-dinitrophenyl hydrazone was characterized by absorption bands around 3451 cm<sup>-1</sup> due to NH stretch, 1602 cm<sup>-1</sup> due C=N, 1599 cm<sup>-1</sup> due C=C stretch and 1334, 1468 cm<sup>-1</sup> due to the -NO<sub>2</sub> groups. The presence of the hydrazones functional groups in the infrared and Nuclear magnetic resonance indicates the successful preparations of the said compound and also the data from the results of the experimental, IR and NMR analysis, suggested it to be the composition of the prepared hydrazones. The analytical properties of the reagent APGH on the metals Cd, As, Pb, and Cr revealed a maximum absorption at a wavelength range of between 385.0 (Cr) to 440.0nm for (Pb) at a working pH of 6.5 to 7.5 room temperature (37°C). The reagent had a molar absorptivities (L mol<sup>-1</sup> cm<sup>-1</sup>) ranging from 2.006 x 10<sup>4</sup> (Pb) to 2.407 x 10<sup>4</sup> (Cd), a mole ratio of metal to ligand of 1:1, a detection limit (µg/g) ranging from 0.3272 (As) to 0.4456 (Cd) and the metal-ligand complex was stable spectrophotometrically for 0-36 hours. The reagent had a Beer's law validity range (mgL<sup>-1</sup>) of 0.001 to 100. The preliminary investigations on APDH as possible chelating reagents for the UV-Vis spectrophotometric determination of lead (Pb) on waste water and soil from tannery water was carried out, and the result were compared with results from Atomic absorption spectroscopy (AAS) methods. The results obtained were satisfactory with good precision and accuracy for the APDH method.

**Index Terms**— elemental analysis, APDH method .

## I. INTRODUCTION

Highlight The analytical potentials of hydrazones and its derivatives for the Uv-Vis spectrophotometric determination of heavy metals have been reviewed by Singh *et al* 1992. Hydrazones are important class of known analytical reagents. Hydrazones and its derivatives reacts with many metals ions forming colour complexes and acts as chelating agents. Various approaches are described in the literatures for detailed analysis of metal in environment, biological, water, waste water and food samples. Analytical methods frequently require sample pre-concentration and or pretreatment for the destruction of the organic matrix such as wet digestion, dry ashing, and microwave oven dissolution or extraction. Research has been carried out on sample collection, preservation, pre-treatment, quantitative determination, speciation and microscopic analysis. Most of the new information about chemistry of heavy metals results mainly from continuing improvement in speciation and quantitative trace elements analysis (Ortega, 2002). Many organic compounds react with metal ions and form coloured precipitates or solutions. Hence, they are extensively used as analytical reagents, though it is difficult to predict with certainty which organic compound is suitable for the analysis of a particular metal ion. It has been observed that the reactivity of organic reagents with metal ions in the use of the former as analytical reagents requires the presence of certain acidic or basic groupings and coordinating atoms. While most of the reagents are not selective, various means are known where by the selectivity of reagent may be improved. These include adjustment of the pH, and the use of masking agents which form complexes with the interfering elements in the determination of the test ion. Within the organic reagent molecule, there is generally a single acidic or basic group, or a combination of these two, which is the key to the reactivity of the reagent, Survey has revealed that organic compounds capable of forming chelates or inner complex salts give better results than those containing only acidic or basic groupings, in the field of inorganic analysis. The element in the organic molecule through which the metal is bonded is generally oxygen or nitrogen, less usually it is sulphur. The oxygen

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containing groups most often met in organic reagents were -OH, -CHO, -COOH, and -CO. The nitrogen containing groups (-NH<sub>2</sub>, =NH, heterocyclic N) met with in general functional groups are amines (usually aliphatic), heterocyclic rings (usually pyridine), oximes (in which bonding tends to be coordinated to the nitrogen instead of replacement of hydrogen) and azo groupings (Zhang and Zhang, 2003). The work is aimed at to Synthesize, characterization and evaluate acetylpyridine-2, 4-dinitrophenylhydrazone as chromogenic reagents for UV-Visible spectrophotometric determination of selected heavy toxic (Pb, Cd, Cr and As) metals in biological and environmental samples.

## II. 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<sup>-1</sup> 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, acetylpyridine Phenyl hydrazine, Lead nitrate, Arsenic trioxide, 2,4-dinitrophenylhydrazine.

### 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 (Deepael. *at.*, 2015). 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<sup>3</sup> volumetric flasks, 2.0 cm<sup>3</sup> solution (1.0 x 10<sup>-4</sup> M), of the salt of metal of interest, 2.0 cm<sup>3</sup> of the hydrazone solution (1.0 x 10<sup>-4</sup> M) and 4 cm<sup>3</sup> 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 glutaraldehyde phenylhydrazone was tested in different organic and aqueous solvents. The organic solvent tested and yielded were N, N-dimethylformamide (DMF), demethylsulfoxide (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

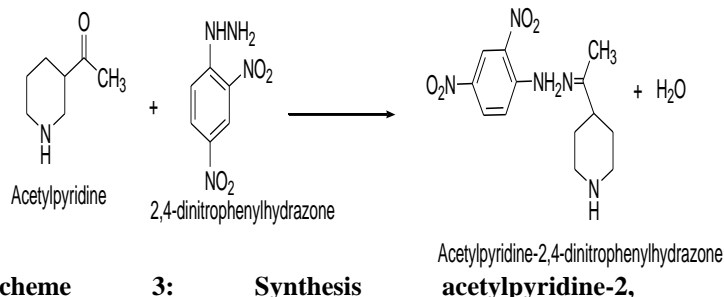
oxide. The solutions were serially diluted to the required working standards of interest. The various chromogenic reagents in 1.0 x 10<sup>-4</sup> M were prepared in each solvent (N, N-dimethylformamide, demethylsulphuroxide and 1, 4-dioxane) and diluting it to 100 cm<sup>3</sup> in volumetric flask (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<sup>3</sup> volumetric flask containing 5.0 cm<sup>3</sup> 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 of acetylpyridine-2,4-dinitrophenylhydrazone (Gopalaet al., 2010).

The reaction mixture containing one equivalent 2,4-dinitrophenylhydrazine (1.0 mol, 0.198 g) and one equivalent acetyl pyridine (1.0mol, 0.121 cm<sup>3</sup> in 15 cm<sup>3</sup> methanol) were dissolved in hot condition taken into round bottom flask and reflux for 8hours. On cooling the resulting mixture gave an orange colour product. It was collected by filtration. The compound was recrystallized twice with ethanol.



## Scheme 3: Synthesis of acetylpyridine-2,4-dinitrophenylhydrazone

The resultant compounds were characterized by FT-IR and NMR for spectral studies. The preliminary purity of the products obtained was confirmed by elemental analysis (Cristofolet *et al.*, 1991).

## Nitrogen content of the acetylpyridine-2,4-dinitrophenylhydrazone (Jamaluddin and Tasnima, 2012).

Preliminary investigations of the elemental constituent present in the products were 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 4.0 cm<sup>3</sup> 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 100 cm<sup>3</sup> 0.1M hydrochloric acid. The distillation was continued until all the ammonia gas evolution ceased. The excess acid was titrated

against standard 0.1 M sodium hydroxide using phenolphthalein indicator (Jamaluddin and Tasnima, 2012).

#### **Analytical properties of the synthesized hydrazone for Uv-Vis spectrophotometric analysis**

The following analytical parameters were analysed on the synthesized hydrazones to ascertain their 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 ( $1.0 \times 10^{-4}$  M) and ( $1.0 \times 10^{-4}$  M), of the salt of metal of interest in a 25.0 cm<sup>3</sup> volumetric flask and made to the mark with deionized water. The absorbance were scanned between 190-800 nm in a 1.0 cm<sup>3</sup> cuvette to determine the maximum wavelength of absorption ( $\lambda_{max}$ ) 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<sup>3</sup> of  $5 \times 10^{-4}$  M of the various metals of interest was taken into 10.0 cm<sup>3</sup> volumetric flask. Then 5.0 cm<sup>3</sup> of  $5.0 \times 10^{-4}$  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<sup>3</sup> of  $5.0 \times 10^{-4}$  M of the various metals of interest was taken into 25 cm<sup>3</sup> volumetric flask. Then 5.0 cm<sup>3</sup> of  $5.0 \times 10^{-4}$  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<sup>3</sup> solutions, each containing constant volume of 4.0 cm<sup>3</sup> of buffer (desired pH), 3.0 cm<sup>3</sup> of  $1.0 \times 10^{-4}$  M of reagent hydrazone and 2.0 cm<sup>3</sup> of corresponding salt of metal of interest ranging from  $0.1 \times 10^{-4}$  to  $1.0 \times 10^{-4}$  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, 2011).

### III. COMPOSITION AND STABILITY CONSTANT STABILITY CONSTANT OF THE REAGENT

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

##### ***Molar ratio method***

To 25.0 cm<sup>3</sup> volumetric flask, 5.0 cm<sup>3</sup> 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<sup>3</sup> 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 state, Nigeria for analysis. The waste water collected (500.0 cm<sup>3</sup>) 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<sup>3</sup> of concentrated H<sub>2</sub>SO<sub>4</sub> and 10.0 cm<sup>3</sup> concentrated HNO<sub>3</sub> 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<sup>3</sup> of distilled water. After cooling the solution was neutralized with dilute NH<sub>4</sub>OH solution and the obtained solution was filtered into 25.0 cm<sup>3</sup> standard flask and made up to the mark with distilled water (Adiet. 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<sup>3</sup> of 5M of HNO<sub>3</sub> was added and evaporated 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<sup>3</sup> of concentrated HCl was added and the sample was evaporated to dryness, removed, and the 5.0 cm<sup>3</sup> 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<sup>3</sup> flask by making it with distilled water (Zeng-Yei, 2004).

### IV. RESULTS AND DISCUSSION

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 acetylpyridine-2, 4-dinitrophenylhydrazone. The ligand generally was soluble and stable in dimethylformamide (DMF), dimethylsulfoxide (DMSO) and 1, 4-dioxane for between thirty six to forty eight hours as shown in table 1, 2, 3 and 5. The colour formation and development were instantly. To avoid precipitation of the DMF, DMSO and 1,

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4-dioxane content of the final solution, the solvents used must not be below 20% total volume as recommended by Cristofalet *al.*, 1991. The results of nitrogen content for acetyl-2, 4-dinitrophenylhydrazone yielded 17.62% (calculated value 18.84%). The infrared spectrum of acetylpyridine-2, 4-dinitrophenylhydrazone showed band at

1599.0  $\text{cm}^{-1}$  1599.0 $\text{cm}^{-1}$  (1690-1520 $\text{cm}^{-1}$  for C=N), 3451 $\text{cm}^{-1}$  (3500-3300 $\text{cm}^{-1}$  for  $\text{NH}_2$ ). The NMR spectra of the acetylpyridine-2, 4-dinitrophenylhydrazone showed bands at 139.433 (C=N), 13.5 ( $\text{CH}_3$ ), 105-130(aromatic ring) as tabulated in table 4.

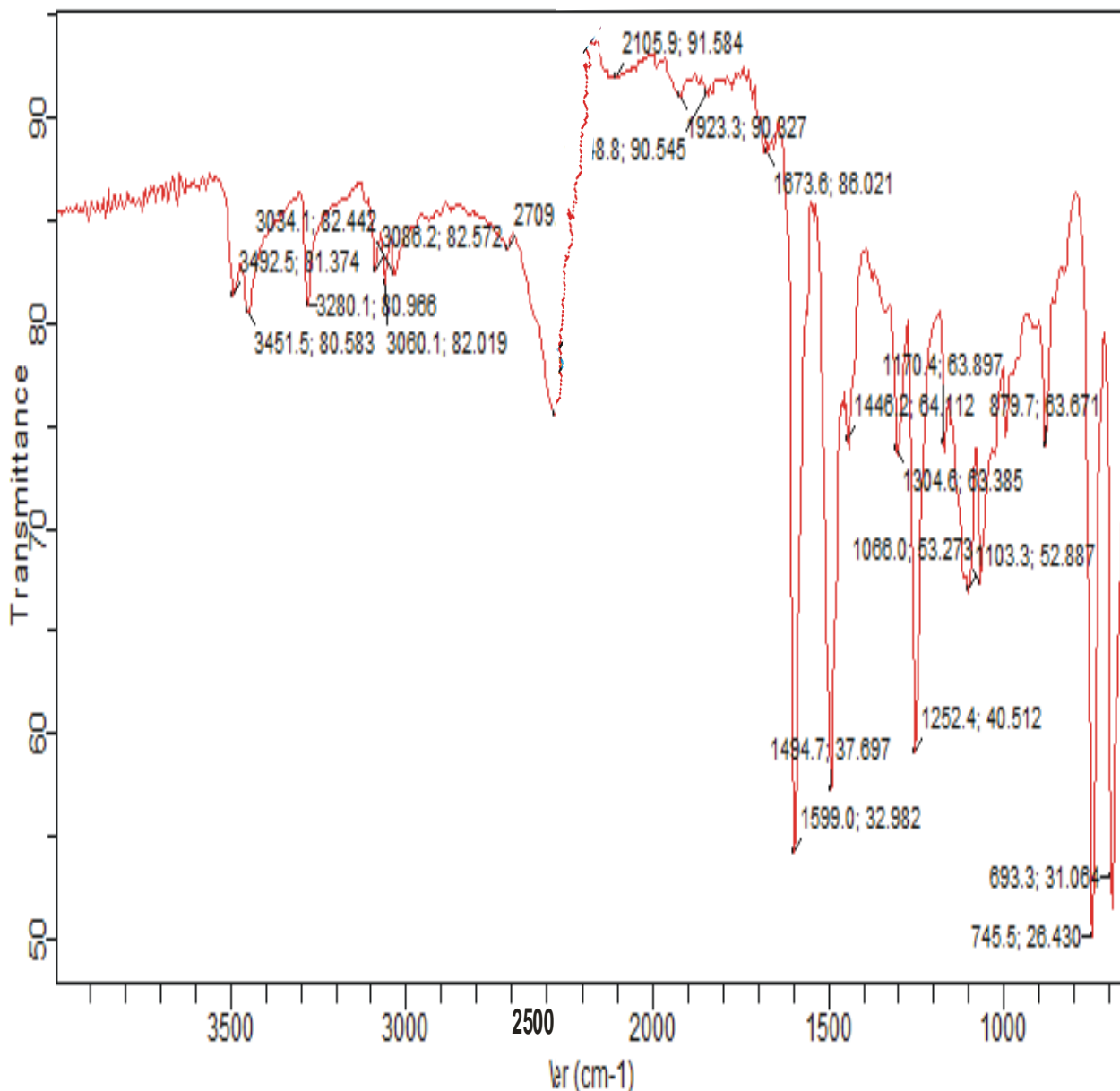


Figure 1: IR spectrum of acetylpyridine-2, 4-dinitrophenylhydrazone





Agilent Technologies

SAMUEL\_ECHIODA\_D1

Sample Name	SAMUEL_ECHIODA_D1	Pulse sequence	CARBON1	Temperature	31
Date collected	2017-06-19	Solvent	dmso	Spectrometer	Agilent-NMR-vnmr400
				Study owner	vnmr1
				Operator	vnmr1

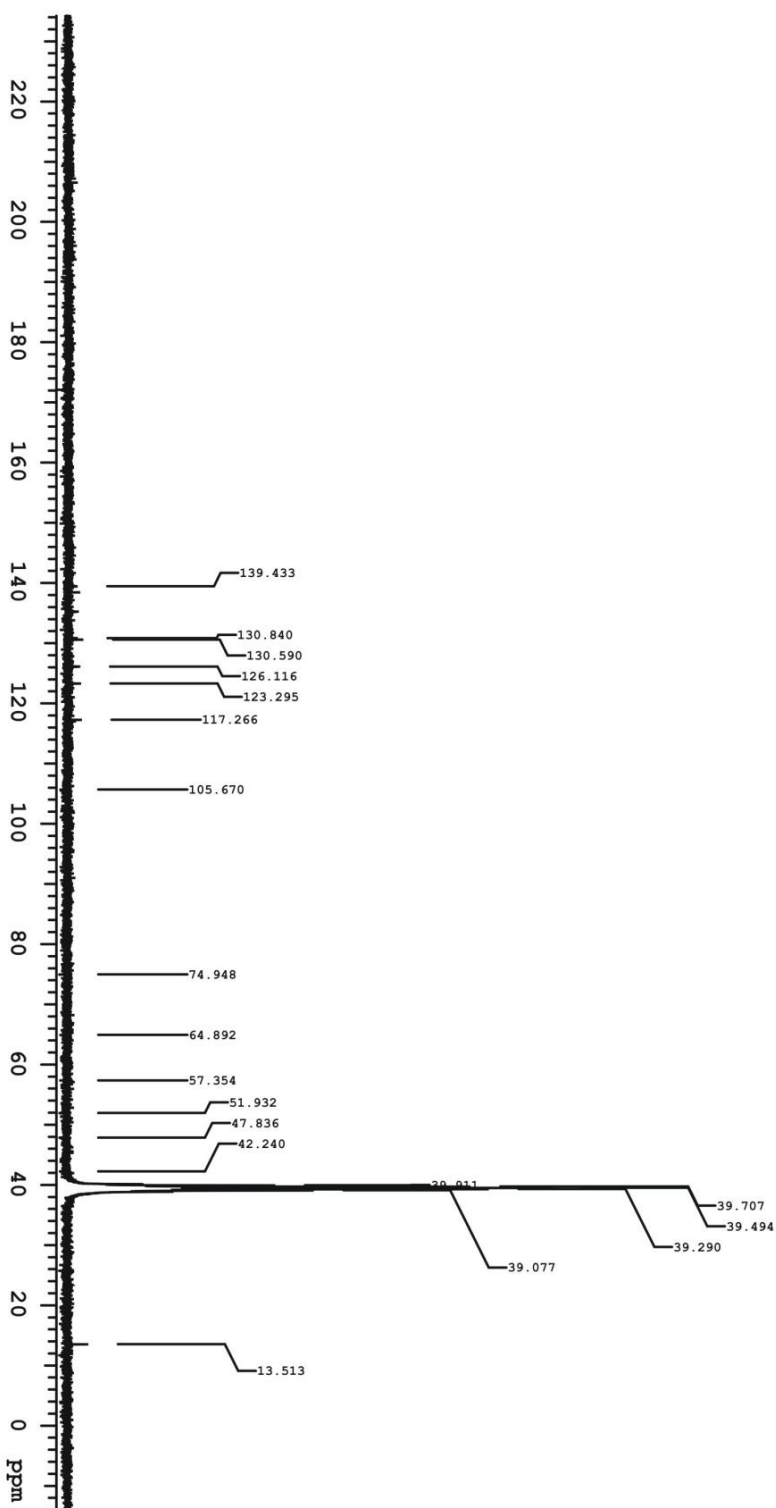


Figure 5: Carbon NMR Spectrum of acetylpyridine-2,4-dinitrophenylhydrazone

Data file: /home/vnmr1/vnmr/systems/data/SAMUEL\_ECHIODA\_D\_20170619\_01/CARBON\_01

Plot date: 2017-07-26

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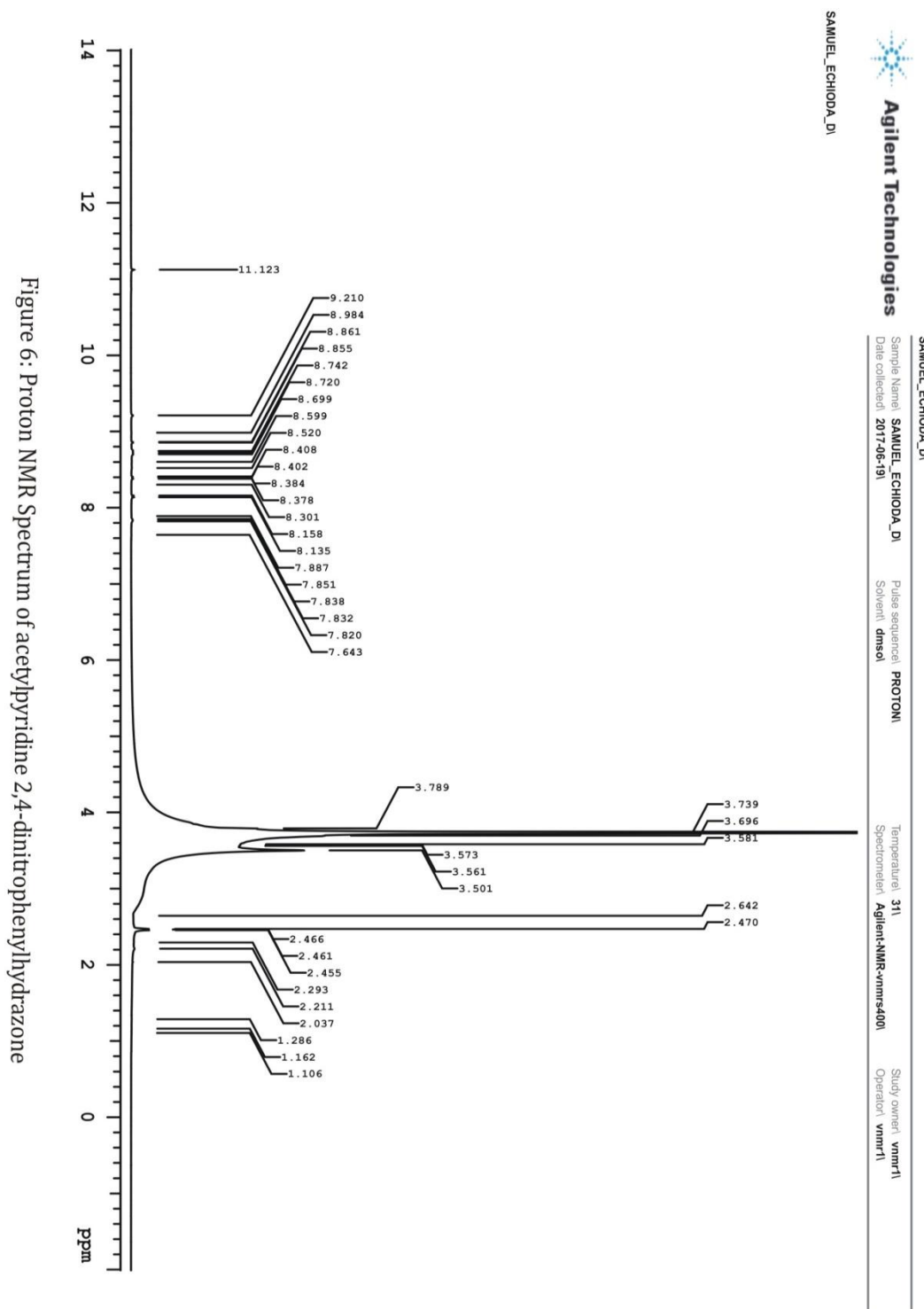


Figure 6: Proton NMR Spectrum of acetylpyridine 2,4-dinitrophenylhydrazone

Plot date 2017-07-26

Table .1: Physical properties of the synthesized Acetylpyridine-2, 4-dinitrophenylhydrazone

Properties of synthesized hydrazone	Acetylpyridine-2, 4-dinitrophenylhydrazone
Yield (%)	79
Melting point (°C)	211-214
Colour	Orange
Nitrogen content (%)	18.62

Table 2: Solubility of the synthesized hydrazone in different solvent

Solvent used	Acetylpyridine-2,4-dinitrophenylhydrazone (APDH)
Water	Not completely soluble at room temperature
Ethanol	soluble
Dimethylformide	Soluble
Dimethylsulfoxide	Soluble
1,4-dioxane	Soluble

Table 3: Absorbance of the hydrazone in various solvent

Solvent (50 % v/v)	Absorbance of APDH
Methanol	0.219
Chloroform	0.347
DMF	0.421
DMSO	0.410
Dioxane	0.359

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Table 4: FT-IR and NMR properties of acetylpyridine-2, 4-dinitrophenylhydrazone

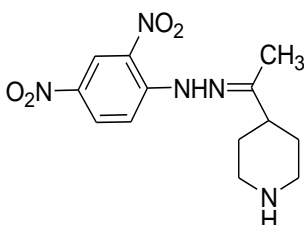
Structure	FI-IR Analysis		<sup>13</sup> C-NMR		<sup>1</sup> HNMR	
	Absorption (cm <sup>-1</sup> )	Inference	δ(ppm)	Inference	δ(ppm)	Inference
 <p>Acetylpyridine-2,4-dinitrophenylhydrazone</p>	3451	secondary amino NHstretch	139.4	Due to cyano carbon atom.	1.105(s)	-CH <sub>3</sub> proton
	1602	C=N stretch		Assigned to aromatic carbons	2.037(s)	-NH- proton on pyridine ring
	1599	Due to phenyl C=C stretch	105.6 130.8		2.211(m)	-CH- proton on pyridine ring
	1334,1468	-NO <sub>2</sub> groups	13.5	Due to CH <sub>3</sub> carbon	2.470(q)	-CH <sub>2</sub> - proton on pyridine ring
					3.561(t)	-CH <sub>2</sub> - proton on pyridine ring
					7.643(s)	Aromatic -CH stretch on C <sub>6</sub> of phenyl group
					7.887	Aromatic C-H stretch on C <sub>5</sub> of phenyl group
8.408					Aromatic C-H stretch on C <sub>3</sub> of phenyl group	
8.984						

Table 5: Physiochemical properties of the hydrazone under observation

characteristics	Cd-APDH	As-APDH	Pb-APDH	Cr-APDH
Selected wavelength (λ <sub>max</sub> ) nm	395.0	405.0	440.0	385.0
Selected pH	6.5-7.5	6.5-7.5	6.5-7.5	6.5-7.5
Working temperature (°C)	3337±2	37±2	37±2	37±2
Molar absorptivity (ε) (Lmol <sup>-1</sup> cm <sup>-1</sup> )	2.407x10 <sup>4</sup>	2.445 x10 <sup>4</sup>	2.006 x10 <sup>4</sup>	2.207 x10 <sup>4</sup>
Sandell's sensitivity (μg/cm <sup>2</sup> )	0.00416	0.00409	0.00499	0.00453



Mole ratio ( M:L)	1:1	1:1	1:1	1:1
Detection Limit ( $\mu\text{g/g}$ )	0.4456	0.3272	0.3572	0.4202
Quantification limit ( $\mu\text{g/g}$ )	1.3495	0.9916	1.0824	1.2735
Complex Stability (h)	0-36	0-36	0-36	0-36
Beer's Law validity range $\text{mgL}^{-1}$	0.001-100	0.001-100	0.001-100	0.001-100

Table 6: Results of concentration of lead from AAS and APDH methods

Name of Sample	AAS method (ppm) $(\bar{x} \pm SD)$	APDH method (ppm) $(\bar{x} \pm SD)$
Waste water (ww)	0.878 $\pm$ 0.0003	0.878 $\pm$ 0.070
Waste water sand (wws)	1.173 $\pm$ 0.0002	1.174 $\pm$ 0.030

Note:  $\bar{x}$  is mean from the set of results

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

The ligand acetylpyridine-2,4-dinitrophenylhydrazone 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 region as shown in table 2, 3 and 5 which is in agreement with the report of Okoye et. al.,2013. The colour reactions were instantaneous and the method does not involve heating of the reaction mixture or pre-extraction of the components. The reagents gave colour reactions with metal ions in slightly acidic and slightly neutral regions. The working pH for the metal-reagent complex were selected based on the method reported by Nityananda et al., 2015 and tabulated in table 6. In a series of 10 cm<sup>3</sup> volumetric flasks, 2.0 cm<sup>3</sup> solution (1.0 x10<sup>-4</sup> M), of the salt of metal of interest, 3.0 cm<sup>3</sup> of the hydrazone solution (1.0 x 10<sup>-4</sup>M) and 4 cm<sup>3</sup> of the buffer of varying pH were added and made up to the mark with deionized water and the absorbances were measured against the ligand blank at the scanned and recorded wavelength as shown in table 3 and 5. The pH with the highest absorbance was determined as the working pH for each metal of interest. The molar absorptivities from the data generated ranged from 2.006 x 10<sup>4</sup> for Pb-APDH to 2.445 x 10<sup>4</sup> L mol<sup>-1</sup>cm<sup>-1</sup> for

As-APDH respectively. The values of the molar absorptivities were higher than the values of Fahrudinet. al., 2011, Jamaluddin and Tasnima 2012, and Srikanth and Chandra 2013, Saritha et al., 2014 and were improved by using appropriate masking agents. The molar ratio method was used to study of the complex formation equilibrium in solution. The concentration of the metal ion was kept constant while the total concentration ratios rose linearly from the origin and breaks sharply to a straight line at mole ratio of the components in the complex. However, a complex that undergoes appreciable dissociation in solution gives a continuous curve, which only becomes parallel to the mole ratio axis, when an excess of the variable component is added. 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 reagent acetylpyridine-2, 4-dinitrophenylhydrazone (APDH) has a detection limit which ranged from 0.3272  $\mu\text{g/g}$  (As) – 0.4456  $\mu\text{g/g}$  (Cd). 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

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complex for metal-APDH studied (Cd, As, Pb, and Cr) were followed spectrophotometrically. The preliminary investigations on APDH as possible chelating reagent 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 hydrazones was easy to synthesize and purify with available chemicals. The most favourable characteristic of these reagents is that they form 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. The sensitivity in terms of molar absorptivity as shown in figure 4.9 to 4.18 and precision in terms of standard deviation as shown in table 4.33 for the determination of lead, shows the present could be very reliable for determination of lead in waste water, and waste water sand samples at room temperature.

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