Original Research Article

Preparation, Characterization and Investigation of Extraction Efficiency of m- and p- Substituted Hydroxamic Acids with some metals

Abstract:

Two hydroxamic acids, N- phenyl-N-p- nitrobenzohydroxamic acid (i) and N-phenyl-N-m-nitrobenzohydroxamic acid (ii) were prepared by the partial reduction of nitro benzene with zinc dust and ammonium chloride to give β- phenyl hydroxyl amine which was coupled with p- nitrobenzoyl chloride to give (i) and with m- nitrobenzoyl chloride to give (ii). They were identified by their characteristic-colored reaction with vanadium (V) and iron (lll), melting point, I.R. spectra, ^{1}H n.m.r. and mass spectrometry. The extractive properties of hydroxamic acids towards the metal ions like Fe (lll), Cu (ll), Ni (ll), Co (ll) and V (V) were examined using appropriate organic solvent, which show an increasing with the pH. Also, the effect of para and meta substituted nitro groups was examined and found that there are an increasing in the extraction percent of metal ions by hydroxamic acid containing para substituted compared with meta position.

Keywords: Extraction, coupling, hydroxamic acid, efficiency.

1. Introduction:

The chemistry of the hydroxamic acids, R-CO-NH OH, began in 1869 when W-Lossen, isolated oxalohydroxamic acid from the reaction product of ethyl oxalate and hydroxyl amine. Later W-Lossen obtained a mixture of mono-, di -, and tri- benzoyl derivatives from the reaction of hydroxyl amine with benzoyl chloride [1, 2].

Hydroxamic acid is the name given to N-acyl or aryl derivatives of hydroxylamine. They can be classified as primary, secondary and cyclic. Muzukami, S and Nagata, K (1968) replaced the oxygen donor atom of hydroxamic acids by sulfur atom to get thiohydroxamic acids [3]. Hydroxamic acids are white or light-yellow solids, except iodo- and cinnamo- substituted which are pink and light yellow respectively [4, 5]. They are soluble in chloroform, hot benzene, diethyl ether, dioxane and ethanol, sparingly

soluble in carbon tetrachloride and cold benzene, and insoluble in water; they are of low melting point [6, 7].

Hydroxamic acids are very weak acids, although they are several times stronger than phenol [8]. The monohydroxamic acids have been prepared by many methods. The most general is the reaction between an ester and hydroxylamine [9, 10]. The other methods have limited application like the reaction of acid anhydride, carboxylic acid, acid chloride [11, 12], and amides [13] with hydroxylamine.

The most important uses of hydroxamic acids are their application as analytical reagents for gravimetric analysis, solvent extraction and spectrophotometric determination of metals [14]. They are also finding wide uses in the analysis of trace metal by flow injection analysis and high-performance liquid chromatography. They used also as colorimetric reagents due to the formation of complexes with intensive colors with many metal ions under controlled pH, also they are used in qualitative organic analysis, and since, they form complexes with metal ions they found application in complexometric titration [15]. Also, they used in biochemical processes [16, 17].

Solvent extraction or liquid - liquid extraction is a technique in which a solution (usually aqueous) is brought in to contact with a second solvent (usually organic), essentially immiscible with the first. In the case of inorganic solutes, we are concerned largely with samples in aqueous solution so that it is necessary to produce substances, such as neutral metal chelates and ion – association complexes, which are capable of extraction in to organic solvent [18]. The efficiency of extraction depends on the magnitude of D (distribution ratio) and on the relative volumes of liquid phases. The percentage extracted (%E) is given by:

$$\%E = \frac{100D}{\{D + (Vaq./Vor.)\}}$$

Where:

v_{aq}: the volume of aqueous layer

v_{org}.: the volume of organic layer

Thus, the percentage of extraction varies with the volume ratio of the two phases and the distribution ratio.

In this study the extraction efficiency of para and meta substituted hydroxamic acids has been investigated using different metals.

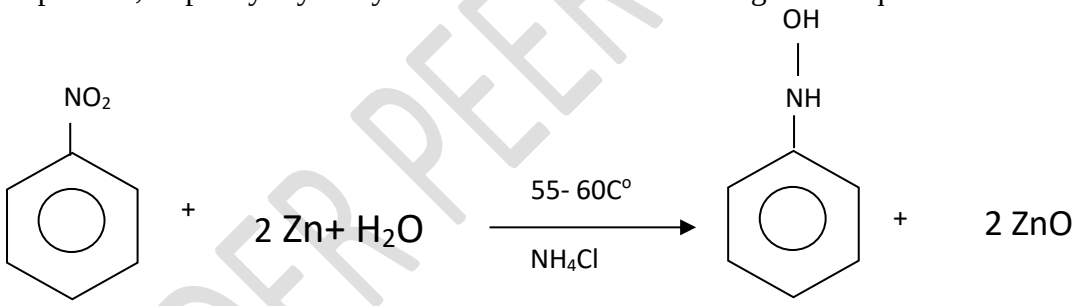
2. Experimental part:

2.1 Preparation of N-phenyl–N-p-nitrobenzohydroxamic acid:

2.1.1 Preparation of N-phenyl hydroxyl amine:

In a two-liter beaker equipped with a thermometer and mechanical stirrer, placed (25 g, 0.47 mole) of ammonium chloride in 800 cm^3 of water and (41.6 cm^3, 0.4 mole), of nitrobenzene then the mixture was stirred vigorously (59.5 g. 0.9 mole) of zinc powder were added during about 15 minutes. The rate of addition was adjusted such that the temperature rapidly raised to 55-60 ^0C and remained in this range until all the zinc was added, stirring was continued for 15 minutes. The warm solution was filtered at the pump to remove zinc oxide and washed with 100 cm^3 of hot water. The filtrate was placed in a conical flask and saturated with common salt and cooled in an ice bath for one hour. The pale-yellow crystals were filtered and recrystallized from benzene. Yield (23.5 g, 54 %), m.p. 81 ^0C, (lit. 81 ^0C) [19].

The product, N-phenyl hydroxylamine was formed according to the equation:



2.1.2 Preparation of p-nitro benzoyl chloride:

33.40g (0.2 mole) of pure p-nitro benzoic acid and 35.7g of redistilled thionyl chloride (22 cm^3, 0.3 mole) were refluxed on a water bath for 8 hours, till the evolution of sulphur dioxide and hydrogen chloride gases ceased. Then the excess of thionyl chloride was evaporated, the resulting yellow solid, P-nitro benzoyl chloride was recrystallized from carbon tetrachloride. Then dried and weighed, the yield 27.8 g (75%), m.p. 73 ^0C (lit 72- 74 ^0C) [20].

2.1.3 Coupling of N-phenyl hydroxyl amine and p-nitro benzoyl chloride:

10.9 g (0.1 mole) of freshly prepared N-phenyl hydroxyl amine was dissolved in 150 cm^3 of diethyl ether in a 500 cm^3 of three neck round bottomed flask equipped with a

mechanical stirrer, and placed in an ice – bath at 0 ^{0}C. A suspension of sodium hydrogen carbonate (8.4 g, 0.1 mole) was added. The mixture was stirred gently, 18.55 g (0.1 mole) of p-nitro benzoyl chloride was dissolved in 100 cm^3 diethyl ether and placed in a separatory funnel and added dropwise to the cooled reaction mixture during a course of one hour. Stirring was continued for further 30 minutes.

A pale-yellow precipitate separated and filtered off under suction and washed with water. The filtrate was placed in a separatory funnel and the ether layer was separated and evaporated under vacuum. Any solid matter was added to the product. The product was placed in a beaker and stirred mechanically for 30 minutes with 100 cm^3 of 10 % sodium hydrogen carbonate to remove unreacted acid chloride. The product washed with cold water and dried, yield 16.5 g (64 %).

2.1.4 Characterization of N-phenyl–N-P-nitro benzohydroxamic acid:

i. m.p. 166 ^{0}C (lit. -).

ii. i.r. (KBr disc), figure (1): showing absorption bands, 3184.26 cm^{-1} for (-OH) 1612.38 cm^{-1} for (C=O), 1350.08 cm^{-1} for C – N and 916.12 cm^{-1} for N-O.

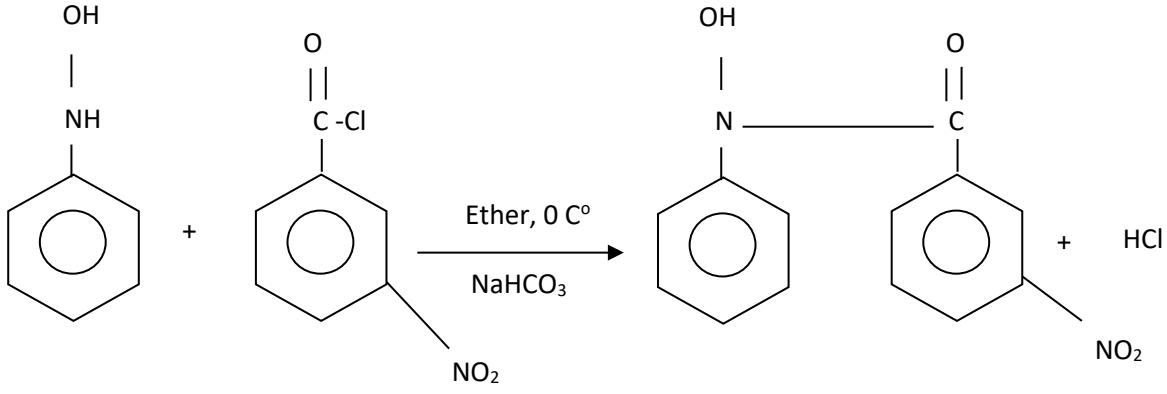
iii. ^{1}H n.m.r (sample dissolved in $CDCI_3$): Figure (5): showing chemical shifts: 8.164, 7.627, 7.379 and 7.261 ppm for aromatic protons, 9.045ppm for (-NOH).

iv. Mass spectrum, Figure (3): 258 is the molecular mass of N-phenyl–N-p-nitrobenzohydroxamic acid, and fragment $C_6H_4.NO_2.CON$ for 164.

v. G.C. - M.S. spectrum, appendix (1 E), page (176): fragments 77, 150, 212, 226 and 242, corresponding to C_6H_5, $C_6H_4NO_2CO$, $C_{12}H_9NOH.CO$, $C_{12}H_9CONOH.N$ and $C_{12}H_9CO.NOH.NO$ respectively.

2.2 Preparation of N-phenyl–N-m-nitrobenzohydroxamic acid:

This ligand was prepared by the coupling reaction of N-phenyl hydroxyl amine and m-nitro benzoyl chloride according to the equation:



2.2.1 Preparation of N-phenyl hydroxyl amine:

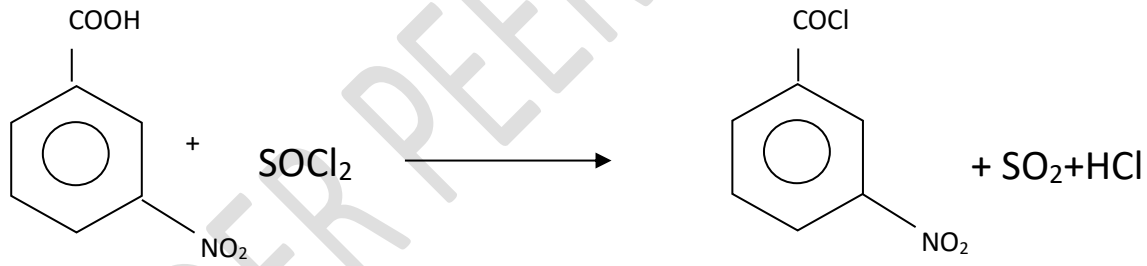
It was prepared as in 2.1.1.

2.2.2 Preparation of m-nitro benzoyl chloride:

98.53g (0.59 mole) of pure m-nitro benzoic acid was mixed with 62.05cm^3 (0.85 mole) of redistilled thionyl chloride in 250 cm^3 round bottomed flask. The flask was fitted with double surface reflux. The flask was heated on a water bath with an occational shaking for 90 minutes until the evolution of hydrogen chloride HCI and sulfur dioxide (SO_2) almost ceased.

The reaction mixture was allowed to cool and then was connected with a water-cooled condenser and receiver. The excess of thionyl chloride (b.p. 79 ^{0}C) was distilled off slowly and the temperature was raised rapidly to about 120 ^{0}C, this will ensure that all the thionyl chloride was removed [21].

The content was allowed to cool, and the residual m-nitro benzoyl chloride was distilled under reduced pressure. The resulting m-nitrobenzoyl chloride weight 85.597g (78.2%) with melting point 34 ^{0}C.



2.2.3 Coupling of N-phenyl hydroxyl amine and m-nitro benzoyl chloride:

In to a 500 cm^3, three necked flasks, equipped with stirrer, dropping funnel and thermometer, about 100 cm^3 of diethyl ether, 10.9 g (0.1mole) of freshly crystallized N-phenyl hydroxyl amine and the suspension of 8.6g (0.1 mole) of sodium hydrogen carbonate in 25cm^3 of distilled water were added. The mixture was cooled to 0 ^{0}C and then 18.55g (0.1 mole) of m-nitro benzoyl chloride dissolved in a mixture of about 150 cm^3 of diethyl ether and petroleum ether (boiling point range 40 – 60 ^{0}C) was added drop wise over a period of one hour. An additional time of 30 minutes was allowed and the temperature was maintained at 0 ^{0}C or lower. Some of the product was precipitated as a pale yellow solid while the ether layer separated and the ether was removed under vacuum, the residue combined with the precipitated solid. This solid was placed in a beaker and stirred mechanically for 30 minutes with 100 cm^3 of 10% sodium hydrogen

carbonate to remove un reacted acid chloride, filtered and washed with cold water.Yield 14.90g (57.8 %).

2.2.4 Characterization of N-phenyl-N-m-nitro benzohydroxamic acid:

i. m.p. 120 C^o (lit.-).

ii. i.r. (KBr disc), figure (2): showing absorption bands: 3082.22 cm^{-1} for (OH), 1639.82 cm^{-1} for (C=O), 1341.82 cm^{-1} for C-N and 907.81 cm^{-1} for N-O.

iii. ^1H n.m.r (sample dissolved in $CDCI_3$) figure (6) : showing chemical shifts: 9.229 ppm, for (-NOH), 8.32, 7.76, 7.496 and 7.351ppm for aromatic protons.

iv. Mass spectrum figure (4): 258 is the molecular mass of N-phenyl-N-m-nitro benzohydroxamic acid, fragments $C_{12}H_9$.NOH.CO for 213 and 164 for $C_6H_4NO_2$.CO.N.

2.3 Extraction of metal ions:

2.3.1 Reagent:

1. 100 ppm of Fe (lll), Co (ll), Cu (ll), Ni (ll) and V (v) were prepared by diluting 25 cm^3 from 1000 ppm stock solution to 250 cm^3 with water in a volumetric flask.
2. Buffer solution from 1 to 7.
3. $2x10^{-2}$ M of hydroxamic acids solutions in organic solvents:

For each extraction, 1.29 g of hydroxamic acids were dissolved in 250 cm^3 of chloroform.

2.3.2 General extraction procedure: -

First the metal stock solution (1000 ppm) was diluted to a reasonably extractable concentration. Then an aliquot of 5 cm^3 portions from the diluted metal standard were transferred to six or seven, 25 cm^3 volumetric flasks and diluted to the mark with buffer solutions (selected range). The solutions were transferred quantitatively to six or seven 100 cm^3 separatory funnel. 25 cm^3, portions of $2x10^{-2}$ M hydroxamic acid dissolved in organic solvent were added to each separatory funnel. The mixtures were shaken gently for two minutes and then allowed to separate. The aqueous layers (A) were separated in 25 cm^3 volumetric flasks, and analyzed for the percentage of metal unextracted by the hydroxamic acid.

3 Result:

3.1 Analysis for metal ions content using AAS:

Standards of Fe (lll), Cu (ll), Co (ll), Ni (ll) and V (V) were sprayed first in the atomic absorption spectrophotometer to calibrate the instrument, and then followed by the extracted aqueous layers (A).

Table (1): Result of extraction of Fe (lll) with N-phenyl-N-p-nitrobenzohydroxamic acid:

pH	Conc. of A(ppm)	% Unextracted	%Extracted
1	9.2637	46.30	53.70
2	8.1627	40.80	59.20
3	7.4559	37.30	62.70
4	6.8240	34.10	65.90
5	2.5472	12.70	87.30
6	5.3224	26.60	73.40

Table (2): Result of extraction of Fe(lll) with N-phenyl-N-m-nitrobenzohydroxamic acid:

pH	Conc. of A(ppm)	% Unextracted	%Extracted
1	9.8434	49.20	50.80
2	8.7301	43.70	56.30
3	7.7320	38.70	61.30
4	7.0303	35.20	64.80
5	3.3735	16.90	83.10
6	7.8493	39.20	60.80

Table (3): Result of extraction of Cu (ll) with N-phenyl-N-p-nitrobenzohydroxamic acid:

pH	Conc. of A(ppm)	% Unextracted	%Extracted
1	17.1400	85.70	14.30
2	0.4472	2.20	97.80
3	0.1084	0.54	99.46
4	0.0917	0.46	99.54
5	0.0796	0.40	99.60
6	0.0219	0.10	99.90
7	0.0371	0.20	99.80

Table (4): Result of extraction of Cu (ll) with N-phenyl-N-m-nitrobenzohydroxamic acid:

pH	Conc. of A(ppm)	% Unextracted	%Extracted

1	11.6600	58.30	41.70
2	0.3782	1.90	98.10
3	0.1035	0.50	99.50
4	0.0842	0.40	99.60
5	0.1313	0.70	99.30
6	0.0632	0.32	99.68
7	0.0595	0.30	99.70

Table (5): Result of extraction of Ni (ll) with N-phenyl-N-p-nitrobenzohydroxamic acid:

pH	**Conc. of A (ppm)**	**% Unextracted**	**%Extracted**
1	18.3800	91.90	8.10
2	8.1350	40.70	59.30
3	12.7100	63.55	36.45
4	12.7425	63.70	36.30
5	13.8194	69.10	30.90
6	10.1487	50.70	49.30
7	0.1773	0.90	99.10

Table (6): Result of extraction of Ni (ll) with N-phenyl-N-m-nitrobenzohydroxamic acid:

pH	**Conc. of A (ppm)**	**% Unextracted**	**%Extracted**
1	14.7400	73.70	26.30
2	12.5100	62.55	37.45
3	12.3900	62.00	38.00
4	11.415	57.00	43.00
5	11.8770	59.40	40.60
6	6.8250	34.10	65.90
7	0.7740	3.90	96.10

Table (7): Result of extraction of Co (ll) with N-phenyl-N-p-nitrobenzohydroxamic acid

pH	Conc. of A(ppm)	% Unextracted	%Extracted
4	13.3690	66.80	33.20
5	17.6000	88.00	12.00
6	15.8580	79.30	20.70
7	1.8957	9.48	90.52
8	0.2330	1.17	98.83
9	1.7057	8.50	91.50
10	0.7590	3.80	96.20

Table (8): Result of extraction of Co (ll) with N-phenyl-N-m-nitrobenzohydroxamic acid

pH	Conc. Of A (ppm)	% Unextracted	%Extracted
4	19.0647	95.30	4.70
5	18.1449	90.70	9.30
6	13.6242	68.10	31.90
7	2.5034	12.50	87.50
8	0.2763	1.40	98.60
9	1.4351	7.20	92.80
10	2.2556	11.30	88.70

Table (9): Result of extraction of V (v) with N-phenyl-N-p-nitrobenzohydroxamic acid

pH	Conc. of A (ppm)	% Unextracted	%Extracted
1	0.6261	03.13	96.87
2	2.077	10.39	89.61
3	14.00	70.00	30.00
4	13.37	66.85	33.15
5	3.392	16.96	83.04
6	1.279	06.40	93.60

Table (10): Result of extraction of V (v) with N-phenyl-N-m-nitrobenzohydroxamic acid

pH	Conc. of A (ppm)	% Unextracted	%Extracted

1	1.224	6.12	93.88
2	2.634	13.17	86.83
3	12.77	63.85	36.15
4	13.50	67.50	32.50
5	2.539	12.70	87.30
6	5.179	25.90	74.10

Table (11): The effect of nitro group in the p- and m- position and pH on maximum extraction percentage

	Fe	Cu	Ni	Co	V
N-phenyl-N-p-nitrobenzohydroxamic acids	87.30 pH 5.0	99.90 pH 6.0	99.10 pH 7.0	98.830 pH 8.0	96.87 pH 1.0
N-phenyl-N-m-nitrobenzohydroxamic acids	83.10 pH 5.0	99.70 pH 7.0	96.10 pH 7.0	98.60 pH 8.0	93.88 pH 1.0

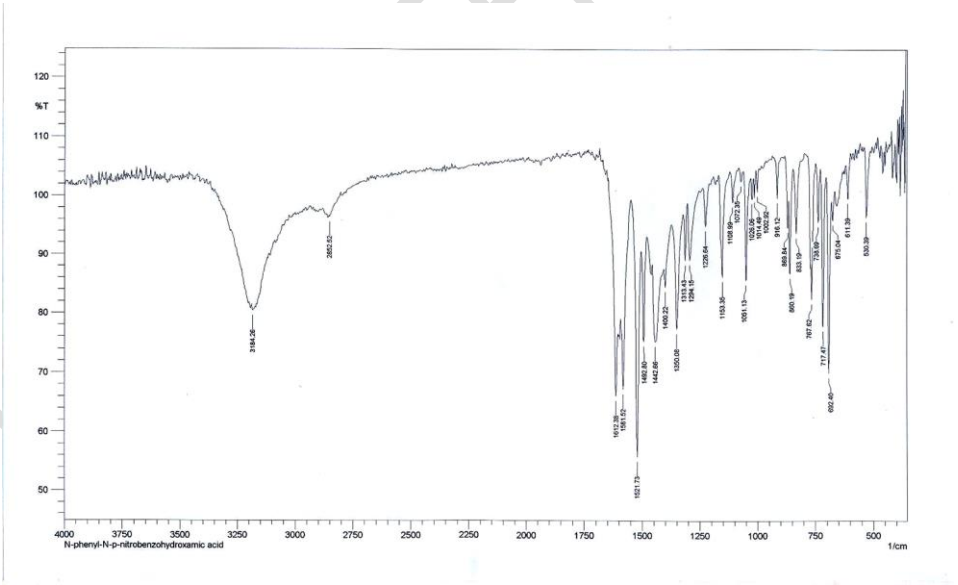


Figure (1): I.R spectrum of N-Phenyl-N-P-nitro benzo hydroxmic acid

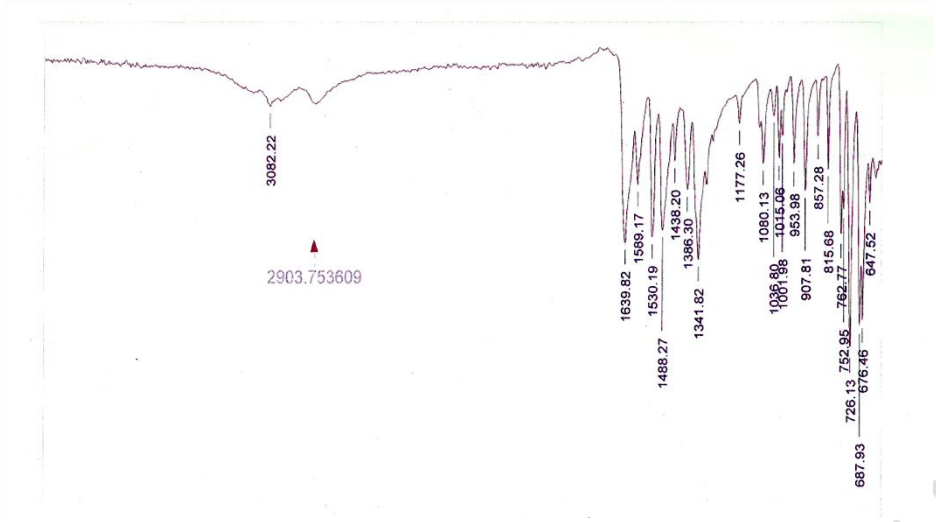


Figure (2): I.R spectrum of N-Phenyl-N-m-nitro benzo hydroxmic acid

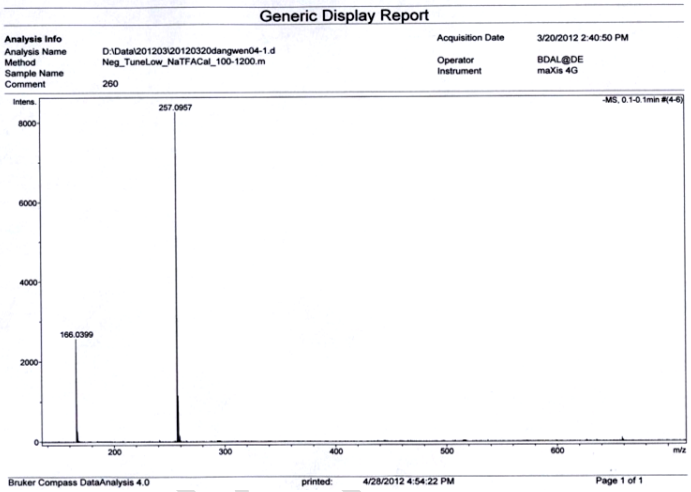


Figure (3): Mass spectrum of N- Phenyl-N-P- nitro benzo hydroxmic acid

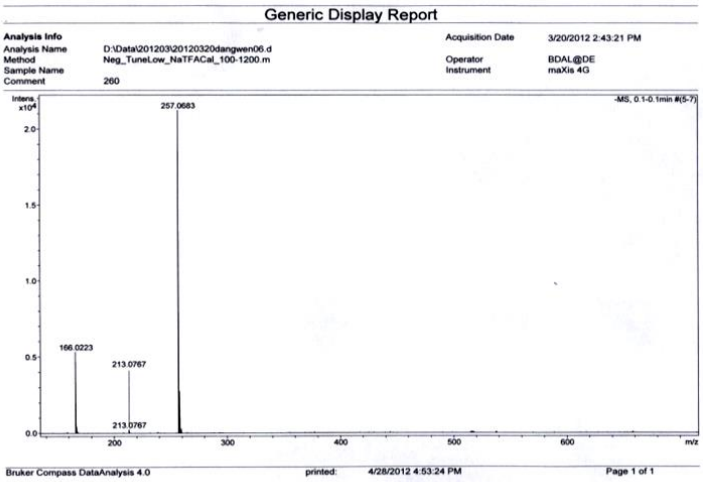


Figure (4) Mass spectrum of N- Phenyl-N-m- nitro benzo hydroxmic acid

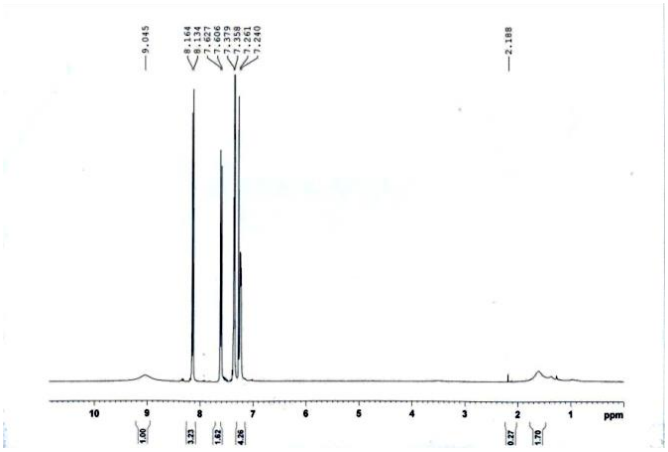


Figure (5): H1 NMR spectrum of N-Phenyl -N-P- nitro benzo hydroxmic acid

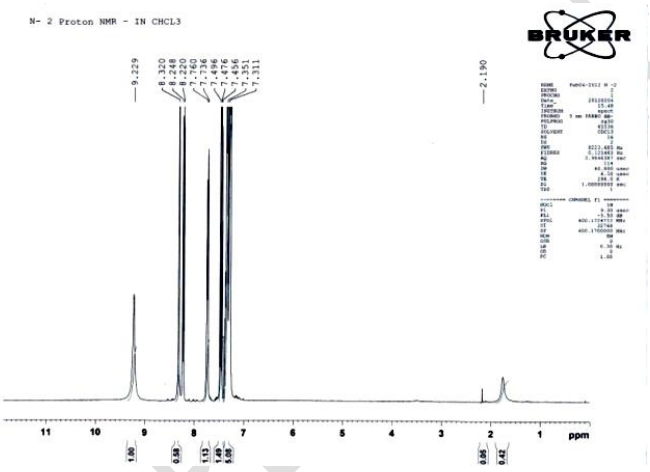


Figure (6): H1 NMR spectrum of N-Phenyl -N-m- nitro benzo hydroxmic acid

4 Discussion and conclusion:

Hydroxamic acids were prepared by many methods, but the coupling reaction between the substituted acid chloride and hydroxylamine under cold ether process, was found to be more applicable than the aqueous process, due to the relative purity of the final product obtained which is mainly the monohydroxamic acid.

The four hydroxamic acids prepared are pale yellow crystalline solids. They are sparingly soluble in water but are readily soluble in benzene, alcohol and chloroform.

The high yield N-phenyl-N-p-nitrobenzohydroxamic acid can be attributed to the p-substituent of the nitro group which cause electronic effect that decrease the tendency to form o- and di- derivatives.

The hydroxamic acids prepared were quantitatively identified by their reaction towards ferric chloride and vanadium (v) solution, giving blood-red and a deep- violet color respectively in the chloroform extract.

They were also characterized by their melting points, (166 ^{0}C) for N-phenyl-N-p-nitro benzohydroxamic acid, (120 ^{0}C) for N-phenyl-N-m-nitro benzohydroxamic acid.

The hydroxamic acids prepared show the most characteristic bands associated with hydroxamic acid functional grouping that is due to OH, C=O, N-O and C-N.

The ^{1}H NMR spectra of hydroxamic acids under investigation show the characteristic of the proton of the hydroxyl group attached to the nitrogen atom in the region 9.045 – 9.229 ppm. The shifting of the resonance signal of hydroxyl proton to lower field supports intermolecular hydrogen bonding. The protons of aromatic ring appear in the region 7.24 – 8.32 ppm.

The ^{13}C NMR spectra exhibit absorption signal due to carbonyl (C=O) in the region 163.31 and 178.59 ppm. The chemical shifts of aromatic carbons appear in the region 123.56 – 149.21 ppm.

The mass spectrum of N-phenyl-N-p-nitro benzohydroxamic acid gave the correct molecular mass (258) and fragments sequence of 164.0399 and 257.0957 corresponding to $C_6H_5NO_2CON$. And (M – H) respectively.

The mass spectrum of N-phenyl-N-m-nitro benzohydroxamic acid gave the correct molecular mass (258) and fragments sequence of 164.0223, 213.0767 and257.0653, corresponding to $C_6H_5NO_2CON$, (M – NO_2) and (M – H) respectively.

For extraction and separation work, the acidity of the ligands is affected by the electron-donating or electron- withdrawing groups attached to the hydroxamic acids. The electron- withdrawing groups increase the acidity and hence the extractability of a metal with a ligand.

The effect of nitro group in the p- and m- position can be observed through the comparison between N-phenyl-N-p-nitro benzohydroxamic acid and N-phenyl-N-m-nitro benzohydroxamic acid as shown in table (11).

The most likely cause for this is the decrease in the formation of metal chelate owing to the steric hindrance of the nitro group in the meta- position, while the para- nitro group has no effect on the formation of the metal complex.

Generally, the meta–nitro group has slight effect in the maximum extraction percentage.

The extractability of the substituted hydroxamic acids indicates a general increase of the amount of metal extracted with an increase in pH, as shown in table (11).

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