International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Index Copernicus Value (2015): 78.96 | Impact Factor (2015): 6.391

Preparation, Characterization and Evaluation of the Extraction Efficiency of Phthalohydroxamic Acid towards Nickel and Cobalt Cations

Dr. Egbal Eltom Bakheet[1], Dr. Elmugdad Ahmed Ali[2]

[1, 2]Sudan University of Science and Technology, Khartoum, Sudan

Abstract: ***The study deals the extractive ability of Phthalohydroxamic acid. The acid was prepared through coupling of the parent ester with the free hydroxylamine. It was characterized by color test, m.p., infrared and G.C- mass spectrometry. The extractive properties of the acid towards the metal: Ni^{+2} and Co^{+2} cations were determined under different pH values. The extractability it found to: Ni (II) 24.4% at pH 6 and Co (II) 35.5% at pH 9***

Keywords: chelation, coupling, partition coefficient, phase distributions

1. Introduction

Hydroxamic acids have the general formula , where (R and R- = hydrogen, alkyl or aryl) and a large number of derivatives are available with different R and R-groups. Hydroxamic acid have the bidentate functional grouping, that fulfils the basic requirements of complex formation with metal ions. Hydroxamic acid [1, 2], began in 1869 when H. Lossen, isolated oxalohydroxamic acid from the reaction product of ethyl oxalate and hydroxylamine. Later H. Lossen obtained a mixture of mono, di and tribenzoyl derivatives from the reaction of hydroxylamine with benzoyl chloride.

2. Literature Survey

Hydroxamic acids are in general prepared by the reaction of an activated acyl or aryl group with hydroxylamine in presence of an alkali as catalyst. Substrates that undergo this reaction are carboxylic acid, ester, acid chlorides, amides, lactams, acid anhydrides and imides. They are identified by V(v) solution and Fe (III) solution, m.p, infrared and G.C-mass spectra.

Hydroxamic acids find many applications in organic and inorganic analytical gravimetry [2,3] spectrophotometry [4,5] titrimetry [6,7] , ion exchange and other uses. Gravimetric methods the most important applications of hydroxamic acids as analytical reagents are their uses as complexing agent for metal ions. It is some- times possible to separate interfering ions by controlling the pH and the uses of the masking agents. Most spectrophotometric methods of hydroxamic acids have dealt with those metals which exist as cations of block (d) and block (f) element in dilute acidic solution. Colors are intensified by extraction with suitable solvents.

Most of hydroxamic acids can be titrated against alkalis in non-aqueous media with phenolphthalein as an indicator, however, the end point is not sharp [8]. The strong base potassium methoxide (in methanol / benzene 1 : 10 v/v) gives a sharp end point in the titration of hydroxamic acid.

Most of hydroxamic acids are important substances in the medical field. Their biological activity being attributed to their ability to chelate specifically with iron. The trihydroxamic acid desforrioxamine Bis currently used for the treatment of iron overload disease. It is usually sold as a salt under the trade name desferal. Dihydroxamic acid finds similar application [9].

The exchange solvent extraction or liquid – liquid extraction is based on the distribution of solute between two essentially immiscible solvents. Usually one is an aqueous phase and the other is an organic liquid. Solvent extraction is widely used as separation technique because of its ease, speed, selectivity and convenience [10].

For all phase distributions, the classical phase rule of Gibbs is applied:

$$P+V = C+2 \quad (1)$$

P≡ number of phases
V≡ variance or degree
C≡ number of components

In a particular case of solvent extraction we are dealing with two essentially immiscible solvents and one solute distributed between them so that, P =2, and C=3. At constant temperature and pressure, the rule predicts a variance of unity. This means that if we choose the concentration of solute in one phase, the solute concentration in the other phase is fixed, hence there will be a definite relationship between the solute concentrations in each of the solvent phase. This relation is described in distribution law.

The distribution law was first stated by [11] and then elaborated by [12]. The law states that: at equilibrium a given solute is distributed between two immiscible liquids in the same proportions which can be expressed mathematically as:

$$KD = [\ Aorg\ ] / [\ Aaq] \quad (2)$$

Where: K_D is the distribution or partition coefficient, A_{org} and A_{aq} are known as the concentration of solute (A) distributed between immiscible phases provided that its molecular state is the same in both liquids and that the temperature is constant.

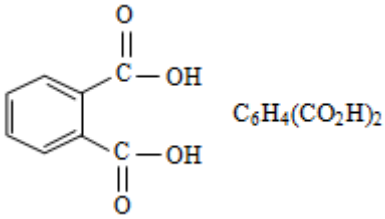
Licensed Under Creative Commons Attribution CC BY

The distribution

$$D = [C_A]_{org} / [C_A]_{aq} \quad (3)$$

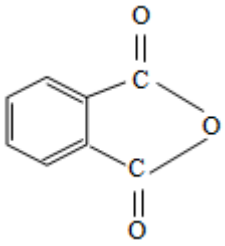
Where C_A is the total concentration of solute A is all forms. When D is very large only one extraction is enough to remove a substance from the solution, otherwise, several extractions are required.

Phthalic acid is an aromatic dicarboxylic acid, with formula $C_6H_4(CO_2H)_2$ it is an isomer of isophthalic acid and terephthalic acid. Although phthalic acid is of modest. Commercial importance, the closely related derivative phthalic anhydride is a commodity chemical produced on a large scale [13].



$C_6H_4(CO_2H)_2$

Phthalic acid is produced by the catalytic oxidation of naphthalene or ortho- xylene directly to phthalic anhydride and a subsequent hydrolysis of the anhydride phthalic acid.
Phthalic anhydride is the organic compound with formula $C_6H_4(CO)_2O$. It is the anhydride of phthalic acid. Phthalic anhydride is a principle commercial form of phthalic acid. It was the first anhydride of a dicarboxylic acid to be used commercially. This colourless solid is an important industrial chemical, especially for the large – scale production of plasticizers for plastics.



$C_6H_4(CO)_2O$

Phthalic anhydride was first reported in 1836 by [14]. More contemporary routes include catalytic oxidation of ortho – xylene and naphthalene (Gibbs phthalic anhydride process), although use of naphthalene has declined starting from o-xylene, the oxidation follows the following stoichiometry.

$$C_6H_4(CH_3)_2 + 3\ O_2 \longrightarrow C_6H_4(CO)_2O + 3\ H_2O \quad (4)$$

The reaction proceeds with about 70% selectivity. About 10% of maleic anhydride is also produced.

$$C_6H_4(CH_3)_2 + 7.5\ O_2 \longrightarrow C_4H_2O_3 + 4H_2O + 4CO_2 \quad (5)$$

The reaction is catalysed by a vanadium pentoxide (V_2O_5) between 320°- 400° C. Phthalic anhydride can also be prepared from phthalic acid [13].

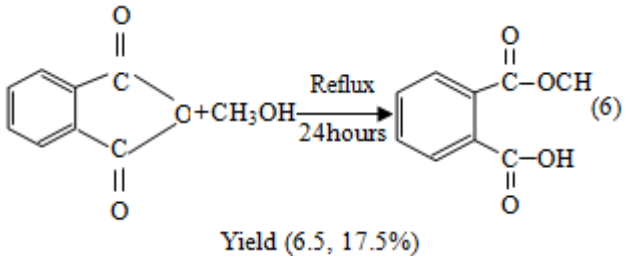
Hydroxamic acid chelating resins were prepared by converting a cross – linked poly carboxylic acids via ester, acid chloride or other alternative methods, these resins have been found to be effective for the following ions: Ni(II), Co(II). The chelating hydroxamic acid resins have been found of great industrial benefits specially in metal recovery and hydrometallurgy.

Although Phthalohydroxamic acid has not been reported, its monohydroxylamine analog is known, namely, O-carboxybenzohydroxamic acid. It was the product of reaction of phthalic anhydride and hydroxylamine. In the present work it was found that although sodium Phthalohydroxamate was obtainable by interaction of phthalic ester, hydroxylamine and sodium ethoxide, precautions were necessary to prevent formation of (phthaloxime) thus, temperature control (5° C) is important and temperature must not be allowed to rise spontaneously, the solvent must be nearly an hydrous, and the salt must not be allowed to stand in moist air. The salt gave the ferric chloride color reaction typical of hydroxamic acids but it contained less sodium than that calculated for the disodium salt. Attempts to purify it by crystallization were un successful, as were attempts to obtain the free Phthalohydroxamic acid; instead, phthaloxime was obtained when the salt was acidified. Treatment of a concentrated aqueous solution of the salt with carbon dioxide yielded red plates and further acidification with hydrochloric acid yielded phthaloxime. The coloured substance was probably a salt of phthaloxime when is known to form several coloured salts [15].

3. Methodology

Materials
All chemical are purified.

Methods
Preparation of phthalohydroxamic acid:
Preparation of phthalate ester
Equimolar quantities of phthalic anhydride and methanol (0.25 mole each) were refluxed for different periods of time (5,10,15,20,24 and 48 hrs) and the optimum conditions for the preparation of the ester was found. It was concluded that, refluxing for 24 hrs is the reasonable time to convert almost all the anhydride to the corresponding ester [16]. The ester formed had a melting point of 86° C which fits quite well with the literature value 85° C. The reaction can be represented as.



(6)

Yield (6.5, 17.5%)

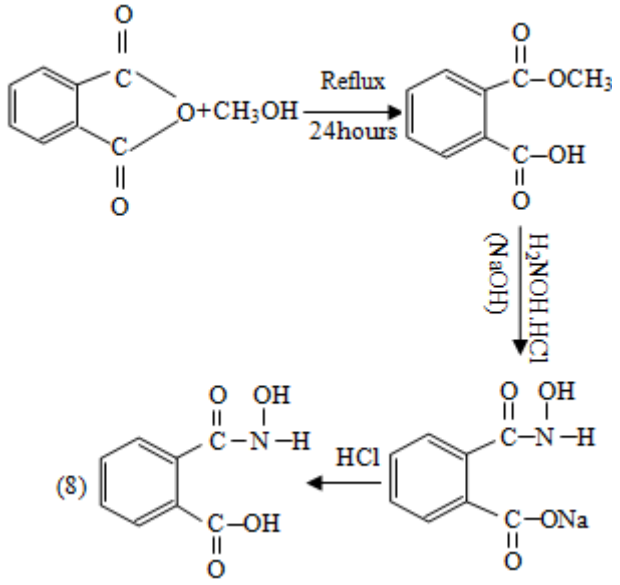
Preparation of free hydroxyl amine
The free hydroxylamine was prepared by adding (6.95g, 0.1mole) of $NH_2OH.HCl$ to an exess of 4.0% methanolic sodium hydroxide. The sodium chloride formed was filtered off leaving solution of hydroxylamine in methanol.

$$H_2NOH.HCl + NaOH = H_2NOH.CH_3OH + NaCl + HO_2 \quad (7)$$

Licensed Under Creative Commons Attribution CC BY

Preparation of phthalohydroxamic acid

The ester product was refluxed with an equal number of mole of hydroxylamine free from hydrochloric acid (0.036 mole each) in methanol for 7.0 hrs and in basic media using sodium hydroxid pellets. The exess methanol was distilled off and the product was acidified with dilute HCl (1M) and recrystallized from methanol and water. The yield obtained is 4.5g. The product has a melting point of 242°C.



Characterization of PHA

1) M.pt. 242 °C.
2) i.r. spectrum. Showing absorption bands ; 3091 cm^{-1} for (-OH), 1689 cm^{-1} for (C=O) , 906 cm^{-1} for (N-O) and 1282 cm^{-1} for (C-N).
3) G.C-mass spectrum.

Molecular mass 181 for PHA, and fragments
$C_6H_4CO.COOH$= 149, $C_6H_4CO.NHO$= 135,
$C_6H_4CO.NHOH$= 136, $C_6H_4CO.N.COOH$= 163,
$C_6H_4.COOH$= 121, $CO.NHOH.COOH$= 105, C_6H_4= 76.

Extraction:

Phthalohydroxamic acid

0.905 g (0.0056 mole) of phthalohydroxamic acid were dissolved in 250 cm^3 of amyl alcohol and filtered.

General extraction procedure

The metal stock solution (1000 ppm) was diluted to a reasonably extractable concentration. Then 5 cm^3 portions from the diluted metal standard were transferred by a pipette to 6 or 7 , 25 cm^3 volumetric flasks and completed to the mark with buffer solution to make a solution of (certain ppm) in each. The contents were transferred quantitatively to 6 or 7. 100 cm^3 separatory funnels. 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 were separated in 25 cm^3 volumetric flask and analyzed for the percentage of metal unextracted by the hydroxamic acid.

Extraction of metals

Nickel (II)

Reagents:

1) 100 ppm Ni (II) solution, prepared by diluting 25 cm^3 from the 1000 ppm stock solution to 250 cm^3 with water in a volumetric flask.
2) Buffer solutions range from 1 to 7.
3) $2x10^{-2}$ M PHA in Amyl alcohol.

Extraction

5 cm^3 portions of 100 ppm Ni (II) solution were transferred by a pipette to seven 25 cm^3 volumetric flasks, completed to the mark with buffer solutions from 1 to 7 respectively, this constituted 20 ppm Ni (II) in each. The content of each flask was transferred quantitatively to seven 100 cm^3 separatory funnels. 25 cm^3 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 the layers were allowed to separate.

The aqueous layers, were separated in 25 cm^3 volumetric flask.

Preparation of standard nickel solution for instrument calibration (AAS)

Standards containing 0.5, 1.0, 1.5, 2.5 and 5 ppm Ni (II) were prepared by pipetting 0.125, 0.25, 0.375 and 0.625cm^3 of 100 ppm Ni (II) solution into 25cm^3 volumetric flasks and completed to the mark with water.

Cobalt (II):

Reagents:

1) 100 ppm Co (II) solution prepared by transferring 25 cm^3 from the 1000 ppm stock solution to 250 volumetric flasks and diluted to the mark with water.
2) Buffer solutions range from 4 to 10.
3) $2x10^{-2}$ M PHA in Amyl alcohol.

Extraction

5 cm^3 portions of 100 ppm Co (II) solution were transferred by a pipette to seven 25 cm^3 volumetric flasks, completed to the mark with buffer solutions from 4 to 10 respectively; the content of each flask was transferred quantitatively to seven 100 cm^3 separatory funnels. 25 cm^3 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 the layers were allowed to separate. The aqueous layers, were separated in 25 cm^3 volumetric flask.

Preparation of standard Co (II) solution for instrument calibration (AAS)

Standards containing 0.1,0.15, 0.2 and 0.3 ppm Co (II) were prepared by pipetting 0.025, 0.0375, 0.05 and 0.075 cm^3 of 100 ppm Co (II) solution into 25 cm^3 volumetric flasks and completed to the mark with water.

4. Results

Analysis for Nickel (II) content:

Standard calibration curve:

The standard concentration in ppm:
0.50, 1.00, 1.5, 2.5, 5.00 and the concentration reading in the AAS (Absorption): 0.0018, 0.0034, 0.0051, 0.0083, 0.0146

Licensed Under Creative Commons Attribution CC BY

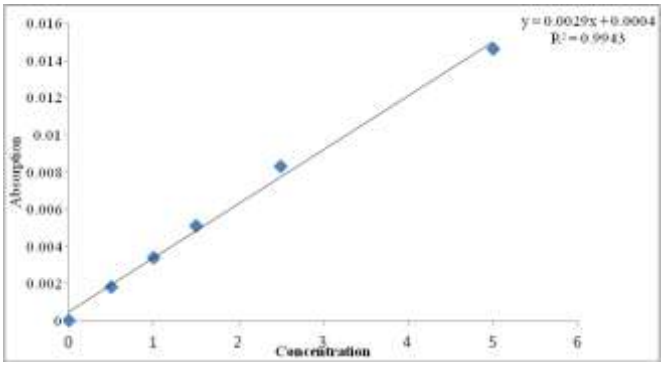


Figure 1: Calibration graph for atomic absorption spectrometric determination of Ni (II) with hydroxamic acids.

Table 1: Extracted of Ni (II)

pH:	1	2	3	4	5	6	7
Conc.:	18.2671	17.2788	17.1376	169258	16.2904	15.1256	15.7963
Unextracted%	91.34	86.40	85.69	84.63	81.45	75.63	78.98
Extracted%	8.66	13.61	14.31	15.37	18.55	24.37	21.02

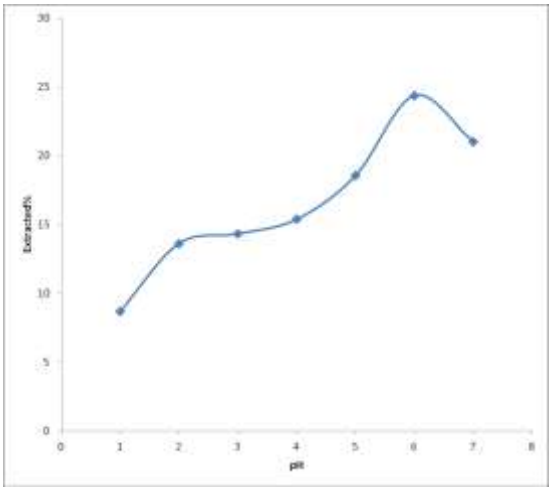


Figure 2: Extraction curve showing distribution of Ni (II) as a function of pH for the PHA.

Analysis for cobalt (II) content

Standard calibration curve:
Concentration in ppm: 0.10, 0.15, 0.20, 0.300 and the concentration reading in the AAS (Absorption): 0.0069, 0.0089, 0.0123, 0.0186.

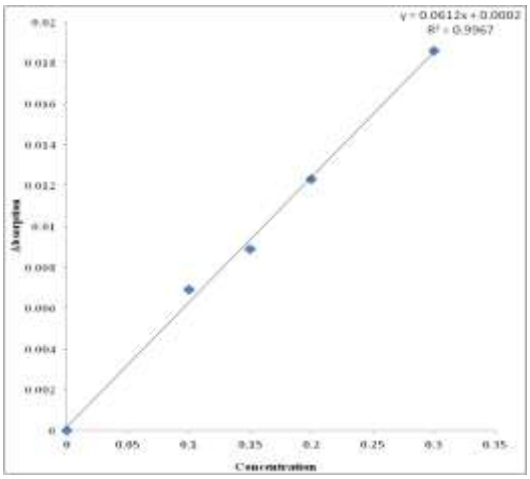


Figure 3: Calibration graph for atomic absorption spectrometric determination of Co (II) with hydroxamic acids.

Table 2: *Extracted of Co (II)*

pH:	4	5	6	7	8	9	10
Conc.:	15.50	15.00	14.70	13.90	13.50	12.90	13.20
Unextracted%	77.50	75.00	73.50	69.50	67.50	64.50	66.00
Extracted%	22.50	15.00	26.50	30.50	32.50	35.50	34.00

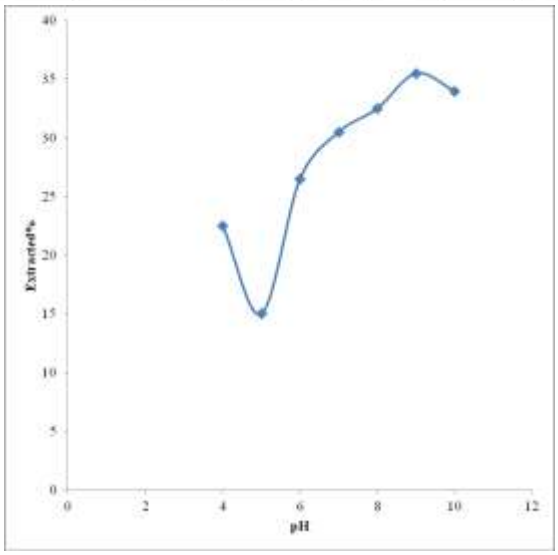


Figure 4: Extraction curve showing distribution of Co (II) as a function of pH for the PHA.

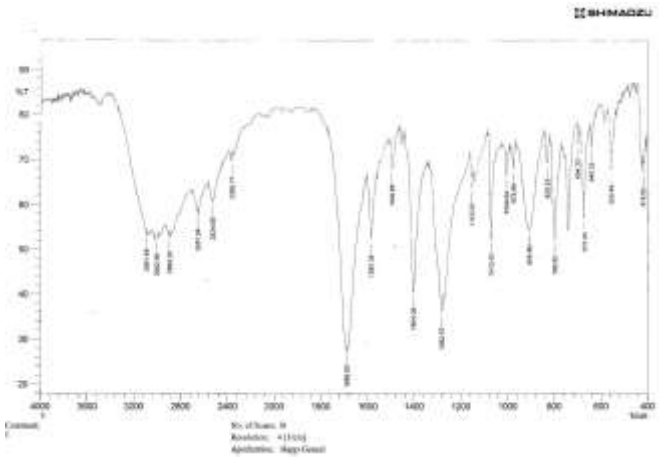


Figure 5: infra red spectra of phthalohydroxamic acid

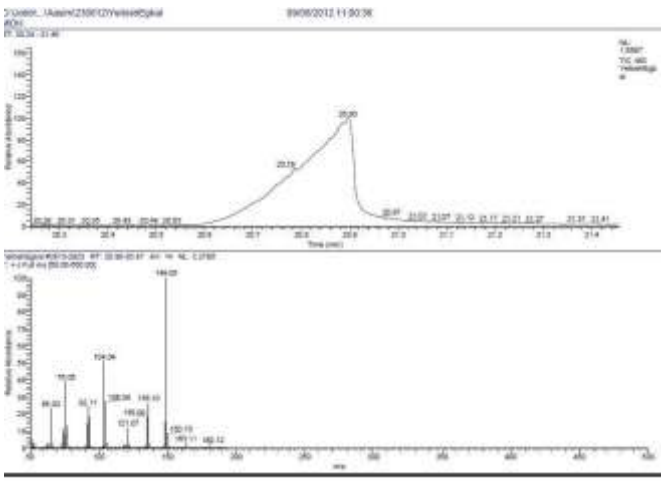


Figure 6: G.C Mass spectra of phthalohydroxamic acid

Licensed Under Creative Commons Attribution CC BY

5. Discussion and Conclusions

Carboxylic acids are the starting materials for the preparation of hydroxamic acids either through ester or acid chloride route. It has been shown that hydroxamic acids exhibt an extra complexing capacity toward a very great number of metal ion.

When a solution of a hydroxamic acids is added to an acidified vanadium solution (or ferric solution) violet and blood red colour are developed respectively. Such reactions indicate that the compounds exhibit hydroxamic acid properties.

The phthalohydroxamic acid (PHA) are prepared, purified and recrystallized from appropriate solvent. It was identified by melting point, infra-red, G.C-mass spectroscopy.

The melting points of PHA is 242°C.
The IR spectrum of PHA showed γ (KBr) 906 (N-O), 1282 (C-N), 1689 (C=O) and 3091 cm^{-1} (OH).
The G.C mass spectrum of PHA gave m/z 181 corresponding to (M^+) and a sequence of fragmentation at m/z 149, 135, 136, 163, 121, 105,76. Corresponding to the loss of NHOH, CO.OH.H, CO.OH, H_2O, CO.NHOH, C_6H_4 and CO.OH.CO.NHOH respectively.
181- 149 = 32 corresponds to loss of NHOH group.
181- 135 = 46 corresponds to loss of CO.OH.H group.
181-136 = 45 corresponds to loss of CO.OH group.
181- 163 = 18 corresponds to loss of H_2O group.
181- 121 = 60 corresponds to loss of CO.NHOH group.
181- 105 =76 corresponds to loss of C_6H_4 group.
181- 76 =105 corresponds to loss of CO.OH.CO.NHOH group.

The reagents containing aromatic hydroxamic acid functional group are less soluble in aqueous media and they generally form coloured extractable chelates.

The high percentage of extraction due to the acidity of phthalohydroxamic acid prepared and metal ions which formed stable complexes according to Irving-william series.
Mn (II) < Fe (III) < Co (II) < Ni (II) < Cu (II) < Zn (II).

Ni (II)
PHA extract Ni (II) up to 24.37% at pH 6.

Co (II)
PHA extract Co (II) up to 35.5% at pH 9.

References

[1] Yale, H.L. (1943) Chem. Rev, 33, 209.
[2] Majumadar, A.K. (1972) "N. Benzoylphenylhydroxylamine and its Analogues", Pergamon Press, Oxford. Vol. 50.
[3] Chatterjee, B.J. (1968) Ind. Chem. Soc., 45:1061, 48:929, (1971).
[4] Bhaduri, A.S. ; Ray, D. (1957) Anal. Chem., 103:154.
[5] Baroneeli, F.; Grossi, G. (1965) J. Inorg. Nucl. Chem., 25:1085.
[6] Shendricat, A.D. (1962) Talanta, 10:611.
[7] Kaimal, U.R.M.; Shome, S.C. (1963) Anal. Chim. Acta., 27:786.
[8] Vernon, F.; Khorassani, J.W. (1978) Talanta, 25 : 410.
[9] Agrawal, Y.K. (1972) Analyst., 97 : 578.
[10] Barry, L.K.; Synder, L.R; Casba, H. (1973) Introduction to Separation Science, John Wiley , New York.
[11] Berthelot, M.; Jungfleisch, J. (1872) Ann , Chem et Phys , 26 ,396.
[12] Nernst, Wo.Zo. (1891) Physik, Chem , 8, 110.
[13] Peter, M.; Lorz; Friedrich, K.; Towae; Walter Enke; Rudolf Jackh; Naresh Bhargava; Wolfgang Hillesheim (Phthalic Acid and Derivatives) in Ullmann,s Encyclopedia of Industrial Chemistry, 2007, Wiley-VCH,Weinheim. Doi : 10 . 1002/ 14356007. 920 – 181. Pub 2
[14] Auguste Laurent, (1836) (sur I, acid naphthaligue et ses combinaisons (on naphthalic acid and its compounds).
[15] Charles, D.; Hurd; Charles, M.; Buess; Ludwing; Bauer. (1953) The journal of Organic Chemistry. Vol 19.
[16] Cool, H.A.; Bunbury, M.H.; Hey, H.D.(1965) Dictionary of organic compound, 4th ed.

Author Profile

Dr. Egbal Eltom Bakheet, received the B.S. honor in Chemistry in 2002 from Sudan University of Science and Technology (SUST), and M.S. degrees in Chemistry in 2007 from Elgazeera University– Sudan , and PhD in Chemistry, Sudan University of Science and Technology 2012 – Khartoum, Sudan. She joint the staff of SUST as Teaching Assistant in 2003, and promoted as Assistant Professor 2013 in SUST. She now with the University of Hafr Albatin, chemistry department in Kingdom of Saudi Arabia as Assistant Professor. Member of Sudanese Chemical Society.

Dr. Elmugdad Ahmed Ali, received the B.S in General Chemistry, University of Khartoum Sudan. And M.Sc. in Analytical Chemistry, Queen's University of Belfast, United Kingdom. Ph.D. Chemistry, University of Khartoum, Sudan. Memberships in: Sudanese Medical Council, National Arabization Committee, Representative of the college of science in industrial technology & engineering college council. Extra Curricula Activities: Secretary – General, Sudanese Chemical Society, Scientific Advisor, Sudanese Consumer Protection Association, Active member in Environment Protection Society, Organizer of Faculty of Science weekly forum. Several publications internal and external Sudan. Full Professor and Head Department of Chemistry, College of Science, Sudan University of Science & Technology – Khartoum , Sudan.



Licensed Under Creative Commons Attribution CC BY