A new method for determination of Nickel ion (II) using the organic detector ferrozine

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ABSTRACT

The study includes the determination of Ni (II) using azo reagent Benzenesulfonate, 4,4'-[3-(2-pyridinyl)-1,2,4-triazine-5,6-diyl]bis-, hydrogen sodium salt (1:1:1) spectrophotometric at (λ_{max} 562 nm) wave length. The effect of different parameters on determination is evaluated. The study shows that best PH=(7±0.1). The study includes obey concentration of Beer-Lambert law to determination of the calibration graph of Ni(II) by reagent. From this graph we note obey the concentration of law was between (2-50) μg of Ni(II) after this values the absorbance increased. The stoichiometry of complex Nickel ion determined by molar ratio method. Result indicated reagent to metal ratio was (1:2) the stability constant of the complex determination through mole ratio method and its value indicated good stability. The UV-Vis spectra and the IR spectra of the complex and reagent were measured. From all mentioned studies proposed structural formula of Ni(II) complex.

Introduction

Nickel is a chemical element with symbol Ni and atomic number 28. It is a silvery-white lustrous metal with a slight golden tinge. Nickel belongs to the transition metals and is hard and ductile. Pure nickel shows a significant chemical activity that can be observed when nickel is powdered to maximize the exposed surface area on which reactions can occur, but larger pieces of the metal are slow to react with air at ambient conditions due to the formation of a protective oxide surface. Even then, nickel is reactive enough with oxygen that native nickel is rarely found on Earth's surface, being mostly confined to the interiors of larger nickel–iron meteorites that were protected from oxidation during their time in space. On Earth, such native nickel is found in combination with iron, a reflection of those elements' origin as major end products of supernova nucleosynthesis. An iron–nickel mixture is thought to compose Earth's inner core.[4]

The use of nickel (as a natural meteoric nickel–iron alloy) has been traced as far back as 3500 BCE. Nickel was first isolated and classified as a chemical element in 1751 by Axel Fredrik Cronstedt, who initially mistook its ore for a copper mineral. The element's name comes from a mischievous sprite of German miner mythology, Nickel (similar to Old Nick), that personified the fact that copper-nickel ores resisted refinement into copper. An economically important source of nickel is the iron ore limonite, which often contains 1-2% nickel. Nickel's other important ore minerals include garnierite, and pentlandite. Major production sites include the Sudbury region in Canada (which is thought to be of meteoric origin), New Caledonia in the Pacific, and Norilsk in Russia.[5]

Because of nickel's slow rate of oxidation at room temperature, it is considered corrosion-resistant. Historically, this has led to its use for plating metals such as iron and brass, coating chemistry equipment, and manufacturing certain alloys that retain a high silvery polish, such as German silver.[6] About 6% of world nickel production is still used for corrosion-resistant pure-nickel plating. Nickel-plated items are noted for provoking nickel allergy. Nickel has been widely used in coins, though its rising price has led to some replacement with cheaper metals in recent years.[7]

Nickel is one of four elements that are ferromagnetic around room temperature. Alnico permanent magnets based partly on nickel are of intermediate strength between iron-based permanent magnets and rare-earth magnets.[8] The metal is chiefly valuable in the modern world for the alloys it forms; about 60% of world production is used in nickel-steels (particularly stainless steel). Other common alloys, as well as some new superalloys, make up most of the remainder of world nickel use, with chemical uses for nickel compounds consuming less than 3% of production.[9] As a compound, nickel has a number of niche chemical manufacturing uses, such as a catalyst for hydrogenation. Enzymes of some microorganisms and plants contain nickel as an active site, which makes the metal an essential nutrient for them [10].

The present study was conducted to estimate the ion Nickel(II) spectrally using a reagent Benzenesulfonate, 4,4'-[3-(2-pyridinyl)-1,2,4-triazine-5,6-diyl]bis-, hydrogen sodium salt (1:1:1) at λ_{max} 562 nm wavelength which contains inhomogeneous loop in its structure different atoms is nitrogen [11], which owns electronic pairs nonbonding qualifies them to link with the different elements especially metallic ones to form complexes, fig.(1).

Practical Part

Prepared Solutions

Reagents

Ferrozine (0.01M ferrozine)

Make 100ml of ferrozine solution by diluting 0.508g of ferrozine using Distil water. *Keep in the dark only for a month as this solution oxidises over time.*

Buffer pH 9.5 (5M ammonium acetate adjusted to pH9.5 with a 28-30% ammonium hydroxide (NH_4OH).

Make 100ml, dissolving 38.54g of ammonium acetate in 30mL Distil water.

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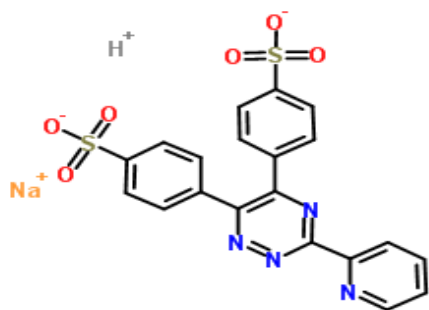
Fig 1. The chemical composition of organic reagent Benzenesulfonate, 4,4'-[3-(2-pyridinyl)-1,2,4-triazine-5,6-diyl]bis-, hydrogen sodium salt (1:1:1) Molecular Formula $C_{20}H_{13}N_4NaO_6S_2$, Average mass 492.460 Da Monoisotopic mass 492.017426 Da

Adjust to pH 9.5 by adding ammonium hydroxide solution (28-30% NH4OH)

Standards

Prepare the calibration immediately before running the analysis as Fe(II) oxidises with air, keep standards in closed bottles in the dark prior to adding the reagents.

100 ppm Ni^{2+} Stock Solution

Weigh out 0.0702 g of Mohr's salt $NiCl_2$. and dissolve in Distil water, make up to 100 mL in a volumetric flask. This will yield a slightly acid solution.

Standards for a calibration curve between 0.5-2.5 ppm

Prepare standards of 0.5, 1.0, 1.5, 2.0 and 2.5 ppm from the Ni^{2+} stock solution by dilution. Take the appropriated aliquots (below) of the 100ppm Fe stock solution and make up to 100 mL with Distil water.

To make 100 mL of standards at different concentration, please follow the equation:

$$\text{Concentration}_{std} \times 100\ mL = \text{Concentration}_{stock\ std\ solution} \times V_{needed}$$

The used devices

1 - PH measurement device (PH meter Hanna/ Italy).
2 - (UV-Vis) Spectroscopy measuring device (PG/ USA 990).
3 - Spectroscopy FTIR measuring device (Shimadzu 66x).
4 - Melting point measuring device (Thermo/ Germany).

Procedure

1. Switch on the instrument 15 minutes before the measurements and set wavelength to 562nm. This is to enable the bulbs in the spectrometer to warm up.

2. Prepare the spectrophotometric cuvettes, always hold them from the opaque sides. Cuvettes must be inserted in the same orientation all the time, there is a small arrow at the top to help ensure they are used the same way round.

3. Add 1mL of blank solution to a spectrophotometric cuvette. Repeat the same operation with the standards and samples.

4. Add 100 μL of ferrozine solution to all cuvettes, including the blank, standards and samples.

5. Add 50 μL of buffer to each cuvette and wait for 5 minutes for colour to develop in fully.

6. Put the blank into the spectrophotometer and push the zero key.

7. Measure the standards and samples in the same manner and record their absorbance values. Measure as soon as possible to avoid degradation of the coloured complex. If the absorbance of your samples is too intense for the spectrophotometer to measure, dilute the solution and repeat the analyses (steps 3-7).

8. Plot absorbance (y axis) against Ni^{2+}(aq) concentration (in ppm iron) (x axis)

9. Use the graph to find the concentration of Ni^{2+} (aq) as ppm iron in the samples. Or alternatively use analogue output of your results if your spectrophotometer has that option.

This method must be applied with caution in these situations:

● Samples with organic matter; as Ni^{2+} organic complexes may precipitate at acidic pHs and quantification of Ni^{2+} is incomplete.

● Ni^{2+} in solution form complexes with ferrozine. Although absorbance of, it is accounted for in the determination for Ni^{2+}.

● Any modification or adaptation of the current method must be carefully evaluated based on the reactions occurring during the determination and nature of the sample. It is not always possible to apply a similar spectrophotometric method from the published literature to samples of different nature.

Results and Discussion

The effect of different factors was studied to determine the optimum conditions for the process of complexity of Nickel ion (II) and reagent Benzenesulfonate, 4,4'-[3-(2-pyridinyl)-1,2,4-triazine-5,6-diyl]bis-, hydrogen sodium salt (1:1:1), these factors are:

Acidic function

Buffer solutions of metal ion were prepared in a concentration of (1×10^{-5}) Molar with acidic function ranged between (4-10),then the same volume of the organic reagent added to them, of an equivalent concentration to the metal ion, it observed variation the complexity of the process with variation of the acidic function as shown in Fig.(2), the complex showed higher absorption when the acidic function (7) so it is the best function of the consistency process between all of the mentioned ion and the reagent, this results are consistent with previous studies to set the Nickel ion (II) [12,13] because it is the best acidic function in which the reagent can give non covalent electronic couples to participate in the consistency process on the one hand and on the other hand the aggregates viable consistency become more freedom to contribute in the complexity process at this point. While the acidic function (9) showed high absorption value but the color of the reagent has change, the reason may be attributed to aggregates arrangement change and ties in the structure of the organic reagent along the lines of the principle of chemical indicators.
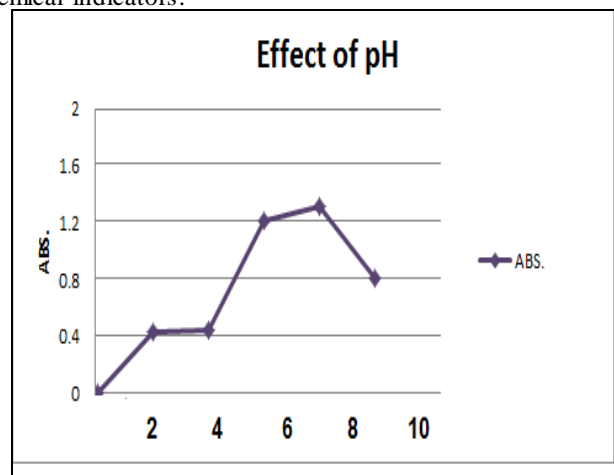
Fig 2. The relationship of the acidic function with the absorption for Nickel ion complex(II).

Metallic ion concentration

Different concentrations of Nickel ion(II) were prepared to determine the obey concentrations of Beer's- Lambert law ranged between (2-50)μg/ ml, then the same volume of organic reagent of the concentration (0.001%) was added for each

solution, then measured at the optimum acidic function and the results were as set out in fig.(3), we note that obey of the mentioned law is located between the concentrations (10-40) μg/ml equivalent the concentrations (1.5×10^{-4} - 15×10^{-4}) molar after these concentrations absorbance values deviate a positive deviation, the reason may be due to increasing of the mentioned ion concentration comparing to the organic reagent concentration which upset the balance process and distort the reaction to back according to Le Shateli principle and in fig.(3) we note that the value of the molar absorption constant is (1.5×10^4), where this value indicates the good stability of the formative complex.

Table 1. The values of the molar absorption coefficient to set the Nickel ion (II) using different reagents.

The ion	Molar Absorption	Reagents
Ni(II)	6.86×10^4	Dithzone
	4×10^4	4-(-2- Pyridylazo)resorcinol
	1×10^4	6-MBTABP
	4.9×10^4	5-(5- BrmoPyridylazo)-5-diethylamino phenol
	1.04×10^4	Xylenol orang
	1.5×10^4	1-Hydroxy-7-azabenzotriazole
	1.24×10^4	reagent Benzenesulfonate, 4,4'-[3-(2-pyridinyl)-1,2,4-triazine-5,6-diyl]bis-, hydrogen sodium salt

Table(1) shows that this method using organic reagent Benzenesulfonate, 4,4'-[3-(2-pyridinyl)-1,2,4-triazine-5,6-diyl]bis-, hydrogen sodium salt fall within the most accurate, sensitive and selective for the appointment of Nickel ion (II).
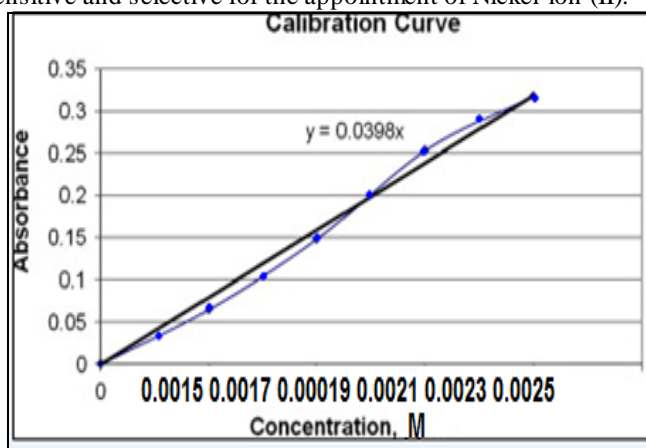

Fig 3. The standard calibration curve for duo ion Nickel using the new organic reagent reagent Benzenesulfonate, 4,4'-[3-(2-pyridinyl)-1,2,4-triazine-5,6-diyl]bis-, hydrogen sodium salt (1:1:1)

The formative complex valence

Molar ratio adopted for the study of valence of Nickel complex(II), where different concentrations of organic reagent were prepared in the range between (0.25×10^{-4} - 2.5×10^{-4}) molar and constant concentration of the metal ion, the results are shown in Fig.(4), and the proportion of the organic reagent to the metal ion was found equal to 1:2 and by which the stability constant of the complex was calculated[14], which amounted (0.904×10^4), this value refers to the good stability of this complex.

A concentration of 50 mg/liter of a group of positive and negative ions separately added to the mentioned ion solution and reagent to find out the effect of the presence of a number of positive and negative ions on the spectral estimation process of Nickel ion (II). The results displayed in table (2).
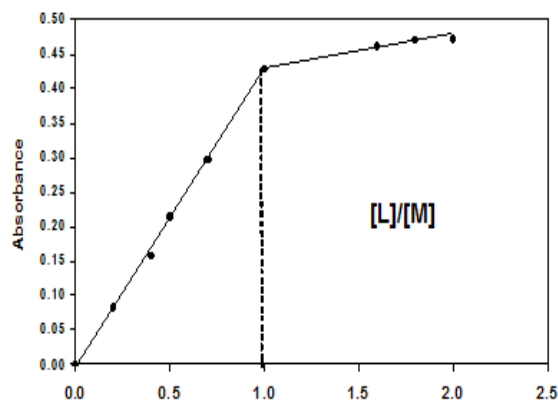
Fig 4. The relationship between the molar ratio M:L and the absorption of Nickel complex (II) at the greatest wavelength The effect of positive and negative ions

Those results showed influence of negative ions on the complexity process and the reason has been attributed to the fact that negative Nickel ion (II) produces stable complexes with both Tartrates Sulfates ion and less stable complexes with Chloride ion [15] on the one hand and on the other hand the presence of positive ions affects the consistency process, especially Cadmium ion (II) and Nickel (II) with the organic reagent [16], which affects negatively on the basic consistency process.

Table 2. The effect of the presence of some ions on the process of complexity through the values of the relative deviation (E) *

Positive ion	Relative Deviation E	Negative ion	Relative Deviation E
Cd++	0.324	Tartrate	0.046
Zn++	0.326	IO_4^{---}	0.237
Ba++	0.297	SO_4^{--}	0.311
K+	0.209	MnO_4	0.365
Mg++	0.329	CrO_4^{--}	0.092
Na+	0.105	-	-

* The concentration of the metal ion 1×10^{-4} molar

Also the melting point of the Nickel ion complex(II) and the reagent Benzenesulfonate, 4,4'-[3-(2-pyridinyl)-1,2,4-triazine-5,6-diyl]bis-, hydrogen sodium salt (1:1:1) were measured, the melting point of a metalloproteinase ion complex was (490 ºC) while for the detector one was (185 º C), referring to an increase in the molecular weight of the complex, resulting from the complexity process face increasing in the melting point. Table (3) shows some chemical characteristics for each of the organic reagent and complex.

Table 3. Some qualities of each of the complex and the organic detector

The substance	Color	Melting point ºC	Wave length λ_{max} nm	Molecular weight g. mol^{-1}
The reagent	Blue-Green	169	460	364.12
The complex	Red	245	562	490

A spectral study was conducted such as of UV-visible spectroscopy (Uv-Vis) and infrared spectroscopy FT-IR for both of the organic reagent and complex, the spectroscopy study of the ultraviolet-visible(UV-Uv-Vis) showed absorption spectrum in the ultraviolet - visual region for the metallic ion solution fig.(5-1) at the wave length of 217 nm and for the organic reagent Benzenesulfonate, 4,4'-[3-(2-pyridinyl)-1,2,4-triazine-5,6-diyl]bis-, hydrogen sodium salt (1:1:1) dissolving in ethanol fig.(5-2), and shown absorption peak at the greatest wavelength

of 440nm, and showed the absorption spectrum of the complex dissolved in the mentioned solvent the greatest absorption at the wavelength of 562 nm fig.(5-3), and when comparing the two values red shift is took place of the complex spectrum comparing to the organic reagent spectrum of 145nm and this could be due to obtain a correlation between the metal ion and donor atoms in the reagent which is both of nitrogen and oxygen atom.
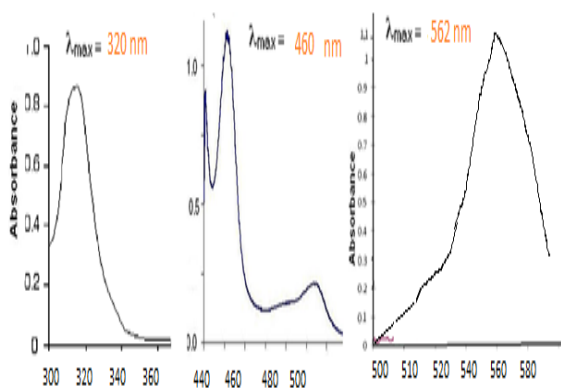

Fig (5-1): The spectrum of metal ion solution only Fig(5-2) the spectrum of reagent only Fig (5-3) the spectrum of complex

The complex have been diagnosed using spectroscopy Infrared IR fig.(6), and when comparing its spectrum with the organic detector spectrum fig.(7) we note clear changes, that appeared new packages were not already present before in the spectrum of the detector sometimes or disappearance of some packages or change its shape at other times as indicated in table(4) where we note the frequencies of the most important peaks and the changes that have obtained shows that the frequencies of the hydroxyl group(OH) move away from its position toward the higher frequency at consistency, and the reason of this attributed to break the implicit hydrogen bonds in the detector particle and involve the group in the overall episode of the complex after losing its proton by the effect of metalloproteinase ion and the acidic function of the solution [17-19]

Table 4. The values of the infrared spectra frequencies FTIR (cm^{-1}) for both the organic and the complex detectors.

Compound	υ O-H str.	C-N strυ	υ C-H alp.str	υ C-H arm.str	υ C=O
The reagent	-	1530.37(s)	2920. (m) 2905.2 (m)	3054.4 (w)	1740.2(s)
The complex	3260 (s)	1590 (s)	2924.42(m) 2850 (m)	3096(w)	1742. (s)

Also the (C = N) pack suffer from change in its shape, that refer to force it in the consistency process [18]. Changes got to vibrations of other groups such as (N = N), which are affected by the consistency process as well as the emergence of new packages such as (M-O). In the complex spectrum, we note the presence of a broad package at $3550cm^{-1}$ is attributed to the presence of water molecule within the complex structure and which confirms this conclusion is the weight difference of amount of the complex before and after the heating process to the degree of 105 ºc. Fig. (6) and (7) confirm the results we have obtained.
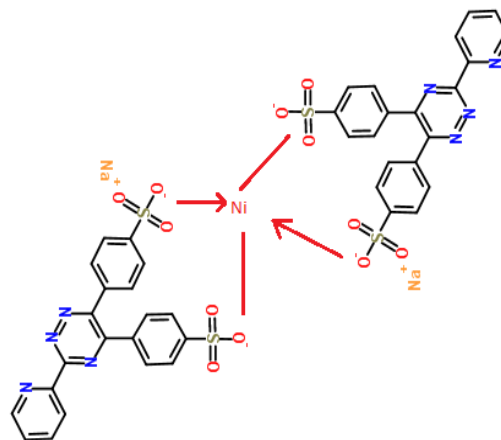
Depending on the mentioned above studies, vacuum figure of the formative complex have been proposed as shown in Fig.(8).
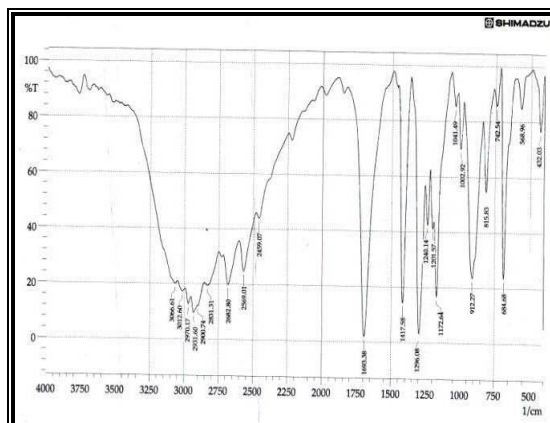
Fig 6. Infrared image of the detector Benzenesulfonate, 4,4'-[3-(2-pyridinyl)-1,2,4-triazine-5,6-diyl]bis-, hydrogen sodium salt (1:1:1)
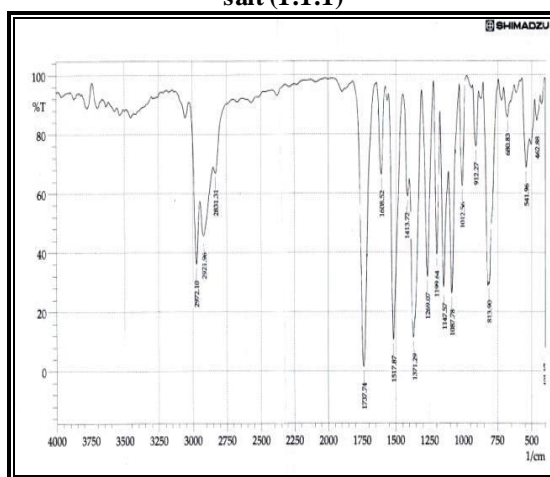
Fig 7. Infrared image of the complex

Fig 8. The proposed vacuum Figure of Nickel ion complex(II).

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