

# DETERMINING THE AMOUNT OF NICKEL IN BRONZE ON SOLID PHASE USING CATION EXCHANGER ON STRONG ACID

Sadouh Massoud\*

Department of Basic Sciences, Faculty of Pharmacy, Al Andalus University for Medical Sciences, AL-Kadmous, Tartous, Syrian Arab Republic

\*Corresponding author: E-mail: ws.sarah2005@gmail.com; Phone number: 00963991485107

## ABSTRACT

A method was designed for the determination the amount of nickel in bronze. It was based on the adsorption of nickel on positive ion exchange of strong acid Amberlit CG-120 in form-H. HCl:acetone medium at pH=1 was used in order to separate other positive ions as chloride complexes. The fluids were filtered and the cation exchanger was treated with ammonium buffer solution pH=8-9, then it was treated with an ethanolic solution of Dimethylglyoxime. The determination of Nickel content was carried out using a spectrophotometer. Results indicated a content of  $0.29 \pm 0.02\%$ , whereas the nickel theoretical content was 0.31%. Using IR spectra, it was found that the adsorption of nickel on Amberlit CG-120 was due to covalent bonds with groups-SO<sub>3</sub><sup>-</sup>, in the form of ammonium complexes.

**Key Words:** Nickel, Bronze бРАжM-114, Amberlit CG-120, Dimethylglyoxime (DMG).

## INTRODUCTION

The great increase in manufacturing production nowadays causes a negative effect on the environment. Therefore, it is necessary to improve analytical methods in order to control different manufacturing process. These methods should be accurate, sensitive, rapid and simple in order to determine the specific element with a high LOD and LOQ. One of these methods is the spectrophotometer on solid phase methods. The first step in the conventional determination of nickel in Bronze is the isolation of preinstalled existing template from the Matrix. Cations were isolated as chlorinate complexes on cation exchanger Ky-2. They were also isolated using an anion exchanger (Dayekc-1) pretreated with different concentrations of hydrochloric acid solution ranging between 0.1-12 M, the isolation was mainly performed due to the difference in the stability of chloride-metal complexes. The following metals are isolated by Ky-2 ion-exchanger: Fe<sup>3+</sup>, Zn, Mn, Co and Ni (Guixia et al., 2011), while (Dayekc-1) is used for the isolation of: Cu, Cd, Zn, Ni, Mn, Fe<sup>2+</sup> and Fe<sup>3+</sup> (Li et al., 2004).

All cations adsorbed on Ky-2 ion-exchanger are sequentially washed with increasing concentration solutions of hydrochloric acid. While chloride-Nickel complex is not formed in these circumstances, and can be washed from the ion exchanger using concentrated hydrochloric acid.

When Ky-2x8 ion-exchanger is used, the complex is precipitated on the cation exchanger despite the presence of an ion exchanger in the filtrate. Nickel is therefore isolated from Cd, Bi, Mn, Zn, Fe (III), Co, and other elements in the form of chloride complex (Dayekc-50) which can be eluted using a mixture of 90% acetone and 10% hydrochloric acid solution 6M (Yavuz et al., 2003). The stability of the complexes is to a large extent related to the nature of the solvent and its composition. The presence of organic solvents affects the equilibrium position displacement of complexes engaged in ion exchange process. Due to the very low and gradual dielectric constants of different solvents, complexes are less dissociated in acetone compared to water. That is why the ion exchange appears more clearly when performed gradually from a neutral medium using an aqueous solution of strong electrolyte (Hague et al., 1954).

In that case, the treatment of the cation exchanger using a mixture of acetone and hydrochloric acid will lead to the formation of cations-chloride complexes which can be isolated from cation exchanger except for Nickel which remains on cation exchanger. This characterization was used in order to isolate the nickel in bronze. After its isolation, the adsorbed nickel was identified on the ion exchanger using a specific reagent which gave a color that can be measured by spectrophotometer in the solid phase, and so both processes of concentration and determination are combined in a single process. The absorption specter of the reagent differs from its specter after the adsorption of Nickel, this allows the identification of the ionic exchanger treated with the same reagent before the adsorption of Nickel. The colorless Nickel reagent "Dimethylglyoxime" was chosen, and the string acid exchanger Amberlit CG-120 which has a yellow to light pink coloration at pH=1, in the form of H was used as a carrier. The cation exchanger has a sterol structure and contains functional groups SO<sub>3</sub>H<sup>-</sup> which are characterized by forming complexes with metal ions which will be adsorbed on the exchanger (Rao et al., 2007). The Cations adsorption of heavy metals on the cation

exchanger of strong acid is characterized by the fact that it is formed in an acidic medium. While the hydroxylated complexes are formed on the cation exchanger of weak acids at pH=4 or more.

## EXPERIMENTAL

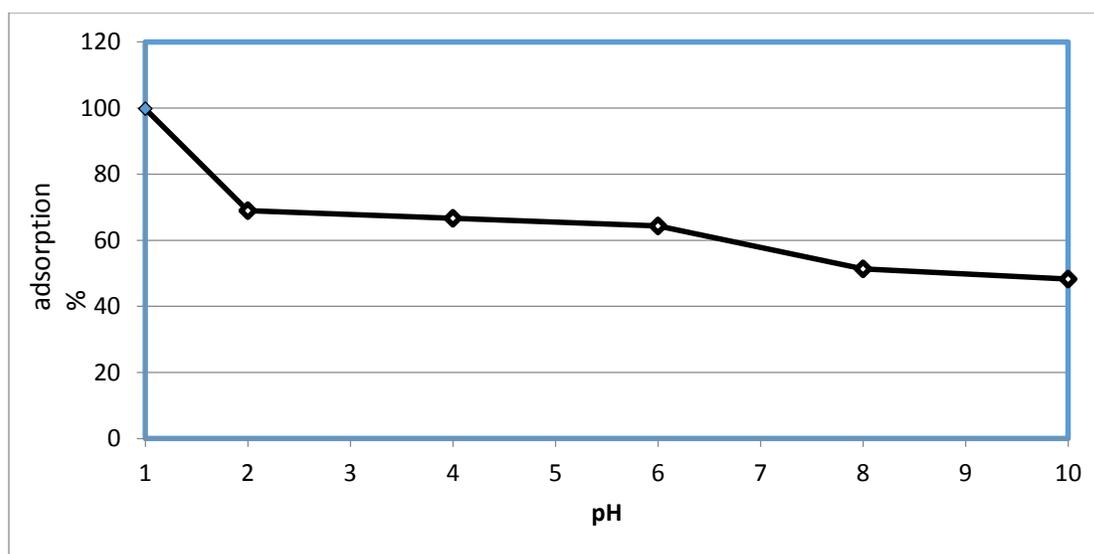
The nickel solution  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  of pure chemical feature (PDH, Titer  $T_{\text{Ni}} = 1\text{mg}$ ) was used for this process. The solution has been calibrated using EDTA, whereas the less concentrated solutions were prepared by dilution. The cation exchanger Amberlit CG-120 prepared in the form of  $\text{H}^+$  was used, the diameter of the granules was (0.1-0.2) mm. The identification of Nickel was performed using 1% solution of Di methyl Gliuksym in ethanol. Measurement was conducted under static conditions on spectrophotometer (KФK) and on general photocolormeter (ФOУ). The Bronze бРАЖМ-114, was tested by means of the pH value using pH-meter 262, and the infrared spectra was measured on a Specord-80.

## RESULTS

**The effect of pH on the adsorption:** The relation between the adsorption of nickel on Amberlit CG-120 and PH with/without the addition of NaCl was studied. As shown in table 1 and figure 1, the maximum adsorption of Nickel was observed at pH=1 and its minimum absorption was at pH=10 (99.8% and 48.3%, respectively) without the addition of NaCl. Results indicated that Nickel absorption decreases as pH increases and this correlate with different previous studies (Harter, 1983). Following experiments were conducted on nickel adsorption at pH=1 without the addition of NaCl. In this experiments, the full adsorption of nickel is obvious.

**Table.1. The adsorption of nickel on Amberlit CG-120 at different pH without the addition of NaCl**

pH	1	2	4	6	8	10
adsorption of nickel %	99.8	69.0	66.6	64.3	51.3	48.3

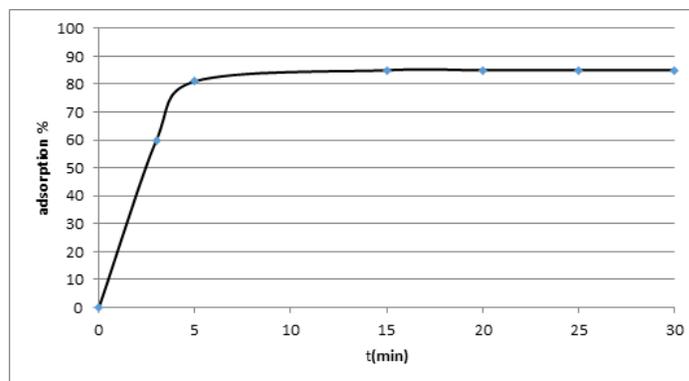


**Figure 1. The adsorption of nickel on Amberlit CG-120 at different pH without the addition of NaCl**

The partial adsorption is linked with the ionic strength of the solution. The presence of trace amounts of sodium ions displaces the equilibrium, although the adsorption of trace amounts of nickel is incomplete. The adsorbed nickel was treated at pH=1 (without the addition of NaCl) using a solution of ammonia buffer (pH=8-9), and a solution of Di methyl Gliuksym in ethanol, this led to a pink coloration correlated with the amount of Nickel. The use of a strong acid cation exchanger will give a negative result due to its high adsorption of cations and the absence of selectivity. This, in turn, leads to a partial adsorption of the selected item. At the same time, the effect of the ionic strength on the adsorption is minimum on weak acids cation exchanger. Amberlit CG-120 can be colored using a specific reagent, whereas both Amberlit CG-50, and KБ-4П-2 are almost non-colored.

**The effect of time on adsorption:** In order to study the effect of time on the adsorption of nickel at pH=1, the speed of the nickel adsorption was set on cation exchanger Amberlit CG-50 in the form of H-as follows:

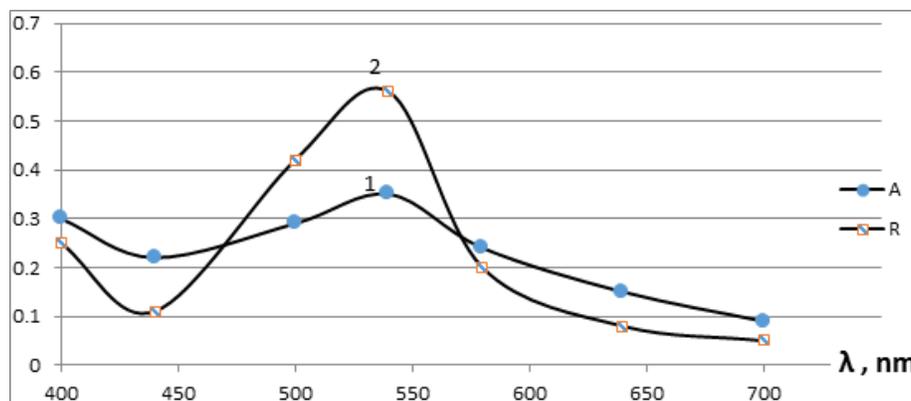
In a 200 ml beaker, 5ml of nickel chloride solution ( $T_{Ni} = 1 \text{ mg}$ ) was mixed 0.500 g of cation exchanger and the pH was set at 1 by adding hydrochloric acid solution (1:1). the mixture was diluted until 100 ml and the pH value was tested using a pH - meters 262. The solution was mixed using a magnetic stirrer, samples were taken at different times and the nickel content was identified. Results illustrated in Figure 2 indicate that the equilibrium occurs within 15 minutes and it is related to the maximum adsorption.



**Figure 2. Effect of time in the adsorption of nickel on Amberlit CG-120 in the form of H- at pH=1**

The Cation exchanger was treated with a solution of Dimethylglyoxime in order to determine its Nickel content. A pink color formed in the presence of Nickel and its intensity is linked to its content. The possibility of Nickel adsorption on the cation exchanger pretreated with Dimethylglyoxime was examined. Results showed no pink coloration when it is in contact with Nickel. This means absence of adsorbed Dimethylglyoxime on Amberlit CG-120 which can be explained by the characteristics of the cation exchanger structure and the chemical composition of Dimethylglyoxime. So, the pink coloration correlated with the Nickel content can only be formed after the Nickel adsorbed on the cation exchanger is treated with the Dimethylglyoxime solution. In comparison with 1 - (2 - Pyridyl azo -2 - naphthol) (PAN-2) (Morozko et al., 1995; Morozko et al., 1996; Vasi et al., 2004; Zen et al., 1993), and the reagent TAN-3.65 (Morozko et al., 1996), Dimethylglyoxime is characterized by being not adsorbed on the cation exchanger and having no coloration. The cation exchanger itself doesn't give a noticeable coloration when its spectrum is measured by spectrophotometer.

**The reaction between the adsorbed nickel and Dimethylglyoxime:** To find the ideal conditions for the spectrophotometer analysis, the reaction between the adsorbed nickel on the ion exchanger and the ethanolic solution of Dimethylglyoxime 1% was studied. Results show that at pH=1 a colored complex between Nickel and Dimethylglyoxime is formed on the ion exchanger, and the color intensity is linked to the content of adsorbed Nickel. The absorbance spectrum of the complex formed on the solid phase is similar to the absorbance spectrum of the complex formed in solution. The maximum absorbance wavelength  $\lambda_{max}=540 \text{ nm}$  as results indicate in (Figure 3).



**Figure 3. 1. The absorption spectrum of Nickel - Dimethylglyoxime in ethanol; 2. The spectrum of reflection on the solid phase**

**Determining the amount of Nickel in Bronze:** (0.1-0.05) g of the mixture of nickel metal content was dissolved in 5ml of diluted nitric acid (1:1) with heating. After the dissolution, 5ml of hydrochloric acid was added and evaporated in a water bath until the acid was almost gone. The process was repeated twice in order to transform all the nitrate into chlorides. A mixture consisting of 2ml of concentrated hydrochloric acid 6M and 18ml acetone, and (0.200) g Amberlit CG-120 in the form of H was added to the remaining amount of chlorides. Then the content of the beaker was well stirred, and within 15 minutes the exchanger was isolated through filter paper and washed 4 to 5 times by a mixture of HCl:acetone (1:9) (Yavuz et al., 2003). The fluids were filtered and the cation exchanger was treated twice with 5ml of ammonium buffer solution pH=8-9, then it was treated with 2ml of an ethanolic solution of Dimethylglyoxime 1%. The cation exchanger was dried in the air. It turned pink, and the reflection was measured by a spectrophotometer at 540 nm using as blank an ion-exchanger treated with an ammonium buffer solution and the ethanolic solution of Dimethylglyoxime. This method is known as the standard addition method. It was used instead of the standard curve method because the curve design requires to be at the same circumstances of nickel determination which in turn will slow down the analysis. Results are presented in Table (2).

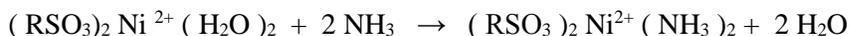
**Table 2: Content of nickel in bronze (alloy brand BRAЖM-114); n=5, P=0.95**

Alloy brand	Composition of Bronze alloy %	Nickel content %		S <sub>r</sub>
		in catalogue (Theoretically)	Practical result	
BRAЖM 114	Al - 11.07 ; Fe - 2.11; Mn -1.40 ; Si - 0.136; Sn - 0.078 ; Sb - 0.0013 ; Pb - 0.024 ; Zn - 0.81 ; P - 0.01	0.31	0.29 ± 0.02	0.071

## DISCUSSION

The adsorption was conducted on cation exchanger Amberlit CG-120 in the form of H- from acetone - hydrochloric acid medium. The maximum adsorption of nickel was obtained at pH=1. The equilibrium occurs within 15 minutes and the diffusion constant in a solution of 0.02M equals  $20.2 \times 10^3 \text{ cm}^2/\text{sec}$ . The presence of organic solvents affects the equilibrium position displacement of complexes engaged in ion exchange process. The stability of the complexes is associated with the nature of the solvents and their structure. Due to the very low and gradual dielectric constants of different solvents, complexes are less dissociated in acetone compared to water. Therefore, the ion exchange is particularly clear when the exchange is accompanied by the adsorption of neutral compounds [4]. The referenced combination was used to isolate the nickel from bronze, and it was identified in the spectrophotometer method on the solid phase.

The adsorption of Nickel on the exchanger is due to the covalent bonds formed between Nickel and the functional group -SO<sub>3</sub>H in a medium of ammonium hydroxide (Vasi et al., 2004):



In the ion-exchanger phase, a displacement of the equilibrium can occur with complexes of different composition. The presence of ammonia does not strongly affect the adsorption of Nickel because when the complex Alamonyakal is formed, its charge and the charge of Nickel hydrate are equal and they remain similar. Infrared spectra were measured (IR) for the exchanger Amberlit CG-120 which was treated in the form of H- and the same exchanger (Amberlit CG-120) after the adsorption of nickel and its treatment with buffer solution at pH=9. Measurement was done using Specord-80, and the highest point of absorption was noticed at 300 Cm<sup>-1</sup>. This indicates the presence of the bond (N-Ni-N), and this is in agreement with the references (Pellerano et al., 2007; Martín-Calero et al., 2009; Prado et al., 2011; Kalluru et al., 2013). (Table 3).

**Table.3. The values of wave numbers (cm-1) of the cation exchanger Amberlit CG-120 treated in the form of H-, and the exchanger Amberlit CG-120 after Nickel adsorption and treatment with buffer solution at pH=9**

Amberlit CG-120 treated in the form of H-	276	-	672	832	1118	1392
Amberlit CG-120 after Nickel adsorption	256	300	682	816	1100	1320

The infrared IR spectra for both samples show a sharp absorption peaks at  $(1392-1118) \text{ cm}^{-1}$  which indicates the presence of S=O. But after the adsorption of Nickel, the peak at  $1392 \text{ cm}^{-1}$  shifts a little, and its intensity is reduced, while a new absorption peak appears at  $1320 \text{ cm}^{-1}$ . This can be explained by the transformation of the cation exchange to its metallic form.

## CONCLUSION

The proposed method allows the quantification of nickel after its isolation from the matrix of the bronze alloy БРАЖМ-114 using the selective reagent Dimethylglyoxime. Other cations present in the bronze alloy БРАЖМ-114 do not interact with this process and the limit of quantification is reduced comparing with the traditional spectroscopic methods.

## ACKNOWLEDGMENT

Writing assistance provided by Dr. Wissam Zam and Dr. Oussama Mansour from the Faculty of Pharmacy at Al-Andalus University for Medical Sciences (Syria) is greatly appreciated.

## REFERENCES

- Guixia Z, Xilin W, Xiaoli T, Xiangke W. Sorption of Heavy Metal Ions from Aqueous Solutions: A Review. *The Open Colloid Science Journal*, 4, 2011, 19-31.
- Hague JL, Maczkowske EE, Bright HA. Determination of Nickel, Manganese, Cobalt, and Iron in High-Temperature Alloys, Using Anion-Exchange Separations. *Journal of Research of the National Bureau of Standards*, 53(6), 1954, 353-359.
- Harter RD. Effect soil pH on adsorption of lead, copper, zinc, and nickel. *Soil Sci. Soc. Am. J.*, 47, 1983, 47-51.
- Kalluru VR, Kishore K, Venkateswarlu P. Solid Phase Extraction Method for the Determination of Ni(II), Cu(II) and Zn(II) by Flame Atomic Absorption Spectrometry Using Schiff Base in Various Water Samples. *Chem Sci Trans.*, 2(1), 2013, 213-221.
- Li YH, Ding J, Luan Z, Di J, Zhu Y, Xu C, Wu D, Wei B. Competitive adsorption of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ions from aqueous solutions by multiwalled carbon nanotubes. *Carbon.*, 41, 2004, 2787-2792.
- Martín-Calero A, Ayala JH, González V, Afonso AM. Ionic liquids as desorption solvents and memory effect suppressors in heterocyclic aromatic amines determination by SPME-HPLC fluorescence. *Anal. Bioanal. Chem.*, 394(4), 2009, 937-46.
- Morozko SA, Ivanov VM. Test Methods in Analytical Chemistry: Immobilized 1-(2-Pyridylazo)-2-Naphthol as an Analytical Reagent. *Anal. Khim.*, 50, 1995, 629-635.
- Morozko SA, Ivanov VM. Test Methods in Analytical Chemistry: Immobilization of 4-(2-Pyridylazo)resorcinol and 1-(2-Pyridylazo)-2-Naphthol on Cellulose and Silica Adsorbents. *Zh. Anal. Khim.*, 51, 1996, 631-637.
- Pellerano RG, Romero CH, Acevedo HA, Vazquez FA, Marchevsky EJJ. Chemical Fractionation of Cadmium in natural water from Parana river in Corrientes-Argentina. *Argentine Chemical Society*, 95(1), 2007, 70-79.
- Prado AGS, Pescara IC, Evangelista SM, Holanda MS, Andrade RD, Suarez PAZ, Zara LF. Adsorption and preconcentration of divalent metal ions in fossil fuels and biofuels: Gasoline, diesel, biodiesel, diesel-like and ethanol by chitosan microspheres and thermodynamic approach. *Talanta*, 84, 2011, 759.
- Rao GP, Lu C, Su F. Sorption of divalent metal ions from aqueous solution by carbon nanotubes: A review. *Sep. Purif. Technol.*, 58, 2007, 224-231.
- Vasi V, Savi J, Vukeli N. Sorption-spectrophotometric method for the determination of Pd (II) in aqueous solutions. *J.Serb.Chem.Soc.*, 69(4), 2004, 309-317.
- Yavuz Ö, Altunkaynak Y, Güzel F. Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite. *Water. Res.*, 37, 2003, 948-952.
- Zen JM, Lee ML. Determination of traces of nickel(II) at a perfluorinated ionomer/dimethylglyoxime mercury film electrode. *Anal. Chem.*, 65(22), 1993, 3238-3243.