DETERMINATION OF NI(II) IN ALLOYS USING A NEW REAGENT DERIVED FROM L-DOPA

Wagner José Barreto*[+], Herica Aparecida Magosso*, Miriam Fátima Soares*, Bruno Marco Oliveira Silveira*, Ieda Spacino Scarminio[+], Dílson Norio Ishikawa**, Sônia Regina Giancoli Barreto*

*Laboratory of Environmental Physical Chemistry, Department of Chemistry, CCE, Londrina State University, Londrina, PR, 86051-990, Brazil.
[+]Laboratory of Chemometrics in Natural Sciences, Department of Chemistry, CCE, Londrina State University, Londrina, CP 6001, 86051-990, Brazil.
**Department of Chemistry, CCE, Londrina State University, Londrina, CP 6001, 86051-990, Brazil
[+]barreto@uel.br

Abstract: A simple and sensitive UV-Vis spectrophotometric method was developed using a new chromogenic reagent, L-dopasemiquinone, for the quantification of Ni(II) in metallic alloys: Inox, Co-Cr, and Ni-Ti. The complex $[Ni(II)(L^{1-})_3]^{1-}$ presents an intense band at 591 nm, $\varepsilon = 2.4 \times 10^3$ L mol^{-1} cm^{-1}. Beer's law is obeyed from 4.02×10^{-5} to 2.01×10^{-4} mol L^{-1} with limits of detection and quantification of 4.15×10^{-5} mol L^{-1} and 5.02×10^{-5} mol L^{-1}, respectively. The method was compared with atomic absorption spectrophotometry and inductively coupled plasma atomic emission spectroscopy obtaining good results. Cobalt and Titanium cause low interference in the method.

INTRODUCTION

Nickel determination is important in metallurgy, biological sciences and environmental analytical chemistry. There is a growing need for the development of analytical procedures with high sensitivity for nickel determination.

The usual methods for determination of nickel using chemical reagents like; dimethylglyoxime, sodium diethyldithiocarbamate, (ethylenedinitrilo) tetraacetica acid disodium salt (Titriplex® III), 2,2'-Furil dioxime and dithioxamide [1]. The dimethylglyoxime method present $\varepsilon = 14 \times 10^3$ L mol^{-1} cm^{-1} at 450 nm and Co, Cr(III) Cu(II), Mn(II), Fe and Zn higher 1 µg mL^{-1} interfere and it is advisable to isolate the nickel by extraction with dimethylglyoxime/chloroform before the determination in aqueous solution. The method involves the addition of various chemical reagents (hydrochloric acid, bromine water and ammonia) and the times stated for which addition are to be strictly adhered [2]. In the
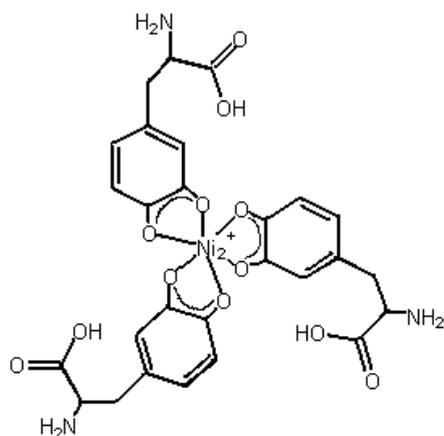
sodium diethyldithiocarbamate method Cu, Bi, Co and Fe are interferents and should be removed by the prior extraction with dimethylglyoxime. The method presents $\varepsilon = 35 \times 10^3$ L mol^{-1} cm^{-1} but in ultra-violet region (325 nm). The method is time consuming and use extractions with carbon tetrachloride [3]. The method using Titriplex® III gives a coloured complex utilized for determination of nickel by spectrophotometric observation of the band at 1000 nm [4]. The 2,2'-Furil dioxime forms with nickel a yellow, water insoluble complex which is extractable with chloroform and it can be utilized for photometric determination [5]. The method utilizing dithiooxamide is very sensitive (limit of detection about 0.01µg nickel) but copper and cobalt interfere seriously in the method [6].

Others analytical procedures have been proposed including voltammetry [7, 8], ion selective electrodes [9,10], polarography [11], derivative spectrophotometry [12], fluorescence spectrometry [13,14] and inductively coupled plasma atomic emission spectroscopy ICP-AES [15,16]. The search for new chromogen-

ic reagents for spectrophotometric methods is important because these methods have the advantages of simplicity, rapidity, low costs and wide application [17-23].

The chemical behaviors of nickel, iron and cobalt are very similar, and these elements are frequently found together in real samples, notably in metal alloys used to improve the material properties, for example, the mechanical and chemical resistance of steel. The Inox used in orthodontics has an austenitic structure, with a composition of 18% chromium, 8% nickel, and 0.08 to 0.15% carbon, the remaining content being iron. The chromium-cobalt alloy contains 40% cobalt, 20% chromium, 15% nickel, 15.8% iron, 7% molybdenum, 2% manganese, 0.16% carbon and 0.04% beryllium and its properties are very similar to those of the steel, however, with greater formability.

Catecholates, semiquinones and quinones are highly reactive dioxolenes, with important participation in biological structures performing essential functions in living organisms. The dioxolene molecules show interesting magnetic and redox behaviors, forming colorful complexes with heavy metals [24, 25]. Studies on the preparation and spectrophotometric (UV-Vis, IR, EPR and Raman) analysis of the Co(II), Ni(II), Zn(II) and Fe(III) water soluble compounds with dioxolene derived from dopamine oxidation in a sodium thiosulfate environment, have shown that L-dopa-semiquinone has a high affinity for the transition metals under study [26]. The compound resulting from the complexation reaction of the L-dopa-semiquinone and Ni(II) at a pH of 7 was proposed to be a soluble $[Ni(II)(L^{1-})_3]^{1-}$ anion with the structure showed in Figure 1. The absorption spectrum shows an intense absorption band at 591 nm with $\varepsilon = 2.4 \times 10^3$ L mol^{-1} cm^{-1}, assigned to an inter-ligand charge transfer [26].

The aim of this study was to develop a UV-Vis spectrophotometric methodology for determination of Ni(II) using a new reagent, prepared from L-dopa, and to test it in the determination of Ni(II) in three commercial metallic alloys; Inox, nickel-titanium (Ni-Ti), and nickel-cobalt (Ni-Co). The results are compared with those of the established methods of atomic absorption spectroscopy (AAS) and inductively coupled plasma optical emission spectrometry (ICP-AES).
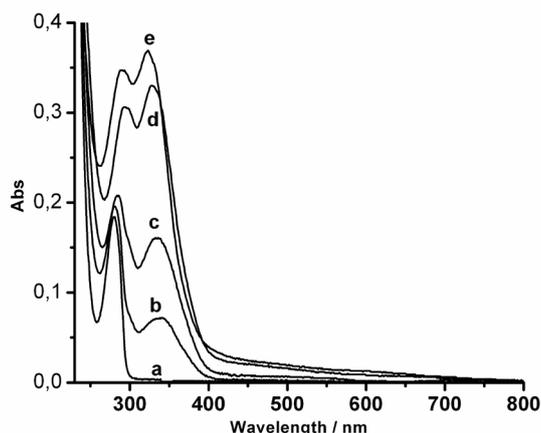
EXPERIMENTAL

Preparation of the chromogenic reagent (L-dopasemiquinone)

All of the solutions were prepared with ultra-pure water (Helga). Sodium thiosulfate (0.3131 g) (Aldrich Chemical 99.9%) was dissolved in 500 mL of water ($3.96 \ 10^{-3}$ mol L^{-1}), following by 0.1008 g of L-dopa [(S)-2-amino-3-(3,4-dihydroxyphenyl) propanoic acid, $C_9H_{11}NO_4$] (Aldrich Chemical 99.9%) ($1.06 \ 10^{-3}$ mol L^{-1}) with O$_2$ bubbling at a constant flow of 0.5 L min^{-1}. After 48 hours of reaction the absorption band at 278 nm, a characteristic electronic transition of the L-dopa, disappeared and a band at 337 nm, characteristic of the L-dopasemiquinona, emerged (Fig. 2). The resulting dark green solution was stored in polyethylene flasks at 4°C.

Stock solution of NiCl$_2$

A stock solution of Ni(II) was prepared dissolving nickel chloride (Aldrich Chemical 99.9%) in water (1.00×10^{-3} mol L^{-1}). Aliquots were transferred to 25 mL volumetric flasks and completed with buffer solution pH 7.5 (KH$_2$PO$_4$/NaOH) resulting in solutions with concentrations of 4.02×10^{-5}, 8.04×10^{-5}, 1.206×10^{-4}, 1.608×10^{-4}, and 2.01×10^{-4} mol L^{-1}. The solutions were standardized with EDTA.

Figure 1. Proposed structure for the soluble [(Ni(II)(L1-)3]1- anion complex where L1- is the L-dopasemiquinone radical.

Figure 2. UV-Vis absorption spectra obtained during the reaction to obtain the chromogenic reagent (L-dopasemiquinone). Aqueous solution containing 1.06 10-3 mol L-1 L-dopa and 3.96 10-3 mol L-1 of Na2S2O3 with O2 bubbling at a constant flow of 0.5 L min-1. Reaction times (h): (a) 0; (b) 24; (c) 48; (d) 72; (e) 96.

Obtaining the Analytical Curves

The analytical curves (n=5) (Y = -0.0572 + 2483 X, r = 0.998) were obtained mixing 5 mL of the chromogenic solution with 5 mL of Ni(II) solution. A blank was obtained using 5 mL of buffer solution pH 7.5 and 5 mL of the chromogenic solution. The test tubes were sealed and the homogenized mixtures were placed in ultra-thermostatic bath at 25 ± 0.01 °C, for 30 min. Aliquots (3 mL) were transferred to a quartz cuvette (10 mm) and the absorbances were measured at 591 nm (Thermo Scientific, Genesys 2).

Determination of the Limits of Detection (LOD) and Quantification (LOQ)

To seven test tubes were added 5 mL of buffer 7.5 and 5 mL of chromogenic solution. After 30 minutes at 25 °C the absorbances were measured at 591 nm. The limit of detection (LOD) was calculated using the equation LOD = X + 3 s, where X is the mean of the measured values and s is standard deviations. The limit of quantification (LOQ) was determinate using the expression LOQ= X + 10 s.

Digestion of the Alloys

Samples of the metallic alloys (0.055g of Inox, 0.035 g of Co-Cr and 0.0135 g of Ni-Ti) were digested in 10 mL of aqua regia solution (3:1 HCl:H-NO$_3$) at 105 ± 5 °C. Two blanks containing all reagents but not including the samples, accompanied the alloys digestion. After complete digestion, the resulting solutions were maintained under heating until they were almost dried. The obtained residues were redissolved with water and completed up to 50 mL in volumetric flasks.

For the spectrophotometric determination of Ni(II) in the alloys, 1 mL of the digested solution of Inox was transferred to 100 mL volumetric flask and for the Co-Cr or Ni-Ti 2 mL of the digested solutions were transferred for 25 mL of volumetric flask and the volumes completed with buffer solution pH 7.5.

The procedure for the spectrophotometric determination of Ni(II) followed the same procedure used to obtain the analytical curve. The analytical curve Y = -0.0572 + 2483 X (n=5) was used to determinate the Ni(II). Aliquots of the same solutions of Ni(II) were used to determine Ni(II) using atomic absorption atomic spectrophotometry (AAS) and inductively coupled plasma (ICP-AES).

Study of Interference from Metals

After the determination of the best conditions for the complexation reaction between Ni(II) and dopa-semiquinone, the possibility of interference from the transition metals Co, Cr, Cu, Fe, Mn, Cd, Pb and Zn in the determination of Ni(II) was studied. The solutions used in the interference studies to determinate 8.04×10^{-5} mol L^{-1} of Ni(II) were prepared by the addition of aliquots of 1000 mg L^{-1} standard solutions of Cr(III), Co(II), Cu(II), Fe(III), Mn(II), Zn(II), Cd(II), Pb(II) (Merck) and Zn(II) (Carlo Erba) with a 7.5 pH buffer. The solution of Ni(II) with the interfering metal was prepared adding to a test tube 5 mL of the nickel solution, 5 mL of the metal interfering solution and 5 mL of the chromogenic solution. The mixture was maintained at 25 °C by 30 minutes. A blank was prepared in the same conditions with 5 mL of buffer pH 7.5 and 5 mL of chromogenic solution. Aliquots of 3 mL were transferred to a quartz cuvette

(10 mm) and the absorbances measured at 591 nm. All experiments were carrying out in duplicates.

A study on the interference of anions was also performed. Solutions $1 \, 10^{-3}$ mol L^{-1} of salicylate, nitrate, carbonate, sulfate, citrate, tartrate, oxalate and acetate were prepared from their sodium salts. To 25 mL volumetric flasks were added 2 mL of 1.00×10^{-3} mol L^{-1} $NiCl_2$, the anion solutions and completed with buffer pH 7.5. Aliquots of 5 mL of the solution were mixed with 5 mL of chromogenic solution at 25°C for 30 minutes. A blank was prepared using 5 mL of buffer pH 7.5 without the anions. Several solutions for each anion were prepared growing the concentration until to observe interference in Ni(II) determination. All the experiments were made in duplicates.

Nickel Determination by Atomic Spectroscopy (AAS and ICP-OES)

The determination of Ni(II) in the metallic alloys by AAS (Shimadzu AA-6601F) was carried out using a nickel hollow cathode lamp and atomic transition at 232 nm. The analytical curve from 8.50×10^{-6} to 4.25×10^{-5} mol L^{-1} was obtained diluting 1.70×10^{-2} mol L^{-1} of Ni(II) stock solution previously standardized with EDTA.

The ICP-AES (Perkin Elmer Optima 5200DV) analysis was performed with the same solutions used for the spectrophotometric and AAS methods with the quantification limits of: Fe (0.0012 mg L^{-1}), Ni (0.0018 mg L^{-1}), Co (0.0015 mg L^{-1}), Ti (0.001 mg L^{-1}) and Cr (0.0019 mg L^{-1}). The analytical curves were obtained using the 1000 mg L^{-1} standard solutions for each metal from 0.1 to 10.0 mg L^{-1}.

RESULTS AND DISCUSSION

The complex formed between Ni(II) and the chromogenic reagent, formulated as the soluble anion $[Ni(II)(L^{1-})_3]^{1-}$ (Fig. 1) presents an intense interligand charge transfer at 591 nm ($\varepsilon = 2.4 \times 10^3$ L mol^{-1} cm^{-1}) resulting in an intense blue coloration (Fig. 3) [26]. The complex is stable at pH 7.5 and 25 °C. The best reaction parameters for obtaining higher absorbance values were determined using a 2^4 factorial design.
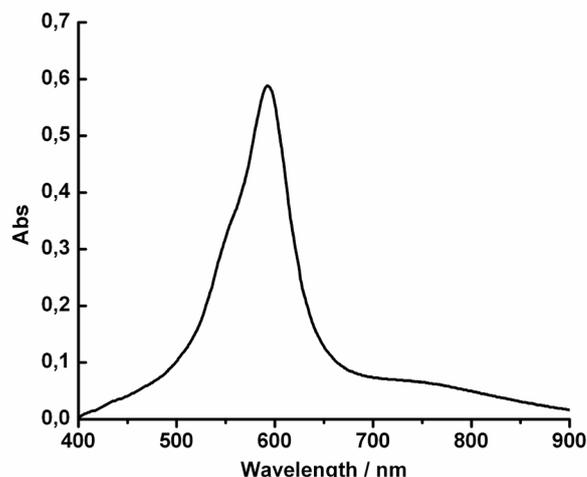
Figure 3. UV-Vis absorption spectrum of the complex [(Ni(II)(L1-)3]1- formed in aqueous solution, pH 7.5 (buffer KH2PO4/NaOH), temperature of 25 °C, reaction time of 30 minutes and 1.16 10-4 mol L-1 of Ni(II).

The results showed that the effects of reaction time, pH and concentration of nickel were significant for obtaining high absorbance (analytical signal). The analytical signal increased at higher pH values and concentration of Ni(II) and shorter reaction times. It was verified that the analytical signal showed little variation with temperature, and therefore a temperature of 25 °C was used for subsequent experiments. The results of the factorial design, with the temperature fixed at 25 °C, showed that the best reaction conditions in terms of the analytical signal were: 30 minutes of reaction time, pH 7.5 and Ni(II) concentration range of 1.00×10^{-5} to 2.00×10^{-5} mol L^{-1}.

The limits of detection and quantification of the method were 4.15×10^{-5} mol L^{-1} and 5.02×10^{-5} mol L^{-1} respectively. The maximum concentrations (mol L^{-1}) of metals that can be present without interfering in the determination of Ni(II) were: 6.81×10^{-7} for Co(II), 7.65×10^{-7} for Cr(III), 8.10×10^{-8} for Cu(II), 6.50×10^{-8} for Mn(II), 1.23×10^{-6} for Zn(II), 6.00×10^{-7} for Fe(III), 1.07×10^{-4} for Cd(II), 5.74×10^{-5} for Pb(II). The salicylate, nitrate, carbonate, sulfate, citrate, tartrate, oxalate and acetate anions do not cause interference until they are present in the same concentration as the Ni(II) to be determined, in the case studied this being 8.04×10^{-5} mol L^{-1}.

One of the major problems with spectrophotometric methods for Ni(II) determination is cobalt interference, because many of the reagents used when working with nickel also react with cobalt. In general, this interference is eliminated by procedures involv-

ing operations such the extraction, ion exchange and precipitation of nickel with dimethylglyoxime. However, the methodology developed has a very low level of interference from Co(II), being significant only at ca. 7.0×10^{-7} mol L^{-1}, corresponding to 0.04 mg L^{-1}. Table 1 gives the recovery test results for Ni(II) in very complex samples (orthodontic alloys). ICP-AES analysis was used to determine the major elements contained in the alloys, and it showed the complexity of the samples. The following contents were found (mass percentage, %): 69.4 % Ni and 30.6 % Ti for the Ni-Ti alloy; 8.97 % Ni, 73.0 % Fe and 18.3 % Co for the Inox; and 18.0% Ni, 15.8% Fe, 45.4% Co and 20.8% Cr for the Co-Cr alloy.

Table 1. Mass percentage (%) of Ni(II) in metallic alloys determinate by the spectrophotometric, Atomic Absorption Spectrophotometry (AAS) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) methods.

Alloy	Spectrophotometric[1]	AAS[2]	ICP-AES[3]
Inox	11 ± 3	9.7 ± 0.5	9
Ni-Ti	72 ± 8	76 ± 1.1	70
Co-Cr	16 ± 1.5	18 ± 0.6	21

[1]n= 4, [2]n=3, [3]n=1

The results were compared to those obtained with AAS and ICP-AES, two very widely used methodologies, and the results showed that the spectrophometric method was able to quantify Ni(II) in alloys, including the Co-Cr alloy, which presents high levels of the cobalt. The results indicated that the other elements that comprise the alloys did not interfere to a great extent in the determination of Ni(II).

CONCLUSION

The results obtained showed that the spectrophotometric method is sensitive, fast, can be used at room temperature (25 °C) and does not require solvent extraction. The preparation of the new chromogenic is simple and safe, and complex experimental procedures or equipment are not needed. The study of metal interferences showed that Mn(II) and Cu(II) interfere more significantly, whereas the traditionally most problematic metal in terms of interference in nickel determination, that is, cobalt, showed low interference. The methodology was tested on real complex samples, Inox, Ni-Ti and Co-Cr alloys, and good results were obtained.

REFERENCES

[1] J. Fries, H. Getrost, *Organic reagents for trace analysis*, E. Merck Darmstadt, 1977.

[2] H. Specker, H. Kartkamp, Z. Anal. Chem. **145** (1955) 260

[3] O. R. Alexander, E. M. Godar, N. J. Linde, Ind. Eng. Chem. Anal. Ed. **18** (1946) 206.

[4] L. D. Brake, W. M. McNabb, J. F. Hazel, Anal. Chim. Acta **19** (1958) 42.

[5] A. R Gabler, A. M. Mitchel, M. G Mellon, Anal. Chem. **23** (1951) 500.

[6] W. D. Jacobs, J. H.Yoe, Anal. Chim. Acta, **20** (1959) 332.

[7] M. Korolczuk, Talanta, **53** (2000) 679.

[8] D.V.Vukomanovic, J. A. Page, G. W. Vanloon, Anal. Chem. **68** (1996) 829.

[9] V. K. Gupta, R. Prasad, P. Kumar, R. Mangla, Anal. Chim. Acta **420** (2000) 19.
[10] A. Abbaspour, A. Izadyar, Microchem. J. **69** (2001) 7.

[11] H. B.Mark, D. Koran, L. Gierst, J. Electroanal. Chem. **498** (2001) 228.

[12] S. L. C. Ferreira, A. C. S. Costa, D. S. deJesus, Talanta **43** (1996) 1649.

[13] V. Rigin, Anal. Chim. Acta **283** (1993) 895.

[14] O. W. Lan, S. Y. Ho, Anal. Chim. Acta **280** (1993) 269.

[15] T. Kempf, M. Sonneborn, Mikrochim. Acta. **2** (1983) 445.

[16] J. L. Fernandez-Turiel, J. F. Llorens, F. Lopez-Vera, C. Gomez-Artola, I. Morell, D. Gimeno, Fresenius J. Anal. Chem. **368** (2000) 601.

[17] S. Zhao, X. Xia, Q. Hu, Anal. Chim. Acta **39** (1999) 365.

[18] K. Ohshita, H. Wada, G. Nakagawa, Anal. Chim. Acta **140** (1982) 291.

[19] A. Izquierdo, J. Carrasco, Analyst **109** (1984) 605.

[20] Q. Hu, G. Yang, Z. Huang, J. Yin, Anal. Sci. **19** (2003) 1449.

[21] S. K. Kumar, P. S. Rao, L. Krishnaiah, B. Jayaraj, P. Chiranjeevi, Anal. Sci. **20** (2004) 951.

[22] Z. J. Li, J. M. Pan, J. Tang, Anal. Lett. **35** (2002) 167.

[23] Y. Liu, X. Chang, S. Wang, Y. Guo, B. Din, S. Meng, Talanta **64** (2004) 160.

[
24]. U. ElAyaan, E. Herlinger, R. F. Jameson, W. Linert, J. Chem. Soc., Dalton Trans., (1997) 2813 (1997).

[25]. R. C. Hider, B. Howlin, J. R. Miller, A. R. Mohd-Nor, J. Silver, Inorg. Chim. Acta, **80** (1983), 51(1983).

[26] W. J. Barreto, R. A. Ando, P. S. Santos, W. P. Silva, Spectrochim. Acta A **68** (2007) 612.