

FLOW-INJECTION EXTRACTION SPECTROPHOTOMETRIC DETERMINATION OF NICKEL USING NAPHTHAZARIN REAGENT.

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ABSTRACT

Attempts had been made to determine of nickel by using Naphthazarin (Naph) for the extraction and spectrophotometric method both manually and flow injection system. This was the first use of Naphthazarin (Naph) for the extraction and determination of nickel in the extracted samples. This method was successfully applied to detect nickel in nickel-based alloys, pig feeds or electroplating solutions.

Two procedures had been developed for the determination of nickel, manual spectrophotometry and flow injection spectrophotometry. Nickel could be determined spectrophotometrically at 370 nm after extraction of the chelate into chloroform in the first procedure. The calibration graph was linear up to 50 mg per ml of nickel at 370 nm. The relative standard deviation for the determination of 50 mg per ml of nickel was 1.40 % (n=10). Nickel could be determined by flow injection spectrophotometry at 370 nm after extraction of the chelate into chloroform. The carrier stream was deionized water and the reagent streams were acetate buffer (pH 5) and 0.226 % (w/v) Naph solution. The sampling rate was 30 per h. The calibration graph was linear up to 100 mg per ml of nickel. The percent relative standard deviation was 1.75% (n=10) for 20 mg per ml of nickel. It was found that the reagents used in this work were most suitable for the flow injection systems. The system was successfully applied to determine nickel existing in nickel-based alloys and pig feeds.

Keywords: Spectrophotometry, flow system, extraction, Naphthazarin, Nickel.

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INTRODUCTION

Several methods are available for the determination of trace nickel existing in the extraction of samples using spectrophotometry. The Naphthazarin (5,8-dihydroxy-1,4-naphthoquinone) was first introduced as a chromoric reagent for the spectrophotometric determination of nickel in a manitol buffer, pH 5, and 1,4-dioxane solvent (Underwood, 1949). Its capability of forming chelate polymers with some divalent metal ions including nickel ion has been studied for quite sometimes (Agnihotri et al., 1993; Akihisa et al., 2011). Agnihotri used this reagent for the determination of beryllium, aluminum, thorium, and uranium in a micellar medium containing Triton X-100 and ammonium acetate. Acid-base characteristics of the naphthazarin in 50%v/v of the ethanol/water medium have been investigated (Idriss and Saleh, 1993). Nickel-containing materials play major roles in our everyday lives, such as food preparation equipment, medical equipment, transport, buildings, and power generation. (Chromatog Ernst et al., 1999; Khalafy et al., 2010; Khalafy et al., 1987a; Khalafy et al., 1987b) They are selected because they offer better corrosion resistance, better toughness, better strength at high and low temperatures, and a range of special magnetic and electronic properties when they were compared with other materials.

To date, the most important compound is the alloy of nickel with stainless steels, which are used widely and in the largest volume. Nickel based alloys-like stainless with higher nickel contents are used for more demanding applications, such as gas turbines and some chemical plants. In addition, nickel alloys were used in electronics and section engineering, while copper-nickel alloys were used for coinage and marine engineering (Byeong-Churl et al., 2009).

The Naphthazarin (Naph) is used in the extraction and the spectrophotometric determination of nickel for the first time. Attempts to develop the procedures are carried out both systems, i.e., manually and flow injection systems. The procedures are successfully applied to determine the trace nickel element in several samples, i.e., nickel-based alloys, pig feeds, and electroplanting solutions (Khalafy et al., 2009).

Naphthazarin derivatives (5,8-dihydroxy-1,4-naphthoquinone; Naph) have been isolated from *n*-hexane extract of the root parts of the herb (Scalia et al., 1999). The characteristics of Naphthazarin compounds, i.e., alkanin, shikonin and their derivatives, are lypophilic red pigments (Assunta et al., 2003). They are found in the plant roots of several genera of *Boraginaceae* (Mark et al., 2009).

Naphthazarin has been successfully used as a complexing reagent for the determination of Nickel (II) by spectrophotometry. The complexing reagent used in the spectrophotometric technique is prepared from the polynuclear complex of nickel-naphthazarin at the molar ratio of 4:6, which is formed in 50%v/v ethanol/water medium containing 0.1 M ammonium acetate and 1.5% (w/v) sodium dodecyl sulfate. This method can detect nickel as low as 0.9-4.5 ppm by using naphthazarin reagent in such optimized conditions.

The use of naphthazarin was first documented over 50 years ago (Combes, 1252), but it was found in the list of analytical reagents in 1993 (Townshend et al., 1993). The applications of naphthazarin were described as a complexing agent for the determination of several elements, i.e., Co, Cu, Ni, Pd, and Pt, and was used in the photometric determination of Co as described by Pandolfi (2003), and of Fe (III) as described by Jang et al. (2009). It was also described the use of β Ketoamines *per se* but brief mentioned by Li et al. (1993) for the determination of nickel using gas chromatography (Yachao et al., 2011), and by using X-ray fluorescence (Huot and Brassard, 1974). However, the colorimetric application was never done in a massive review by Sasaki (2002) and Pietrosiuk (2003), which covered more than 1,800 individual reagents (Li et al., 1993). Several other studies have mentioned the use of naphthazarin to determine copper and nickel by chromatography (Pandolfi, 2003; Ernst-Russel, 1999), which emphasized mainly in the connection with the determination of copper(II) and nickel(II). Thus, the objective of this study was aimed to study the use of spectrophotometric method for the determination of nickel by using Naphthazarin as a complexing reagent.

MATERIALS AND METHODS

A spectrum of absorbance was measured at 370 nm with a Jasco Uvidec-4 spectrophotometer. The spectrophotometer was fitted with a 30 μ l (10-mm) special quartz flow cell (Hellma), and the spectrum was recorded with a Pharmacia recorder, Model REC-482. The solution was pumped through the spectrophotometer using a variable-speed peristaltic pump (MS-Reglo Ismatec), which was fitted with the Viton pump tubes for the organic phase, and with Tygon pump tubes for the aqueous phases.

Samples were injected using an Omnifit four-way valve fitted with a by-pass coil. The PTFE tube (0.8 mm in diameter) was used as flow lines. The schematic diagram of the flow system is summarized in Figure 2. Omnifit three-way connectors were used at mixing points, i.e., "Hex" for mixing aqueous phases, and "Tee" for segmenting the aqueous and organic phases. The phase separator was constructed following the design, which was reported by Al-Wehaid that fitted with a 0.075 mm Fluolion PTFE thread tape (Walker).

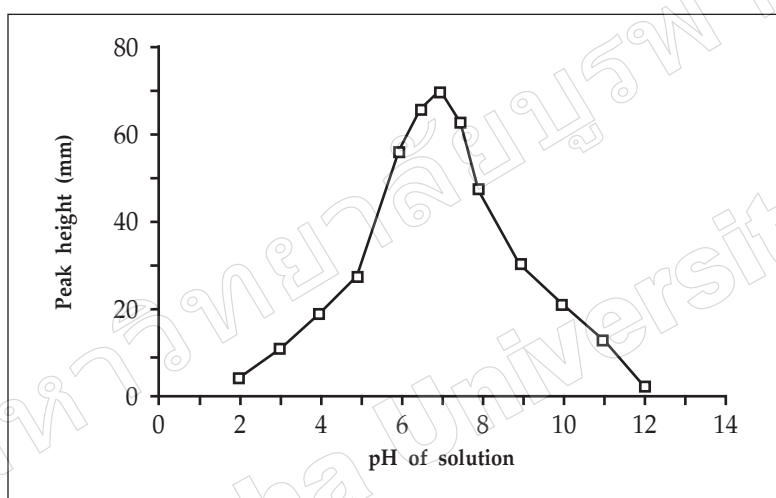


Figure 1. Illustrating the relationship among pH of the buffer solution and the peak heights (mm).

Reagents and chemicals

The naphthazarin reagent was prepared by the reduction of 1,5-dinitro-naphthalene in the acid solution with metals or with sulfur sesquioxide. Since naphthazarin was easy to soluble in water, as well as in the sulfuric acid solution, in which it was prepared and had here-to-fore been separated as an insoluble metal salt such as the zinc salt. The mixture was stirred for 30 min and diluted with water. The crystals were filtered and recrystallized immediately from ethanol after cooling. The melting point range of crystal was at 110-112°C. Results of element analysis were 64.2% of C, 9.9% of H, 12.1% of N, where an theoretical analysis of $C_{10}H_6O_4$ was 64.3% of C, 8.9% of H, and 12.5% of N.

The naphthazarin solution, 0.2% (w/v), should be freshly prepared daily before use by dissolving a 0.2 g amount of naphthazarin in 100 ml of 10% (v/v) ethanol. The buffer solution at pH5 was prepared by mixing of 180 ml of 0.5 M acetic acid with 320 μ l 0.5 M sodium acetate solution. A solution of 1000 mg per ml of Ni^{2+} as nitrate was used as a Nickel standard solution. All other reagents were of analytical grade, and deionized water was used throughout.

General procedure

Sample and standard solutions were examined using the flow system and conditions, as shown in Figure 1.

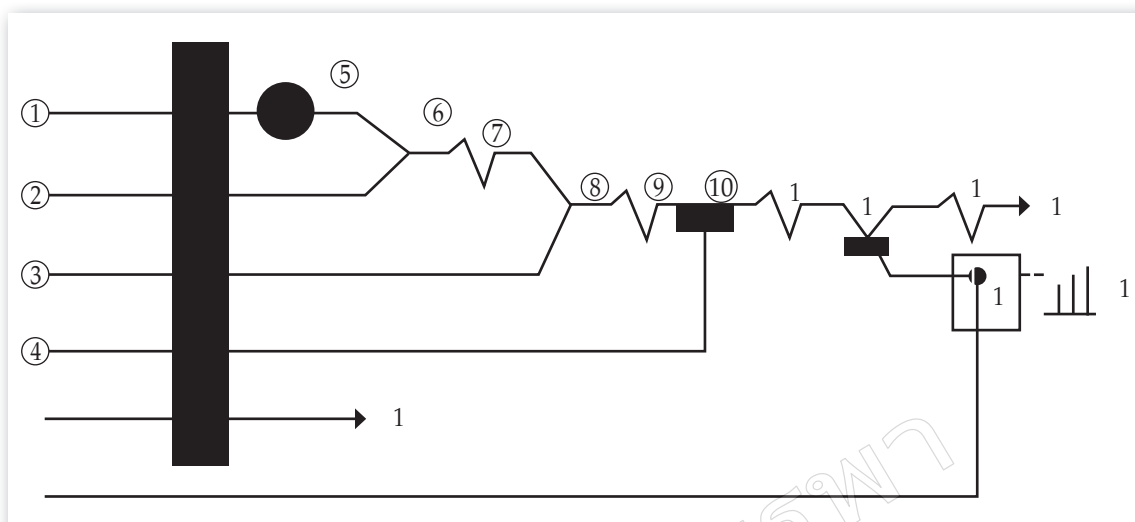


Figure 2. A schematic diagram of the flow-injection system: (1) distilled water; (2) phosphate buffer; (3) Naphthazarin; (4) chloroform; (5) sample injector; (6,8) mixing points ("Hex"); (7,9) mixing coils; (10) segmentor ("Tee"); (11) extraction coil; (12) phase separator; (13) restriction coil; (14) aqueous waste; (15) spectrophotometer; (16) recorder; (17) organic waste.

Sample preparation procedures

a) Procedure for nickel-based alloys

One-tenth gram of a sample of nickel-based alloys was dissolved in 8 ml of 50 % (v/v) HCl, and subsequently dissolved in 2 ml of 50 % (v/v) HNO₃ in a 100 ml conical flask. The mixture was allowed to dissolve completely by gently warming on a hot plate. The solution was allowed to cool and subsequently transferred to a 100 ml volumetric flask, and filled up to a volume of 100 ml with water. The solution was saved as diluted aliquots for further use with water.

(b) Procedure for pig feeds

A 0.3-0.4 gram of a portion of pig feed was placed in a 100 ml Kjeldahl flask, and a 5 ml of water was added. Ten ml of concentrated perchloric acid (70 %, w/w) and five ml of 30 % hydrogen peroxide (Xiao-Ling, 2009) were added into the flask. The solution was heated gently with occasional swirling until frothing ceases, and the solution was subsequently boiled briskly until the solution was clear. The solution was air cooled, and a 20 ml of water was subsequently added and

filtered through a Whatman No.1 filter paper into 100 ml volumetric flask, and finally added up to 100 ml with water for further use.

Examination of all main experimental variables

The optimum experimental conditions were determined in univariate searches using a 40 µg per ml of nickel (II) sample solution that prepared in Figure 1.

Effect of reagent concentrations

It was found that the peak heights increased rapidly with increasing pH of the buffer solution up to the level of 4.5 when the concentration of Naphthazarin was fixed at 0.2% (w/v), then it was slightly increased up to the peak at pH level 5.5 and gradually decreased. A buffer solution at the level of pH 5 was, therefore, adopted.

Once the buffer solution was fixed at pH 5, the peak heights were found to increase with the increasing of naphthazarin concentration from 0.05 % (w/v) to 0.15 % (w/v) and were constant thereafter. So, a naphthazarin concentration of 0.226 % (w/v) was used in the subsequent experiments in Figure 3.

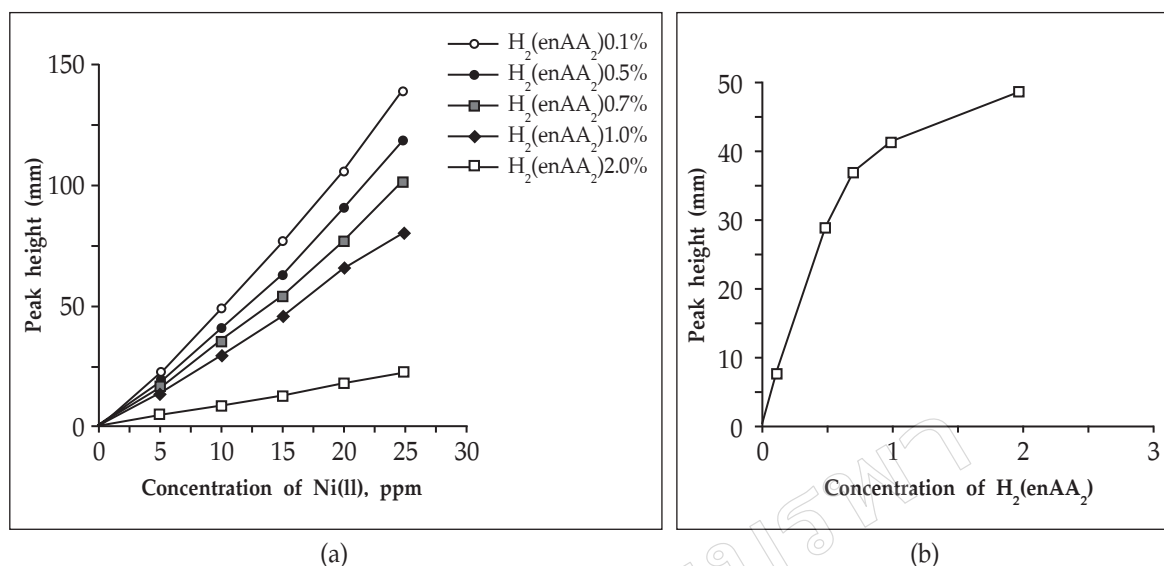


Figure 3. (a) Illustrating the relationship among nickel (II) concentration, ppm and the peak heights (mm) at various Naph concentration. (b) Illustrating the relationship among Naph (%w/v) concentration and the peak heights (mm) at Ni(II) concentration 10 ppm.

Effect of operating variables

The effects of extraction coil length and sample injection volume were individually studied under the above optimum concentrations of the reagents, as shown in Figure 4.

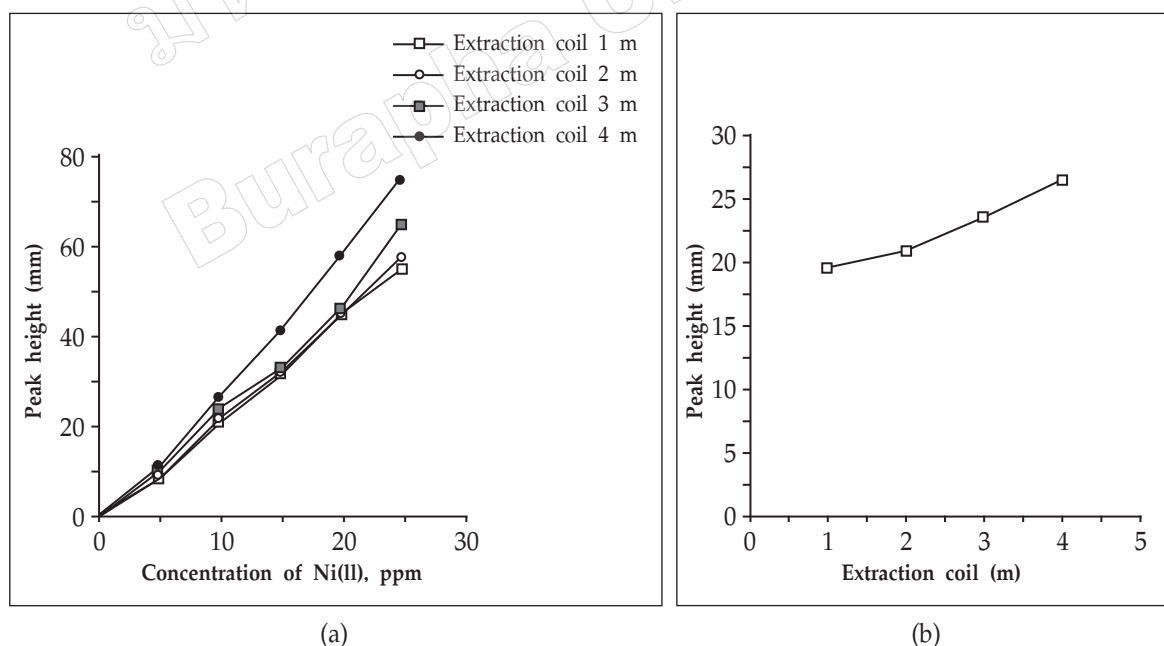


Figure 4. (a) Illustrating the relationship among nickel (II) concentration, ppm and the peak heights (mm) at various extraction coil. (b) Illustrating the relationship among extraction coil (m) and the peak heights (mm) at Ni(II) concentration 10 ppm.

The extraction coil length was varied from 100 to 500 cm. It was found that the peak heights were almost constant with length of extraction coil. An extraction coil length of 400 cm was, therefore, used.

The volume of injected sample was varied from 30 to 500 μl when the length of sample

loops in the injection valve was changed. The peak heights increased non-linearly with increasing sample size and the peak widths also became broader. The volume of 250 μl was a compromise between sensitivity and sample injection rate, as shown in Figure 5.

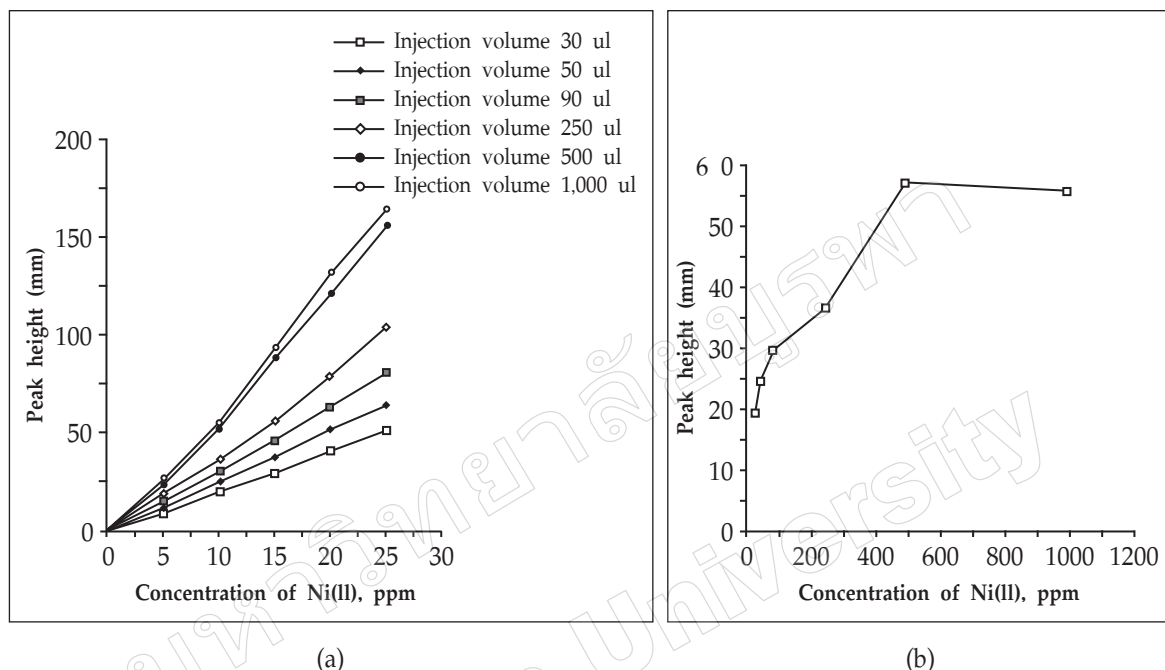


Figure 5. (a) Illustrating the relationship among nickel (II) concentration, ppm and the peak heights (nm) at various Naph concentration.

(b) Illustrating the relationship among Naph (%w/v) concentration and the peak heights (nm) at Ni(II) concentration 10 ppm.

RESULTS AND DISCUSSION

Linear calibration graphs were obtained for 0-100 μg per ml of nickel based on peak height measurements using the flow system and conditions, as shown in Figure 1. Typical calibration data are shown in Figure 2. The relative standard deviation for the determination of 20 μg per ml of nickel was 0.226 % (10 replicates). The limit of detection (three times the baseline noise) was 0.42 μg per ml.

The possible interferences of other ions on the determination of 40 μg per ml of nickel were examined using the flow system and conditions given in Figure 1. It was found that the mixture of Ca(II), Mn(II), Mg(II), Zn(II), Cr(VI), and Pb(II) in the weight ratio (w/w) of 100:1; the mixture of

Ni(II) and Cr(III) in the weight ratio of 10:1; the mixture of Al(III) and Fe(III) in the weight ratio of 5:1; the mixture of NO_3^- , Cl^- , and SO_4^{2-} in the weight ratio of 20,000:1; an ion of ClO_4^- in the weight ratio of 8,000:1; and ion of F^- in the weight ratio of 20:1 did not show any interfering effect in peak heights (3% change in peak heights were regarded as non-interfering). The interference caused by nickel (II) is much less in the FIA method as compared to the manual extraction due to the slow rate of formation of the nickel(II) Naph complex at ambient temperatures.

Results of the determination of nickel in nickel-based alloys are agreed with certified values, where the nickel in pig feeds is also agreed with

results obtained with the atomic elements (see Tables 1 and 2). The method is simple to operate, based on a very cheap reagent, and is yielded more rapid results (30 injection hours) than those of the conventional extraction method.

Table 1. Results of the determination of nickel in nickel-based alloys.

Sample BCS CRM no.	Certified Nickel content (%w/w)	Nickel found ^a (w/w)
364	80.67	80.3±0.4
10 g	60.8	61.2±0.9 HT Brass

^a Mean±S.D. for 5 replicates

Table 2. Determination of nickel in pig feeds^a.

Sample No.	Nickel found ^b (%w/w)		
	FIA	Flame-AAS	ICP-AES
Pig-Finisher 5.0	2.24±0.15	2.17±0.22	2.14±0.12
Pig-Finisher 5.0	2.79±0.14	2.74±0.16	2.64±0.18

^a Product of Groupnet Medicine Co., Ltd., Samutsakorn, Thailand.

^b Mean±S.D. for 5 replicates

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