**Statistical evaluation of spectrophotometric determination of nickel(II) using Micelle-mediated extraction.**

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**Abstract.** An organic reagent namely 2-(2-bromophenyl)imino)methyl)-4-(5,6-dimethylpyridin-2-yl)diazenylphenol was synthesized and used for the determination of nickel after preconcentration using Micelle-mediated extraction. In this preconcentration method the ligand (2-(2-bromophenyl)imino)methyl)-4-(5,6-dimethylpyridin-2-yl)diazenylphenol was used as a chelating agent for the extraction of Ni(II), using the nonionic surfactant Triton X-114 medium. UV-Vis spectrophotometry was applied for the quantitation of the analyte at \( \lambda_{\text{max}}(650) \) nm. All factors affecting the extraction and determination of Ni(II) ion using micelle mediation extraction (e.g. pH, surfactant and reagent concentrations, incubation time and temperature) were executed by using a classical optimization, the calibration plot was subjected to the statistical evaluation by using the analysis of variance (ANOVA). The method was applied to the determination of Ni (II) in environmental samples.

**Introduction**

The main reasons for the choice of Nickel in this study lay in its important as ultra-trace nutrient essential for proper function of the human body, it is involved in lipid metabolism, increases hormonal activity and participate in degradation of urea, but at high concentration it can become toxic. Allergic reaction, skin disorder and respiratory cancer may be caused by nickel toxicity.⁹ Thus the quantification of Nickel in environmental and food samples is very important considering the toxicity of this metal. Therefore the monitoring of Nickel in such samples even at ultra trace level is very essential, but such analyses are difficult because such samples contain low concentration of nickel. Several preconcentration procedures to determine nickel have been devised involving separation techniques such as, solid phase extraction,²-⁴ liquid-liquid extraction,⁵-⁶ ion exchange,⁷ dispersive Liquid–Liquid microextraction⁸ and Micelle-mediated extraction(MME),⁹ the use of Micelle-mediated extraction for separation and pre-concentration has attracted more attention in the last few years, mainly because it is in continuation with our development of suitable methods for the determination of metal ions and it is in agreement with the “green chemistry” principles.¹⁰ By means of Micelle-mediated extraction, the metals are extracted into micelles with a complexing agent in the presence of a surfactant. Above the critical micelle concentration, a separate phase is created.

Different conventional spectrophotometric techniques have been already combined with Micelle-mediated extraction for trace analysis of nickel.¹⁵-²⁷ Among them, UV-Vis has been, by far, the most widely used due to its cost-effectiveness, simplicity, availability, versatility, speed, precision
and accuracy. This technique is generally used in analytical chemistry for determination of different analytes such as transition metal ions, and highly conjugated organic compounds.

In the current work, a new azo–schiﬀ base reagent, namely 2-(2-bromophenyl)imino)methyl)-4- (5,6-dimethylpyridin-2-yl)diazenyl)phenol was synthesized, characterized, and used as a complexing agent to study the Micelle-mediated extraction methodology for preconcentration of ultra trace amounts of nickel ion using triton x-114 as surfactant and their determination by UV-Vis spectrophotometry. The developed method was applied for the determination of ultra trace amounts of nickel (II) in different water samples.

**Experimental Apparatus**

(FTIR)Spectra(4000-400cm-1)in KBr disk were recorded on" SHIMADZU FTIR-8400S fourier. Transform". A "PG Instrument T80+ UV/Vis"spectrometer (England) was used for the scanning study of absorption spectra of the complexes formed, while absorbance measurements were carried out with a "spectrophotometer UV-7804C (China) ". The pH measurements were conducted with a "pH meter Philip PW model 9421( Holland )" with an accuracy of ±0.01 pH unit. The effect of temperature was tested by using a water bath "WB 710 model (OPTIMA, Japan)". melting point were measured using” Stuart, UK. Elemental Analysis 3764,carlo erba Europ". 1HNMR were recorded on fourier transformation bruker spectrometer, operating at (400MHz) with (DMSO-ds) measurments were made at Department of chemistry, kashan university, Iran.

**Reagents and Solutions**

All the chemicals used were of analytical reagent grade, and used without further purification. Deionized and Distilled water was used for diluting the samples and reagents. A 2-amino-5,6dimethylpyridine, 2-bromoaniline,salicylaldehyde and ethanol were purchased from (GCC, England). Stock solutions of Ni(II) ion (1000 mg L⁻¹) were prepared by dissolving (4.032 g)NiCl₂·6H₂O (Merck) in deionized water, respectively. Working standard solutions of metal ion were daily prepared by appropriate dilution of the stock standard solution.. The aqueous solution (5% v/v) of Triton X-114 was prepared by diluting 5 mL of concentrated solution to 100 mL with water. A acetate buffer solution (0.1 mol L⁻¹) was prepared from sodium acetate and acetic acid at different pH.

**Synthesis procedure of 2-(2-bromophenyl)imino)methyl)-4- (5,6-dimethylpyridin-2-yl)diazenyl)phenol (R)**

**Synthesis of 5-((5,6-dimethylpyridin-2-yl)diazenyl)-2-hydroxybenzaldehyde (I)**

Dissolved 2-Amino-4,6-dimethylpyridine (0.01mol) in mixture of 4 ml hydrochloric acid. and 50 ml distilled. The solution was diazotized with (0.75 gm, 0.01 mol in 25 ml distilled water) sodium nitrate (NaNO₂)was cooled and added drop wise to solution of 2-Amino-4,6-dimethylpyridine). The resulting reaction mixture was stirred of 25 minutes ,formed a clear yellow solution. In the resulting diazonium chloride solution,drop-wise, with cooled condition and stirring at(0-5)°C,was added to solution of salicylaldehyde (0.01 mol) dissolved in 50 ml ethanol. The reaction mixture was stirred for another 2 hours at (0-5)°C in ice-bath. After completion of reaction ,the reaction mixture was added to the ice cold water (100 ml) with stirring. The crude product was separated by filtration, washed with distilled water and dried. The solids obtained recrystallized with ethanol to get brown crystals colored. The purity of the azo dye ligand (I) was determined by thin layer chromatography (TLC). The yield of the reaction was 88%. 
Synthesis of 2-((2-bromophenyl)imino)methyl)-4-((5,6-dimethylpyridin-2-yl)diazenyl)phenol \( (R) \)

A mixture of (0.01 mol) of 2-bromobenzaldehyde and (0.01 mol) (1) was refluxed for 3 h in 20 mL of ethanol and Add drops of acetic acid. The reaction mixture was cooled and kept for 24 h. The crystals found was filtered, dried and recrystallized from ethanol to give compound (R).

![Synthetic path of reagent](image)

**Figure 1:** Synthetic path of reagent (2-((2-bromophenyl)imino)methyl)-4-((5,6-dimethylpyridin-2-yl)diazenyl)phenol (R)

**Micelle-mediated extraction procedure:**

To an aliquot of 2 mL of a solution containing known amount Ni(II) standard or sample solution, 0.4 mL of 1.0x10^-3 mol L^-1 organic reagent solution, 1.0 mL of acetate buffer solution at pH = 5.0, 0.3 mL of Triton X-114 (5%) were mixed in a 5-mL volumetric flask and diluted to mark with deionized water. The contents of the flask were transferred into a 10 mL centrifuging tube and the phase separation was induced by heating the contents in a water bath at 50 °C for 10 min. The separation of the phases was accelerated by centrifuging at 5000 rpm for 10 min. The viscosity of the surfactant-rich phase was increased by cooling the mixture in an ice-bath for 5 min. After decantation, the surfactant-rich phase that remained adhered to the tube was dissolved with a 3 mL of ethanol and the concentration of the Ni(II) ions was determined spectrophotometry at \( \lambda_{max} \) of 650 nm.

**Infrared spectra**

The synthesized ligand and its complexes were characterized by FT-IR, compound (1) show absorption at (2707) cm^-1 for (C-H)aldehyde,( 1724) cm^-1 for (C=O), (1450) cm^-1 (-N=N-), and show band at (3008) cm^-1 (C-H)aromatic 'and band for (C-H) aliphatic at (2823) cm^-1, 1627 cm^-1 for (C=C) aromatic. (1535) cm^-1 for (C=N)pyridine, (3309) cm^-1 (OH) for phenol.

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The synthesized organic reagent (2) were characterized by FT-IR show absorption at (1650) cm$^{-1}$ for new(C=N), (3394) cm$^{-1}$ (OH) for phenol, (1488) cm$^{-1}$ (-N=N-)and show band at(2923) cm$^{-1}$ for (C-H) aliphatic and (3062) cm$^{-1}$ for (C-H)aromatic.

The $^1$H NMR (DMSO) spectrum data of compound (1) show δ: 6.8-8.9 (m, 5H, Ar-H), 1.7 (s, 6H, -CH3), 9.3 (s, 1H, OH), 11.6 (S, 1H, C-H) Ald.
The $^{1}$H-NMR(DMSO) spectrum data of compound (R) show $\delta$: 6.9-8.9 (m, 9H, Ar-H), 1.8 (s, 6H, -CH$_3$), 6.02 (s, 1H, CH-N).

Figure (5) 1H NMR Spectra For compound (R)

$^{13}$C-NMR Spectra
The $^{13}$C-NMR(DMSO) spectrum data of compound (1) show $\delta$: 153 (C9), 191(C12), 152(C1), 149(C5), 141(C6), 133-122(C aromatic), 134(C4), 29(C13,C14).

Figure (6) $^{13}$C NMR Spectra For compound (1)

The $^{13}$C-NMR(DMSO) spectrum data of compound (R) show $\delta$: 151 (C9), 135(C13), 150(C1), 149(C5), 135(C4), 147(C6), 112-132(C aromatic), 25(C13,C14).

Figure (7) $^{13}$C NMR Spectra compound (R)
Absorption spectra

The absorption spectra of [(R)_2Ni] complex was recorded against a reagent blank prepared under the identical conditions. The spectra of Ni(II) complex show the absorption maxima of 650 nm with molar absorptivities of $16.19 \times 10^5$ L mol$^{-1}$ cm$^{-1}$. Whilst, the ligand (R) gave the absorption maxima of 484 nm as depicted in Figure 8.

![Absorption spectra](image)

**Figure 8:** Absorption spectra (a) Reagent = $1 \times 10^{-3}$ M (b) [(R)_2Ni] complex, Ni(II) =40 ng mL$^{-1}$, [R] =0.3 mL of $1 \times 10^{-3}$ M, Buffer pH = 5

The Reagent (R) reacts with Ni(II) ion at pH 5 forming a green complex, and the absorbance remained stable, for at least 24 h. The stoichiometry of [(R) 2Ni] complex was studied, under the established experimental conditions, by mole ratio and Job’s methods. The obtained results indicated that the composition of complexes was (1: 2) In addition this complexes was characterized on the basis of spectroscopic techniques and the suggested related chemical structur is shown in Figure 9.

![Chemical structure](image)

**Figure 9:** The probable chemical structure of the complex

Optimization of MME Procedure

The influence of most experimental variables which impact the MME procedure for the Ni ion such as, pH, concentration of reagents and non-ionic surfactant, temperature, centrifugation times and incubation time were investigated using one variable-at-a-time (OVAT) strategy in searching of the optimum conditions, to maximize analytical Figureures of merit such as sensitivity and detection limit and recovery percentage Ni (II) ion in the selected samples. Each experiment of the stutdying variable was conducted followed the general MME procedure.
Effect of pH

The solution pH acting an important role in the formation of metal complexes with the chelating agent and their extraction by MME methodology. Thus, the influence of pH was studied in the range of 3 to 9 using different pH acetate buffer solutions. The results are depicted in Figure 10. As can be seen from Figure 10 that the absorbance first increased with increasing pH and reached a maximum at pH 5.0. Thereafter, the absorbance decreased because of partial dissociation of the complexes at higher pH, which may result in incomplete extraction of Ni (II) complex. Therefore, pH 5.0 was selected as the optimum pH's for complete formation of for Ni (II) complex.

![Figure 10](image_url)

**Figure 10** Effect of pH on the formation of [(R) 2Ni] complex by MME [Conditions: 40 ng mL⁻¹ Ni(II) or , 0.4 mL of 1x 10⁻³ M chelating agent, 0.3 mL of 5 % (v/v) Triton X-114, X pH, Temp. 50 °C, Time 10 min ]

Effect of chelating agent concentration

The influence of 2-(2-bromophenyl)imino)methyl)-4- (5,6-dimethylpyridin-2-yl)diazenyl)phenol concentration was investigated by measuring the absorbance signal according to the general MME procedure of solution containing 40 ng mL⁻¹ Ni(II) and varying volume from 0.2 to 0.7 mL of 1 x 10⁻³ mol L⁻¹ organic reagent. the analytical responses increase rapidly as the volume of organic reagent increases and reach maximum up to 0.4 mL and decrease thereafter with further increase in the chelating agent. Representative that any excessive amount of chelating reagent was not necessary (Figure 11). Consequently, 0.4 mL of 1 x 10⁻³ mol L⁻¹ of the prepared reagent was chosen as the optimum.

![Figure 11](image_url)

**Figure 11** Effect of concentration of chelating agent on the MME of Ni (II) [Conditions: 40 ng mL⁻¹ Ni (II) , X mL of 1x 10⁻³ M chelating agent , pH 5, 0.4 mL of 5 % (v/v) Triton X-114, Temp. 50 °C, Time 10 min ]
Effect of Triton X-114 amount

TX-114 was chosen as nonionic surfactant in the present study because of its, low toxicological properties, low cost, commercial availability with high purity, and also its high viscosity gives the opportunity for easy phase separation by centrifugation. The influence of concentration of Triton X-114 on the absorbance for the determination of Ni (II) ion was evaluated. Different volumes of Triton X-114(5% v/v) ranging from 0.1 to 0.6 mL were used in this study at conventional optimum conditions. As shown in Figure 12, the absorbance for Ni complex increased by increasing the Triton X-114 concentration up to 0.3 of 5% (v/v) then suddenly decreased at higher amounts. Therefore 0.3 mL of 5% (v/v) Triton X-114 was used as the optimum amount for Ni (II) for subsequent experiments.

![Figure 12](image1.png)

Effect of the equilibrium temperature and the incubation time

To attain efficient phases separation by MME method, the effect of the equilibrium temperature and the incubation time were tested. Consequently, the temperature was varied from 30 °C to 90°C at incubation time of 10 min keeping other variables are constant to seek the optimum value. It was exposed (Figure 13) that a maximum absorbance signal was achieved when the temperature at 50 °C. Thus, an equilibration temperature of 50°C for maximum extraction of Ni(II) was chosen as optimal. and it was observed that the incubation time of 10 min was sufficient for the maximum absorbance for the Ni (II)complex (Figure 14).

![Figure 13](image2.png)
Effect of incubation time on the MME of Ni (II)
[Conditions: 40 ng mL$^{-1}$ Ni (II), 0.4 mL of 1x $10^{-3}$M chelating agent, pH 5, 0.3 mL of 5% (v/v) Triton X-114, Temp. 50 °C].

**Calibration graphs**

Under the optimized conditions established by MME procedure, a series of standard Ni(II) solutions ranging from 20-80 ng mL$^{-1}$, was taken and subjected to the general MME in order to test the linearity of the method. The statistical evaluation for the calibration graphs has shown that a strong correlation between signal and Ni(II) concentration may exist ($r = 0.9996$). The statistical analytical results for the calibration data for Ni(II) is summarized in Table 1.

The analysis of variance (ANOVA), On the other hand, also proved that the linear regression equations [$y=0.062\pm0.00322+(6.841 \pm0.00256)x$] for Ni (II) , were statistically valid. This because of the ratio (MSreg/MSerror) for 1 and 8 dof, bigger than critical value (F1,8= 5.32 at 95% CI),

**Table 1** Method validation of the determination Ni complex

| Parameter | Value |
|-----------|-------|
| Regression equation | $y = 0.062 + 6.841x$ |
| Std. dev. of regression line ($s_{y/x}$) | 0.00565 |
| Correlation coefficient ($r$) | 0.9996 |
| Concentration range (ng mL$^{-1}$) | 20-80 |
| Limit of Detection (ng mL$^{-1}$) | 2.48 |
| Limit of Quantitation (ng mL$^{-1}$) | 8.25 |
| Sandell’s sensitivity (g cm$^{-3}$) | $0.146 \times 10^{-3}$ |
| Molar absorptivity (L.mol$^{-1}$.cm$^{-1}$) | $16.19 \times 10^{5}$ |
| Composition of complex (M: L)* | 1:2 |
| RSD% (n=7) | 1.23 |
| Enrichment factor (EF)** | 78 |

**| **EF is calculated as the ratio of slope of calibration curves obtained with and without MME

**Table 2**: Analysis of Variance table of regression line for Ni (II)

| Source | dof | SS | MS | F | P |
|--------|-----|----|----|---|---|
| Regression | 1 | 1.23561 | 1.23561 | 154451.25 | 0.000 |
| Error | 8 | 0.00007 | 0.000008 | Residual |
| Total | 9 | 1.23568 |

SS: sum of squares, MS: mean of squares, Dof=degrees of freedom ,F (Fisher F-test)

The proposed method has achieved enriching factor of 78 fold and this is what was allowed to get on the detection limit of 2.48 ng mL$^{-1}$ for Ni (II) in aqueous solution. It can be concluded that the
prepared ligand in the current work beside MME-Spectrophotometry gave satisfactory analytical Figureures of merit for Ni (II) which were much better than with those obtained by some previous studies that used analytical methods in combination with MME (Table 3).

Table 3: Comparison of the proposed Method with reported methods in chemical literatures for the determination of Ni (II) ion.

| preconcentration technique | LOD μg / L | Linear range μg / L | sample | Ref |
|---------------------------|------------|----------------------|--------|-----|
| MME - FAAS                | 1.7        | -                    | Water  | 34  |
| DLLME-HPLC               | 0.8        | -                    | Water  | 35  |
| MME-UV-VIS              | 4.05       | -                    | Soil, Cabbage Chicken liver, Fish | 36  |
| SPE- UV-VIS               | -          | 0.01-0.1            | spiked water, natural water | 37  |
| MME-UV-Vis             | 4          | 10-150               | Water  | 38  |
| MME-UV-Vis             | 2.805      | 5-50                | Waste water | 39  |
| MME-UV-Vis              | -          | 0.43-8.56          | Tap water and alloy | 40  |
| MME-UV-Vis              | 2.48       | 20-80               | Different water samples | This work |

Interference Study
The influence of most diverse ions on the determination of 40 ng/mL–Ni (II) solutions were studied following the MME procedure. It is agreed that co-existing ion deemed to interfere seriously when it gives a relative error percent greater than ±5%. The results showed that some of metal ions like Na (I), Ca (II), K (I), and Zn(II) have no appreciable effect on the Nickel ion responses, while the other metal ions such as Cu (II), Co(II) and Cd(II) have exceeded the allowable limits of interferences for Ni(II) as shown in Table 4.

Table 4. Effect of divers ions on the absorption signal of Ni (II) (40 ng mL−1, Abs=0.313) by MME-spectrophotometry

| Erel (%) | A | A | Interferent / Ni(II) | Interfering ion |
|----------|---|---|----------------------|-----------------|
| 0.318    | 0.001 | 0.314 | 1000 | Na⁺       |
| -1.29    | -0.004 | 0.309 | 1000 | K⁺        |
| 0.94     | 0.003 | 0.316 | 1000 | Cd²⁺      |
| 5.15     | 0.017 | 0.33  | 500  | Co (II)   |
| -7.93    | -0.023 | 0.29  | 500  | Cu (II)   |
| -11.78   | -0.033 | 0.28  | 500  | Cd (II)   |
| -0.64    | -0.002 | 0.311 | 1000 | Zn (II)   |

A mixture of 0.05M tartaric acid, oxalic acid, and sodium fluoride used to control the interferences of Cd(II), Cu (II) and Co (II), without any appreciable masking of Ni ion.

Determination of Nickel ion in real samples
To test the applicability of the proposed MME method, different water sample (Tap water, river water and Mineral water) were collected from al- Dewanyia city. The river water sample was filtered through whatman filter paper.
results (Table 5) indicate that the proposed method is applicable for the determination of Ni(II) in water samples.

**Table 5.** Determination of Nickel ion in different water samples.

| Sample         | Added (ng.ml⁻¹) | Found (ng.ml⁻¹) | Recovery % |
|----------------|-----------------|-----------------|------------|
| Tap water      | -               | 9.3±0.2         | -          |
|                 | 10              | 18.9±0.6        | 96         |
|                 | 20              | 28.6±0.1        | 96.5       |
| River water    | -               | 13.6±0.5        | -          |
|                 | 10              | 22.9±0.2        | 93         |
|                 | 20              | 33.1±0.1        | 97.5       |
| Mineral water  | -               | 5.6±0.2         | -          |
|                 | 10              | 14.9±0.1        | 93         |
|                 | 20              | 25.4±0.8        | 99         |

*The mean value and its standard deviation (n=3) at 95% confidence level.(x± t. s/√n)*

**Conclusions**

In this work, we have using laboratory-made azo–schiff base reagents for cloud point extraction in the selective separation and enrichment of Nickel(II) ion as a prior step for the determination of ultra-trace quantities in environmental samples by means of spectrophotometric techniques. The analytical figures of merit and enrichment for Nickel(II) was a satisfactory compared with those using expensive instrumentation and sophisticated such as SPE-ETV-ICP-OES, FO-LADS, FIA-Optical sensor etc.

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