Introduction

In last decades, toxic effects of elements for the environment and human health at trace levels have been extensively investigated in pollution and nutrition studies.\(^1\) Although many elements are essential for human beings and animals, some elements, such as nickel, can cause harmful effects on living organisms when they are taken in excessive and/or lower amounts than required. In general, nickel naturally exists with different oxidation steps such as –1, +1, +2, +3 and +4 in the various minerals and the +2 oxidation state is the most common one.\(^2\) The color of ceramics, electroplating, battery, production and reclamation are different application areas for nickel and/or its compounds.\(^3\)

Industrial activities cause nickel contamination in air, soil, water and food samples. Normally, human beings ingest about 100 - 300 μg of nickel per day.\(^4\) In general, the nickel content in foodstuffs is considered to be lower than 0.2 mg kg\(^{-1}\), oatmeal (1 mg kg\(^{-1}\)), roasted cashew (up to 5 mg kg\(^{-1}\)), cocoa (up to 12 mg kg\(^{-1}\)), chocolate (up to 6 mg kg\(^{-1}\)), soy products (2 - 6 mg kg\(^{-1}\)), legumes (2 mg kg\(^{-1}\)), almonds (0.8 mg kg\(^{-1}\)), black tea (up to 3 mg kg\(^{-1}\)) can be given as examples for nickel-rich food sources.\(^4,5\) The nickel concentration in drinking water is generally found to be less than 10 μg L\(^{-1}\). The average intake of nickel is around 7.5 and 15.0 μg for adults who drink 1.5 L water per day.\(^2\) If it is taken in more than the allowed amount, various diseases, such as lungs, gastrointestinal and kidneys problems, pulmonary fibrosis, skin dermatitis and respiratory cancer, may occur.\(^5,6,4\) Therefore, the sensitive, accurate and precise determination of nickel in environmental samples is very important.\(^9\)

In the literature, there are many methods for the determination of metal ions at trace levels. Some of them are flame atomic absorption spectroscopy (FAAS),\(^10\) graphite furnace atomic absorption spectroscopy (GFAAS),\(^11\) inductively coupled plasma mass spectroscopy (ICP-MS),\(^12\) atomic fluorescence spectroscopy (AFS),\(^13\) inductively coupled plasma optic emission spectroscopy (ICP-OES).\(^14\) Among them, FAAS is a robust analytical method that gives accurate and precise measurements, and it is ideal for routine laboratory usage. As the detection limits recorded for most elements using FAAS are in the upper parts of per billion level, the sensitivity is not high enough to determine metals at trace levels.\(^15-17\) However, its sensitivity can be increased using either simply modified systems or some preconcentration procedures,\(^15\) such as cloud point extraction (CPE),\(^18\) dispersive liquid-liquid microextraction (DLLME),\(^19\) solid-liquid-solid dispersive extraction, ionic liquid-based dispersive liquid-liquid microextraction (SLSDE-ILDLLME)\(^20\) and solid phase extraction (SPE).\(^21\) Recently, SPE has been widely used for the preconcentration and separation of elements owing to such as advantages a high enrichment factor, rapid separation and low cost. Furthermore, it can be easily combined with different detection methods in the on-line or off-line modes.\(^7,22\)

A novel method was developed for the selective and simultaneous preconcentration of Ag, Cd and Ni in real water samples using a multi-step cloud-point extraction procedure, AAS was used for determining these ions, respectively. In this

Separation and Preconcentration of Nickel(II) from Drinking, Spring, and Lake Water Samples with Amberlite CG-120 Resin and Determination by Flame Atomic Absorption Spectrometry

Yasin ARSLAN,*, Burcu KABAK,** Diğdem TRAK,** and Erdal KENDÜZLER***†

* Nanoscience and Nanotechnology Department, Faculty of Arts & Science, Mehmet Akif Ersoy University, 15030 Burdur, Turkey
** Chemistry Department, Faculty of Arts & Science, Mehmet Akif Ersoy University, 15030 Burdur, Turkey

In this study, Amberlite CG-120 adsorbent was used for the separation/preconcentration of Ni(II) ions in commercial drinking, spring and lake water samples before detection by flame atomic absorption spectrometry. Various optimization parameters for Ni(II) determination, such as pH, eluent type and concentration, sample and eluent flow rates, amount of adsorbent, were investigated to obtain better sensitivity, accuracy, precision and quantitative recovery. Furthermore, the interference effects of some ions on the recovery efficiency of Ni(II) were also investigated. The optimum experimental parameters were obtained in the case of pH 1; 5 mL of 4 mol L\(^{-1}\) HCl for eluent and 0.3 g for the adsorbent amount. The limit of detection was found to be 0.58 μg L\(^{-1}\) and linearity ranged from 5 to 50 μg L\(^{-1}\). The accuracy of the method was tested by the certified reference material of TMDA-70.2 Ontario Lake Water at a 95% confidence level.

Keywords: Amberlite CG-120 resin, water samples, nickel(II), solid phase extraction

(Received February 25, 2018; Accepted May 29, 2018; Published October 10, 2018)
study, the linearity ranged from 10 to 150 μg L⁻¹ for Ag, 5 to 100 μg L⁻¹ for Cd and 10 to 200 μg L⁻¹ for Ni. The enhancement factors were 42 for Ag, 54 for Cd and 41 for Ni and limit of detection values were 0.58 μg L⁻¹ for Ag, 0.29 μg L⁻¹ for Cd and 1.12 μg L⁻¹ for Ni. In another study, a simple micro extraction method was used for the determination of Ni and Pb by solid–liquid–solid dispersive extraction, followed by ionic liquid-extraction method was used for the determination of Ni and Pb and Ni(II) was prepared by dissolving 0.495 g of Ni(NO₃)₂·6H₂O in food samples, such as chicken, fish and meat. In this study, solid-liquid-solid dispersive extraction, followed by ionic liquid-based dispersive liquid-liquid microextraction (SLSDE-ILDLMME), was applied for the extraction of Ni and Pb ions. The effect of some experimental parameters, such as the extraction time, pH and volume of the complexing agent of ammonium pyrrolidine dithiocarbamate (APDC), were investigated for extracting these ions. Under the optimum conditions, the limits of detection (LODs) calculated using 3(SD)ₙₙₙ/ₙ were found to be 0.17 μg L⁻¹ for Ni(II) and 0.79 μg L⁻¹ for Pb(II) for aqueous solutions with 125 enrichment factor (EF). In another study, modified magnetic nanoparticles were used as sorbents for the preconcentration and determination of Ni ions in food and environmental water samples. The calibration plot was linear between 30 and 5000 μg L⁻¹ and the detection limit was found to be 3.9 μg L⁻¹. In another study, Co and Ni ions were separated and preconcentrated in water, black tea and tomato samples using a column solid-phase extraction procedure with FAAS detection. The limit of detection was 0.25 μg L⁻¹ for Co and 0.18 μg L⁻¹ for Ni and the enhancement factor was 250 for both elements.

In this study, separation and/or preconcentration of Ni(II) was performed in a column containing Amberlite CG-120 resin prior to FAAS detection. Amberlite CG-120 is a strongly acidic cation exchange resin and the optimum pH values of this resin have been obtained to be around 0.4 – 10. The functional groups of this resin are named as Na⁺ form and sulfonic acid groups. As a result of the interaction with these groups, Ni(II) is adsorbed on Amberlite CG-120 resin. Some preconcentration methods were developed for Mn, Cd, Cu and Zn by using Amberlite CG-120 resin. As far as we can ascertain, Amberlite CG-120 was the firstly used resin for the preconcentration and determination of Ni(II) with FAAS detection. In this study, Ni(II) was selectively determined in all water samples supplied from Burdur, Turkey province and the certified reference material of TMDA-70.2 Lake Ontario Water using optimum experimental conditions.

**Apparatus**

In this study, ATI Unicam 939 Model FAAS was used in the detection step of Ni(II) equipped with a Ni hollow cathode lamp as a light source (current, 15 mA; wavelength, 232 nm; bandwidth of the slit, 0.2 nm) and acetylene flow rate, 1.0 L min⁻¹. The pH values were controlled with a Thermo Orion 3 Stars Model pH meter and an Memmert, UN-110 Model oven was used for drying all glass materials; 18 M₂-cm deionized water from a PURIS purification system (Model: Expe-UP Series) was used preparing all solutions. In the separation and/or preconcentration of Ni(II) prior to FAAS detection, the glass column used in this study has a solution volume of 250 mL, 15 cm in length and 0.8 cm in internal diameter.

**Column preparation**

In the preparation step of the column, a small glass wool wad was placed at the bottom of the column and 0.3 g of Amberlite CG-120 resin was added on it. Afterwards, another small glass-wool wad was inserted onto the top of the resin. Before use, the Amberlite CG-120 resin in the column was washed consecutively with ethanol, 1 mol L⁻¹ HCl, 1 mol L⁻¹ HNO₃, and deionized water. After each usage, the column was filled with deionized water and stored so as to prevent drying of the resin until the next experiment.

**Samples preparation**

In this study, the Ni(II) was selectively determined in all water samples supplied from Burdur, Turkey province and the certified reference material of TMDA-70.2 Lake Ontario Water using optimum experimental conditions.

**Results and Discussion**

In this study, some of the experimental parameters, such as pH, volume and flow rate of sample solution, volume, flow rate, type and concentration of eluent solution, and adsorbent amount, were optimized for the separation and/or preconcentration of Ni(II) in a column containing Amberlite CG-120 adsorbent prior to FAAS detection.

**pH effect**

In the solid-phase extraction technique, the pH is a significant parameter to obtain the quantitative recovery of elements, because it affects the sorbent surface charge. It also plays a role in the ionization degree of the adsorbent. Therefore, the column was first conditioned at different pH values in the range of 1 – 10. Then, model solutions (25 mL of solutions containing 50 μg Ni(II)) were prepared and conditioned at different pH values in the range of 1 – 10, respectively. The model solutions were passed through the column separately by adjusting the sample solution flow rate of 2 mL min⁻¹, and then recovered from the column using 10 mL of a 2 mol L⁻¹ HCl solution. As can be seen in Fig. 1, the quantitative similar recovery of Ni(II) was obtained for pH 1 – 5. pH 1 was chosen as the optimum pH value because various real samples, such as biological and/or geological, were usually dissolved by using acids and the precipitation of metal ions could occur at high pH values.

**Eluent type and volume**

A series of eluent solutions, viz. 10 mL of 2 mol L⁻¹ HNO₃, HClO₄, HCl and pure ethanol, were employed in order to find out the suitable eluent type. The highest recovery of Ni(II) was achieved with 10 mL of 2 mol L⁻¹ HCl among these eluents.
After that, the optimum concentration and volume of HCl was also optimized. To this purpose, various concentrations and volumes of HCl were investigated (Table 1). It was found that quantitative elution was achieved by using 5 mL of 4 mol L–1 HCl. Therefore, 5 mL of a 4 mol L–1 HCl solution was employed in all studies. There were some studies existing in the literature to use HCl for the elution of Ni(II) ion.7,29

Sample and eluent solution flow rate

The sample and eluent flow rate through the column filled with Amberlite CG-120 resin are significant parameters that influence both the recovery efficiency of the analyte and the time of analysis. In order to perform, the model solution was passed through the column at a flow rate changing from 0.25 to 5 mL min–1. Quantitative recovery was obtained for all sample flow rates, and 5 mL min–1 was chosen in order to shorten the analysis time. Furthermore, when sample flow rate was higher than 5 mL min–1, the preconcentration factor was decreased because of the fact that Ni(II) ions in the sample was not efficiently adsorbed on the resin, and it was difficult to control higher flow rates in our system. The eluent solution was passed through the Amberlite CG-120 resin at flow rates ranging from 0.25 to 2 mL min–1. With all eluent flow rates, quantitative recovery was achieved and 2 mL min–1 was selected to shorten the analysis time. The effect of the flow rates of the sample and the eluent on the recovery of Ni(II) is shown in Fig. 2. A 2000-mL volume of the sample solution was passed through the column at 400 min and 5 mL of the eluent solution was passed through the column at 2.5 min. This result is consistent with studies in the literature.30–32

Amberlite CG-120 resin amount

For an efficient extraction procedure, the optimization of Amberlite CG-120 resin amount is another significant parameter. The amount of 0, 0.01, 0.1, 0.3 and 0.5 g of the Amberlite CG-120 resin for the Ni(II) adsorption was investigated, and quantitative recovery was obtained from 0.3 to 0.5 g. Preliminary studies showed that when the amount of the Amberlite CG-120 resin was higher than 0.5 g, all of the adsorbed Ni(II) ions were not sufficiently recovered from the resin by the eluent. Therefore, the maximum resin amount was chosen to be as 0.5 g. The capacity of resin for Ni(II) adsorption decreased when the amount of resin was less than 0.3 g, owing to an insufficient number of adsorption sites. Therefore, 0.3 g was chosen in further experiments to use a smaller amount of Amberlite CG-120 resin.

Sample volume

To obtain the highest preconcentration factors, volumes in the range from 25 to 4000 mL of sample solution containing 25 μg Ni(II) were passed through the Amberlite CG-120 resin. The recovery of Ni(II) was quantitative (≥95%) for sample volumes ranging from 25 to 2000 mL of the sample volume, as shown in Fig. 3. When the sample and eluent volumes were chosen to be as 2000 mL and 5 mL, respectively, the preconcentration factor was obtained as 400-fold.

Interference studies

Interference effects should be investigated, since interfering ions present in high amounts in the real samples, may affect the Ni(II) signal positively and/or negatively. For this, different cations prepared from nitrate or chloride salts were added individually to the model solution of Ni(II), and then the proposed preconcentration method was applied. The tolerance limits for interfering ions on the Ni(II) recovery are given in Table 2. There was no obvious influence on the recovery of Ni(II) by the presence of interfering ions.
Ni(II) for Al(III), Mn(II), Fe(III), Cu(II), Zn(II), Ca(II) and Mg(II) up to 250-fold, and for Na and K up to 5000-fold excess electrolytes. The tolerance limits for interfering ions on the Ni(II) recovery were a significant advantage of this study compared with other studies in the literature.\textsuperscript{22,23,33}

**Method validation**

The accuracy of the method was tested by the determination of Ni(II) in the certified reference material, TMDA-70.2 Lake Ontario Water. By using optimum analytical parameters, Ni(II) concentration in the certified reference material was found to be 318 ± 25 μg L\(^{-1}\) with a relative error of –4.2%, based on 3 replicate measurements at the 95% confidence level, which is a good agreement with the certified value of 332 ± 23 μg L\(^{-1}\). Therefore, it seems that this method is useful for the preconcentration of trace levels of Ni(II) in the presence of other cations which shows the applicability of the method.

**Real samples analysis**

The developed method was used for the determination of Ni(II) ions in commercial drinking water samples purchased from local market in Burdur province and different spring waters supplied from Burdur province (Kurna village and Ağlasun county) and Isparta province (Eyüpler village and Tepeli village) and the lake water supplied from Isparta province ( Eğirdir lake) at Turkey. The accuracy was also tested by measuring the recovery of Ni(II) spiked as different amounts in the water samples, as shown in Table 3.\textsuperscript{34,35} The results show the applicability of the method in the water samples without any interference effect of other ions for Ni(II) determination.

**Table 2** Effect of interfering ions on the recovery of Ni(II)

<table>
<thead>
<tr>
<th>Ions</th>
<th>Tolerance level/mg L(^{-1})</th>
<th>R, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^+)</td>
<td>5000</td>
<td>95 ± 1</td>
</tr>
<tr>
<td>K(^+)</td>
<td>5000</td>
<td>97 ± 2</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>250</td>
<td>100 ± 1</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>250</td>
<td>97 ± 4</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>250</td>
<td>96 ± 2</td>
</tr>
<tr>
<td>Zn(^{2+})</td>
<td>250</td>
<td>98 ± 2</td>
</tr>
<tr>
<td>Mn(^{2+})</td>
<td>250</td>
<td>100 ± 1</td>
</tr>
<tr>
<td>Al(^{3+})</td>
<td>250</td>
<td>96 ± 1</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>250</td>
<td>98 ± 2</td>
</tr>
</tbody>
</table>

pH, 1; sample volume, 25 mL; eluent volume, 5 mL of 4 mol L\(^{-1}\) HCl; amount of Ni(II), 25 μg; flow rate of sample, 5 mL min\(^{-1}\); flow rate of eluent, 2 mL min\(^{-1}\); resin amount, 0.3 g. N = 3.

**Table 3** Determination of Ni(II) in water samples (N = 3)

<table>
<thead>
<tr>
<th>Water sample</th>
<th>Added Ni(II)/μg L(^{-1})</th>
<th>Found Ni(II)/μg L(^{-1})</th>
<th>Relative error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^a)</td>
<td>100</td>
<td>102 ± 6</td>
<td>+2.0</td>
</tr>
<tr>
<td>2(^b)</td>
<td>200</td>
<td>195 ± 9</td>
<td>–2.5</td>
</tr>
<tr>
<td>3(^c)</td>
<td>100</td>
<td>96 ± 4</td>
<td>–4.0</td>
</tr>
<tr>
<td>4(^d)</td>
<td>100</td>
<td>102 ± 9</td>
<td>+2.0</td>
</tr>
<tr>
<td>5(^e)</td>
<td>100</td>
<td>188 ± 5</td>
<td>–6.0</td>
</tr>
<tr>
<td>6(^f)</td>
<td>100</td>
<td>98 ± 5</td>
<td>–2.0</td>
</tr>
<tr>
<td>7(^f)</td>
<td>100</td>
<td>209 ± 9</td>
<td>+5.0</td>
</tr>
</tbody>
</table>

a. Commercial drinking water.

b. Kurna village spring water.

c. Ağlasun county spring water.

d. Eyüpler village spring water.

e. Tepeli village spring water.

f. Eğirdir lake water.

**Conclusions**

In this study, the pH, concentration and type of eluent, flow rates of eluent and sample, sample volume and amount of adsorbent were optimized so as to obtain more sensitive, precise and accurate separation and/or preconcentration of Ni(II). All experiments were repeated at least 3 times, and the relative standard deviation (RSD%) was found as below 5% at the 95% confidence level. The method was performed in a strongly acidic medium, and there was no necessity of using buffer and chelating agents for the separation and preconcentration of Ni(II) on the column containing Amberlite CG-120 resin. Using this rapid, simple, economic, accurate and precise method, enrichment factor and the limit of detection were found to be as 400-fold and 0.58 μg L\(^{-1}\), respectively. The method was used to determine Ni(II) in water samples, and the accuracy of the method was tested by certified reference material, TMDA-70.2.

**Table 4** Comparison of the analytical performance of this proposed method with different methods in the literature

<table>
<thead>
<tr>
<th>Study</th>
<th>pH</th>
<th>LOD/μg L(^{-1})</th>
<th>Enhancement factor</th>
<th>Method</th>
<th>Samples</th>
<th>Measuring instrument</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5</td>
<td>1.12</td>
<td>41</td>
<td>MS-CPE</td>
<td>Water samples</td>
<td>FAAS</td>
<td>18</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>1.0</td>
<td>200</td>
<td>SPE</td>
<td>Tobacco, brewed tea, water samples</td>
<td>FAAS</td>
<td>32</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>5.2</td>
<td>10</td>
<td>LL-SHS-LPME</td>
<td>Tobacco, tea, food samples</td>
<td>FAAS</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>0.18</td>
<td>250</td>
<td>SPE</td>
<td>Mineral water, black tea, spring water, tomato</td>
<td>FAAS</td>
<td>23</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>0.14</td>
<td>357</td>
<td>SPE</td>
<td>Various vegetables</td>
<td>Electrothermal AAS</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>7</td>
<td>0.80</td>
<td>100</td>
<td>SPE</td>
<td>Various food and water samples</td>
<td>FAAS</td>
<td>34</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>2.3</td>
<td>100</td>
<td>SPE</td>
<td>Food samples</td>
<td>FAAS</td>
<td>36</td>
</tr>
<tr>
<td>8</td>
<td>9</td>
<td>0.9</td>
<td>100</td>
<td>SPE</td>
<td>Waste water and lake water</td>
<td>FAAS</td>
<td>37</td>
</tr>
<tr>
<td>This study</td>
<td>1</td>
<td>0.58</td>
<td>400</td>
<td>SPE</td>
<td>Water samples</td>
<td>FAAS</td>
<td>—</td>
</tr>
</tbody>
</table>
Ontario Lake Water, at a 95% confidence level based on t-test calculations. Comparisons of the analytical performance of this proposed method with different methods are given in Table 4. Therefore, the most important advantage of this method is to have the highest preconcentration factor.

References