Research Paper

Extractive Spectrophotometric Determination of Nickel with 2-hydroxy-5-iodothiophenol and Diphenylguanidine

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Abstract

Nickel(II) forms well chloroform-extractable ternary complex with 2-hydroxy-5-iodothiophenol (HITP) and diphenylguanidine (DPG). The complex, which has a composition of 1:2:2 (Ni:HITP:DPG) and a two-phase stability constant of Log β = 6.62, could be used for selective, sensitive, and reliable extractive spectrophotometric determination of nickel. The wavelength of maximum absorption, molar absorptivity, Sandell’s sensitivity, optimum pH interval, limit of detection, range of linearity, and relative standard deviation of the developed procedure were 480 nm, 2.64 × 10⁴ L mol⁻¹ cm⁻¹, 2.23 ng cm⁻², 4.5-6.8, 0.02 µg mL⁻¹, 0.07-3.6 µg mL⁻¹ and ≤1.8%, respectively. It was applied for nickel determination in metallic magnesium and a geological sample-carnallite.

Keywords: Nickel(II), 2-Hydroxy-5-Iodothiophenol, Ternary Complex, Liquid-Liquid Extraction

1. Introduction

Nickel is a transition metal with wide application in industry and important roles in the biology of microorganisms and plants. It is used in many recognizable products, such as stainless steels, alloys, coins, rechargeable batteries, permanent magnets, magnetic shields, superconductors, electric guitar strings, microphone capsules, green tint in glass, and catalysts for various industrial processes, such as hydrogenation of vegetable oils, cracking of petroleum, purification of coal gas, synthesis of organic and inorganic compounds, etc. Most of the produced nickel (ca. 96%) is applied for production of stainless steels, alloys, and nickel plating. The chief criteria of use are nickel’s resistance to alkalis, acids, and air oxygen, malleability, attractive finish and appearance, and excellent ability to alloy with both ferrous and nonferrous metals. Over 3000 alloys containing nickel are known (Chatterjee, 2007), including these with Mg, which are considered promising materials for optical switching (Richardson et al, 2001 and Yoshimura et al, 2002), gaseous hydrogen storage (Leiva et al, 2012 and Révész et al, 2014) and production (Huang et al, 2014).

In the Earth’s crust, nickel occurs most often in combination with sulphur (pentlandite, millerite), iron (pentlandite, kamagate, taenite), arsenic (nickelite, nickel galena), and magnesium (garnierite). It is present in all types of soils, in fossil fuels, volcanic emissions, and iron meteorites. As for most metals, the toxicity of nickel is dependent on the route of exposure and the solubility of the corresponding compound (Das et al, 2008). An important feature of this element is that it can cause allergic reactions in some people through skin contact (Thyssen, 2011).

Several analytical methods have been used for nickel determination, including flame atomic absorption spectrophotometry (Avci et al, 2013), graphite furnace atomic absorption spectrometry (Dobrowolski & Otto, 2012), electrothermal atomic absorption spectrometry (Sadeghi et al, 2011), atomic fluorescence spectrometry (Zeng et al, 2012), inductively coupled plasma-optical emission spectrometry (Beiraghi et al, 2012), and spectrophotometry (Uesugi & Yamaguchi, 1982; Ishii et al, 1987; Fan et al, 1998; Fan & Zhu, 1998; Chimpalee et al, 2000; Malik &

The methods involving spectrophotometry are rather popular due to their simplicity, inexpensive instrumentation and easy automation. They are often based on ion-association complexes composed of intensively coloured anionic chelate and bulky organic cation which makes the complex hydrophobic and easily extractable into organic solvents (Töei et al, 1979; Ishii et al, 1987; Purohit et al, 1989; Rao et al, 1998; Terra et al, 1999; Balogh et al, 2005 and Marczenko & Balcerzak, 2007).

In the present paper we study the complex formation in a liquid-liquid extraction system containing Ni(II), 2-hydroxy-5-iodothiophenol (HITP) and diphenylguanidine (DPG), and show the potential of this system for Ni(II) determination in real samples. HITP, an iodine-containing reagent, has -OH and -SH groups in ortho-position. Hence, we expected that this reagent would form stable chelate structures with metal ions, like Ni(II), which have ionic radii close to 0.07-0.08 nm.

2. Materials and Methods

2.1. Reagents and Instruments

Stock solution of Ni(II) was prepared by dissolving NiCl$_2$, 6H$_2$O (Sigma-Aldrich, puriss. p.a.) in distilled water; it was standardized gravimetrically with dimethylglyoxime. Working Ni(II) solutions (0.1 mg mL$^{-1}$) were prepared by appropriate dilution of the stock solution. HITP was synthesized according to the procedure (Kuliev et al, 1976). DPG was a Sigma-Aldrich product (97%). Chloroform solutions of HITP (0.01 mol L$^{-1}$) and DPG (0.025 mol L$^{-1}$) were used. To create the optimum acidity, 0.1 mol L$^{-1}$ solutions of HCl, NaOH, or ammonium acetate buffers were applied. The organic solvent was alcohol-free chloroform. The absorbance of the extracts was measured using a SF 26 spectrophotometer (USSR), KFK 2 photocolorime-ter (USSR), and a Camspec M508 spectrophotometer (UK). Glass cells with optical path of 5 or 10 mm were used. pH of aqueous phase was measured using an I-120.2 potentiometer with a glass electrode.

2.2. Procedure

An aliquot containing no more than 90 µg of nickel was placed in a calibrated tube with ground-glass stopper. Then chloroform solutions of HITP (0.6 mL) and DPG (0.4 mL) were added and the chloroform phase was adjusted to 5 mL; the volume of the aqueous phase and pH were adjusted to 25 mL and 5.0, respectively. After 10 min of shaking, a portion of the organic extract was transferred through a filter paper into a cell and the absorbance was read at $\lambda$=480 nm against chloroform. The nickel content was found from a calibration graph.

2.3. Dissolution of Magnesium

A 0.5-0.6 g sample of magnesium was carefully dissolved in 10 mL of HNO$_3$ (1:2) and the solution was evaporated to moist salts on an electric heater. After cooling, 3 mL of water were added to dissolve the salts and pH was adjusted to ca. 6 with NaOH. The solution was quantitatively transferred into a 25 mL calibrated flask; then distilled water was added to the mark.

2.4. Dissolution of Carnallite

A ca. 2.0 g sample of carnallite was placed in a 50 mL beaker. 0.5 mL of a 3% NaF solution and 5 mL of HNO$_3$ (1:20) were added and the beaker was heated on an electric heater. After cooling, the obtained solution was neutralised with ammonia to pH 6 (universal paper indicator); then it was transferred through a filter paper into a 50 mL calibrated flask and diluted to the mark with distilled water.

2.5. Preparation of a Solid Complex

Solutions of Ni(II), HITP and DPG were mixed in a 1:2:2 molar ratio and the extraction was performed at the optimum pH. The procedure was carried out several times and the extracts were collected in a beaker. Then the beaker was carefully heated up to 70-85 °C for complete evaporation of the solvent (Genç et al, 2010).

3. Results and Discussion

3.1. Optimum Operating Conditions

In a slightly acidic medium, HITP reacts with nickel(II) to produce a coloured anionic complex. In the presence of the cationic ion-association reagent DPG a ternary complex is formed; it is sparingly soluble in water but is easily soluble in organic solvents. The following organic solvents were tested in our experiments: chloroform, 1,2-dichloroethane, carbon tetrachloride, benzene, chlorobenzene, toluene, xylene, isobutanol, isopentanol, and diethylether. The distribution coefficients and extraction rates with these solvents were evaluated. The best ones were chloroform (extraction rate of 97.6%), 1,2-dichloroethane, and carbon tetrachloride. All further investigations were performed with chloroform. The extraction equilibrium with this solvent is achieved for ca. 6-7 min, but we carried out the extraction for 10 min. The absorption maximum of the ternary complex lies at $\lambda$=480 nm, while the maximum of HITP is at $\lambda$=288 nm. Therefore the colour reaction is very contrast (bathoc-
hromic shift of 192 nm). The optimum pH for complex formation and extraction is 4.5–6.8 (Figure 1). The optimum concentrations of the reagents in the organic phase are 1.2×10^{-3} \text{ mol L}^{-1} (HTP) and 2.0×10^{-3} \text{ mol L}^{-1} (DPG).

3.2. Composition, Structure and Stability

The molar ratios between the components of the ternary complex were found by several methods: Starik-Barbanel relative yield method (Barbanel’, 1964), straight line method (Asmus, 1960), equilibrium shift method (Bulatov & Kalinkin, 1986) and crossed lines method (Shevchenko, 1965) (Figure 2). The results suggest the complex composition of 1:2:2 (Ni:HTP:DPG). Additional experiments by the Akhmedly’s method (Akhmedly et al, 1974) showed that the complex exists in monomeric form in the organic phase (the obtained coefficient of polymerization γ was equal to 1).

The existence of clearly defined absorption bands at 2410–2415 cm^{-1} in the IR-spectrum of the complex indicates the coordination of the DPG in the protonated form (Fritz & Schenk, 1974). The disappearance of the band at 2580 cm^{-1}, characteristic for the spectrum of HTP, and appearance of corresponding bands in the spectrum of the complex, which are shifted toward lower frequency, suggests that the sulphur atoms are involved in complex formation. The observed decrease in the intensity of the absorption bands at 3200-3600 cm^{-1} with a maximum at 3460 cm^{-1} and the appearance of a broad band in the region of 3050-3150 cm^{-1} shows that the hydroxyl group participates in the formation of a coordination bond. Proceeding from the obtained data, we propose the following structure for the extracted ternary complex (Figure 3).

3.3. Calibration Graph and Analytical Characteristics

The Ni(II) extracts conform to the Beer’s law in the range of 0.07–3.6 \text{ µg mL}^{-1} with a correlation coefficient of 0.9993 (10 standards used). The limit of detection, calculated according to Aleksovskii et al (1988) was 0.02 \text{ µg mL}^{-1}. The straight-line equation was \(A=0.449C_{\text{Ni}}+0.02\), where \(A\) is the absorbance and \(C_{\text{Ni}}\) is the nickel(II) concentration in µg mL^{-1}. The corresponding molar absorptivity was \(\varepsilon_{430}=2.64\times10^{4} \text{ mol L}^{-1} \text{ cm}^{-1}\); it is higher than the molar absorptivities reported for similar liquid-liquid extraction-spectrophotometric procedures involving pyridoxal-4-phenyl-3-thiosemicarbazone (\(\varepsilon_{430}=1.92\times10^{3} \text{ L mol}^{-1} \text{ cm}^{-1}\)) (Sarma et al, 2008), N-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone (\(\varepsilon_{430}=1.14\times10^{4} \text{ L mol}^{-1} \text{ cm}^{-1}\)) (Ramachandraith et al, 2008), α-furilidoxime (\(\varepsilon_{435}=2.0\times10^{4} \text{ L mol}^{-1} \text{ cm}^{-1}\)) (Marzenko & Balcerzak, 2007), sodium isoamyl xantene (\(\varepsilon_{430}=1.20\times10^{4} \text{ L mol}^{-1} \text{ cm}^{-1}\)) (Malik & Rao, 2000),

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1-hydroxy-2-acetonaphthoneoxime (ε\textsubscript{396}=5.7×10\textsuperscript{3} L mol\textsuperscript{-1} cm\textsuperscript{-1}) (Reddy & Paul, 1984), 2-hydroxy-1-naphthaldoxime (ε\textsubscript{396}=8.1×10\textsuperscript{3} L mol\textsuperscript{-1} cm\textsuperscript{-1}) (Uesugi & Yamaguchi, 1982), dimethylglyoxime (ε\textsubscript{380}=1.9×10\textsuperscript{3} L mol\textsuperscript{-1} cm\textsuperscript{-1}) (Umland et al., 1971), etc.

### 3.4. Effect of the Foreign Ions

To evaluate the complex applicability for photometric determination of nickel, we examined the influence of foreign ions and reagents. The results showed that great excesses of alkali, alkali earth, and rare earth elements, as well as F-, Cl-, Br-, SO\textsubscript{4}\textsuperscript{2-}, SO\textsubscript{3}\textsuperscript{2-}, and C\textsubscript{2}O\textsubscript{4}\textsuperscript{2-} do not interfere with determination. The influence of Fe(III) was eliminated by thioglycolic acid; Ti(VI), by ascorbic acid; Cu(II), by thiourea; and Mo(VI) and Nb(V), by oxalate (Table 1). If a 0.01 mol L\textsuperscript{-1} solution of EDTA was used, Ti(IV), V(IV), Nb(V), Ta(V), Mo(VI) and Fe(III) exhibited no interference.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Molar Ratio to Nickel</th>
<th>Masking Agent</th>
<th>Found (µg)</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(II)</td>
<td>50</td>
<td>-</td>
<td>30.0</td>
<td>2</td>
</tr>
<tr>
<td>W(VI)</td>
<td>50</td>
<td>-</td>
<td>29.8</td>
<td>2</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>200</td>
<td>-</td>
<td>29.8</td>
<td>3</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>200</td>
<td>-</td>
<td>29.6</td>
<td>4</td>
</tr>
<tr>
<td>Al(III)</td>
<td>180</td>
<td>-</td>
<td>30.0</td>
<td>2</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>60</td>
<td>Thioglycolic acid</td>
<td>30.2</td>
<td>4</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>50</td>
<td>-</td>
<td>29.8</td>
<td>3</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>25</td>
<td>Thiourea</td>
<td>29.6</td>
<td>5</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>40</td>
<td>-</td>
<td>30.2</td>
<td>5</td>
</tr>
<tr>
<td>Ti(IV)</td>
<td>30</td>
<td>-</td>
<td>29.6</td>
<td>3</td>
</tr>
<tr>
<td>V(IV)</td>
<td>20</td>
<td>-</td>
<td>29.6</td>
<td>3</td>
</tr>
<tr>
<td>Mo(VI)</td>
<td>10</td>
<td>EDTA</td>
<td>30.4</td>
<td>4</td>
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<tr>
<td>Cr(III)</td>
<td>120</td>
<td>-</td>
<td>29.8</td>
<td>4</td>
</tr>
<tr>
<td>Nb(V)</td>
<td>50</td>
<td>C\textsubscript{2}O\textsubscript{4}\textsuperscript{2-}</td>
<td>30.1</td>
<td>5</td>
</tr>
<tr>
<td>Ta(V)</td>
<td>50</td>
<td>Ascorbic acid</td>
<td>30.1</td>
<td>5</td>
</tr>
<tr>
<td>UO\textsubscript{2}\textsuperscript{2+}</td>
<td>50</td>
<td>-</td>
<td>29.2</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 1. Influence of Foreign Ions on the Determination of Nickel (30 µg) with HITP and DPG

### 3.5. Determination of Nickel in Magnesium and Carnallite

The developed analytical procedure (as mentioned in Section 2.2) was applied for the analysis of real samples. Four replicates of metallic magnesium and four samples of carnallite were subjected to analysis. The results are shown in Table 2; their reliability was verified by the added-recovered method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Found (%) ×10\textsuperscript{-4}</th>
<th>Added-Recovered Method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Added (%) ×10\textsuperscript{-1}</td>
</tr>
<tr>
<td>1\textsuperscript{a}</td>
<td>7.65±0.01</td>
<td>1</td>
</tr>
<tr>
<td>2\textsuperscript{a}</td>
<td>7.64±0.02</td>
<td>1</td>
</tr>
<tr>
<td>3\textsuperscript{a}</td>
<td>7.70±0.02</td>
<td>1</td>
</tr>
<tr>
<td>4\textsuperscript{a}</td>
<td>7.63±0.02</td>
<td>1</td>
</tr>
<tr>
<td>1\textsuperscript{b}</td>
<td>8.71±0.01</td>
<td>1</td>
</tr>
<tr>
<td>2\textsuperscript{b}</td>
<td>8.69±0.02</td>
<td>1</td>
</tr>
<tr>
<td>3\textsuperscript{b}</td>
<td>8.90±0.01</td>
<td>1</td>
</tr>
<tr>
<td>4\textsuperscript{b}</td>
<td>8.81±0.01</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 2. Determination of Nickel in Metallic Magnesium and Carnallite

\textsuperscript{a}Metallic Magnesium; N=6; P=95\%
\textsuperscript{b}Carnallite; N=5; P=95\%

### 4. Conclusion

In the present work we developed a selective, sensitive, reliable and inexpensive liquid-liquid extraction-spectrophotometric method for Ni(II) determination based on a ternary complex with a new analytical reagent -2-hydroxy-5-iodothiophenol. The method was applied for nickel determination in real industrial and geological samples (metallic magnesium and carnallite) and satisfactory results were obtained.

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**References**


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