Spectrophotometric Determination of Nickel(II) with Some Schiff Base Ligands

M. S. EL-SHAWAWI

Chemistry Department, Faculty of Science at Damiatta, Mansoura University, Damiatta, Egypt

Sensitive and convenient methods for the spectrophotometric determination of nickel(II) with \(N,N'-\text{bis(salicylaldehyde)ethylenediamine, } N,N'-\text{bis(salicylaldehyde)O-phenylenediamine and } N,N'-\text{bis(2-hydroxy-l-naphthaldehyde)O-phenylenediamine} \) have been developed. The optimum concentration range evaluated by Ringbom's method and the effect of diverse ions on the determination were also investigated. The molar absorptivity and the Sandell sensitivity of the complexes were obtained. The present methods have been applied for the analysis of standard samples of nickel(II) in tap water and in industrial wastewater.

Keywords Nickel(II) determination, Schiff base, spectrophotometry, natural water

The Schiff base compounds have been extensively studied because of their biological and structural importance. Several Schiff base ligands have been proposed as spectrophotometric reagents for metal ions. The importance of these compounds lies mainly in their specific and selective reactions with metal ions. There are many effective spectrophotometric methods for the determination of trace amounts of nickel(II) but they require much time for the extraction procedure and the tolerance limit for nickel(II) is low. Work done on bisazomethazine Schiff base ligands involving salicylaldehydediamine and its derivatives revealed that, these compounds behaved as promising reagents for a number of metal ions, because they react with these metal ions to give complexes that are insoluble in water. This paper describes the conditions for the extraction spectrophotometric determination of microgram amounts of nickel(II) with some Schiff base ligands.

Experimental

Apparatus
An Orion pH meter was used for pH measurements. A Varian 634S double beam UV-Visible spectrophotometer was also used for the absorption spectra and the absorbance measurements, with a quartz cell of 10 mm path length.

Synthesis of the reagents
The reagents \(N,N'-\text{bis(salicylaldehyde)ethylenediamine (Salen), } N,N'-\text{bis(salicylaldehyde)O-phenylenediamine (Salop) and } N,N'-\text{bis(2-hydroxy-l-naphthaldehyde)O-phenylenediamine (Napop)} \) were prepared by a method similar to those described previously using the following general procedure. To 50 mmol salicylaldehyde or 2-hydroxy-1-naphthaldehyde in ethanol, 25 mmol ethylenediamine or \(O\)-phenylenediamine were added. The reaction mixture was refluxed for one hour with constant stirring; the resulting precipitates were cooled and filtered off, washed with methanol and dried over silica gel. The Schiff bases and their nickel(II) complexes were characterized on the basis of their electronic spectra, characteristic IR frequencies and elemental analysis. Analysis for hydrogen, nitrogen and carbon of the compounds prepared gave acceptable results, with carbon values within 0.4% of the theoretical values.

Reagents
All reagents used were of analytical reagent grade unless stated otherwise. A stock solution of nickel (1 mg cm\(^{-2}\)) was prepared by dissolving an accurate weight of nickel sulfate in doubly distilled water and standardized by EDTA. Solutions (0.02% g/v) of Salen, Salop and Napop were prepared in chloroform.

Recommended procedures
Into a 100 cm\(^3\) separating funnel, transfer 20 cm\(^3\) of sample solution containing up to 70 mg of nickel(II). Add 5 cm\(^3\) of pH 4.5 – 5 acetate buffer solution and 5 cm\(^3\) of the reagent in chloroform followed by 5 cm\(^3\) of chloroform. Shake the mixture vigorously for 5 min and allow the layers to separate. Transfer the organic phase to a 10 cm\(^3\) volumetric flask after drying it over anhydrous sodium sulfate. Measure the absorbance of the organic phase at the maximum wavelength for each complex against a reagent blank prepared in the same
manner. Calibration curves are obtained under similar conditions. Establish the concentration by reference to the calibration graph with solutions containing 20 - 70 µg of nickel.

Results and Discussion

Chloroform, toluene, carbon tetrachloride, methyl-
enechloride and chlorobenzene were used as possible extracting agents for the tested complexes. All solvents used extract the complexes, but the highest absorbance is obtained in chloroform, the extraction also being more clean and complete in this solvent. Chloroform was selected as a proper solvent for these reasons and because its greater density allows a better separation of phases.

Absorption spectra

Some important infrared absorption frequencies of the solid reagents and their solid nickel(II) complexes are given in Table 1 with their probable assignments. The electronic absorption of the ligands and their complexes in chloroform is also given in Table 1. Representative spectra are shown in Fig. 1. The electronic spectra of the complexes have three bands in the UV-visible region, which are partially resolved, and a broad shoulder of low intensity. The absorption maxima of the complexes were found in the range 310 - 330, 380 - 415 and 450 - 480 nm. The reagents form 1:1 complexes with nickel(II). In the subsequent work, the absorbance measurements for the complexes NiSalen, NiSalop and NiNapop were carried out at 415, 377 and 380 nm, respectively.

Effect of shaking time

The effect of shaking time on the absorbance of the tested complexes was checked from 2 - 30 min. It was observed that the extraction of the chelates into chloroform was fast and rapid. No change in the degree of extraction occurred when the stirring time was varied from 5 - 30 min. Therefore, a 5 min shaking time was adopted in the subsequent work.

Stability of the color complexes and effect of electrolytes

After the extraction of each color complex as described under the recommended procedure, the absorbances were found constant up to 20 h for samples containing 20-60 µg. Samples were stored in stoppered tubes at room temperature; the absorbance values remained constant over this time period. The addition of sodium chloride (0.01 - 0.1 M) did not improve the amount of complex extracted in any system, indicating that the complexes are extracted quantitatively without or with salt effect.

Table 1  Infrared spectra and band assignments of the solid compounds and details of their electronic spectra in chloroform

<table>
<thead>
<tr>
<th>Compound</th>
<th>νC=N</th>
<th>νM-O</th>
<th>νM-N</th>
<th>Peak position in nm with intensity in 1 mol⁻¹ cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salen</td>
<td>1620</td>
<td>—</td>
<td>—</td>
<td>330 (405 (w))</td>
</tr>
<tr>
<td>Salop</td>
<td>1612</td>
<td>—</td>
<td>—</td>
<td>340 (385)</td>
</tr>
<tr>
<td>Napop</td>
<td>1620</td>
<td>—</td>
<td>—</td>
<td>335, 40, 415 (w)</td>
</tr>
<tr>
<td>NiSalen</td>
<td>1625</td>
<td>520</td>
<td>430</td>
<td>334 (1.8x10⁴), 415 (1.26x10⁴), 480 (sh), 560 (sh)</td>
</tr>
<tr>
<td>NiSalop</td>
<td>1610</td>
<td>550</td>
<td>460</td>
<td>310 (2.5x10⁴), 377 (3.9x10⁴), 480 (1.3x10⁴)</td>
</tr>
<tr>
<td>NiNapop</td>
<td>1620</td>
<td>560</td>
<td>430</td>
<td>330 (2.2x10⁴), 380 (3.0x10⁴), 475 (1.8x10⁴)</td>
</tr>
</tbody>
</table>

Fig. 1a Absorption UV-visible spectra of the nickel(II) complexes (1.2x10⁻⁴ M) against reagent blank in chloroform.

Fig. 1b Absorption UV-visible spectra of the Schiff base reagents (2.0x10⁻⁴ M) against chloroform.
Effect of reagent concentration

The effect of an excess of the chromogenic reagents was examined. The absorbance of a series of solutions containing 60 µg of nickel(II) and various amounts of the Schiff base ligand in chloroform was examined. It was found that 3 – 5 cm³ of 0.02% g/ v of each ligand solution sufficed to complex 60 µg or less of nickel. A large excess of the reagent tends to decrease the absorbance, possibly owing to the increased absorbance of the reagent blank.13 Amounts of the reagents smaller than the recommended values gave incomplete complex formation.

Effect of pH

The influence of the pH of the aqueous phase on the extraction of nickel (50 µg) was examined by measuring the absorbance of the organic phase for each nickel complex in chloroform. The final pH of each aqueous solution was measured before the extraction. Other conditions were kept constant. The results are summarized in Fig. 2, from which it can be seen that a maximum and constant absorbance of the organic phase for NiSalen, NiSalop and NiNapop can be obtained over the pH range 4.5 – 7, 4.8 – 7.5 and 5 – 7.5, respectively. The pH values were adjusted with HCl and NaOH. When HClO₄ is used instead of HCl in the preparation of the samples, no significant differences in the range of constancy absorbance of the tested complexes were observed. In more acidic or alkaline solution, the absorbance decreased, possibly because of the incomplete complex formation or the hydrolysis of the complexes, respectively.14 An acetate buffer solution was finally chosen and used as described under the recommended procedure.

Beer's law and sensitivity

Under the optimum experimental conditions described above, calibration curves of the nickel complexes were constructed. A linear graph was obtained for each complex by measuring the absorbance of the organic phase as a function of metal ion concentration. For the Salen reagent, Beer's law was obeyed up to 7 µg cm⁻³ nickel in the organic phase. The optimum concentration range evaluated by Ringbom's plots¹⁵,¹⁶ has been found to be 14 – 52.2 µg metal ion. The molar absorptivity calculated from Beer's law and the Sandell¹⁷ sensitivity for the NiSalen complex have been found to be 1.26×10⁴ 1 mol⁻¹ cm⁻¹ and 0.049 µg cm⁻², respectively at 415 nm. In the case of NiSalop and NiNapop complexes, calibration graphs showed good linearity. Beer's law was obeyed over the concentration range up to 6.5 and up to 5.5 µg cm⁻³ for these two complexes in the organic phase. The molar absorptivity and the Sandell sensitivity have been found to be 3.9×10⁴ 1 mol⁻¹ cm⁻¹ and 0.076 µg cm⁻² for NiSalop and 3.0×10⁴ 1 mol⁻¹ cm⁻¹ and 0.006 µg cm⁻² for NiNapop in chloroform at 377 and 380 nm, respectively. The sensitivities of these reactions are comparable to those of many well known methods for nickel.⁶ Reproducibility tests for five results at 4 µg cm⁻³ of nickel showed a standard deviation of ±0.12.

Effect of diverse ions

The effects of some of the diverse ions which are often in association with the tested metal ion were studied. The selectivity of the proposed method using the reagent Salen was examined by the determination of a fixed concentration (40 µg) of nickel in the presence of a relatively high excess (10 mg) of: NO₃⁻, CO₃²⁻, HCO₃⁻, SO₄²⁻, Cl⁻, Br⁻, PO₄³⁻, TeO₄²⁻, SeO₄²⁻, AsO₄³⁻, AsO₃³⁻, WO₄²⁻, tartrate, EDTA and citrate. The percentage recovery was 100±1.5% and the standard deviation was ±0.27.

The tolerance limits of various cations at 50 µg nickel were also tested in the presence of up to 1 mg of the following ions: Li⁺, Na⁺, K⁺, NH₄⁺, Ca²⁺, Mg²⁺, Ba²⁺, Ag⁺, Al³⁺, Sb³⁺, As³⁺, Ce³⁺. The percentage recovery of nickel(II) was 100±0.7%. In the presence of some other ions, simple modifications were introduced in the aqueous solution to eliminate their interferences in the determination by the proposed method. The results obtained are summarized in Table 2.

Application to natural water

The proposed extraction method involving formation of NiSalen has been applied to the determination of nickel(II) in tap water and in industrial wastewater. The determination of nickel(II) in 20-50 cm³ of tap water was carried out. The results were all negative, indicating the absence of nickel(II). When various amounts of nickel(II) (20 – 50 mg) were added to the tested samples, satisfactory results for the spiked nickel(II) recovery were obtained. In analysis of 50 – 100 cm³ samples of industrial wastewater by the present method, 0.4 mg cm⁻³ nickel(II) content was determined. This was in agreement with the results obtained by the standard methods.¹⁸ Traces of potassium iodide followed by 2 cm³ of sodium thiosulfate (0.2%) in water were added to eliminate any interference due to the presence of copper(II). Results for standard additions
of nickel(II) in industrial water samples gave fairly satisfactory results. The results of these determinations are given in Table 3.

References


(Received December 3, 1990)  
(Accepted February 27, 1991)