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Short communication

Synthesis and analytical application of a novel tetradentate N_2O_2 Schiff base as a chromogenic reagent for determination of nickel in some natural food samples

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Abstract

A novel sensitive chromogenic reagent, *N*,*N*′-bis(3-methylsalicylidene)-*ortho*-phenylene diamine (MSOPD), has been synthesized and used in the spectrophotometric determination of nickel. At pH 8, MSOPD can react with nickel ion at room temperature to form a 1:1 complex. The apparent molar absorptivity is 9.5×10^4 l mol^{-1} cm^{-1} at 430 nm. Beer's low is obeyed over the range 0–1.0×10^{-5} M of nickel with a detection limit of 1.36×10^{-8} M. The relative standard deviation for measurement of 3.41×10^{-6} M nickel is 1.3% ($n = 10$). The method has successfully been applied to determination of trace amounts of nickel in some natural food samples.

Keywords: Nickel determination; Spectrophotometry; Schiff base; Chromogenic reagent; *N*,*N*′-bis(3-methylsalicylidene)-*ortho*-phenylene diamine

1. Introduction

The importance of the determination of heavy metal ions, such as nickel, in environment samples can hardly be overemphasized because they have undoubtedly a serious potential hazard to the human organism. US EPA has classified nickel as one of 13 priority metal pollutants for its widespread use [1]. Also, the knowledge of the nickel content in foods could be of a great interest for the dietary control of nickel-eczema patients. So, the demand for the determination of nickel in biological samples such as plants, foods and similar stuffs is increasing.

Several techniques such as atomic absorption [2], atomic fluorescence [3], X-ray fluorescence [4], voltammetric [5,6], electrothermal atomic absorption or inductively coupled plasma mass spectrometry [7,8] have been used for the determination of this ion in different samples. Spectrophotometric methods based on the UV-visible spectra are widely used due to their simplicity, rapidity, low costs and wide application.

The main reagents available for spectrophotometric determination of nickel are dimethyl glyoxime [9], 5,17-bis(quinolyl-8-azo)-25,26,27,28-tetrahydroxy calix[4]arene [10], 5-(6-methoxy-2-benzothiazoleazo)-8-aminoquinoline [11], benzothiaxolyldiazaoaminoazobenzene [12], 2-[2-(5-methylbenzothiazolyl)azo]-5-dimethylaminobenzoic acid [13], *p*-acetylarsenazo [14], 1-(2-pyridylazo)-2-naphthol-6-sulfonic acid [15], 2-(2-imidazolylazo) phenol-4-sulfonic acid [16], 3-(4-methoxyphenyl)-2-mercaptopropenoic acid [17], 5-(6-methoxy-2-benzothiazoleazo)-8-aminoquinoline [18], 2-(2-benzothiazolylazo)-5-dimethylaminobenzoic acid [19], 7-(4,5-dimethyl-2-thiazolylazo)-8-hydroxyquinoline [20]. However, most of these methods lack sensitivity or selectivity, the procedures are sometimes rather complicated because of the need for extraction to separate interfering ions or expensive surfactants.

The Schiff bases derived from salicylaldehyde (salens) as polydentate ligands are known to form very stable complexes

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with transition metal ions [21,22]. The resulting 1:1 complexes have been frequently used as catalysts in such diverse processes as oxygen and atom-transfer [23], enantioselective epoxidation [24] and mediating organic redox reactions [25]. However, despite extensive scientific reports on the synthesis, characterization and crystalline structure of the transition metal–salen complexes, reports on analytical application of these ligands are quite spare. According to our best knowledge there is no method in the literature based on the use of this group of compounds as chromogenic reagents for determination of metal ions.

In this work, a novel tetradentate Schiff base, *N*,*N*′-bis(3-methylsalicylidene)-*ortho*-phenylene diamine (MSOPD), is synthesized and the optimum conditions for color development of the Ni–MSOPD complex are reported in detail. Also a new method for the spectrophotometric determination of nickel with MSOPD is proposed, and applied to the determination of this ion in some natural food samples.

2. Experimental

2.1. Apparatus

Infrared spectra were taken in KBr disks on a Perkin-Elmer 781 spectrophotometer. ^{1}H nuclear magnetic resonance (NMR) spectra were measured on a Bruker-Avance 300 MHZ spectrometer in $CDCl_3$ with tetramethylsilane as the internal standard. A Shimadzu model UV-160, spectrophotometer equipped with a 1 cm quartz cell was used for all spectrophotometric measurements. Also, a Shimadzu AA-680, flame atomic absorption spectrometer with a hollow cathode lamp at a wavelength of 232.0 nm using an air-acetylene flame and a deuterium background corrector was used. All operating parameters were set as recommended by the manufacturers. The pH was determined with a model 691 Metrohm pH meter with a combined glass–calomel electrode. Melting points were obtained with a Yanagimoto micro-melting point apparatus. The purity determination of the substrates and reactions were accomplished by TLC on silica gel polygram SILG/UV 254 plates.

2.2. Reagents

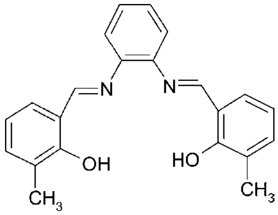
All of reagents were of analytical grade and all solutions were prepared with doubly distilled water.

A 0.01% (w/v) chromogenic reagent solution was prepared by dissolving appropriate amounts of MSOPD in methanol. Requisite amount of high purity powdered nickel in concentrated nitric acid was dissolved, and then the solution was evaporated to remove the excess acid and diluted with water to volume in a calibration flask and mixed well. Working solutions were prepared by appropriate dilution of this stock solution. Dissolve 0.38 g $Na_2B_4O_7{\cdot}10H_2O$ in 100 ml water to give a 0.01 M borax buffer solution at pH 8.

2.3. Synthesis of MSOPD

2-Hydroxy-3-methyl-benzaldehyde (1.36 g, 10 mmol) was dissolved in methanol (15 ml) and then *ortho*-phenylenediamine (0.54 g, 5 mmol) was added to this solution. The resulting mixture was refluxed and stirred for 30 min. The reaction mixture was cooled to room temperature and washed with cold methanol. The product was recrystallized from methanol to give Schiff base MSOPD in 95% yield as yellow crystalline solid, m.p. 113 °C, IR (KBr, cm^{-1}) 740(m), 1290(s), 1520(s), 1640(s, C=N), 2890–2970(m), 3300–3500(m, br); ^{1}H NMR ($CDCl_3$) δ (ppm), 2.23(s, 6H), 6.7–7.3(m, 10H), 8.5(s, 2H), 13.1(s, br, 2H).

2-Hydroxy-3-methyl-benzaldehyde as starting material for synthesis of Schiff base MSOPD was prepared through procedure that was recently reported [26]. Its structure is:



2.4. Determination of nickel

An aliquot of a standard nickel solution containing ca. 5 μg of nickel was transferred to a 25 ml volumetric flask. An amount of 2 ml of borax buffer and 0.5 ml of 0.01% chromogenic reagent solution was added and diluted to the mark with doubly distilled water. The solution immediately represented a change in color and the absorbance was determined at 430 nm after 5 min in a 1 cm quartz cell against a reagent blank.

3. Results and discussion

3.1. Absorption spectra

Under the experimental conditions, the absorption spectra of MSOPD and its nickel complex were scanned and are shown in Fig. 1. The contrast between complex and ligand spectra can be obviously distinguished (110 nm) and was appropriate for quantitative analysis. According to our experiments the absorption at 430 nm shows the best correlation with complex concentration and was chosen as determination wavelength.

3.2. Effect of pH

The effect of pH on the absorbance of Ni–MSOPD complex at 430 nm is shown in Fig. 2. Different pH values were obtained by using 0.01 M of either nitric acid or sodium hydroxide solutions confirmed by pH-meter. It can be seen from

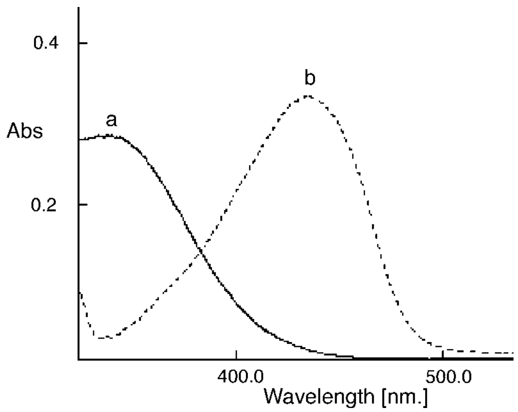


Fig. 1. Absorption spectra of MSOPD and its nickel complex at pH 8.0. Conditions: (a) 5.8×10^{-6} M of MSOPD solution against water blank; (b) the solution containing 5.8×10^{-6} M of MSOPD and 3.4×10^{-6} M Ni^{2+} against corresponding reagent blank.

Fig. 1 that the maximum and constant absorbance of the complex is obtained in the pH range 7–9, and a pH of 8 may thus be chosen for the following experiments. Addition of 1–3 ml borax buffer was sufficient for pH adjustment and less influence on the absorbance. Hence an addition of 2 ml was chosen.

3.3. *Effect of amount of MSOPD*

The effect of amount of MSOPD on the absorbance of nickel–MSOPD was investigated. In 25 ml of solution containing up to 1.0×10^{-5} M of nickel, the addition of 0.2–1.0 ml of 0.01% (w/v) MSOPD solution was enough for the complete reaction and the absorbance spectra remained in a nearly constant level in this range. So, the use of 0.5 ml of reagent solution was selected for following experiments.

3.4. *Rate of color reaction stability and stoichiometry of the complex*

At the optimum conditions, the formation of the colored complex of nickel with MSOPD was completed in 5 min after mixing, which could be monitored by its absorption spectra growth and remained virtually constant for at least 2 h. The stoichiometry of the complex was determined by the continuous variation and molar ratio methods. Both demonstrated that the molar ratio of Ni^{2+} to ligand is 1:1.

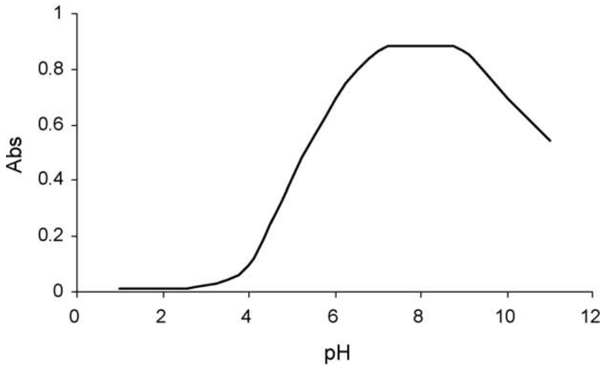


Fig. 2. Effect of pH. Conditions: 5.8×10^{-6} M of MSOPD and 3.4×10^{-6} M Ni^{2+}.

Table 1
Effect of foreign ions on the determination of nickel in a 3.41×10^{-6} M of nickel solution at pH = 8

Ion	Tolerance amount (mg/25 ml)	Ion	Tolerance amount (mg/25 ml)	Ion	Tolerance amount (mg/25 ml)
Cu^{2+}	0.1[a]	Bi^{3+}	0.3	Al^{3+}	1.6[b]
Zn^{2+}	0.2	Fe^{3+}	0.6[b]	Ag^{+}	0.3
La^{3+}	1.2	Ca^{2+}	3.0	Co^{2+}	0.2
Cr^{3+}	1.3	Na^{+}	25[c]	Ba^{2+}	2.9
Cd^{2+}	0.6	K^{+}	25[c]	Pb^{2+}	1.0
Mn^{2+}	0.5	Mg^{2+}	1.0	As^{3+}	1.9
W^{6+}	0.3	Hg^{2+}	1.6	Zr^{4+}	0.3

[a] Masked with 90 mg of thiourea.
[b] Masked with 40 mg of NaF.
[c] Above of which was not tested.

3.5. *Analytical figures of merit*

The calibration graph was constructed by the general procedure. Beer's law was obeyed in the concentration ranges 0–1.0×10^{-5} M of nickel. The linear regression equations obtained were $A = 95324C - 0.0033$ ($r = 0.9985$), where C is expressed as molarity of nickel and A is the absorbance. The apparent molar absorptivity of the complex was 9.5×10^{4} l mol^{-1} cm^{-1}, and the detection limit based on 3σ of the blank was 1.36×10^{-8} M. The relative standard deviation for measurement of 3.41×10^{-6} M nickel was found to be 1.3 ($n = 10$).

3.6. *Effect of foreign ions*

An extensive study was made on the effect of foreign ions on the determination of nickel in a 3.41×10^{-6} M of nickel solution buffered at pH 8. The tolerance amounts of foreign

Table 2
Result of nickel in certified reference material[a]

Sample	Nickel found by the methodology proposed (μg g^{-1})	Certified value (μg g^{-1})
Rice flour (NIES 10)	0.23 ± 0.02	0.19 ± 0.03

[a] Result given is mean ± S.D., confidence level 95% and $n = 3$.

Table 3
Results for the determination of nickel in food samples[a]

Sample	Proposed method (μg g^{-1})	AA method (μg g^{-1})
Starch	0.43 ± 0.01	0.40 ± 0.03
Sugar	0.61 ± 0.03	0.65 ± 0.02
Black tea leaves	0.34 ± 0.02	0.38 ± 0.02
Tobacco	0.40 ± 0.03	0.42 ± 0.03
Rice flour	0.65 ± 0.02	0.61 ± 0.01

[a] Analytical results were expressed as: mean of three determinations ± S.D.

Table 4
Comparison of spectrophotometric reagents for nickel determination

Reagent	λ_{max} (nm)	$\Delta\lambda$[a] (nm)	ε (l mol^{-1} cm^{-1})	pH range	Dynamic range (mol l^{-1})	Comments	Ref.
Dimethyl glyoxime	445	–	1.5×10^4	1.16	$0–3.4 \times 10^{-6}$	Bromine water	[9]
5,17-Bis(quinolyl-8-azo)-25,26,27,28-tetrahydroxy calix[4]arene	580	180	1.28×10^5	10.7	$1.7 \times 10^{-7}–5.1 \times 10^{-6}$	2% DMF	[10]
5-(6-Methoxy-2-benzothiazoleazo)-8-aminoquinoline	623	73	1.28×10^5	9.5–10.5	$0–5.45 \times 10^{-4}$ mol l^{-1}	0.5% CTAB	[11]
Benzothiaxolyldiazaoaminoazobenzene	550	115	1.96×10^5	9–9.8	$0–4.8 \times 10^{-6}$	0.8% OP	[12]
2-[2-(5-Methylbenzothiazolyl)azo]-5-dimethylaminobenzoic acid	640	120	1.32×10^5	5.6	$0–7 \times 0^{-6}$	0.48% SDS	[13]
p-Acetylarsenazo	630	75	6.5×10^4	6	$0–1.4 \times 10^{-5}$	–	[14]
1-(2-Pyridylazo)-2-naphthol-6-sulfonic acid	570	105	5.6×10^4	5–10	$1.7 \times 10^{-6}–1.7 \times 10^{-5}$	Extracted with chloroform	[15]
2-(2-Imidazolylazo)phenol-4-sulfonic acid	510	120	2.7×10^4	5.5	$0–1.4 \times 10^{-5}$	–	[16]
3-(4-Methoxyphenyl)-2-mercaptopropenoic acid	415	60	1.95×10^4	10–12	$6.8 \times 10^{-6}–1.2 \times 10^{-4}$	Extracted with isoamyl alcohol	[17]
5-(6-Methoxy-2-benzothiazoleazo)-8-aminoquinoline	623	73	1.28×10^5	10	$0–5.4 \times 10^{-6}$	0.1% CTAB	[18]
2-(2-Benzothiazolylazo)-5-dimethylaminobenzoic acid	640	120	1.2×10^5	8.5	$8.5 \times 10^{-7}–8.5 \times 0^{-6}$	28% Methanol	[19]
7-(4,5-Dimethyl-2-thiazolylazo)-8-hydroxyquinoline	560	130	1.12×10^5	5.2	$0–9.5 \times 10^{-6}$	0.16% Triton X-100	[20]
N,*N*′-bis(3-methylsalicylidene)-*ortho*-phenylene diamine	430	110	9.5×10^4	7–9	$0–1.0 \times 10^{-5}$	2% Methanol	This work

[a] The contrast between complex and ligand spectra.

ions are shown in Table 1. The tolerance limit of foreign ions was taken as that value which caused an error of not more than ±5% in the absorbance. Most of the cations examined did not interfere with the determination of Ni^{2+}. Only some elements, Cu^{2+}, Fe^{3+} and Al^{3+} interfered, which can be eliminated by masking with thiourea and sodium fluoride solution.

3.7. Accuracy of the method

In order to evaluate the accuracy of the developed procedure, nickel was determined in a reference material, supplied by National Institute for Environmental Studies (NIES), Japan, rice flour (NIES 10). The result is summarized in Table 2 and no significant difference between achieved results by the proposed method and certified values was found. The paired *t*-test was also applied in the results of Table 2. It demonstrated also that there is no significant difference among the achieved results and the certified values for a confidence level of 95%.

3.8. Determination of nickel in food samples

The analytical procedure was used for nickel determination in several natural samples such as starch, sugar, black tea leaves, tobacco and rice flour. These samples were homogenized and dried overnight at 70 °C, and were kept in dry ambient. A dry-ashing sample preparation was carried out for a sample mass of 10 g decomposed at 500 °C for 60 min, followed by a treatment with 20 ml concentrated nitric acid or 30% (v/v) hydrogen peroxide and a second step of heating for 45 min as recommended by the ASTM [27]. The solution was boiled almost to dryness. This was cooled and then 10 ml of water was added to dissolve the salts. The solution was transferred to a 25 ml standard flask, 1 ml of 9% thiourea solution and 2 ml of 2% sodium fluoride solution were added. Then the experimental procedure was followed to complete the determination. Analytical blanks were prepared in the same way. The results are presented in Table 3 and agree well with those obtained by atomic absorption spectrometry.

3.9. Comparison with prior reagents

A comparison of MSOPD with other reported reagents for nickel determination is summarized in Table 4. These data show that a time consuming extraction step and almost expensive surfactants are essential in most of the reported works, while the present one does not require them, showing a simpler feature. Moreover, MSOPD has a longer dynamic range than most of them. Its molar absorptivity is $9.5 \times 10^4\,\mathrm{l\,mol^{-1}\,cm^{-1}}$, better than Refs. [9,14–17] and comparable with the results reported in Refs. [10–13] and [18–20]. Because of these advantages in addition to two units appropriate pH range the proposed method can be used as a substitute for the previous reagents.

4. Conclusion

In this work the new Schiff base, *N*,*N*′-bis(3-methylsalicylidene)-*ortho*-phenylene diamine (MSOPD), was synthesized and used for the spectrophotometric determination of nickel. This reagent can react with nickel immediately at room temperature to form a colored stable complex. With this new tetradentate Schiff base having N_2O_2 donor groups as a chromogenic reagent a very simple, reproducible and highly selective method for the determination of nickel in natural samples was developed. So, the proposed method can be used routinely for the determination of nickel in foods and other natural samples.

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