Solvent Extraction and Spectrophotometric Determination of Nickel(II) with Thiazole-2-carbaldehyde 2-Quinolylhydrazone

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A sensitive method for the extractive spectrophotometric determination of nickel(II) with thiazole-2-carbaldehyde 2-quinolylhydrazone (TAQH) has been described. Nickel(II) reacts with TAQH at pH 8.7–9.5 to form a 1:2 metal to ligand complex that is extractable into many organic solvents. The species when extracted with benzene and measured at 522 nm obeys Beer's law over the range up to $0.7 \mu\text{g ml}^{-1}$ of nickel. The molar absorptivity is $7.17 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 522 nm. The method has been satisfactorily applied to the determination of nickel in two standard alloy steel samples.

Keywords Nickel determination, spectrophotometry, thiazole-2-carbaldehyde 2-quinolylhydrazone, solvent extraction

In a study concerning the analytical possibilities of heterocyclic substituted hydrazones as tridentate ligands, we have proposed the use of thiazole-2-carbaldehyde 2-quinolylhydrazone (TAQH) as a potential chromogenic reagent for the spectrophotometric determination of several transition metal ions including palladium.¹

In this paper the properties of the nickel(II) complex with the above reagent and an extractive spectrophotometric method for determining sub-ppm amounts of nickel are described. The method has been applied to the determination of nickel in two standard alloy steel samples after separation of the metal from interfering ions by an anion-exchanger.

Experimental

Reagents

Unless otherwise stated all inorganic and organic chemicals were of reagent grade quality. Organic solvents were freshly distilled before use.

TAQH solution. The ligand, TAQH, was synthesized as described previously.¹ A stock solution of $6 \times 10^{-4} \text{ M}$ TAQH in benzene was prepared. This solution was stable for at least 1 week, if kept in the dark.

Nickel(II) stock solution. Nickel(II) standards were obtained by dilution of 0.01 M nickel(II) nitrate solution standardized compleximetrically.²

Buffer solution. A solution, which is 0.1 M in sodium tetraborate and 0.06 M in ammonia, was adjusted to pH 9.1 with 6 M hydrochloric acid.

Ion-exchange resin. Dowex 1-X8, 50–100 mesh, was

used in the chloride form. A $9 \times 60 \text{ mm}$ resin bed was prepared.

Apparatus

A Nippon Bunko UVIDEK-1 digital spectrophotometer and a Union Giken SM-401 high-sensitivity recording spectrophotometer with matched 1.00-cm quartz cells were used. A Toa Dempa HM-20E pH meter was used with a combination electrode.

All measurements were made at 25°C .

Procedure

General procedure for the determination of nickel(II).

Transfer an aliquot of sample solution containing up to $7 \mu\text{g}$ of nickel(II) into a 50-ml separatory funnel. Add 5 ml of the buffer solution (pH 9.1) and dilute to 10 ml with doubly distilled water. Equilibrate the mixture with exactly 10 ml of $6 \times 10^{-4} \text{ M}$ TAQH in benzene by mechanical shaking for 30 min. Measure the absorbance of the organic phase at 522 nm against the reagent blank.

Determination of nickel in alloy steel samples. Dissolve 0.1 g of the finely pulverized sample in 10 ml of concentrated hydrochloric acid plus 5 ml of concentrated nitric acid and evaporate almost to dryness on a water-bath. Repeat the acid treatment and evaporation to ensure complete dissolution of the soluble components of the sample. Add 10 ml of hot, 1 M hydrochloric acid and remove insoluble residue by filtration. Dilute the filtrate to 250 ml with water. Use a suitable aliquot of this solution for the nickel(II) determination.

Acidify the sample solution to approximately 9 M in

hydrochloric acid and place on the anion-exchange column. Elute the column with 20–25 ml of 9 M hydrochloric acid at a flow rate of 0.6 ml min⁻¹. Evaporate the effluent to dryness and determine nickel(II) as described.

Results and Discussion

Characteristics of nickel(II)-TAQH complex

The nickel(II)-TAQH complex is sparingly soluble in water, but readily soluble in aromatic hydrocarbons, halogenated hydrocarbons, acetate esters and ketones. The spectral characteristics of the complex depend on the solvent used. Benzene was chosen as the extractant because the highest absorbance of the complex in the visible region was obtained in this solvent. Under the optimum conditions of the reagent and ammonia concentrations, pH and shaking period, nickel(II) can be quantitatively extracted from aqueous solution with one 10-ml portion of TAQH in benzene over the

Fig. 1 Absorption spectra obtained under experimental conditions given in the general procedure. Ni(II) taken, 4.1 µg; (1) reagent blank vs. benzene; (2) Ni(II)-TAQH complex vs. reagent blank.

Fig. 2 Effect of pH. Ni(II) taken, 4.1 µg; TAQH used, 6×10^{-4} M; NH₃ added, 0.03 M.

concentration range studied. The absorption spectra of the reagent and the nickel(II) complex in benzene are shown in Fig. 1. The absorbance measurements were made at 522 nm.

Effects of experimental conditions

Figure 2 illustrates the dependence of the absorbance of the organic phase on the pH of the aqueous phase. A maximum and constant absorbance is obtained between pH 8.7 and 9.5. For the spectrophotometric determination pH 9.1 ± 0.1 was adopted. Addition of 9×10^{-3} – 3.3×10^{-2} M ammonia as an auxiliary complexing agent was effective to some extent for improving the slow chelate formation between nickel(II) and TAQH.

The absorbance of the organic phase was studied as a function of the initial concentration of TAQH in benzene. It was found that about a 50-fold molar excess of TAQH was the minimum required for obtaining a constant and maximum absorbance. A 6×10^{-4} M solution of TAQH is recommended as a suitable concentration of reagent.

A shaking period of 20–60 min did not produce any change in absorbance, provided the volume ratio $V_{\text{org}}(10 \text{ ml}):V_{\text{aq}}$ was between 1:0.5 and 1:2; a shaking time of 30 min was selected.

Stoichiometry

The extraction method^{3,4}, where metal distribution is followed in the presence of a reasonable excess of ligand, was used to establish the stoichiometry of the nickel(II) complex. As the ligand, TAQH, exists in the neutral form, HL, at the acidity investigated¹, a simple logarithmic expression can be derived for the metal distribution:

$$\log D_{\text{Ni}} = \log K_{\text{ex}} - \log \alpha_{\text{Ni}} + n \log [\text{HL}]_{\text{org}} - n \log [\text{H}^+]$$

where D_{Ni} denotes the distribution ratio of nickel(II), K_{ex} is the extraction constant defined by $[\text{NiL}_n]_{\text{org}}/[\text{H}^+]^n/[\text{Ni}^{2+}][\text{HL}]_{\text{org}}^n$, n is the number of hydrazone molecules bound per metal atom, and α_{Ni} is the side-reaction coefficient for nickel(II). At constant pH, a logarithmic plot of the metal distribution against the ligand concentration in the organic phase should be a straight line with slope equal to n . Experimental data showed n equal to 2 and a 1:2 Ni(II):ligand ratio (Fig. 3). The value of K_{ex} was estimated to be 8.13×10^{-10} , by using $\alpha_{\text{Ni}} = 27.4$.⁵

Beer's law and sensitivity

A calibration graph for the determination of nickel(II) was prepared according to the general procedure. A good linearity was obtained between the absorbance of the organic phase and the concentration of nickel(II) up to about 1.2×10^{-5} M ($0.7 \mu\text{g ml}^{-1}$). The molar absorptivity of the complex and the Sandell sensitivity are $7.17 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 522 nm and 0.86 ng cm^{-2} , respectively. In the sensitivity for nickel(II),

Fig. 3 Relationship between nickel(II) distribution and analytical TAQH concentration. Ni(II) taken, 7.0×10^{-6} M; pH, 9.15; NH_3 added, 0.03 M.

the present reagent, TAQH, is fairly or much superior to other *NNN*-tridentate ferriin-type hydrazones, such as pyridine-2-aldehyde-2-pyridylhydrazone⁶, pyridine-2-aldehyde-2-quinolylhydrazone⁷, quinoline-2-aldehyde-2-quinolylhydrazone⁸, pyridine-2-aldehyde-2-benzothiazolylhydrazone⁹, phenanthridine-6-aldehyde-2-pyridylhydrazone⁸, 2,2'-dipyridyl-2-pyrimidinylhydrazone¹⁰, benzothiazole-2-aldehyde-2-benzothiazolylhydrazone¹¹ and some pyradinylhydrazones.¹² TAQH is also more sensitive for nickel(II) than familiar colorimetric reagents, such as dimethylglyoxime (extraction method)¹³, 2,2'-furyl dioxime¹⁴, 1,2-cyclohexanedionedioxime¹⁵ and 1-(2-pyridylazo)-2-naphthol.¹⁶

Effect of diverse ions

The possible interference of various ions was examined by introducing them into a solution containing 4.1 μg of nickel(II). The tolerance limit of an ion was fixed as the maximum amount causing an error not greater than $\pm 2\%$ in the absorbance of the extract solution. The results for metallic ions are summarized in Table 1. Of the non-metallic anions tested, chloride, bromide, fluoride, nitrite, nitrate, thiosulfate and sulfate up to at least 10000-fold molar ratio to nickel(II), and iodide, thiocyanate, sulfite, oxalate and tartrate up to 1000-fold molar amount did not interfere with the determination. Cyanide, citrate and EDTA, however, must be absent.

Application to alloy steel samples

The proposed method has been applied to the determination of nickel in two standard alloy steel samples supplied by the Iron and Steel Institute of Japan.

In basic media, as shown in Table 1, TAQH reacts with several metal ions including cobalt(II), copper(II), zinc(II), bismuth(III), chromium(III), iron(II,III), rho-

Table 1 Effect of metallic ions on determination of 4.1 μg (0.070 μmol) of nickel

Tolerance limit ([Ion]/[Ni(II)])	Ion
140 (at least)	Ag(I), Tl(I), Ba(II), Ca(II), Mg(II), Mn(II), Pb(II), Sr(II), La(III), Sm(III), Pt(IV), Se(IV), As(V), V(V), Cr(VI), Mo(VI)
70	Ir(III), U(VI)
30	Pd(II), Pt(II), Au(III), Ga(III), Re(III), Y(III), W(VI), Os(VIII)
7	Al(III) ^a , In(III) ^a , Th(IV) ^a
3	Cr(III), Ti(IV) ^a , Zr(IV) ^a
0-1	Cd(II), Co(II), Cu(II), Fe(II, III), Hg(II), Zn(II), Bi(III), Rh(III), Ru(III)

a. In the presence of 0.07 M sodium fluoride.

Table 2 Determination of nickel in standard alloy steel samples

Sample	Composition, %	Ni content, %	
		Standard	Found
JSIS 153-1	C 0.24, Si 0.23, Mn 0.77, P 0.049, S 0.018, Cu 0.13, Cr 1.10, Mo 1.26, V 0.22	1.06 ^a	1.04 1.05
JSIS 154-1	C 0.29, Si 0.57, Mn 1.04, P 0.015, S 0.016, Cu 0.21, Cr 1.95, Mo 0.68, V 0.32	0.51 ^b	0.50 0.49

a. An average of 24 analytical data ranging from 1.02 to 1.10%.

b. An average of 24 analytical data ranging from 0.49 to 0.53%.

dium(III) and titanium(IV) to give extractable colored complexes or insoluble precipitates on the boundary of the two phases. A preliminary anion-exchange separation of nickel(II) was therefore adopted for eliminating the possible interference from metal ions, prior to the color development of the nickel(II)-TAQH complex. It was found that under the experimental conditions described, the anion-exchange column permits quantitative separation of nickel(II) (4.1 μg) from each of the following metal ions: cadmium(II), cobalt(II), copper(II), mercury(II), palladium(II) and iron(III) up to at least 100-fold molar amount; iron(II), zinc(II) and bismuth(III) up to about 50-fold molar amount. However, more than 4- to 5-fold molar amounts of chromium(III) and titanium(IV) still interfered with the final determination of nickel(II) by suppressing the color formation of the TAQH complex.

The analytical results shown in Table 2 are in

reasonable agreement with the standard values.

In conclusion, the tridentate hydrazone ligand, TAQH, is worthy of use as a chromogenic reagent for the spectrophotometric determination of nickel(II) at sub-ppm levels.

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