Gravimetric Determination of Nickel with Salicylaldehyde Thiosemicarbazone

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Synopsis. A study of the use of salicylaldehyde thiosemicarbazone (STSC) in the gravimetric determination of nickel is reported. STSC reacts with Ni(II) in aqueous medium in the pH range 6.5—8.2 to form reddish brown water insoluble complex. The complex can be conveniently filtered at the pump using a G_4 sintered glass crucible and dried at 100—120 °C and weighed as $Ni(C_8H_8N_3OS)_2$. Interference of foreign ions were examined. The influence of concentration, temperature, and pH on the precipitation were studied. The reagent tested in this work was compared with classical 1,2-dioximes[1-3] used in the gravimetric determination of nickel. This method was applied to determine nickel in stainless steel.

The commonly employed organic reagents for the gravimetric determination of nickel were dioximes[1-4] and monoximes.[5-9] Thiosemicarbazones have been used as gravimetric reagent for the estimation of some metal ions.[10-12] In this paper a newly developed gravimetric determination of nickel with salicylaldehyde thiosemicarbazone (STSC) will be described. STSC reacts with Ni(II) in aqueous medium in the pH range 6.5—8.2 to form reddish brown water insoluble complex. The complex is soluble in highly acidic medium, highly alkaline medium, and organic solvents like chloroform, 90—100% ethanol etc. The complex is stable at room temperature for over 24 h. The complex can be conveniently filtered at the pump using a G_4 sintered glass crucible and dried at 100—120 °C and weighed as $Ni(C_8H_8N_3OS)_2$.

The present method is superior to other methods that the pH range is wide and the solubility of the complex in cold and hot water is very low and the complex is partially soluble in rectified spirit or 90—100% ethanol. Its lower conversion factor or high relative molecular masses give appreciably higher sensitivities than classical reagents.

Experimental

Reagents. All chemicals were of reagent grade. Stock solution (0.5%) of STSC in methanol was prepared. The nickel solutions were prepared from nickel chloride and standardized with dimethylglyoxime. 2 mol dm^{-3} sodium acetate solution was prepared.

Synthesis of STSC. Mixture of salicylaldehyde[13] and thiosemicarbazide (1:1 ratio) in 80% ethanol or methanol was refluxed for 2 h. The mixture was cooled and the precipitated STSC was filtered off and dried in a desiccator.

Apparatus. Global digital pH meter, Perkin-Elmer 577 Infrared spectrometer, Gouy-type magnetic balance.

Procedure. An aliquot of Ni(II) solution containing 20 to 40 mg of metal was placed in a 250 ml beaker and was diluted to 100 ml with distilled water. The solution was heated to 70—80 °C and the pH was adjusted to 6.5—8.2 with 2 mol dm^{-3} sodium acetate solution. To this 25—50 ml of 0.5% STSC solution was added with constant stirring and the mixture was heated in a water bath for 30 min. The mixture was allowed to cool and filtered through a weighed G_4 sintered glass crucible. Then it was washed with 40—60% hot methanol solution and finally with distilled water and dried at 110—120 °C. Conversion factor for $Ni(C_8H_8N_3OS)_2$ to Ni is 0.1314.

Results and Discussion

Properties of the Reagents. Salicylaldehyde thiosemicarbazone, was poorly soluble in water but soluble in methanol. Solution in methanol stored at room temperatures was stable for at least 1 month.

Study of Nickel Salicylaldehyde Thiosemicarbazone Complex. Elemental analysis of the nickel complex confirmed the formula $Ni(C_8H_8N_3OS)_2$. A study was made to elucidate the structure. The infrared spectra showed a shift in the C=N stretching vibration bands in relation to the reagent at 1600—1620 cm^{-1} and double bands appeared; on the other hand bands due to the C=S group disappeared and C–S vibration bands showed up. The strong band at 3400 cm^{-1} in the spectrum of the ligand may be due to ν_{-OH}. Since this band is retained almost at the same position, it was an evidence for the nonparticipation of the oxygen atom of the phenolic hydroxyl group in coordination (Fig. 1). A study of the magnetic susceptibility showed that the nickel STSC complex is diamagnetic at 293 K.

From these results it can be concluded that the Ni–STSC complex is square-planar. In general thiosemicarbazones usually react as chelating ligands with transition metal ions by bonding through the sulfur and hydrazine nitrogen atoms.[14]

Determination of Optimum Experimental Conditions for Precipitation. The effect of increasing amounts of reagent was investigated. It was found that for every 10 mg of nickel, 15—20 ml of 0.5% methanolic solution of the reagent sufficed.

Experiments were conducted at various temperatures. Precipitation occurred at room temperature and also at high temperatures. Below 50 °C the solution was found turbid. Therefore precipitation was conveniently conducted above 70 °C.

To determine the optimum pH, complex was precipitated from solutions at different pH, adjusted by

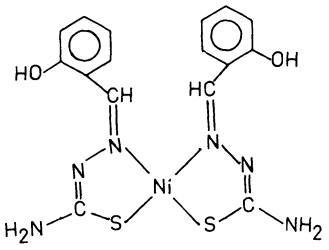

Fig. 1.

Table 1. Effect of Reagent Concentration

Sodium acetate 2 mol dm^{-3} Reagent in ml	Ni=20.09 mg Ni found	Reagent 0.5% Error in mg
5	8.80	−11.29
10	9.20	−10.89
15	10.68	−9.41
20	15.74	−4.35
25	19.67	−0.42
30	20.10	+0.01
35	20.25	+0.16
40	20.55	+0.46

Table 2. Effect of Foreign Ions in the Determination of Ni(II) Using STSC (Ni(II) taken 21.37 mg)

Ions	Tolerance limit in mg
Na^+, K^+, Ag^+, Zn^{2+}, Cl^-, F^-, Br^-, I^-, thiosulfate, thiocyanate, oxalate, tartrate, acetate	100
Pb^{2+}, Hg^{2+}, Cd^{2+}, Mo^{6+}, citrate, phosphate, sulfate nitrate, tetraborate, hydrogen carbonate	50
Mn(II), Bi(III), As(III), Fe(III), Co(II), Th(IV), U(VI)	25
Cu(II), CN^-	10
EDTA	a)

a) Which interfere strongly.

Table 3. Estimation of Metal

Ni(II) added in mg	Ni(II) found in mg	Error in mg	%Error
17.69	17.69	0.00	0
21.37	21.55	+0.18	+0.84
20.09	20.15	+0.06	+0.30
22.41	22.27	−0.14	−0.62
26.53	26.59	+0.06	+0.23
29.24	29.36	+0.12	+0.41

Average of seven determinations.

means of different buffers. The optimum pH was found to be 6.5—8.2.

The influence of various solvents for washing the precipitates was studied. Experiments with different amount of methanol showed that 30—70% methanol water mixture was suitable for washing the precipitate.

Effect of Diverse Ions. Nickel (21.37 mg) was gravimetrically determined in the presence of varying amounts of other cations and anions and the limit of concentration that can be tolerated are given in Table 2.

Composition of the Complex. The amount of precipitate obtained from a known quantity of nickel agreed with the formula $Ni(C_8H_8N_3OS)_2$, which was proved by analysis (Found: C, 42.89; N, 18.58; H, 3.2; S, 13.7%. Calcd: C, 42.98; N, 18.79; H, 3.6; S, 14.3%). The conversion factor is 0.1314. Reproducible results were obtained using varying amounts of nickel as shown in Table 3.

Table 4. Analysis of Stainless Steel

	Ni found using STSC	Ni found using DMG
Sample I	11.29	11.41
Sample II	14.21	14.30
Sample III	29.01	29.21
Sample IV	67.37	67.80

Applications

Determination of Nickel in Stainless Steel. A known weight (1.2 mg) of sample was treated with 50 ml of 12% sulfuric acid and boiled for 1 h nearly to dryness. It was then heated to dryness with 10 ml of concentrated nitric acid, cooled, and added 5 ml concentrated hydrochloric acid. The mixture was boiled, cooled, and made upto 100 ml. Aliquots of this solution (20 ml) was taken, treated with 1:1 ammonia and then filtered through Whatman No. 41 filter paper. The precipitate was dissolved by adding hot hydrochloric acid dropwise and the solution was collected in a beaker, reprecipitated with 50 ml of aqueous ammonia (1:1) and filtered on the same filter paper. The solution was concentrated to 70 ml and nickel was determined with STSC, at pH 7.5 adjusting with sodium acetate solution. The values are given in Table 4.

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