

TABLE 2 — STATISTICAL PREDICTIONS AND EXPERIMENTAL RATIOS FOR THE EQUILIBRIUM CONSTANTS IN THE SYSTEM $[\text{NiS}_n]^{2+} + n\text{L} \rightleftharpoons [\text{NiL}_n]^{2+} + n\text{S}$

Ratio	Statistical predictions	Experimental ratio	
		Thiophenol	<i>p</i> -Toluenethiol
k_2/k_1	0.375	0.354	0.631
k_3/k_2	0.444	0.372	0.479
k_4/k_3	0.375	1.380	1.023

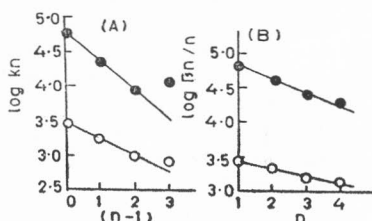


Fig. 2 — (A) Plot of $\log k_n$ versus $(n-1)$. (B) Plot of $\log \beta_n/n$ versus n [Ni(II)-thiophenol (—●—●—), and Ni(II)-*p*-toluenethiol (—○—○—)]

An attempt was made to apply the obtained results to the empirical equation of Van Eck¹¹:

$$\log k_n = \log k_1 - 2\lambda(n-1)$$

where λ is a constant and n is the number of attached ligands. A plot of $\log k_n$ against $(n-1)$ given in Fig. 2A, shows that whereas $\log k_{1-3}$ fall on a linear plot, $\log k_4$ for both the ligands deviates from the linear plot especially of thiophenol. This may be explained on the premise that the fourth thiol molecule after occupying the fourth site in the square planar complex sphere, imparts further stabilization of the configuration by virtue of a relatively high trans-effect. Under such circumstance, one may also argue that solvent-ligand interactions are eventually replaced by ligand-ligand interactions.

Considering the overall formation constants, β_n and applying Van Eck equation in the form^{5d}:

$$\log \beta_n/n = \log \beta_1 - \lambda(n-1)$$

one would expect the plot of β_n/n versus n to be linear. Fig. 2 B gives a fairly good indication of the validity of the above relation.

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Studies on Mixed Ligand Complexes of Mo(VI) & W(VI) with *N-m*-Tolyl-*p*-methoxybenzohydroxamic Acid & Thiocyanate

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N-m-Tolyl-*p*-methoxybenzohydroxamic acid (TMBHA) is used for extraction and spectrophotometric determination of Mo(VI) (λ_{\max} 390nm; chloroform as solvent) and W(VI) (λ_{\max} 400 nm; *n*-hexanol as solvent) from hydrochloric acid medium (8.0 M) containing thiocyanate. The method is applied satisfactorily for the analysis of some of the alloy steel samples. The composition of the extractable species has been found to be 1:1:2 (metal-thiocyanate-TMBHA). The stability constants of the complexes have been evaluated.

MANY hydroxamic acids have been used for extractive photometric determination of Mo(VI)^{1,2}. *N-m*-Tolyl-*p*-methoxybenzohydroxamic acid (TMBHA) has already been used in this laboratory for solvent extraction of Nb(V), Ta(V) and Ti(VI)^{3,4}. Molybdenum(VI) and W(VI) form mixed ligand complexes with thiocyanate and TMBHA which can be extracted by organic solvents from strong HCl medium (8M). The yellow coloured complexes of Mo(VI) and W(VI) can be measured spectrophotometrically at 390 and 400 nm respectively.

A fresh solution of the reagent was used every time. A stock solution of molybdenum was prepared by dissolving ammonium molybdate in dil. hydrochloric acid. Tungsten solution was prepared by dissolving sodium tungstate in doubly distilled water. The solutions were standardized by known methods⁵. Potassium thiocyanate solution (4M) was prepared in doubly distilled water.

General procedure — An aliquot of the metal ion solution containing about 2.0 mg of molybdenum or tungsten was taken and to it was added 0.3 and 1.5 ml of 4 M potassium thiocyanate solution for Mo(VI) and W(VI) respectively. Enough conc. hydrochloric acid was added to maintain acid strength at 8.0M. The volume of the aqueous phase was made up to 10 ml with distilled water, shaken for 10 min with 0.025 M TMBHA solution (10 ml) in organic solvent [(chloroform for Mo(VI) and *n*-hexanol for W(VI)]. The yellow coloured complexes were measured spectrophotometrically at λ_{\max} 390 and 400 nm for Mo(VI) and W(VI) respectively against similarly processed reagents solution as a blank. The amount of metal extracted was computed from calibration curve.

The yellow coloured complexes of molybdenum and tungsten absorb maximally at 390 and 400 nm respectively and the coloured solutions obey Beer's law over the concentration range of 34 to 1016 μg of molybdenum and 29.5 to 750 μg of tungsten per ml of organic solvent. The molar absorptivity and the Sandell's sensitivity values for these com-

plexes are 2.7×10^3 litre mol⁻¹ cm⁻¹ and $0.089 \mu\text{g cm}^{-2}$ for molybdenum and 0.37×10^3 litre mol⁻¹ cm⁻¹ and $0.49 \mu\text{g cm}^{-2}$ for tungsten respectively.

Optimum extraction is found to occur at 8.0 M hydrochloric acid and decreases thereafter. The optimum thiocyanate concentration required for the quantitative extraction of Mo(VI) and W(VI) is 0.12 and 0.60 M respectively. A 10 ml of 0.025 M TMBHA is adequate for the quantitative extraction. The complexes are stable for 20 hr. It is found that equilibration for 10 min is sufficient for complete extraction of the metal complexes.

Effect of diverse ions — Several ions were examined for their effect on the extraction of Mo(VI) and W(VI). The tolerance limit was taken as the amount of foreign ion required to cause $\pm 2\%$ error in the recovery of metal ion. These metals can be extracted satisfactorily in the presence of large amounts of most of the associated ions. Ions showing strong interference are Cu(II), Fe(III), Nb(V), Ti(IV), V(V) and F⁻. Mo(VI) and W(VI) interfere with each other.

The relative standard deviations obtained from ten determinations are found to be ± 0.9 for Mo(VI) and ± 0.8 for tungsten.

Nature and composition of the extractable species — From Job's,⁶ mole ratio⁷ and slope ratio⁸ methods, the composition of metal to organic ligand (TMBHA) comes out to be 1:2 in the presence of thiocyanate. This is further supported by the plot of log D (distribution ratio of metal) versus log [TMBHA]₀ (concentration of TMBHA in organic phase at equilibrium) which gives a slope of two. A plot of log D versus log [SCN⁻] affords a slope of one which shows the presence of one thiocyanate ion in the neutral extractable complex. On the basis of these observations, the probable extractable species formed in presence of thiocyanate may be MoO₂.SCN.R.HR and WO₂.SCN.R.HR.

Metal-ligand stability constants — The conditional metal-ligand stepwise stability constants of the extractable complexes have been computed from the spectrophotometric data employing Yatsimirskii's^{9,10} and Leden's¹¹ methods in modified forms¹². The values of log K₁, log K₂ and log β₂ of the molybdenum complex are 2.81, 2.53 and 5.34 by Yatsimirskii's method and those by Leden's method are 3.00, 2.70 and 5.70 respectively. The respective values for tungsten complex are 3.31, 2.87 and 6.18 by Yatsimirskii's method and 3.12, 2.44 and 5.56 by Leden's method.

Application to alloy steels — The usefulness and wide applicability of the present method is shown by satisfactory analysis of some of the alloy steel samples.

An alloy steel sample (100 mg) was dissolved in HNO₃ (1:1) by warming and the solution evaporated to small volume and cooled conc. sulphuric acid (1 ml) was added and heated to fumes to drive off HNO₃. The residue was cooled and then heated with water (50 ml) to dissolve the soluble salts, any insoluble matter was filtered off and the solution made up to 100 ml with distilled water. A 20-ml aliquot was taken, evaporated to small volume and to this

was added few drops of dil. potassium permanganate solution until a faint pink colour persisted. This treatment ensured that vanadium in the sample solution was in +5 state. The acidity of the aqueous solution was adjusted to 4.0 M HCl. V(V) was extracted and separated as a violet coloured complex with 0.025 M TMBHA solution in chloroform¹³. The aqueous phase after the separation of vanadium was adjusted to about pH 2.5 after the addition of ammonium thiocyanate. Fe was then extracted with 3 portions of tributyl phosphate. The acidity of aqueous phase was then adjusted to 8.0 M HCl and W(VI) or Mo(VI) determined as already described. The average of the triplicate analyses of steel samples [BAS No. 60 B and 64 B (Mo) and BCS 241/1(W)] gave a result of 0.427%, 4.92% and 19.50% (certified values are 0.430%, 4.95% and 19.61% respectively).

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Mixed Adduct Formation : A Spectrophotometric Study

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Stronger shifts in the visible spectrum of nickel-5-nitro-8-quinolinolate, in chloroform, have been observed on the addition of 4-methyl-8-quinolinol than those observed with 5-nitro-8-quinolinol. This has been attributed to the formation of the strongest mixed adduct by the addition of the most basic analogue (4-methyl-8-quinolinol) to the nickel chelate of the least basic analogue, (5-nitro-8-quinolinol) of the parent ligand i.e. 8-quinolinol.

IN a systematic study, Freiser and coworkers¹ reported that zinc-8-quinolinolate was extracted as a monoadduct, ZnQ₂HQ, in chloroform or carbon