

Raman Spectrometer that can stand comparison with any industrial infrared spectrophotometers, both with respect to the convenience of use and reliability, and with respect to the optical qualities. In this equipment the optical, mechanical and electronic elements have been specially designed to take into account the properties and the special geometry of the laser beam. The source is a He: Ne laser 50 mW 6328 Å (or Argon or ionized Krypton). The optics consist of a double monochromator—a grating followed by either a grating or a prism. The manufacturers claim that this equipment which is rapid, true, and automatised should

satisfy the most exacting researcher as well as the routine analyst.

The possibilities offered by this equipment are illustrated by the two figures reproduced here. Figure 1 presents a part of the toluene spectrum. The effect of polarisation of the lines 1208, 1030 and 1004, as well as the different resolutions on the last two lines could be seen. It is to be noted that the entire set of these results were obtained in about 10 minutes. Figure 2 represents a quantitative estimation of NO₃ ion, in an aqueous solution of NaNO₃ at different concentrations. In this case the entire set of results were obtained in 60 minutes.

SPECTROPHOTOMETRIC STUDIES OF MOLYBDENUM (VI) COMPLEX OF 3-PHENYLDAPHNETIN

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THOUGH the most common procedure for the colorimetric determination of molybdenum is based upon its colour formation with thiocyanate in presence of stannous chloride,¹ several phenolic compounds, e.g., catechol,² protocatechuic aldehyde,³ disodium-1, 2-dihydroxybenzene-3, 5-disulphonate,⁴ gallic acid⁵ have also been employed. Recently esculetin (6, 7-dihydroxycoumarin) and its derivatives have been used⁶ because they produce orange-coloured aqueous ethanol-soluble complexes with molybdenum. The present study deals with the complex of this metal with another dihydroxycoumarin, 3-phenyldaphnetin, i.e., 3-phenyl-7, 8-dihydroxycoumarin. Daphnetin derivatives have been used for a long time as mordant dyes, they can be expected to form stabler complexes useful for analytical work.

3-Phenyldaphnetin in ethanolic solution forms a yellow complex with molybdenum, which is soluble in 40% ethanol. This complex has molar composition of 1:1 and obeys Lambert-Beer's law, at 400 mμ, between the concentration limits of 1.7 to 5.7 ppm. of molybdenum in solution.

EXPERIMENTAL

3-Phenyldaphnetin was prepared by the method of Bargellini⁷ as improved by Krishnaswamy,⁸ and its standard ethanolic solution was used. Standard molybdenum solution was prepared using sodium molybdate (Analar BDH).

Beckman pH-meter model H2 was used for measurement of pH, which was adjusted with hydrochloric acid and sodium hydroxide.

Unicam spectrophotometer model SP 600 was used for spectrophotometric measurements.

Absorption spectrum of the complex.—The complex showed maximum absorption at 400–410 mμ between pH 1–7, thereby indicating the presence of only one complex. In this pH range of 1 to 7, the complex showed maximum absorption at pH 6, at 400–410 mμ. The subsequent studies were carried out at 400 mμ and at pH 6.

Minimum amount of the reagent for full colour development.—The study of the optical density of a series of solutions, containing the metal and the reagent in the ratio varying from 1:1 to 1:13, showed that the full colour development required a tenfold concentration of the reagent. During the subsequent studies, however, the molar ratio of the reagent to metal was maintained at 12.

Molar composition of the complex.—The molar composition of the complex was determined employing three different methods:

- Job's method of continuous variation⁹:**
This gives a composition of 1:1 as is indicated in Fig. 1.
- Mole-ratio method¹⁰:** The molar composition of the complex was also determined by the mole-ratio method of Harvey and Manning. The results indicate the composition to be 1:1 (Fig. 2).
- The composition was finally verified by Asmus method.¹¹** The straight line at $n=1$ shows the composition to be 1:1 (Fig. 3).

The complex was found to be negatively charged by passing it through ion-exchange resins.

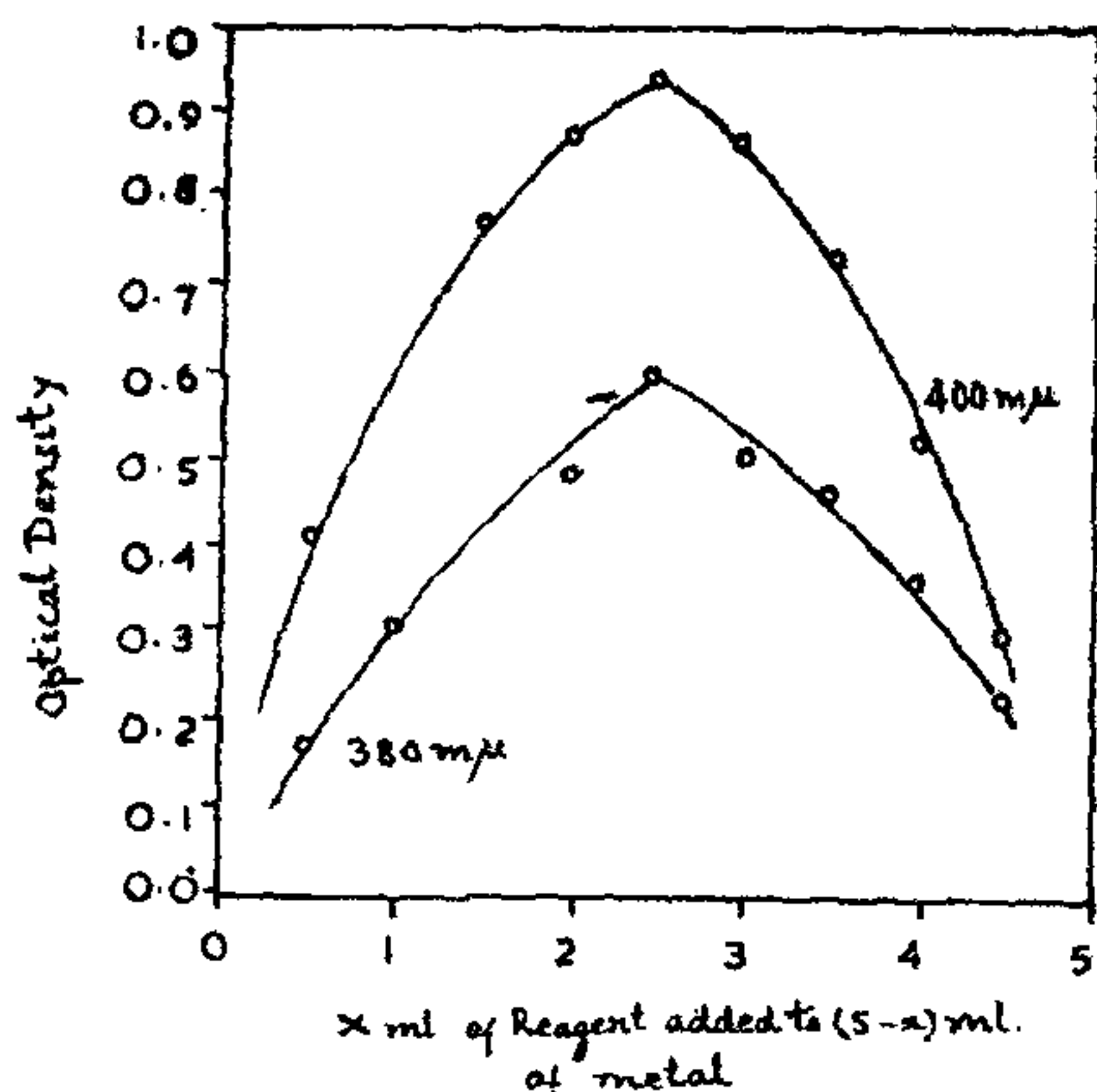


FIG. 1

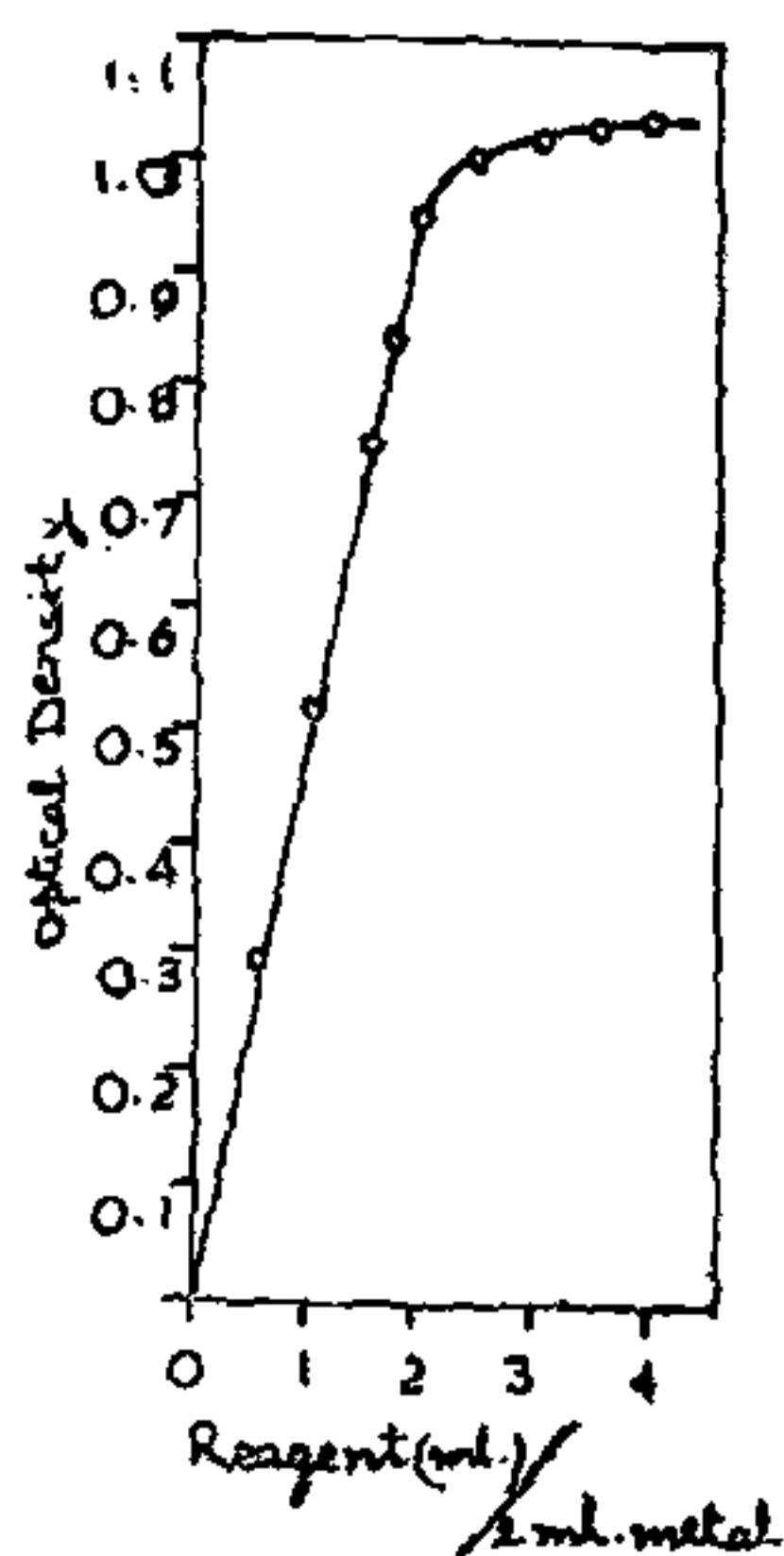


FIG. 2

Further studies regarding the structure of the complex are in progress.

Stability of the complex.—The optical density of the complex has been found to remain constant for 12 hours. The complex obeys Lambert-Beer's law between the concentration limits of 1.7 ppm to 5.7 ppm of molybdenum in solution. Stability constant of the complex was determined by two different methods:

- (1) From the curve of the molar composition of the complex, the value of α , the degree of dissociation of the complex

was calculated. This value of α was then employed to calculate the value of the stability constant. This gives the average value of $\log K$, at an ionic strength of 0.2 M (maintained by the addition of KCl solution) in 40% alcoholic medium, at $32^\circ \pm 2^\circ \text{C}$. to be 4.5 ± 0.2 .

- (2) The intercept made by the straight line with the Y-axis in Asmus' method (Fig. 3) is given by $-(b_0/v)^n \cdot 1/K_c$, where b_0 is the molar strength of reagent solution employed, v is the final volume made, K_c is the dissociation constant and $n=1$ in this case. This method gives the value of $\log K$, under the conditions mentioned above (except that ionic strength in this case was not kept constant), to be 4.39.

Interference due to foreign ions.—Ce (III & IV), Fe (II & III), titanium (IV), thorium (IV), tungsten (VI), vanadium (V), uranium (VI), niobium (V) cause serious interference even when present in small quantities.

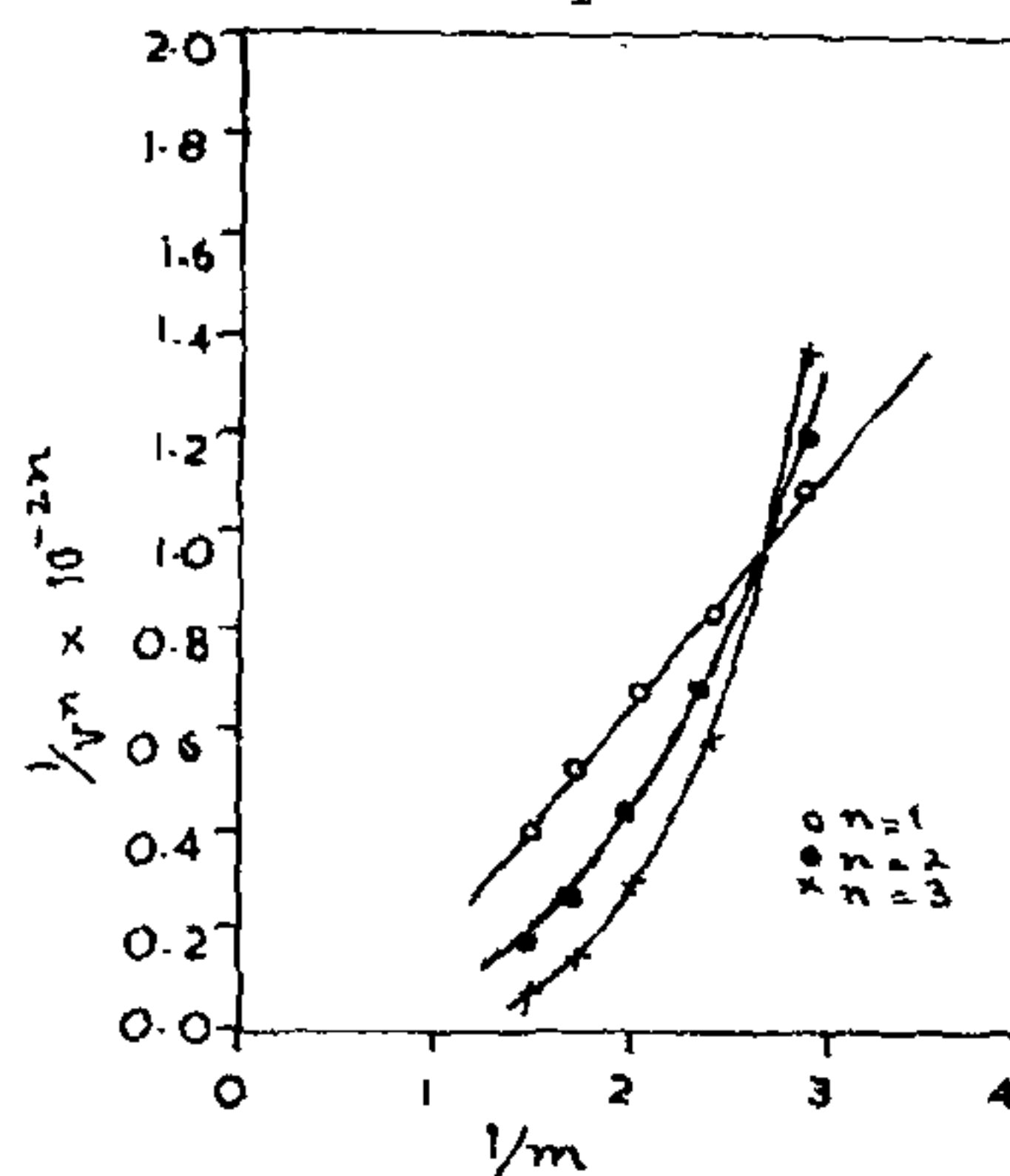


FIG. 3

Among the anions studied acetate, sulphate and thiosulphate did not cause interference. Citrate and oxalate could be tolerated as far as the amount present was less than that of molybdenum itself. Phosphate and fluoride do not cause interference even when present in 100-fold and 30-fold concentrations respectively.

Recommended procedure for estimation.—An aliquot of molybdenum solution containing not more than 5.7 ppm of molybdenum is mixed with the required amount of the reagent. The pH of the resultant solution is adjusted to the appropriate value and its optical density

measured, using the reagent, under corresponding conditions as reference. Concentration of molybdenum can then be determined from the calibration curve obtained earlier using solutions of known strength.

SUMMARY

3-Phenyldaphnetin (3-phenyl-7, 8-dihydroxycoumarin) in ethanolic solution forms aqueous alcohol soluble yellow complex with molybdenum. The complex obeys Lambert-Beer's law between 1.7 ppm to 5.7 ppm of molybdenum in solution and has the composition of 1:1. Interference due to various ions has been studied. Stability constant of the complex under the experimental conditions is 4.5 ± 0.2 .

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ARE TENDRILS OF VITACEAE AXILLARY?

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TENDRILS of Vitaceae are of considerable interest from morphological and ontogenetic view-points. The tendril is considered a modification of an entire shoot apex or a part of the shoot apex due to dichotomy or unequal division of the shoot apex (refer Shah¹ for detailed references). If the tendril is homologized with a lateral branch, several types of morphogenetic development are considered. It is stated that the tendril has developed from (a) an extra-axillary bud opposite to the leaf, (b) an axillary bud with its axillant leaf aborted, (c) an axillary bud originating at the node below and carried upward by intercalary growth of the internode, (d) a branch of the aborted prophyll of the bud axillant to the leaf opposite the tendril which rotates around the vine-shoot through 180° to have an opposite position and (e) a tendril is a composite structure consisting of a "hypoclade" bearing a displaced leaf of the main stem. The bud axillant to this leaf is differentiated as the other part of the tendril (Shah,¹ Chadeaud,² Bugnon,³ Millington⁴).

Shah¹ discussed these various interpretations and on the basis of ontogenetic study, he concluded that the tendril and the inflorescence of *Cissus* (and perhaps of other genera of the Vitaceae) are interrelated morphological organs whose development from the extra-axillary bud meristem depends upon the vegetative and reproductive phases of the shoot. Recently Millington⁴ interpreted the tendril of *Parthenocissus*

inserta as a modification of an axillary bud of type C as mentioned above. The present communication deals with this interpretation along with our observations based on the ontogenetic studies of adult shoot apices of *Parthenocissus quinquefolia*, Planch (obtained from the Arnold Arboretum), *Cayratia carnosae*, Gagnep., *Cissus rotundifolia*, Vahl., and *Vitis japonica*, Thumb. About 26 species of the Vitaceae obtained from U.S.A., Canada and India are under investigation.

The general arrangement of tendrils and leaves in the investigated species, including *P. inserta* is illustrated in A. According to Millington,⁴ T₁, T₄ are lower and T₂, T₅ are upper tendrils. The tendril T₁, T₂, T₄ and T₅ is a modification of the bud axillant to leaf L₁, L₂, L₄ and L₅ respectively and carried upward by an intercalary growth of the internode so as to lie exactly opposite the leaf above. The ontogenetic evidences put forth by him are as follows:

(a) The tendril is initiated at the second plastochron. It is axillary in origin though its position at the time of initiation is at the flank meristem and its final displacement is extra-axillary.

(b) The bud meristem of a tendril-less leaf, L₀ and the tendril meristem supposed to be axillant to this leaf (T₁ and L₁, T₄ and L₄ in A) are initiated simultaneously forming a "tendril-bud complex" (of T and AX in C) from which