

## Spectrophotometric determination of *N*-*o*-tolylbenzohydroxamic acid with vanadium(V)

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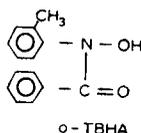
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**Abstract.** A rapid and reliable method for the spectrophotometric determination of the established analytical reagent *N*-*o*-tolylbenzohydroxamic acid (*o*-TBHA) with vanadium(V) has been developed. The chloroform extractable violet complex formed by *o*-TBHA with vanadium(V) in hydrochloric acid (> 2M) media, showing a broad absorption band at 520 nm, is utilized for this purpose. The molar absorptivity of the extracted complex in terms of *o*-TBHA is  $2500 \pm 100 \text{ l. mole}^{-1} \text{ cm}^{-1}$ . The effects of several experimental variables such as the time of shaking of the phases, volume and temperature of aqueous phase, mole ratio of *o*-TBHA to vanadium(V) and concentration of mineral acids on the determination of *o*-TBHA have been investigated. *o*-TBHA has been determined in the presence of several classes of organic compounds such as amides, esters, anhydrides, etc. The new method is successfully applied for the determination of distribution ratios of *o*-TBHA between different organic solvents and water and solubilities in different solvents.

**Keywords.** *N*-*o*-Tolylbenzohydroxamic acid ; spectrophotometric determination.

### 1. Introduction

*N*-*o*-Tolylbenzohydroxamic acid (trivial name *o*-TBHA) is an established analytical reagent (Majumdar and Pal 1965 ; Gupta and Tandon 1973 ; Lahiri 1974 ; Bag and Lahiri 1975).



Studies involving kinetics of hydrolysis and redox reactions of *o*-TBHA and physico-chemical measurements of distribution ratios and solubilities, etc., warrant reliable method for determining micro quantities of *o*-TBHA. Hence, based on our earlier experience in this laboratory (Rao and Tandon 1972 ; Tandon and Tandon 1973) we used the reaction with vanadium(V) in concentrated hydrochloric acid media for developing a spectrophotometric method for the determina-

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tion of *o*-TBHA. Apparently the vanadium(V) reaction should have general analytical applicability; however, experience has shown that the method for each hydroxamic acid is to be standardized individually because of variation in  $pK_a$  and distribution constants with substitution in hydroxamic acid functional grouping. Hence, the effects of various experimental variables such as optimum range of hydrochloric acid concentration, mole ratio of *o*-TBHA to vanadium(V), optimum concentration of vanadium(V), volume and temperature of aqueous phase and the time of shaking of the phases, etc., have been investigated. The results of these studies are presented in this communication.

## 2. Experimental

### 2.1 Chemicals

All chemicals were of CP grade unless otherwise stated. *o*-TBHA, m.p. 106° C, was prepared by the method reported earlier (Priyadarshini and Tandon 1967). Its solution was freshly prepared by dissolving about 50-100 mg of *o*-TBHA in 100 ml chloroform and diluting appropriately. An aqueous saturated solution of ammonium metavanadate, A.R. Hungary, was prepared. Ethyl alcohol was freed from chloroform by the procedure reported earlier (Priyadarshini and Tandon 1961).

### 2.2 Apparatus

Absorption spectra were scanned on SPECORD UV-VIS Carl-Zeiss, Jena recording spectrophotometer using 1 cm matched cells. For accurate measurement of absorbance Electronic Corporation of India, grating spectrophotometer model GS 865 was used. It was observed that measurement of absorbance on SPEKOL Carl Zeiss, Jena Spectrocolorimeter was equally satisfactory.

### 2.3 Recommended analytical method

Transferred an aliquot of chloroform solution of *o*-TBHA (containing not more than 1.35 mg of it) into a 125 ml pear-shaped separatory funnel. Concentrated hydrochloric acid and ammonium metavanadate solutions were added so that acidity of the aqueous phase was between 3.2 and 8.2 M and volume of aqueous phase equal to that of chloroform phase. On shaking for one minute violet chloroform extract was obtained.

(i) The extract was collected in a dry stoppered test tube, or

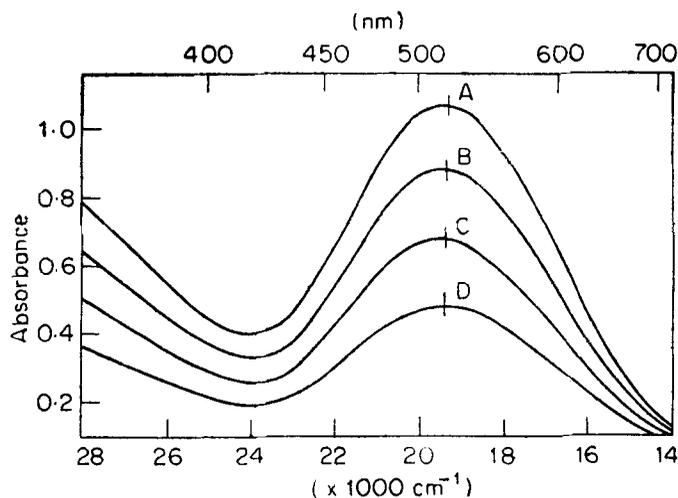
(ii) The extract was collected in a 50 ml beaker containing 1.5 to 2 g of anhydrous sodium sulphate and transferred to a 25 ml volumetric flask. The aqueous layer and the sodium sulphate crystals were washed free of colour with small portions of chloroform, washings transferred to the volumetric flask and the solution made up to the mark.

The absorbance of extract was measured at 520 nm using chloroform as blank. The quantity of *o*-TBHA corresponding to the absorbance reading was calculated from the calibration curve.

Both (i) and (ii) gave satisfactory results although in (i) the detection limit improved considerably; results were, however, slightly more accurate with (ii).

**Table 1.** Effect of acids and their concentrations on the absorption spectra of extracts of *o*-TBHA with vanadium(V).

Acid	Acid, M	Extract, colour	$\lambda_{\max}$ , nm
Hydrochloric	5.0	Violet	520
	1.0	Reddish-violet	502
	0.1	Brownish	465
	0.01	Orange	456
Hydrobromic	5.0	Violet	530
Sulphuric	6.0	Reddish-violet	504
Perchloric	5.0	Reddish-violet	500
Nitric	5.0	Reddish	492
Acetic	5.0	Reddish	480
Phosphoric	1.7	Orange	462



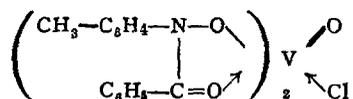
**Figure 1.** Absorption spectra of violet extracts with vanadium(V) from 5 M HCl in chloroform *o*-TBHA.

A, 4.230; B, 3.478; C, 2.687; D,  $1.897 \times 10^{-4}$  M.

#### 2.4 Colour reaction

The chloroform solutions of *o*-TBHA react with vanadate ions and yield extracts, the colours of which depend on the concentration and type of acid used. The colours of the chloroform extracts from aqueous solutions containing more than 2.0 M hydrochloric acid are violet and show a broad absorption band around 520 nm. Below 2 M hydrochloric acid the extracts display hypsochromic effect (table 1). The absorption spectra of typical chloroform extracts from 5 M HCl are presented in figure 1. The solid complex isolated from extracts has the

formulae  $(C_{14}H_{12}O_2N)_2 VOCl$ ; vanadium being in oxidation state + 5 (Koshy 1981). The complex has the following structure, as evidenced by spectral and other studies (Koshy and Tandon 1981).



Various other acids such as acetic, hydrobromic, nitric, perchloric, phosphoric, sulphuric, etc., have been examined for the adjustment of acidity of the aqueous phase. The colours and positions of absorption bands of typical fresh extracts thus obtained are given in table 1. Hydrochloric acid was chosen for adjusting the acidity of aqueous phase. Extracts obtained from other acids have a tendency of slowly turning violet with bathochromic shift of absorption band of decreased intensity if the containers are contaminated with even trace impurity of hydrochloric acid.

### 2.5 Solvents for the extraction of the coloured complex

Various organic solvents such as benzene, cyclohexane, carbon tetrachloride, chloroform, ethyl acetate, chlorobenzene and *o*-dichlorobenzene, etc., were examined for the solvent extraction of the coloured species. However, chloroform was the preferred solvent for quantitative extraction, colour stability and ease of operation.

## 3. Results and discussion

### 3.1 Beer's law

Studies made in the concentration range 2–130  $\mu\text{g/ml}$  of *o*-TBHA showed that Beer's law is obeyed for it from 10–116  $\mu\text{g/ml}$  of chloroform extract. The optimum concentration range works out between 18 and 64  $\mu\text{g/ml}$  as per the recommendations of Sandell (1959). The molar absorptivity of the extracted complex in terms of *o*-TBHA is  $2500 \pm 100$  litre mole<sup>-1</sup> cm<sup>-1</sup> at 520 nm. The molar absorptivity for the determination of vanadium(V) with *o*-TBHA under identical conditions comes out to be  $5000 \pm 100$  (calculated on the basis of vanadium) against the reported values of  $5000 \pm 100$  (Gupta and Tandon 1973) and 4743 (Majumdar and Das 1964).

### 3.2 Effect of acidity

The absorbance remains constant in the range 3.2 to 8.2 M hydrochloric acid. Generally, studies were made at 5 M HCl.

### 3.3 Shaking time and stability

The colour is extracted from the aqueous phase in almost a minute. The absorbance of the extract is unaffected up to 10 min of shaking but beyond this a slight decrease in absorbance is noted.

The extracts are stable for several days, if stored in cool dark place. In typical analyses the absorbance decreased after seven days by about 2%.

### 3.4 *Volume and temperature of the aqueous phase*

The absorbance of the chloroform extracts remains unchanged if the volume of the aqueous phase is varied between 1 and 50 ml for 10 ml of chloroform phase presumably because of large value of distribution ratio of extracted metal species. Volume ratio of organic and aqueous phases should be unity or more for satisfactory extraction efficiency. Variation of temperature from 25 to 35° C did not produce any measurable change in the absorbance of chloroform extracts. At higher temperatures there is excessive loss of chloroform due to evaporation.

### 3.5 *Effect of vanadium(V) concentration*

The absorbance of chloroform extracts were studied as a function of mole ratio of *o*-TBHA to vanadium(V) from 1 : 0.25 to 1 : 55. Constant absorbance is obtained with 1 : 3 mole ratio of *o*-TBHA to vanadium(V). At least a tenfold molar excess of vanadium(V) is, therefore, recommended.

### 3.6 *Order of addition*

The order of addition of reagents is not critical but to avoid any possible oxidation of *o*-TBHA by vanadium(V), ammonium metavanadate was added in the last step and phases shaken immediately. The extracted metal species is protected in the organic phase.

### 3.7 *Effect of foreign acids*

The effect of common acids upon typical determination of *o*-TBHA with vanadium(V) was examined. The data presented in table 2 show that acetic, perchloric, phosphoric and sulphuric acids were tolerated in large quantities.

### 3.8 *Effect of other foreign materials*

The effect of the other foreign materials encountered in practical analysis of *o*-TBHA was studied. *o*-TBHA (1.00 mg/25 ml) was determined satisfactorily in the presence of acetone (1 ml), acetic anhydride (1 ml), acetone (1 ml), acetic anhydride (1 ml), acetamide (80 mg), benzamide (20 mg), benzoic acid (5 mg), carbon tetrachloride (4 ml), cyclohexane (8 ml), 1.4 dioxane (4 ml), ethylacetate (1 ml), and urea (1000 mg). Alcohols are not tolerated because the extracts turn red.

### 3.9 *Precision and accuracy*

Statistical analysis on the results at three different concentration levels of *o*-TBHA shows that the new method is both precise and accurate.

### 3.10 *Sensitivity*

The Sandell sensitivity (Sandell 1959) of the system is 0.0897/ $\mu\text{g. cm}^{-2}$  at 520 nm.

**Table 2.** Effect of foreign acids  
 $o$ -TBHA =  $2.254 \times 10^{-4}$  M, HCl = 5 M

Foreign acid	Foreign acid, N	Absorbance, 520 nm
..	..	0.550*
Acetic	1.7	0.550
	3.5	0.560
	5.2	0.590**
Perchloric	0.8	0.550
	1.6	0.545
	2.4	0.535
Phosphoric	4.1	0.540
	8.2	0.510
	12.3	0.485
Sulphuric	3.6	0.550
	5.4	0.545
	7.2	0.530
	10.8	0.500

\* Average of 10 replicate measurements ; standard deviation in absorbance,  $\sigma = 0.0055$ .

\*\* Extract reddish-violet.

### 3.11 Applications of methods

The method is successfully applied in this laboratory for studying the kinetics of hydrolysis of *o*-TBHA, catalysed by different mineral acids and alkalies. Distribution ratios of *o*-TBHA between organic solvents and water determined by the use of the present analytical method are as follows : chloroform ( $360 \pm 20$ ), chlorobenzene ( $106 \pm 8$ ), benzene ( $100 \pm 10$ ), *o*-dichlorobenzene ( $91 \pm 6$ ), toluene ( $48 \pm 4$ ), xylene ( $39 \pm 3$ ), carbon tetrachloride ( $36 \pm 3$ ), cyclohexane ( $6.0 \pm 0.5$ ) and *n*-hexane ( $3.6 \pm 0.3$ ).

Data on solubility (g/litre) of *o*-TBHA are : chloroform, 438 ; acetone, 278 ; ethyl alcohol, 95%, 202 ; ethyl acetate, 154 ; benzene, 149 ; chlorobenzene, 105 ; *o*-dichlorobenzene, 85 ; toluene, 68 ; carbon disulphide, 51 ; xylene, 38, carbon tetrachloride, 36 ; cyclohexane, 4 ; and water, 0.53 (Temperature being  $28 \pm 2^\circ$  C).

## 4. Conclusions

The method is rapid, reliable and sensitive. It gives precise and accurate results if due care is exercised to minimise the possible error due to oxidation of *o*-TBHA by vanadium(V). This is achieved by following rigorously the recommended procedure.

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