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SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM(V) WITH 2, 2'-DIPYRIDYL-2-QUINOLYLHYDRAZONE (DPQH)

SYNTHESIS of DPQH and its application in the spectrophotometric determination of micro amounts of cobalt(II) have been reported earlier¹.

DPQH forms magenta violet (1:1) complex with vanadium(V), having maximum absorbance at 550 nm in the pH range 3.7-5.9. The Sandell's sensitivity and molar extinction coefficients are 0.0022 $\mu\text{g}/\text{cm}^2$ and 2.28×10^4 l. mole⁻¹ cm⁻¹, respectively. The range of validity for Beer's law is upto 2.29 ppm and optimum concentration range for determination of metal is 0.38-2.04 ppm.

Working Procedure

To a suitable aliquot containing 3.8-20.4 μg of vanadium(V), add 2 ml of ethanolic 10⁻² M solution of DPQH. Adjust the pH within 3.7-5.9 with dilute solutions of hydrochloric acid and sodium hydroxide. Make up the volume to 10 ml, keeping 50% (v/v) ethanol-water medium. Measure the absorbance against reagent blank prepared under identical conditions.

Effect of Diverse Ions

The ions Cl⁻, Br⁻, I⁻, SO₄²⁻, SO₃²⁻, NO₂⁻, NO₃⁻, ClO₄⁻, CH₃COO⁻, thiosemicarbazide, Ca(II), Sr(II), Ba(II), Mg(II), Al(III), In(III), Sb(III), Mo(VI), W(VI), Th(IV), Ta(V), lanthanides and Pt metals except Pd (in cold) did not interfere, but the ions CN⁻, C₂O₄²⁻, citrate, EDTA, Co(II), Fe(II) and Pd(II) interfered seriously. * The tolerance limits (in ppm) are given in Table I.

TABLE I
Effect of diverse ions

| Anions | | Cations | |
|---|--------|--------------|-----------------|
| Foreign ions | V-DPQH | Foreign ions | V-DPQH |
| F ⁻ | 1000 | Cu(II)* | 20 ^a |
| CNS ⁻ | 600 | Ag(I)* | 5 ^b |
| S ₂ O ₃ ²⁻ | 400 | Zn(II) | 10 |
| Tartrate | 500 | Cd(II) | 10 |
| BO ₃ ³⁻ | 250 | Hg(II)* | 15 ^a |
| Thiourea | 500 | Ni(II) | 5 |
| PO ₄ ³⁻ | 250 | Pb(II) | 15 |
| S ₂ O ₈ ²⁻ | 100 | Mr (II) | 10 |
| | | Ti(IV) | 15 |

* Masked with ^a thiosemicarbazide; ^b CNS⁻.

Comparison with Other Reagents

The present method using DPQH as a reagent for the determination of vanadium(V) compares favourably with other methods known for the purpose. Sensitivities of different methods for determinations of vanadium are compared with the present method in Table II.

TABLE II
Sensitivities of methods for determination of vanadium(V)

| Method | Sensitivity ($\mu\text{g V cm}^{-2}$) | Reference |
|--|---|----------------|
| PAR (in presence of DCTA) | 0.0014 (550 nm) | 2 |
| Xylenol orange | 0.0026 (530 nm) | 3 |
| 5, 7-Diiodo-8-quinolinol | 0.0084 (420 nm)) 0.0106 (475 nm) } | 4 |
| PAN (CHCl ₃) | 0.0030 (615 nm) | 3 |
| 2-Naphthohydroxamic acid | 0.009 (450 nm) | 5 |
| N-(4-chlorophenyl)-4-methoxy-benzohydroxamic acid | 0.009 (545 nm) | 6 |
| N-(4-dimethyl amino-phenyl)-3-methoxy-2-naphthohydroxamic acid | 0.0042 (570 nm) | 7 |
| DPQH | 0.0022 (550 nm) | Present method |

PAR is one of the most sensitive reagent for determination of vanadium. Reagent also absorbs strongly at the wavelength of maximum absorption. It is quite selective in presence of DCTA. However, even in presence of DCTA, uranium, niobium, titanium and zirconium interfere. Complete colour development requires 30 min. and complex is stable for 2 hr only. Xylenol orange is also a sensitive reagent; however molybdenum and tungsten interferes seriously. The reagent 5, 7-dihydro-8-quinolinol is quite sensitive and also selective. The colour is extractable into chloroform but starts fading immediately. Strict control of acidity is required to extract the complex into *n*-heptyl alcohol and procedure is quite lengthy.

In the present method DPQH does not absorb at all at λ_{\max} 550 nm which is an advantage since water reference can also be used. Furthermore determination can be carried out even in the presence of large amounts of molybdenum, tungsten, thorium, tantalum and moderate amount of titanium.

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OCCURRENCE OF THE RARE ALKALOID MARITIDINE IN *ZEPHYRANTHES ROBUSTA* AND *Z. SULPHUREA*

THE plant members of Amaryllidaceae are known to possess poisonous and medicinal properties¹. *Zephyranthes robusta*² and *Z. sulphurea*³ were examined chemically and the alkaloids tazettine, haemanthamine, lycorine and a new alkaloid m.p. 262–64° were reported. Further work was carried out on the above alkaloid (m.p. 262–64°) and it was identified as maritidine.

The bulbs of *Z. robusta* and *Z. sulphurea* obtained from a nursery in Sikkim were examined separately. The bulbs were extracted with alcohol and concentrated to a small bulk adding water towards the end. This aqueous suspension was adjusted to pH 6 and extracted with ether and chloroform. The remaining aqueous suspension was then made alkaline (pH 8) and extracted with chloroform (A).

Z. robusta: The extract A on crystallization directly gave lycorine (Fraction I) m.p. 255–57°, $[\alpha]_D^{30} = -100^\circ$ (alcohol), $C_{16}H_{17}NO_4$; acetate m.p. 216°. The mother liquor was subjected to chromatography on alumina when two crystalline fractions were obtained (Fractions II and III). Fraction II was identified as haemanthamine m.p. 201–03°, $[\alpha]_D^{30} = +37.5^\circ$ (chloroform), $C_{17}H_{19}NO_4$; picrate m.p. 220°. Fraction III was obtained from chloroform eluates, m.p. 260–62°. It answered tests for alkaloids and analysed for $C_{17}H_{21}NO_3$.

Z. sulphurea: The extract A on direct crystallization gave stout prisms (Fraction IV). The mother liquor on chromatography gave Fraction V in benzene-chloroform eluates and Fraction VI in chloroform eluates. Fraction IV, tazettine, m.p. 204°, $[\alpha]_D^{30} = 166^\circ$ (chloroform), $C_{18}H_{21}NO_5$; hydrochloride m.p. 218°. Fraction V, haemanthamine, m.p. 203°. $[\alpha]_D^{30} = 33.5^\circ$ (chloroform), $C_{17}H_{19}NO_4$; picrate m.p. 222°. Fraction VI, stout prisms from methanol, m.p. 262–64°. The compound was soluble in methanol and almost insoluble in chloroform. It answered all tests for alkaloids. $[\alpha]_D^{30} = +28^\circ$ (methanol), Found: C, 71.54; H, 7.20; N, 4.95%. $C_{17}H_{21}NO_3$ (287.4) requires C, 7.43; H, 7.33; N, 5.06%. I.R. ν_{\max} (KBr) 3610, 3020, 2820, 1270, 1120, 1100, 1080, 740 cm^{-1} . Picrate m.p. 192–94°; oxidation with manganese dioxide gave an α , β -unsaturated ketone, m.p. 140–43°. Fractions III and VI possessed same properties and were identical in TLC and I.R. This alkaloid was found to have similar properties as those of the new alkaloid (alkaloid 16) reported by Sandberg and Michel⁴ from *Pancreatum maritimum*. Wildman⁵ elucidated the constitution of the alkaloid 16 in an unpublished work and named it maritidine at the same time of our isolation of this new alkaloid from *Zephyranthes* species. Thus the above alkaloid isolated was identified as maritidine and further confirmation of the identity was obtained by m.m.p., TLC and I.R. comparison with authentic maritidine.

Maritidine is the first alkaloid with 5, 10 *b* ethanophenanthridine nucleus containing dimethoxy rather than methylenedioxy substituents at C-8, C-9.

This is the second report of isolation of the rare alkaloid maritidine from Amaryllidaceae and first report from *Zephyranthes* genera.

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