in such extreme cases, this is the only method which gives us reliable ages provided large surface areas are scanned for fossil tracks. There is a large statistical error in our result due to paucity of fossil tracks and the f.t. age obtained is an order of magnitude higher than the value found by French group<sup>5</sup>.

The rate of ocean bottom spreading is estimated from the f.t. age of oceanic basalt and its distance of location from the axis of Mid-Atlatic Ridge which is nearly 1 km in our case. Assuming, the last magmatic activity around the median valley of the Ridge occurred around 3000 years ago<sup>6</sup>, the spreading rate is found to be 1 cm/year. It has been observed6 that the spreading rate depends upon the distance of location from the axis of Mid-Atlantic Ridge and with increase of distance the spreading rate decreases rapidly. It has also been verified that spreading rate is asymmetric about the median axis of the Ridge, Our result is comparable with the values inferred from the magnetic data<sup>10</sup> (0.7-1.5 cm/year) but it is not in agreement with the values obtained by French group<sup>5</sup> on the basis of fission track analysis.

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- 1. Wegner, A. L., The Origin of Continents and Oceans, Methuen, London (English edition 1924).
- 2. Hess, H. H., History of the Ocean Basins, Buddington Vol (A. E. J. Engel et al., eds.), Geol. Soc. Amer., 1962, pp. 599-620.
- 3. Aumento, F., Can. J. Earth Sci., 1969, 6, 1431.
- 4. Fleischer, R. L., Viertl, J. R. M., Price, P. B. and Aumento, F., Rad. Eff., 1971, 11, 193.
- 5. Storzer, D. and Selo, M., C.R. Acad. Sci. Paris, 1974, 279, 1649.
- 6. and —, Bull. Soc. Geol. France, 1976, 18, 807.
- 7. Virk, H. S. and Koul, S. L., Curr. Sci., 1975, 44, 211.
- 8. Fleischer, R. L., Price, P. B. and Walker, R. M., Nucl. Sci. and Engg., 1965, 22, 153.
- 9. Nagpaul, K. K., Gupta, M. L. and Mehta, P. P., Him. Geol., 1973, 3, 249.
- Planet. Sci. Lett., 1974, 22, 29.

## PROPERICIAZINE AS A SELECTIVE AND SENSITIVE REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM AND ITS APPLICATION TO VANADIUM STEELS

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#### ABSTRACT

Propericiazine is shown to be a selective and sensitive spectrophotometric reagent for vanadium. It forms an orange red species with vanadium(V) in phosphoric acid medium. The orange red species exhibits maximum absorption at 496 nm with a molar absorptivity of  $9.0 \times 10^3$  1 mole-1 cm<sup>-1</sup>. Beer's law is valid over the concentration range of 0·1-6·6 ppm. The proposed method has been used successfully for the determination of vanadium in vanadium steels.

### Introduction

OST of the reagents proposed for the spectrophotometric determination of vanadium are unsatisfactory for one reason or the other. The authors have now developed propericiazine (PP), Cyano-3 [(hydroxy-4-piperidino)-3-propyl]-10-phenothiazine as a sensitive and selective reagent for the spectrophotometric determination of vanadium(V). The proposed method offers the advantage of simplicity, rapidity, stability, sensitivity and selectivity without the need for extraction or heating.

## EXPERIMENTAL

Stock solution (0.01 N) of vanadium(V), prepared from AnalaR sodium metavanadate in distilled water, was standardised against a standard Fe(II) solution and further diluted as needed. Solution of PP [0.1% (m/V)] was prepared in distilled water containing a few drops of hydrochloric acid and stored in an amber bottle in a refrigerator. Beckman Model DB spectrophotometer with matched 1 cm silica cells was used for absorbance measurements,

TABLE I	
Effect of diverse lons	
[Amount of vanadium taken,	3 ppm]

Ion added	Tolerance limit (opm)	lon added	Tolerance límit (ppm)	Ion added	Tolerance limit (ppm)
Fe(III)	8000	U(VI)	1500	C1-	3800
Cu(II)	329	Ti(IV)	600	Br-	4000
Ni(II)	480	Zr(IV)	750	I-	8.0
Co(II)	180	Zn(U)	1300	NO <sub>a</sub> -	4000
Cd(II)	1800	Pb(11)	500	SO <sub>4</sub>	10000
Hg(II)	1200	As(III)	800	Acetate	3400
$Mg(\Pi)$	1200	Pd(II)	1.5	Oxalate	4000
Ca(II)	1200	Pt(IV)	24	Tartrate	2200
A1(111)	1000	Os(VIII)	50	Citrate	1400
Mo(VI)	1600	Cr(UI)	1300	EDTA	360
•		Mn(II)	1200		
W(VI)	200	F-	6000		

Procedure for the Determination of Vanadium

An aliquot of the stock solution containing 2.5-165 µg of vanadium(V), 15 ml of 10 M phosphoric acid, and 1 ml of 0.1% PP solution were made upto 25 ml with distilled water. The solution was mixed well, and the absorbance was measured at 496 nm against a reagent blank prepared under similar conditions. The amount of vanadium in the sample solution was then deduced from the standard calibration curve.

## RESULTS AND DISCUSSION

PP reacts with vanadium(V) in sulphuric, hydrochloric, phosphoric or acetic acid medium forming orange red coloured species believed to be a radical cation.1,2 The intensity and stability of the colour depend on the nature and concentration of the acid employed. The orange red colour is not stable in hydrochloric acid or acetic acid. It is stable for 50-60 min. in sulphuric acid in which the reaction is less sensitive. Phosphoric acid has therefore been selected for further studies because the reaction is more sensitive and the coloured species is more stable. The maximum colour development takes place instantaneously at room temperature (27° C) in 3-9 M phosphoric acid. The stability of the colour increases from 5-120 min with increasing acid concentration from 3-9 M. maximum colour intensity is not observed below 3 M phosphoric acid. The reagent gives light orange-red colour in phosphoric acid concentration higher than 9 M. Hence 6 M phosphoric acid medium in which the absorbance is stable for about 2 hours was selected for the determination of vanadium. A 46-fold molar excess of the reagent over vanadium is required for full development of colour.

The orange-red species exhibits maximum absorption at 491-498 nm. Absorption measurements are therefore made at 495 nm. Beer's law is obeyed in the range 0.1-6.6 ppm of vanadium. The optimum concentration of vanadium, evaluated by Ringbom's method<sup>3,4</sup>, is 0.5-6.2 ppm. For  $\log (I_0/I) = 0.001$ . the sensitivity of the reaction as calculated from Beer's law data is 5.66 ng cm<sup>-2</sup>. The molar absorptivity is  $9 \times 10^{-3}$  1 mole<sup>-1</sup> cm<sup>-1</sup>. The relative error calculated from ten determinations with 3 ppm of vanadium is  $\pm 1\%$  and a standard deviation is 0.04. The absorbance readings remained constant in the temperature range 10-60°C. The absorbance gradually decreased with a rise in temperature. The order of addition of reagents was not critical.

## Effect of Diverse Ions

The tolerance limits for various diverse ions which gave less than 2% error in absorbance readings are given in Table I. The major advantage of this method is that Fe(!!!) is tolerated up to 8000 ppm.

## Determination of Vanadium in Vanadium Steels

About 0.5 g of vanadium steel containing C: 0.14-1.04%; Si: 0.10-0.35%; Mn: 0.36-0.88%; P: 0.015-0.027%; S: 0.008-0.011%; Ni: 0.1-0.37%; Cr: 0.02-1.32%; Mo: 0.03-0.94%; Cu: 0.1-0.11%; Al: 0.032%; Ti: 0.061%; B: 0.0046% and V: 0.19-0.96% was accurately weighed and brought to solution. A suitable portion of the solution was then treated with the reagent and the volume made up 25 ml and the absorbance was measured as above. The results given in Table II confirm the usefulness of the method.

TABLE II

Determination of vanadium in vanadium steels

£' 1 -	Vanadium content of solution, ppm		
Sample	Certified value	Found	
1. No. 4. CrlMo95-		•	
V85T1B	0.9625	0.9648	
-	1.9250	1.9120	
	3.850	3.8450	
2. H No. 7, 2034,	0.7656	0.7580	
15CDY6	1.860	1.865	
	2.714	2.695	
3. $T_{100}V_{25}$	1.006	1.000	
	2.012	2.018	
	3.024	3.000	

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- Dwivedi, P. C., Gurudath Rao, S. N., Bhat, S. N. and Rao, C. N. R., Spectrochim. Acta, 1975, 31A, 129.
- 2. Forrest, I. S., Forrest, F. M. and Berger, M., Biochim. Biophys. Acta, 1958, 29, 441.
- 3. Ringbom, A., Z. Anal. Chim., 1939, 115, 332.
- 4. Ayres, G. H., Anal. Chem., 1949, 21, 652.
- 5. Sanke Gowda, H. and Narayana Achar, B., Micro-chemical Journal, 1979, 24, 40.

# SYNDIAGENETIC MICROSTRUCTURES DUE TO INTERNAL FILLING IN TERMITE MOUNDS

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### ABSTRACT

Pedographic study of the thin sections of the termite mounds, occurring on different geologic formations, revealed certain microstructures consisting of 'birdseye', cyclic depositional zones, Leisegang structures, and rim cement resulting from the internal fillings of the soil framework during the syndiagenesis of the termite mound. All these microstructures are similar to those developed during the diagenesis of carbonate sediments.

TERMITES construct their mounds on the ground surface with a widely varied size, shape, and architectural style. For the construction of these mounds, the termites carry in their mandibles the scil particles which are placed in position and are cemented with a mortar consisting of their saliva or excrement mixed with clay. This mechanical process of construction has been observed directly by several workers (Beaumont<sup>7,4</sup> Hill<sup>8</sup>, Emerson<sup>6</sup> Grasse, Stuart<sup>166</sup> and others). Thus lithification of the mound is initially carried out by the termites. The physical and chemical changes, involved in the formation of termite soils, have been discussed by Lee and Wood<sup>11</sup>.

The important constituents in the termite soils are various types of clay mineral and iron oxides which are mainly formed by chemical weathering of the silicate minerals. The organo-mineral colloids which are a mixture of floccules and gels (Tyulin<sup>18</sup>) are commonly developed by the clay and iron compourds

together with organic matter. Iron in the presence of organic matter is mobilised (Jackson<sup>10</sup>, p. 128). Hence the organo-mineral colloids are mobilised and reconstituted leading to the diagenesis of the termite mounds.

In order to investigate the processes of diagenesis involved in the development of termite mounds, samples of the mounds, developed on the soils derived from different geological formations, were collected. Thin sections of these samples, for microscopic study, were prepared after impregnating them with xylene and Canada balsam, a suggested by Ireland<sup>9</sup>. Stoops<sup>15</sup> has also carried out the petrographic study of the thin sections of the termite mounds.

The thir section study, in the present work, revealed certain excellent microstructure, involving the development of the birdseye, cyclic deposition, Leisegang phenomenon, and rim cementation leading to the diagenesis of the termite soils in the fermation of the mounds. All these microstructures are open-space