

A RAPID SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF VANADIUM(V) IN SEDIMENTARY ROCKS

RAJENDRA SHARMA

Geology Division, KDMIPE, Dehradun 248 001, India.

THE colorimetric methods available for the determination of vanadium in traces are lengthy, tedious and involve the removal of interfering ions by solvent extraction¹⁻³. L- α -Methyl-3,4-dihydroxyphenylalanine⁴ or α -methyldopa (known as M-dopa, Alphadopao or Sembrina commercially) is a pharmaceutical preparation (British Pharmacopoeia)⁵ used in the treatment of hypertension. In the present studies it was observed that M-dopa forms a purple-coloured complex with vanadium(V) in acidic medium and can be used as a colorimetric reagent.

The chemicals used were of analytical grade. All measurements were done in triplicate. Absorption spectra (visible light) were recorded on a Carl Zeiss VSU-2 spectrophotometer. Ammonium metavanadate (AMV, 2.296 g) was dissolved in distilled water (1 l) to give a concentration of 1000 ppm vanadium. M-dopa (10 mg) was dissolved in 0.1 N H₂SO₄ (50 ml), this gives a concentration of 200 μ g/ml. Solutions B of rock samples were prepared by employing the standard method of Riley⁶. Clay fraction was fused with HF and HClO₄ in a platinum crucible and the residue was dissolved in distilled water.

Aliquots of standard AMV were taken in measuring flasks and diluted with distilled water to make different concentrations ranging from 10 to 100 ppm vanadium. These solutions were pipetted out (2 ml) into a series of stoppered test tubes. To these test tubes M-dopa solution (2 ml) was added. An unstable pink colour developed immediately. The reaction mixture was then heated on a steam bath for 10 min and cooled to room temperature. The stable purple-coloured complex formed had absorption maximum (λ_{\max}) at 560 nm (figure 1). The developed colour was stable for up to 12 h.

Absorbance was measured for different concentrations of vanadium at 560 nm using reagent as blank. Beer-Lambert law was obeyed up to 500 ppm of vanadium (figure 2). Molar absorptivity of the complex was $2 \times 10^2 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 560 nm. The method is quite reproducible (SD + 2 ppm, $P < 0.05$). The working pH range was observed to be between 1 and 3.

Most of the common ions present in rocks do not interfere with the determination of vanadium(V) by

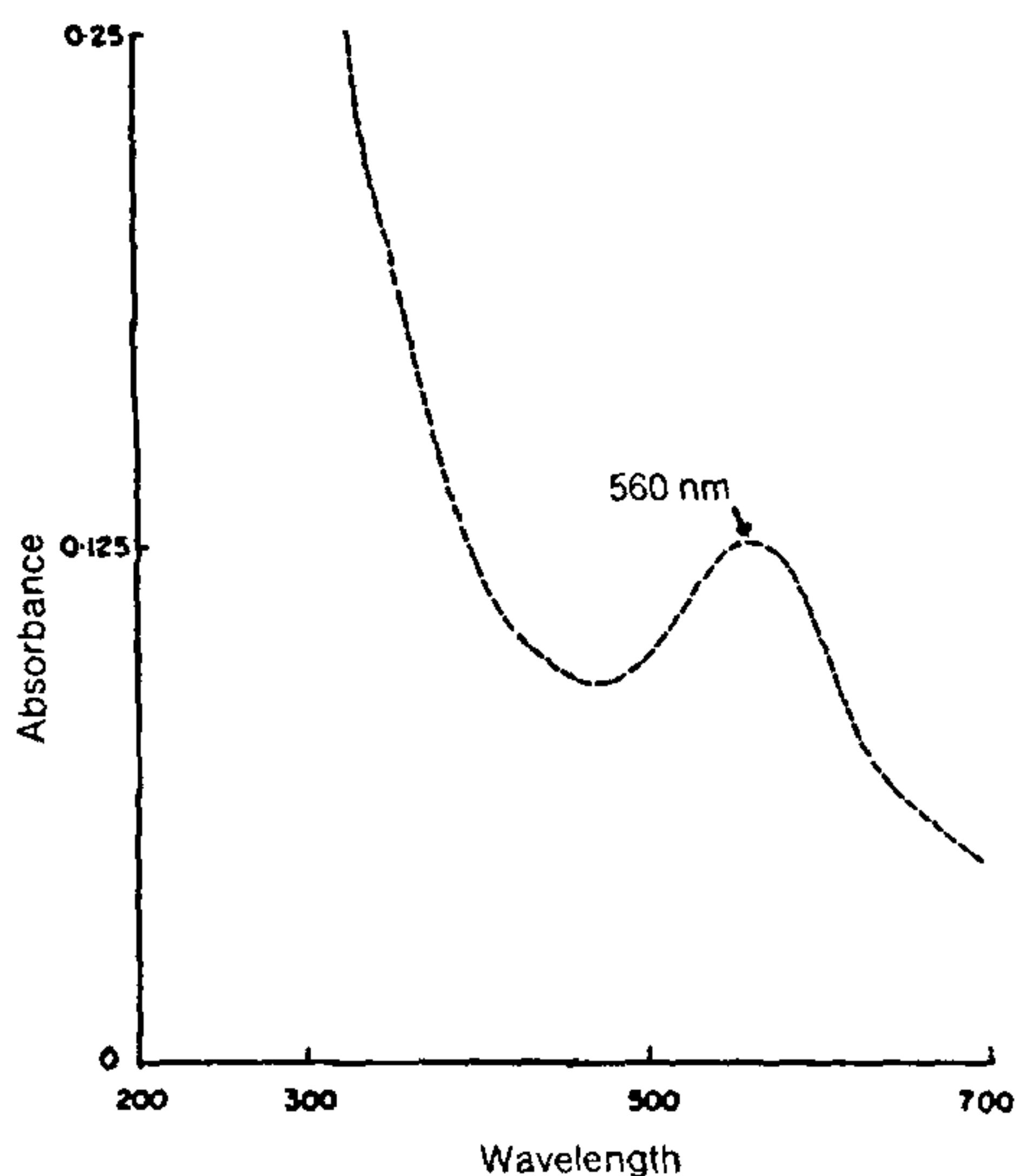


Figure 1. Absorption spectrum of vanadium complex with α -methyldopa (1-cm cell).

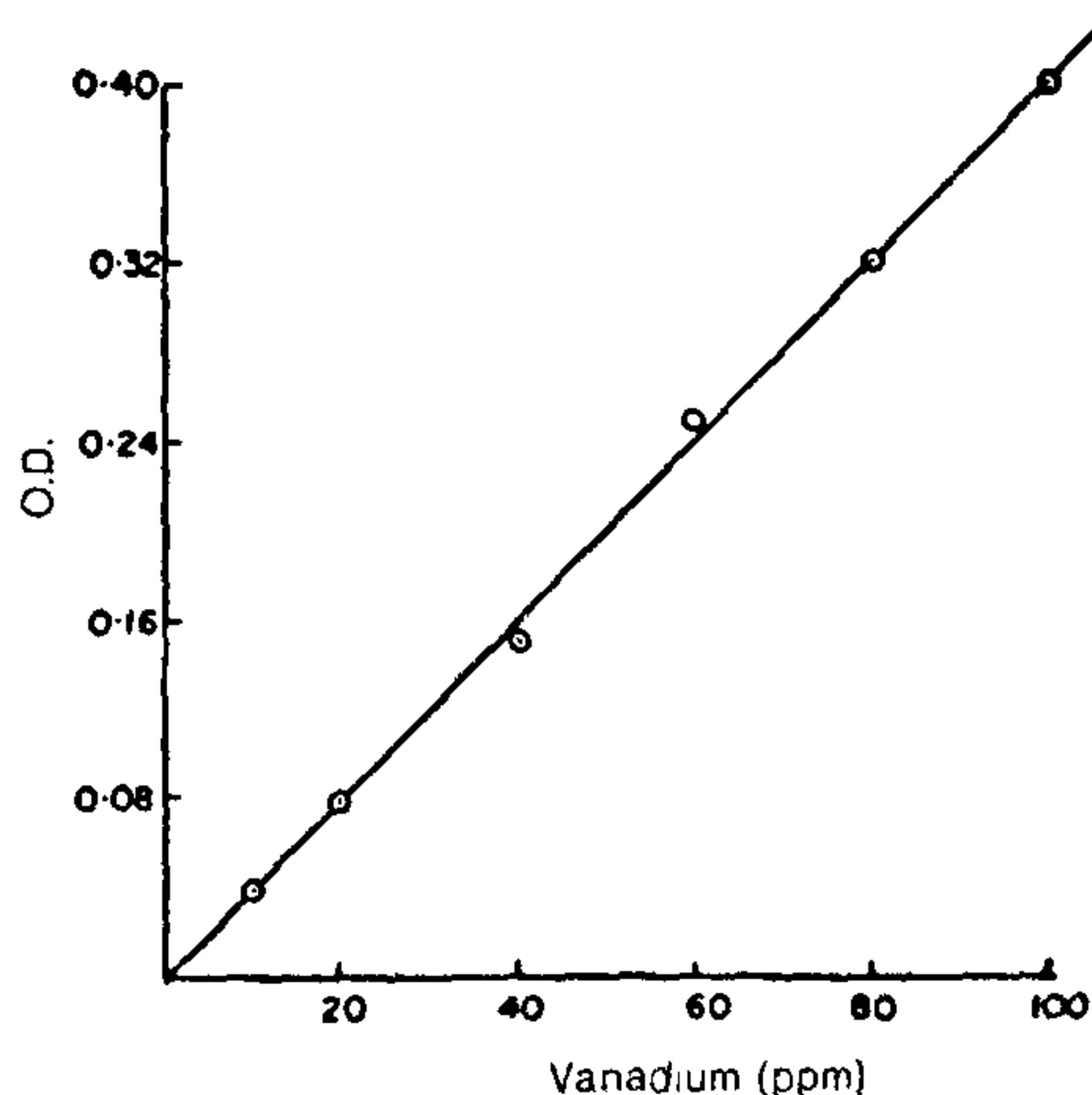


Figure 2. Calibration graph for vanadium using α -methyldopa (1-cm cell, 560 nm).

this method. However, to evaluate the tolerance limit of different ions synthetic solutions containing 100 ppm V(V) and different amounts of various ions were prepared. Tolerance limits in ppm (error $\pm 2\%$)

for different metal ions are given in brackets below: Ca(II) (2000), Mg(II) (1000), Sr(II) (1000), Na(I) (2000), K(I) (1500), Fe(III) (500), Mn(IV) (1000), Ti(IV) (1200), Ga(III) (50), Ni(II) (500), Cu(II) (500), Zn(II) (500), Co(II) (200), B (200) and Cr(III) (150).

The reaction mixture was heated gently on a steam bath. It was observed that rapid heating leads to the formation of a brownish complex or precipitation of the purple-coloured complex. Use of strong concentrated acids may also lead to precipitation of the complex.

To an aliquot of solution B of rock sample, an acidic solution of M-dopa was added and the reaction mixture was heated in the manner described for standard vanadium samples. The results for a few samples analysed by this method were compared with those of Majumdar and Das² using *N*-benzoyl-*o*-tolylhydroxylamine, and are summarized in table 1.

It has been reported earlier⁷ that vanadium(V) forms a green-coloured complex with absorption maximum at 680 nm with M-dopa. In fact M-dopa and vanadium(V) form a purple-coloured complex with λ_{\max} at 560 nm (figure 1). To examine the earlier reported method, various concentrations of M-dopa and vanadium(V) were mixed in separate tubes and heated for different periods in acidic medium. A green-coloured complex with absorption maximum at 680 nm could never be obtained.

The molar absorptivity and Sandell's⁸ sensitivity of the reaction are $2 \times 10^2 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $0.035 \mu\text{g/cm}^2$ respectively. The Job's⁹ method and mole ratio method suggest that a 1:2 complex is formed between metal and the reagent. The $\log k$ was found to be 8.86 at $25 \pm 0.5^\circ\text{C}$, pH 2.0.

It seems that vanadium(V) in acidic solution forms VO_2^+ ions which in turn react with $-\text{NH}_2$ and $-\text{COOH}$ groups of the phenylalanine moiety of M-dopa to give a distorted octahedral complex.

Table 1 Vanadium analysis data for sedimentary rock samples from Bhima Basin

Sample No.	Present method		<i>N</i> -Benzoyl- <i>o</i> -tolyl-hydroxylamine method ²	
	OD at 560 nm	Vanadium (ppm)	OD at 510 nm	Vanadium (ppm)
BV-I	0.27	67	0.84	70
BV-7	0.24	60	0.70	58
BV-II	0.30	75	0.90	75
BV-14	0.32	80	0.94	78
BV-25	0.38	95	01.15	96

Cell- 1 cm.

Attempts to dissociate the vanadium-M-dopa complex are in progress and a detailed study to elucidate its structure will be carried out.

5 May 1988

1. Bennette, W. H. and Pick up, R., *Colon. Geol. Min. Res.*, 1952, 3, 171.
2. Majumdar, A. K. and Das, G., *Anal. Chim. Acta*, 1964, 31, 147.
3. Cheng, K. L., *Talanta*, 1961, 8, 658.
4. Suzuki, M. *et al.*, *Chem. Ind. (London)*, 1972, 687.
5. *British Pharmacopoeia*, H. M. Stationary Office, London, 1980, Vol. 1, p. 289.
6. Riley, J. P., *Anal. Chim. Acta*, 1958, 19, 413.
7. Shukla, S., Pathak, V. N. and Shukla I. C., *J. Inst. Chem.*, 1985, 57, 115.
8. Sandell, E. B., *Colorimetric Determination of Trace Metals*, Interscience, New York, 1959.
9. Job, *Ann. Chim.*, 1928, 9, 113.

A NOTE ON THE RADIOACTIVE INTRAFORMATIONAL CONGLOMERATE IN PAKHAL BEDS NEAR BANGARUCHILKA, KHAMMAM DISTRICT, ANDHRA PRADESH

YAMUNA SINGH, S. D. RAI and T. M. RAMACHAR

Atomic Minerals Division, Department of Atomic Energy, AMD Complex, Begumpet, Hyderabad 500 016, India.

BANGARUCHILKA ($17^\circ 46' 15'' \text{ N}$; $80^\circ 36' 46'' \text{ E}$), is a small village located about 5 km north of Mailaram Copper Mines in Khammam district, Andhra Pradesh (T.S. No. 65 C/9). The area exposes schists and gneisses of the Dharwar age and acid intrusives. Acid intrusives include pink granite and associated pegmatites and vein quartz. All these are unconformably overlain by Pakhal/Gondwana sediments. The radioactive intraformational conglomerate occurs within quartzite of Pakhal Supergroup in Turpu Gutta, about half a kilometre due north-east of Bangaruchilka village.

Field data indicate that the radioactive intraformational conglomerate is a polymictic conglomerate, consisting mainly of pebbles of quartz and lesser feldspars, with a length of up to 18 cm and length/breadth ratio of 1.5–2.0. The conglomerate passes into gritty arkose and finally to arkose. It is