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1 - PHENYL - 3 - METHYL - 4 - TRIFLUOROACETYL - PYRAZOLONE - 5 (HPMTFP) AS AN EXTRACTION AND SPECTROPHOTOMETRIC REAGENT FOR VANADIUM (V)

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Abstract : A rapid and efficient method for the determination of a large quantity of vanadium(V) in an aqueous medium using 1 - phenyl - 3 - methyl - 4 - trifluoroacetyl - pyrazolone - 5 (HPMTFP) is described. The percentage extraction as a function of pH of aqueous medium is reported and it shows that quantitative extraction of V(V) occurs in the pH range of 1.7-2.3. The properties of the colour of the extracted complex species with respect to pH of solution, various solvents, time and presence of diverse ions are reported. Beer's law was found to be valid up to 100 ppm of vanadium (V) ($\mathcal{E} = 1.1 \times 10^{2}$ l. mol^{-1} $.cm^{-1}$).

Key words : Vanadium (V) determination, 1-phenyl-3-methyl-4-trifluoroacetyl-pyrazolone-5, pH, extraction, spectrophotometry

INTRODUCTION

1-Phenyl-3-methyl-4-acyl-pyrazolones, as chelating agents, have been used for the efficient extraction and separation of trace amounts of metals[1-5] of which the 4-benzoyl derivative has been extensively studied. Apart from this, very few studies have been carried out using these chelating reagents in other practical applications such as colorimetry and extraction of large concentrations of these metals from aqueous solutions. Quite recently the 4-trifluoroacetyl derivative HPMTFP has attracted the attention of research workers[6,7] because its pK_a (2.76 ± 0.13) is lower than that of the 4-benzoyl derivative (HPMBP)[5] which has been extensively studied.

This paper describes the use of HPMTFP for the extraction of large quantities of vanadium(V) at the 200 ppm level from various buffer solutions and spectrophotometric determination of V(V) extracted into the organic phase.

METHODS AND MATERIALS

Apparatus : A Pye Unicam SP6-400 spectrophotometer was used for absorbance measurements. The measurement of pH of solutions were made with Kent EIL 7050 pH meter. Shaking of phases were carried out with a Stuart flask shaker. The extraction bottles used were made of polythene material.

Reagents : All solvents and reagents used were of analytical grade. HPMTFP was synthesized according to established method[1] and was twice recrystallized from aqueous ethanol; m.p., 139^0 C. A solution of 0.02 M HPMTFP in methyl isobutyl ketone (MIBK) was used as organic extraction and spectrophotometric reagent.

A stock solution of vanadium (V) , 2000 ppm, was prepared by dissolving 0.4593 g of NH_4VO_3 (ammonium metavanadate) in 2 ml of 10 M H_2SO_4 and diluted to 100 ml with distilled water. Buffer solutions were prepared from mixtures of 0.1 M solutions of the following reagents: HCl/KCl, pH 0.5-2.2; HCl/CH_3COONa, pH 2.3-3.5; CH_3COOH/CH_3COONa, pH 3.6-5.8.

Measurement of extraction : A 0.5 ml aliquot of the stock solution was diluted with a buffer solution of pH 0.5-5.8, to give a 5 ml aqueous phase, thus, containing 200 ppm of V(V) ion in an extraction bottle. This was shaken for 15 minutes with an equal volume (5 ml) of various organic solvents containing 0.02 M HPMTFP or a mixture of it with 0.01 M tri-octylphosphine oxide (TOPO). The percentage extraction was calculated as the percentage ratio between the concentration of V(V) in the organic phase and that in the aqueous phase. The pH of aqueous phase was measured after extraction in all the experiments.

Analysis of V(V) in aqueous raffinate : A 2 ml portion of the aqueous raffinate was introduced into a 10 ml volumetric flask to which 1.5 ml of 4 M H_2SO_4 was added. The solution was later made up to 10 ml with a methylated spirit solution containing 0.01M NHPMBP. The absorbance of the wine-red complex was measured[8] at 480 nm against a reagent blank prepared in a similar way and compared with a standard calibration curve.

Determination of V(V) in the organic phase : 0.2 ml aliquot of stock V(V) solution containing 2000 ppm of V(V) ion was introduced into an extraction bottle and adjusted to a total volume of 5 ml and pH of 1.9 with solution mixtures of HCl/KCl. 5 ml of MIBK containing 0.02 M HPMTFP + 0.01 M TOPO was added and both immiscible phases shaken vigorously for 15 minutes. The phases were allowed to settle before they were separated. The absorbance of the greenish-brown organic extract containing the V(V) - PMTFP complex species was measured at 480 nm against a reagent blank. Beer's law was obeyed for 10-100ppm V(V) concentration ($\varepsilon = 1.1 \times 10^2$ l. mol^{-1} .cm^{-1}).

RESULTS AND DISCUSSION

Effect of experimental variables on extraction : The extraction of 200 ppm of V(V) using 0.02 M HPMTFP in various organic solvents studied as a function of pH of aqueous phase is shown in figure 1. The figure shows that the percentage extraction of

V(V) is a function of the pH of aqueous solution, type of solvent used and presence of synergists like TOPO. It shows that extraction with organic reagent in the following solvent systems: benzene, chloroform and cyclohexanone are not quantitative, giving a maximum of 48% (pH 3) , 51% (pH 2.3) and 60% (pH 2.4) extractions into these solvents respectively. 80% extraction was obtained at pH 2 when the MIBK solvent system was used. Figure 1 shows that the presence of 0.01 M of TOPO synergistically enhanced the extraction of V(V) with 0.02 M HPMTFP, resulting in the quantitative extraction of V(V) in the pH range 1.7-2.3.

The rapid fall in percentage extraction of V(V) after pH 2.6 (graph A) with all the organic solvents studied is probably due to the formation of polyhydroxy and oxo-bridged vanadyl complex species which are probably pronounced after pH 2.6 due to the large concentration of V(V) ions in solution.

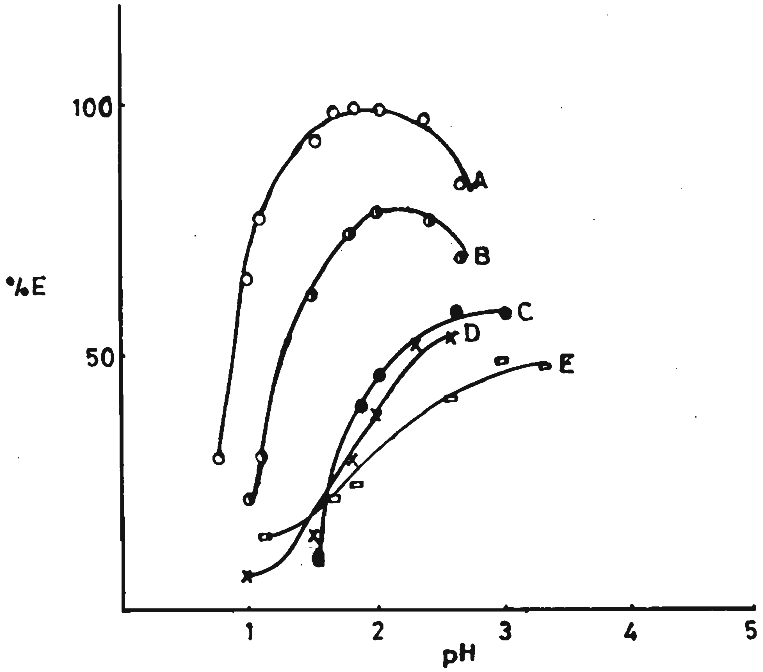

Figure 1: Percentage extraction of 200 ppm V(V) as a function of pH of solution using : A. 0.02 M HPMTFP + 0.01 M TOPO in MIBK, B. 0.02 M HPMTFP in MIBK, C. 0.02 M HPMTFP in cyclohexanone, D. 0.02 M HPMTFP in chloroform and E. 0.02 M HPMTFP in benzene.

Effect of Experimental Variables on the Spectrophotometric Determination of V(V) in the Organic Phase: The absorbance spectra of the extraction reagent and extracted V(V) complex species show that the MIBK solution containing the HPMTFP and TOPO mixture absorb strongly below 400 nm. The 480 nm wavelength was used for determining the concentration of the extracted complex species because the absorbence of the extraction reagent at 480 nm is negligible.

The optimum absorbance of the extracted organic phase using 0.02 M HPMTFP and 0.01 M TOPO mixture in MIBK occurs between pH 1.7-2.3 which is where the optimum percentage extraction also occurred. Thus, the pH of the aqueous phase was adjusted to pH of 1.9 in all subsequent extraction-spectrophotometric studies. The absorbances of the different amounts of V(V) studied are given in Table 1.

Table 1. Variation of absorbance of organic phase extract with concentration of V(V) extracted from aqueous phase of pH 1.9

V(V) concentration (ppm) in the aqueous phase	20	40	80	120	160	200
Absorbance of organic extract	0.042	0.082	0.170	0.230	0.285	0.345

The colour of the extracted complex is stable for 5 hours.

The use of various solvents (Figure 1) showed that benzene, chloroform and cyclohexanone are poor extraction systems and the sensitivity of the colour of the extracted complex species in these solvents is also poor. In some cases emulsions were obtained as was with the cyclohexanone system.

Interferences: The effects of various ions on the determination of V(V) were examined by extracting a 5 ml aqueous solution containing 80 ppm of V(V) ion and various amounts of a foreign ion and measuring the absorbance of the organic extract at 480 nm against a reagent blank. The results are given in Table 2.

Table 2. Determination of 80 ppm of V(V) in the presence of diverse ions

Ion	Amount of ion added (ppm)	Added as	Vanadium (V) found (ppm)	% Recovered
None	0	-	80.0	100.0
Ag^{+}	500	$AgNO_3$	80.0	100.0
Ba^{2+}	500	$BaNO_3$	79.0	98.8
Be^{2+}	500	$BeSO_4.4H_2O$	80.1	100.1
Ca^{2+}	500	$Ca(CH_3COO)_2$	79.1	98.9
Cd^{2+}	500	$Cd(NO_3)_2.4H_2O$	81.2	101.5
Co^{2+}	500	$Co(CH_3COO)_2.4H_2O$	80.3	100.4
Cu^{2+}	200	$Cu(ClO_4)_2.6H_2O$	98.8	123.5
Cu^{2+}	100	$Cu(ClO_4)_2.6H_2O$	84.1	105.1
Mg^{2+}	500	$Mg(ClO_4)_2$	79.4	99.3
Mn^{2+}	500	$MnSO_4.4H_2O$	80.0	100.0

Table 2 Contd.

Ion	Amount of ion added (ppm)	Added as	Vanadium (V) found (ppm)	% Recovered
Ni^{2+}	500	$Ni(NO_3)_2.6H_2O$	79.2	99.0
Pb^{2+}	500	$Pb(NO_3)_2$	78.8	98.5
Sr^{2+}	500	$Sr(CH_3COO)_2.1/2H_2O$	80.0	100.0
Fe^{3+}	10	$NH_4Fe(SO_4)_2.12H_2O$	105.9	132.4
Fe^{3+}	2	$NH_4Fe(SO_4)_2.12H_2O$	81.2	102.0
Ce^{4+}	100	$Ce(SO_4)_2.4H_2O$	96.5	120.6
Ce^{4+}	50	$Ce(SO_4)_2.4H_2O$	83.0	103.8
V^{4+}	500	$VOSO_4.H_2O$	101.2	126.5
V^{4+}	250	$VOSO_4.H_2O$	80.5	100.6
Cr^{6+}	50	$K_2Cr_2O_7$	188.2	235.3
Cr^{6+}	10	$K_2Cr_2O_7$	85.8	107.3
Mo^{6+}	200	$Na_2MoO_4.2H_2O$	76.9	96.1
Mo^{6+}	100	$Na_2MoO_4.2H_2O$	80.0	100.0
U^{6+}	100	$UO_2(NO_3)_2.6H_2O$	104.3	130.4
U^{6+}	20	$UO_2(NO_3)_2.6H_2O$	82.3	102.9
W^{6+}	100	$Na_2WO_4.2H_2O$	70.6	88.0
W^{6+}	50	$Na_2WO_4.2H_2O$	76.6	95.8
F^-	200	NaF	79.5	99.4
PO_4^{3-}	200	Na_2HPO_4	78.6	98.3
EDTA	200	Na_2EDTA	72.9	91.1
EDTA	100	Na_2EDTA	79.5	99.4
Oxalate	200	$(NH_4)_2$ oxalate	72.2	90.2
Oxalate	100	$(NH_4)_2$ oxalate	80.0	100.0
Tartrate	200	Na (Tartrate)	80.0	100.0

Some of the interferences observed were due to colour reaction between the metal ion introduced and vanadium (V) ion, resulting in enhanced intensity of the extracted organic complex species. Table 2 shows that V(V) can be determined in the presence of up to 250 ppm of V(IV) with little or no interference from V(IV) ion.

Analysis of water samples: Some water samples collected from Port Harcourt metropolis were digested with hydrochloric -nitric acid (3:1) mixture. 10 ml of the residue was adjusted to pH 4.0 and extracted with 0.02 M HPMTFP in benzene. This reagent system will extract Fe(III) completely at pH 4.0 without extracting V(V)[9] if both ions are present in the water sample. 5 ml of the aqueous raffinate above was adjusted to pH 2 and extracted with 5 ml of a mixture of 0.02 M HPMTFP and 0.01 M TOPO in MIBK. The average result of three determinations are shown in Table 3 (1).

Table 3: Analysis of samples for V(V) ion

(1) Water samples-May'90

Sample source	Amount (ppm) of V(V) added to water sample	% Recovered
Aluu stream	0.00	0.0
Aluu stream	40.00	99.1
Uni Port Delta Park tap	0.00	0.0
Uni Port Delta Park tap	60.00	100.4

(2) Determination of vanadium (V) in the presence of mixtures of the following ions M^{n+} (ppm): Ba^{2+}(50), Cd^{2+}(70), Ca^{2+}(50), Co^{2+}(70), Cu^{2+}(10), Cr^{6+}(2), U^{6+}(5) and V^{4+}(50). Average of three determinations are given.

V(V) (ppm) added to synthetic mixture	40.0	60.0	80.0
V(V) (%) recovered	98.7	101.2	99.1

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References

1. Jensen B.S. (1959). The synthesis of 1-phenyl-3-methyl-4-acyl-pyrazolones-5. *Acta Chemica Scandanavica* **13:** 1668 -1670.

2. Mirza M.Y. & Nwabue F. I. (1980). Studies on the extraction of Ti(IV), Ce(IV) and U(VI) with 1-phenyl-3-methyl-4-benzoyl-pyrazole-5-one from different mineral acids. Separation of thorium from titanium, uranium and rare earths. *Radiochimica Acta* **27:** 47-50.

3. Mirza M.Y. (1970). Preparation of ^{28}Mg in a nuclear reactor. *Radiochimica Acta* 27: 47-50 .

4. Rao G.N. & Arora H.C. (1977). Solvent extraction of uranium(VI) with 4-acyl 2,4-dihydro 5-methyl 2-phenyl 3H-pyrazol 3-ones. *Journal of Inorganic and Nuclear Chemistry* 39: 2057-2060.

5. Akama Y., Sato K., Ukaji M., Kawata T. & Kajitani M. (1985). Studies on extraction of copper(II) with 1-phenyl-3-methyl-4-acyl-5-pyrazolone. *Polyhedron* 4(1): 59-63.

6. Hasany S.M. & Qureshi I.H. (1977). Extraction of group IB, IIB and III-VA elements with 1-phenyl-3-methyl-4-trifluoroacetyl-pyrazolone-5. *Journal of Radioanalytical Chemistry* **40**: 28-39.

7. Umetani S. & Freiser H. (1987). Mixed-ligand chelate extraction of lanthanides with 1-phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolone and some phosphine oxide compounds. *Inorganic Chemistry* **26**: 3179-3181.

8. Uzoukwu B.A. (1991). Synthesis, structure, uv-visible and ir spectral studies of 1-phenyl-3-methyl-4-acyl-pyrazolone-5-complexes with vanadium(V). *Synthesis and Reactivity in Inorganic and Metalo-Organic Chemistry* 21(5): 881-896.

9. Uzoukwu B.A. & Jack B. (1993). 1-Phenyl-3-methyl-4-trifluoroacetyl-pyrazolone-5 as an extraction and spectrophotometric reagent for Fe(III). *Journal of the National Science Council, Sri Lanka*. 21(1):83-92.