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1 - PHENYL - 3 - METHYL - 4 - TRIFLUOROACETYL - PYRAZOLONE - 5 AS AN EXTRACTION AND SPECTROPHOTOMETRIC REAGENT FOR Fe (III)

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Abstract: A rapid, simple and sensitive extraction method for the determination of iron (III) spectrophotometrically in buffer solutions using 1-phenyl-3-methyl-4-trifluoroacetyl-pyrazolone-5 (HPMTFP) is described. The properties of the colour of the extracted complex species with respect to pH of aqueous media, presence of synergists, various solvents, time and diverse ions are reported. Up to 500 ppm of Ag^+, K^+, Na^+, Ba^{2+}, Be^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Sr^{2+} and Zn^{2+} do not interfere. The tolerence level of the following ions which interfere were determined (ppm) : $Cu^{2+} \leq 20$, $Ce^{4+} \leq 8$, $Cr^{6+} \leq 100$, $Mo^{6+} \leq 8$, $U^{6+} \leq 50$, $V^{4+} \leq 300$, $V^{5+} \leq 20$ and $W^{6+} \leq 8$. Beer's law is valid up to 10 ppm iron (III) ($\mathcal{E}$, $7.32 \pm 0.08 \times 10^3$ $1\ mol^{-1}\ cm^{-1}$) within an optimum pH range of 1.5 - 4.5.

INTRODUCTION

Acyl-pyrazolones have long been known for their versatile application in the solvent extraction of metals[1-4] from acid solutions. However, there have been very few studies of these promising chelating agents in other aspects of practical application. Apart from the spectrophotometric determination of Fe (III)[5] and V(V)[6-8] using the 4-benzoyl derivative, other 4-acyl derivatives have not been studied in this direction. During our solvent extraction studies the trifluoroacetyl derivatives of pyrazolone-5 (HPMTFP) was observed to be much more sensitive in both the extraction and spectrophotometric determination of Fe (III) than the 4-benzoyl derivative (HPMBP).[5]

This paper describes the use of HPMTFP as a reagent which offers a wider pH range and a more sensitive extractive spectrophotometric method for the determination of iron (III) than the 4-acyl-pyrazolone-5 derivative previously reported.[5]

METHODS AND MATERIALS

Apparatus: A Pye Unicam SP6-400 spectrophotometer was used for absorbence measurements. pH was measured with a Kent EIL 7050 pH meter. Mixing of phases was carried out with a Stuart flask shaker.

Reagents: All reagents and solvents used were of analytical grade. Aqueous solutions were prepared with glass distilled water.

HPMTFP was synthesized according to an established method[2] and twice recrystallized from aqueous ethanol. The chelating agent was confirmed pure from the following : m.p., 139^0 C ; calculated for $C_{12}H_9O_2N_2F_3$: C, 53.34% ; H, 3.36% , N, 10.37% . Found: C, 53.11% ; H, 3.88%; N, 10.25%. A solution of 0.02 M HPMTFP was prepared by dissolving 0.5405 g of HPMTFP in 100 ml of chloroform. A stock solution of iron (III), 100 ppm, was prepared by dissolving 0.8634 g of ferrric alum ($NH_4Fe(SO_4)_2.12H_2O$) in 100 ml of 0.1 M HCl and diluted to 1 litre.

Buffer solutions were prepared by mixing 0.1 M solutions of reagents as follows: pH 0.5 - 2.2, HCl/KCl; 2.3 - 3.8 , HCl/CH_3COONa ; 3.9 - 5.8 , CH_3COOH/CH_3COONa and 5.9 - 7.0 citric acid / NaOH.

Procedure: A 1 ml sample solution in an extraction bottle containing up to 100 μg of iron (III) was adjusted to a volume of 10 ml and pH 3 with buffer solution (HCl/CH3COONa). Ten ml of 0.02 M HPMTFP dissolved in chloroform was added and shaken vigourously for 20 min. The immiscible phases were transferred to a separating funnel and the phases allowed to settle before separation. The absorbence of the intense wine-red organic phase containing the extracted complex species was measured at 480 nm against a reagent blank containing 0.02 M HPMTFP in chloroform. Beer's law was obeyed from 1 ppm to 10 ppm of Fe(III) extracted into the organic phase.

For other extraction studies , as a function of pH of aqueous solution, a 10 ml solution containing 6 ppm in Fe(111) was used. This was adjusted to the desired pH value and extracted with an equal volume of organic phase containing HPMTFP or a mixture of it and trioctylphosphine oxide (TOPO) or 2-thenoyltrifluoroacetone (HTTA). For interference studies, the solution containing the appropriate ion was first introduced before adjusting to pH 3.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of 0.02 M HPMTFP and its iron (III) complex species extracted from aqueous solution (pH 3) into chloroform are shown in Figure 1. The extracted iron(III) complex species exhibited a broad absorbence between 420 nm and 510 nm with a maximum absorbence at 480 nm. Figure 1 shows that HPMTFP does not absorb at 480 nm. Thus, all subsequent studies were carried out at 480 nm.

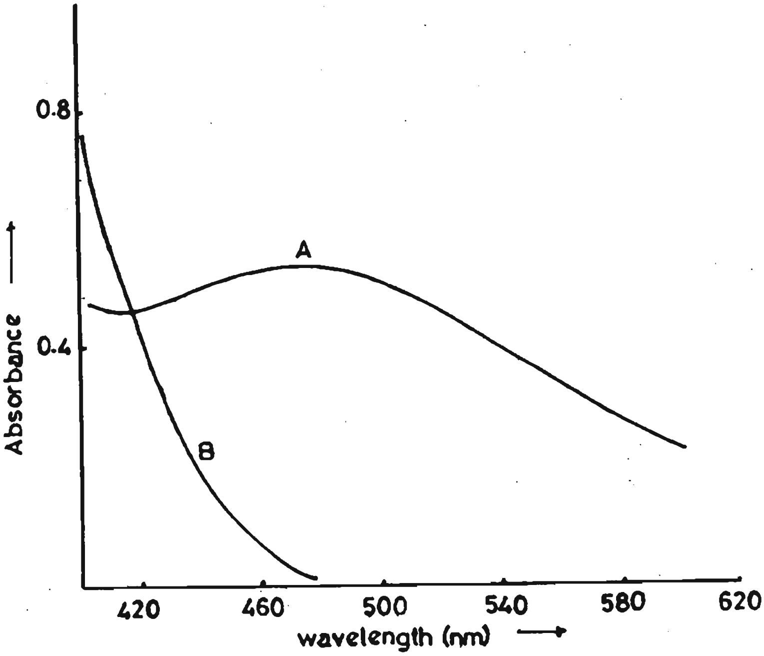

Figure 1: **Absorption spectra of HPMTFP and Iron(III) - PMTFP complex extracted into chloroform. Fe(III)$_{conc.}$ = 4 ppm; HPMTFP$_{conc.}$ = 0.02 M. A, Iron(III)-PMTFP complex extracted at pH 3; and B, reagent blank.**

Effects of experimental variables

pH : The effect of pH of the aqueous phase on the percentage extraction of Fe(III) into the organic phase containing one or two mixtures of chelating agents is shown in Figure 2. The absorbence is maximal and percentage extraction quantitative over the pH range 1.5 - 4.5 (curve C). Synergism is observed when the extraction regent is HPMTFP + TOPO (curve A) or HPMTFP + HTTA (curve B), resulting in quantitative extraction also occurring further down the pH value at 1.0 and 1.2 respectively,. Since the optimum pH range is 1.5 - 4.5 (curve C) all subsequent extraction studies with 0.02 M HPMTFP in chloroform were done with aqueous solution of pH 3 adjusted with acetate buffer.

Reagent concentration: A reagent concentration greater than 0.02 M HPMTFP did not alter the absorbence values. Enhancement of the colour intensity of the extracted complex species occurred when the organic phase contained 0.02 M HPMTFP + 10^{-3} M HTTA, while increase in the concentration of HTTA to 10^{-2} M in

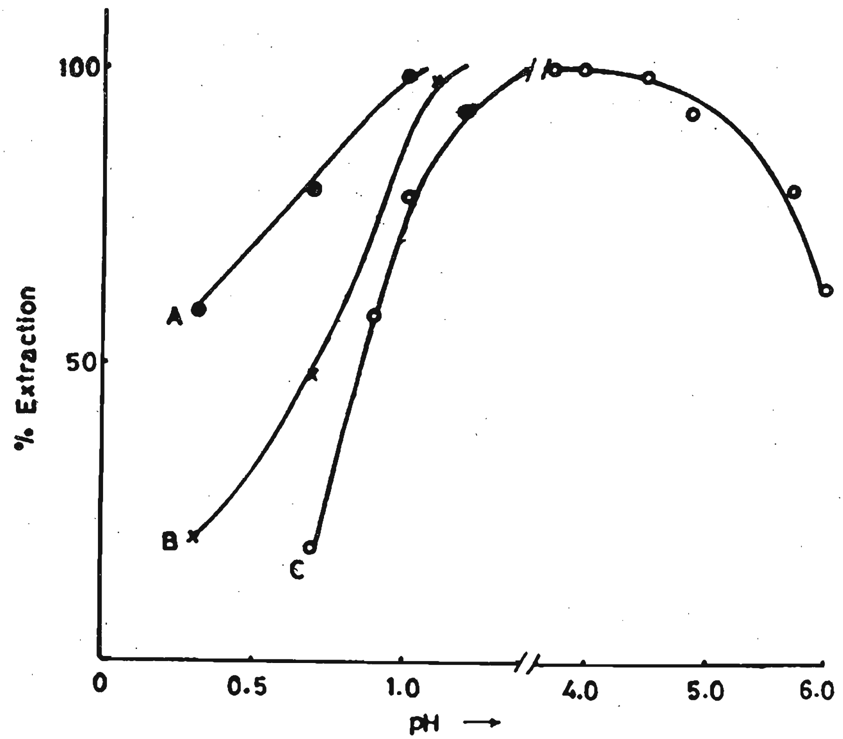

Figure 2: Extraction graphs of 6 ppm Fe(III) from different buffer solutions into chloroform solutions of: A, 0.02 M HPMTFP + 10^{-2} M TOPO; B, 0.02 M HPMTFP + 10^{-2} M HTTA; and C, 0.02 M HPMTFP.

the mixture has no effect on the colour intensity of the extracted complex species. However, increase in the concentration of TOPO from 10^{-3} M - 10^{-2} M in a mixture with 0.02 M HPMTFP showed a significant reduction in the colour suppression from increased TOPO concentration in the reagent mixture. Details of the sensitivity and molar absorptivities of the extracted complex species by the various reagent mixtures are given in Figure 3 and Table 1.

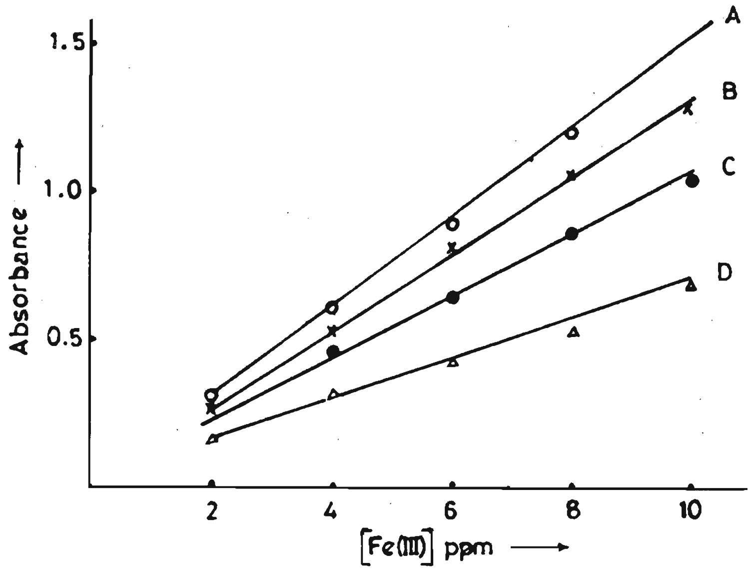

Figure 3: Plots of absorbance of extracted complex species in organic phase vs concentration of Fe(III) in aqueous phase (pH 3) extracted by the following organic reagents: A, 0.02 M HPMTFP + 10^{-3} M HTTA in chloroform; B, 0.02 M HPMTFP in chloroform; C, 0.02 M HPMTFP in MIBK; and D, 0.02 M HPMTFP + 10^{-2} M TOPO in chloroform.

Table 1 : Effects of various reagent concentrations and solvents on the intensity of extracted Fe(III) complex species : λ = 480 nm, pH = 3.

Solvent	Reagent	Molar absorptivity ε x 10^{-3} 1^{-1} mol. cm.	Beer's limit (ppm)
Chloroform	0.02 M HPMTFP	7.32 ± 0.08	1 - 10
"	0.02 M HPMTFP + 10^{-3} M HTTA	8.60 ± 0.19	1 - 9
"	0.02 M HPMTFP + 10^{-2} M HTTA	7.32 ± 0.08	1 - 10
"	0.02 M HPMTFP + 10^{-3} M TOPO	6.74 ± 0.14	1 - 10
"	0.02 M HPMTFP + 10^{-2} M TOPO	4.49 ± 0.11	1 - 12
MIBK	0.02 M HPMTFP	6.03 ± 0.22	1 - 10
Benzene	0.02 M HPMTFP	4.76 ± 0.17	1 - 12
Cyclohexanone	0.02 M HPMTFP	3.45 ± 0.09	2 - 15

Solvents: The use of different organic solvents was studied . The details of the molar absorptivitites of the extracted complex species in these various solvents are contained in Table 1. The Fe(III) complex is quantitatively extracted by benzene, methyl-isobutylketone (MIBK) and cyclohexanone but the colour of the extracted complex species compared is of slightly lower intensity in these solvent systems when compared to that of chloroform. The colour of the extracted complex species in these solvent systems is stable for days. In cyclohexanone the extracted complex species at low concentration appeared pale brown.

Stability of colour

The stability of the colour of the extracted complex species was studied at room temperature. The maximum absorbence of 0.805 ± 0.005 recorded for 6 ppm Fe(III) extracted into chloroform was measured at 1, 10, and 30 min and 1, 10, 24, 48 and 168 h after extraction. The colour of the extracted complex species was found to be stable for at least a period of one week.

Calibration range and sensitivity

Beer's law was obeyed up to 10 ppm of Fe(III) extracted into chloroform. The range increases slightly when solvents such as methyl isobutylketone, benzene or cyclohexanone are used. However, when these solvent systems are used the relative sensitivity also decreases slightly.

Tests for interference

The effects of various ions on the determination of iron(III) extracted into the organic phase were examined. This was carried out by introducing different amounts of ionic species to a 10 ml solution containing 60 μg of iron(III) at pH 3 and extracting with 10 ml of 0.02 M HPMTFP in chloroform. The absorbence of the extracted complex species was measured at 480 nm against reagent blank. The results are shown in Table 2.

Interferences observed from some metal ions came from colour reactions e.g., U^{6+}, Cr^{6+} or formation of emulsion with the extracted complex as was the case with Cu^{2+}. The interferences observed from some anions were as a result of masking of Fe(III) in the aqueous phase by these anions which are also complexing agents, e.g., EDTA and oxalate ions.

Table 2 : Determination of 6 ppm of iron(III) in the presence of diverse ions.

Ion	Amount of ion added (ppm)	Added as	Iron(III) found (ppm)	% Recovery
None	0	-	6.00	100.0
Ag^+	500	$AgNO_3$	5.91	98.5
K^+	500	KCl	6.00	100.0
Na^+	500	$NaNO_3$	5.96	99.3
Ba^{2+}	500	$BaNO_3$	5.86	97.7
Be^{2+}	500	$BeSO_4..4H_2O$	6.00	100.0
Ca^{2+}	500	$Ca(CH_3COO)_2$	5.97	99.5
Cd^{2+}	500	$Cd(NO_3)_2.4H_2O$	5.87	97.8
CO^{2+}	500	$Co(CH_3COO)_2.4H_2O$	6.00	100.0
Cu^{2+}	500	$Cu(ClO_4)_2.6H_2O$	11.70	195.0
"	100	"	8.70	137.0
"	50	"	7.05	117.5
"	20	"	6.21	103.5
Mg^{2+}	500	$Mg(ClO_4)_2$	5.94	99.0
Mn^{2+}	500	$MnSO_4.4H_2O$	5.85	97.5
Ni^{2+}	500	$Ni(NO_3)_2.6H_2O$	5.87	97.8
Pb^{2+}	500	$Pb(NO_3)_2$	5.90	98.3
Sr^{2+}	500	$Sr(CH_3COO)_2.½H_2O$	6.00	100.0
Zn^{2+}	500	$ZnCl_2$	5.91	98.5
Ce^{4+}	15	$Ce(SO_4)_2.4H_2O$	5.48	91.3
"	8	"	6.05	100.8
V^{4+}	500	$VOSO_4.H_2O$	7.20	120.0
"	300	"	6.10	101.7
V^{5+}	50	NH_4VO_3/H_2SO_4	6.66	111.0
"	20	"	6.05	100.8
Cr^{6+}	500	$K_2Cr_2O_7$	7.65	127.5
"	200	"	6.75	112.5
"	100	"	6.07	101.2

Table 2 Contd.

Ion	Amount of ion added (ppm)	Added as	Iron(III) found (ppm)	% Recovery
Mo^{6+}	15	$Na_2MoO_4.2H_2O$	5.42	90.3
"	8	"	5.90	98.3
W^{6+}	15	$Na_2WO_4.2H_2O$	5.05	84.2
"	8	"	5.92	98.7
U^{6+}	500	$UO_2(NO_3)_2.6H_2O$	10.21	170.2
"	100	"	7.05	117.5
"	50	"	5.98	99.6
F^-	200	NaF	5.90	98.3
PO_43-	200	Na_2HPO_4	5.93	98.8
EDTA	50	Na_2EDTA	0.00	00.0
"	5	"	5.11	85.2
"	1	"	5.78	96.3
Oxalate	50	$(NH_4)_2$oxalate	2.42	40.3
"	10	"	5.88	98.0

Analyses of water samples

The extraction and spectrophotometric procedures were applied to various water samples collected from Port Harcourt metropolis. Each of the sample was subjected to the following method of analysis. 100 ml of the sample in a beaker was evaporated to 10 ml using a heating mantle. After cooling, 20 ml of concentrated hydrochloric acid-nitric acid (3:1) mixture was added and the sample heated until digestion was completed. The residue was dissolved in 10 ml 0.1M HNO_3 . A 5 ml aliquot of this solution was pipetted into an extraction bottle, adjusted to pH 3 with acetate buffer solution and extracted with 5 ml of chloroform solution of 0.02 M HPMTFP. The determination was carried out three times and the results are shown in Table 3.

Table 3 : Analyses of water samples-May 90

Water sample source	Iron(III) (ppm) found by method	Iron(III) (ppm) found by AAS*
Aluu stream	0.29 ± 0.05	0.30
Aluu well	0.84 ± 0.07	0.88
Aluu bore hole	0.22 ± 0.03	0.21
Uni Port Delta Park tap	0.25 ± 0.01	0.22
Port Harcourt city tap	0.46 ± 0.01	0.47
New Calabar River	0.98 ± 0.05	1.01

* Atomic Absorption Spectrometry.

CONCLUSION

The 4-trifluoroacetyl-pyrazolone-5 derivative is more sensitive and superior to the 4-benzoyl-pyrazolone-5 derivative proposed by Rao and Arora.[5] The optimum pH range is also wider than the range obtained by Chmutova and Kochetkova[4] using the same 4-benzoyl-pyrazolone-5 for their studies. Compared to 0.1 M HPMBP used by these workers[4,5] HPMTFP has proved to be less expensive since 0.02 M of the ligand is more efficient and more sensitive when employed for the same purpose of extraction and spectrophotometric determination of iron(III) in aqueous media.

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References

1. Mirza M.Y. (1968). Carrier-free separation of ^{115m}In from irradiated Cd by solvent extraction with 1 - phenyl - 3 - methyl - 4 - caproylpyrazolone - 5. *Talanta* **15** : 137-140.

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

3. 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.

4. Chmutova M.K. & Kochetkova N.E. (1969). Extraction of iron(III) with 1-phenyl-3-methyl-4-benzoylpyrazolone-5. Separation of plutonium from iron. *Journal of Analytical Chemistry of the USSR*. **24**: 112-115.

5. Rao G.N. & Arora H.C. (1976). Extraction and spectrophotometric determination of iron(III) with 4-benzoyl-2, 4-dihydro-5-methyl-2-phenyl-^{3}H-pyrazol-3-one. *Microchemical Journal* **21**: 1-4.

6. Akama Y., Nakai T. & Kawamura F. (1981). Spectrophotometric determination of vanadium(V) using 4 - benzoyl - 3 - methyl - 1 - phenyl - 5 - pyrazolone. *Analyst*, **106**: 250-253.

7. Peshkova V.M., Khalitova A.I. & Mel'Chakova N.V. (1984). Determination of vanadium(V) with 1-phenyl-3-methyl-4-benzoyl-pyrazolone in aqueous ethanol medium. *Journal of Analytical Chemistry of the USSR* **39**: 1640-1644.

8. Shcherbakova S.A., Mel'Chakova N.V. & Peshkova V.M. (1976).Determination of vanadium(IV) and vanadium(V) in a vanadium catalyst using 1 - phenyl - 3 - methyl - 4 - benzoyl - pyrazolone. *Journal of Analytical Chemistry of the USSR* **31**: 318-322.