

ligand stretching modes for the different possible chromophores namely NiN_4 (T_d , D_{4h}), NiN_4O (C_{2v} , C_{4v}) and NiN_4O_2 (C_{2v} , D_{4h}) were derived by the method described by Cotton³ and on this basis the spectrum conforms to octahedral coordination to Ni(II) with the two H_2PO_4^- ions in the axial positions [D_{4h} , one $\nu_{\text{Ni-N}}$ (Eu) and one $\nu_{\text{Ni-O}}$ (A_{2u})]. The bands at 262 cm^{-1} (m) and 230 cm^{-1} (s) were attributed to Ni-O stretching⁴ and Ni-N stretching⁵ modes respectively. The spectral features of coordinated pyridine were similar to those for related complexes⁶. The absorption bands due to H_2PO_4^- were noticed at the following frequencies (cm^{-1}): 2850 (br,m), 2400 (br,m), 1250 (m), 1175 (vs), 1100 (s), 1050 (m), 958 (sh), 950 (s), 890 (m), 880 (sh), 850 (sh), 535 (sh), 525 (s), 505 (w), 400 (w), 385 (w) and 350 (w). These bands were shifted⁷ to different extents relative to those of non-coordinated H_2PO_4^- .

The electronic absorption spectrum of the complex showed five $d-d$ transition bands at $26,670\text{ cm}^{-1}$, $16,130\text{ cm}^{-1}$, $13,890\text{ cm}^{-1}$ (shoulder on the $16,130\text{ cm}^{-1}$ band), 8930 cm^{-1} (br) and $10,640\text{ cm}^{-1}$ (shoulder on the 8930 cm^{-1} band). The broad band at 8930 cm^{-1} showed a spike at 8416 cm^{-1} which is attributed to H_2PO_4^- (8405 cm^{-1} in KH_2PO_4). The spectrum of $\text{Ni}(\text{py})_4(\text{H}_2\text{PO}_4)_2$ is characteristic of trans-octahedral complexes like $\text{Ni}(\text{py})_4\text{X}_2$ ^{8,9} ($\text{X} = \text{Cl}, \text{Br}$ or I) thereby substantiating axial coordination of H_2PO_4^- ion as revealed by IR results. It appears from the electronic spectrum that the ligand field due to H_2PO_4^- is comparable to that of halide ions. The lack of solubility of the complex in organic solvents possibly indicates extensive intermolecular hydrogen bonding.

The magnetic moment of the complex (3.26 B.M.) is in the range expected for octahedral complexes¹⁰.

The IR spectrum of $\text{Cu}(\text{py})_2\text{Cl}_2 \cdot \text{O} \cdot \text{O} \cdot 5\text{H}_3\text{PO}_4$ in the region of $300-200\text{ cm}^{-1}$ (metal-nitrogen and metal-halogen stretching modes) was similar to that reported for $\text{Cu}(\text{py})_2\text{Cl}_2$ ¹¹ and therefore $\text{Cu}(\text{py})_2\text{Cl}_2 \cdot \text{O} \cdot \text{O} \cdot 5\text{H}_3\text{PO}_4$ is also very likely to have a chlorine-bridged distorted polymeric octahedral structure as for $\text{Cu}(\text{py})_2\text{Cl}_2$ ¹¹, with H_3PO_4 remaining uncoordinated in the lattice. The x-ray powder diffraction patterns of $\text{Cu}(\text{py})_2\text{Cl}_2 \cdot \text{O} \cdot \text{O} \cdot 5\text{H}_3\text{PO}_4$ and $\text{Cu}(\text{py})_2\text{Cl}_2$ were conspicuously different as expected. The room temperature magnetic moment of the complex (1.82 B.M.) is in the expected range¹⁰.

As no Cu(II) complexes with coordinated orthophosphate ion have been obtained in the present work, alternative routes should be explored to obtain such complexes.

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HYDRAZINE CARBOTHIOAMIDE, 2-[(4-HYDROXY-3-METHOXY PHENYL) METHYLENE], AS A SELECTIVE REAGENT FOR THE RAPID SPECTROPHOTOMETRIC DETERMINATION OF COBALT(II)

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GHUHA-SIRCAR *et al.*¹ have prepared hydrazine carbothioamide-2-[(4-hydroxy-3-methoxy phenyl) methylene], [HCHMM] and used as a colour reagent for a few metal ions in inorganic analysis. A survey of chemical literature shows that no attempt has been made to use HCHMM as spectrophotometric reagent for cobalt(II). The present investigation deals with the study of the colour reaction of HCHMM with cobalt(II) for the rapid spectrophotometric determination of cobalt(II). The proposed method offers the advantages of simplicity, rapidity, sensitivity and selectivity

for the determination of cobalt(II) at room temperature without the need for extraction.

A stock solution of cobalt(II) was prepared from AR grade cobaltous sulphate and standardised². HCHMM was prepared from hydrazine carbothioamide and vanillin³. A 0.3% solution of HCHMM was prepared in 85% ethanol. Beckman model DB spectrophotometer with 1 cm silica cells was used for absorbance measurements.

Procedure for the determination of cobalt

To a sample solution containing 1–50 μg of cobalt(II) was added 5 ml of ethanol, 3.5 ml of 0.3% HCHMM and 3 ml of 1 M sodium hydroxide. The solution was diluted to 25 ml with distilled water, and the absorbance was measured at 404 nm against the reagent blank. The amount of cobalt(II) was then deduced from the standard calibration curve.

HCHMM forms an yellow coloured complex with cobalt(II) instantaneously at room temperature in the alkaline medium. The optimum concentration of sodium hydroxide was found to be 0.06–0.25 M. The absorbance decreases above and below this range Co(II)-HCHMM complex is not studied in acid medium because of its low sensitivity and stability (<2 min). The effective ethanolic concentration has been found to be 24–76% (v/v). Below this range, turbidity is obtained and above 76% ethanol, the maximum colouration is not obtained due probably to the dissociation of the complex. A 32% ethanolic medium containing 0.12 M sodium hydroxide was conveniently chosen for all further investigations.

The maximum absorbance of cobalt-HCHMM complex in 0.12 M sodium hydroxide solution was found at 400–406 nm, where the reagent and cobalt(II) sulphate under similar conditions do not absorb appreciably around this wavelength. The effect of the reagent concentration was examined by measuring the absorbance at 404 nm of the solutions containing a known concentration of cobalt(II) and varying amounts of the reagent. A fifty-two-fold molar excess of the reagent over cobalt(II) is required to obtain maximum absorbance. There is appreciable change in the absorbance, if the order of addition of reagents is varied. The addition of the reagents should be in the order: cobalt(II), ethanol, HCHMM, sodium hydroxide and water. The complex is stable for two days. The absorbance readings remain constant in the temperature range 4–55°C. Above 55°C the absorbance gradually decreases.

Beer's law is valid over the concentration range 0.04–2 ppm of cobalt(II). The optimum concentration range evaluated by Ringbom's method is 0.2–1.9 ppm. The molar absorptivity is $1.95 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at

404 nm. According to Sandell's expression the sensitivity of the reaction is $3 \mu\text{g cm}^{-2}$. The precision of colorimetric measurement of pure cobalt solutions containing 0.4–1.8 μg of cobalt/ml was better than 1.5% (1s; $n=8$).

The equilibrium shift method⁴ and Asmus method⁵ indicate the formation of 1:1 complex between cobalt(II) and HCHMM with a log K value of 3.7 at 27°C. The ion-exchange experiments showed that cobalt(II)-HCHMM complex is cationic in nature.

Effect of Diverse ions:

In order to assess the possible analytical applications of cobalt(II)-HCHMM complex the effect of some ions which often accompany cobalt was studied by adding different amounts of the diverse ions. An error of 2% in absorbance readings was considered toler-

TABLE I

Amount of cobalt(II) taken, 1.0 ppm

Ion added	Tolerance limit (ppm)	Ion added	Tolerance limit (ppm)
Fluoride	6700	Copper(II)	31 ^a
Chloride	3400	Nickel(II)	14
Bromide	6800	Nickel(II)	18 ^c
Iodide	2400	Silver(I)	15
Nitrate	5600	Molybdenum (VI)	51
Sulphate	9000	Iron(III)	68
Phosphate	850	Iron(III)	109 ^b
Thiosulphate	4000	Bismuth(III)	18
Acetate	6300	Manganese(II)	21.5
Citrate	9600	Sodium(I)	6800
Oxalate	400	Potassium(I)	4700
Tartrate	7300	Tungston(VI)	1400
EDTA	132	Titanium(IV)	12
Palladium(II)	2	Vanadium(V)	90
Ruthenium(III)	3	Zinc(II)	12
Iridium(III)	10	Barium(II)	4
Rhodium(III)	5	Mercury(II)	20
Rhodium(III)	8 ^b	Chromium(VI)	16
Osmium(VIII)	16	Chromium(III)	89
Osmium(VI)	1	Tin(II)	140
Platinum(IV)	8	Magnesium(II)	48
Gold(III)	13	Lead(II)	136
Copper(II)	20	Aluminium(III)	48
		Arsenic(III)	42

^a citrate; ^b tartrate; ^c phosphate.

able. The tolerance limits given in table I show that many cations and anions do not interfere in the determination of cobalt(II). The interference of certain metals can be reduced by using tartrate, citrate, and phosphate as masking agents.

The sensitivity of HCHMM is more than that of Bis (thiosalicylidene) ethyldiamine⁶, 5-chloro-7-iodo-8-quinolinol⁷, 1-naphthamide oxime⁸, ferrozine⁹, sulphosalicylic acid¹⁰ which have been proposed as sensitive spectrophotometric reagents for cobalt.

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OSCILLATORY REACTION UNRAVELLED BY A NOVEL DIAGNOSTIC APPROACH

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OSCILLATIONS in the acid-bromate system involving Mn(II), Ce(III) or Fe(II) ions (Belousov-Zhabotinskii or B-Z reaction) have been reported¹⁻³ with different organic substrates. The iodate-hydrogen peroxide system with Mn(II) (Briggs-Rauscher or B-R reaction)^{4,5} is known to oscillate with only a few organic substrates. Uncatalysed bromate oscillations (UBO)

have been observed in many instances; however the species causing oscillations have hitherto evaded identification^{6,7}.

The results obtained in the acid-bromate-pyrogallol system with and without the inclusion of [iron($\alpha\alpha'$ -bipyridyl)₃]²⁺ provides valuable information regarding the species responsible for the oscillations in these systems. The course of the oscillatory reaction is followed by keeping all the other constituents, except one, well-stirred and thermostated in a polythene beaker. The platinum and/or Ag/AgBr electrode immersed in the solution is coupled to a saturated calomel electrode through a salt bridge and connected to a *x-t* recorder for a continuous follow-up of the reaction. The addition of the thermostated last constituent triggers off the oscillation.

The uncatalysed pyrogallol system yields oscillations of large amplitude (about 400 mV) in the range 0.6 to 1V (vs SCE) (figure 1). The spectrophotometric follow up at 390 nm as well as the simultaneous recordings obtained with a platinum and Ag/AgBr electrode establish that at the peak [Br₂] = 10⁻⁴M and

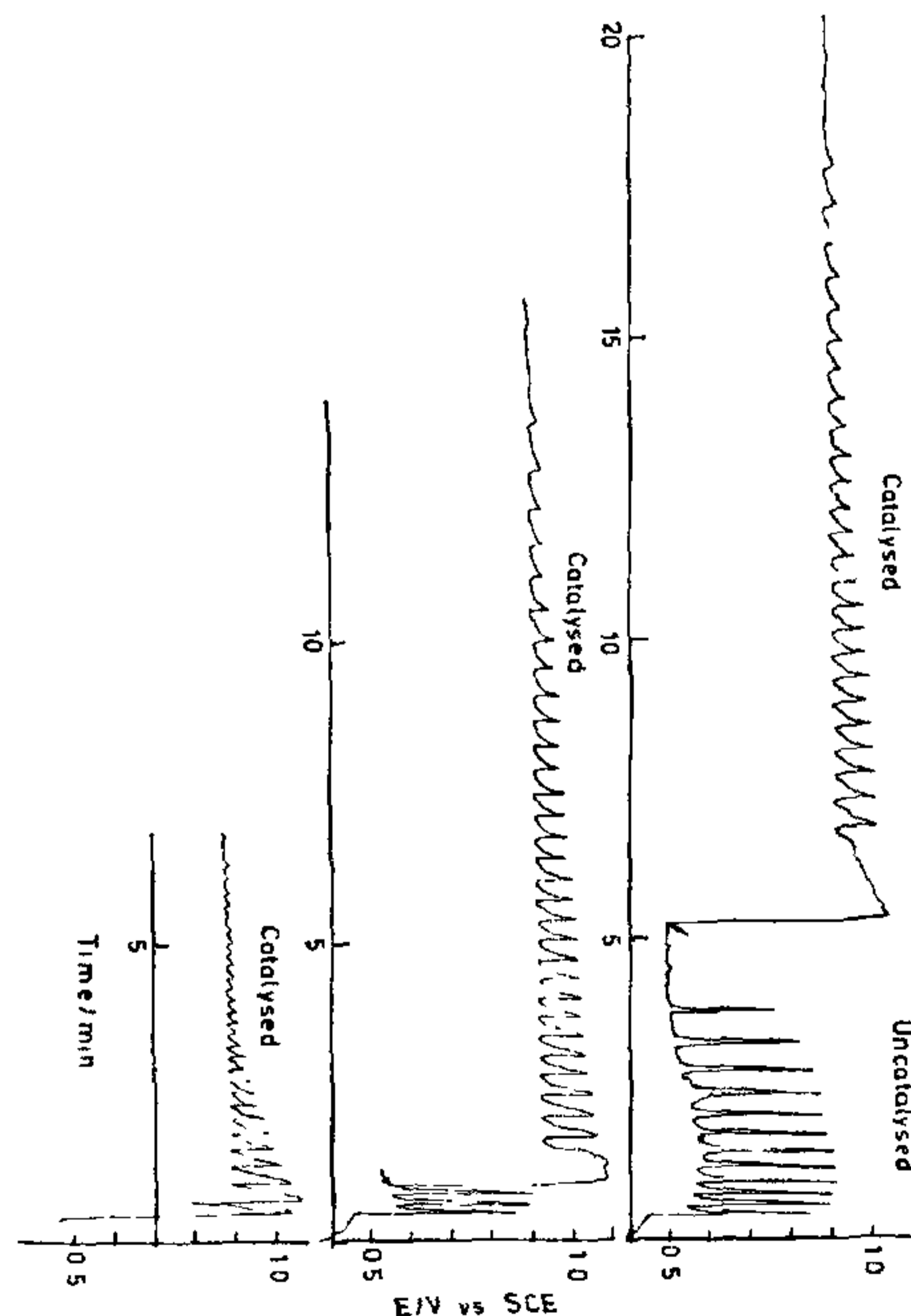


Figure 1. Oscillations in the pyrogallol-bromate system with [iron($\alpha\alpha'$ -bipyridyl)₃]²⁺ = 0.002 M PG = 0.05 M; H₂SO₄ = 2 M; KBrO₃ = 0.1 M Temperature = 30° C.