

Polarographic determination of Cr (VI) in Environmental samples using Catalytic hydrogen currents

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Abstract: - A sensitive polarographic method for the determination of Chromium is proposed, based on the catalytic hydrogen wave of Cr (VI) - xanthate complexes in the presence of NH_4Cl at mercury electrode. The Cr(VI)-xanthate complexes produce a catalytic hydrogen wave at -1.48 V vs SCE with potassium octyl xanthate (Koxan) and at -1.60 V vs SCE with potassium secondary butyl xanthate (Ksbxan) in $\text{NH}_4\text{Cl-NH}_4\text{OH}$ medium (pH 9.0 for Koxan and 8.5 for Ksbxan). The peak height is proportional to metal ion concentration. The proposed method is free of interference from other metal ions except for Mo (VI), and is evaluated to micro level Cr (VI) down to 0.2 ppm by the determination of Chromium content in drinking water samples, industrial effluents, tannery waste water and agricultural materials.

Keywords: - polarographic catalytic hydrogen wave, Cr (VI), Potassium octyl xanthate, Potassium secondary butyl xanthate, Environmental samples.

I. Introduction

Chromium is one the essential trace metal nutrient for animals and man. The tolerance limits of chromium contents according to US Public Health Service is 0.05 mg/L for drinking water and 2.1 mg/L for industrial effluents discharged into sewages. Chromium metal and Cr (III) are relatively nontoxic [1-3] where as water soluble chromium (VI) is extremely irritating and toxic to human body tissue [4-5]. In tannery industries severe environmental contamination [6-7], the corrosive active hexavalent chromium induces chronic ulcers in workers and cancer of the nose and lungs [8] among the workers is also reported. To assess the environmental hazards of chromium (VI) and the quality of water, methods capable of determining chromium in water are needed. In the present study a simple, sensitive, selective and rapid procedure for the determination of chromium in water and agriculture samples using potassium octyl xanthate, potassium secondary butyl xanthate as reagents by simple d.c. polarographic technique is developed.

Chromium gives catalytic currents at mercury electrode in the presence of organic reagents such as amines and arsines. The chromium (VI) and (III) content in water samples has been studied by polarographic catalytic waves using the system, ethylene diamine-sodium nitrate at pH 8 [9]. Chromium in mineral samples estimated by Chou and Pao [10] using N-nitrosophenyl-hydroxyl amine-ammonium chloride-ammonium hydroxide medium. The adsorption of the reduced form of the complex of chromium with As (III) in ammonium or borate buffer was found to give a catalytic hydrogen wave in d.c. polarography and was used for the determination of chromium at concentrations as low as 10^{-8}M [11]. The chromium content of clays and ores was determined by the catalytic wave of chromium in an electrolyte solution of sodium nitrate -O-phenanthroline-ammonium chloride-ammonium hydroxide at pH 9.3 [12]. Lin et al. [13] reported the study of traces of chromium in sea water using ethylene diamine- NaNO_2 -EDTA system. The chromium (VI) content in water samples is estimated by Su et al. [14] using ammonium acetate - cupferron at pH 6-6.5. The mechanism of the catalytic wave of chromium in 1, 10-phenanthroline-nitrite -ammonium chloride-ammonia medium at pH 9.4 was explained by Han et al. [15]. Trace amounts of Cr(VI) in steel and water was determined by using a catalytic polarographic method of O-phen- NaNO_2 - CTAB [16].

Catalytic hydrogen waves are due to the presence in the solution of certain catalytic substances, which contribute to the evolution of molecular hydrogen on the mercury electrode with simultaneous consumption of hydrogen ions. These waves are observed at less negative potentials than the usual waves of hydrogen discharge in the same solution. In addition to having considerable theoretical significance, the catalytic hydrogen wave is of great practical interest because it has a higher analytical sensitivity than other polarographic catalytic waves.

The catalytic hydrogen waves of oraganic thio compounds in the presence of Cr(VI) and Cr(III) at DME have been reported for the first time from these laboratories [17-21]. An attempt has been made with Potassium octyl xanthate (Koxan) and Potassium secondary butyl xanthate (Ksbxan) and found to give catalytic hydrogen currents in the potential range -1.48 and -1.60 V vs. SCE with Cr(VI) in $\text{NH}_4\text{Cl-NH}_4\text{OH}$ medium at

the pH 9.0 and 8.5 respectively (Fig 1&2). The quantitative experimental conditions have therefore been developed, the details of which are shown in Table 1.

II. Experimental

2.1 Reagents

All chemicals used are of analytical reagent grade unless specified other wise. The solutions are prepared in double distilled water and diluted to required strength. 5% NH₄OH and 1% HCl are used for pH adjustments. Gelatin and Triton X-100 are prepared and diluted as per requirement.

Koxan and Ksbxan are prepared and recrystallized according to standard procedures reported [22-25]. Water samples are preconcentrated by evaporation and standard addition method is used for analysis. Dry ash method [26] is used for agricultural products for preparation of the sample solutions.

2.2 Apparatus

The equipment used is d.c. Polarograph model CL-357 coupled with model LR-101 P strip chart recorder supplied by Elico Private Limited (Hyderabad, India).

The pH measurements are made by using pH meter; model LI-120(Elico Private Limited) with glass electrode of pH range 0-13.

The temperature is maintained at $25 \pm 0.2^\circ$ C and the flow of mercury at 2.5 seconds per drop.

2.3. Preparation of Cr (VI) of real samples

2.3.1. Drinking water samples

One liter of the samples collected from Kalyani Dam, Bore wells and Kapilatheertham water falls (Tirupati, Chittoor District, India) are preconcentrated to 100ml.

2.3.2. Industrial effluents

One liter of the industrial effluents collected from Upper India Steel Limited and Pioneer Alloy Castings Limited, Gajulamandyam Industrial Estate, near Tirupati Town, Chittoor District, India and tannery waste water from SKS Industries Limited, Chrompet, Chennai, India are preconcentrated to 100ml.

2.3.3. Agricultural material

10g of *Oryza sativa* sample (Unpolished rice) and 5g of piper betle (Betle leaves) collected from Tirupati Town, Chittoor District are digested by dry ash method and brought into solution (10g Unpolished rice/25 ml and 5g of betle leaves/500 ml triple distilled water).

Aliquots of the above solution are taken in a beaker and the quantitative experimental conditions are maintained as already mentioned in the Table 1. The precipitates of metal xanthates given by interfering metal ions are filtered off and the filtrate is polarographed after deaeration. The results are presented in Table 2 to 4.

The standard addition method is used for the analysis of chromium content in all the samples. These results are further supported by the values obtained using atomic absorption spectrophotometric method.

III. Results and discussion

The catalytic hydrogen waves of Cr (VI) are recorded in neutral and alkaline media such as NH₄Cl – NH₄OH, KH₂ PO₄ sodium tetraborate, HOAc-NaOAc, sodium citrate- HCl and tartaric acid–sodium tartarate supporting electrolytes containing xanthates as the ligands. The current of the catalytic hydrogen wave in NH₄Cl – NH₄OH supporting electrolyte is about twice that in other reported media. 0.4 M and 0.8 M NH₄Cl – NH₄OH supporting electrolyte is therefore selected respectively, for detailed study.

3.1. Effect of pH

Maintaining the concentration of metal ion (3.4 ppm) and xanthates concentration constant (3.4 mM of Koxan and 2.8 mM of Ksbxan) in 0.4M and 0.8 M ammonium chloride, pH is varied from 6.5 to 10.0 adjusting with NH₄OH/HCl. The heights of the catalytic wave increased pH gradually up to 9.0 for Koxan and 8.5 for Ksbxan and decreased beyond these values. The peak potential is also shifted towards negative value with increase in pH. Therefore, pH 9.0 for Koxan and 8.5 for Ksbxan are fixed as quantitative parameters.

3.2. Effect of supporting electrolyte concentration

With an increase in the concentration of ammonium chloride from 0.05 to 1.0 M at pH values selected above the height of the chromium(VI) wave is found to increase up to a certain value (0.4 M for Koxan and 0.8 M for Ksbxan). With further increase in NH₄Cl the wave height decreased and therefore, 0.4 M and 0.8 M NH₄Cl was maintained for respective xanthates for further studies.

The peak potential of the catalytic wave shifted towards less negative potentials with increase in NH₄Cl throughout the concentration range of NH₄Cl studied.

3.3. Effect of reagent concentration

The concentration of xanthates was varied from 0.2 to 4.0 mM keeping the metal ion at 3.4 ppm and ammonium chloride at 0.4 M at respective pH values selected earlier. For two xanthates the catalytic current peak height is maximum with xanthate concentration of 3.4mM of koxan and 2.8mM of ksbxan xanthates and independent beyond this concentration could be indicate that the complexes obtain stabilized. The peak potential of the catalytic wave shifted towards more negative values on increasing the xanthate concentrations up to optimum concentrations 3.4mM of koxan and 2.8mM of ksbxan xanthates. The peak current is not varied linearly with all concentrations of ligand which is a characteristic nature of catalytic waves.

Plot of $\{[Xan] / i_p\}$ vs $[Xan]$ is a straight line (Fig.2) confirming the adsorption behavior in the electrode reaction process [27].

3.4. Supporting evidence of catalytic hydrogen waves

The catalytic behavior of chromium-xanthate systems are further supported by the effect of mercury column height on the peak current and temperature coefficient values. The catalytic current as well as i_c / \sqrt{h} decreased with the increase of the mercury column indicating that the current is catalytic in nature. The diminishing of the wave height increased with increase in temperature and temperature coefficient values decreased gradually from 15 to 30°C (data not shown).

The surfactant like gelatin suppresses the catalytic wave sharply up to 0.01% and by about 2% beyond and up to maximum permissible concentrations. The suppression with Triton X-100 is small when compared to gelatin. The peak potential shifted towards less negative potentials in both cases. It could be shows that the wave is of catalytic in nature and adsorption involved in these waves.

3.5. Effect of metal ion on peak current

The peak current increased proportionally with Cr (VI) concentration in the range of 0.1 to 3.4 ppm in for both xanthates. However, the sensitivity of the method is more with Koxan compared to Ksbxan because of strong complex of Cr (VI) with Koxan and therefore increased catalytic activity [28]. (Fig 3)

The linear relationship between metal ion concentration and the catalytic current suggests that the method can be used successfully to determine trace amounts of Cr (VI) in environmental samples.

3.6. Interference studies

Most of the transition metal ions do not interfere with catalytic wave of Cr (VI) under the conditions developed and Ni (II) gets precipitated which can be removed by filtration. The only metal ion, Mo (VI) interferes seriously by increasing the wave height of Cr (VI). Anions such as carbonate and EDTA interfere by completely suppressing the chromium catalytic wave, where as nitrite and nitrate interfere as they also give catalytic current with Cr (VI).

3.7. Effect of indifferent cations

The effect of neutral salts on the chromium-xanthate systems is studied using lithium, sodium, potassium and calcium chlorides. With increase in concentration of chlorides the wave height decreased continuously and the decrease is less with sodium chloride to that of potassium chloride. The decrease in wave height is more for lithium chloride and much more for calcium chloride indicating that Cr (VI) xanthate complexes have adsorption properties on mercury electrode use of platinum. The peak potential is shifted towards less negative potentials with all cations of the neutral salts used.

3.8. Electrocapillary curves

The presence of xanthates in NH_4Cl solution shifted the electrocapillary maximum to more negative value and the electrocapillary curve is suppressed on the positive side of the electrocapillary maximum indicating that adsorption is involved in the reaction process (Fig 4).

3.9. Application of the catalytic method to real samples

The developed method is applied to the analysis of trace quantities of chromium in drinking water samples, industrial effluents, tannery waste water and agricultural materials.

The results in Table 2 show that the drinking water drawn from bore wells and supplied to Tirupati town by Municipality from Kalyani Dam is free from chromium content. Though the water from the water falls of Kapilatheertham of Tirupati Town Table 3 is found to have traces of chromium it is within the tolerance limits. Chromium (VI) detected from the industrial effluent, Table 4 indicates that the metal is present in trace levels and therefore, does not cause any hazards to the environment through the waste water that is discharged into public sewers. The chromium levels analyzed in agricultural samples (Table 5) are in agreement

with the reported values [29]. The results obtained using two ligands are in good agreement with atomic absorption spectrophotometric values.

The method reported here may therefore, be successfully applied for the determination of traces of chromium in water samples, industrial effluents and agricultural materials without interference from other transition metal ions excepting molybdenum.

IV. Conclusions

The result of this investigation shows that Cr (VI) gives catalytic hydrogen waves in the presence of xanthate at DME due to chromium–xanthate complex formation. The linear dependence of the current on the pH and ligand concentration upto certain values shows that the waves are catalytic in nature due to chromium complexes with the xanthates and adsorption of complexes are responsible for catalytic currents. The effect of height of the mercury reservoir and temperature coefficient values is also indicative of catalytic nature of the complexes. Further support of adsorption is indicated by the Langmuir adsorption isotherm curve.

Yet another support for the idea about participation of adsorption of the catalytic metal-xanthate complexes in catalytic hydrogen waves is seen with the decrease of the height of the peak current with indifferent electrolytes and from the shape of the electrocapillary curves [30].

From the results obtained for Cr (VI)–xanthate complex study it may be concluded that the procedure developed for the determination of Cr (VI) using the catalytic hydrogen waves at DME in the presence of Koxan and Ksbxan is selective without much interferences due to other metal ions except Mo (VI). The method is also sensitive with the lowest detection limit of 0.1 ppm, rapid and specific compared to diffusion current of Cr (VI) in classical polarography.

Table 1: Quantitative Experimental Conditions for Cr (VI) Determination through Catalytic Hydrogen Waves

Conditions	Koxan	Ksbxan
pH	9.0	8.5
NH ₄ Cl, M	0.4	0.8
Xanthate, mM	3.4	2.8
Chromium(VI), ppm	0.1-3.4	0.1-3.4

Table 2: Determination of Cr (VI) in water samples of Tirupati town

Sample	S.No	Cr(VI)added, ppm	Koxan		Ksbxan		AAS Method	
			Cr(VI) found, ppm	%Recovery	Cr(VI) found, ppm	%Recovery	Cr(VI) found, ppm	%Recovery
Kalyani Dam	1	0.80	0.80	100.00	0.80	100.00	0.80	100.00
	2	1.00	0.98	98.00	1.00	100.00	0.98	98.00
	3	1.20	1.20	100.00	1.18	98.33	1.20	100.00
	4	1.40	1.38	98.57	1.38	98.59	1.40	100.00
	5	1.50	1.50	100.00	1.50	100.00	1.49	99.33
			Average	99.31%	Average	99.38%	Average	99.46%
Bore well	1	0.80	0.80	100.00	0.80	100.00	0.80	100.00
	2	1.00	0.98	98.00	0.98	98.00	0.98	98.00
	3	1.20	1.19	99.16	1.19	99.16	1.20	100.00
	4	1.40	1.38	98.57	1.40	100.00	1.38	98.57
	5	1.50	1.50	100.00	1.48	98.66	1.49	99.33
			Average	99.15%	Average	99.16%	Average	99.18%

Table 3: Determination of Chromium (VI) in Water Samples

Sample* / xanthate		Cr(VI), ppm		Cr(VI) in the sample, ppm	
		Added	Total found**	Catalytic method	AAS method
Kapilatheertham water falls	a	0.5	0.88	7.60	7.68
	b	0.5	0.87	7.40	

* 5 ml of the concentrated sample is used.

** Average of five individual determinations.

Table 4: Determination of Chromium (VI) in industrial effluents

Sample* / xanthate		Cr(VI), ppm		Cr(VI) in the sample, ppm	
		Added	Total found**	Catalytic method	AAS method
I .Upper India limited	a	1.0	1.625	12.48	12.50
	b	1.0	1.625	12.50	
II Pioneer Alloy Castings limited	a	1.0	1.451	9.02	9.00
	b	1.0	1.451	9.02	
III S.K.S Industries limited	a	0.5	2.000	150.00	150.00
	b	0.5	1.982	148.20	

* 5 ml (I, II) and 1 ml (III) of the sample is used.

** Average of five individual determinations.

Table 5: Determination of Chromium (VI) in Agricultural materials

Sample* / xanthate		Cr(VI), ppm		Cr(VI) in the sample, ppm	
		Added	Total found**	Catalytic method	AAS method
I Oryza sativa (Unpolished rice)	a	1.0	1.056	0.14	0.145
	b	1.0	1.052	0.13	
II Piper betle (Betle leaves)	a	0.5	1.793	1292.00	1290.00
	b	0.5	1.790	1290.00	

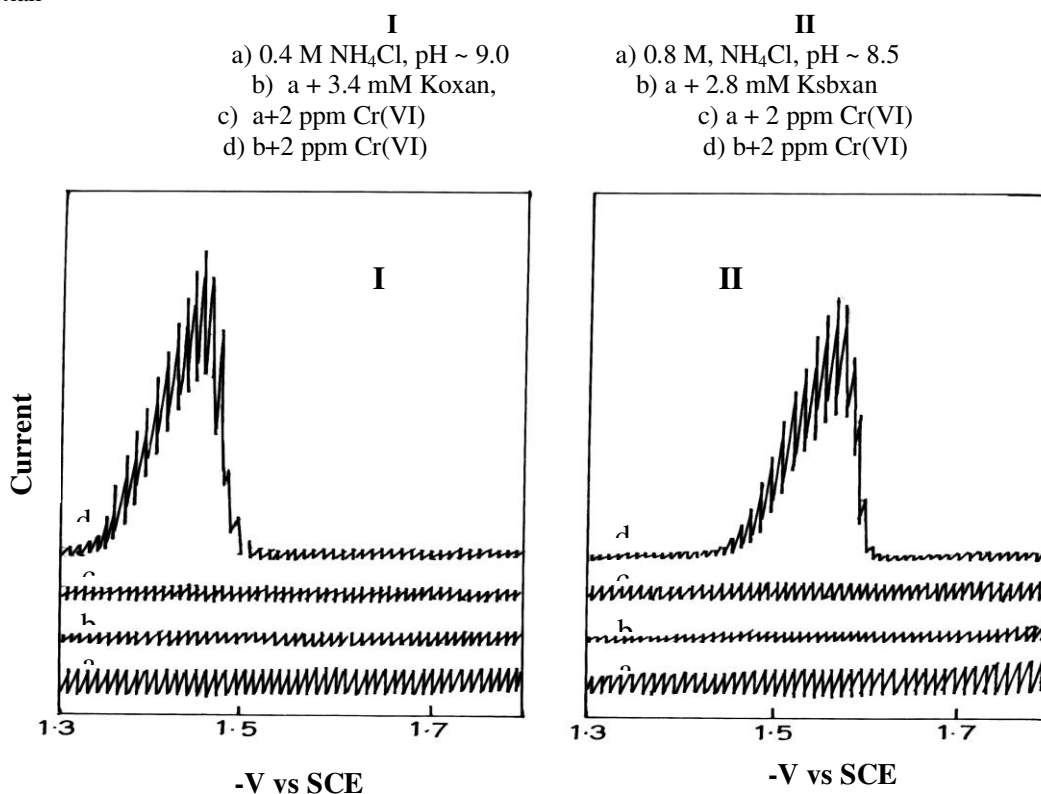
* 1.0 ml (I,II) of the sample is used.

** Average of five individual determinations.

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Fig. 1: Polarographic curves of Chromium(IV) in $\text{NH}_4\text{Cl} - \text{NH}_4\text{OH}$ medium in the presence of Koxan and Ksbxan



Current, μA

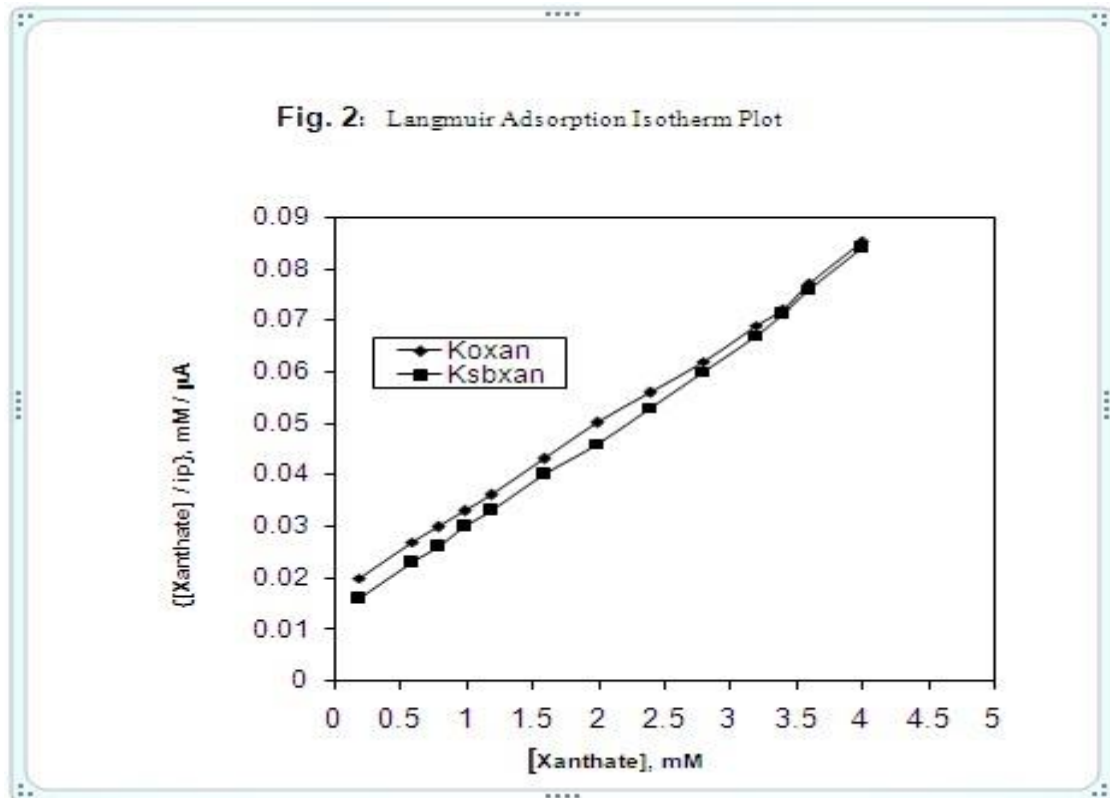


Fig. 3: Effect of Chromium (VI) on Peak Current

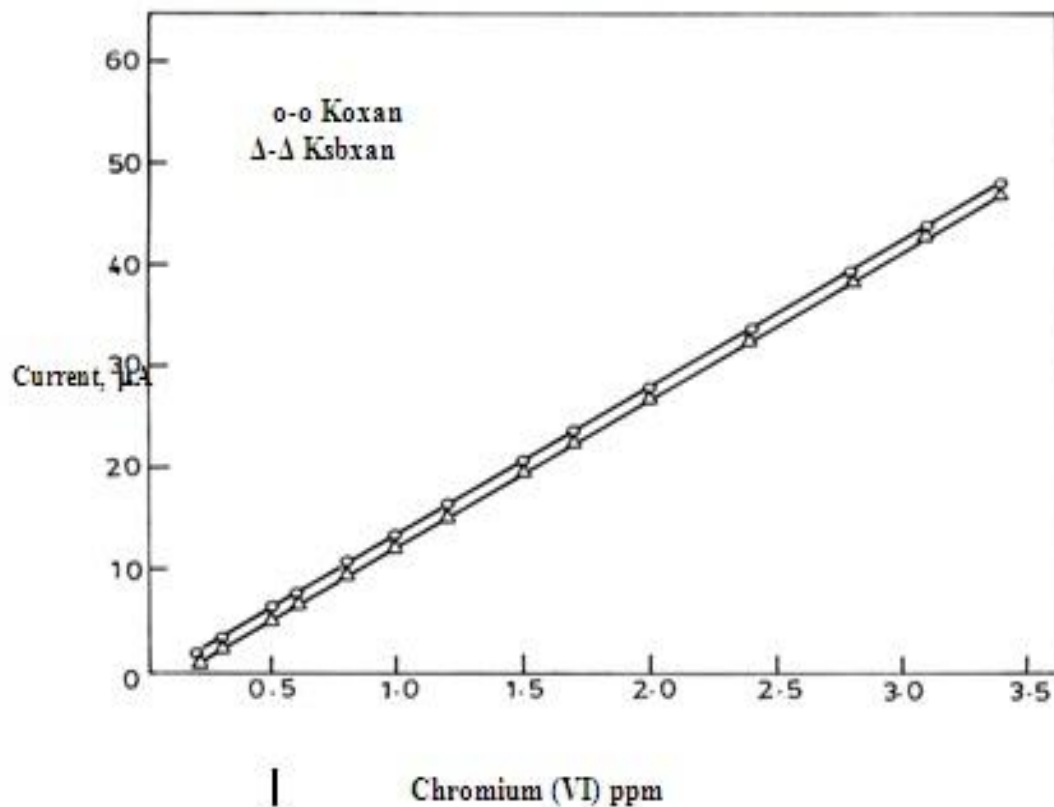


Fig.4: Electrocapillary Curves

