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Sensitive determination of Cr(VI) in environmental samples using catalytic hydrogen currents at DME

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ABSTRACT

Novel, robustic, simple, mobile and inexpensive method developed for determination of Chromium in milk and water samples with three novel and facile ligands potassium allyl xanthate, potassium isoamyl xanthate and potassium cinamyl xanthate in presence of NH_4Cl*-*NH_4OH *at pH 8.2 for Kaxan/Kixan and 8.6 for Kcxan. The ligands produce catalytic hydrogen currents with Chromium at peak potential -1.48 V vs SCE with Kaxan/Kixan and -1.5 V vs SCE with Kcxan. In this paper, several experimental parameters have influence on the catalytic hydrogen wave, which are study to optimize the experimental parameters for determination chromium ion and this method was compared with AAS method.*

Key Words: D. C. Polarography, Ligands, Catalytic hydrogen wave, milk and water samples.

INTRODUCTION

Chromium is found throughout the environment in 3 major oxidation states: Chromium(0), Chromium(III) and Chromium(VI) [1].The most stable form, Chromium(III) occur in naturally in the environment, while Chromium(VI) and Chromium(0) are generally produced by industrial process [2]. Chromium(VI) is known to be a strong oxidizing agent. The trivalent and hexavalent states of Chromium are the most biologically significant. Chromium(VI) compounds toxicity derives from it's ability to diffuse through cell membrane and oxidize biological molecule [3]. Chromium in biological tissues is almost always trivalent and helps to maintain the normal metabolism of glucose, protein and fat [2,4]. Chromium(VI) is highly toxic to human and animals due to carcinogenic and mutagenic properties [2]. Chromium compounds that are inhaled have been linked with lung cancer, while those ingested cause kidney and liver damage [5].

Toxicity of Chromium to plants depends on its valence state. Chromium(VI) is highly toxic and mobile, Chromium(III) is less toxic. Chromium also causes deleterious effect on plant physiological process such as photosynthesis, water relations and mineral nutrition [6].

It is known that an increase in the content of Chromium in soil makes them infertile and that the toxic effect depends on the oxidation state of Chromium. On the other hand, the introduction of Chromium salts in to soils has been some positive effects due to oxidation of some bio-chemical processes [7].

Milk is a complex, bioactive substance, optimal source of nutrition to promote proper growth and development of infant mammals. In fact milk is ideal source for micro, macro elements and can be found even heavy metals [8].

Varieties of minerals are essential for health, especially during growth and old age and deficiencies and/or may results in metabolic irregularities and pathological changes. Chromium was essential trace elements in human nutrition, for this reason, toxic elements need to be detected, measured and adequate concentrations of essential elements ensured. Hence the determination of Chromium in environmental and biological samples is great importance.

There are many sensitive techniques for Chromium determination such as ICP-MS [9-11], ICP-AES [13], adsorbtion [14], NAA [15,16], UV-Visible [12-16], degradation by photocatalyst [17] and AAS [18-19]. More over such techniques are not available in many laboratories. Because, of cost the above instruments the researchers are interested in voltametric techniques. Voltametry is applied in the present work in view the low cost, high sensitivity, mobile, rapid and easy to measure facilities.

MATERIALS AND METHODS

Reagents

All the metal salts used were of AR reagent grade. The stock solutions of Chromium(0.01M) in triple distilled water are prepared from accurately weight potassium chromate and diluted to required strength. Kaxan/Kixan/Kcxan is prepared according to method described by Keskyula [20] and 0.01M solutions are prepared by double distilled water. 5% NH_4OH and 1%HCl was used for pH adjustments. Gelatin and TX-100 solutions was prepared in W/V basis and diluted as per requirement.

Apparatus

Polarograms are recorded at 25 ±0.2^{0}C using Elico recording D.C.polarograph model CL-357. pH measurements are made with a LI-120 pH meter (Elico Pvt.Ltd, India).

RESULTS AND DISCUSSION

Factors affecting the catalytic hydrogen currents

Several factors influence the catalytic peak such as effect of pH, effect of supporting electrolyte and its concentrations, effect of reagent concentration, effect of metal ion concentration, mercury column height, temperature, suppressing agents and interfering ions.

Selection of supporting electrolyte

Preliminary experiments were conducted with few types of supporting electrolytes. The peak current and shape of the catalytic hydrogen peak are improved in the presence of ammonium chloride and therefore, ammonium chloride is used as a supporting electrolyte in the present method for all three xanthates.

Optimization of the experimental parameters

Effect of pH

The effect of pH on the catalytic peak is studied by recording the polarograms at various pH values (6.0 to 10.0) keeping Cr(VI) ion at 3.0 ppm and xanthate concentration constant (2.8 mM of Kaxan/Kiaxan and 3.0 mM Kcxan) in ammonium chloride (0.3M for Kaxan/Kiaxan and 0.4M for Kcxan respectively and adjusting the pH with NH_4OH. The pH where the catalytic wave height is maximum and well defined is selected as optimum pH. These valves are 8.2 for Kaxan/Kixan and for Kcxan. At higher pH values the peak height is diminished and peak potential is shifted to negative values.

Effect of Supporting Electrolyte Concentration

The wave height increases up to 0.3M NH_4Cl for Kaxan/Kixan and 0.4M NH_4Cl for Kcxan at pH at fixed metal ion 3.0 ppm Cr(VI), 2.8 mM Kaxan/Kixan and 3.0mM Kcxan at pH 8.2 for Kaxan/Kixan and 8.6 for Kcxan and decreased beyond this concentration for all xanthates. The peak potential is shifted considerably to words less negative potential with increase in NH_4Cl concentration.

Effect of Reagent Concentration

The wave heights obtained at 2.8 mM Kaxan/Kiaxan and at 3.0 mM Kcxan, are maximum, at 3.0 ppm of Cr(VI) in 0.3M (for Kaxan and Kiaxan) and 0.4M (for Kcxan) NH_4Cl supporting electrolyte at pH 8.2 for Kaxan/Kiaxan and 8.6 for Kcxan.

The potential of the peak shifted towards more negative potentials on increasing the xanthate concentration. The variation of the wave height as a function of xanthate concentration is not linear but tends to a limiting value at higher concentration of xanthate which is a typical of catalytic wave [21]. The shapes of the waves are indicative of adsorption [21-23].

The non-linear portion has the shape of a curve resembling a Langmuir adsorption isotherm, and the plot of {[Xanthate]/ip} vs [Xanthate] is a straight line obtained. The relationship shows the involvement of adsorption process in the electrode mechanism [23].

Effect of Mercury Pressure

Polarograms of 3.0 ppm Cr(VI) in 0.3M NH_4Cl at pH~8.2 for 2.8 mM Kaxan/Kiaxan and 0.4M NH_4Cl at pH~8.6 for 3.0 mM Kcxan are studied at different mercury column heights. The wave height decreased slightly with increase in height of the mercury column and $i_C/\sqrt{h}$ also decreased. The diminishing of the wave height with the increase of the height of the mercury reservoir is characteristic of catalytic hydrogen waves [24].

Effect of Maximum Suppressor

The catalytic wave height is reduced by 19% by the addition of 0.005% gelatin and above this it decreases slightly. The catalytic wave reduced 10% by addition of 0.002% TX-100 and above this concentration of TX-100 the current decreased very slightly in case of all three xanthates. The peak potential shifted towards less negative potentials in all cases. This shows that the wave is of catalytic in nature and adsorption is involved in these waves [25-26].

Effect of Temperature

The catalytic wave height increased with increase in temperature and the temperature coefficient values decrease with increase in temperature up to 30°C and iC becomes temperature independent beyond 30°C [22].

Effect of Cr(VI) on peak current

Maintaining all the conditions previously selected, the concentration of chromium is varied and the sensitivity is tested. The peak current increased proportionally with the concentration of Cr(VI) in the range of 0.1 to 4.5 ppm for all three xanthates. The linear relationship obtained between the catalytic current and metal ion concentration within a limited range as is expected with catalytic currents [21] show that the determination of the microgram quantities of Cr(VI) in unknown samples using xanthates as complexing agents is possible.

Effect of Foreign Ions

Co(II) is oxidized to Co(III) by atmospheric oxygen before oxygen is removed by the passage of nitrogen and was precipitated with xanthate. Vanadium interferes and it is masked by adding 2 ml of 1% sodium fluoride solution. Ni(II) also precipitates in the pH range of chromium-xanthate system. Among these metal ions only Mo(VI) seriously interferes as the catalytic wave of Mo(VI) is obtained even in the absence of xanthate.

However, carbonate and EDTA interfere severely by suppressing the catalytic wave of Cr(VI) as they give strong complexes with the metal ion. Nitrite and nitrate give catalytic currents with Cr(VI) in the absence of xanthate also.

Effect of Indifferent Cations

The effect of alkali chlorides on the Cr(VI) xanthate system is studied using lithium, sodium, potassium and calcium chloride, keeping ammonium chloride in the solution constant at 0.3 mM (Kaxan/Kiaxn) and 0.4 mM (Kcxan). The wave height decreases continuously with increase in the concentration of sodium chloride and potassium chloride .The decrease in height is due to lithium chloride and is much more with calcium chloride.

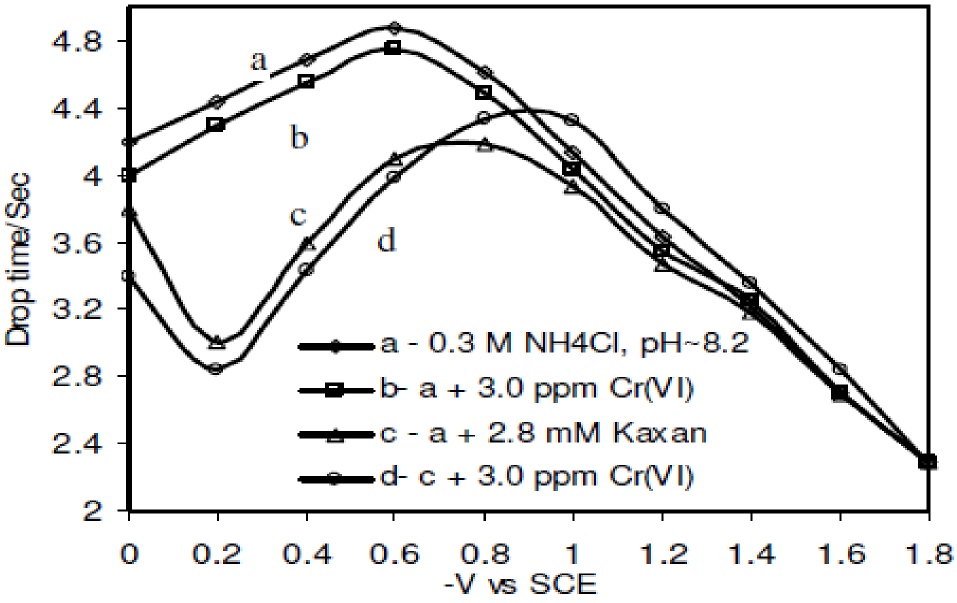
The peak potential of the catalytic waves shifted towards less negative potentials with increase in chloride concentration in all cases. The suppression of wave height in the presence of indifferent electrolytes shows that the chromium-xanthate complexes have adsorption properties on the mercury electrode [22-24].

Eletrocapillary curves

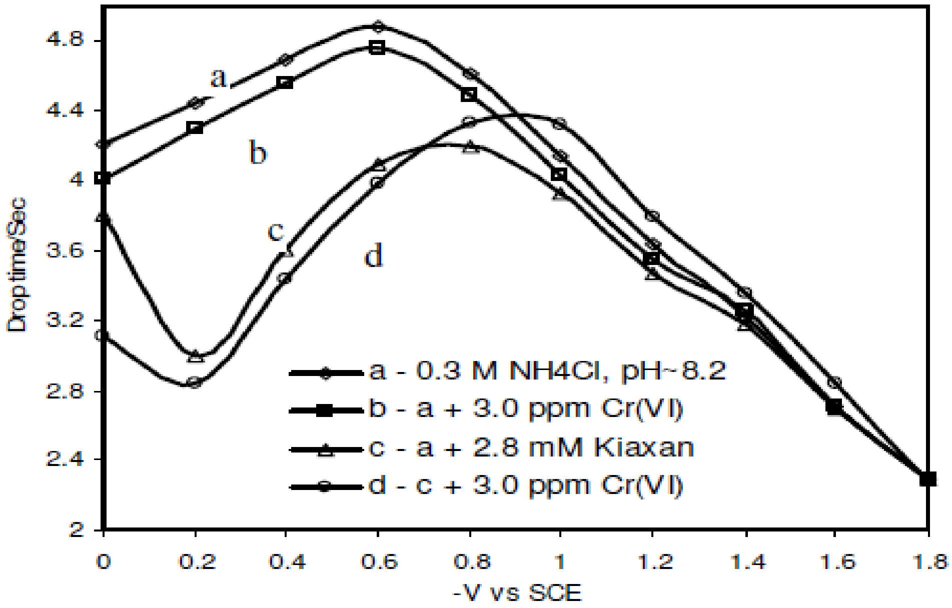
The curves are drawn by plotting potential vs drop time. The electrocapillary curves obtained with the supporting electrolyte alone (a) and in the presence of xanthate (b) and Chromium(VI) plus xanthate (c) are shown in **fig-1**(a. Kaxan, b. Kiaxn, c. Kcxan). In the presence of xanthate the electrocapillary maximum potential is shifted to more negative values and the curve is in the form of minima on the positive side of the electrocapillary maximum corresponding to the adsorption wave of xanthate [27] (curve c). The surface activity of xanthate is further increased in the presence of Cr(VI) and curve (d) coincide with the curve(a) close to the potential where hydrogen evolution starts [28] .

Fig 1. Electrocapillary curves

a. Kaxan electrocapillary curves



b. Kiaxan electrocapillary curves



c. Kcxan electrocapillary curves

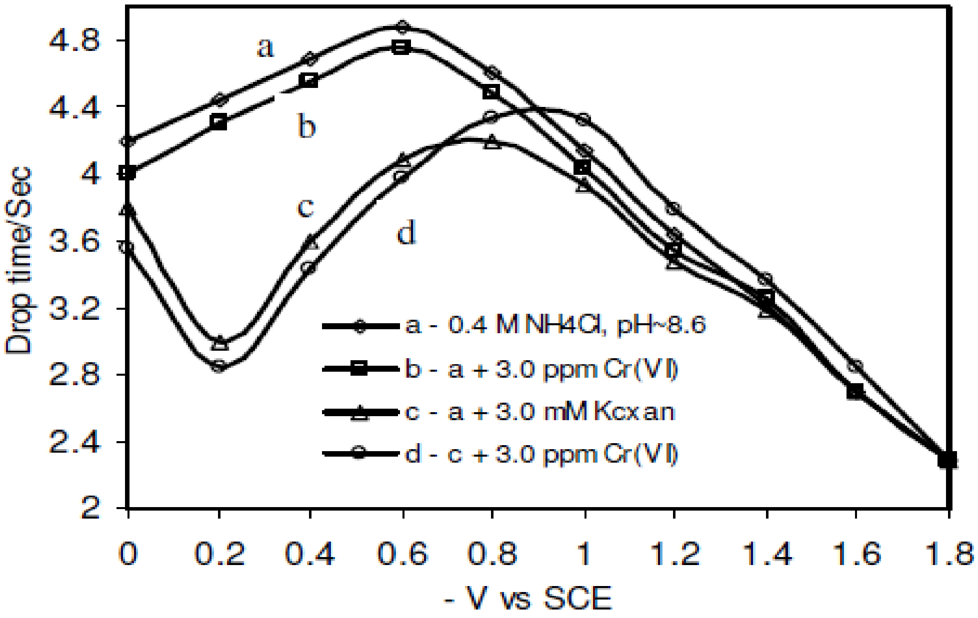


Table-1: Determination of Chromium(VI) in Milk Samples:

1. Cow Milk
2. Goat Milk
3. Buffalo Milk

	Kaxan	Kiaxan	Kcxan
NHCl :	0.3	0.3	0.4
Xanthate, mM :	2.8	2.8	3.0
pH :	8.2	8.2	8.6

Cr(VI) Found in samples, ppm*				
Sample	**Present Method**			**AAS Method**
	Kaxan	Kiaxan	Kcaxan	
		Cow Milk		
001C-08	0.11(±0.628)	0.13(±0.532)	0.13(±0.684)	0.14
002C-08	0.14(±0.515)	0.09(±0.715)	0.10(±0.588)	0.12
003C-08	0.12(±0.843)	0.11(±0.418)	0.10(±0.617)	0.12
004C-08	0.15(±0.494)	0.15(±0.662)	0.13(±0.489)	0.16
005C-08	0.12(±0.734)	0.14(±0.483)	0.11(±0.585)	0.14
		Goat Milk		
001G-08	0.30(±0.559)	0.32(±0.813)	0.32(±0.488)	0.34
002G-08	0.33(±0.746)	0.34(±0.449)	0.34(±0.439)	0.35
003G-08	0.30(±0.722)	0.28(±0.682)	0.28(±0.599)	0.3
004G-08	0.35(±0.416)	0.37(±0.496)	0.37(±0.731)	0.38
005G-08	0.30(±0.821)	0.30(±0.773)	0.30(±0.518)	0.32
		Buffalo		
001B-08	0.36(±0.522)	0.35(±0.498)	0.33(±0.555)	0.38
002B-08	0.36(±0.588)	0.36(±0.683)	0.37(±0.489)	0.38
003B-08	0.33(±0.495)	0.35(±0.519)	0.35(±0.718)	0.35
004B-08	0.33(±0.912)	0.33(±0.692)	0.33(±0.581)	0.35

**1 ml of the sample is used*
** SD for 5 individual samples*

Table-2: Determination of Chromium (VI) in water samples

		Kaxan	Kixan	Kcxan
NH_4Cl	:	0.3	0.3	0.4
Xanthate, mM	:	2.8	2.8	3.0
pH	:	8.2	8.2	8.6

Samples	Cr(vi) Added, ppm	Kaxan		Kixan		Kcxan		AAS Method	
		Cr(vi) found,ppm	% Recovery	Cr(vi) found,ppm	% Recovery	Cr(vi) found,ppm	% Recovery	Cr(vi) found,ppm	% Recovery
1.	0.5	0.48	96	0.48	96	0.5	100	0.5	100
2.	1.0	0.99	99	0.98	98	1.0	100	1.0	100
3.	1.5	1.47	98	1.49	99.3	1.49	99.3	1.49	99.33
4.	2.0	1.99	99.5	1.99	99.5	1.98	99	1.99	99.5
5.	2.5	2.5	100	2.5	100	2.5	100	2.5	100
		Average	98.5	Average	98.57	Average	98.5	Average	98.77

**5 ml of the concentrated samples used.*

Table-3: Determination of Chromium(VI) in Swarnamukhi River Water, Sri kalahasthi.

		Kxan(a)	Kiaxan(b)	Kcxan(c)
NH_4Cl	:	0.3	0.3	0.4
Xnthate, mM	:	2.8	2.8	3.0
pH	:	8.2	8.2	8.6

Sample	Xanthate	Rainy season				Summer season			
		Cr(vi),ppm		Cr(vi) in the Sample,ppm		Cr(vi),ppm		Cr(vi) in the Sample,ppm	
		Added	Found**	present Method	AAS method	Added	Found**	present Method	AAS method
1.	a.	2.0	2.85	7.37	7.68	2.0	2.95	7.82	7.82
	b.	2.0	2.9	7.63		2.0	2.93	7.76	
	c.	2.0	2.82	7.49		2.0	2.95	7.82	

**5 ml of the concentrated samples were used.*
***Average of five individual determination.*

CONCLUSION

The results of this investigation shows that Cr(VI) gives catalytic hydrogen currents at DME due to the complexation of –SH containing ligands. The linear dependence of the current on the pH and ligand concentration up to certain values shows that the waves are catalytic in nature due to chromium complexation with xanthates and adsorption phenomenon is involved. The effect of height of the mercury reservoir and temperature coefficient values is also indicative of catalytic nature of the waves. Further support of adsorption is indicated by the Langmuir adsorption isotherm curve.

Still another support for the idea about participation of adsorption and the metal xanthate complexes in catalytic hydrogen waves is seen with the decrease of height of the current with indifferent electrolytes and the shape of the electrocapillary curves and further increase in surface activity (curve d) due to the adsorption of chromium-xanthate complexes on the mercury surface.

From the results obtained for Cr(VI)-xanthate complex study it may be concluded that the procedure developed for the detection and determination of Cr(VI) using the catalytic hydrogen waves at DME in the presence of xanthates (Kiaxan, Kaxan and Kcxan) 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 d.c. polarography.

Application of the Catalytic method

The developed method is applied to the analysis of trace quantities of chromium in milk and water samples. Samples are preconcentrated by evaporation and standard addition method is used for analysis. The method reported here may therefore successfully applied for the determination of chromium in cow, got and buffalo milk samples and water samples without inferences from other metal ions except molybdenum.

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