Trade Science Inc.

ISSN : 0974-7419 Volume 10 Issue 10

Analytical CHEMISTRY

An Indian Journal

Full Paper

ACAIJ, 10(10) 2011 [691-694]

Simple catalytic currents at DME for trace amounts of chromium(III) in agricultrual samples

A.Varaprasad, T.Niranjan, K.Meenakumari, N.V.S.Naidu*, K.Saraswathi

Electro Analytical Research Lab, Department of Chemistry, S.V. University, Tirupati - 517 502, A.P., (INDIA)

E-mail: prof.nvsn@gmail.com

Received: 2nd May, 2011 ; Accepted: 2nd June, 2011

ABSTRACT

A catalytic polarographic method for the determination of microgram quantities of Cr(III) is developed based on the catalytic currents of chromium(III) in the presence of antipyrine in potassium chloride medium. The procedure is applied for the estimation of Cr(III) in agricultural samples. The method is simple, sensitive and free from interference of many metal ions.

KEYWORDS

Catalytic currents;
Chromium(III);
Antipyrine;
Potassium chloride;
Agricultrual samples.

INTRODUCTION

Chromium compounds that are inhaled have been linked with lung cancer, skin allergy, asthma and renal diseases while those ingested can cause kidney and liver damage[1]. Trivalent chromium is an essential trace element for humans. Together with insulin it removes glucose from the blood, and it also plays a vital role in fat metabolism, chromium deficits may exacerbate diabetes symptoms and heart problems[2]. Chromium(III) is an essential nutrient for maintaining normal physiological function[3], where as chromium(VI) is toxic[4] and carcionogenic for the human body[5-7]. Chromium may exist in water supplies in both the hexavalent and trivalent state although the trivalent form rarely occurs in potable water[8]. The most important application of chromium in the metallurgic industry is its use as an alloying element in steels. In these materials, chromium contributes to increase the hardness, tempering and oxidation resistance[9].

There are many sensitive techniques for chromium determination, such as ICP-MS[10-14], ICP-AES[15-18], HPLC[19-21], Stripping Voltammetry[22-26], AAS[27-31], spectrophotometry[32-36]. Cr(III) reacts with many organic reagents at high temperature due to the inert nature of $[Cr(H_2O)_6]^{3+}$ complex. The time required varied from 20 minutes to 2 hours depending on the nature of reagents[37-39]. The need to monitor chromium in the environment has led to the application of increasingly complex analytical techniques[40,41].

In continuation of our earlier work on development of catalytic polarographic methods[42-44] using antipyrine as complexing agent, a simple procedure is developed for the determination of chromium at low concentrations.

The polarographic studies on chromium(III) in the presence of antipyrine in potassium chloride medium revealed that in the presence of even microgram quantities of Cr(III) catalytic currents with peak values at -1.5 V Vs SCE, respectively are observed. At microgram concentrations chromium(III) exhibits negligible current in the absence of antipyrine.

EXPERIMENTAL

Reagents

A 99% pure antipyrine obtained from Aldrich Chemical Laboratory, USA is accurately weighed and dissolved in double distilled water and is used as the stock solution. Stock solutions of the Cr(III) {$Cr_2(SO_4)_3K_2SO_4.24H_2O$} are prepared from accurately weighed potassium chromic sulphate AnalaR samples by dissolving in distilled water and diluted to required strength with double distilled water. The supporting electrolyte, potassium chloride used in the present study is of AnalaR grade. Triton X-100 is weighed and is made upto 100ml in a standard flask and is diluted as per requirement.

Equipment

Current-Voltage curves are obtained with a DC recording polarograph (Model CL-25, Elico Pvt. Ltd., India) and a strip chart recorder (LR-101P). Atomic absorption studies are made by using Perkin-Elmer Model-2380 AAS. The capillary characteristics of the DME used are t=4.0 sec and m=2.15 mg/sec in 0.1M potassium chloride solution. All the experiments are performed at 25±0.2^{0}C using freshly prepared solutions in double distilled water. Deoxygenation is accomplished by passing pure nitrogen for 15-20 minutes through the test solutions.

Procedure

A measured amount of the supporting electrolyte, ligand and maximum suppressor are added to the required aliquots of Cr(III) solution under study and the solution is made upto 25ml with triple distilled water. This is then transferred to the polarographic cell and deoxygenated by passing nitrogen and polarographed. A test run of the supporting electrolyte without the electroactive species is also taken in order to record residual current (Figure 1).

RESULTS AND DISCUSSION

A detailed experimental procedure on the polarographic behaviour of Cr(III) in the presence of complexing agent, antipyrine in potassium chloride medium is mentioned below.

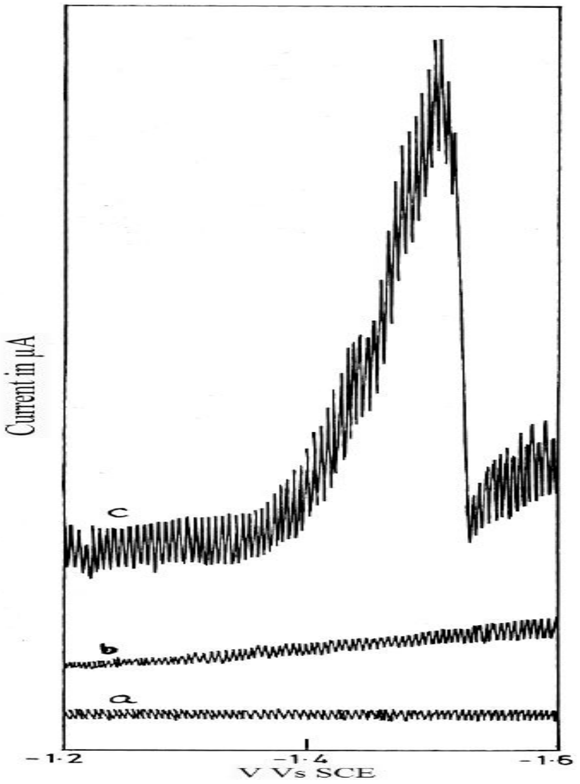

Figure 1 : Current voltage curves of (a) KC1 (0.1M) + antipyrine (0.1M); (b) KC1 (0.1M) + chromium(III) (5.71 ppm); and (c) KC1 (0.1M) + chromium(III) (5.71 ppm) + antipyrine (0.1M)

Effect of potassium chloride concentration

Keeping the concentrations of Cr(III) (5.71 ppm) and (0.1M) constant, the concentration of the reagent, potassium chloride is varied from 0.05 to 0.2M. The results reveal that the peak is maximum only when the antipyrine concentration is 0.1M.

Effect of height of the mercury column

The variation in the height of the mercury column has no effect on both the nature and height of the Current-Voltage curves indicating the catalytic nature of the waves.

Effect of triton X-100

Triton X-100 ranging from 0.001 to 0.004% has been added for both solutions containing analytical concentrations of metal ions, antipyrine and potassium chloride and the effect is studied. It is found that this surface active agent does not change the nature of the catalytic wave.

Effect of temperature

The current voltage curves for the systems containing (5.71 ppm) Cr(III), 0.1M potassium chloride and

0.1M antipyrine is recorded at various temperatures and the increase in the height of the wave with rise in temperature is noticed. The catalytic current is found to increase with temperature and the temperature coefficient calculated is above 3% which shows the catalytic nature of the waves.

Effect of chromium ion concentration

The effect of increased concentration of metal ion in the range of 1.0 to 6.0 ppm, on the catalytic peak current is studies at the fixed concentrations of the reagent antipyrine (0.1M) and potassium chloride (0.1M).

The shape and the peak potentials of the current-voltage curves remained same, but the peak height increased with increase in concentration of chromium ion. A linear plot obtained between the peak height in μA and the amount of Cr(III) in ppm reveals the usefulness of the method for the determination of microgram quantities of the metal ion by the present method from 1.0 to 6.0 ppm.

Effect of foreign ions on the polarographic behaviour of chromium (III)-Antipyrine system

The effect of various metal ions that are known to be associated with chromium(III) in ores and alloys like cobalt(II), copper(II), manganese(II), iron(II) and nickel(II) on the polarographic characteristics of chromium(III) is maintained at 5.71 ppm, antipyrine 0.1M and potassium chloride at 0.1M. Masking agents like fluoride, oxalate, citrate and tartrate have been tried. Fluoride masks chromium also along with Co(II) and therefore it could not be used in the present studies. The other anions are found to be of no help in masking the metal ions like manganese, nickel and iron which interfere with the wave of chromium(III)-antipyrine system. Copper(II) does not interfere because of its reduction at much positive potentials.

The results above indicate that chromium(III) may be determined in the samples of ores and alloys in the absence of manganese(II), nickel(II), iron(II) and cobalt(II).

Applications

The catalytic polarographic method is extended for the analysis of trace amounts of chromium in agricultural materials.

Agricultural materials

5g of piper betle (Betle leaves), Ocimum sanctum leaves, Oryza sativa (Unpolished Rice) are collected and digested by dry ash method[45].

Aliquots of the above sample solutions are taken and quantitative experimental conditions are maintained and the solutions are polarographed. Standard addition method is used for agricultural materials. The results obtained by this method are further supported by AAS method (TABLE 1).

TABLE 1 : Determination of chromium in agricultural samples

Agricultural materials

1) **Piper betle (Betel leaves)**
2) **Ocimum sanctum leaves**
3) **Oryza sativa (Unpolished Rice)**

Antipyrine = 0.1M **Potassium chloride = 0.1M**

Sample*	Cr(III), ppm		Cr(III) in the sample, ppm	
	ppm added	Total found	Catalytic method	AAS method
1	0.5	1.786	1286.00	
	0.5	1.790	1290.00	1290.00
2	1.0	1.63	0.89	
	1.0	1.67	0.91	0.89
3	1.0	1.056	0.14	
	1.0	1.052	0.13	0.145

***1.0 (1 & 2) ml of the sample is used.**

ACKNOWLEDGEMENTS

The authors are highly thankful to The Head of the Department of Chemistry SVU for providing necessary facilities.

REFERENCES

[1] R.Prakash, R.Bansal, A.Kaur, S.K.Rehani; Talanta, **38**, 1163 **(1991)**.

[2] D.G.Barceloux; J.Toxicol.Clin.Toxicol., **37**, 173-194 **(1999)**.

[3] J.Versiek, R.Cornelis; Anal.Chim.Acta, **116**, 217 **(1980)**.

[4] J.M.Eckert, R.J.Judd, P.A.Lay, A.D.Symons; Anal. Chim.Acta, **255**, 31 **(1991)**.

[5] International Agency for Research on Cancer; World Health Organization: Chromium, Nickel and Welding. IARC Monographs on the Evaluation of Carcionogenic Risks to Humans, IARRC, WHO, Lyon, 49 **(1990)**.

[6] National Toxicology Program; Chromium Hexavalent Compounds, Ninth Report on Carcinogens, NTP, Department of Health and Human Services, **(2000)**.

[7] S.A.Katz, H.Salem; J.Appl.Toxicol., **13**, 217 **(1993)**.

[8] Standard Methods for the Examination of Water and Wastewater; American Public Health Association, 19th Edition, Washington, 3.

[9] K.Other; Encyclopedia of Chemical Technology, John Wiley & Sons, New York.

[10] C.F.Wang, C.J.Chin, S.K.Luo, L.C.Men; Anal. Chim.Acta, **389**, 257-266 **(1999)**.

[11] H.Gurleyuk, D.Wallschlaeger; J.Anal.Atom. Spectrom., **16**, 926-930 **(2001)**.

[12] A.Makishima, K.Kobayashi, E.Nakamura; Geostandards Newsletter, **26**, 41-51 **(2002)**.

[13] K.Takeda, S.Watanabe, H.Naka, J.Okuzaki, T.Fujimoto; Anal.Chim.Acta, **47**, 377 **(1998)**.

[14] E.Skrzydlewska, M.Balcerzak, F.Vanhaecke; Analytica Chimica Acta, **479**, 191-202 **(2003)**.

[15] S.Balasubramanian, V.Pugalenthi; Talanta, **50**, 457-467 **(1999)**.

[16] T.Y.Peng, Z.C.Jiang, B.Hu, Z.H.Liao; Fresen.J. Anal.Chem., **364**, 551-555 **(1999)**.

[17] S.Satyaveni; Preconcentration and Determination of Trace Metals by ICP-AES, Ph.D. Thesis, S.V. University, Tirupati, India, **(2007)**.

[18] K.Oktor, S.Yilmaz, G.Turker, E.Erkus; Environ. Monit.Assess., **141**, 97-103 **(2008)**.

[19] A.Imran, Y.A.Hassan; Chemosphere, **48**, 275 **(2002)**.

[20] M.Bittner, J.A.C.Broekaert; Analytica Chimica Acta, **364**, 31 **(1998)**.

[21] J.Posta, A.Alimonti, F.Petrucci, S.Caroli; Analytica Chimica Acta, **325**, 185 **(1996)**.

[22] Z.Gao, K.S.Siow; Electroanalysis, **8**, 602 **(1996)**.

[23] J.Wang, J.Lu, K.Olsen; Analyst, **117**, 1913 **(1992)**.

[24] D.V.Vukomanovic, G.W.VanLoon, K.Nakatsu, D.E.Zoutman; Microchemical Journal, **57**, 86 **(1997)**.

[25] M.Paneli, A.V.Voulgaropoulus, K.Kalcher; Mikrochimica Acta, **110**, 205 **(1993)**.

[26] M.Boussemart, C.M.G.Van den Berg, M.Ghaddaf; Analytica Chimica Acta, **262**, 103 **(1992)**.

[27] A.Gaspar, C.Sogor, J.Posta; Fresen.J.Anal.Chem., **363**, 480-483 **(1999)**.

[28] M.N.Amin, H.Okada, S.Itoh, T.Suzuki, S.Kaneso, K.Ohta; Fresen.J.Anal.Chem., **371**, 1130-1133 **(2001)**.

[29] P.Tiglea, J.Lichtig; J.Anal.Lett., **33(8)**, 1615-1624 **(2000)**.

[30] K.S.Subramanian; Analytical Chemistry, **60**, 11 **(1988)**.

[31] M.A.El-Shahat; Anal.Sci., **16**, 151 **(2000)**.

[32] M.J.Ahmed, I.Jahan, S.Banoo; Anal.Sci., **18**, 805 **(2002)**.

[33] H.D.Revanasiddappa, T.N.K.Kumar; Anal.Sci., **17**, 1309 **(2001)**.

[34] A.Joseph, B.Narayana, C.H.R.Nambiar; Anal.Sci., **16**, 985 **(2000)**.

[35] M.I.C.Monteiro, I.C.S.Fraga, A.V.Yallouz, N.M.M.Oliveira, S.H.Ribeiro; Talanta, **58**, 629 **(2002)**.

[36] B.Narayana, T.Cherian; J.Braz.Chem.Soc., **16(2)**, 197-201 **(2005)**.

[37] B.K.Puri, M.Gautam; Talanta, **25**, 485 **(1978)**.

[38] S.K.Jain, B.K.Puri, A.L.Singla, A.L.J.Rao; Microchemical Journal, **37**, 167 **(1988)**.

[39] A.C.S.Costa, J.C.R.Assis, A.L.C.Torres, S.L.C.Ferreira, M.D.G.Korn, L.S.G.Teixeira; Quimica Nova, **22**, 194 **(1999)**.

[40] S.Peraniemi, M.Ahlgren; Anal.Chim.Acta, **315**, 365 **(1995)**.

[41] Y.Inoue, T.Sakai, H.Kumagai; J.Chromatog.A, **706**, 27 **(1995)**.

[42] K.Saraswathi, K.Meenakumari, K.Padmaja; Trans.SAEST, **34(1)**, 28 **(1999)**.

[43] K.Saraswathi, K.Meenakumari, N.V.S.Naidu, K.Padmaja; J.Electrochem.Soc., **48(3)**, 264 **(1999)**.

[44] K.Saraswathi, N.V.S.Naidu, K.Meenakumari, K.Padmaja; Chem.Environ.Res., **8(3&4)**, **(1999)**.

[45] T.T.Gorusch; Analyst, **84**, 135 **(1959)**.