

ELECTROANALYSIS OF TITANIUM AND OTHER METALS IN BAUXITE ORE

P. K. Tamrakar and K. S. Pitre

*Department of Chemistry
Dr. Hari Singh Gour University
Sagar - 470 003 (M.P.) India*

ABSTRACT

Convenient and accurate direct current and differential pulse polarographic and differential pulse anodic stripping voltammetric procedures were developed for the simultaneous trace determination of metals in bauxite ore. The analysis was performed using three different supporting electrolytes i.e. 0.1 M(NH₄)₂ tartrate, 1M HCl and 0.01M EDTA. The results indicated the presence of Tl, Ni, Zn, Fe, V and Ti metals in the sample. Titanium gave a well defined wave/peak with $E_{1/2}/E_p = -0.18V/-0.22V$ vs SCE in 0.01M EDTA supporting electrolyte. The accuracy of the methods was verified by a statistical approach and also by comparing the observed results with those obtained using atomic absorption spectroscopic method.

INTRODUCTION

Bauxite is a known ore of aluminum. In bauxite ore aluminium is associated with a large number of elements, such as Si, Fe, Mn, Ti, V Cu, Zn, Sb etc. /1-3/. Trace analysis of bauxite has been carried out mainly by using atomic absorption spectroscopy (AAS) /4/, neutron activation analysis /5/ and X-Ray fluorescence /6/ methods. Although these methods are highly useful for such analysis, they cannot be advocated for routine analysis because of the high cost of their instrumentation. The development of low cost electroanalytical instrumental techniques which are very well suited for trace analysis of metals in samples of geological origin /7, 8/, has led to the use of differential pulse polarography (DPP) and differential pulse anodic stripping voltammetry (DPASV) for the simultaneous determination of metals /9-11/.

These methods are highly sensitive and dependable up to nanogram per gram levels.

The present paper deals with the trace analysis of bauxite ore samples using direct current polarography (DCP), differential pulse polarography (DPP) and differential pulse anodic stripping voltammetry (DPASV) methods. The electrochemical results were compared with those obtained using the AAS method.

EXPERIMENTAL

Sample

The bauxite ore sample was collected from the Katni area of M.P. India.

Instrumentation

Polarographic and voltammetric measurements were made on an Elico (India) Model CL-90 pulse polarograph coupled with a Model LR-108 X-Y polarocard. The electrode system consisted of a dropping mercury electrode (DME) as the working electrode, a coiled platinum wire as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. The electrochemical cell used had provision for inserting a bubbler for deaerating the solutions and passing nitrogen gas. A glassy carbon fibre electrode (NF 12 Sigtitelectrode, UK) was used for DPASV.

The pH measurements were made on a Systronics digital pH meter (model 335).

Chemicals & Reagents

All the chemicals used were of analytical reagent grade (BDH). Stock solutions of 1M $(\text{NH}_4)_2$ tartrate, 11M HCl, 0.1M EDTA, Ti, Ni, Zn, Fe, V and Ti (0.01M) were prepared in doubly distilled water. Gelatin solution (0.1%) was prepared in hot distilled water. The solutions were standardized by known methods and diluted as required.

Preparation of Sample Solution

The bauxite ore sample solution was prepared by fusion method. Finely pulverized 1g bauxite ore samples were fused with 10g KHSO_4 for about 2 hours. The melt was dissolved in water and acidified with 10ml conc. HCl. Then the final volume of the sample solution was made up to 100ml with distilled water.

Preparation of Analyte and Recording of Polarograms/Voltammograms.

To 10ml of the sample solution, 10ml of 1M $(\text{NH}_4)_2$ tartrate/ 0.1M EDTA disodium salt solution as supporting electrolyte with 1M of 0.1% gelatin as a maximum suppressor were added. For the analysis of V the analyte, 11M HCl, was prepared. The final volume of each analyte was made up to 100ml by distilled water. The pH of the test solution was first adjusted to 9.5 ± 0.1 in the case of 0.1M $(\text{NH}_4)_2$ tartrate, 0.7 ± 0.1 in the case of 11M HCl and 2.0 ± 0.1 in the case of 0.01M EDTA supporting electrolyte. Then the analyte was placed in a polarographic cell equipped with the electrode assembly specified above. Pure nitrogen gas passed through the test solution for 15 min at the beginning of the experiment. The polarograms and voltammograms were then recorded with the instrumental parameter as follows: Pulse amplitude, 50mV, Drop time, 0.5s; I.R. compensation, 4; C. C. Compensation, 5, Time constant, 10 ms; Sensitivity, $1\mu\text{A/V}$; Scan rate, $12\text{mV}\cdot\text{s}^{-1}$. For DPASV the deposition potential was fixed at -2.0V, deposition time 60s and resting period 10s.

RESULTS AND DISCUSSION

The D. C. polarogram and D. P. polarogram [Fig.1(A) and (B)] of the bauxite ore sample in 0.1M $(\text{NH}_4)_2$ tartrate gave four well defined waves/peaks with $E_{1/2}/E_p = -0.46\text{V}/-0.52\text{V}$, $-1.10\text{V}/-1.14\text{V}$, $-1.34\text{V}/-1.34\text{V}$ and $-1.56\text{V}/-1.58\text{V}$ vs SCE, indicating the presence of T^+ , Ni^{2+} , Zn^{2+} and Fe^{3+} metal ions in the sample. The D.P.A.S. voltammogram [Fig. 1(C)] of the sample in 0.1M $(\text{NH}_4)_2$ tartrate also showed four distinct peaks with $E_p = -1.54\text{V}$, -1.12V , -1.30 and -1.58V vs SCE corresponding to the presence of T^+ , Ni^{2+} , Zn^{2+} and Fe^{3+} metal ions in the sample.

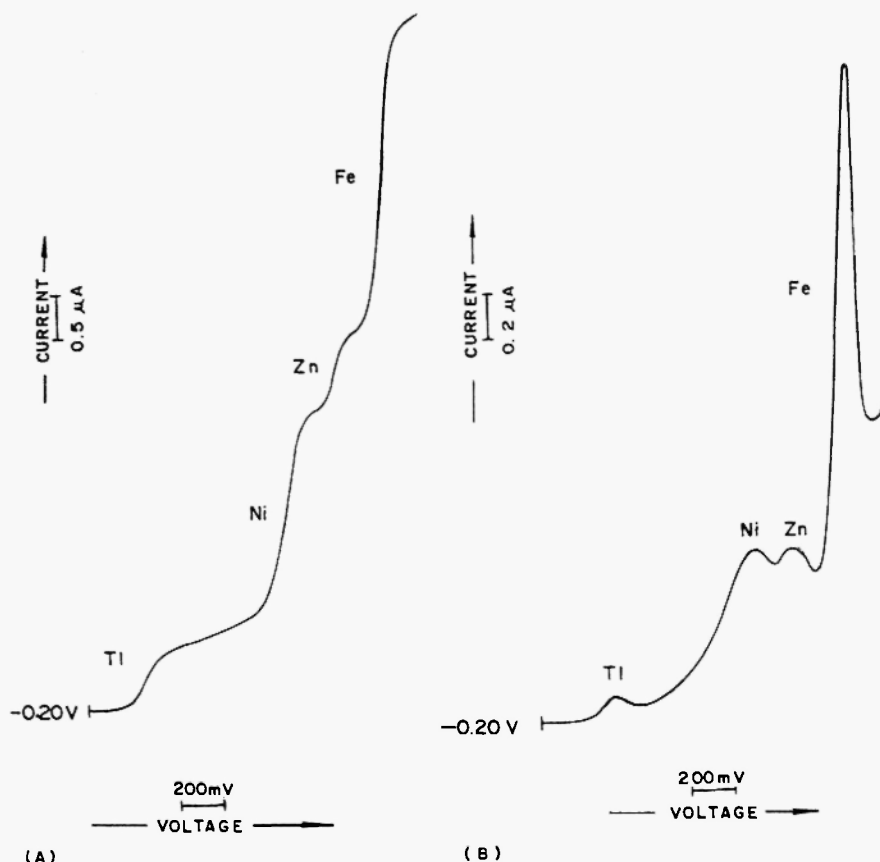


Fig. 1: (A) Direct current polarogram,
(B) Differential pulse polarogram of bauxite ore sample in 0.1 M ammonium tartrate + 0.001% gelatin. pH 9.5 ± 0.1 .

The D.C. polarogram and D. P. polarogram [Fig 2(A) and (B)] of the sample in 11M HCl showed a well defined wave/peak with $E_{1/2} / E_p = -0.52\text{V} / -0.56\text{V}$ vs SCE, indicating the presence of V^{3+} metal in the sample. The D.P.A.S voltammogram [Fig. 2(C)], of the sample in 11M HCl also produced a well defined peak with $E_p = -0.54\text{V}$ vs SCE revealing the presence of V^{3+} in the sample.

To investigate the presence of other trace metals in the sample the polarograms/voltammograms were recorded in 0.01M EDTA disodium salt supporting electrolyte. The D. C. polarogram and D. P. polarogram [Fig 3(A)

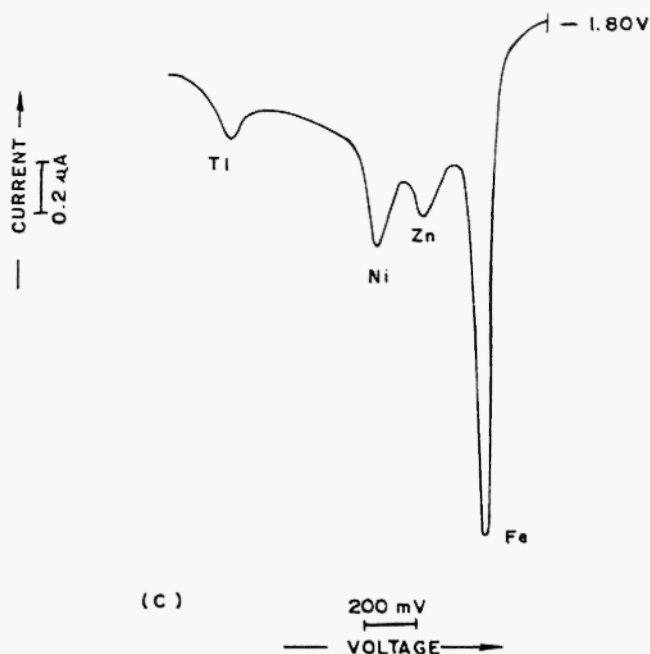


Fig. 3 cont'd: (C) Differential pulse anodic stripping voltammogram of bauxite ore sample in 0.01M EDTA+ 0.001% gelatin. pH 2.0 ± 0.1 .

and (B)] of the sample in 0.01 M EDTA showed one well defined wave/peak with $E_{1/2}/E_p = -0.18V/-0.22V$ vs SCE, indicating the presence of Ti^{4+} in the sample. The D.P.A.S. voltammogram [Fig 3(C)] of the sample also showed one well defined peak with $E_p = -0.18V$ vs SCE, corresponding the presence of Ti^{4+} in the sample.

To confirm the presence of the said metal ions in the sample a known quantity of standard solution of each metal ion was added to analyte and then polarograms/voltammograms were recorded under the identical experimental conditions. An increase in wave and peak height of each metal ion signal was observed without any change in half wave and peak potential values.

Based on the presence of the above mentioned metal ions some synthetic samples [Table 1] with varying concentrations were prepared and their polarograms and voltammograms were recorded under identical experimental conditions as indicated earlier. The results indicated no change in $E_{1/2}$ and E_p

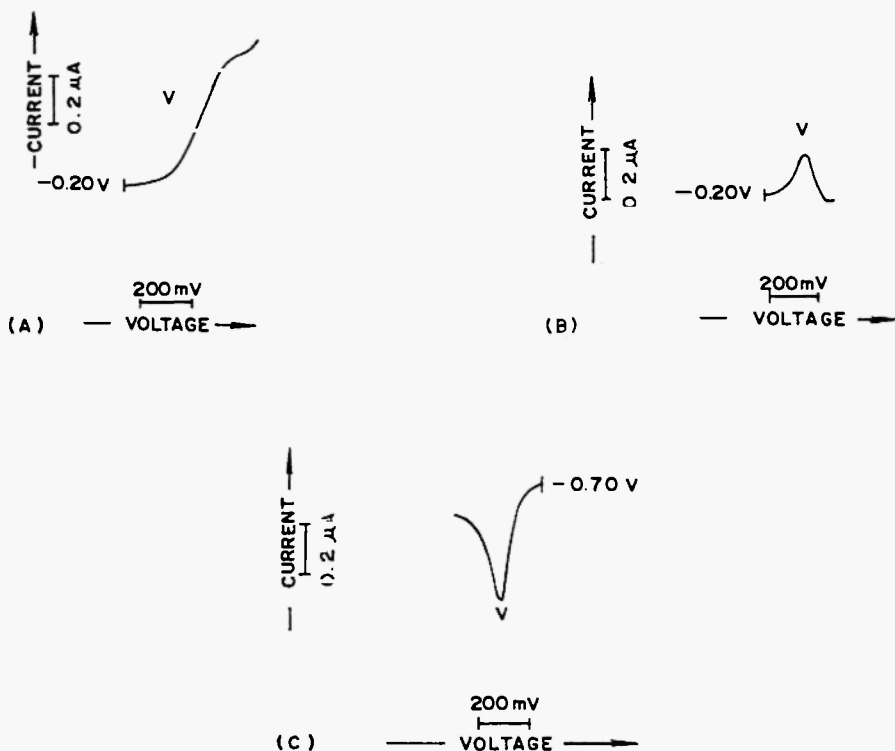


Fig. 2: (A) Direct current polarogram,
 (B) Differential pulse polarogram,
 (C) Differential pulse anodic stripping voltammogram of bauxite ore sample in 11M HCl + 0.001% gelatin. pH 0.7 ± 0.1 .

values of the metal ions under studying each of the synthetic samples; it was also observed that the concentration of each metal ion is directly proportional to its wave and peak height, thus confirming the possibility of an accurate simultaneous qualitative and quantitative determination of the above mentioned metal ions in the sample.

Minimum Tried Detection Limits

The detection limits of the DCP, DPP and DPASV techniques for measurements of the individuals and combined metal ions are given in Table 2. Except V and Ti, all the metal ions in the sample could be determined in

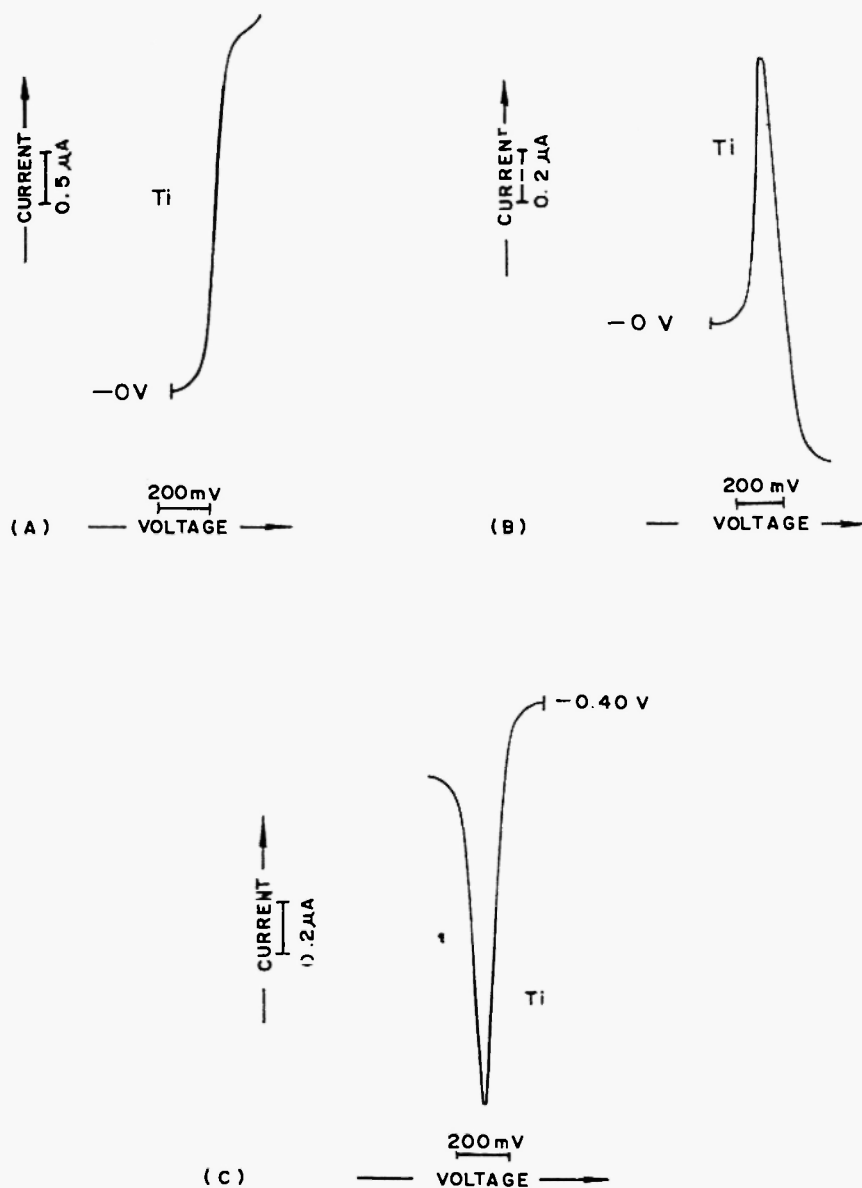


Fig. 3: (A) Direct current polarogram,
 (B) Differential pulse polarogram,
 (C) Differential pulse anodic stripping voltammogram of bauxite ore sample in 0.01M EDTA+ 0.001% gelatin. pH 2.0 ± 0.1 .

Table 1
Analysis of synthetic samples.

	Composition of synthetic samples (mg/100ml analyte)			
Ti ⁺	0.40 (0.38)*	0.82 (0.81)	1.02 (1.02)	2.04 (2.03)
Ni ²⁺	0.19 (0.16)	0.58 (0.54)	0.58 (0.53)	0.70 (0.68)
Zn ²⁺	0.06 (0.06)	0.13 (0.12)	0.26 (0.21)	0.78 (0.74)
Fe ³⁺	11.55 (11.50)	13.95 (13.98)	16.74 (16.73)	18.14 (18.12)
V ³⁺	1.19 (1.16)	1.78 (1.72)	2.49 (2.46)	2.62 (2.60)
Ti ⁴⁺	2.77 (2.74)	4.15 (4.15)	4.70 (4.68)	5.26 (5.23)

Average of four determinations.

() * Amount found using DPP (mg per 100ml analyte).

Table 2
Minimum tried detection limits.

Metal Ion	DCP μg l ⁻¹	DPP μg l ⁻¹	DPASV ng l ⁻¹
Ti ⁺ <i>Individual</i>	20.4	0.204	20.4
<i>Combined</i>	20.4	0.204	20.4
Ni ²⁺ <i>Individual</i>	5.8	0.58	5.8
<i>Combined</i>	5.8	0.58	5.8
Zn ²⁺ <i>Individual</i>	6.4	0.64	12.8
<i>Combined</i>	6.4	0.64	12.8
Fe ³⁺ <i>Individual</i>	5.6	0.56	2.8
<i>Combined</i>	5.6	0.56	2.8
V ³⁺ <i>Individual</i>	5.1	0.51	5.1
<i>Combined</i>	5.1	0.51	5.1
Ti ⁴⁺ <i>Individual</i>	4.8	0.048	4.8
<i>Combined</i>	4.8	0.096	9.6

Table 3
Results on bauxite ore sample for its trace metals content (mg.g^{-1})

Metal ions	Parameter	DCP		DPP		DPASV	
Ti^+	Amount	-	3.89	-	3.89	-	3.89
		3.88	7.75	3.88	7.74	3.88	7.76
	R%	99.74%		99.61%		99.87%	
	S.D.	0.034		0.029		0.070	
	C.V.	0.87%		0.74%		1.80%	
Ni^{2+}	Amount	-	1.88	-	1.88	-	1.88
		1.82	3.64	1.82	3.66	1.82	3.68
	R%	98.64%		98.91%		99.46%	
	S.D.	0.059		0.052		0.052	
	C.V.	3.14%		2.76%		2.76%	
Zn^{2+}	Amount	-	0.24	-	0.24	-	0.24
		0.23	0.45	0.23	0.46	0.23	0.46
	R%	95.74%		97.87%		97.07%	
	S.D.	0.018		0.018		0.041	
	C.V.	7.5%		7.5%		17.08%	
Fe^{3+}	Amount	-	115.60	-	115.60	-	115.60
		115.50	230.85	115.50	230.85	115.50	230.88
	R%	99.89%		99.89%		99.90%	
	S.D.	0.091		0.064		0.091	
	C.V.	0.078%		0.055%		0.078%	
V^{3+}	Amount	-	11.88	-	11.88	-	11.88
		11.70	23.49	11.70	23.49	11.70	23.52
	R%	99.62%		99.62%		99.74%	
	S.D.	0.073		0.044		0.059	
	C.V.	0.62%		0.37%		0.50%	
Ti^{4+}	Amount	-	27.72	-	27.72	-	27.72
		27.20	54.38	27.20	54.86	27.20	54.86
	R%	99.92%		99.89%		99.89%	
	S.D.	0.059		0.044		0.059	
	C.V.	0.22%		0.16%		0.22%	

Results are average of four determinations

R% = Recovery (%)

S.D. = Standard Deviation

C.V. = Coefficient of Variation

one run. For V and Ti changing the supporting electrolyte was necessary. The detection limits were examined by preparing synthetic samples. The data in Table 2 show that the DPASV method using a glassy carbon fibre electrode is highly sensitive in determining the reported metal ions down to the nanogram level.

Quantitative Analysis of the Sample

After ascertaining the presence of the said metal ions in the sample the method of standard addition was used for quantitative analysis. The results are given in Table 3. The statistical data are also reported in this table. The recovery is over 99% for most of the metal ions, with high accuracy and precision of determination. The standard deviation and coefficient of variation clearly speaks for the reliability of the observed data.

The final results on the analysis of bauxite ore sample are reported in Table 4. These results were compared with those obtained using AAS methods. The agreement between the data demonstrates the utility of voltammetric methods for such analysis. Further, the voltammetric methods are simple, fast and economic.

Table 4
Final results on bauxite ore sample and the comparison with the results by AAS method.

Metal Ions	Amount found in mg.g ⁻¹	
	Voltammetry	AAS
Ti ⁺	3.89	3.86
Ni ²⁺	1.88	1.84
Zn ²⁺	0.24	0.23
Fe ³⁺	115.60	115.50
V ³⁺	11.88	11.83
Ti ⁴⁺	27.72	27.66

ACKNOWLEDGEMENT

The authors thank Prof. V. K. Saxena, Head, Department of Chemistry, Dr. H. S. Gour University, Sagar (M.P.) India, for providing the necessary laboratory facilities. One of the authors (P.K.T.) is thankful to the CSIR, New Delhi (India) for providing Senior Research Fellowship (S.R.F.).

REFERENCES

1. R. J. Batra and A. N. Garg, *J. Geol. Soc. India*, **32**, 351(1988).
2. A. K. Gupta and K. De, *Indian J. Technol*, **25**(6), 294 (1987).
3. N. Sasaok, K. Morisige, T. Shigematsu and Y. Nishikawa, *Bunseki Kagaku*, **36**(11), 722 (1987).
4. M. R. Winchester and R. K. Marcus, *Appl. Spectrosc.*, **42**(6), 941 (1988).
5. R. J. Batra and A. N. Garg, *J. Indian Chem. Soc.*, **63**(9), 832 (1986).
6. K. J. S. Sawhney, G. S. Lodha and B. R. Singh, *Nucl. Geophys.*, **3**(2), 125(1989).
7. I. M. M. Kenway, M. A. H. Hafez, A. A. El-Khouly and Y. C. Goudah, *Indian J. Chem. Technol.*, **2**(5), 266 (1995).
8. P. K. Tamraker and K. S. Pitre, *J. Indian Chem. Soc.*, **78**, 482 (2001).
9. A. A. Ensafi and S. Abbasi, *Anal. Sci.*, **16**(4), 377 (2000).
10. E. Desimoni, P. Genevini, F. Tambone, S. Pikovic and P. Banfi, *Electroanalysis*, **12**(5), 337 (2000).
11. P. K. Tamraker and K. S. Pitre, *Bull. Electrochem.*, **18**(1), 35 (2002).

