VOLTAMMETRIC ANALYSIS OF GALENA FOR ITS METAL CONTENT

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ABSTRACT

Direct current polarography (DCP), differential pulse polarography (DPP) and differential pulse anodic stripping voltanunetry (DPASV) have been successfully used for simultaneous determination of some metal ions in a galena ore sample obtained from Chouraiya village, Chhatarpur District (M.P.), India.

Ammonia-ammonium chloride has been used as a supporting electrolyte and 0.001% gelatin as maximum suppressor. The sample indicated the presence of Ag(I) (0.18 mg/g), Pb(II) (715.20 mg/g), Cu(II) (12.70 mg/g), Cd(II) (1.85 mg/g), Cr(II) (0.30 mg/g), Ni (0.17 mg/g) and Zn(II) (0.72 mg/g).

The method of standard addition was used for quantitative analysis. The obtained voltammetric results were compared with those observed using an AAS method.

INTRODUCTION

Galena is a known source of silver /1-4/. In this ore Pb constitutes the major part of the sample and Ag, Cu, Cd, Cr, Ni and Zn are present in trace amounts. During the last two decades, AAS, X-RF and NAA have dominated the field of trace analysis of natural origin substances for their metal contents, but the accuracy may be poor /5/. In recent years voltammetry and related techniques have been applied increasingly to such analyses /6-8/. DPP and DPASV have been used for the simultaneous determination of metals. These metals are highly sensitive, rapid and economic.

In view of the accuracy and reliability /9,10/ of trace determination by voltammetric methods, the authors have undertaken the trace analysis of galena samples for their metal content in general and silver in particular. The results are discussed in this paper.

EXPERIMENTAL

Samples

The galena sample was procured from the Geology Department of Dr. Hari Singh Gour University, Sagar (M.P.), India. According to information received from that source, the sample originated from Chouraiya village, Chhatarpur District (M.P.), India.

Apparatus

Polarographic and voltammetric measurements were made on an Elico (India) pulse polarograph model CL-90 coupled with a model LR-108 X-Y Polarocard. The electrode system consisted of a dropping mercury electrode (DME) as a working electrode, a coiled platinum wire as an auxiliary electrode and a saturated calomel electrode (SCE) as a reference electrode. A glassy carbon fibre electrode was used for DPASV studies. pH measurements were made on an Elico digital pH-meter model LI-120.

Chemicals and Reagents

Anal-R.BDH grade chemicals were used. Stock solutions of ammonia, ammonium chloride (1M), Ag, Cu, Cd, Pb, Cr, Ni and Zn (0.01 M) were prepared by dissolving their requisite amounts in double-distilled water. The solutions were standardised by known methods and diluted as required.

Preparation of Sample Solution

1.0 g of finely pulverised ore sample was dissolved in 10 ml of hydrobromic acid and evaporated to dryness. This dry residue was dissolved in 10 ml of (1M) ammonium hydroxide containing 3g of tartaric acid and final volume was made up to 100 ml with distilled water /11/.

Preparation of Analyte and Recording of Voltammogram

10 ml of sample solution was mixed with 0.1M ammonia-ammonium chloride as supporting electrolyte and 0.001% gelatin as maximum suppressor in the polarographic cell and the final volume was made up to 100 ml with distilled water. The pH of the test solution was adjusted to 8.0 ± 0.02 with ammonia solution. The analyte was placed in a polarographic cell. Pure hydrogen gas was bubbled through the solution for 15 minutes before recording polarograms. To determine the trace amounts of metals in the presence of lead in the sample, the polarograms were recorded by changing the current sensitivity, i.e. for voltage scan from 0.0V to –0.58V and from –0.70V to –1.62V, to 0.2 μA per cm in DCP and DPP modes and to 0.5 μA per cm in DPASV mode, for the determination of Ag, Cu, Cd, Cr, Ni and Zn, and for voltage between –0.58V and –0.7V, to 2 μA/cm in all three modes for the determination of Pb.

RESULTS AND DISCUSSION

The DC polarogram and DP polarogram (Fig. 1a and 1b) of the sample solution showed seven well defined polarographic signals with $E_{½}/E_p$ values equal to -0.08V/–0.08V, –0.44V/–0.44V, –0.66V/–0.64V, –0.76V/–0.78V, –0.94V/–0.94V, –1.32V/–1.32V and –1.54V/–1.54V, indicating the presence of Ag(I), Cu(II), Pb(II), Cd(II), Cr(II), Ni(II) and Zn(II) respectively.

However, the DPAS voltammogram (Fig. 2) showed six voltammetric peaks with E_p equal to –0.16V, -0.44V, –0.62V, –0.90V, –1.06V, -1.26V, corresponding to Ag-Cu, Pb(II), Cd(II), Cr(II), Ni(II) and Zn(II). The difference in peak potential in DPP and DPASV modes may be explained on the basis of the increased ease of reduction on glassy carbon fibre electrode

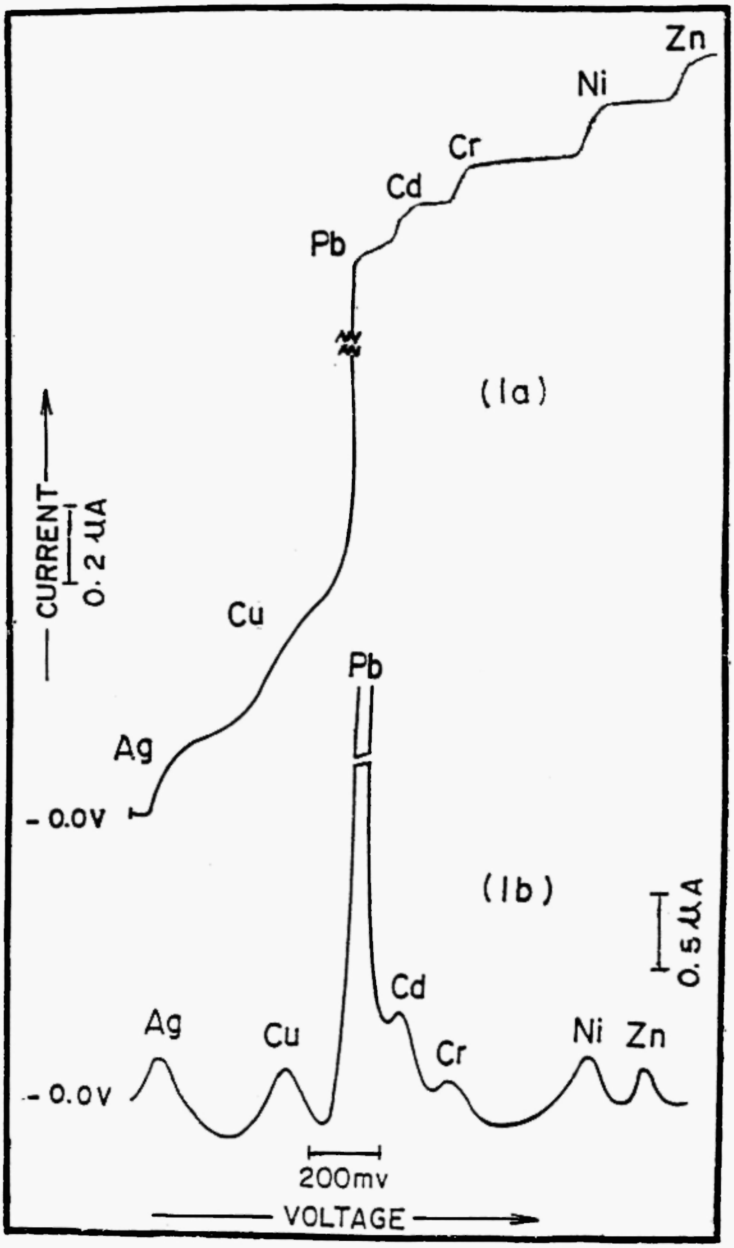

FIG. 1: (a) Direct Current Polarogram and (b) Differential Pulse Polarogram of Galena sample (100 mg / 100 ml) in 0.1 M ammonia-ammonium chloride buffer + 0.001 % gelatin; pH 8.00 ± 0.02

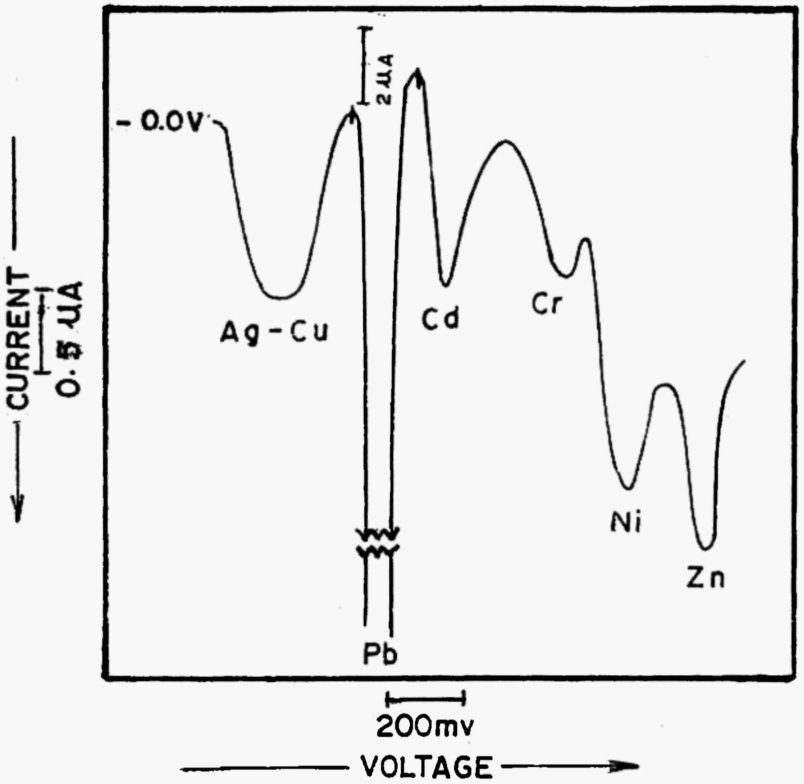

FIG. 2 : Differential Pulse Anodic Stripping Voltammogram of Galena sample (100mg / 100ml) in 0.1 M ammonia-ammonium chloride buffer + 0.001 % gelatin; pH 8.00 ± 0.02

/12,13/. In the DPAS voltammogram, the peak of Ag is merged with that of Cu, which may be due to the increased detection sensitivity of DPASV which results in enlarged peaks as compared to DPP ones. Since their peak potentials are very close to each other, they produce only one single peaked signal; whereas, in the case of the relatively less sensitive DPP method, the peaks due to Ag(I) and Cu(II) are comparatively small and are not merged. To confirm the presence of the said metal ions in the sample a definite quantity of standard solution of each metal ion was added to the analyte and polarograms were recorded, which increased the wave height of each metal ion signal without any change in $E_{1/2}/E_p$ values (Table 1).

Table 1

Results of galena sample analysis for metal ions (mg/100 mg)*

METAL ION	AMOUNT ADDED	BY DCP		BY DPP		BY DPASV	
		% Recovery (S.D.**)	Found	% Recovery (S.D.**)	Found	% Recovery (S.D.**)	Found
Ag	–	100%	0.018	100%	0.018	–	–
	0.012	(0.002)	0.030	(0.001)	(0.030	–	–
Cu	–	99.2%	1.270	99.2%	1.270	–	–
	1.270	(0.011)	2.520	(0.001)	2.520	–	–
Pb	–	99.3%	71.52	99.4%	71.52	99.4%	71.52
	62.16	(0.020)	132.90	(0.02)	133.00	(0.050)	133.00
Cd	–	99.0%	0.185	99.2%	0.185	99.3%	0.185
	0.124	(0.004)	0.306	(0.003)	0.306	(0.003)	0.307
Cr	–	99.1%	0.030	99.6%	0.03	99.6%	0.03
	0.03	(0.004)	0.059	(0.003)	0.059	(0.003)	0.059
Zn	–	100%	0.072	100%	0.072	100%	0.072
	0.065	(0.004)	0.137	(0.003)	0.137	(0.002)	0.137
Ni	–0.015	99.6%	0.017	100%	0.017	100%	0.017
		(0.007)	0.031	(0.005)	0.032	(0.006)	0.032

*Results are averages of four determinations.

**Standard deviation (mg Kg^{-1})

Based on the presence of these metal ions in the sample, some synthetic samples of varying concentrations of the ions were prepared and their polarograms were recorded under identical experimental conditions (Fig. 3, Table 2). There was no change in $E_{½}/E_p$ of the aforesaid metal ions, and also the proportionality of the concentration of each metal ion to its wave/peak height was maintained. Thus, the possibility of accurate qualitative as well as quantitative oligo determinations of the metal ions in the sample was re-confirmed.

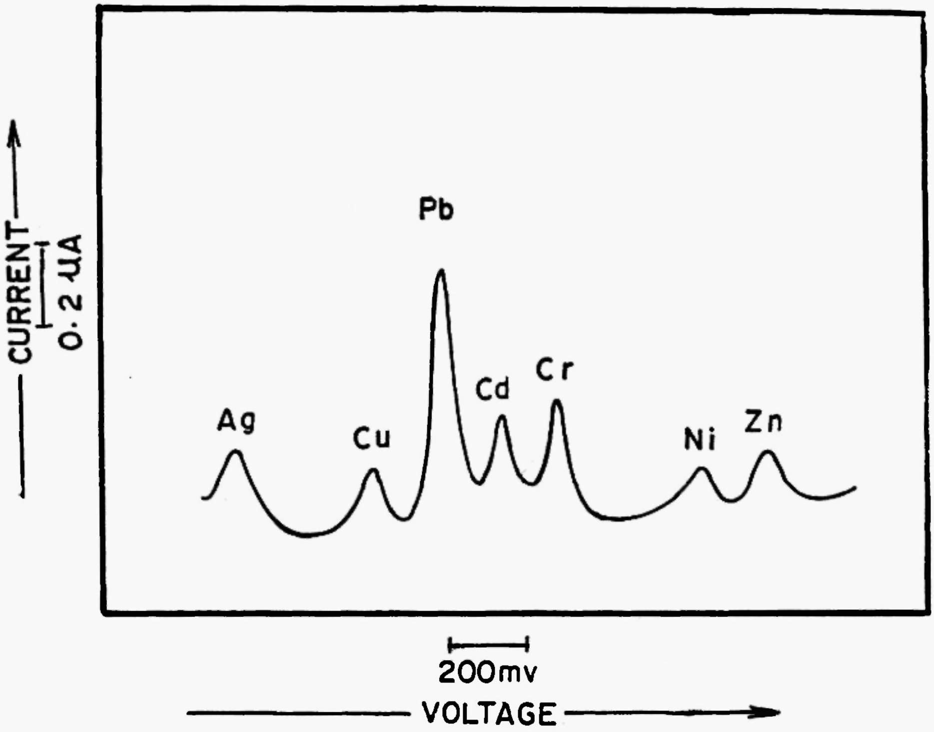

FIG. 3 : Differential Pulse Polarogram of a synthetic sample containing: Ag(I) 0.01mg, Cu(II) 1.26mg, Pb(II) 10.72mg, Cd(II) 0.56 mg, Cr(II) 0.50mg, Ni (II) 0.59mg, Zn(II) 0.56mg / 100 ml in 0.1 M ammonia-ammonium chloride buffer + 0.001 % gelatin; pH 8.00 ± 0.02

Table 2

Analysis of synthetic samples

Composition of synthetic samples (mg/100 ml)							Amount found using DPP (mg/100 ml)*						
Ag	Cu	Pb	Cd	Cr	Ni	Zn	Ag	Cu	Pb	Cd	Cr	Ni	Zn
0.01	1.27	10.73	0.56	0.51	0.59	0.56	0.01	1.26	10.72	0.56	0.50	0.59	0.56
0.02	2.52	21.42	1.12	1.0	1.17	1.12	0.02	2.52	21.42	1.11	1.0	1.18	1.12
0.04	5.04	42.84	2.24	2.0	2.34	2.24	0.04	5.02	42.80	2.23	2.0	2.33	2.24
1.08	0.63	2.07	1.12	0.51	0.54	0.63	1.08	0.63	2.06	1.11	0.51	0.54	0.62

*Results are averages of four determinations.

Quantitative Analysis of the Sample

The principal use of DCP, DPP and DPASV was shown for the quantitative oligo determination of Ag(I), Cu(II), Pb(II), Cd(II), Cr(II), Ni(II) and Zn(II) in the sample. The precision and percentage recovery of the spiked samples for the determination of the above mentioned metal ions has been reported in Table 1. The results indicated that the percentage recovery is over 99% for all the metal ions.

Table 3 shows the final analysis results of the sample. These results were compared with those obtained using the AAS method. The comparative data are also shown in the table, which are in excellent agreement. However, the statistical data express the superiority of the polarographic method over the AAS method for such an analysis.

Table 3
Comparison of voltammetric and AAS trace analysis data on galena sample

Metal Ion	By Voltammetry*	By AAS
Ag	0.18	0.14
Cu	12.70	12.56
Pb	715.20	715.20
Cd	1.85	1.80
Cr	0.30	0.30
Ni	0.17	0.16
Zn	0.72	0.70

*Amount in mg/g

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