

# Polarographic analysis of zinc ore concentrates for the determination of lead, copper, cadmium and zinc

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**I**N the field of inorganic analysis, the polarograph has been applied successfully for the determination of many elements under favourable conditions to obtain somewhat greater accuracy than the other instrumental or chemical methods with far less expenditure of time.

The present work was taken up to find out a rapid and reliable polarographic method for the analysis of a large number of samples of zinc ore concentrates required to be analysed during the beneficiation of zinc ores in this laboratory. The difficulties encountered for the determination of lead, copper, cadmium and zinc by existing wet chemical methods are well-known. It is often required to separate the metals from each other and the interfering elements also, which makes the process time-consuming.

For the polarographic determination of lead various methods have been described by different authors<sup>1-4</sup> from time to time. Using 0.25 M ammonium acetate as supporting electrolyte, Bachman and Astle<sup>5</sup> found that metals whose half-wave potentials are more negative than -0.3 Volts vs. S.C.E. yield normal polarograms and their diffusion currents are directly proportional to their concentration. Polarographic characteristics of a number of cations in ammonium acetate medium were also studied by Desesa<sup>6</sup> et al. It is evident from these works that lead can be determined quantitatively in ammonium acetate medium. Solubility of lead sulphate in ammonium acetate has been utilised in the present work for the determination of lead.

The sample was dissolved in hydrochloric and nitric acid mixture and lead was separated by fuming with sulphuric acid. The precipitate was filtered off. Lead sulphate in the precipitate was extracted with ammonium acetate solution and lead was estimated polarographically. From the filtrate, copper, cadmium and zinc were determined polarographically making the solution ammoniacal in presence of ammonium chloride.

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## SYNOPSIS

*A rapid method for the determination of copper, cadmium, zinc and lead in zinc ore concentrates has been described. After taking the sample in solution with nitric acid and hydrochloric acids, lead was separated as lead sulphate by fuming with sulphuric acid and dissolved in ammonium acetate. From the polarogram obtained with the above solution, lead was estimated by comparing the step-height of the lead wave with the standard calibration graph. After removal of lead, the filtrate was treated with ammonium chloride and ammonia and polarographed. From the step-heights obtained for copper (second wave), cadmium and zinc, their percentages were calculated from the standard calibration graphs. It has also been found that even small amounts of lead can conveniently be determined by this method where it is separated as lead sulphate.*

## Experimental

### Apparatus

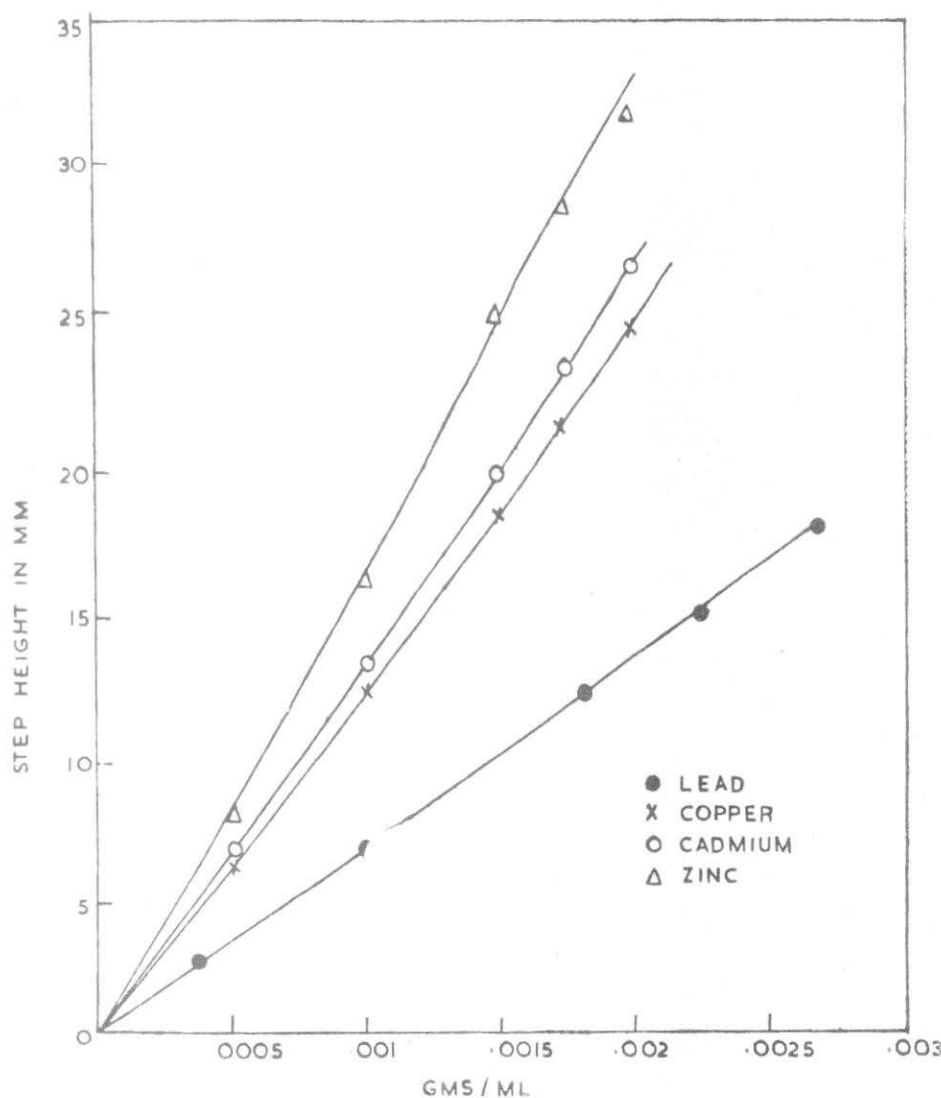
The polarograph used was a Cambridge Polarograph having photographic recording arrangement with dropping mercury electrode assembly. Saturated calomel electrode was used as reference cell. The temperature was controlled at 25°C ( $\pm 0.5$ ) with a thermostat.

### Reagents and chemicals

All the reagents used for the work were of chemically pure quality and the metals used for the preparation of standard solutions were of spectrographically pure variety. Developing and fixing solutions were prepared according to the composition recommended by the manufacturers of the particular type of photographic paper used.

### Preparation of standard solutions and calibration graphs

For the preparation of standard solutions spectrophotometrically



1 Determination of lead, copper, cadmium and zinc

cally pure copper, cadmium, lead and zinc metals were separately dissolved in nitric acid. Mixing different aliquot portions of the above solutions, five standard solutions were prepared.

One gram each of spectrographically pure copper, cadmium, lead, iron and zinc were weighed accurately and dissolved separately in nitric acid and made up to 100 ml in measuring flasks. Five synthetic solutions containing 0.0005 to 0.003 g of the above metals were prepared by mixing the individual metal solutions. From these solutions lead was precipitated as lead sulphate by fuming with sulphuric acid.

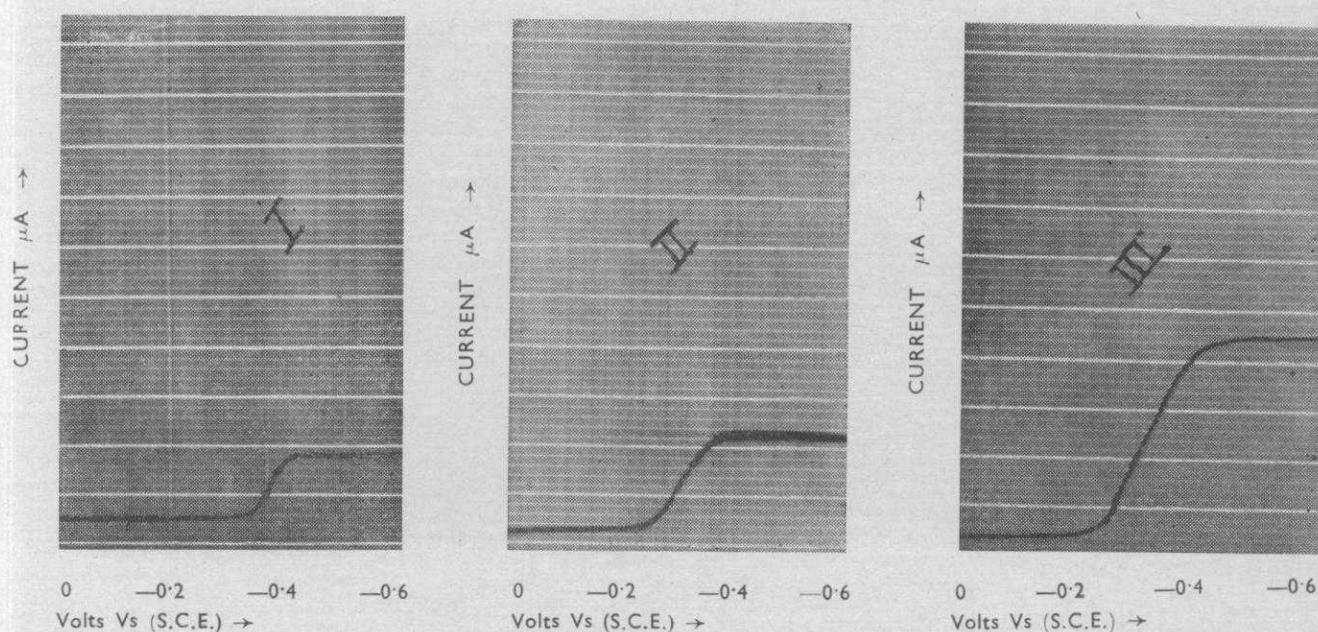
After filtering and washing, the precipitates were dissolved and diluted to 100 ml with 5% ammonium acetate solution (w/v). The solutions were polarographed and the wave heights of lead were measured and plotted against g of lead to obtain the calibration graph for lead.

To the filtrate obtained after separation of lead 10 g

solid ammonium chloride was added and the solutions were made ammoniacal. The volumes were made up to 100 ml in measuring flasks and allowed to settle the precipitate of ferric hydroxide. A suitable portion of the supernatant liquid was taken from each flask and after removal of dissolved oxygen, polarograms were recorded. The step heights for copper (second wave), cadmium and zinc were measured and plotted against their respective concentrations in g/ml to obtain the standard calibration graphs. The calibration graphs obtained for lead, copper, cadmium and zinc are given in Fig. 1.

#### Procedure

The quantity of sample taken for analysis depended on its composition. For concentrates less amount of the sample is preferable. In case a larger amount of sample is necessary e.g. for the determination of



2 Polarograms of three unknown samples for lead only in presence of 5% ammonium acetate as supporting electrolytes and 0.01% gelatin; sensitivity was 1/15, galvanometer damping 2, and counter current 3

cadmium, the solution may be diluted to a convenient volume to bring the concentrations of other constituents within the range of the determination. The procedure given here is for general use.

2.5 g of the finely ground sample was taken in 250 ml beaker and covered with a watch glass. A mixture of 20 ml concentrated HCl and 10 ml concentrated HNO<sub>3</sub> was slowly added to the sample and digested on a hot plate until a clear solution was obtained. 5 ml concentrated H<sub>2</sub>SO<sub>4</sub> was added to the cooled solution, fumed to almost dryness, again cooled, diluted with 20 ml water and the process of fuming repeated. After cooling, 40 ml water was added to the solution and boiled. The precipitate was filtered off and washed with dil H<sub>2</sub>SO<sub>4</sub> (1:99). The filtrate and washings were collected in a 100 ml measuring flask and were reserved for determination of copper, cadmium and zinc.

0.5 g of solid ammonium acetate was added to the precipitate on the filter paper and then a hot solution of 5% ammonium acetate was added. The filtrate with the filter paper was collected in a 100 ml measuring flask and shaken well in order to have the precipitate of PbSO<sub>4</sub> completely dissolved. The solution was cooled by placing under tap water. 10 ml of 0.1% freshly prepared gelatine solution was added to it and the volume was made up to the mark with 5% ammonium acetate solution. A portion of the supernatant liquid was taken in the polarographic cell. Dry hydrogen was passed for ten minutes through the cell to remove dissolved oxygen. The polarogram was recorded from -0.3 volt to -0.8 volt vs. S.C.E. and step heights for lead was measured at -0.48 volts vs. S.C.E. Typical polarograms for Pb are given in Fig. 2.

10 gm of solid ammonium chloride was added to the filtrate after removal of Pb and the solution was

made up to the mark after adding 10 ml of 0.1% gelatin solution. Taking an aliquot portion of the supernatant solution into the cell, hydrogen was passed for ten minutes to remove oxygen and polarogram was recorded from -0.2 volt to -1.6 volts vs. S.C.E. polarograms for copper and zinc are given in Fig. 3.

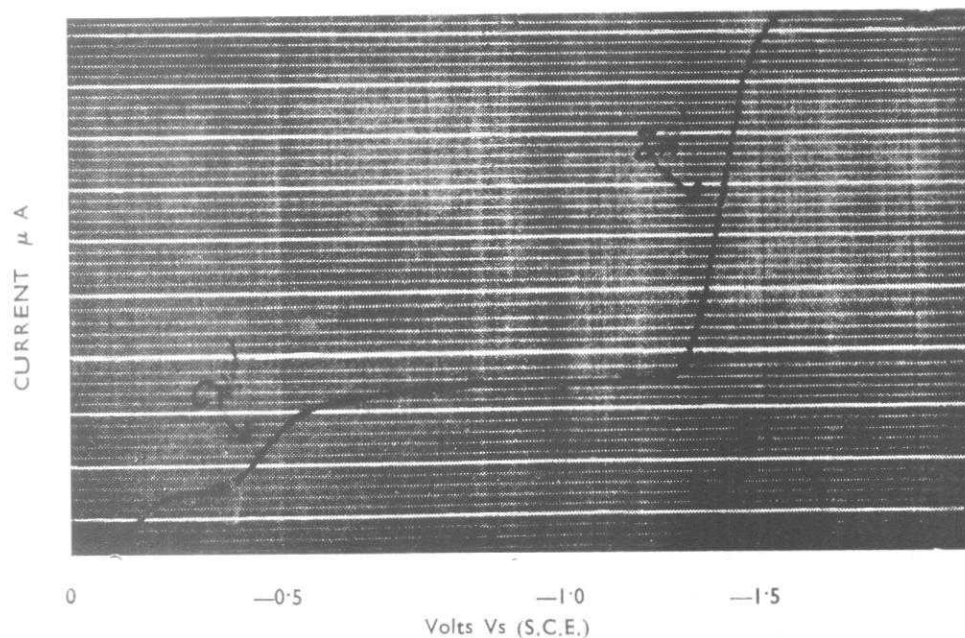
The step heights were measured at -0.45, -0.8 and -1.4 vs. S.C.E. respectively for Cu, Cd, Zn and compared with those of calibration curves. Second wave of copper was taken for determination of copper. Table I shows the values obtained polarographically. Results obtained by the usual chemical method are given for comparison.

### Discussion

The concentration of cadmium in zinc ore concentrate is very low and more sample may be required for its determination. In that case, for the determination of other constituents an aliquot portion of the solution may be diluted to a suitable volume maintaining the concentration of ammonium chloride identical to prevent precipitation of zinc by hydrolysis.

Solubility of PbSO<sub>4</sub> in ammonium acetate is retarded by the presence of barium, silica, tin and antimony which can be eliminated by using sufficient amount of the reagent even when BaSO<sub>4</sub> is 100 times more than lead. Free sulphuric acid when present to the extent of 10% will prevent the extraction of PbSO<sub>4</sub> with ammonium acetate completely. But in the procedure described there is little chance of getting this concentration of sulphuric acid after washing. To separate lead from silica, the precipitate may be hydrofluorised by the usual procedure.

Gelatin was found to have a marked effect on the



3 A polarogram of unknown sample in presence of ammonium chloride and ammonium hydroxide as supporting electrolytes showing the waves of copper and zinc

wave of lead. 0.01% gelatin was found sufficient to suppress the lead maxima. Greater concentrations of gelatin may decrease the step height of the wave consi-

derably. Concentration of ammonium acetate was also found to reduce the step height of the lead wave when it was present in excess. Final concentration of

TABLE I Results of ore samples analysed polarographically and chemically

	Chemical values				Polarographic values			
	% Cu	% Pb	% Zn	% Cd	% Cu	% Pb	% Zn	% Cd
1.	6.28	11.79	13.79	—	6.32	11.56	13.53	—
2.	2.41	5.98	18.62	—	2.43	5.86	18.02	—
3.	0.34	1.14	41.52	—	0.33	1.12	40.35	—
4.	3.84	20.7	12.71	—	3.76	19.88	19.46	—
5.	4.21	9.61	13.11	—	4.03	9.56	13.33	—
6.	3.61	1.59	36.77	0.1	3.07	1.54	38.25	0.08
7.	2.58	2.27	14.38	0.2	2.46	2.29	14.25	0.17
8.	0.52	1.92	37.29	0.1	0.53	1.95	37.89	0.13
9.	5.95	11.37	14.11	—	5.88	11.23	14.21	—
10.	2.55	7.12	14.05	—	2.45	7.16	14.02	—
11.	5.05	3.02	52.05	0.08	5.04	3.31	50.73	0.05*
12.	6.01	2.07	51.02	0.07	6.00	2.08	50.68	0.05*

\*The results were also checked spectrographically.

the test solution was controlled to avoid any detrimental effect on the lead wave.

For determination of lead in some other alloys, few experiments were carried out with 'clad metal' by the same procedure. It was found to be suitable for its accurate determination with far less expenditure of time required by usual chemical method.

#### Acknowledgement

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## Discussions

Mr Sunil Dey (Chemical and Metallurgical Design Company Private Limited, New Delhi) : Is polarographic analysis possible to determine Ni, Co, Zn, Cu, Cd and Al in an acidic solution of nickel sulphate containing about 45 g/p.l Ni.

Dr H. P. Bhattacharya (Author) : It may be possible

to determine Cu and Cd directly from the solution as both the metals give well defined waves in sulphuric acid solution. They may also be determined along with Ni in ammonia and ammonium chloride supporting electrolyte. But for determination of Co and Zn, Ni will have to be separated first. As regards Al it may not be possible to determine it polarographically.