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

H. P. BHATTACHARYA and P. C. DEBNATH

In 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 from time to time. Using 0.25 M ammonium acetate as supporting electrolyte, Bachman and Astle 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 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 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 (±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 spectrophotically 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 spectographi-
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
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.

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 PbSO₄ 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 BaSO₄ is 100 times more than lead. Free sulphuric acid when present to the extent of 10% will prevent the extraction of PbSO₄ 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
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 con-
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

![Image: A polarogram of an unknown sample in presence of ammonium chloride and ammonium hydroxide as supporting electrolytes showing the waves of copper and zinc.](image)

TABLE I Results of ore samples analysed polarographically and chemically

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Polarographic</th>
<th>% Cu</th>
<th>% Pb</th>
<th>% Zn</th>
<th>% Cd</th>
<th>% Cu</th>
<th>% Pb</th>
<th>% Zn</th>
<th>% Cd</th>
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<tbody>
<tr>
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<td>% Pb</td>
<td>% Zn</td>
<td>% Cd</td>
<td>% Cu</td>
<td>% Pb</td>
<td>% Zn</td>
<td>% Cd</td>
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<td>% Pb</td>
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<td>13.79</td>
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*The results were also checked spectrographically.
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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

Thanks are due to Dr T. Banerjee, Scientist-in-charge, National Metallurgical Laboratory, for his kind permission to publish the paper.

References


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/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.