International Journal of Chemical Research and Development

Manisha Bhattacharya
Department of Chemistry, R.J.
College Ghatkopar, Mumbai,
Maharashtra, India

Pintu B
Merck Life Sciences Pvt. Ltd.,
Maharashtra, India

SG Dixit
Department of Chemistry, R.J.
College Ghatkopar, Mumbai,
Maharashtra, India

Corresponding Author:
Manisha Bhattacharya
Department of Chemistry, R.J.
College Ghatkopar, Mumbai,
Maharashtra, India

Chronopotentiometric study of CuO in aqueous and nonaqueous solvents

Manisha Bhattacharya, Pintu B and SG Dixit

Abstract
Chronopotentiometry technique was employed to study the nature of CuO leaching in various solvent systems. Chronopotentiometry curves were obtained using a carbon paste electrode as the working electrode. The potential-time curve was obtained applying a constant potential of 2V and varying the current from $10 \times 10^{-6}A$ to $200 \times 10^{-6}A$. The slope of the curves varied between -4.27 at $10 \times 10^{-6}A$ to -29.63 at 50×10^{-6} A to -5.85 V/s at $200 \times 10^{-6}A$. Correlation values obtained were between -0.972 to -0.948. For the chronopotentiometric curve at a particular current density, the $it^{1/2}$ term becomes independent of further change in current value. This indicates that copper oxides dissolution is controlled by solid-state diffusion.

Keywords: Chronopotentiometry, aqueous and nonaqueous solvents leaching

Introduction

Copper ore generally found in nature are mainly sulphides or oxides or a mixture of these two. To recover copper from ores of carbonate origin it is difficult by conventional metallurgical techniques [1-3]. Oxidised copper minerals cannot be effectively separated from carbonate gangue minerals by floatation and direct acid leaching is not economical because of excessive acid consumption. The recovery of copper from oxidised copper ores by ammonia or cyanide leaching is technically feasible, but leachant generation faces a problem. The chemistry of copper oxide leaching [4, 5] depends upon various factors of which leachant and solvent system plays an important role. The leaching of metal oxides is favoured in the presence of an added oxidising or reducing agent. The leaching of copper oxides with aqueous solution of sulphur dioxide [6-10] is of broad commercial interest. DMSO was chosen as the non-aqueous solvent for the electrochemical studies due to its unique properties [11-13]. In the present work, Chronopotentiometry an electrochemical technique is used, in which a current signal is imposed on a quiescent electrochemical cell and a response signal, usually the potential of the working electrode is measured and plotted as a function of time. Here the current step is impressed across an electrochemical cell containing unstirred solution [14-18].

Materials and Methods

All chemicals used throughout these studies were either of AR grade or were purified using known techniques [19]. CuO obtained from S.D. Fine chemicals was used as received. DMSO was of AR grade and was purified by keeping in $3A^0$ molecular sieves to absorb water [20]. AR grade TBAP was obtained from Fluka and was oven dried for 1 hour at 100 °C before the experiment. KCl was AR grade and was used as such. Sodium sulphate, Iodine, EDTA of AR grade were used and were obtained from S. D. Fine Chemicals. Graphite powder and paraffin oil used were of reagent grade. Nitrogen gas was obtained from Industrial Oxygen Ltd. with 99% purity. Sulphur dioxide gas was supplied by INOX Ltd. in small volume capacity and was used directly.

Electrode systems: Electrochemical studies were conducted using a five necked round bottom flask. Electrochemical measurements were carried out using a three electrode system i.e., working electrode (WE), an auxiliary or counter electrode (CE) and a reference electrode (RE) [21, 22]. The WE was made up of graphite paste [23-27], platinum wire served as a CE and the RE electrode used was SCE for aqueous solution and a silver wire which served as a quasi-reference electrode (QRE) in non-aqueous solution.

The solution was purged for about 1 hour before each experiment with pure nitrogen gas to remove any dissolved oxygen. The studies were performed in the inert nitrogen atmosphere which was maintained during the run of the experiment. The QRE was placed very close to the WE to eliminate any iR potential drop in the solution. An unstirred solution at room temperature was used for the measurements.

Estimation of copper: Copper was estimated by EDTA method [28]. About 200 mg of copper oxide was taken in a beaker and then 2 ml of conc. HNO_3, 2 ml of conc. H_2SO_4 and about 1-2 drops of 70% perchloric acid was added in it. The solution was heated strongly to dryness. The sample treated above was dissolved in 5 ml of 2N HCl, then 10 ml of conc. Ammonia solution was added. The resulting solution was titrated against 0.01 M EDTA solution using Fast Sulphon Black F as an indicator. The colour changed from blue to pale green in the vicinity of endpoint. The metal % was calculated as:

1000 ml of 1M EDTA = 63.54 gm of Cu.

Determination of Sulphur dioxide concentration: In a conical flask known volume of standard 0.1 N iodine solution (10-25ml) depending upon the concentration of sulphur dioxide in the solution was taken and diluted with distilled water to about 150 ml and acidified with 5 ml of 2 N HCl [29]. Then the known volume of aqueous sulphur dioxide solution was taken in a pipette and was slowly added to the solution in the conical flask and the excess iodine was titrated against standard 0.1 N sodium thiosulfate solution, using starch as an indicator. The total volume of standard iodine solution taken minus the burette reading gave the amount of iodine which has reacted with aqueous sulphur dioxide. From the following reaction.

$$SO_3^{-2} + I_2 + H_2O = SO_4^{-2} + 2H^+ + 2I^-$$
$$HSO_3^- + I_2 + H_2O = SO_4^{-2} + 3H^+ + 2I^-$$
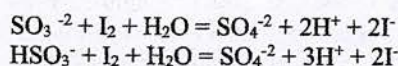
It follows that
1 ml 0.1 N I_2 = 0.0032 gm SO_2
In case of determination of sulphur dioxide in DMSO, due to high concentration of sulphur dioxide very low volume of the solvent mixture i.e.; 0.1 ml was taken for iodometric analysis.

pH Meter: The pH of the solution was measured with the Elico pH-meter instrument. The instrument was standardised using buffer tablets before each experiment.
Potentiostat: Electrochemical measurements were performed using a E.G & G Princeton Applied Research Corporation 273 Potentiostat/Galvanostat model. M270 electrochemical software was used for various functions of the instrument. The instrument was connected to a 386 computer along with a printer.

Results and Discussions
Chronopotentiometry study of CuO in water: Chronopotentiometry technique was employed to study the nature of CuO leaching in water system. Chronopotentiometry curves were obtained using carbon paste electrode as working electrode. The potential-time curve was obtained by keeping the potential constant and by varying the current density. The variation of potential as a function of time was measured.

Table 1: Chronopotentiometric data of CuO in water at various current range.

Current (10^{-6}A)	Time (s)	Area (Vs)	Area ($Vs^{1/2}$)	Slope 10^{-3} V/s	Chi-square	Correl
10	120	-25.8	1.84	-9.21	0.07	-0.94
10	40	-14.5	2.73	-15.83	0.21	-0.95
10	30	-12	3.23	-18.88	0.16	-0.97
50	100	-16.2	4.48	-13.36	0.07	-0.97

An initial potential of 1.0 V was fixed and the current densities were varied from 10 x 10^{-6} A to 50x 10^{-6} A. The transition time was measured in different current ranges keeping the step time constant at 10 seconds. The plot of E versus t at a particular current range shows that as the current range is increased i.e.; 10 x 10^{-6} A to 50 x 10^{-6} A, the potential value decreases in an increasing trend. The potential value initially decreases up to 30 seconds, and then almost remains constant at a particular current range. Both at very low and very high current value, the plots show irregular behaviour.
It was observed that after a certain current value, the $it^{1/2}$ term becomes almost constant. There is no further change in potential with increase in current density. The term $it^{1/2}$ becomes independent of current density as shown previously. The behaviour of $it^{1/2}$ can be effectively used to study mechanisms of electrode reactions. A constant value of $it^{1/2}$ over a wide range of i indicates simple, diffusion-controlled electrode reaction with no kinetic or adsorption phenomena at a planar electrode.
The area of the curve using chronopotentiometry data for both E versus t and E versus $t^{1/2}$ has been obtained. Table 1 shows the value at different current ranges. The area of the curve decreases from -25.79 Vs to -12.02 Vs for E versus t and 1.84 to 4.48 $Vs^{1/2}$ for E versus $t^{1/2}$. It was observed a gradual increase in area at a fixed time period of 10 seconds. The area of the curve above 0.5 x 10^{-4} A increases rapidly and later on becomes irregular.
The slopes of CuO in water were obtained at different current ranges using E versus t plots are shown in Table 1. The slope value increased from -9.21 x 10^{-3} V/s at 10 x 10^{-6} A and 120 seconds to 18.88 x 10^{-3} V/s at 10 x 10^{-6} A and 30 seconds. Above 50 x 10^{-6} A, the slope value decreased to 13.36 x 10^{-3} V/s. The slope value is maximum around 10 x 10^{-6} A. The chi-square and correlation value were calculated using E versus t plots. The chi-square decreased from 0.17 to 0.07 at 10 x 10^{-6} A. The correlation value varied from -0.977 to -0.947.

Chronopotentiometry study of CuO in water-sulphite system: Chronopotentiometry curves were employed to determine the nature of CuO in the water-sulphite system. The current densities applied were 10, 25, 50, 75 and 100 x 10^{-6} A with the initial potential fixed at 1.0 V. The step time was kept constant throughout the experiment. The E-t plots were obtained at various pH. It was observed that with the increase in current range from 5 x 10^{-6} A to 100 x 10^{-6} A, the potential value decreases in an increasing trend. The potential value initially decreases upto 0.5 seconds and then almost remains constant at a particular current range. It was seen that at current ranges lower than 10 x 10^{-6} A and higher than 100 x 10^{-6} A the chronopotentiometric plots are ill-defined. This trend is seen at all the pH values studied.
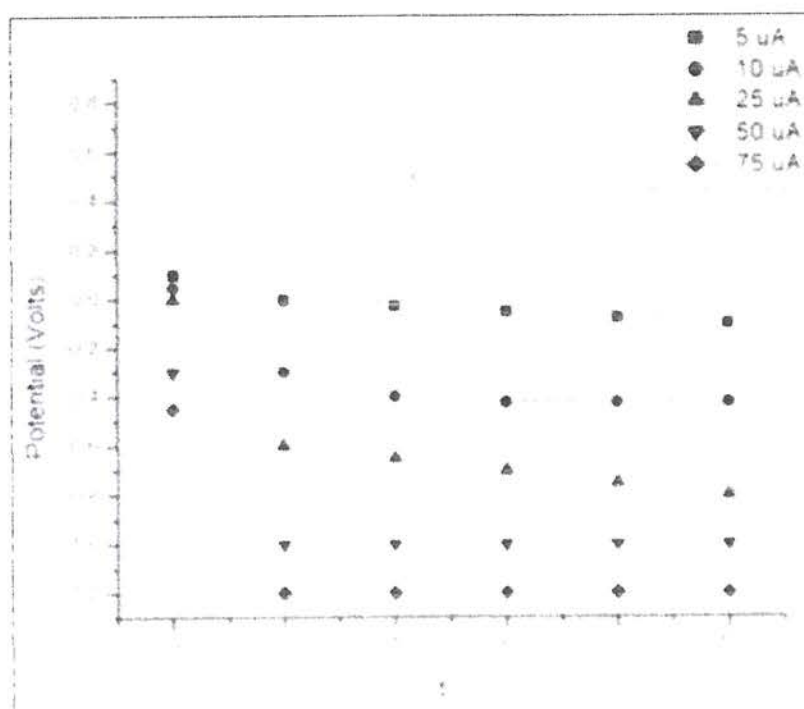
Table 2: Chronopotentiometric data of CuO in water +sodium sulphite system at various current range and at various pH.

Current (10^{-6}A)	Time (s)	Area (Vs)	Area ($Vs^{1/2}$)	Slope 10^{-3} V/s	Chi-square	Correl.
at pH 8.8						
5	10	-2.82	-0.53	-73.48	0.82	-0.96
10	10	-5.03	-1.07	-96.35	6.78	-0.84
25	10	-7.63	1.99	-43.15	2.42	-0.76
50	10	-8.09	-2.17	-35.57	3.06	-0.65
75	10	-9.11	-2.50	-27.06	3.06	-0.55
100	10	-8.79	-2.52	-16.85	2.88	-0.39
at pH 3.0						
5	10	-0.67	-0.11	-27.80	0.04	-0.98
10	10	-3.87	-0.96	-42.15	0.89	-0.88
25	10	-6.80	-1.83	-37.33	1.50	-0.79
50	10	-9.57	-2.69	-27.28	3.49	-0.53
100	10	-11.94	-3.36	-26.34	4.37	-0.47
at pH 2.2						
10	10	-3.04	-0.75	-38.33	0.75	-0.88
25	10	-6.69	-1.72	-46.42	0.94	-0.89
50	10	-8.99	-2.41	-41.00	2.47	-0.74
75	10	-10.25	-2.80	-34.26	3.67	-0.60
100	10	-9.55	-2.69	-32.94	5.63	-0.51
at pH 1.8						
5	10	-0.26	-0.11	-13.64	0.15	-0.97
10	10	-1.69	-1.34	-39.59	0.40	-0.93
25	10	-4.81	-1.23	-40.92	1.12	-0.85
50	10	-9.29	-2.52	-42.63	5.26	-0.62
75	10	-10.52	-2.90	-39.61	7.09	-0.53
100	10	-11.44	-3.22	-37.22	8.02	-0.49
at pH 1.5						
10	10	-2.46	-0.64	-30.68	0.35	-0.91
25	10	-6.42	-1.47	-98.06	3.40	-0.91
50	10	-8.08	-1.92	-84.30	7.32	-0.80
75	10	-9.81	-2.52	-54.38	10.03	-0.59
100	10	-9.94	-2.62	-46.34	9.20	-0.54

When we plot E versus $t^{1/2}$, we found that after a certain current value the $it^{1/2}$ term becomes independent of any increase in current density. It was noted that the current density and the transition time becomes constant after a certain current value. It can be represented by the equation: $it^{1/2}$ = constant

Fig 1: Chronopotentiometric plot of CuO in water + sulphite system at pH=1.8

The area of the curve for the E vs t plots were calculated at different current ranges and pH values. The data has been tabulated in Table 2 gradual increase in area at a fixed time period of 10 seconds was observed at almost all the pH values. However the magnitude of area was lower at pH=1.8 as compared to other pH values.

The slopes, chi-square and correlation value were calculated for CuO in the water-sulphite system from the E-t curves. These were obtained at different current ranges and pH values. Table 2 shows the data calculated for slope, chi-square and correlation value from the E-t curves. The slope value increased with the increase in current range upto 25 x 10⁻⁶ A and then again decreased gradually. This trend is seen in almost all pH values studied. However at pH=1.8, the slope value increased upto 50 x 10⁻⁶ A and then decreased again. It was seen that with further rise in current value, the slope remains constant. The chi-square value increased with increase in current range and decrease in pH value. At pH=1.8, the magnitude of chi-square was comparatively lower than other pH values. The correlation value varied from -0.492 to -0.988 at different pH values. As studied by Youzbashi and Dixit [30] in leaching of cuprous oxide with aqueous SO₂ solution the dissolution was controlled by surface reactions and leaching rate depended on particle size.

Chronopotentiometry study of CuO in DMSO

Chronopotentiometry curves were obtained for CuO in DMSO using carbon paste electrode as working electrode. The current densities applied were 5, 10, 50, 75 and 100 x 10⁻⁶ A with a fixed initial potential of 1.0 V. The step time was kept constant at 10 seconds. The transition time (t) was measured in a different current range. It was observed that when the current range is increased from 5 to 100 x 10⁻⁶ A, the potential value decreases in an increasing trend. At very high or very low current range, the chronopotentiometry plots are ill-defined.

It was observed that the $it^{1/2}$ becomes constant with further increase in current density. The transition time also becomes constant with further increase in current density.

The area of the curve for E versus t and E versus $t^{1/2}$ has been obtained with a different current range. A gradual increase in area at a fixed time period of 10 seconds was observed for both types of plots. When the current range was increased to value more than 100 x 10⁻⁶ A, the nature of the curve became ill-defined.

Table 3: Chronopotentiometric data for area of CuO in DMSO at various current ranges.

Current (10⁻⁶A)	Time (s)	Area (Vs)	Slope 10⁻³ V/s	Chi-square	Correl.
5	10	-3.57	-30.38	0.935	-0.94
10	10	-4.45	-42.23	2.76	-0.92
50	10	-8.15	-48.26	1.80	-0.95
75	10	-11.24	-40.03	2.55	-0.91
100	10	-12.73	-30.88	3.86	-0.82

Table 3 shows the slope values of CuO in DMSO using E versus t plots. The slope value varied from -30.38 V/s at 5 µA to -30.88 at 100 µA. It was observed that with the increase in current range, the slope value increases to -48.26 V/s at 50 µA, further at higher current value the slope value decreases again to -30.88 V/s at 100 µA. Similar findings were observed for E versus $t^{1/2}$ plots. Firstly the slope increases from -0.12 $V/s^{1/2}$ at 5 µA to have a maximum value of -0.19 $V/s^{1/2}$ at 50 µA and then decreases again to -0.12 $V/s^{1/2}$ at 100 µA. The values are shown in Table 3 along with statistical calculation of chi-square and correlation coefficient. The chi-square vales increases from 0.12 at 5 µA to 0.69 at 100 µA. The correlation value varies from -0.958 to -0.995. It was observed that the area increases with an increase in current. The slope value increases at 5 x 10⁻⁶A, reaches a maximum value near 50 x 10⁻⁶A and then decreases rapidly.

4. Chronopotentiometry study of CuO in DMSO + SO₂

Chronopotentiometry technique was used to study the nature of CuO leaching in DMSO + SO₂ solvent system.

An initial potential of 1.0V was fixed and the current densities were varied from 10 x 10⁻⁶ A to 200 x 10⁻⁶ A. The transition time was measured in different current range keeping the step time constant at 10 seconds. The plot of E versus t at a particular current range has been shown in Fig. 3a. It was seen that as the current range is increased i.e.; 10, 50, 75, 100 and 200 x10⁻⁶A, the potential value decreases in an increasing trend. The potential value initially decreases up to 0.5 seconds, and then almost remains constant at a particular current range. Both at very low and very high current value, the plots shows irregular behaviour.

The plot of E versus $t^{-1/2}$ at different current range was obtained as shown in Fig. 2. It was observed that after certain current value, the $it^{1/2}$ term becomes almost constant. There is no further change in potential with increase in current density. The term $it^{1/2}$ becomes independent of current density.

Table 4: Chronopotentiometric data for area of CuO in DMSO+ SO₂ at various current ranges.

Current (10⁻⁶A)	Time (s)	Area (Vs)	Area (Vs¹ᐟ²)	Slope 10⁻³ V/s	Chi-square	Correl.
10	10	-0.54	-0.16	-4.91	0.01	-0.89
50	10	-2.12	-0.49	-33.42	0.41	-0.91
75	10	-4.84	-1.27	-31.62	0.79	-0.83
100	10	-5.69	-1.57	-20.30	1.48	-0.58
200	10	-7.71	-2.20	-18.95	2.50	-0.45

The area of the curve using chronopotentiometry data for both E versus t and E versus $t^{-1/2}$ has been obtained. The area of the curve increases from -0.54 Vs to -7.71 Vs for E versus t and -0.16 to -2.20 $Vs^{1/2}$ for E versus $t^{-1/2}$. It was observed a gradual increase in area at fixed time period of 10 seconds. The area of the curve above 200 x10⁻⁶A increases rapidly and later on becomes irregular.
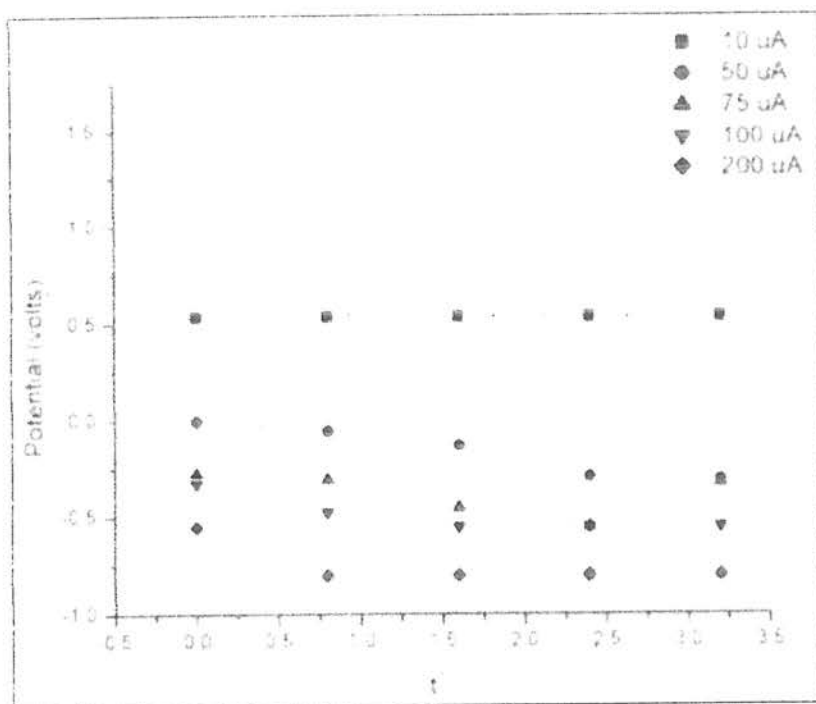
Fig 2: Chronopotentiometric plot of CuO in DMSO + SO₂ system

The slopes of CuO in DMSO + SO₂ were obtained at different current range using E versus t plots are shown in Table 6. The slope value increased from -4.91 x 10^{-3} V/s at 10 x10^{-6}A to 33.42 x 10^{-3} V/s at 50 x10^{-6}A. Above 50 x10^{-3}A, the slope value decreased from 31.62 x 10^{-3} V/s at 75 x10^{-6}A to 18.95 x 10^{-3} V/s at 200 x10^{-6}A. The slope value is maximum around 50 x10^{-6}A. The chi-square and correlation value were calculated using E versus t plots. The chi-square first decreased from 11.07 x 10^{-3} at 10 x10^{-6}A to 0.41 x 10^{-3} at 50 x10^{-6}A. The value increased from 0.41 x 10^{-3} to 2.50 x 10^{-3} at 200 x10^{-6}A at 10 seconds. The correlation value varied from -0.913 to -0.458.

The slope value calculated using E versus $t^{-1/2}$ curve. Initially the slope value decreased from -15.88 x 10^{-3} V/s$^{1/2}$ at 10 x10^{-6}A to 0.11 x 10^{-3} at 75 x10^{-6}A. Later on the slope increased to -19.49 x 10^{-3} at 200 x10^{-6}A. The slope value is lowest around 75 x10^{-6}A. The chi-square value increased from 49.64 x 10^{-3} at 10 x10^{-6}A to 85.88 at 75 x10^{-6}A to 52.92 at 200 x10^{-6}A. The correlation value varied from -0.999 to -0.654.

Conclusion

1. It can be seen that for the chronopotentiometric curve at a particular current density, the it$^{1/2}$ term becomes independent of further change in current value. This indicates that copper oxides dissolution is controlled by solid-state diffusion.
2. The it$^{1/2}$ behaviour at very low and at very high values of current density does not remain constant in a particular solvent system. The it$^{1/2}$ value varies with change in concentration.
3. The pH of the solution influences the overall dissolution process. A series of experiments were conducted at various pH to investigate the effects of pH on the leaching potential.
4. The pH of the solution was varied by keeping the concentration of CuO constant. The results showed that potential of the system decreases with the decrease in pH. This can be explained as due to decrease in pH, the concentration of oxides decreases in the system.
5. Chronopotentiometric study confirms that the dissolution in copper oxides is under solid-state diffusion control.

References
1. Lee J-C, Song HT, Yoo JM. Present status of the recycling of waste electrical and electronic equipment in Korea. Resour. Conserv. Recycl. 2007;50(4):380-397.
2. Park YJ, Fray DJ. Recovery of high purity precious metals from printed circuit boards. J Hazard Mater. 2009;164(2-3):1152-1158.
3. Pradhan JK, Kumar S. Metals bioleaching from electronic waste by *Chromobacterium violaceum* and *Pseudomonads* sp. Waste Manag. Res. 2012;30(11):1151-1159.
4. Donald MB. Leaching in Chem. Eng. Practice. In: Cremer HW, Davis T, eds. London Butterworths. 1958;6:369.
5. San Jose MT, Espinosa AM, Tascon ML, Vazquez MD, Batanera PS. Electrochim Acta. 1991;36(7):1209.
6. Lee JH, Gilze J, Fernando Q, Zeitlin H. Environ. Sc. Tech. 1978;12:1428.
7. Barneveldvan EC, Leaver ES. U.S. Bureau of Mines Tech. Paper: c1923. p. 312.
8. Selby JH, James GS. Fr. Demande. 1974;2:193,089.
9. Okuwaki A, Kanabe A. Koiggyo Kagaku Zashi. 1964;67(7):993.
10. Warren IH, Hay MG. Inst. Min. Met. Trans. Sect C. 1975;84:49.
11. Graham NK, Gill JB, Goodall DC. J. Chem. Soc. (D.T.). 1983, 1363.
12. Raisoni PR, Dixit SG. Ind. Eng. Chem. Res. 1990;29(1):14.
13. Vaisman II, Berkowitz ML. J. Amer. Chem. Soc. 1992;114:7889.

14. Adams RN. Electrochemistry at Solid Electrodes. New York: Marcel Dekker; c1969. p. 19.

15. Delahay P. New Instrumental Methods in Electrochemistry. New York: Interscience; c1954. p. 46.

16. Davis DC. Applications of CP to Problems in Anal. Chem. In: Bard AJ, ed. Electroanal. Chem. New York: Dekker; c1965, 87.

17. Paunovic J. J. Electroanal. Chem. 1967;14:447.

18. Delahy P. Treatise in Anal. Chem., Part I. In: Kolthoff IM, Elving PJ, eds. Wiley Interscience. New York. 1963;4:2233.

19. Perrin DD, Armarego WLF. Purification of Laboratory Chemicals. New York: Pergamon Press; c1988. p. 65.

20. Martin D, Hauthal HG. Dimethylsulfoxide. New York: John Wiley & Sons; c1975. p. 41.

21. Delahay P. New Instrumental Methods in Electrochemistry. New York: Interscience; c1954. p. 72, 115, 179.

22. Bond AM. Modern Polarographic Methods in Analytical Chemists. New York: Marcel Dekker; c1980. p. 169.

23. Adams RN. Anal Chem. 1958;30:1576.

24. Kuwana T, French WG. Anal Chem. 1964;36:241.

25. Gruner W, Kunath J, Kalnishevskaja LN, Poskin JV, Brainina KhZ. Electroanalysis. 1993;5:243.

26. Bauer D, Gaillochet MPh. Electrochim Acta. 1974;19:597.

27. Lamache M, Bauer D. Anal Chem. 1979;51:1320.

28. Vogel AI. A Textbook of Quantitative Inorganic Analysis. ELBS & Longman; c1975. p. 441.

29. Vogel AI. A Textbook of Quantitative Inorganic Analysis. ELBS & Longman; c1975. p. 370.

30. Youzbashi AA, Dixit SG. Metal Trans. Leaching of Cu2O with aqueous solution of sulphur dioxide. 1993;24B:563-570.