Simultaneous Electrochemical Determination of Glue and Thiourea in Copper Refining by Using Artificial Neural Network

EFAT REZAEI
Hydrometallury department
R& D division,Sarcheshme copper complex,Kerman,IRAN
ef_rezaei@yahoo.com

Abstract: - In this research an artificial neural network was invented for simultaneous determination of both glue and thiourea in industrial electrolytes. First, a network was designed, which electrochemical data was its input. This network consisted of three layers of nodes, and back propagation rule was used for training the network. Sigmoid transfer function was applied in the hidden and output layers. The precision and accuracy of model was tested. The resulting MSE (Mean Square Error) for prediction of glue and thiourea were 0.0011 and 0.0008 respectively.

Key-Words: - ANN, glue, thiourea, copper refining, electrochemical determination, sigmoid transfer function.

1 Introduction

Glue and thiourea are additives used in copper electro refining. These additives concentrations must be controlled carefully because the electro deposition process is often very sensitive to very small fluctuations in the value of these additives. These additives prevent rough and nodular electro deposition. The nodular may grow and cause short circuits which results in lose of energy. Additives agents are effective in controlling metal crystal growth since they modify the normal nucleation and lattice growth phenomenon in refining the grain structure; moreover, they adjust tiny nodules dendrite or other spikes by selective adsorption at the peak of these protrusion. Different method such as fluorimetric[1], chemiluminescens[2], voltammetric method[3], Raman spectroscopy, kinetic method, high performance liquid chromatography and electro kinetic reversal phase chromatography, were reported for determination of glue and thiourea. All of these techniques have been used for determination of glue and thiourea in simple matrixes, and some of them used to determine only one of the additives.

None of these techniques were utilized for determination of additives in copper refining with complex matrix. The suggested method is applicable in industrial electrolyte media in copper refining process.

2 Experimental

Electrochemical analysis system BHP2061-C^{++} was used for recording I-E curves (by the use of differential pulse voltammetry technique).

Pt working electrode and reference $Hg/Hgso_4/SO_4$ electrode were used for recording current potential curves; a copper wire was as an anode electrode. Essentially, between each measurement,there must be precise cleanup of the Pt electrode, which was implemented dipping the Pt electrode in concentrated HNO3 to remove deposited Cu, and then washing it with doubly distilled water The ANN (artificial neural network) program was written by the Matlab (version 6.5) software; the resulting program was run on a personal computer.

2.1 Reagent

All chemicals were of analytical purity, and doubly distilled water was used through the experiments. The solutions of electrolyte were prepared by purring 40 ml of matrix electrolyte to 100 ml volumetric flask and diluting it to the mark with distillated water.

2.2 Sample preparation and recommended procedure

In the beginning, the industrial electrolytes were heated to release additives (3 h, t= 90 ^{0}C, V= 4 lit) and pure matrixes were yielded. These matrixes were used to prepare blank and different concentrations of glue and thiourea. For recording voltammograms in each step, 40 ml of pure matrix and different values of standard solutions of glue and thiourea were transferred into a 100 ml volumetric flask. Having completely mixed and transferred to cell, N_2 gas bubbled for 5 minutes. Afterwards, voltammograms were recorded in the range of 0 to -0.5 volts. The values of current in different potentials were recorded and entered to the model as input data. This model is composed of three layers and was trained by applying a back propagation learning rule. Sigmoid transfer function was used in the hidden and output layer. Prior to the start of training, all of the weights in the network were selected as random values.

Experiments were done in two steps: calibration set and prediction set. First, the model was trained with calibration set and its parameters were optimized. After that, prediction set was analyzed and its inputs were entered to the model. Outputs of prediction set were obtained by using optimized parameters in the first step. Predictions set tests were done for accuracy of the model.

3 Results

In this research it was found that the polarization potential of copper (DPV) varies with changing the concentration of glue and thiourea. This relation is nonlinear and ANN was used for the model analyzed. Glue and thiourea form a complex with copper. Cu^+ makes up complexes of glue and thiourea at the surface of the electrode in copper solution. These complexes adsorb at the electrode surface and the polarization potential of cathode changes to negative potentials by increasing concentration of glue and thiourea (fig. 1). Glue and thiourea have the same effect on the shifting polarization potential [8, 9, 10, 11]. Therefore, usual method do not use for the determination of glue and thiourea. Fig. 1 shows the voltammograms of electrolyte in the presence of different concentrations of glue and thiourea.

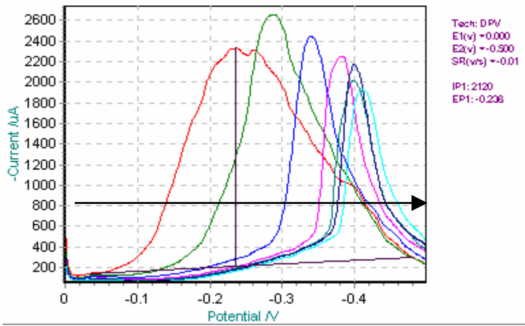

Fig1. Fig1. Polarization potentials increase with raising the concentrations of glue and thiourea in industrial electrolytes (from left to right)

3.1 Influence of variables

For obtaining voltammograms, our studies showed that when the scan rate and Hpulse (Height pulse) were 8 mV/s and 40 mV respectively, the shape of voltammograms were suitable, so in all stages voltammograms were plotted in this condition and potentials were recorded in the current of 1.4*10 $^{3-}$ A. The effect of variable parameters such as concentration of Cu^{2+} and hydro sulfuric acid concentration were studied as well.

The effect of Cu^{2+} concentration in the range of 35-45 g/lit was examined, and its results are shown in fig. 2. For making different concentrations of copper, first an electrolyte with 35g/lit Cu^{2+} was selected and the voltammogram of this solution was obtained; then, different values of standard solutions of Cu^{2+} were added until desired Cu concentrations were in hand.

Finally, voltammograms were plotted and potentials in the current of $1.4 * 10^{3-}$ A gained.

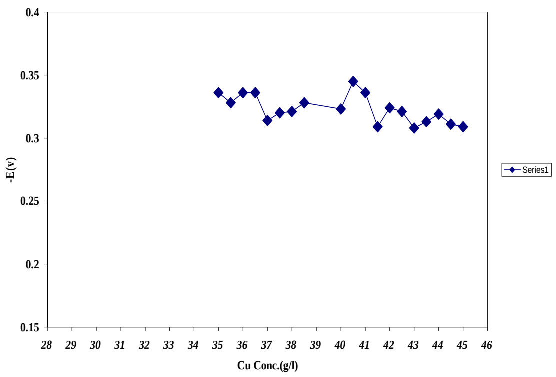

Fig2. The effect of Cu concentrations in glue and thiourea determination.

Conditions: industrial blank electrolyte, $C_{\text{sulfuric acid}}$= 168.9 g/lit, C_{thiourea} =2 ppm, Hpulse= 40 mV, scan rate = 8 mVs^{-1}

The fluctuation of acid concentrations in NICICO (National Iranian Copper Industries Company) is in the range of 160-180 g/lit; therefore, the effect of acid concentration in this range was studied. For this experiment an industrial electrolyte contained 160 g/lit was selected and its voltammogram was plotted. By adding different values of H^+ standard solution to initial solution (160g/lit), another acid concentration was obtained. The results of this experiment are shown in fig. 3.

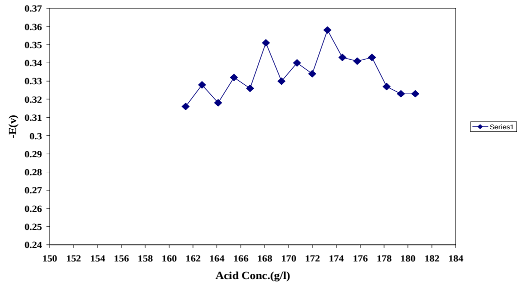

Fig 3. The effect of acid concentrations in glue and thiourea determination.

Conditions: industrial blank electrolyte, C_{cu2+} = 40.45 g/lit, C_{thiourea} =2 ppm, Hpulse= 40 mV, scan rate = 8 mVs^{-1}

4. Calibration graph and precision

In optimized conditions, scan rate and Hpulse are 8 mVs^{-1} and 40 mV respectively. In different currents, the potential of voltammograms were recorded (such as showing in fig 1), and then these potentials made up the data matrix in calibration set.

Calibration curve for calibration set was obtained to evaluate the performance of the model. The calculated concentrations against experimental (expected) concentrations was plotted (R_g^2=9945 and R_t^2= 0.999). The high correlation coefficient confirms the good performance of the model. In another words, based on the R^2 value, it can be concluded that the model is able to simulate the response data.

To test the performance of the model, a new situation (prediction set) was introduced to the model (R_g^2 = 0.9883 and R_t^2 = 0.9983).

The dynamic rang for glue and thiourea was 0- 12 ppm and 0-11.75 ppm respectively,

The precision of the method for glue and thiourea determination were established by replicate determination (n=10). Standard deviations (SD) of the results are shown in table 1 and 2.

Table1. Analysis of refinery sample for glue determination

Actual value (ppm)	Obtained value (ppm) ± (SD)	%Recovery
0.50	0.47(± 0.043)	97
1.0	1.02 (±0.047)	102
1.75	1.71(± 0.042)	96
2.70	2.74(± 0.056)	101
3.70	3.65(± 0.066)	95
4.30	4.31(± 0.033)	101

Table2. Analysis of sample for thiourea determination

Actual value (ppm)	Obtained value (ppm) ± (SD)	%Recovery
0.50	0.51(± 0.072)	102
1.20	1.16 (±0.065)	96.6
2.00	2.04(± 0.085)	102
3.20	3.14(± 0.073)	98.1
4.10	4.13(± 0.078)	100.7
5.00	4.98(± 0.029)	99.6

Some results of glue concentrations determined by the use of this method are represented in the figures as 4 and 5.

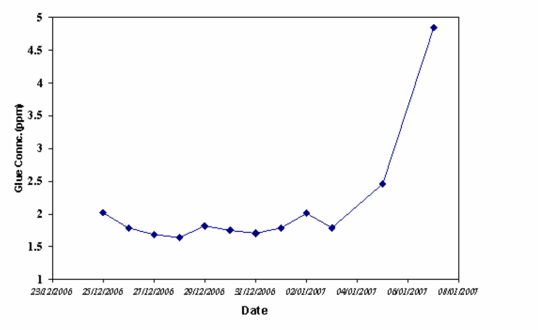

Figure 4 .Glue concentration values in COMI circuit in NICICO
(National Iranian Copper Industries Company)

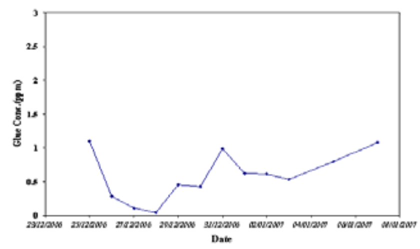

Figure 5. Glue concentration values in EXP. circuit in NICICO

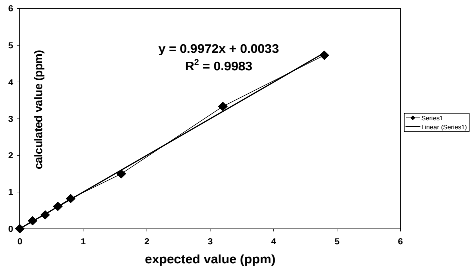

Fig6. Calibration curve for calibration set in glue determination

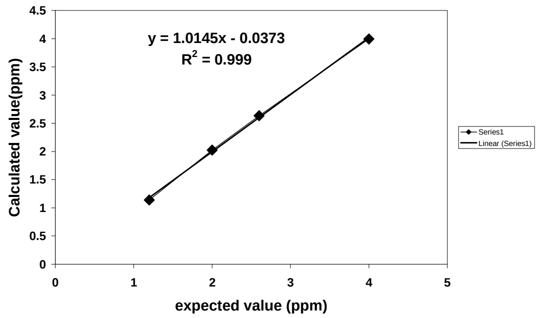

Fig7. Calibration curve for prediction set in glue determination

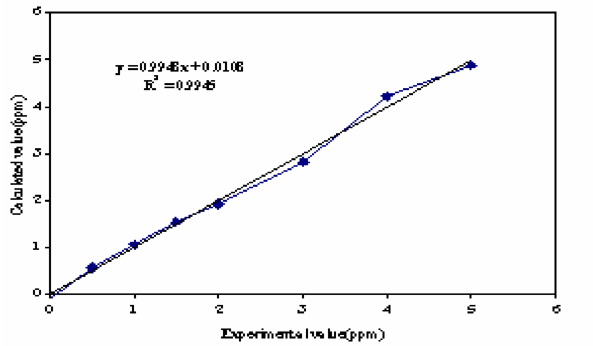

Fig8. Calibration curve for calibration set in thiourea determination

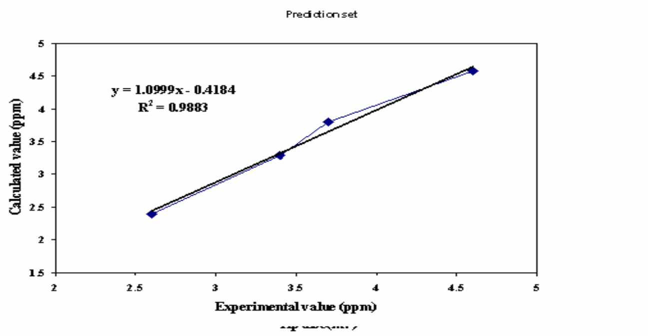

Fig9. Calibration curve for prediction set in thiourea determination

5 Conclusions

These experiments were conducted by industrial electrolytes that contained different ions; none of these ions interfered in glue and thiourea determination. Glue and thiourea have the same effect in polarization potentials, and for this reason, the normal techniques cannot be used for glue and thiourea determination in industrial electrolyte with complex matrixes.

Consequently, the suggested method is highly precise, accurate, selective, cheap and fast for determination trace amounts of glue and thiourea in industrial electrolytes which have complex matrixes. This method was very successfully to determine the glue and thiourea concentrations in different electrolytes in Sarcheshmeh Copper refinery in Iran with no need to separate any interfering and/or additive substances.

6 Acknowledgments

The author is grateful to R&D department and refinery plant at Sarcheshmeh Co. for supporting this research work.

7 References

[1] T1. Perez-Ruiz, C. Martinez- Lozano, V. Tomas, R. Casajus, "Flow Injection Fluorimetric Determination of Thiourea"Talanta, Vol 42 (3), 391-396, 1995.

[2] Z. He,F. Wu, H. Meng, L. Ling, J. Liang, Q. Yuan, Z. Lu ," Chemiluminescence Determination of Thiourea Using Tris(2,2'-bipyridyl) Ruthenium" Anal. Sci., Vol 15, pp 381-383, 1999.

[3] N.R. Baharucha., Z. Zauorsky, L. Leroy, Metallurgical Transactions B, Vol 7B, pp 509-514,1978.

[4] E.Rezaei, thesis of master degree in analytical chemistry, Isfahan University of Technology, Isfahan, Iran, 2003.

[5] T.N. Andersen, R.D. Badd, A. Strachan, ", "A Rapid Electrochemical Method for Measuring the Concentration of Active Glue in Copper Refinery Electrolyte Which Contains Thiourea""Metallurgical Transaction B", Vol7B, pp 333-338, 1978.

[6] M. Goffman, T. Jordan, "Method of Thiourea Addition to Electrolytic Solutions Useful for Copper Refining"United State Patent, No (4,511,443), 1985.

[7] B.R.Conard, B. Rogers, R. Brisebois,
C. Smith, ""Inco copper Refinery Addition Agent Monitoring Using Cyclic Voltammetry""Proceedings of the InternationalSy Electrometallurgical Plant Practice, October 21-24, pp292-307,1990.

[8] G.Fabricius,K. Konitturi,G. Sundholm, "J.Appl. Electrochem" Vol26 (11), 1179-1183, 1996.

[9] S.Krzewska, L. Pajdowski, H. Podsiadly, J. Podsiadly, "Electrochemical Determination of Thiourea and Glue in the Industrial Copper Electrolyte",Metallurgical Transactions B, Vol 15B,1984,PP 451-459.

, 1 [10] R.C.Kerby,H.E.Jackson, T.J.Okeefe,Y.M.Wang, "Evaluation of Organic Additives for Use in Zinc Electro winning", Metallurgical Transactions B, Vol 8E, 1977, PP 661-668.

[11] S.A. Campbell,E.E. Farndon,F.C. Walsh M.Kalaji, "Trans.Inst.Met", Vol 75(1), 10-17,1997.