# Applying Artificial Neural Network for Simultaneous Electrochemical Determination of Glue and Thiourea in N.I.C.I.CO

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*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

Electrorefining is electrolytic process that involves anodically dissolving a metal at the positive electrode in the cell and simultaneously redepositing the same metal at the negative electrode. purity of cathode in this process is about 99.999%.

In refinery impure anodes is converted to pure cathodes, in refinery factories there are rectangular cells that contain about 51 negative and 52 positive electrodes and additional positive electrode is required in each cell in order to ensure plating occurs on both side of each negatives.

Thiourea is a compound of nitrogen, sulfur and hydrogen and carbon, glue is a kind of protein that contain different amino acid, both of them have atoms with free pair electrons or in another word they have functional groups that can form a complex with ions such as copper, Cobalt and so on. 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

#### 2-1 electrochemical definition

Any process measured in electroanalytical chemistry occurs at the surface of the electrode. Therefore electrochemical measurements reflect an inherently surface process rather than a solution process. Hence, the surface itself, the distance of the analyte from the surface, the rate at which the analyte reaches the surface and interactions of analyte with the surface will all affect the measurement. The type and magnitude of the effect depends on the type of measurement. The measurement types are detailed below. **Potential** (E). One of the more common electrochemical measurements is that of

Potential (E). Potential is more accurately called a "potential difference" since it always reflects the force at which the electrons move between electrodes. However, since it is impossible to measure the potential at one electrode, the two terms are used interchangeably. Potential is related to the free energy ( $\Delta G$ ) of the overall reaction. Potential is determined by the specific reaction. concentration (more accurately. activity) of products and reactants and temperature according to the Nernst equation.

 $E = E^{0} + RT/nF \ln([ox]/[red])$  (1) where E is the experimental potential (V), E<sup>0</sup>is the standard potential (V) which is dependent on the identity of the reaction, R is the gas constant  $(J/mol^{0}K)$ , T is temperature (K), n is the number of electrons transferred (mol e/mol), F is Faraday's constant (C/mol e), [ox] is the activity of the oxidized form of the analyte and [red] is the activity of the reduced form of the analyte. If other Species, such as H+ participate in the reaction their activities must be also be included. Since the reaction of interest normally occurs at only one electrode, an electrode potential is measured. The term "electrode potential" superficially refers to the potential at one electrode. Since this is an experimental impossibility, what it really refers to is the potential versus some known half-cell, such as one of the reference electrodes mentioned above. Therefore, when referring to a electrode potential the reference electrode must always be cited. For example, the potential of a copper electrode in a solution with [Cu2+] = 1.0 M is about +0.3 V vs. SHE. Most tables of electrode potentials use SHE (NHE) as the reference electrode. Experimental data is more likely to use Ag/AgCl or SCE as the reference electrode. Conversions between reference electrodes are easily accomplished by using the value of the experimental

reference electrode versus SHE. For example, since the SCE electrode is +0.241 V vs. SHE, to convert the potential versus SHE (ESHE) from the potential versus SCE (ESCE), you could use the equation 0.241 - ESCE = ESHE (2) One of of the features many electroanalytical measurements is the ability to control potential. Changing the potential can force nonspontaneous reactions to occur and increase the rate of reaction. By definition, a more positive potential induces and/or speeds up oxidation reactions while a more negative potential induces and/or speeds up reduction reactions.

**Charge (Q)**. Charge is a measurement of the number of electrons. Faraday's constant

Relates coulombs (C), the electrical measurement of charge, to the number of electrons where

96,484 C = 1 mole of electrons (3)

The half reaction can then be used to relate the moles of electrons to moles of analyte.

**Current (i)**. The current is the rate at which electrons travel. It is expressed in amperes

Or amps (A) which is the same as coulombs per second. Consequently, a measurement of current is proportional to the instantaneous rate of the reaction.

There are many factors which influence the rate of reaction. These include: electrode

Surface area, reactant concentration, temperature, viscosity of solution, and applied potential. To use current as a signal to measure reactant concentration, the other factors must be kept constant. In addition to the current from the chemical reaction, there is also a background current. This current can be due to electrolysis of impurities, electrolysis of solvent, electrolysis of the electrode surface material, and capacitive currents. Electrolysis of the solvent and electrode can be minimized or eliminated by working in only at potentials where these reactions do not occur at

any significant rate. This range of potentials is called the potential window. Capacitive current is caused by the electrode-solution interface behaving like an electrical capacitor, storing charge. As the potential difference increases, more charge is stored at the electrode. Therefore capacitive current can also be called charging current. Generally background current can be determined by measuring a

blank and subtracting its current from the analyte signal

**Pulse Techniques.** In sweep techniques, the potential gradually and consistently changed. However, in pulse techniques the initial potential (where no reaction occurs) is directly changed to the final potential (where the reaction rate is at maximum). Hence it is referred to as a step or pulse instead of a sweep. Because there are only two potentials, the signal is graphed as a function of time rather than potential. The appropriate initial and final potentials are normally determined using voltammetry. The initial potential (Ei) should be a value before the peak begins and the final potential (Ef) at a value in the diffusion-limited region, when the current levels off after the peak.

**Voltammetry**. Voltammetry is a series of techniques where potential is controlled and current is measured. In this technique, the current is due to a redox half-reaction induced by the applied potential. The graph of current versus potential, called a voltamogram, provides information about the chemical reaction. It is important that the voltamogram reflect the analyte's reaction at the working electrode. Thus, it is important that the potentials measured be in a region where solvent, electrolyte and electrode are not reacting. This range of potentials is called the potential window.

#### Differential pulse voltammetry:

Differential pulse voltammetry is often used to make electrochemical measurements. It can be considered as a derivative of linear sweep voltammetry or staircase voltammetry, with a series of regular voltage pulses superimposed on the potential linear sweep or stair steps. The current is measured immediately before each potential change, and the current difference is plotted as a function of potential. By sampling the current just before the potential is changed, the effect of the charging current can be decreased. The system of this measurement is usually the same as that of standard voltammetry. The potential between the working electrode and the reference electrode is changed as a pulse from an initial potential to an inter level potential and remains at the inter level potential for about 5 to 100 milliseconds; then it changes to the final potential, which is different from the initial potential. The pulse is repeated, changing the final potential, and a constant difference is kept between the initial and the inter level potential. The value of the current between the working electrode and auxiliary electrode before and after the pulse are sampled and their differences are plotted versus potential.

In this study for electrochemical determination, voltammetry techniques and differential pulse voltammetry was used.

#### 2-2 artificial neural network

A neural network is, in essence, an attempt to simulate the brain. Neural network theory revolves around the idea that certain key properties of biological neurons can be extracted and applied to simulations, thus creating a simulated (and very much simplified) brain. The first important thing to understand then is that the components of an artificial neural network are an attempt to recreate the computing potential of the brain. The second important thing to understand, however, is that no one has ever claimed to simulate anything as complex as an actual brain. Whereas the human brain is estimated to have something on the order of ten to a hundred billion neurons, a typical artificial neural network (ANN) is not likely to have more than 1,000 artificial neurons.

#### Multilayer Neural networks

Multilayer neural networks are undoubtedly the most popular networks used in applications. While it is possible to consider many activation functions, in

practice it has been found that the logistic (also called the sigmoid) function  $g(v) = (e^v / 1 + e^v)$  as the activation function (or minor variants such as the

tanh function) works best. In fact the revival of interest in neural nets was sparked by successes in training neural networks using this function in place of the historically (biologically inspired) step function (the "perceptron"). Notice that using a linear function does not achieve anything in multilayer networks that is beyond what can be done with single layer networks with linear activation functions. The practical value of the logistic function arises from the fact that it is almost linear in the range where g is between 0.1 and 0.9 but has a squashing effect on very small or very large values of v. In theory it is sufficient to consider networks with two layers of neuronsone hidden and one output layer-and this is certainly the case for most applications. There are, however, a number of situations where three and sometimes four and five layers have been more effective. For prediction the output node is often given a linear activation function to provide forecasts that are not limited to the zero to one range. An alternative is to scale the

output to the linear part (0.1 to 0.9) of the logistic function. Unfortunately there is no clear theory to guide us on choosing the number of nodes in each hidden layer or indeed the number of layers. The common

practice is to use trial and error, although there are schemes for combining optimization methods such as genetic algorithms with network training for these parameters. Since trial and error is a necessary part of neural net applications it is important to have an understanding of the standard method used to train a multilayered network:

#### Training Multilayer Perceptrons

Once the number of layers, and number of units in each layer, has been selected, the network's weights and thresholds must be set so as to minimize the prediction error made by the network. This is the role of the training algorithms. The historical cases that you have gathered are used to automatically adjust the weights and thresholds in order to minimize this error. This process is equivalent to fitting the model represented by the network to the training data available. The error of a particular configuration of the network can be determined by running all the training cases through the network, comparing the actual output generated with the desired or target outputs. The differences are combined together by an error function to give the network error. The most common error functions are the sum squared error (used for regression problems), where the individual errors of output units on each case are squared and summed together, and the cross entropy functions (used for maximum likelihood classification).

In traditional modeling approaches (e.g., linear modeling) it is possible to algorithmically determine the model configuration that absolutely minimizes this error. The price paid for the greater (non-linear) modeling power of neural networks is that although we can adjust a network to lower its error, we can never be sure that the error could not be lower still.

A helpful concept here is the error surface. Each of the N weights and thresholds of the network (i.e., the free parameters of the model) is taken to be a dimension in space. The N+1th dimension is the network error. For any possible configuration of weights the error can be plotted in the N+1th dimension, forming an error surface. The objective of network training is to find the lowest point in this many-dimensional surface.

In a linear model with sum squared error function, this error surface is a parabola (a quadratic), which means that it is a smooth bowlshape with a single minimum. It is therefore "easy" to locate the minimum.

Neural network error surfaces are much more complex, and are characterized by a number of unhelpful features, such as local minima (which are lower than the surrounding terrain, but above the global minimum), flat-spots and plateaus, saddle-points, and long narrow ravines.

It is not possible to analytically determine where the global minimum of the error surface is, and so neural network training is essentially an exploration of the error surface. From an initially random configuration of weights and thresholds (i.e., a random point on the error surface), the training algorithms incrementally seek for the global minimum. Typically, the gradient (slope) of the error surface is calculated at the current point, and used to make a downhill move. Eventually, the algorithm stops in a low point, which may be a local minimum (but hopefully is the global minimum).

#### The Back Propagation Algorithm

The best-known example of a neural network training algorithm is back propagation. Modern second-order algorithms such as conjugate gradient descent and Levenberg-Marquardt (both included in ST Neural Networks) are substantially faster (e.g., an order of magnitude faster) for many problems, but back propagation still has advantages in some circumstances, and is the easiest algorithm to understand. We will introduce this now, and discuss the more advanced algorithms later. There are also heuristic modifications of back propagation which work well for some problem domains, such as quick propagation and Delta-Bar-Delta and are also included in ST Neural Networks.

In back propagation, the gradient vector of the error surface is calculated. This vector points along the line of steepest descent from the current point, so we know that if we move along it a "short" distance, we will decrease the error. A sequence of such moves (slowing as we near the bottom) will eventually find a minimum of some sort. The difficult part is to decide how large the steps should be.

Large steps may converge more quickly, but may also overstep the solution or (if the error surface is very eccentric) go off in the wrong direction. A classic example of this in neural network training is where the algorithm progresses very slowly along a steep, narrow, valley, bouncing from one side across to the other. In contrast, very small steps may go in the correct direction, but they also require a large number of iterations. In practice, the step size is proportional to the slope (so that the algorithm settles down in a minimum) and to a special constant: the learning rate. The correct setting for the learning rate is application-dependent, and is typically chosen by experiment; it may also be time-varying, getting smaller as the algorithm progresses.

The algorithm is also usually modified by inclusion of a momentum term: this encourages movement in a fixed direction, so that if several steps are taken in the same direction, the algorithm "picks up speed", which gives it the ability to (sometimes) escape local minimum, and also to move rapidly over flat spots and plateaus.

The algorithm therefore progresses iteratively, through a number of epochs. On each epoch, the training cases are each submitted in turn to the network, and target and actual outputs compared and the error calculated. This error, together with the error surface gradient, is used to adjust the weights, and then the process repeats. The initial network configuration is random, and training stops when a given number of epochs elapses, or when the error stops improving (you can select which of these stopping conditions to use).

backpropagation. It is no exaggeration to say that the speed of the backprop algorithm made neural nets a practical tool in

the manner that the simplex method made linear optimization a practical tool. The revival of strong interest in neural nets in the mid 80s was in large

measure due to the efficiency of the back prop algorithm.

# 2-3 the applied network and instrumental conditions

Electrochemical analysis system BHP2061-C<sup>++</sup> 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 (auxiliary) electrode. Essentially, between each measurement, there must be precise cleanup of the Pt electrode, which was implemented dipping the Pt electrode in concentrated HNO<sub>3</sub> to remove deposited Cu, and then washing it with doubly distillated water.

#### 2.4 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.

The ANN (artificial neural network) program was written by the Matlab (version 6.5) software; 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 resulting program was run on a personal computer.

# 2.5 Sample preparation and recommended procedure

In the beginning, the industrial electrolytes were heated to release additives (3 h, t=90 <sup>0</sup>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<sub>2</sub> gas bubbled Afterwards, for 5 minutes. 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**

# 3.1 Effect of complex formation on polarographic waves

The potential for the oxidation or reduction of metallic ion is greatly affected by the presence of species that form complexes with that ion, that similar effects are observed for reduction of metal complex is generally more negative than that for reduction of the corresponding simple metal ion, in fact this negative shift in potential permits the elucidation of the complex ion and the determination of its formation constant provided that the electrode reaction is reversible, for the reactions

 $M^{n}$ + + ne M(Hg)

And  $M^n + + x A^ MA_x^{(n-x)}$ 

Lingane derived the following relationship between the molar concentration of ligand Cl and the shift in half wave potential brought about by its presence,

#### 3.2 discussions

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

Potential Av

-0.3

-0.4

-0.2

#### **3.1 Influence of variables**

-0.1

0

For obtaining voltammograms, different instrumental and chemical parameters were studied; the effect of scan rate was investigated, in scan rate of 10 mv/s the voltammogram shapes and theirs recording time were suitable, the results of this factor are shown in fig2.



Fig 2. the effect of scan rate in glue and thiourea determination Conditions: industrial electrolyte contain acid concentration= 165 g/lit, cu concentration= 38 g/lit, glue concentration= 1ppm, thioura concentration= 1.2 ppm and Hpulse= 40 mv,

Another parameter was height pulse (Hpulse), this study confirmed the effect of Hpulse on limited diffusion current were rather than polarization potential, so this parameter aren't so important in polarization potential, but because of the voltammogram shape( better recognize and investigation of the potential ), Hpuls 40 mv was selected. The results are shown in fig 3.

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Fig3. the effect of Hpulse in glue and thiourea determination Conditions: industrial electrolyte contain acid concentration = 165 g/lit, cu concentration= 38 g/lit,glue concentration = 1ppm, thioura concentration = 1.2 ppm and scan rate = 10 mv/s

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  $1.4*10^{-3-4}$  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. 4. 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.



Fig4. The effect of Cu concentrations in glue and thiourea determination. Conditions: industrial blank electrolyte, C <sub>sulfuric acid</sub>= 168.9 g/lit, C<sub>thiourea</sub>=2 ppm,Hpulse= 40 mV, scan rate = 8 mVs<sup>-1</sup>

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<sup>+</sup> standard solution to initial solution (160g/lit), another acid concentration was obtained. The results of this experiment are shown in fig. 5.

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Fig 5. The effect of acid concentrations in glue and thiourea determination.

Conditions: industrial blank electrolyte, C  $_{cu2+}$  = 40.45 g/lit, C<sub>thiourea</sub> =2 ppm, Hpulse= 40 mV,

scan rate =  $8 \text{ mVs}^{-1}$ 

#### 4. Calibration graph and precision

In optimized conditions; Epoch numbers: 60000, learning rate: 0.06, Momentum: 0.95, Gain: 1, Function: sigmoid transfer function, Number of neuron in hidden layer: 4, scan rate and Hpulse are 8 mVs<sup>-1</sup> 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	Obtained value (ppm)	%Recovery
(ppm)	$\pm$ (SD)	
0.50	$0.47(\pm 0.043)$	97
1.0	1.02 (±0.047)	102
1.75	$1.71(\pm 0.042)$	96
2.70	2.74(±0.056)	101
3.70	3.65( ± 0.066 )	95
4.30	$4.31(\pm 0.033)$	101

Table2. Analysis of sample for thiourea determination

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



Fig6. Calibration curve for calibration set in glue determination

Condition: Hpulse= 40 mV, scan rate = 8  $mVs^{-1}$ 

Epoch numbers: 60000, learning rate: 0.06 Momentum: 0.95, Gain: 1, Function: sigmoid transfer function, Number of neuron in hidden layer: 4 Also the residual curve for this curve is shown in the fig 7. It can be seen there are not any systematic errors in this data.



experimental

Fig7. the residual curve for calibration set



Fig8. Calibration curve for prediction set in glue determination

Condition: Hpulse= 40 mV, scan rate = 8  $mVs^{-1}$ 

Epoch numbers: 60000, learning rate: 0.06 Momentum: 0.95, Gain: 1, Function: sigmoid transfer function, Number of neuron in hidden layer: 4



Fig9. Residual curve for prediction set of glue



Fig10. Calibration curve for calibration set in thiourea



Fig11. the residual curve for thiourea calibration set



Fig12. Calibration curve for prediction set in thiourea

#### determination

Condition: Hpulse= 40 mV, scan rate = 8  $mVs^{-1}$ 

Epoch numbers: 60000, learning rate: 0.06 Momentum: 0.95, Gain: 1, Function: sigmoid transfer function, Number of neuron in hidden layer: 4



Fig13. Residual curve for thiourea prediction set

Some results of glue concentrations determined by the use of this method (trained model) are represented in the figures 14 and 15.



Figure 14 .Glue concentration values in COMI circuit in NICICO (National Iranian Copper Industries Company)



Figure 15. Glue concentration values in EXP. circuit in NICICO

By attended to SEM and metallurgical studies the suitable ranges of glue and thiourea concentration were obtained.

### **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.

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