

Chemistry

Simultaneous Determination of the Effect of Changes in Amperage, Temperature and Time of Electrolysis on the Electrodeposition of Nickel from Solution, Using a Novel Electrodeposition Device

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Introduction

It is often difficult or prohibitively costly to study a multivariant system by isolating each variable for study. In cases where multiple dependent variables need to be tested or when an interactive effect between the variables is expected, a simultaneous determination of these effects is desirable and sometimes necessary. In these cases, a response surface methodology should be used.¹

A response surface is defined by Mason *et al.*² as: “the geometric representation obtained when a response variable is plotted as a function of one or more quantitative factors.” A face centered design was chosen to reduce the likelihood of exceeding the reasonable bounds of the system. While a detailed discussion of composite designs is outside the scope of this paper, the reader can find more complete information on this subject from a number of sources.³

In this experiment, the system to be modeled was an electrochemical reaction described by the reaction equation:



The discipline of electrochemistry is substantial, containing as one element, the analytical determination of metal ions in solution. The experiment in this report is a continuation of the work begun by R.H. Parker of the LaGrange College Chemistry Program, in which a novel method of quantitatively determining the amount of nickel by electrogravimetric means was devised.⁴ In his design, the electrode-

1 Box, G.E.P.; Draper, N.R.; *Empirical Model-Building and Response Surfaces*; Wiley Interscience: New York, 1987.

2 Mason, R.L.; Gunst, R.F.; Hess, J.L.; *Statistical Design and Analysis of Experiments with Applications to Engineering and Science*; Wiley Interscience: New York, 1989, p. 205.

3 see References 1 and 2, among many others

4 R.H. Parker, *J. Chem. Educ.*, 2011, 88 (10), 1428–1430.

position process required that the reaction proceed overnight. The goal of the experiment in this report was to improve on this original design by testing the effects of amperage, temperature and time on the electrodeposition reaction and, from those results, determine optimal conditions in which this reaction could be carried out.

Experimental Design

The intent of Parker's original experiment was to design a method of quantitatively determining the concentration of nickel in a solution, using a non-standard method. The work in this report utilizes the same method, modified to test the conditions over the response surface. For each experimental run, nickel was plated onto the surface of a cleaned copper wire of known mass from a solution of known nickel concentration. The gain in mass of the copper wire after precipitation of the nickel was determined and used to determine the percent of the nickel, available in the solution, that was plated onto the copper.

Boundary conditions were chosen and cited in Figure 1. A nickel solution of known concentration was prepared from which aliquots were drawn. The experimental procedure for determining a single data point follows. The solution conditions have been adapted for solutions used for the electrodeposition of nickel ion, described in the literature.⁵

Experimental Procedures

1. Preparation of the nickel solution

A solution of nickel(II) sulfate⁶ containing 10.00 g/L of nickel was used for this study. Twenty mL of this solution was transferred to a beaker followed by: 30 mL of distilled water, 5.00 grams of ammonium chloride⁷, and 5.00 grams of tartaric acid⁸. To this solution was added a measured excess of ammonium hydroxide solution. An aliquot of 2.00 grams of sodium sulfite was added and the solution was placed in a controlled temperature bath.

2. Preparation of the copper electrode

A 32 cm section of 18 gauge copper wire was wrapped around a cylinder to form a loose spiral. This coil was cleaned by dipping in concentrated

5 Dale, J.M.; Banks, C.V.; Nickel. In *Treatise on Analytical Chemistry, Part II, Volume 2*; Koltoff, I.M., Elving, P.J., Sandell, E.B., Eds.; p. 408.

6 Nickel(II) sulfate hexahydrate, 98.5% purity, Acros Organics.

7 Ammonium Chloride, Fisher Scientific.

8 L-(+) Tartaric Acid, Fisher Chemical.

HCl, rinsed with deionized water then acetone, and dried to constant mass at 100°C.

3. Reaction Conditions

The copper coil was connected to the negative (-) lead of the power source⁹ and a 12 cm length of a graphite pencil lead¹⁰ was attached to the positive (+) lead. The electrodes were suspended in the nickel solution with 1 cm of each electrode protruding above the solution. The solution was exposed to current of the desired amperage for the desired time. After that period, the electrode was removed from the solution, washed with deionized water, then acetone and dried to constant mass at 100°C. The percent recovery was determined by dividing the measured amount of nickel plated onto the wire by the calculated nickel content of the aliquot tested, multiplied by 100%.

Determination of the Model Equation and Response Surface

The amount of nickel plated onto the copper wire (stated as a percent of the nickel ion available, plated onto the wire) was determined in twenty experiments, defined by the composite design. The results were modeled to a predictive equation, using linear regression, in the manner of Box and Draper.¹¹

A linear model, $Y = \theta_1 x_1 + \theta_2 x_2 + \theta_3 x_3 + \theta_{11} x_1^2 + \theta_{22} x_2^2 + \theta_{33} x_3^2 + \theta_{12} x_1 x_2 + \theta_{13} x_1 x_3 + \theta_{23} x_2 x_3$, was chosen for this purpose, where x_1 , x_2 and x_3 are the variables under study. A matrix, \mathbf{Z} , constructed of rows denoting each experiment, (each containing the appropriate values of x for that experiment) and a vector, \mathbf{Y} , containing the corresponding experimental results of those experiments were used to determine the coefficients, θ , using¹²:

$$\theta = (\mathbf{Z}'\mathbf{Z})^{-1} \mathbf{Z}'\mathbf{Y}$$

9 GW Laboratory DC Power Supply; Model GPS-1850

10 Mars-Lumograph Pencil Lead 2.00 mm dia. HB, Staedtler/Mars.

11 Reference 1, Chapter 3.

12 Reference 1, Chapter 3.3

These calculations resulted in the model equation,

$$Y_{\text{(percent recovery of Ni from solution)}} = 14.043x_1 + 1.451x_2 + 0.075x_3 - 7.855x_1^2 - 0.019x_2^2 - 0.026x_3^2 + 0.454x_1x_2 - 0.210x_1x_3 + 0.051x_2x_3 - 47.608$$

where: x_1 = amperage, x_2 = temperature and x_3 = time.

The fit of the model equation to the data was made by ANOVA, using the method described in Mason, *et al.*¹³ The values of F, calculated for this data not only exceeded the minimum F values for 95% and 99% confidence in the fit, but exceeded the “Draper 4F rule”¹⁴ that requires that the F value must exceed the specified value by a factor of four.

Supplemental Materials

a. Figure 1. Boundary Conditions

Temperature (°C)		Amperage (A)		Time (Min)	
Min	Max	Min	Max	Min	Max
35	65	0.5	1.5	10	30

b. Figure 2. Solution Properties

Analyte Source	Purity	Solution Concentration	Aliquot Size	Analyte in Aliquot
$\text{NiSO}_4(\text{H}_2\text{O})_6$	98.5%	44.853gL^{-1}	20.00mL	0.1974g

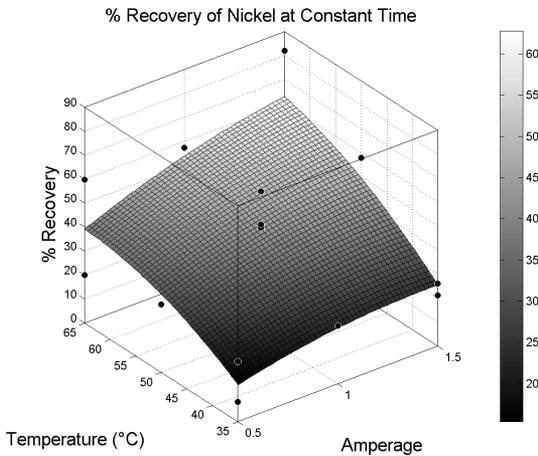
¹³ Reference 2, p. 473 – 475.

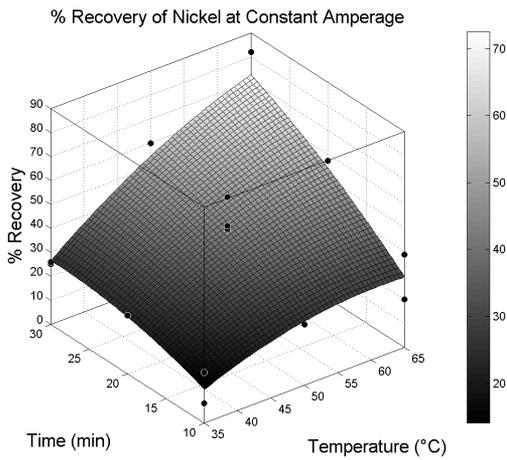
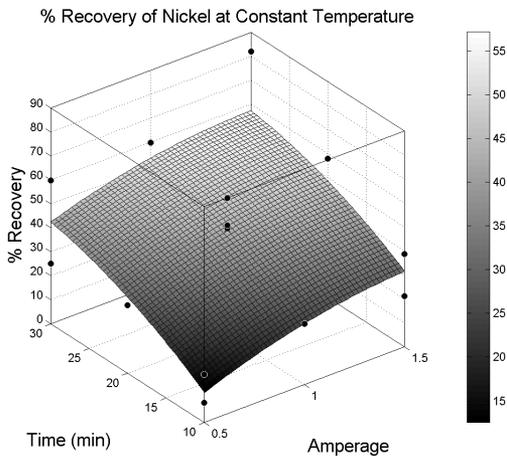
¹⁴ Draper, N.; Smith, H.; *Applied Regression Analysis*; Wiley & Sons: New York, 1966, p. 64.

c. Results of the Matrix Calculation to Determine the Model Equation

Percent Recovery	Calculated Recovery		Percent Recovery	Calculated Recovery
8.36	7.81		45.94	44.22
21.17	19.94		43.61	44.22
24.36	24.65		57.94	50.67
25.17	22.39		59.72	55.54
26.03	30.31		20.06	16.23
25.38	27.75		38.75	41.98
28.36	33.84		57.28	55.20
43.56	44.22		59.77	61.45
44.47	44.22		82.00	83.00
39.91	44.22			
45.94	44.22			

d. Plots showing Response Surfaces by Isolating Two Variables.





e. ANOVA Evaluation of the Fit of the Model Equation to the Data

	dF	SS	MS	F	F Crit _(9,9,0.01)
Regression	9	5815.92	646.21	30.70	5.35
Residual	9	189.42	21.04		
Total	18	6005.35		F _{mult}	5.74

R ²	0.9684
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