Design Experiment Optimization for the Determination of Copper in Water Samplesby Adsorptive Stripping Voltammetry.

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ABSTRACT

A new method is presented for the determination of copper based on adsorptive stripping voltammetry of complexes of Cu(II) with calcon at a hanging mercury drop electrode (HMDE)has been optimized. The selection of the experimental conditions was made using experimental of respon surface methodology. The influence of several parameters were studied: variations of calcon concentration, pH, accumulation potential and accumulation time. The design experiment was a central composite design with 4 factors/variables, 3 levels and 31 treatment combinations. Fromanalysis of variance, it was decided to accept the second-order model and the independent variable, concluded that a significant effect on the response variable (peak current). Based on data analysis with response surface method, the determination of copper obtained optimum conditions were: calcon concentration 0.39mM, pH 8, 11, accumulation potential -0.61Volt and accumulation time 81.85 seconds with a maximum peak current 48.77nA. Attheoptimum condition were obtained relative standard deviation 2.0%, recovery 98%, the linear range 0.2-105µg/L, coefficient of correlation 0.93 with a detection limit of 1.21µg/L. The procedure was successfully applied to the determination of copper in water samples without prior treatment.
Keywords: copper, adsorptive stripping voltammetry, water samples, respon surface method

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INTRODUCTION

Copper is an essential trace element for humans and animals. In the human organism, copper exists in two forms, the first and second oxidation form which exists the most in the human organism [1]. Although it is believed to be non-toxicto mammals, to lerance levels vary considerably with species. On the other hand, the toxicity of copper is much acute in aquatic species. Copper ideficiency can lead to number of potentially fatal conditions such as the expression of Menkes syndrome, occipital hornsyndrome, mcrocytic anemia and neutropenia and bone disorders [2].

The toxicity of copper depending on the level of concentration. The maximum tolerable daily intake for copper is 0.5 mg kg^{-1} (WHO, Technical Report Series, No. 683, 1982) body weight [3]. In bio systems copper exists in two characteristic forms, with oxidation levels of I and II and takes part in oxidation-reduction processes. One notable function of copper is its influence on the metabolism of iron [4]. Excess of copper enters the body as a pollutant present in water, food contamination and certain plant foods rich in copper.

The concentration of copper in various samples is low, so sensitive and selective methods for determination of copper in environmental samples are required. Sensitive methods for the determination of trace amounts of metal ions in natural samples have received much attention and many techniques have been employed. In recent years, we need a sensitive and selective method for determining the levels of trace amounts of metal ions, namely the adsorptive stripping voltammetry. Adsorptive stripping voltammetry is a useful method for determining trace levels of copper since it combines excellent sensitivity, selectivity, accuracy and precision with low cost of instrumentation. This technique is based on adsorptive accumulation of a complex of the element with an added specific ligand on a hanging mercury drop electrode, followed by lector chemical reduction of either the element or the ligand in the complex [5-8].

The previous study, to find optimization in the determination of trace metals C d, Cu, P band Zn[6-8] and trace metals Fe, Co, Niand Cr [9] in both individual and simultaneous by adsorptive stripping voltam metry (AdSV), carried out by observing the effect of one variable is changed, while the other variables are kept at a constant level. This optimization technique is called optimization of one variable or a factor at the current time. The main drawback of the results of the optimization of the factors that such optimization does not take into account the effect of the interaction between the variables studied. Therefore, this technique does not describe the full effect on there sponse parameter [10]. Another disadvantage of optimization of these factors is the increase in the number of trials required to do research, which leads to increased time and increased consumption of reagents and materials. To overcome this problem, an optimization technique of analytical procedures is by using multivariate statistical techniques [11].

The most relevant multivariate techniques used in analytical optimization is the Response Surface Method (RSM) with a Central Composite Design (CCD). RSM is a collection of mathematical and statistical techniques, which are used for modeling and analysis of problems in a response that is influenced by several variables, whose purpose is to optimize the response or optimize these variables to achieve the best system performance [10-13]. The RSM was done using Minitab.

Adsorptive stripping voltammetry is a highly sensitive technique [14], the response obtained in the form of the peak current (Ip) is influenced by variables (parameters) the following, namely: calcon concentration, pH, accumulation potential and accumulation time. Therefore it is very important to determine the optimization of these parameters, which will affect the measurement of the peak flow in order to improve the quality of analytical results [11, 15]. The research design used in this study, as a tool for optimization was central composite design with 4variables, 3level/degree and 31acombination of treatments. The first step of 2k factorial design optimizations are: provide the code, where the value of the highest level (+1), the lowest level (-1) and code (0) as the center point. Programs for statistical data processing Mini tab 16 using Response Surface Methodology.

The purpose of this study was to obtain the optimum condition of Cu, so it can be applied to the analysis of Cu in tap water. To achieve these objectives, required an optimization technique using analytical procedures that RSM with aCCD [10-13, 15-16] Some parameters were studied: variations of calcon concentration, pH, accumulation potential and accumulation time.

EXPERIMENTAL PROCEDURE

Material and Equipment:

Reagents were used in this study is a pure reagent, because stripping voltammetry is an ultra-sensitive method of analysis. The most important principle to remember is that an ultra-sensitive method of analysis, all chemicals must be pure (pa) and the equipment to be very clean and should be careful in its use. It aims to avoid or protect from contamination.

Voltammetric measurements were carried out using a Metrohm 797 VA. Electrode stand with a multimode electrode (MME) operating in the HMDE mode. An Ag/AgCl/KCl reference electrode and a platinum wire auxilary electrode were used. pH meter 80 models Griffin, Griffin & George Lough borough, England; and analytical balance Mettler AE 200, Toledo OH-USA; and glassware used in the laboratory.

Procedures:

Voltammeter into the vessel, put 10 ml of standard solution of Cu(II) 10 ug/L, added 0.2 mL and 0.2 mL of 0.1 MKCl in 20 mL calcon, this variable is set constant during the experiment. Calcon concentration, pH, accumulation potential and accumulation time is set according to experimental design of the CCD, used 4 factors and 3 levels, level of each factor is coded -1, 0, and +1, with 2 replications. Variables of experimental design were calcon concentration, pH, accumulation potential and accumulation time can be seen in Table 1.

Table 1: Experimental Design of Copper

Run	Factor				Peak current (Y)
	Calcon Concentration (X_1)	pH (X_2)	Accumulation Potential (X_3)	Accumulation time (X_4)	
1	0.2	5	-0.6	70	10.61
2	0.2	5	-0.4	70	11.02
3	0.2	5	-0.6	110	4.98
4	0.2	5	-0.4	110	24.93
5	0.2	7	-0.6	70	39.71
6	0.2	7	-0.4	70	35.57
7	0.2	7	-0.6	110	43.45
8	0.2	7	-0.4	110	35.94
9	0.4	5	-0.6	70	38.06
10	0.4	5	-0.4	70	44.24
11	0.4	5	-0.6	110	43.24
12	0.4	5	-0.4	110	44.44
13	0.4	7	-0.6	70	43.97
14	0.4	7	-0.4	70	31.45
15	0.4	7	-0.6	110	44.20
16	0.4	7	-0.4	110	26.45
17	0.3	6	-0.5	90	45.95
18	0.3	6	-0.5	90	46.01
19	0,3	6	-0.5	90	**46.04**
20	0.3	6	-0.5	90	46.03
21	0.3	6	-0.5	90	46.02
22	0.3	6	-0.5	90	46.01
23	0.3	6	-0.5	90	46.02
24	0.14	6	-0.5	90	24.18
25	0.3	4.4	-0.5	90	32.15
26	0.3	6	-0.76	90	35.79
27	0.3	6	-0.5	58.1	28.21
28	0.46	6	-0.5	90	42.17
29	0.3	7.6	-0.5	90	21.20
30	0.3	6	-0.34	90	35.69
31	0.3	6	-0.5	121.9	19.15

RESULTS AND DISCUSSION

Optimization of Copper Using One Variable:

The optimization of one variable in the determination of trace metal copper in the presence of calcon has been done [6-8]. The optimum condition as follow: calcon concentration 0.3mM, accumulation potential -0.5 V, pH 6, accumulation time 90 seconds.

This technique does not describe the full effect on the response parameters and optimization of these factors is the increase in the number of trials required to do research, which leads to increased time and increased consumption of reagents and materials. Therefore to overcome this problem, an optimization technique of analytical procedures is by using Respon Surface Methodology.

Optimization of Copper Using RSM:

Analysis of RSM First-Order Model of Copper:

The data processing was done using software Minitab16, and the results can be seen in Table2 the following:

Table 2: Model Order I regression coefficient

Term	Coef
Constant	34,7505
X1	6,8650
X2	4,9513
X3	- 0,8863
X4	0,8125

Based on Table2, regression equation of first-order model was:

$\hat{Y} = 34.7505 + 6.8650X_1 + 4.9513X_2 - 0.8863X_3 + 0.8125X_4$

Where X_1 = calcon concentration (µg/L), X_2 = pH, X_3 = accumulation potential (µg/L), X_4 = accumulation time (seconds), and $\hat{Y}$ = peak current (nA), where as the results of Analysis of Variance(ANOVA) of first-order model can be seen at Table3.

Table 3: ANOVA of First-Order Model of Copper

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regresi	4	1169,42	1169,42	292,355	2,09	0,137
Linear	4	1169,42	1169,42	292,355	2,09	0,137
X1	1	754,05	754,05	754,052	5,38	0,036
X2	1	392,24	392,24	392,238	2,80	0,117
X3	1	12,57	12,57	12,567	0,09	0,769
X4	1	10,56	10,56	10,563	0,08	0,788
Residu Error	14	1962,27	1962,27	140,162		
Lack of Fit	12	1962,27	1962,27	163,522		0,000
Pure Error	2	0,00	0,00	0,002		
Total	18	3131,69				

Table3 test procedure used to determine when there first-order models can be used or not. This hypothes is test was used to test the significance of regression models, which test whether there was a independent variable that significantly influence the response/dependent variable,

H_O: βi = 0,
H_1: βi≠0; i= 1,2,3,4

Based on Table3, the test regression parameters simultaneously produce p-value of 0.137, meaning that the p-value is greater than the significance level used in the amount of $\alpha=0.05$. Thus it was decided notto reject H_O and conclude that none of the independent variables that significantly influence the response variable, so the first-order model cannot be used

Analysis RSM Second-Order Model of Copper:

First-order model cannot be used, then proceed with the second-order model by using aquadratic effect and interaction. Results of second-order model data processing obtained (Table4) the following results:

Table 4: Regression Coefficients in the Second-Order Model

Term	Coef
Constant	44,3394
X1	3,84580
X2	1,66905
X3	-0,393866
X4	-0,0614595
X1*X1	-0,770434
X2*X2	-1,58253
X3*X3	-0,449967
X4*X4	-1,95672
X1*X2	-2,80652
X1*X3	-0,698096
X1*X4	-0,260240
X2*X3	-1,53890
X2*X4	-0,316352
X3*X4	0,131666

Based on Table4, the model regression equation:

$$\hat{Y} = 44.3394+6.4686X_1+2.8073X_2-0.6625X_3-0.1034X_4-2.1797X_1^2-4.4772X_2^2-1.2730X_3^2$$
$$-5.5358X_4^2-7.9400X_1X_2-1.9750X_1X_3-0.7362X_1X_4-4.3537X_2X_3-0.8950X_2X_4+0.3725X_3X_4$$

Where X_1 = calcon concentration (µg/L), X_2= pH, X_3 = accumulation potential (µg/L), X_4 = accumulation time (seconds), and $\hat{Y}$ = peak current (nA). Results of ANOVA second-order model data were presented in Table5.

Table5: ANOVA of Second-Order Model

Sumber	DF	Seq SS	Adj SS	Adj MS	F	P
Regresi	14	3555,68	3555,68	253,98	5,58	0,001
Linear	4	1086,68	1086,68	271,67	5,97	0,004
X1	1	906,25	906,25	906,25	19,91	0,000
X2	1	170,69	170,69	170,69	3,75	0,071
X3	1	9,51	9,51	9,51	0,21	0,654
X4	1	0,23	0,23	0,23	0,01	0,944
Square	4	1070,90	1070,90	267,73	5,88	0,004
X1*X1	1	128,59	79,60	79,60	1,75	0,205
X2*X2	1	389,48	335,85	335,85	7,38	0,015
X3*X3	1	39,37	27,15	27,15	0,60	0,451
X4*X4	1	513,45	513,45	513,45	11,28	0,004
Interaction	6	1398,10	1398,10	233,02	5,12	0,004
X1*X2	1	1008,70	1008,70	1008,7	22,16	0,000
X1*X3	1	62,41	62,41	62,41	1,37	0,259
X1*X4	1	8,67	8,67	8,67	0,19	0,668
X2*X3	1	303,28	303,283	303,28	6,66	0,020
X2*X4	1	12,82	12,82	12,82	0,28	0,603
X3*X4	1	2,22	2,22	2,22	0,05	0,828

Residu Error	16	728,28	728,28	45,52		
Lack of Fit	10	728,28	728,28	72,83		0,000
Pure Error	6	0,01	0,01	0,00		
Total	30	4283,96				

$$H_O: \beta i = 0, H_1: \beta i \neq 0; i = 1,2,3,...,k$$

Based on Table 5 test procedure against the second order model. This hypothesis test was used to test the significance of regression models, which test whether there is a independent variable(including quadratic and interaction effects) significantly affects the response variable. Test regression parameters simultaneously produce p-value of 0.000, meaning that the p-value obtained is smaller than the significance level used in the amount of a=0.05. Thus it was decided to reject H_O and conclude that there was a independent variable that significantly influence the response variable, so that the second-order model can be accepted.

Based on the regression coefficient values in Table3 can be arranged matrix b and Bas follows:

$$b = \begin{bmatrix} 3.84580 \\ 1.66905 \\ -0.39387 \\ -0.06146 \end{bmatrix} \quad dan \quad B = \begin{bmatrix} -0.77043 & -1.40326 & -0.349048 & -0.13012 \\ -1.40326 & -1.58253 & -0.769450 & -0.15818 \\ -0.34905 & -0.76945 & -0.449967 & 0.06583 \\ -0.13012 & -0.15818 & 0.065833 & -1.95672 \end{bmatrix}$$

In order to obtain a stationary point as follows:

$$x_0 = -\frac{B^{-1}b}{2} = \begin{bmatrix} 0.88991 \\ 2.11415 \\ -4.80281 \\ -0.40737 \end{bmatrix}$$

Thus, the solution in response to the stationary point is obtained as follows:

$$\hat{y} = \hat{\beta}_0 + \frac{1}{2}x_0'b = 44.3394 + \begin{bmatrix} 0.88991 & 2.11415 & -4.80281 & -0.40737 \end{bmatrix} \begin{bmatrix} 3.84580 \\ 1.66905 \\ -0.39387 \\ -0.06146 \end{bmatrix} = 48.7733$$

Further more, the stationary point can be restored to the true value, acquired conditions that provide the optimal solution (Table6) was as follows:

Table6: Optimal Value of Copper

Variable	Optimal value (with coding)	Optimal value(without coding)
X_1	0.88991	0.388991
X_2	2.11415	8.11415
X_3	-4.80281	-0.980281
X_4	-0.40737	81.8526

Where X_1 = calcon concentration (µg/L), X_2 = pH, X_3 = accumulation potential (µg/L), and X_4 = accumulation time (seconds). To get an idea of the character is tics of the surface of the response calculating eigen values(λ) of the matrix B and obtained:
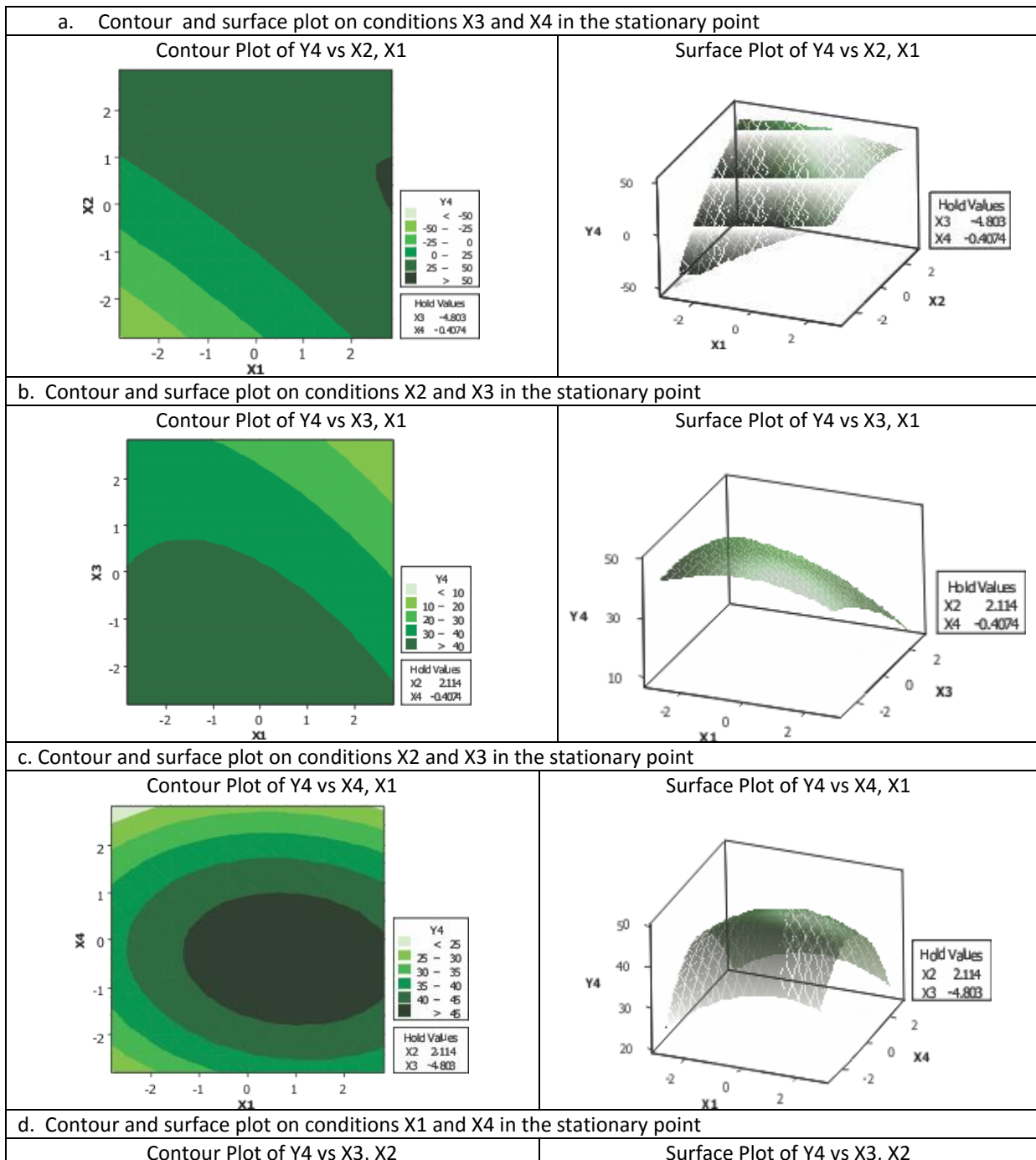
$$\lambda = [-2.94492 \quad -1.93573 \quad -0.34414 \quad -0.22314]$$

Because all foureigen values is negative, then the surface shape is the maximum response. It can be seen plot contour and response surface plot. By making constans two of the four factors were observe data stationary point, then it may be possible to plot contour and response surface as shown in Figure1.

Based on data analysis with response surface method, it is concluded that the peak flow will reach its maximum value at the time of calcon concentration 0.388991mM, pH8.11, accumulation potential -0.61 Volt and accumulation time 81.85seconds with a maximum peak current value of copper 48.77nA.

Contour and surface plot of Copper at stationary point:

By making constant two of the four factors used, then it can be shown that the shape and surface contour is the maximum response. The following will be presented contour plot and the surface on every possible pair of factors used.
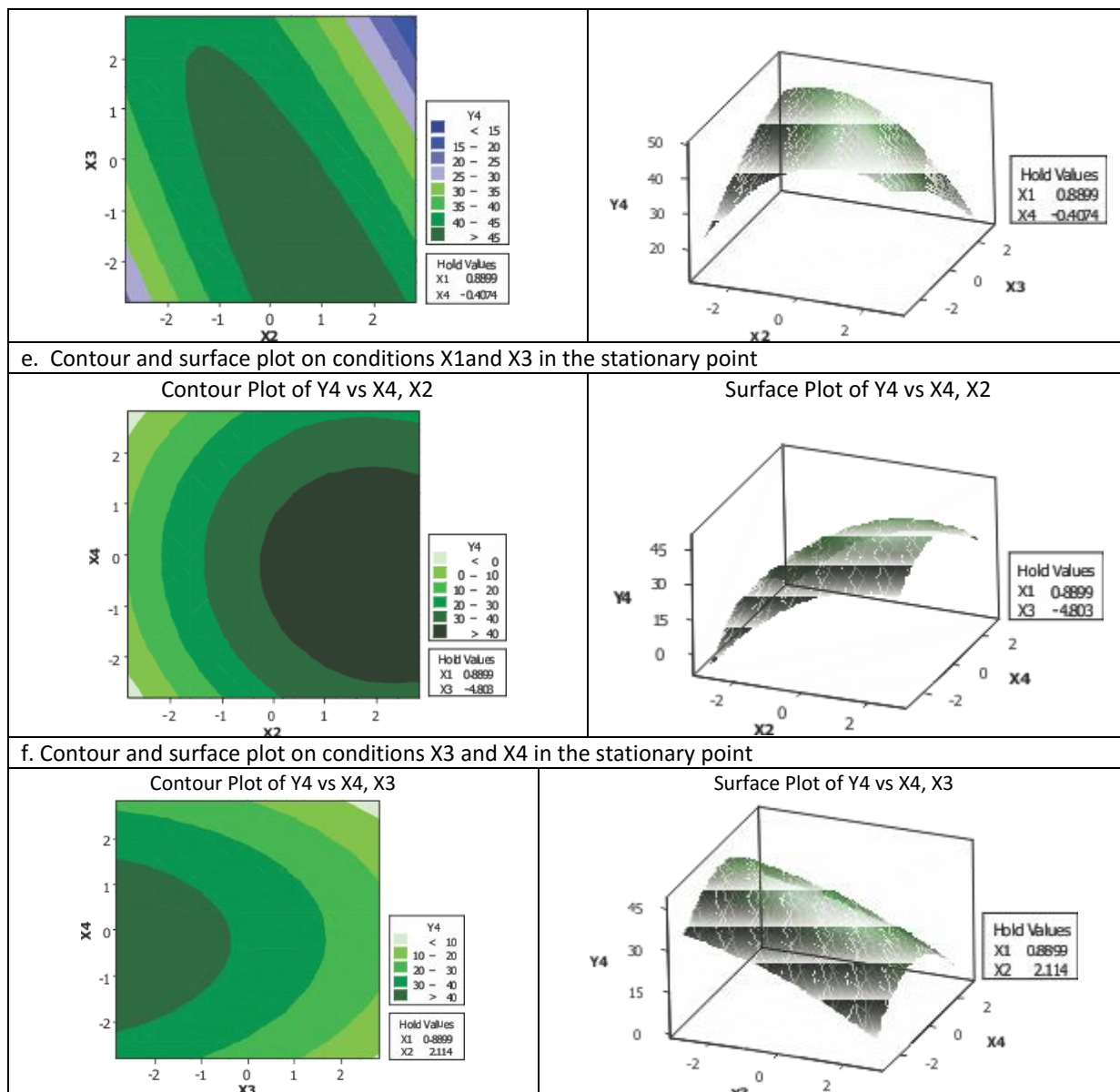
a. Contour and surface plot on conditions X3 and X4 in the stationary point

b. Contour and surface plot on conditions X2 and X3 in the stationary point

c. Contour and surface plot on conditions X2 and X3 in the stationary point

d. Contour and surface plot on conditions X1 and X4 in the stationary point

Contour Plot of Y4 vs X3, X2	Surface Plot of Y4 vs X3, X2

e. Contour and surface plot on conditions X1and X3 in the stationary point

f. Contour and surface plot on conditions X3 and X4 in the stationary point

Figure1: Contour and surface plot of Copper

Parameter Analytical overview:

This method has been successfully applied to a sample of tap water in which were obtained relative standard deviation 2.0%, recovery 98%, the linear range 0.2-105µg/L, coefficient of determination 0.93 with a detection limit 1.21µg/L. More information can be seen in the Table 7 and 8.

Table7: Overview of Analytical Parameters

Parameters	Cu
Tap water sample	33.50 µg/L
RSD	2.0 %
Recovery	98 %
Linier range	0.2-105 µg/L
R^2	0.93
LOD	1.37 µg/L

Table8: Fixed Variable for adsorptive stripping voltammetry procedure

	Cu
working electrode HMDE	HMDE
stirrer speed	2000 rpm
drop size	4
mode	DP
purge time	300 s
deposition potential	-0.61 V
deposition time	48.39 s
equilibration time	5 s
pulse amplitude	0.05005 V
start potential	0.01V
end potential	-0.3 V
voltage step	0.005951 V
voltage step time	0.5 s
sweep rate	0.0119 V/s
peak potential	-1 V

Interference studies:

Possible interference by other metals with the adsorptive stripping voltammetry of copper was investigated by the addition of the interfering ion to the solution containing 10.0 mg/L of this metal using the optimized conditions. The results of this study are summarised in Table 9. Based on the results, it were found that most of the foreign ions did not interfere for copper determination.

Table 9: Tolerance ratio of interfering ions in the determination of 10 μg/L of Copper

Ions	Tolerance limit Cu (ppm)
Zn^{2+}, Pb^{2+}, Cd^{2+} Al^+, Ca^+, Li^+, K^+, Ba^{2+}, Cr^{+3}, Cl^-, F^-, Br^-, SO_4^{2-}, I^-, Ni^{2+}, $Co^{2+,}$	10
Fe^{3+},Na^+	1

CONCLUSION

Based on data analysis with response surface method, the determination of copper obtained optimum conditions, namely: calcon concentration of 0.39mM, pH8.11, accumulation potential-0.61 Volt and accumulation time 81.85seconds with a maximum peak current value of copper 48.77 nA. The response surface method can be applied to the determination of copper in water sample quickly, effectively and efficiently. At the optimum condition were obtained relative standard deviation 2.0%, recovery 98 %, the linear range0.2 -105μg/L, coefficient of correlation 0.93 with a detection limit of 1.21μg/L.

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