

APPLICATION OF CENTRAL COMPOSITE DESIGN FOR OPTIMIZATION THE DETERMINATION OF LEAD USING ADSORPTIVE CATHODIC STRIPPING VOLTAMMETRY

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ABSTRACT

This paper describes an optimization method for rapid determination of lead from Maninjau lake waters by adsorptive cathodic stripping voltammetry using central composite design. The influence of several parameters were studied : variations of calcon concentration, pH, accumulation potential and accumulation time. The design study was a central composite design with 4 factors/variables 3 levels and 31 treatment combinations. From analysis of variance, concluded to accept the second-order model and a significant effect on the response variable (peak current). Based on central composite design, obtained the optimum conditions of lead were : concentration of calcon 0.76 mM, pH = 5.88, accumulation potential -0.45 Volt and accumulation time 88.38 seconds with a maximum peak current 42.56 nA. This method has been successfully applied to water was obtained : relative standard deviation 1.5%, recovery 97.33%, the linear range 0.2-105 µg/L, coefficient of determination 0.92 with a detection limit 1.02 µg/L.

Keywords: central composite design, lead, adsorptive cathodic stripping voltammetry

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INTRODUCTION

Heavy metals such as lead are very important, because it shows toxic effect on living system. Monitoring low levels of lead in the environments has received much attention as consequence of being serious cumulative body poison and it is capable to enter through air, water and food. This metal exhibits severe deleterious effects on human. In particular, it is strongly effects the mental and physical development of children. Acute lead poisoning in humans causes severe damage in the liver, brain, kidneys, reproductive system and central nervous system and sometimes causes death. Mild lead poisoning causes anemia, headache and the victim may feel fatigued and irritable. Besides, chronic exposure to lead causes nephritis, scaring and the shrinking of kidney tissues¹.

Therefore, several methods have already been developed for the determination of lead in water samples. Flame absorption atomic spectrometry (FAAS) and inductively coupled plasma emission spectrometry (ICP-OES) have high detection limit for lead determination and preconcentration procedures are required. Electrothermal atomic absorption spectrometry (ETAAS) has been extensively used for determination of lead in several samples because of the high sensitivity achieved. In the same sense, inductively coupled plasma mass spectrometry (ICP-MS) has high sensitivity and wide linear dynamic range. However, this method is costly for the operation, costs maintenance are quite expensive and less practical but it also cannot measure the levels of metal ions are very small². Although it has previously been carried out preconcentration (concentration) to reduce or eliminate the salt content is high enough of a sample of sea water using solvent extraction method³.

In recent years, we need a sensitive and selective method for determining the levels of trace amounts of metal ions, namely the adsorptive cathodic stripping voltammetry (AdCSV). AdCSV method chosen as an alternative because it has many advantages such as: high salinity of the sea water does not interfere in the analysis, has a high sensitivity, low detection limit on a scale µg/L (ppb), the use of simple and convenient sample preparation, analysis fast, inexpensive infrastructure⁴⁻⁶. In addition, with this method

it is possible to study chemical species of heavy metals⁷, which cannot be done with other methods, this method can be performed for simultaneous determination of Cd, Cu and Pb in seawater using calcon as complexing⁸, simultaneous determination of Cu, Pb and Cd in fresh water using calcein as complexing agent⁹. Heavy metal toxicity is determined from chemical species^{2,10}. Almost all methods of determining the metal in very small quantities requires considerable time on the stage of pre-concentration before measurement. On AdCSV preconcentration stage shorter time, generally less than 1 minute¹¹.

From the results of previous research, to find the optimum conditions of metal ions Cd, Cu, Pb and Zn^{4,8} and metal ions Fe, Co, Ni and Cr¹² in both the singular and simultaneous AdCSV, 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 the response parameter¹³. 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.

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 performance¹³⁻¹⁴.

AdCSV is a highly sensitive technique⁷, the response obtained in the form of the peak current (I_p) 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 results¹⁵. The research design used in this study, as a tool for optimization are: CCD with 4 variables, 3 level/degree and 31 a combination of treatments. The first step of 2k factorial design optimization 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 Minitab using RSM.

The purpose of this study was to obtain the optimum condition of lead, so it can be applied to the analysis of lead in water of Maninjau Lake. To achieve these objectives, required an optimization technique using analytical procedures CCD¹⁶⁻¹⁹. Some parameters were studied: variations of calcon concentration, pH, accumulation potential and accumulation time.

EXPERIMENTAL

Apparatus

Apparatus used in this study were : 797 Metrohm Computrace with HMDE working electrode, reference electrode in the form of Ag/AgCl/KCl, and a Pt electrode as the electrode support; pH meter 80 models Griffin, Griffin & George Loughborough, England; and analytical balance Mettler AE 200, Toledo OH-USA; and glassware used in the laboratory.

Reagents

Reagents to be used in this study is a pure reagent, because AdCSV 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.

Procedures

Voltammeter into the vessel, put 10 ml of standard solution of Pb(II) 10 µg/L, added 0.2 mL and 0.2 mL of 0.1 M KCl in 20 mL calcon, this variable is set constant during the experiment. Calcon concentration, pH, accumulation potential and accumulation time is set according to CCD. Central composite design used 4 factors and 3 levels, level of each factor is coded -1, 0, and +1, with 2 replications. The numbers -1, 0, and +1 is a symbol (code) that indicates the value of the variable. -1 figures show the value of the lowest variable, +1 figures showed the highest variable values, and the

number 0 indicates the value of the variable medium¹⁵⁻¹⁶. Variables of this research design were the calcon concentration, pH, accumulation potential and accumulation time can be seen in Table 1.

Table-1: Central Composite Design (CCD) of Lead

Run	Factor				Peak current (Y)
	Calcon Concentration (X ₁)	pH (X ₂)	Accumulation Potential (X ₃)	Accumulation time (X ₄)	
1	0.6	6	-0.6	70	6.07
2	0.6	6	-0.4	70	30.52
3	0.6	6	-0.6	110	30.00
4	0.6	6	-0.4	110	30.71
5	0.6	8	-0.6	70	19.86
6	0.6	8	-0.4	70	17.56
7	0.6	8	-0.6	110	14.98
8	0.6	8	-0.4	110	18.41
9	0.8	6	-0.6	70	29.62
10	0.8	6	-0.4	70	34.53
11	0.8	6	-0.6	110	21.97
12	0.8	6	-0.4	110	30.82
13	0.8	8	-0.6	70	17.78
14	0.8	8	-0.4	70	13.32
15	0.8	8	-0.6	110	12.96
16	0.8	8	-0.4	110	18.11
17	0.7	7	-0.5	90	39.81
18	0.7	7	-0.5	90	39.99
19	0.7	7	-0.5	90	40.03
20	0.7	7	-0.5	90	39.94
21	0.7	7	-0.5	90	39.92
22	0.7	7	-0.5	90	39.93
23	0.7	7	-0.5	90	39.92
24	0.54	7	-0.5	90	32.18
25	0.7	5.4	-0.5	90	35.42
26	0.7	7	-0.66	90	38.13
27	0.7	7	-0.5	58.1	30.18
28	0.86	7	-0.5	90	38.30
29	0.7	8.6	-0.5	90	28.18
30	0.7	7	-0.34	90	25.33
31	0.7	7	-0.5	121.9	17.23

RESULTS AND DISCUSSION

Optimization of Lead Using One Variable

From the results of previous research, to find the optimum conditions (optimization) the determination of lead using AdCSV, 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 optimum conditions were as follow : calcon concentration 0.7 mM, accumulation potential -0.5 V, pH 7, accumulation time 90 seconds⁴.

This optimization does not give the effect of the interaction between the variables studied. Therefore, this technique does not describe the full effect on the response parameter¹². 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. Therefore to overcome this

problem, an optimization technique of analytical procedures is by using central composite design.

Optimization of Lead Using Central Composite Design

First-Order Model of Lead

The data processing was done using software Minitab-16, and the results can be seen in Table-2 the following :

Table- 2: Model Order I regression coefficient

Term	Coef
Constant	24.5974
X1	0.6875
X2	-5.0788
X3	2.5463
X4	0.5437

Based on Table 2, regression equation of first-order model was :

$$\hat{Y} = 24.5974 + 0.6875X_1 - 5.0788X_2 + 2.5463X_3 + 0.5437X_4$$

Where X_1 = calcon concentration ($\mu\text{g/L}$), X_2 = pH, X_3 = accumulation potential ($\mu\text{g/L}$), X_4 = accumulation time (seconds), and $\hat{Y}$ = peak current (nA). Analysis of Variance (ANOVA) of first-order model can be seen at Table-3.

Table-3: ANOVA of First-Order Model of Lead

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	4	528.73	528.73	132.182	1.37	0.296
Linear	4	528.73	528.73	132.182	1.37	0.296
X1	1	7.56	7.56	7.563	0.08	0.784
X2	1	412.70	412.70	412.699	4.26	0.058
X3	1	103.73	103.73	103.734	1.07	0.318
X4	1	4.73	4.73	4.731	0.05	0.828
Residual Error	14	1355.46	1355.46	96.819		
Lack-of-Fit	12	1355.32	1355.32	112.944	1619.65	0.001
Pure Error	2	0.14	0.14	0.070		
Total	18	1884.19				

Table-3 test procedure used to determine whether first-order models can be used or not. This hypothesis 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,

$$H_0: \beta_i = 0,$$

$$H_1: \beta_i \neq 0; i = 1, 2, 3, 4$$

Based on Table 3, the test regression parameters simultaneously produce p-value 0.296, meaning that the p-value is greater than the significance level used in the amount of $\alpha = 0.05$. Thus it was decided not to reject H_0 and conclude that none of the independent variables that significantly influence the response variable, so the first-order model can not be used.

Second-Order Model of Lead

First-order model can not be used, then proceed with the second-order model by using a quadratic effect and interaction. Results of second-order model data processing obtained in Table-4.

Table-4: Regression Coefficients in the Second-Order Model

Term	Coef
Constant	40.8228
X1	0.584527
X2	-2.56491
X3	0.527336
X4	-0.359105
X1*X1	-1.02934
X2*X2	-1.45912
X3*X3	-1.46787
X4*X4	-2.47050
X1*X2	-0.624752
X1*X3	-0.261565
X1*X4	-0.695445
X2*X3	-0.819600
X2*X4	-0.371581
X3*X4	-0.0985287

Based on Table-4, the model regression equation :

$$\hat{Y} = 40.8228 + 0.584527X_1 - 2.56491X_2 + 0.527336X_3 - 0.359105X_4 - 1.029342X_1^2 - 1.45912X_2^2 - 1.46787X_3^2 - 2.47050X_4^2 - 0.624752X_1X_2 - 0.261565X_1X_3 - 0.695445X_1X_4 - 0.819600X_2X_3 - 0.371581X_2X_4 - 0.0985287X_3X_4$$

Where X_1 = calcon concentration ($\mu\text{g/L}$), X_2 = pH, X_3 = accumulation potential ($\mu\text{g/L}$), X_4 = accumulation time (seconds), and $\hat{Y}$ = peak current (nA).

Results of ANOVA second-order model data were presented in Table-5.

Table-5: ANOVA of Second-Order Model

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	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	1008.70	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	303.28	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
Residual Error	16	728.28	728.28	45.52		
Lack-of-Fit	10	728.28	728.28	72.83	85920.52	0.000
Pure Error	6	0.01	0.01	0.00		
Total	30	4283.96				

$H_0: \beta_i = 0,$

$H_1: \beta_i \neq 0; i = 1, 2, 3, \dots, k$

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 $\alpha = 0.05$. Thus

it was decided to reject H_0 and conclude that there was a independent variable that significantly influence the response variable, so that the second-order model can be accepted (Table-5). Based on the regression coefficient values in Table-3 can be arranged matrix b and B as follows:

$$b = \begin{bmatrix} 0.58453 \\ -2.56491 \\ 0.52734 \\ -0.35911 \end{bmatrix} \quad \text{and} \quad B = \begin{bmatrix} -1.02934 & -0.31238 & -0.13078 & -0.34772 \\ -0.31238 & -1.45912 & -0.40980 & -0.18579 \\ -0.13078 & -0.40980 & -1.46787 & -0.04926 \\ -0.34772 & -0.18579 & -0.04926 & -2.47050 \end{bmatrix}$$

In order to obtain a stationary point as follows:

$$x_0 = -\frac{B^{-1}b}{2} = \begin{bmatrix} 0.59507 \\ -1.12016 \\ 0.44205 \\ -0.08101 \end{bmatrix}$$

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

$$\hat{y} = \hat{\beta}_0 + \frac{1}{2} x_0' b = 40.8228 + [0.59507 \quad -1.12016 \quad 0.44205 \quad -0.08101] \begin{bmatrix} 0.58453 \\ -2.56491 \\ 0.52734 \\ -0.35911 \end{bmatrix} = 42.5644$$

Furthermore, the stationary point can be restored to the true value, acquired conditions that provide the optimal solution (Table-6).

Table-6: Optimal Value of Lead

Variable	Optimal value (with coding)	Optimal value (without coding)
X_1	0.59507	0.759507
X_2	-1.12016	5.87984
X_3	0.44205	-0.455795
X_4	-0.08101	88.3798

Where X_1 = calcon concentration ($\mu\text{g/L}$), X_2 = pH, X_3 = accumulation potential ($\mu\text{g/L}$), and X_4 = accumulation time (seconds).

To get the surface of the response calculating eigen values (λ) of the matrix B obtained :

$$\lambda = [-2.63499 \quad -1.87237 \quad -1.09470 \quad -0.82478]$$

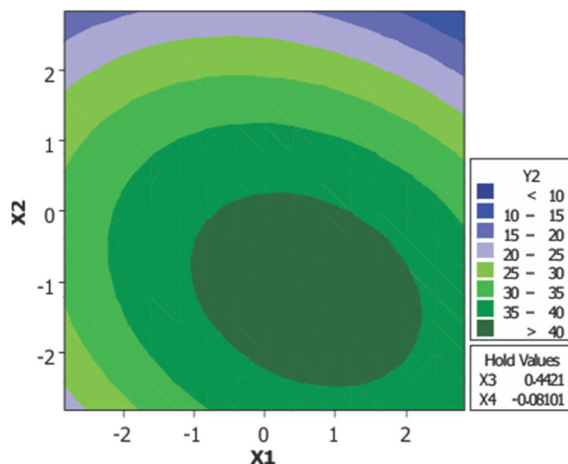
Because all four eigen values is negative, then the surface shape is the maximum response. It can be seen contour and response surface plot. By making constans two of the four factors were observed at a stationary point, then it may be possible to plot contour and response surface as shown in Figure 1.

Based on data analysis with response surface method, it is concluded that the peak flow will reach maximum value of calcon concentration 0.76 mM, pH 5.88, accumulation potential -0.45 Volt and accumulation time 88.38 seconds with a maximum peak current value 42.56 nA.

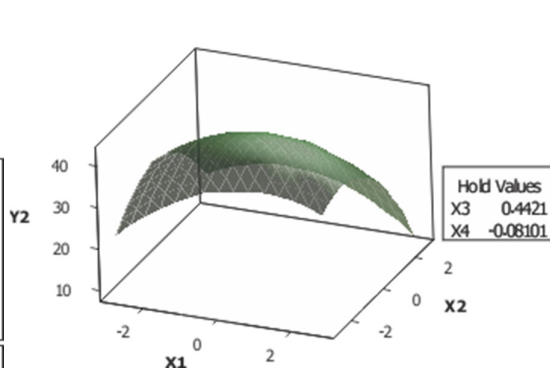
By making constant two of the four factors used, then it can be shown that the shape and surface contour is the maximum response. The following will be presented contour and the surface plot on every possible pair of factors used.

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

Contour Plot of Y2 vs X2, X1

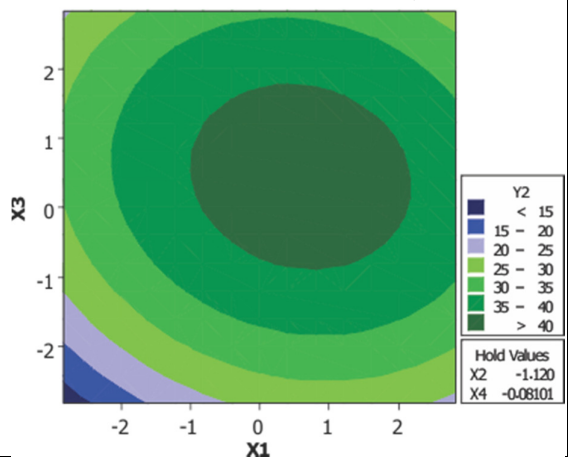


Surface Plot of Y2 vs X2, X1

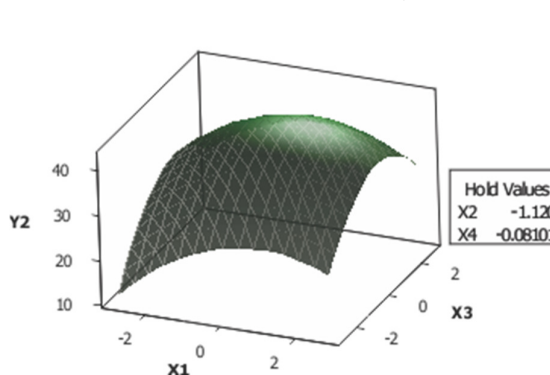


b. Contour and surface plot on conditions X2 and X4 in the stationary point

Contour Plot of Y2 vs X3, X1

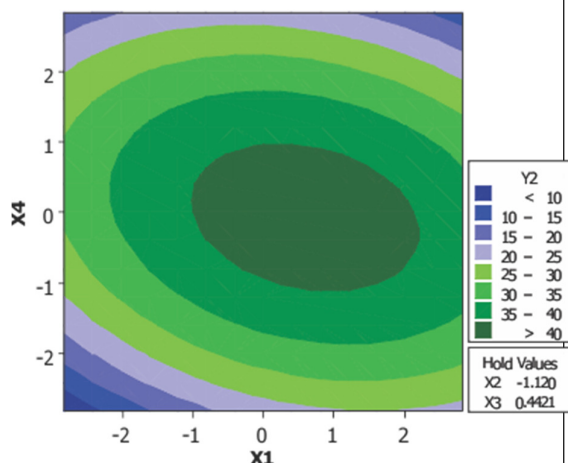


Surface Plot of Y2 vs X3, X1

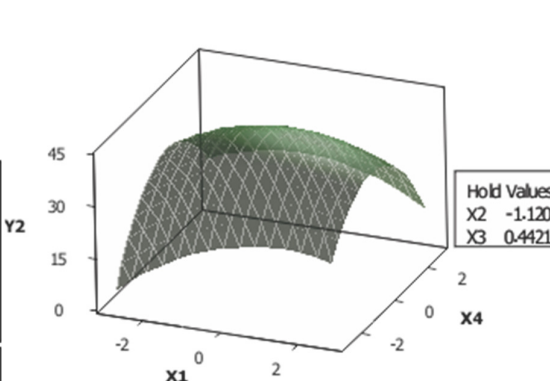


c. Contour and surface plot on conditions X2 and X3 in the stationary point

Contour Plot of Y2 vs X4, X1

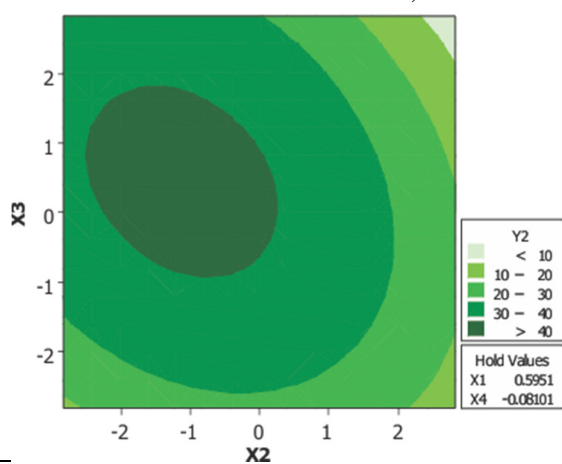


Surface Plot of Y2 vs X4, X1

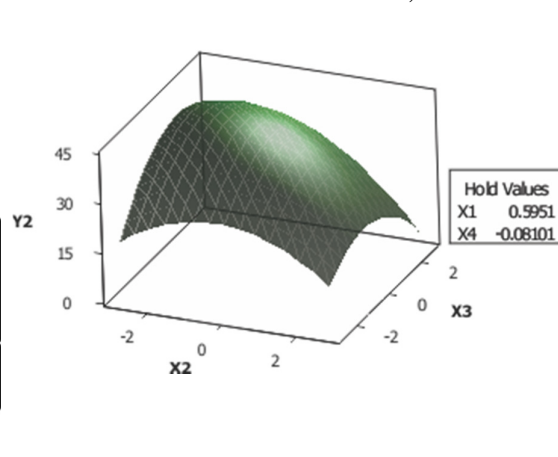


d. Contour and surface plot on conditions X1 and X4 in the stationary point

Contour Plot of Y2 vs X3, X2

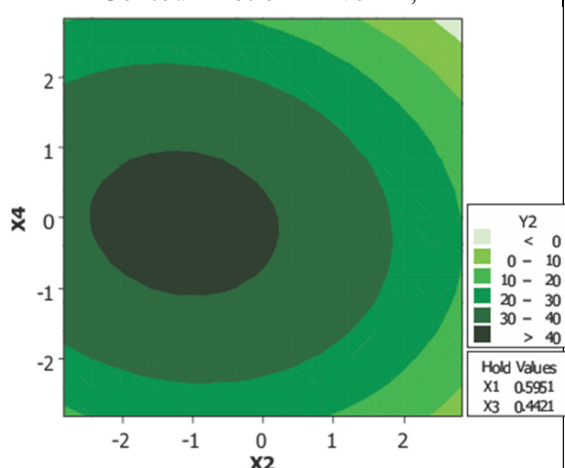


Surface Plot of Y2 vs X3, X2

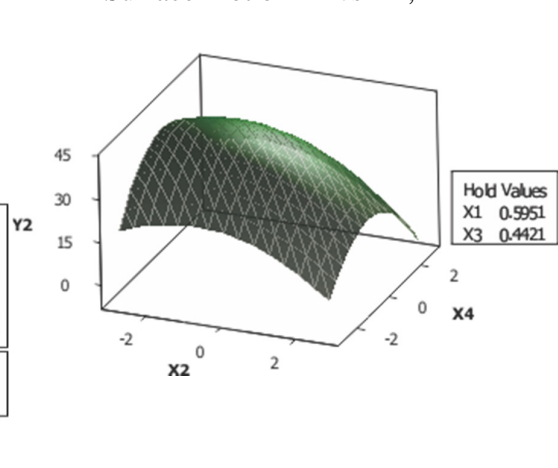


e. Contour and surface plot on conditions X1 and X3 in the stationary point

Contour Plot of Y2 vs X4, X2

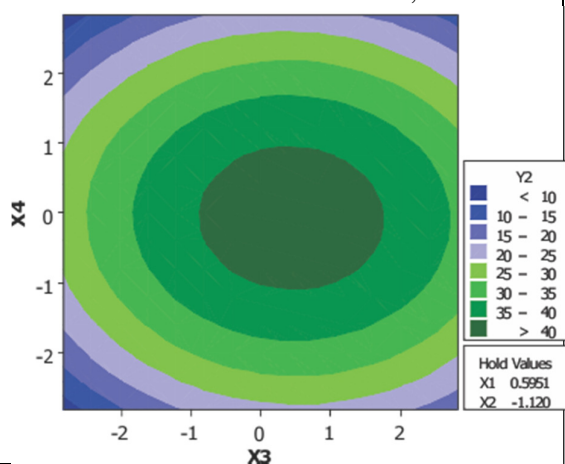


Surface Plot of Y2 vs X4, X2

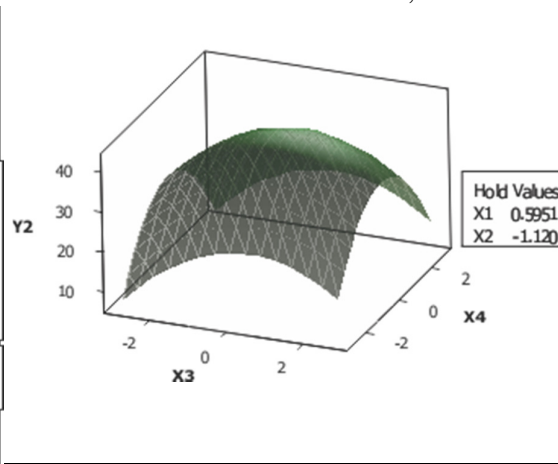


f. Contour and surface plot on conditions X1 and X2 in the stationary point

Contour Plot of Y2 vs X4, X3



Surface Plot of Y2 vs X4, X3



Parameter Analytical overview

This method has been successfully applied to water sample were obtained : relative standard deviation 1.5%, recovery 97.33%, the linear range 0.2-105 µg/L, coefficient of determination 0.92 with a detection limit 1.02 µg/L. More information can be seen in the Table-7.

Table-7: Overview of Analytical Parameters

Parameters	Pb
Tap water sample	33.504 µg/L
RSD	1.5 %
Recovery	97.33 %
Linier range	0.2 - 105 µg/L
R ²	0.92
LOD	1.02 µg/L

Interference studies

Possible interference by other metals with the AdCSV of lead was investigated by the addition of the interfering ion to the solution of this metal using the optimized conditions. Based on the results, it were found that most of the foreign ions did not interfere for lead determination (Table-8).

Table-8: Tolerance ratio of interfering ions in the determination of 10 µg/L of lead

Ions	Tolerance limit Pb (ppm)
Zn ²⁺ , Cu ²⁺ , Cd ²⁺ , Al ³⁺ , Ca ²⁺ , Li ⁺ , K ⁺ , Ba ²⁺ , Cr ³⁺ , Cl ⁻ , F ⁻ , Br ⁻ , SO ₄ ²⁻ , I ⁻	10
Fe ³⁺ , Ni ²⁺ , Co ²⁺ , Na ⁺	1

CONCLUSION

Based on data analysis with central composite design, the determination of lead obtained optimum conditions, namely: calcon concentration of 0.76 mM, pH 5.88, accumulation potential -0.45 Volt and accumulation time 88.38 seconds with a maximum peak current value of lead 42.56 nA. The response surface method can be applied to the determination of lead in water sample quickly, effectively and efficiently. The optimum condition were obtained : relative standard deviation 1.5%, recovery 97.33%, linear range 0.2-105 µg/L, coefficient of determination 0.92 with a detection limit 1.02 µg/L.

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