ICP-OES Method for the Determination of Fe, Co, Mn, Cu, Pb, and Zn in Ore Samples From the Keban Region Using Experimental Design and Optimization Methodology

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INTRODUCTION

Nowadays, the qualitative and quantitative analysis of metals in food products, environmental inorganic pollutants, biological fluids, fruits, vegetables, drug preparation, and ore samples from the mining industry (1–4) are of vital importance in the fields of science and industry. In previous studies, several methods including atomic absorption spectrometry (AAS), atomic emission spectrometry (AES), and inductively coupled plasma optical emission spectrometry (ICP-OES), etc., have been reported for the analysis of these types of samples. The determination of metals in samples can be accomplished via single reagent leaching, ion exchange resins, and sequential extraction procedures (SEP) (5–10). Measurement of total metal concentrations is useful to evaluate the heavy metal burden, but their mobility depends strongly on their specific chemical forms or ways of binding (11–19), and it is normally accepted that total metal concentration gives less information about the metal behavior than fractionation analysis (20–22). Fractionation methods consist of extraction/lixiviation procedures carried out under operationally defined conditions (23,24). However, the determination of specific chemical species or binding forms is difficult and often hardly possible (25). Hence, sequential extraction methods are widely used for the estimation of availability and mobility of relevant metals in solid matrices (26). Sequential extraction

ABSTRACT

A new approach based on the use of inductively coupled plasma optical emission spectrometry (ICP-OES) is presented for the quantitative determination of Fe, Co, Mn, Cu, Pb, and Zn in ore samples obtained from the Keban Region, Turkey. A 3³ full factorial design with 27 sample runs was used to find the optimal sequential extraction conditions for the analysis of these samples. Under optimized conditions for each step of the sequential extraction procedure, calibration curves for the respective metals were obtained by measuring the absorbance values at 238.2 nm for Fe, 228.6 nm for Co, 257.6 nm for Mn, 327.4 nm for Cu, 220.4 nm for Pb, and 206.2 nm for Zn. The proposed ICP-OES method was successfully applied to the quantitative analysis of real ore samples containing Fe, Co, Mn, Cu, Pb, and Zn. Good agreement was found for the analytical results of these metals.

approaches used in trace metal analysis were introduced by Tessier et al. (27) and improved by the Commission of the European Communities Bureau of Reference (BCR) based on the schemes of Salomons and Förstner (28) and Kersten and Förstner (29). Minor different versions of these schemes related to operating conditions have been used to quantify the trace metal content in samples such as soils, sediments, and related materials. For example; in the application of the BCR method for metal analysis, schemes of sequential

extraction treatments have not been very reliable with regard to the source and characteristics of the samples. The main problems in the application of sequential extraction treatments are the ability to find the optimal or desirable reactive volume and concentration for the sub-extraction steps to obtain a higher yield of metal extraction from the samples. Therefore, experimental design optimization is a very suitable tool to solve these problems. An usual strategy of the extraction of metals from samples is based on the one-factor optimization technique. This one-factor approach may give rise to the incorrect interpretation or wrong decision in finding extraction conditions where the other experimental factors are kept constant. A way to eliminate the disadvantages of one-factor optimization technique is the use of the experimental design and optimization techniques (30,31).

In the current study, the experimental conditions of the sequential extraction steps were optimized by using the experimental design optimization technique. In this case, the application of sequential extraction treatment contains four different extraction steps based on the use of CH₃COOH, NH₂OH-HCl, CH₃COONH₄, and *aqua regia*. Before using CH₃COONH₄, a specific amount of H₂O₂ (20 mL in this study) was added. The concentration levels of the mentioned reactives (CH₃COOH, NH₂OH-HCl, and CH₃COONH₄) in the application of the experimental design optimization technique were considered as the variable factors for the optimization of the sequential extraction conditions. In this study, ore

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samples were collected from the Elazig-Keban Region in Turkey, and analyzed using ICP-OES and the optimized sequential extraction procedure. It was observed that ICP-OES is very suitable for the quantitative evaluation of Fe, Co, Mn, Cu, Pb, and Zn in ore samples.

EXPERIMENTAL

Instrumentation and Software

Metals analyses were performed with an Optima™ 2100 DV inductively coupled plasma optical emission spectrometer (ICP-OES) (PerkinElmer, Inc., Shelton, CT, USA). The instrumental operating conditions are listed in Table I. The selection of instrumental parameters and optical wavelengths were based on obtaining good sensitivity, reasonable detection limits, and eliminating interferences (32).

Data treatments and calculations used in the experimental design, optimization, calibration and prediction were performed by means of Microsoft® Excel® and Matlab® software (MathWorks, Inc., USA).

Reagents

In all experiments, deionized water was used throughout and

obtained from a Milli-Q® system (Millipore Corporation, USA). Ultra-pure HNO₃ (Fluka, Switzerland), H₂O₂ (Merck, Germany), CH₃COONH₄ (Merck), analytical grade CH₃COOH (Sigma-Aldrich Corporation, Germany), and NH₂OH-HCl (Sigma-Aldrich) were used as the sequential extraction reagents. Calibration solutions were obtained by diluting the stock solutions.

Stock and Standard Solutions

Stock solutions of 1000 mg/L for Fe, Co, Mn, Cu, Pb, and Zn, prepared in 10, 25, 50, 75, 100 mg/L calibration solutions, were diluted with the respective stock solution for each metal ion.

Sequential Extraction Procedure

An analytical technique consisting of sequential chemical extractions is proposed for the analysis of Fe, Co, Mn, Cu, Pb, and Zn into four sub-fractions: (a) Acetic acid to extract all exchangeable, acid- and water-soluble metals, (b) hydroxylammonium chloride and ammonium acetate to extract all reducible metals (bound to Fe-Mn oxides), (c) hydrogen peroxide to extract all oxidizable metals (bound to organic matter), and (d) *aqua regia* to extract all remaining non-silica-bound metals. For this study, sequential chemical extractions in four sub-fractions were optimized by application of a 3³ full factorial design and the optimization technique. Under the optimized extraction conditions, spectral determination of the metals by ICP-OES was performed by measuring absorbance at the maximum wavelength of 238.2 nm for Fe, 228.6 nm for Co, 257.6 nm for Mn, 327.4 nm for Cu, 220.4 nm for Pb, and 206.2 nm for Zn.

Optimization Methodology

In the chemical studies, experimental design and optimization approaches were applied for the

demonstration of the relationship between one or more responses and experimental factor variables. By using the mathematical model obtained from the factors and factor interactions with response variables, the optimization methodology provides optimal experimental conditions and obtains desirable analytical results in a very short time. Various designs, the full and fractional factorial designs and the more complex central composite designs, Box-Behnken, Doehlert, and use of mixed designs were applied to obtain the expected analytical response surfaces. To compute the mathematical model based on the independent factor variables and their dependent response function, the following second-order polynomial equation was used:

Eq. (1)

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^k \sum_{t=2}^k \beta_{it} x_i x_t$$

where Y represents the predicted response, β_0 is the intercept, β_i and β_{ij} are the linear effect and squared effect, respectively, β_{ij} denotes the interaction effect, x_i and x_j are the independent factor variables. The mathematical solution of Equation 1 allows the prediction of factor levels that produce extreme point maximum or minimum response values corresponding to optimal experimental conditions (30, 31).

RESULTS AND DISCUSSION

In chemical studies of metals, the fundamental problem of quantitative analysis of complex mixtures containing two or more metals (Fe, Co, Mn, Cu, Pb, and Zn for this study) in the same sample is to find the optimal sequential extraction conditions due to the different characteristics of the analyzed metals and their different sample sources. In order to obtain optimized sequential extraction in each sub-step of the procedure for each metal, it is very useful to apply the experimental design and opti-

TABLE I
ICP-OES Instrumental Parameters

Parameters	
RF power	1450 W
Plasma gas flow rate	15 L min ⁻¹
Auxiliary gas flow rate	0.2 L min ⁻¹
Nebulizer gas flow rate	0.8 L min ⁻¹
Sample flow rate	1.5 L min ⁻¹
View mode	Axial
Read	Peak area
Source equilibration time	15 s
Read delay	50 s
Replicates	3
Purge gas	Nitrogen
Shear gas	Air
Plasma gas	Argon

mization approach instead of the manual procedure. Details of the experimental design and optimization methodology are outlined below.

Experimental Design and Optimization Procedure

The 3^3 full factorial design was used in order to find the optimal reactive concentration and optimal volume as used in the sequential extraction process of the metals (Fe, Co, Mn, Cu, Pb and Zn) before the application of the experimental design and optimization. It was concluded that a 3^3 full factorial design was very suitable to optimize the steps of the extraction procedure using different concentrations and volumes of CH_3COOH , $\text{NH}_2\text{OH}\cdot\text{HCl}$, and $\text{CH}_3\text{COONH}_4$; constant concentrations and volumes of H_2O_2 (20 mL) and *aqua regia* (5 mL HNO_3 /15 mL HCl). After some preliminary experiments, the CH_3COOH concentration (x_1), the $\text{NH}_2\text{OH}\cdot\text{HCl}$ concentration (x_2), and the $\text{CH}_3\text{COONH}_4$ concentration (x_3) were considered as factor variables, and then the levels of

the chosen factors in the investigated design were determined as listed in Table II.

Starting from the numerical values of the factors and their levels (see Table II), the design matrix of the 27 sample runs was prepared. After treatment of the samples with model sequential extraction, the metals were measured and computed using ICP-OES. The results are listed in Table III. As can be seen, the quantities of the analyzed metals for each experiment were used as responses for EDO (Experimental Design and Optimization) application. From this full factorial design based on the 27 sample runs, the following second-degree model for each metal was computed for the studied factors and their responses:

$$\text{Eq. (2)} \\ y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 - b_4x_1^2 - b_5x_2^2 + b_6x_3^2 + b_7x_1x_2 + b_8x_1x_3 + b_9x_2x_3$$

where y is the response of the quantity of metal; x_1 , x_2 , and x_3 represents independent factor variables (CH_3COOH , $\text{NH}_2\text{OH}\cdot\text{HCl}$ and

$\text{CH}_3\text{COONH}_4$); b_0 is the intercept which is a real constant number, and real number b_i indicates the coefficients of the model obtained by multiple regression analysis. The above second-order quadratic regression equation for the metals Fe, Co, Mn, Cu, Pb and Zn was obtained as follows with Equations 3 to 8 (see below).

The predicted responses calculated using the second-order quadratic function for Fe, Co, Mn, Cu, Pb and Zn are shown in Table III. A significant test was applied to the regression terms of the mentioned second-order quadratic models and then the $p\text{-value} < p = 0.05$ with $F\text{-calculated} > F\text{-table}$ for each model was reported. From the significant test results, it was concluded that the proposed second-order models were appropriate to optimize the independent variables (x_1 , x_2 , and x_3). From Equations 3 to 8, the optimal values of CH_3COOH concentration (x_1), $\text{NH}_2\text{OH}\cdot\text{HCl}$ concentration (x_2), and $\text{CH}_3\text{COONH}_4$ concentration (x_3) in the sequential extraction procedure were calculated.

In order to demonstrate the factor effect and the factor interactions on the response, the surface graphs for the related metals were plotted. Figure 1 (a - c) shows the factor effect and factor interactions of CH_3COOH (mol/L) and $\text{NH}_2\text{OH}\cdot\text{HCl}$ (mol/L); CH_3COOH (mol/L)

TABLE II
Factors and Their Levels of Experimental Design

Levels	CH_3COOH (mol/L)	$\text{NH}_2\text{OH}\cdot\text{HCl}$ (mol/L)	$\text{CH}_3\text{COONH}_4$ (mol/L)
-1	0.05	0.30	0.55
0	0.10	0.55	1.00
1	0.50	1.00	1.50

$$y_{\text{Fe}} = 52074.05 + 145.36x_1 + 1559.70x_2 + 544.47x_3 - 80.50x_1^2 - 1506.40x_2^2 + 73.23x_3^2 - 70.26x_1x_2 - 667.10x_1x_3 + 168.05x_2x_3 \quad (3)$$

$$y_{\text{Co}} = 3691.00 - 2.10x_1 - 0.07x_2 + 0.56x_3 + 10.20x_1^2 - 1.48x_2^2 - 0.03x_3^2 + 1.47x_1x_2 + 0.09x_1x_3 - 0.65x_2x_3 \quad (4)$$

$$y_{\text{Mn}} = 1243.65 - 55.28x_1 + 0.41x_2 + 7.16x_3 + 11.66x_1^2 - 46.08x_2^2 - 12.19x_3^2 + 41.15x_1x_2 + 31.02x_1x_3 - 25.50x_2x_3 \quad (5)$$

$$y_{\text{Cu}} = 4594.16 + 2867.63x_1 - 990.25x_2 - 1266.26x_3 + 4191.77x_1^2 + 1295.81x_2^2 + 1203.57x_3^2 - 1592.99x_1x_2 - 1877.86x_1x_3 - 1619.03x_2x_3 \quad (6)$$

$$y_{\text{Pb}} = 91.91 + 63.13x_1 + 7.25x_2 + 1.92x_3 + 60.75x_1^2 - 4.28x_2^2 - 0.56x_3^2 + 9.74x_1x_2 + 0.90x_1x_3 + 1.97x_2x_3 \quad (7)$$

$$y_{\text{Zn}} = 151.44 + 272.16x_1 + 1.55x_2 + 3.85x_3 + 282.01x_1^2 - 6.27x_2^2 + 1.26x_3^2 + 7.61x_1x_2 + 4.80x_1x_3 + 2.21x_2x_3 \quad (8)$$

Equations 3 to 8.

TABLE III
Full Factorial Three-Level Design With Responses and Predicted Responses

Run	Exp	Factors			Response (mg/kg)						Predicted Response (mg/kg)					
		X1	X2	X3	Fe	Co	Mn	Cu	Pb	Zn	Fe	Co	Mn	Cu	Pb	Zn
1	11	-1	-1	-1	47432.6	47.9	1312.0	7438.9	85.2	161.1	47741.6	48.1	1291.4	8822.4	88.1	163.0
2	13	-1	-1	0	48334.7	49.9	1317.3	7570.6	89.1	155.0	48711.9	49.3	1305.2	6611.4	87.8	161.1
3	27	-1	-1	1	48935.2	49.7	1329.7	7389.6	86.2	167.0	49828.6	50.4	1294.7	6807.5	86.2	156.7
4	2	-1	0	-1	50834.6	48.9	1299.9	7633.4	88.2	165.2	50709.9	48.7	1322.3	6510.3	88.0	161.0
5	3	-1	0	0	52793.5	50.1	1269.9	7562.8	85.8	157.0	51848.2	49.2	1310.6	5918.3	89.5	161.3
6	26	-1	0	1	52893.4	49.9	1179.0	7573.8	87.2	152.0	53133.0	49.7	1274.5	7733.5	90.0	159.1
7	22	-1	1	-1	50359.2	46.5	1251.5	7689.7	81.9	153.4	50665.3	46.3	1261.0	6789.8	79.2	146.4
8	19	-1	1	0	52684.6	46.0	1236.2	7638.8	85.0	145.3	51971.7	46.2	1223.8	7816.9	82.8	149.0
9	20	-1	1	1	53767.0	45.0	1250.2	7763.3	88.3	150.5	53424.6	46.0	1162.2	11251.1	85.2	149.0
10	5	0	-1	-1	48301.7	33.6	1180.8	6293.9	83.7	135.1	48704.8	34.3	1152.3	10969.1	79.9	140.7
11	21	0	-1	0	50536.4	34.5	1195.2	6335.4	86.5	136.9	49008.0	35.5	1197.2	6880.2	80.4	143.6
12	18	0	-1	1	51413.2	38.5	1217.8	6258.6	87.5	162.8	49457.7	36.7	1217.6	5198.5	79.8	144.0
13	15	0	0	-1	52202.7	35.3	1200.7	6257.0	83.6	146.8	51602.8	36.3	1224.3	7064.0	89.4	146.3
14	6	0	0	0	51271.0	36.5	1240.4	6252.8	89.7	155.3	52074.0	36.9	1243.7	4594.2	91.9	151.4
15	23	0	0	1	51390.7	37.2	1258.7	6151.9	85.6	141.5	52691.7	37.4	1238.6	4531.5	93.3	154.0
16	4	0	1	-1	50830.9	36.4	1231.3	6289.8	91.6	145.2	51488.0	35.4	1204.1	5750.5	90.4	139.4
17	14	0	1	0	51722.1	35.1	1216.6	6261.9	93.3	139.2	52127.3	35.4	1198.0	4899.7	94.9	146.7
18	9	0	1	1	52398.7	36.1	1101.8	6242.5	96.8	155.0	52913.1	35.2	1167.5	6456.1	98.2	151.5
19	24	1	-1	-1	49489.2	41.8	1000.8	31767.3	195.0	693.1	49507.0	40.8	1036.5	21499.3	193.1	682.5
20	1	1	-1	0	48352.9	42.4	1084.3	10398.4	178.5	676.5	49143.1	42.1	1112.4	15532.6	194.5	690.2
21	25	1	-1	1	48232.5	42.3	1133.4	10841.3	193.1	689.5	48925.7	43.4	1163.9	11973.0	194.8	695.4
22	8	1	0	-1	52658.4	45.0	1176.9	10669.6	218.2	702.5	52334.8	44.3	1149.7	16001.3	212.4	695.7
23	12	1	0	0	52097.9	45.1	1264.4	10983.7	228.0	723.3	52138.9	45.0	1200.0	11653.6	215.8	705.6
24	7	1	0	1	52480.7	45.4	1300.0	10634.5	222.1	703.9	52089.5	45.6	1226.0	9713.0	218.1	713.0
25	10	1	1	-1	52794.6	43.9	1158.4	12461.8	216.5	669.0	52149.7	44.9	1170.6	13094.8	223.2	696.4
26	16	1	1	0	51351.9	45.1	1162.1	11268.5	230.2	729.0	52121.9	44.9	1195.5	10366.1	228.5	708.5
27	17	1	1	1	53193.1	45.2	1170.6	10853.2	231.6	718.5	52240.6	44.9	1196.0	10044.6	232.7	718.1

TABLE IV
Optimal Experimental Conditions for the
Concentration of CH₃COOH, NH₂OH-HCl, and CH₃COONH₄
Used in the Sequential Extraction Procedure

Metals	CH ₃ COOH (mol/L)	NH ₂ OH-HCl (mol/L)	CH ₃ COONH ₄ (mol/L)
Fe	0.42	0.97	1.00
Co	0.31	0.81	1.47
Mn	0.30	0.82	1.50
Cu	0.21	0.22	1.24
Pb	0.19	0.11	0.61
Zn	0.18	0.17	0.77

Fig. 1. Surface graphs for Fe (a), Co (b), and Mn (c) obtained by plotting the response variable vs. CH_3COOH (mol/L) and $NH_2OH-HCl$ (mol/L); the response variable vs. CH_3COOH (mol/L) and CH_3COONH_4 (mol/L); the response variable vs. $NH_2OH-HCl$ (mol/L) and CH_3COONH_4 (mol/L).

Fig. 2. Surface graphs for Cu (a), Pb (b), and Zn (c) obtained by plotting the response variable vs. CH_3COOH (mol/L) and $NH_2OH-HCl$ (mol/L); the response variable vs. CH_3COOH (mol/L) and CH_3COONH_4 (mol/L); the response variable vs. $NH_2OH-HCl$ (mol/L) and CH_3COONH_4 (mol/L).

and $\text{CH}_3\text{COONH}_4$ (mol/L); $\text{NH}_2\text{OH-HCl}$ (mol/L) and $\text{CH}_3\text{COONH}_4$ (mol/L) on the responses and corresponds to the quantities of Fe, Co, and Mn. In Figure 2 (a - c), the factor effect with factor interactions of CH_3COOH (mol/L) and $\text{NH}_2\text{OH-HCl}$ (mol/L); CH_3COOH (mol/L) and $\text{CH}_3\text{COONH}_4$ (mol/L); $\text{NH}_2\text{OH-HCl}$ (mol/L) and $\text{CH}_3\text{COONH}_4$ (mol/L) on the responses corresponds to the quantities of Cu, Pb, and Zn. The surface plots in Figure 1 (a - c) and Figure 2 (a - c) show a strong effect of the studied factors on the related response variables.

The optimal experimental conditions for the concentration of CH_3COOH , $\text{NH}_2\text{OH-HCl}$, and $\text{CH}_3\text{COONH}_4$ used in the sequential extraction procedure for the determination of Fe, Co, Mn, Cu, Pb, and Zn by ICP-OES were obtained by solving Equations 3 to 8. Their opti-

mal numerical values are listed in Table IV.

Under the optimized experimental conditions of the sequential extraction procedure, calibration graphs of the analyzed metals were obtained by using the relationship between concentration and absorbance at 238.2 nm for Fe, 228.6 nm for Co, 257.6 nm for Mn, 327.4 nm for Cu, 220.4 nm for Pb, and 206.2 nm for Zn using the ICP-OES method. The calibration data and statistical results are illustrated in Table V. The computed calibration graphs were used for the determination of the respective metals in the samples.

Sample Preparation and Analysis

In this study, sequential chemical extractions in four sub-fractions were optimized by application of the 3^3 full factorial design and the

optimization technique. The extraction procedure was performed using the reagents as listed in Table II. In the first step, a different volume of acetic acid was added to 5 g ore sample and shaken overnight. The solution mixture was centrifuged to separate the extract from the residue and then the supernatants were filtered through a 0.45- μm GF/C filter membrane. The metal ions in each sample were determined by ICP-OES. In the second step, the volume of hydroxylammonium chloride was added to the residue obtained in step 1. The mentioned extraction procedure was applied to the above supernatants. In the third step, the residue from the second step was treated with 20 mL of hydrogen peroxide. Then the volume of ammonium acetate specified in Table II was added and the extraction procedure performed as explained above. The residual fraction obtained after the sequential extraction procedure was digested in 20 mL of *aqua regia* (5 mL HNO_3 /15 mL HCl). The extraction procedure applied was the same as in the first step. The optimized ICP-OES method was applied to the quantitative analysis of Fe, Cu, Co, Mn, Cu, Pb, and Zn in ore samples. The analysis results listed in Table VI for Fe, Cu, Co, Mn, Cu, Pb, and Zn were computed using the above-mentioned calibration graphs.

CONCLUSION

In this study, an ICP-OES method was applied for the determination of Fe, Co, Mn, Cu, Pb, and Zn in ore samples. Prior to the application of ICP-OES, the experimental conditions of the proposed sequential extraction procedure were optimized by solving the second-order quadratic function for each metal, obtained from the 3^3 full factorial design methodology. The optimized sequential extraction procedure followed by ICP-OES

TABLE V
Calibration Data Obtained by Regression Analysis

Metals	Linear Range (mg/L)	Intercept	Slope	Correlation Coefficient (R^2)	LOD ($\mu\text{g/L}$)	LOQ ($\mu\text{g/L}$)
Mn	0-100	177331.0	319300	0.9979	15.0	49.9
Fe	0-100	12940.3	14410	0.9936	7.1	23.6
Co	0-100	15344.2	52860	0.9960	15.0	49.9
Cu	0-100	33592.8	287300	0.9998	5.5	18.3
Zn	0-100	3132.8	35240	0.9993	10.0	33.3
Pb	0-100	1698.5	12510	0.9998	25.0	83.2

TABLE VI
Optimal Total Response Values for the Optimal Concentration Levels for CH_3COOH , $\text{NH}_2\text{OH-HCl}$, and $\text{CH}_3\text{COONH}_4$

Metals	CH_3COOH (mol/L)	$\text{NH}_2\text{OH-HCl}$ (mol/L)	$\text{CH}_3\text{COONH}_4$ (mol/L)	Total Response (mg/kg)
Fe	0.42	0.97	1.00	655121 ± 30642
Cu	0.21	0.22	1.24	8973 ± 397
Mn	0.30	0.82	1.50	1564 ± 126
Zn	0.18	0.17	0.77	890 ± 46
Pb	0.19	0.11	0.61	144 ± 15
Co	0.31	0.81	1.47	77 ± 8

provided successful analysis results with adequate precision and accuracy and a high extraction yield of the analytes in the related samples.

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