Optimization of sample preparation method of total sulphur measurement in mine tailings

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Optimization of sample preparation method of total sulphur measurement in mine tailings

A. H. Khan · J. Q. Shang · R. Alam

Abstract A sample preparation method of total sulphur measurement of reactive mine tailings was optimized. The total sulphur was measured by inductively coupled plasma optical emission spectroscopy, and ultrasound technique was used for sample digestion. The optimization process was adopted by a combined approach of experimental design and response surface methodology. The digestion time, temperature and acid-oxidant combination (i.e. effect of H_2O_2 with a fixed amount of acid mixture) were investigated. A two-level and three-factor (2^3) full factorial design of experiment was applied to identify the most significant factors, and a central composite design was used to optimize the digestion procedure. KZK-1, a sericite schist, was selected as the certified reference material. The optimum methodology at 95 % confidence level ($P < 0.05$) was identified to be 10 min of digestion at 77 °C, with a solution of 1 ml HNO_3:1 ml HCl:1.35 ml H_2O_2. This combination resulted in 100 % sulphur recovery. The investigated method was verified by X-ray diffraction analysis. The optimum digestion level was applied to a reactive mine tailings, which achieved satisfactory results with a percentage relative standard deviation < 3 %.

Introduction

Acid mine drainage (AMD) is generated on many mine sites from reactive mine tailings and has a significant impact on the ecosystem. The reactive mine tailings contain metal sulphides such as iron sulphides [pyrite (FeS_2) and pyrrhotite [$Fe_{1-x}S$, ($0 < x < 0.125$)]. AMD is generated when these tailings are exposed to atmospheric oxygen and water (Shaw et al. 1998; Wang et al. 2006; Zhuang 2009). Accurate and fast measurement of total sulphur in reactive mine tailings is important for day-to-day tailings management. The present work is a continuation of previous works on total sulphur measurement by the inductively coupled plasma optical emission spectroscopy (ICP-OES) (Khan et al. 2012).

Complete dissolution of solid samples is one of the most important steps for spectroscopy analysis (Tuzen 2003). Acid-oxidant combination is suitable for the dissolution of solid samples. Different combinations of acid-oxidant mixture are able to facilitate different elements in the extraction process (Kazi et al. 2009). The use of hydrogen peroxide (H_2O_2), an oxidant, in combination with acid

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mixtures is reported to be advantageous for the extraction of many elements by ultrasound- and microwave-assisted digestion processes for spectroscopy analysis (Bermejo-Barrera et al. 2000; Bermejo-Barrera et al. 2001; Santos et al. 2000; Kazi et al. 2009). Recently, ultrasound-assisted digestion for total sulphur measurement of reactive mine tailings has identified to be an accurate and fast procedure for ICP-OES technique (Khan et al. 2012). Investigations on other types of samples by ultrasound-assisted digestion, followed by ICP-OES detection technique for different elements, have been reported by many authors (Hristozov et al. 2004; Ilander and Väisänen 2009; De-Souza et al. 2006; Santos et al. 2009). In the present study, the influence of hydrogen peroxide (an oxidant) is tested in combination with an acid mixture for total sulphur measurement of reactive mine tailings by ultrasound-assisted digestion technique.

For accurate results, the affecting factors of an experimental method are required to be optimized. The traditional one factor at a time approach, i.e. the univariate technique, may bring a wrong conclusion, especially when the factors are co-related and interact (Hashemi et al. 2005). Multivariate statistical techniques are advantageous because they can reduce the number of laboratory experiments, better evaluate interactions among the variables and reduce costs (Tarley et al. 2009). In addition, multivariate techniques are better suited for mathematical models for prediction of responses as well as for assessing significant variables and experimental conditions (Escudero et al. 2010). During a multivariate optimization process with many factors, the most significant factors are identified by applying a full or fractional factorial design (Ferreira et al. 2004). Then, the optimum conditions are attained by using response surface methodology (RSM), which is predominantly of four types, three level full factorial design (FFD), Doehlert design, central composite design (CCD) and Box–Behnken design (Dias et al. 2007; Ferreira et al. 2007). The RSM provides an extra advantage of measuring the quadratic effects of factors compared to the FFD, which is limited to the linear and interaction effects (Khataee et al. 2010). This quadratic effect helps to analyse the curvature of experimental data (Lima et al. 2007). In this investigation, the factors (digestion time, hydrogen peroxide (H_2O_2) and digestion temperature) are first screened using the FFD and the most significant factors are then optimized by RSM using CCD. The ultrasound energy is applied in the sample digestion process, and the total sulphur is measured by ICP-OES. The influence of hydrogen peroxide (H_2O_2) on the digestion process is tested by statistical means.

Although combined approaches of factorial design and RSM are common practice for the optimization in many analysis procedures (Escudero et al. 2010; Dias et al. 2007; de Amaro and Ferreira 2004; Brasil et al. 2006), this is the first time such an approach is adopted to optimize the total sulphur measuring procedure from reactive mine tailings. This work is also aimed at further improving the digestion time of total sulphur measurement procedure of mine tailings. The present study was carried out between the year 2011 and 2012 at Western University, Department of Civil and Environmental Engineering, Canada.

Materials and methods

Samples and Reagents

KZK-1 was used throughout the experiment as a certified reference material (CRM) of total sulphur content 0.8 ± 0.01 %, which was collected from Canadian Certified Reference Materials Project. The collection, storage procedure and particle-size distribution of mine tailings from Musselwhite mine tailings (MMT) sites were described in our previous work (Khan et al. 2012).

Chemicals and reagents used in this experiment were same as of our previous work unless otherwise stated. Analytical reagent grade nitric acid (HNO_3) of 70 % v/v (Caledon Laboratories ltd., Canada) and hydrogen peroxide (H_2O_2) of 30 % solutions (EMD chemicals, USA) were also used. Atomic absorption grade standard stock solution of sulphur from 'Accu standard, USA' was used for calibration points of 1, 5, 10, 50 and 100 mg L^{-1} in a linear range of $R^2 = 0.999$.

Equipment

Ultrasonic cleaning bath, ICP-OES and X-ray diffraction were the major equipment in the experiment. Experimental setup and all other equipment specifications were described in our previous work. The operating conditions of ICP-OES, including the lowest detection limit, were also cited in the same literature. The wavelength chosen for sulphur measurement by ICP-OES was 181.972 nm (Alam et al. 2012).

Statistical design of experiments

Two major statistical designs were followed to optimize the experimental procedure. The factors such as the

digestion time (A), hydrogen peroxide (B) (an oxidant added to a fixed amount of acid mixture) and digestion temperature (C) were first screened by the FFD, and subsequently, the most influential factors were optimized by the CCD. The analysis of the regression model for both of the designs was carried out at a 95 % confidence level by using graphical analysis software Minitab 15 (Prakash et al. 2008), and all experiments were conducted in duplicates ($n = 2$).

Full factorial design

The FFD contain 2^k experiment (k factors, at two levels) is important for screening of the investigated factors as well as for initial optimization (Ferreira et al. 2004). The factors [i.e. the digestion time (A), hydrogen peroxide (B) and digestion temperature (C)] were first screened by applying the 2^3 FFD, where the factor levels were coded as low (-1), central point (0) and high ($+1$). The uncoded values of the selected levels are presented in Table 1. The run at the central point (0) between the low (-1) and high ($+1$) levels of a chosen factor was performed to evaluate the experimental error (Dias et al. 2007). The number of runs required for the 2^3 (two-level three-factors) FFD is calculated as (N) $= 2^3 = 8$. The FFD matrix in a coded form for the selected reference material KZK-1 is shown in Table 2. The mean values

of duplicate runs for the percentage of total sulphur, percentage recovery of total sulphur (%S_{FFD}) and percentage of relative standard deviation (%RSD) of all eight runs are presented in the same table (Table 2, runs 1–8). In addition, the duplicate run of the central point is also performed, and the mean values are presented (Table 2, run 9).

The average of %S_{FFD} (Table 2, runs 1–8) is 97.35, which is less than the value obtained from the central point run (%$S_{FFD} = 99.3$; Table 2). As a result, the optimum value of the total sulphur measurement for KZK-1 is expected to present between the chosen ranges of the experimental variables; hence, it is not necessary to follow the steepest ascent technique for the optimization process (Li et al. 2001). The screening of the investigated variables was performed by a regression model analysis to identify the factors with a significant effect on the response. The effect, coefficient and probability value (P value) of the experimental data were calculated. The factors identified as significant were then optimized by the CCD for the optimum recovery of total sulphur for the selected reference material KZK-1.

Central composite design

The CCD is the most accepted second-order regression model in the RSM, which was introduced by Box and Wilson in 1951 (Angelopoulos et al. 2009). In a CCD, the

Table 1 Factors and levels (with uncoded values) applied in FFD

Factors with units	Symbols	Low level (-1)	Central point (0)	High level ($+1$)
Digestion time (minute)	A	10	15	20
H_2O_2 (ml); [1 ml HNO_3:1 ml HCl is fixed throughout the experiment]	B	1	1.5	2
Temperature (°C)	C	60	70	80

Table 2 FFD matrix (2^3) and the results for KZK-1

Run	Digestion time (minute), (A)	H_2O_2 (ml), (B)	Digestion temperature (°C), (C)	Percentage of total sulphur	Percentage recovery of total sulphur (%S_{FFD})	%RSD
1	-1	$+1$	$+1$	0.799 ± 0.002	99.9	0.25
2	-1	-1	$+1$	0.796 ± 0.001	99.5	0.13
3	$+1$	$+1$	$+1$	0.793 ± 0.003	99.1	0.38
4	$+1$	$+1$	-1	0.764 ± 0.005	95.5	0.65
5	$+1$	-1	-1	0.768 ± 0.001	96.0	0.13
6	-1	-1	-1	0.781 ± 0.001	97.6	0.13
7	-1	$+1$	-1	0.739 ± 0.003	92.4	0.41
8	$+1$	-1	$+1$	0.79 ± 0.008	98.8	1.01
9	0	0	0	0.794 ± 0.002	99.3	0.25

No. of all experiments is $n = 2$

investigated factors were studied at five levels ($-\alpha$, -1, 0, $+1$, $+\alpha$) that include a full or fractional factorial design with central points that are augmented with star points located at a distance of α from its centre points (Myers and Montgomery 2002). The central points (0) identify the experimental error as well as the reproducibility of data, and the star points ($\pm\alpha$) represent the extreme high ($+\alpha$) and low ($-\alpha$) values (Chang et al. 2011). In a CCD, the star points (α) and total number of runs (N) can be calculated by the following equations, respectively, (Prakash et al. 2008),

$$\alpha = 2^{k/4} \tag{1}$$

$$N = 2^k + 2k + N_0 \tag{2}$$

where k is the number of factors, N is the number of runs, N_0 is the number of central points, 2^k is the total factorial points (cubic points) and $2k$ is the total axial points. The experimental data obtained in a CCD are subject to a multiple regression analysis and represent a relationship between the dependent and independent variables. The second-order regression model obtained from a CCD can be represented as follows (Myers and Montgomery 2002),

$$
\begin{aligned}
Y = {} & s_0 + s_1 x_1 + s_2 x_2 + \ldots + s_k x_k + s_{11} x_1^2 + \ldots + s_{kk} x_k^2 \\
& + s_{12} x_1 x_2 + s_{13} x_1 x_3 + \ldots + s_{k-1,k} x_{k-1} x_k + \varepsilon
\end{aligned}
\tag{3}
$$

where Y is the dependent variables or the response, X_1 is the coded levels of independent variables and so on. S_0, S_1, S_{11} and S_{12} are the regression coefficients for the intercept, linear, quadratic and interaction terms of factors, respectively, and so on. The error term is expressed by ε.

The coefficient of the second-order regression equation and the probability value (P value) was calculated by the software (Minitab 15). The analysis of variance (ANOVA) was carried out to estimate the significance of variables in their linear, interaction and quadratic states. A two-dimensional (2D) contour plot was used to identify the optimum value of the digestion process.

Selection of factors levels

The factors investigated in the optimization process were the digestion time (A), hydrogen peroxide (B) and digestion temperature (C). The upper and lower levels of H_2O_2 and the digestion time were selected by a trial and error method. According to the previous experiments of the authors, the mixture of 1 ml HNO_3:1 ml HCl provided 100 % recovery of total sulphur from the selected reference material KZK-1. For the selection of acid-H_2O_2 (oxidant) combination, a trial was carried out by using HNO_3 and H_2O_2 mixture, without HCl on KZK-1. The results of total sulphur measurement from KZK-1 were inconsistent, and accuracy was low. This observation supports the significance of HCl in the tailings digestion process (Khan et al. 2012). As a result, the acid combination of 1 ml HNO_3:1 ml HCl was fixed throughout the experiment. The temperature levels for the present work were kept the same as of the previous work.

Digestion procedure

Working principle of ultrasound-assisted digestion of mine tailings and the detail digestion procedure of mine tailings for total sulphur measurement by ICP-OES technique were described elsewhere (Khan et al. 2012). For further improvement of the digestion procedure, predetermined quantity of hydrogen peroxide (H_2O_2) was added in the solution of 1 ml HNO_3:1 ml HCl in a digestion tube. After the addition of 1 ml HNO_3 into the sample, it was allowed to stand for 1 min and then, a designated amount of H_2O_2 was added, followed by 1 ml of HCl. The screw cap was

Table 3 Regression analysis results of 2^3 FFD for %S_{FFD} from KZK-1

Term	Effect	Coefficient	Standard error of coefficient	T values	P values
Constant		97.3448	0.1634	595.90	0.000
Time (A)	-0.0014	-0.0007	0.1634	-0.00	0.997
H_2O_2 (B)	-1.2266	-0.6133	0.1634	-3.75	0.006
Temperature (C)	3.9481	1.9741	0.1634	12.08	0.000
Time $\times$ H_2O_2 (AB)	1.1704	0.5852	0.1634	3.58	0.007
Time $\times$ Temperature (AC)	0.7609	-0.3804	0.1634	-2.33	0.048
H_2O_2 $\times$ Temperature (BC)	1.5829	0.7914	0.1634	4.84	0.001
Time $\times$ H_2O_2 $\times$ Temperature (ABC)	-1.1891	-0.5946	0.1634	-3.64	0.007

$R^2 = 96.41$ %, R^2 (adj) $= 93.28$ %; T values $=$ Coefficient/Standard error of coefficient; P Probability

sealed immediately and placed in the ultrasonic bath for sonication. Hydrogen peroxide (H_2O_2) is unstable and decomposes in the presence of acidic solution, which is catalysed by Fe^{3+} ions, metals (Pt, Ag), dust, etc. (Dimitrijevic et al. 1999). The decomposition of H_2O_2 produces oxygen and water in concentrated acid solutions (Dimitrijevic et al. 1999), which may lead to chemical reactions and increasing temperature. The vigorous reactions in combination with the acid mixture and ultrasound energy improving the extraction efficiency of targeted elements from the solid matrix are supported by other study (Kazi et al. 2009).

Results and discussion

Screening of factors

The results from the regression analysis of the 2^3 FFD for $\%S_{FFD}$ from KZK-1 are shown in Table 3. All factors as well as their interactions are found significant at 5 % probability level ($P < 0.05$), except for the digestion time (A) ($P = 0.997$). The digestion time (A) is also showing the lowest effect (A, -0.0014) (Table 3) among all other factors and their interactions. The model presented correlation coefficient $R^2 = 96.41$ % and adjusted correlation coefficient R^2 (adj) = 93.28 %, which is in very good agreement (Li et al. 2001; Jadhav et al. 2012) between the experimental data and the model. Therefore, the model is statistically significant and predictable within the chosen variables. The negative effect and coefficient of the digestion time (A) reveal that the increase in this factor from low to high level is not influential for $\%S_{FFD}$ (Abdel-Ghani et al. 2009). As a result, the low level of digestion time ($A = 10$ min) is adequate for the maximum $\%S_{FFD}$ from the selected reference material (KZK-1) (Dias et al. 2007), showing significant improvement in digestion time compared to our previous work by ICP-OES method (Khan et al. 2012). Similar digestion time (10 min) by ultrasound-assisted extraction was reported for the extraction of phosphorus and chromium from soil and biological samples, respectively (Kazi et al. 2009; Rondano and Pasquali 2008). On the other hand, the two-way interaction effect of hydrogen peroxide (Table 3; BC and AB) is positive as well as significant ($P = 0.001$ and 0.007). The order of effect of the main factors for $\%S_{FFD}$ as calculated in the regression model (Table 3) is the digestion temperature (C, 3.9481) > hydrogen peroxide (B, -1.2266) > the digestion time (A, -0.0014).

Considering the above discussion, the digestion time (A) could be removed from the next steps of optimization process and was fixed at 10 min for the rest of the experiments. In summary, the 2^3 FFD has identified the most influential factors for $\%S_{FFD}$ from KZK-1, i.e. the digestion temperature (C) and hydrogen peroxide (B).

Final optimization

A CCD is performed to optimize the most influential factors (i.e. hydrogen peroxide (B) and digestion temperature (C) see subsection, screening of factors), for percentage recovery of total sulphur ($\%S_{CCD}$). The levels of CCD studied are presented in Table 4 with coded and uncoded values. The design matrix of CCD is detailed in Table 5, which includes 13 runs (Eq. 2; 4 factorial points, 4 star points and 5 central points). The star points are calculated by Eq. 1, i.e. $\alpha = 1.414$ in coded form. Due to the presence of the star points, the factors B and C vary from 0.8 to 2.2 ml and 56 to 84 °C, respectively. The design matrix of CCD also contains the mean values of duplicate runs for the percentage of total sulphur, percentage recovery of total sulphur ($\%S_{CCD}$), percentage of error and $\%RSD$ (Table 5).

Regression model and ANOVA

The regression model of $\%S_{CCD}$, which is obtained by the least square method for KZK-1, contains the coefficients of the regression analysis, student t test (T value) results and P (probability) values for the linear, quadratic (or square) and interaction terms (Table 6). Now adding the values of regression coefficients for the intercept, linear, quadratic and interaction terms from Table 6 to Eq. 3, an empirical second-order relationship between the dependent ($\%S_{CCD}$) and independent (B and C) variables can be derived (Khataee et al. 2010),

$$\%S_{CCD} = 100.127 + 0.314B + 3.602C - 0.838B^2 - 4.088C^2 - 1.409BC \quad (4)$$

Table 4 Factors and levels (with uncoded values) applied in CCD

Factors with unit	Symbols	Levels				
		Extreme low level ($-\alpha$)	Low level (-1)	Central point (0)	High level ($+1$)	Extreme high level ($+\alpha$)
H_2O_2 (ml)	B	0.8	1.0	1.5	2.0	2.2
Temperature (°C)	C	56	60	70	80	84

Table 5 CCD matrix (2^3) and the results for KZK-1

Run	H_2O_2 (ml), (B)	Digestion Temperature (°C), (C)	Percentage of Total Sulphur	Percentage Recovery of Total Sulphur ($\%S_{CCD}$)	Percentage of Error	Percentage Relative Standard Deviation, (%RSD)
1	−1	−1	0.754 ± 0.01	94.25	5.75	1.33
2	+1	−1	0.77 ± 0.005	96.25	3.75	0.65
3	−1	+1	0.801 ± 0.007	100.13	−0.13	0.87
4	+1	+1	0.794 ± 0.007	99.25	0.75	0.88
5	−1.414	0	0.794 ± 0.003	99.25	0.75	0.38
6	+1.414	0	0.797 ± 0.004	99.62	0.38	0.5
7	0	−1.414	0.737 ± 0.006	92.13	7.87	0.81
8	0	+1.414	0.802 ± 0.001	100.25	−0.25	0.12
9	0	0	0.809 ± 0.004	101.25	−1.13	0.49
10	0	0	0.8 ± 0.003	100	0.0	0.37
11	0	0	0.8 ± 0.004	100	0.0	0.5
12	0	0	0.794 ± 0.006	99.25	0.75	0.76
13	0	0	0.801 ± 0.005	100.13	−0.13	0.63

No. of all experiments is $n = 2$

Table 6 Regression model for $\%S_{CCD}$ from KZK-1

Term[a]	Coefficient	Standard error of coefficient	T values	P values
Constant	100.127	0.2954	339.006	0.000
B	0.314	0.3286	0.955	0.351
C	3.602	0.3286	10.961	0.000
B^2	−0.838	0.4980	−1.683	0.108
C^2	−4.088	0.4980	−8.210	0.000
BC	−1.409	0.6473	−2.176	0.042

$R^2 = 90.64\,\%$, $R^2(adj) = 88.30\,\%$; *T values* = Coefficient/Standard error of coefficient; *P* Probability

[a] B = Hydrogen peroxide (ml), C = Digestion Temperature (°C)

Table 7 ANOVA for $\%S_{CCD}$ from KZK-1

Source	DF	Sequential sum of squares	Adjusted sum of squares	Adjusted mean of squares	F values	F critical (F_{cr})	P values
Regression	5	168.997	168.997	33.7994	38.74	2.71	0.000
Linear	2	105.629	105.629	52.8146	60.53	3.49	0.000
Square or Quadratic	2	59.235	59.235	29.6177	33.95	3.49	0.000
Interaction	1	4.133	4.133	4.1328	4.74	4.35	0.042
Residual Error	20	17.450	17.450	0.8725			
Lack-of-Fit	3	2.153	2.153	0.7177	0.80	3.20	0.512
Pure Error	17	15.297	15.297	0.8998			
Total	25	186.447					

DF degrees of freedom, *F values* = Adjusted mean of squares $_{factor}$/Adjusted mean of squares $_{Residual\ Error}$ and *P* Probability

All independent variables in Eq. 4 are in the coded form as given in the CCD matrix (Table 5). This empirical model, Eq. 4, can be used to predict the value of percentage recovery of total sulphur ($\%S_{CCD}$).

According to P (probability) values (Table 6), the linear and quadratic effects of the factor C (digestion temperature) are significant ($P = 0.000$ and 0.000), whereas the same effects are insignificant for the factor B (hydrogen peroxide) ($P = 0.351$ and 0.108). In addition, hydrogen peroxide (B) is significant when it interacts with the factor C (i.e. BC, $P = 0.042$). In all cases of the central to high temperature (C) levels (Table 5; except for the runs 1, 2, 7), the percentage of error and the $\%$RSD are $< 3\%$, which is excellent in accuracy and precision for the digestion procedure (Jenner et al. 1990).

A positive regression coefficient indicates the synergistic effect (i.e. the increase in factors level increases the response) for $\%S_{CCD}$ from KZK-1 (Prakash et al. 2008). The regression coefficients of the linear effect of factors B and C are positive (Eq. 4), which means the increase in the factors level from low to high increases the $\%S_{CCD}$ (Prakash et al. 2008). On the other hand, the quadratic and interaction effects of factors B and C (i.e. C^2, B^2 and BC) are found negative. Furthermore, the correlation coefficient, $R^2 = 90.64\%$, shows a good agreement for $\%S_{CCD}$ between the experimental data set and the model (Li et al. 2001; Jadhav et al. 2012). Therefore, the model is statistically significant and predictable within the chosen variables.

The summary of ANOVA for $\%S_{CCD}$ from KZK-1 is presented in Table 7. The ANOVA table shows the combined effect of linear and quadratic terms as well as the interaction effect of the experimental factors (i.e. B and C). The F tests, F critical values (Montgomery et al. 2006) and P (probability) values are presented in the same table. High values of $F(F > F_{cr})$ and low values of P ($P < 0.05$) of the regression model of $\%S_{CCD}$ for KZK-1 indicate that all variable terms (linear, quadratic and interaction) are statistically significant and the model is adequate for prediction (Khataee et al. 2010; Chang et al. 2011).
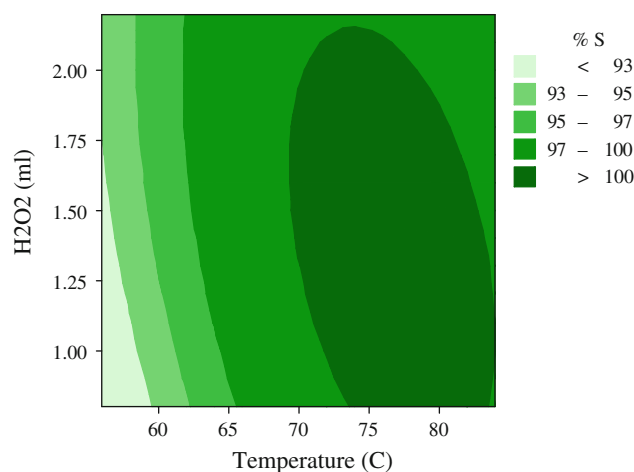

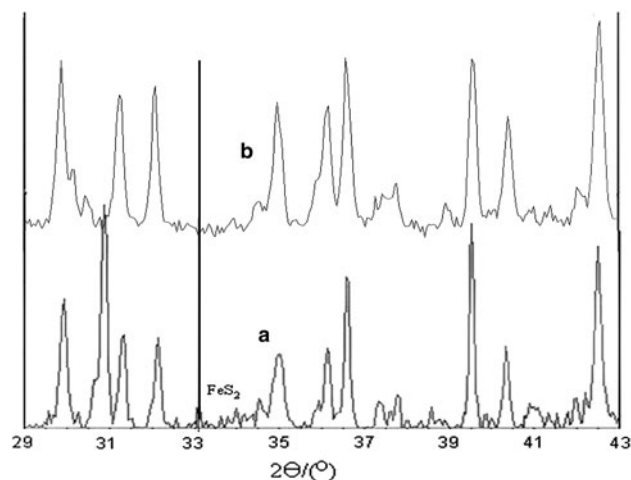**Fig. 1** Contour plot for $\%S_{CCD}$ from KZK-1; digestion temperature (°C) versus H_2O_2 (ml)

Fig. 2 X-ray diffraction analysis of KZK-1 sample: **a** before digestion and **b** after digestion by the optimum levels of investigated factors

2D contour plot

The 2D contour plot (Fig. 1) represents the $\%S_{CCD}$ from KZK-1 by varying the factors B (hydrogen peroxide) and

Table 8 Results of MMT

Run	Digestion time (A), (min)	Acid-oxidant combination (B),(ml)	Digestion temperature (C), (°C)	Total sulphur percentage	Percentage relative standard deviation (%RSD)
01[a]	20	1 ml HNO_3:1 ml HCl	80	0.45 ± 0.002	0.5
02	10	1 ml HNO_3:1 ml HCl:1.35 ml H_2O_2	77	0.43 ± 0.002	0.46
03	10	1 ml HNO_3:1 ml HCl:1.35 ml H_2O_2	80	0.43 ± 0.005	1.16

No. of all experiments is $n = 2$

[a] (Khan et al. 2012)

C (digestion temperature) within the investigated range. The optimum level of the investigated factors is confided on the contour plot where it showed the maximum $\%S_{CCD}$ and was calculated by Minitab-15 to be 76.65 $\sim$ 77 °C of digestion temperature (*C*) and 1.35 ml of hydrogen peroxide (*B*) (Chang et al. 2011). As a result, the optimum digestion levels for the selected reference material (i.e. KZK-1) are 10 min of digestion, 77 °C of digestion temperature and with solution of 1 ml HNO_3:1 ml HCl:1.35 ml H_2O_2. Addition of H_2O_2 in the digestion process significantly improves the digestion time (*A*) to 10 min from 20 min as observed in our previous work (Khan et al. 2012). The reduced digestion time will improve the tailings management technique in the context of monitoring practice. Particularly, the sample preparation for ICP-OES analysis will be short and straightforward.

Validation of the model

Experimental results for $\%S_{CCD}$ are given in Table 5, and the predicted results for the same response can be calculated by Eq. 4. A linear regression model between experimental and predicted results are developed, showing $R^2 = 0.85$, indicating the second-order polynomial equation (Eq. 4.) that is satisfactory for identifying the optimum level of the investigated factors, see supplementary material for the regression model.

XRD analysis

Figure 2a is the XRD (X-ray diffraction) analysis of the selected reference material KZK-1. This figure is reproduced from our previous study (Khan et al. 2012) to compare with Fig. 2b, the XRD result obtained after the digestion of KZK-1 by hydrogen peroxide at their optimum level. Figure 2b clearly shows the absent of pyrite (FeS_2) peak (indicated by the vertical line) (Dold and Fontbote 2002), proving the optimum digestion method can transform the pyrite crystal into amorphous state. The use of H_2O_2 in combination with HNO_3 and HCl in the ultrasound bath has reduced the digestion time to 10 min from 20 min as found in our previous study.

Total sulphur measurement of Musselwhite mine tailings

The optimum digestion levels are applied to measure the total sulphur content in the MMT, and the results are presented in Table 8. The similar sulphur percentage in all three runs support the importance of using H_2O_2 in combination with acid solution to reduce digestion time to 10 min (Run 2 and 3, Table 8) from 20 min (Run 1, Table 8). The results

from the same table of run 2 and 3 also suggest that 77 °C is enough for complete digestion of the tailings samples. The low %RSD (< 3 %) reveals the excellent precision of this digestion process (Jenner et al. 1990).

In summary, the addition of hydrogen peroxide in the solution of nitric acid and hydrochloric acid reduced the digestion time from 20 min, as reported in the previous study (Khan et al. 2012), to 10 min for the same CRM and reactive mine tailings by the ICP-OES method. Ultrasound-assisted sample digestion plays an important role in the digestion process along with the oxidative power of hydrogen peroxide. The %RSD was found to be of < 3 % for both the selected CRM (KZK-1) and the mine tailings (Tables 2, 5 and 8), indicating the excellent precision of the digestion process. The developed method is faster and reproducible compared to other ultrasound-assisted digestion by ICP-OES method, hot plate assisted digestion, X-ray fluorescence and LECO-CNS method for total sulphur analysis of reactive mine tailings as described in our previous paper (Khan et al. 2012).

Conclusion

A fast, accurate and precise sample preparation method for the measurement of total sulphur by ICP-OES of low sulphur content (< 1.0 %) reactive mine tailings is developed. The proposed method is short in terms of sample digestion time and recommended for the routine monitoring of tailings on mine sites. The combined approach of the design of experiment (the FFD) and RSM (the CCD) are found suitable to optimize the digestion process for spectroscopic analysis. The RSM helps to develop a second-order polynomial model equation to predict the digestion procedure. The experimental values are in good agreement with the predicted values, indicating the applicability of the model to the optimization process.

References

Abdel-Ghani NT, Hegazy AK, El-Chaghaby GA, Lima EC (2009) Factorial experimental design for biosorption of iron and zinc using *Typha domingensis* phytomass. Desalination 249: 343–347

Alam R, Shang JQ, Cheng X (2012) Optimization of digestion parameters for analysing the total sulphur of mine tailings by inductively coupled plasma optical emission spectrometry. Environ Monit Ass 184:3373–3387

Angelopoulos P, Evangelaras H, Koukouvinos C (2009) Small, balanced, efficient and near rotatable central composite design. J Stat Plan Infer 139:2010–2013

Bermejo-Barrera P, Muñiz-Naveiro O, Moreda-Piñeiro A, Bermejo-Barrera A (2000) Experimental designs in the optimisation of ultrasonic bath–acid-leaching procedures for the determination of trace elements in human hair samples by atomic absorption spectrometry. Forensic Sci Int 107:105–120

Bermejo-Barrera P, Muñiz-Naveiro O, Moreda-Piñeiro A, Bermejo-Barrera A (2001) The multivariate optimisation of ultrasonic bath-induced acid leaching for the determination of trace elements in seafood products by atomic absorption spectrometry. Anal Chim Acta 439:211–227

Brasil JL, Ev RR, Milcharek CD, Martins LC, Pavan FA, Dos Santos AA Jr, Dias SL, Dupont J, Zapata NCP, Lima EC (2006) Statistical design of experiments as a tool for optimizing the batch conditions to Cr(VI) biosorption on Araucaria angustifolia wastes. J Hazard Mater 133:143–153

Chang SH, Teng TT, Ismail N (2011) Optimization of Cu (II) extraction from aqueous solutions by soybean-oil-based organic solvent using response surface methodology. Water Air Soil Pollut 217:567–576

de Amaro JA, Ferreira SLC (2004) Application of factorial design and Doehlert matrix in the optimisation of instrumental parameters for direct determination of silicon in naphtha using graphite furnace atomic absorption spectrometry. J Anal At Spectrom 19:246–249

De-Souza RM, Saraceno AL, da Silveira CLP, Aucelio RQ (2006) Determination of trace elements in crude oil by ICP-OES using ultrasound-assisted acid extraction. J Anal At Spectrom 21:1345–1349

Dias FDS, dos Santos WNL, Costa ACS, Welz B, Vale MGR, Ferreira SLC (2007) Application of multivariate techniques for optimization of direct method for determination of lead in naphtha and petroleum condensate by electrothermal atomic absorption spectrometry. Microchim Acta 158:321–326

Dimitrijevic M, Antonijevic MM, Dimitrijevic V (1999) Investigation of the kinetics of pyrite oxidation by hydrogen peroxide in hydrochloric acid solution. Miner Engineer 12:165–174

Dold B, Fontbote L (2002) A mineralogical and geochemical study of element mobility in sulfide mine tailings of Fe oxide Cu–Au deposits from the Punta del Cobre belt, northern Chile. Chem Geol 189:135–163

Escudero LA, Cerutti S, Olsina RA, Salonia JA, Gasquez JA (2010) Factorial design optimization of experimental variables in the on-line separation/preconcentration of copper in water samples using solid phase extraction and ICP-OES determination. J Hazard Mat 183:218–223

Ferreira SLC, dos Santos WNL, Quintella CM, Neto BB, Bosque-Sendra JM (2004) Doehlert matrix: a chemometric tool for analytical chemistry-review. Talanta 63:1061–1067

Ferreira SLC, Bruns RE, da Silva EGP, dos Santos WNL, Quintella CM, David JM, de Andrade JB, Breitkreitz MC, Jardim ICSF, Neto BB (2007) Statistical designs and response surface techniques for the optimization of chromatographic systems. J Chromatogr A 1158:2–14

Hashemi P, Bagheri S, Fat'hi MR (2005) Factorial design for optimization of experimental variables in preconcentration of copper by a chromotropic acid loaded Q-Sepharose adsorbent. Talanta 68:72–78

Hristozov D, Domini CE, Kmetov V, Stefanova V, Georgieva D, Canals A (2004) Direct ultrasound-assisted extraction of heavy metals from sewage sludge samples for ICP-OES analysis. Anal Chim Acta 516:187–196

Ilander A, Väisänen A (2009) The determination of trace element concentrations in fly ash samples using ultrasound-assisted digestion followed with inductively coupled plasma optical emission spectrometry. Ultrason Sonochem 16:763–768

Jadhav SB, Surwase SN, Phugare SS, Jadhav JP (2012) Response surface methodology mediated optimization of Remazol Orange decolorization in plain distilled water by Pseudomonas aeruginosa BCH. Int J Environ Sci Technol. doi:10.1007/s13762-012-0088-9

Jenner GA, Longerich HP, Jackson SE, Fryer BJ (1990) ICP-MS A powerful tool for high-precision trace element analysis in earth sciences: evidence from analysis of selected U.S.G.S reference samples. Chem Geol 83:133–148

Kazi TG, Jamali MK, Arain MB, Afridi HI, Jalbani N, Sarfraz RA, Ansari R (2009) Evaluation of an ultrasonic acid digestion procedure for total heavy metals determination in environmental and biological samples. J Hazard Mat 161:1391–1398

Khan AH, Shang JQ, Alam R (2012) Ultrasound assisted extraction for total sulphur measurement in mine tailings. J Hazard Mat 235–236:376–383

Khataee AR, Dehghan G, Ebadi E, Pourhassan M (2010) Central composite design optimization of biological dye removal in the presence of macroalgae chara sp. Clean-Soil Air Water 38(8):750–757

Li C, Bai J, Li W, Cai Z, Ouyang F (2001) Optimization of conditions for bacteriocin extraction in PEG/Salt aqueous two-phase systems using statistical experimental designs. Biotechnol Program 17:366–368

Lima EC, Royer B, Vaghetti JC, Brasil JL, Simon NM, Dos Santos AA Jr, Pavan FA, Dias SLP, Benvenutti EV, da Silva EA (2007) Adsorption of Cu(II) on Araucaria angustifolia wastes: determination of the optimal conditions by statistic design of experiments. J Hazard Mat 140:211–220

Montgomery DC, Runger GC, Hubele NF (2006) Engineering statistics, 4th edn. Wiley, Hoboken

Myers RH, Montgomery DC (2002) Response surface methodology, process and product optimization using designed experiments, 2nd edn. John Wiley & Sons, Canada

Prakash O, Talat M, Hasan SH, Pandey RK (2008) Factorial design for the optimization of enzymatic detection of cadmium in aqueous solution using immobilized urease from vegetable waste. Bioresour Technol 99:7565–7572

Rondano K, Pasquali CEL (2008) Ultrasound method for extraction of phosphorus in soil. Commun Soil Sci Plant Anal 39:2421–2430

Santos C, Moreno FA, Lavilla I, Bendicho C (2000) Total As in seafood as determined by transverse heated electrothermal atomic absorption spectrometry-longitudinal Zeeman background correction: an evaluation of automated ultrasonic slurry sampling, ultrasound-assisted extraction and microwave-assisted digestion methods. J Anal At Spectrom 15:987–994

Santos WPC, Castro JT, Bezerra MA, Fernandes AP, Ferreira SLC, Korn MGA (2009) Application of multivariate optimization in the development of an ultrasound-assisted extraction procedure for multielemental determination in bean seeds samples using ICP OES. Microchem J 91:153–158

Shaw SC, Groat LA, Jambor JL, Blowes DW, Hanton-Fong CJ, Stuparyk RA (1998) Mineralogical study of base metal tailings with various sulfide contents, oxidized in laboratory columns and field lysimeters. Environ Geol 33:209–217

Tarley CRT, Silveria G, dos Santos WNL, Matos GD, da Silva EGP, Bezerra MA, Miró M, Ferreira SLC (2009) Chemometric tools in electroanalytical chemistry: methods for optimization based on

factorial design and response surface methodology. Microchem J 92:58–67

Tuzen M (2003) Determination of heavy metals in fish samples of the middle Black Sea (Turkey) by graphite furnace atomic absorption spectrometry. Food Chem 80(1):119–123

Wang HL, Shang JQ, Kovac V, Ho KS (2006) Utilization of atikokan coal fly ash in acid rock drainage control from musselwhite mine tailings. Can Geot J 43:229–243

Zhuang JM (2009) Acidic rock drainage treatment: a review. Recent Patent Chem Eng 2:238–252