Journal of Environmental Sciences Vol. 10, No. 2, pp. 216—222, 1998 ISSN 1001—0742

Modelling of the relationship between trace elements and three species of sulfur in coal *

Lu Xiao-hua, Zeng Han-cai

National Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, China

Wei Lu-xian

Center of Microanalysis, Wuhan University of Automobile Industry, Wuhan, China

Abstract—Based on the determination of several trace elements in coal particulate of different specific gravity, three-variables regression equations relate the contents of trace elements Be, Cd, Co, Pb, Cu, Ni, As and three species of sulfur in coal were well established. For elements Cd, Co, Pb, Cu and Ni, the regression equations were successfully used for prediction of these trace elements in individual part of coal with different specific gravity. Factor analysis was also used to analyze the data sets. The results showed that a three factor model can interpret the data sets reasonably. Trace elements Cd, Co, Pb, Cu, Ni, inorganic sulfide and total sulfur in coal are high correlated with the first factor. Trace elements Be, sulfate and organic sulfide are high correlated with the second factor and trace elements Cr and As are high correlated with the third factor. The factors can be interpreted by the chemical properties of these elements.

Keywords: trace elements; coal; regression analysis; factor analysis.

1 Introduction

Coal combustion produces not only large amount of gaseous pollutants but also large quantity of particulate matter. The particulate matter emitted through the stack is the most important source of trace heavy metals in atmosphere. Because of the environmental impact of heavy metals, there is a growing interest in the study of trace elements in coal (Solari, 1989; Evans, 1990; Skeen, 1990). From mine to combustion, various trace elements in coal are released into environment and most of them are potentially toxic to plants and animals under certain conditions and concentrations.

The concentration and distribution of trace elements in coal are important for prediction of their behavior on release into atmosphere when coal is burnt. Different trace elements behave differently in coal combustion. Generally trace elements associated with the organic matter and inorganic sulfides volatilize more readily in coal combustion and are enriched in the submicrometer fly ash by volatilization and condensation mechanisms (Linak, 1986; Flagan, 1981).

Depending on their chemical properties and the physicochemical processes which occur during

* This work was supported jointly by the Chinese National Foundation for Climbing Project and the Environmental Science Foundation of HUST.

the coal formation, trace elements can exist in the mineral matter, in the organic matter or in both (Nichols, 1968; Raask, 1985). There have been several studies on the concentration and distribution of trace elements in coal. Gluskoter *et al*. (Gluskoter, 1974) proposed an empirical method to determine the affinity of trace elements with the organic coal matter. Regression analysis and factor analysis are multivariable statistical methods commonly used in studying the correlation relationship between variables. Solari *et al*. (Solari, 1989) developed a multivariable regression model for the partial concentration of trace elements in the organic and inorganic matter. Using Solari's model, Pires and Teixeira (Pires, 1992) studied the concentration and association of these elements in the organic, sulfide and non sulfide fractions of Leao coal. Factor analysis was used to study the distribution of trace elements in seven Chinese coals and the mathematical interpretation was proved by the experimental results (Lu, 1995). The results of these statistical method showed the relationship between trace elements and the organic and inorganic substances in coal. Up to now, no research work on the relationship between the contents of trace elements and three species of sulfur in coal was reported. In order to study the relationship between trace elements and different species of sulfur and to assess the environmental effects of trace elements produced from coal combustion, in this work, based on the determination of some trace elements in particulate of coal with different specific gravity, regression analysis and factor analysis are used for modelling the relationship between the contents of trace elements and three species of sulfur in coal particulate of different specific gravity in this paper. The results of this paper are of significance for the investigation of decreasing the heavy metal pollution of atmosphere caused by coal combustion.

2 Experimental

2.1 Classification of coal into different specific gravity

A coal sample of Qingshan bituminous was crushed to an average particle size of 50—60μm. Six solvents of different specific gravity (Table 1) were used for sequential classification of coal and seven samples of different specific gravity were obtained. In each step, the coal powder on the upper part of the solvent was collected and the bottom part was used in the next step.

Table 1 Preparation of solutions with different specific gravity

No.	1	2	3	4	5	6
Composition	C_2H_5OH	H_2O	CH_2Cl_2	CCl_4	$CCl_4 + CH_3I$	CH_3I
Specific gravity	0.76	1.00	1.30	1.60	1.92	2.28

2.2 Determination of trace elements and three species of sulfur in coal

The seven samples of different specific gravity were digested and then the trace elements Be, Cd, Co, Pb, Cu, Ni, Cr and As were determined by ICP-AES and GFAAS. The sulfate (SO_4) and total sulfur (TS) were determined by $BaSO_4$ gravimetry and inorganic sulfur (IS) was determined by $K_2Cr_2O_7$ oxidation-reduction titration (Bai, 1990). The organic sulfide (OS) was calculated by subtraction.

2.3 Computation

The computer programs of regression analysis and factor analysis in the advanced statistical package SPSS/PC+ (Norusis, 1986) were used to analyze the data sets.

3 Results and discussion

The concentrations of trace elements and three species of sulfur in the coal samples of different specific gravity are listed in Table 2.

Table 2 Concentrations of trace elements and three species of sulfur in coal with different specific gravity

No.	1	2	3	4	5	6	7
Specific gravity	<0.76	0.76—1.0	1.0—1.3	1.3—1.6	1.6—1.92	1.92—2.28	>2.28
TS, %	0.675	0.721	0.873	0.837	0.882	1.873	--
SO_4, %	0.046	0.054	0.063	0.070	0.073	0.075	--
IS, %	0.191	0.248	0.596	0.580	0.657	1.794	--
OS, %	0.498	0.419	0.214	0.187	0.153	0.003	--
Be, μg/g	0.13	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cd, μg/g	1.74	1.86	2.36	2.50	2.30	5.70	10.2
Co, μg/g	6.61	7.18	7.40	7.48	6.90	9.86	10.5
Pb, μg/g	24.5	40.3	49.3	45.9	54.4	111.4	187.9
Cu, μg/g	16.9	19.1	20.5	21.2	21.8	33.8	44.8
Cr, μg/g	12.3	10.5	10.1	18.3	12.4	15.9	28.4
Ni, μg/g	19.2	17.5	22.6	20.1	18.6	24.7	29.3
As, μg/g	24.7	12.9	10.1	27.9	12.0	21.9	39.8

3.1 Regression models

Solari proposed a regression model to study the distribution of trace elements in coal (Solari, 1989). If there are J kinds of organic components and K kinds of inorganic components in coal, then the concentration of a trace element C in coal is:

$$C = \sum_{j=1}^{J} C_{oj} W_{oj} + \sum_{k=1}^{K} C_{ik} W_{ik}, \tag{1}$$

where C_{oj} and C_{ik} are the contents of the trace element in organic component j and inorganic component k in coal respectively. W_{oj} and W_{ik} are the percentages of organic component j and inorganic component k respectively. If the W_{oj} and W_{ik} of all kinds of organic and inorganic components are known, the partial concentration of the trace element in all components can be obtained by regression analysis. In fact it is impossible to get all the W_s, in this paper we assume that the trace elements exist in sulfates, inorganic sulfides, organic sulfides and other unknown components. So the model followed can be used to fit the data of trace elements, three species of sulfur and other unknown components:

$$C = C_o W_o + C_p W_p + C_s W_s + \sum_{i=1}^{I} C_{in} W_{in}, \tag{2}$$

where C_o, C_p and C_s are the concentrations of trace element in organic sulfides, inorganic sulfides and sulfates in coal respectively. W_o, W_p and W_s are percentages of organic sulfides, inorganic sulfides and sulfates in coal respectively. C_{in} and W_{in} are the concentrations of trace elements and percentages of other unknown components in coal. Based on model (2), a linear regression model with three independent variables was used to fit the data sets in Table 2 for every trace element:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3, \tag{3}$$

where X_1, X_2 and X_3 are percentages of sulfates, inorganic sulfides and organic sulfides in coal samples of different specific gravity respectively, Y is the concentration (μg/g) of trace element in corresponding samples. In this paper the samples No. 1, 2, 3, 4, and 6 are used to establish the regression models and the sample No. 5 is used for prediction of these equations. For the eight trace elements the linear regression equations and correlation coefficients are shown in Table 3.

Table 3 Regression models between trace elements and three species of sulfur

Elements	Regression equations	Correlation coefficients
Be	$Y = 0.145 - 2.76X_1 + 0.0389X_2 + 0.122X_3$	0.7760
Cd	$Y = -0.952 + 11.27X_1 + 3.23X_2 + 3.23X_3$	0.9966
Co	$Y = 6.49 - 12.43X_1 + 2.38X_2 + 1.03X_3$	0.9671
Pb	$Y = -51.47 + 791.3X_1 + 57.50X_2 + 67.93X_3$	0.9900
Cu	$Y = -7.99 + 248.8X_1 + 12.84X_2 + 23.25X_3$	0.9970
Cr	$Y = -37.98 + 588.6X_1 + 5.33X_2 + 41.69X_3$	0.6278
Ni	$Y = 81.24 - 716.1X_1 - 1.49X_2 - 58.25X_3$	0.9871
As	$Y = -75.11 + 925.3X_1 + 15.19X_2 + 98.94X_3$	0.3934

The regression equations in Table 3 show that for trace elements Cd, Co, Pb, Cu and Ni, there are good linear relationships between the concentrations of trace elements and the percentages of sulfates, inorganic sulfides and organic sulfides. The large correlation coefficients of these equations show that there are high correlation between these elements and three species of sulfur in coal. Trace elements Be and Cr also show certain correlation with three species of sulfur in coal, while trace element As shows low correlation with three species of sulfur in coal. The results of regression analysis can be interpreted by the association of these trace elements with three species of sulfur. Many research work showed that trace elements Cd, Pb, Co, Cu and Ni exist in coal mainly with inorganic sulfides and trace element Be generally associates with organic sulfides or some times with sulfates (Pires, 1992; Lu, 1995).

Using these regression equations, the concentrations of trace elements in sample No. 5 are predicted in Table 4. It shows that for most of these trace elements the results predicted by these equations are in good agreement with those determinations.

Table 4 Prediction of sample No. 5 by the regression models

	Be	Cd	Co	Pb	Cu	Cr	Ni	As
Predicted	0	2.48	7.30	54.4	22.2	14.9	19.1	17.6
Determined	<0.01	2.30	6.90	54.4	21.8	12.4	18.6	12.0

3.2 Factor models

In this work the original data set was used in factor analysis. Table 5 is the correlation matrix of twelve variables. In factor analysis if the correlation coefficients between variables are small, it is unlikely that the variables are appropriate for the factor model. Table 5 shows that most correlation coefficients are large. All variables have large correlation with others. So the matrix is appropriate for factor analysis.

Table 5 Correlation matrix of twelve variables

	TS	SO_4	IS	OS	Be	Cd	Co	Pb	Cu	Cr	Ni	As
TS	1.000											
SO_4	0.633	1.000										
IS	0.988	0.738	1.000									
OS	−0.781	−0.965	−0.867	1.000								
Be	−0.331	−0.745	0.411	0.679	1.000							
Cd	0.997	0.639	0.986	−0.785	−0.332	1.000						
Co	0.973	0.596	0.953	−0.747	−0.404	0.981	1.000					
Pb	0.982	0.736	0.988	−0.854	−0.491	0.976	0.957	1.000				
Cu	0.990	0.721	0.993	−0.840	−0.439	0.989	0.967	0.995	1.000			
Cr	0.427	0.539	0.470	−0.505	−0.145	0.487	0.464	0.400	0.471	1.000		
Ni	0.818	0.501	0.831	−0.705	−0.227	0.826	0.824	0.778	0.779	0.313	1.000	
As	0.166	−0.029	0.141	0.013	0.421	0.227	0.204	0.044	0.141	0.812	0.137	1.000

The principal component analysis was used to estimate the initial factors. The initial statistics from principal component analysis of the correlation matrix are listed in Table 6. It shows that more than 95% of the total variance is attributable to the first three factors. The remaining nine factors together account for only less than 5% of the variance. So a model with three factors may be adequate to represent the data set.

Table 6 Initial statistics

Factor	Eigenvalue	Percent of variance	Cumulate percent
1	8.39130	69.9	69.9
2	1.89054	15.8	85.7
3	1.18625	9.9	95.6
4	0.31800	2.7	98.2
5	0.21390	1.8	100
6	0.00000	0.0	100
……			
12	0.00000	0.0	100

From the estimation of factor number of 3, the initial factor matrix and the varimax rotated factor matrix were obtained and shown in Table 7. In the rotated factor matrix, the first factor F_1 shows high correlation with variables TS, IS, Cd, Co, Pb, Cu and Ni in coal. It can be interpreted by the similar chemical properties of these elements, i.e., these trace elements have a strong tendency to associate with inorganic sulfides in coal. It is coincide with the results of regression analysis. The second factor F_2 show high correlation with variables SO_4, OS, and Be. It means that Be is generally associated with organic substances and sulfates in coal.

Table 7 Factor matrix of factor analysis

	Initial factor matrix			Rotated factor matrix		
	F_1	F_2	F_3	F_1	F_2	F_3
TS	0.9629	0.0680	0.2377	0.9607	0.2177	0.1348
SO_4	0.7993	-0.2677	-0.4955	0.4396	0.8520	0.1923
IS	0.9884	0.0154	0.1242	0.9243	0.3386	0.1537
OS	-0.9079	0.2215	0.2798	-0.6417	-0.7205	-0.1439
Be	-0.5076	0.6554	0.4627	-0.1710	-0.9102	0.2089
Cd	0.9699	0.1177	0.1955	0.9502	0.2240	0.1992
Co	0.9524	0.0839	0.1967	0.9330	0.2337	0.1667
Pb	0.9788	-0.0862	0.1333	0.9125	0.3830	0.0620
Cu	0.9834	0.0101	0.1171	0.9161	0.3444	0.1518
Cr	0.5407	0.6194	-0.5676	0.2468	0.3083	0.9177
Ni	0.8214	0.0696	0.3091	0.8714	0.1034	0.0707
As	0.1622	0.9584	-0.2245	0.1070	-0.2879	0.9491

According to the three factor model, factor score were calculated and shown in Table 8. The factor score on F_1 and F_2 were used to classify the twelve variable in F_1-F_2 coordinate system. The classification of the variables is shown in Fig. 1. It shows that variables TS, IS, Pb, Cu, Co, Cd, Ni locate closely in F_1-F_2 coordinate system. It also means the similarities of these elements.

Table 8 Factor score coefficient matrix

	Factor 1	Factor 2	Factor 3
TS	0.1993	-0.1122	-0.0480
SO_4	-0.1284	0.4175	0.1132
IS	0.1539	-0.0274	-0.0220
OS	0.0278	-0.2799	-0.0440
Be	0.1611	-0.4936	0.0796
Cd	0.1850	-0.1007	-0.0077
Co	0.1823	-0.0926	-0.0236
Pb	0.1524	-0.0042	-0.0712
Cu	0.1502	-0.0218	-0.0215
Cr	-0.1487	0.1928	0.5302
Ni	0.2136	-0.1631	-0.0813
As	-0.0354	-0.1312	0.5241

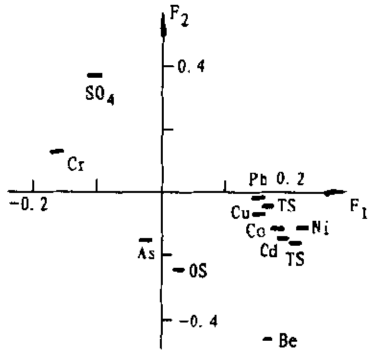

Fig.1 The classification of the variables

4 Conclusions

The factor model and regression model of trace elements in Qingshan bituminous of different specific gravity show that trace elements Cd, Co, Cu, Pb and Ni associate with inorganic sulfides, while trace element Be associates with organic sulfide or sulfates in coal. These results are coincide with those of our experimental research work (Lu, 1995). Because the trace elements associated with organic and inorganic sulfides vaporized easily and enriched in fly ash (Linak, 1986; Flagen, 1981), so it can be predicted that in the process of coal combustion, trace elements Cd, Co, Pb, Cu and Ni are more readily vaporized and enriched in submicrometer fly ash particulate and result in harmful impact to the atmospheric environment than other trace elements.

References

Bai J R, Liu F Q. Coal analysis. Beijing: Coal Industry Press. 1990

Evan J B, Sellers G A, Johnson R G. Energy Fuels, 1990, 4:440—445

Flagen R C, Taylor D D. Eighteenth symposium (international) on combustion. Pittsburgh: The Combustion Institute. 1981.1227

Gluskoter H J, Ruch R R, Shimp N F. Occurrence and contribution of potential volatile trace elements in coal, Urbana: Illinois State Geological Survey. 1974

Linak W P, Peterson T W. Twenty-first symposium (international) on combustion (circular 499). Pittsburgh: The Combustion Institute, 1986. 399

Linak W P, Peterson T W. Twenty-first symposium (international) on combustion. Pittsburgh: The Combustion Institute, 1986. 399

Lu X H, Zeng H C. Huanjing Huaxue, 1995, 14(6): 494—497

Nichols B D. Coal bearing strata (Eds by Murchison D and Weston T S). Edinburgh: Oliver and Boyd, 1968. 269

Norusis M J. Advanced statistics SPSS/PC+, SPSS Inc. 1986

Pires M, Teixeira E C. Fuel, 1992, 71: 1093—1097

Raask E. Prog Energy Combust Sci, 1985, 11: 97—103

Skeen C J, Libby B J, Crandell W B. Energy Fuels, 1990, 20: 63—67

Solari J A, Fiedler H, Schneider C L. Fuel, 1989, 68: 536—541

(Received for review May 26, 1997. Accepted July 18, 1997)