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Elemental Analysis of Coal by Tandem LIBS and LA-ICP-TOF-MS

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Abstract

The capabilities and analytical benefits of combined LIBS and LA-ICP-MS were evaluated for the analysis of coal samples. The ablation system consisted of a Nd: YAG laser operated 213nm. A Czerny-turner spectrograph with ICCD detector and Time-Of-Flight based mass spectrometer were utilized for LIBS and ICP-MS detection, respectively. This tandem approach allows simultaneous determination of major and minor elements (C, Si, Ca, Al, Mg), and trace elements (V, Ba, Pb, U, etc) in the coal samples. The research focused on calibration strategies, specifically the use of univariate and multivariate data analysis on analytical performance. Partial Least Square Regression (PLSR) was shown to minimize and compensate for matrix effects in the emission and mass spectra improving quantitative analysis by LIBS and LA-ICP-MS, respectively. The correlation between measurements from these two techniques demonstrated that mass spectral data combined with LIBS emission measurements by PLSR improved the accuracy and precision for quantitative analysis of trace elements in coal.

Keywords**:** laser ablation, Laser-Induce Breakdown Spectroscopy, inductively coupled plasma mass spectrometry, coal analysis, Tandem.

1. Introduction

Laser ablation for direct solid sampling is a compelling approach for rapid chemical analysis [1][3]. The sampling involves a high-power pulsed laser beam that is directed and focused onto a sample to instantaneously convert a finite volume of the sample into vapor and aerosol constituents for analysis. Laser ablation of solid samples is commonly used in combination with two detection modalities; LIBS (Laser Induced Breakdown Spectroscopy) and LA-ICP-MS (Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry) or LA-ICP-OES (Laser Ablation-Inductively Coupled Plasma Optical Emission Spectrometry).

Individually each of these techniques (LIBS and LA-ICP-MS) possesses a number of distinctive characteristics well documented in the literature. LIBS is based on direct measurement of the optical emission originating from the laser-induced plasma [4][6] whereas LA-ICP-MS involves transport and excitation of the ablated aerosol to a secondary source (ICP), before entering a mass spectrometer [7][10]. LIBS have been recognized for its unique advantages of fast, *in-situ*, multi-elemental analysis from H to Pu of any sample. Recently, a new approach known as Laser Ablation Molecular Isotopic Spectrometry (LAMIS), which is implemented similar to conventional LIBS elemental analysis but measures molecular information from the laser-induced plasma, was proposed for real-time isotopic analysis of samples at ambient pressure [11][14] .The coupling of laser ablation ICP-MS with LIBS provides isotopic information and enhanced sensitivity, essentially expanding the dynamic range of the analysis, and adding complementary elements that each measurement alone would not detect.

Analysis by these two techniques can complement each other quite well, as every laser pulse for ablation provides the optical plasma for emission spectroscopy and particles for ICP mass spectrometry. However, only a few papers have been addressed in which simultaneous data were measured [15][16]. Fernandez et al. [15]used single pulse ablation with simultaneous LIBS and ICP-OES for the detection of brass samples; a linear correlation between measurements from these two techniques was demonstrated. They proposed that LIBS could be used as an internal standard for the ICP-OES measurements. Latkocky et al. [17] combined LIBS with LA-ICP-MS to map the lateral distribution of trace elements in magnesium based alloys. They proposed the use of ICP-MS of one element as an internal standard for those elements measured using LIBS. Stepankova et al. [18] used LIBS, LA-ICP-OES, LA-ICP-MS and simultaneous LIBS and LA-ICP-OES to study urinary stone samples. They compared the analytical performance of these techniques by using standard calibration pellets in phosphate, oxalate and urate matrices.

The analytical benefits of simultaneous measurements go beyond using one measurement to correct the other. Specifically, we demonstrate the use of LIBS for the measurement of major and minor elements simultaneous with ICP-MS for trace elements, for the analysis of coal samples. Coal is the primary source of power generation in many parts of the world. Knowledge of its chemical composition is critical for environmental concerns (pollution) and power generation efficiency. The inorganic ash-forming components are related with thermal efficiency and operation time of power station boilers. LIBS and LA-ICP-MS have been used separately to evaluate coal quality. Chadwick et al. [19][20] investigated lignite samples and reported detection limits for Ca, Al, Na, Fe, Mg and Si. They also reported accuracies for some of the inorganic components (e.g. Al, Si, and Mg) within 10% of the reference values. Ctvrtnickova et al. [21] utilized LIBS and Thermo-Mechanical Analysis (TMA) to determine coal elemental composition including C, H, Si, Al, Fe, Ti, Ca, Mg, Na, K, Mn, Sr and Ba and used this information to predict slag propensity for five coal blends. Lu et al. reported elemental analysis of coal samples including C, H, O, N, Ca, Mg, Fe [22][23], as well as the analysis of volatile matter and ash by using LIBS [24][25]. Chenery et al. [26]reported quantitative determination of 14 trace elements by LA-ICP-MS. This report focused on sample preparation by polishing coal blocks and calibration based on introduction into the ICP of a mixture of ablated material and a nebulized solution. Van Heuzen et al. [27] reported on about 50 elements determined by LA-ICP-MS after sample preparation based on mixing powdered coal with binder material. Stankova et al. [28] utilized LA-ICP-MS to detect and quantify V, Cr, Mn, Ni, Cu, Zn, Sr, Ba, As and Pb in fly ashes. Rodushin et al. [29] used solution nebulization and laser ablation for the multi-element analysis of coal by ICP techniques. LIBS for analysis of major elements alleviates the need to use the ICP-MS detector in a high count mode for high concentrations, and to detect elements difficult (or in some cases impossible) to analyze by ICP-MS like F, O, N, etc. The ICP-MS can complement the LIBS analysis by providing trace elemental and isotopic composition.

In this study we performed simultaneous determination and quantification of major and minor elements by LIBS, and trace elements using LA-TOF-ICP-MS. Univariate calibration and partial least squares regression (PLSR) were used for quantitative analysis of the coal composition (minor and trace elements). The correlation between the major and minor elements from LIBS and the trace elements of ICP-MS was demonstrated; the combined emission and mass spectra by PLSR improved quantitative analysis for trace elements in coal.

2. Experimental

Fig. 1 shows a diagram of the tandem LIBS-LA-TOF-ICP-MS used in this work. The laser ablation-LIBS system (Applied Spectra, Inc. Model J200) consists of a Nd:YAG nanosecond pulsed laser operated at 213 nm and Czerny-Turner ICCD spectrometer. The ablation chamber could accommodate samples up to 100mm diameter with flexibility in volume and wash-out time. The system was interfaced to an ICP-TOF-MS (GBC Scientific). Table 1 lists the experimental conditions used for all measurements. Laser ablation was performed with helium carrier gas; argon was used as a make-up gas before entering the ICP-MS. Laser energy, spot size and repetition rate were 6 mJ, 50 µm and 10 Hz, respectively. The reported emission and mass spectra are the result of signal accumulation from 20 laser shots per sample location. This procedure was repeated at 9 locations on the samples to establish statistics of the measurements. The coal samples, originally in the form of powders were pressed into one-centimeter diameter pellets using 7 tons pressure for 4 min.

Coal standards used in this study include: NIST (1632d) and USGS (SARM-18, SARM-19, SARM-20, CLB-1 and CWE-1). Four samples (NIST 1632d, SARM-19, SARM-20, and CLB-1) were used for calibration and two samples (CWE-1 and SARM-18) were used for the prediction test. The reference concentration values of all samples are listed in Table 2.

3. Results and Discussion

3.1 Univariate and PLSR calibration for LIBS and LA-ICP-MS

Fig.2 (a & b) shows representative emission and mass spectra obtained simultaneously with the LIBS-LA-TOF-MS tandem system. The 240-460 nm wavelength range of the emission spectrum shows major and minor elements C, Al, Ca, Mg, Si, Fe and Si measured by LIBS. The mass spectrum shows trace elements Ba, Mn, Sc, Ce, V, Pb, and U. The blanker device of the instrument was used to remove unwanted portions of the spectra. For LIBS, the grey wavelength range in Fig.2a was removed due to saturation of the calcium signal intensity. For LA-TOF-MS

(Fig.2b), the mass range between 12 and 43 was "blanked out" to avoid abundant species and high intensity from the major elements Al, Si, Mg and Ca, that would reduce the detector life-time.

Similar to previous reports on coal analysis using LIBS, univariate processing of data using single peak intensity did not provide linear calibration curves (Fig.3a); nanosecond pulsed lasers for ablation of coal does not produce the same quantity of mass for every sample matrix [30]. Carbon is the most abundant elements in coal, and can be used as an internal standard to decrease the effect of abated mass variations [31][32] and provide good linearity as shown in Fig. 3b for Si and Mg calibration curves; Al and Ca also showed similar results. Using these normalized calibration curves, two coal samples (CWE-1 and SARM-18) were used for prediction of concentration. Table 3 shows that predicted values using these calibration curves with C as the internal standard are biased when compare to reference values. The use of C as an internal standard partially mitigates differences in the amount of ablated mass. However, matrix effects (for example, excitation efficiency and spatial plasma extent based on quantity of mass ablated) still remain [33]. As we know, effective internal calibration requires an appropriate internal standard. Carbon is the main element in coal, but its concentration is not constant in these different samples. Carbon can be used as the internal standard to improve calibration but there can still be a bias in the prediction.

3.2 PLSR calibration for LIBS and LA-ICP-MS

For coal, it is a heterogeneous material with complex chemical and physical structure, containing many of elements in the periodic table. There is inevitable interference among the emission lines [34]. PLSR is a progressive approach to obtain multivariate calibration that takes into account all intensities at every pixel within a specific wavelength region. A detailed description of PLSR can be found in references [35][36], which has been successfully applied for coal analysis by LIBS [37][38]. Different spectral normalization and pre-treatment methods would influence the accuracy and precision of PLSR analysis [38].For this work, each emission spectrum was normalized to the carbon (CI 247nm) emission intensity before analysis with the PLSR algorithm. Cross validation was used to determine the number of principle components, which showed that three principal components expressed 97% of the total variance of the data were used to construct the prediction model. Plots in Fig. 3c show good agreement between the predicted compared to certified values. The quality of a multivariate analytical calibration model like PLSR is qualified on its predictive ability. Table 3 summarizes data obtained for the "unknown" samples (CWE-1 and SARM-18) used to evaluate the quality of the PLSR model; the multivariate model provides results with lower bias than those obtained with the univariate calibration approach. The only exception was calcium from sample SARM-18; due to the fact that the concentration of this element was outside the working range of the model.

Fig. 4a shows calibration curves for several trace elements (Ba and V) in coal using LA-TOF-ICP-MS; cerium (Ce), manganese (Mn), lead (Pb), and uranium (U) also were measured. Calibration curves from ICP-MS counts per second versus concentration showed relatively good linearity without any normalization. Table 4 shows data obtained from CWE -1 and SARM-18 samples using these LA-ICP-TOF-MS calibration curves. Similar to LIBS, these curves produced poor prediction capability or large biases. As mentioned above, changes in the amount of mass will change the temperature and spatial extent of the LIBS plasma which can be more dramatic than a small change in particle size distribution or mass loading in the ICP. But our results also demonstrated that differences in the matrices between calibration and testing samples also would influence the prediction results of LA-ICP-TOF-MS.

Based on the effectiveness of PLSR on LIBS data, we evaluated its feasibility as a calibration technique for the LA-ICP-TOF-MS data. In this case, different mass ranges were used for different elements. The ranges were selected after testing different combinations including: whole spectra, different range sizes set by selecting the center mass and a fixed number of mass units to both sides of that selected mass, etc. For the case using the whole spectrum, irrelevant information (noise) may be added to the model that negatively affects the efficiency of the prediction step. The best range used for each element is shown in Table 4. Fig. 4a presents the univariate calibration curves and Fig. 4b shows the predicted concentration of the PLSR model against reference values. Three principal components expressed 97% of the variance of the data. Similar to LIBS results, Table 4 shows that PLSR provides better results for LA-ICP-MS data in terms of lower bias for CWE-1 and SARM-18 compared to those from the univariate calibration.

3.3 Correlation analysis between LIBS and LA-ICP-MS

In order to further demonstrate the benefits of tandem LIBS-LA-ICP-MS, we evaluated the correlation between LIBS emission and TOF mass signals. We expect an indirect correlation for the LIBS and LA-ICP-MS data, because the LIBS signal is not only related to the ablated mass, but also related to the plasma temperature whereas the mass signal is related to the ablated mass and many other factors, like the matrix difference. Fig.5 shows the ICP-MS intensity of the measured elements (Sc, V, Mn, Ba, Ce, Pb, U) against the LIBS emission for different coal samples. In Fig.5a the ICP-MS intensity of the measured elements (Sc, V, Mn, Ba, Ce, Pb, U) against the carbon intensity is shown with a noticeable negative correlation. However, it was found that the ICP-MS signal has a significant correlation with the combined emission of the matrix elements (Ca, Si, Al, and Mg) as can be seen in Fig.5b. Carbon in coal is almost exclusively from the organic materials, whereas the minor and trace elements are from the inorganic materials, which indicated that there is a correlation between ICP-MS intensity and carbon emission. This correlation can explain why carbon used as an internal standard improves the calibration curve. However, the prediction was not improved, again due to the change of the carbon concentration in the different coal samples.

As mentioned above, PLSR proved to be a good approach to extract correlation information. From Fig.5b, it is noticeable that each trace element mass signal shows correlation with the emission of the matrix elements acquired from LIBS. Therefore, a combination of the ICP-MS signal form the trace elements with the LIBS signal form the minor elements (Ca, Si, Al and Mg) could be used for PLSR analysis. Due to the differences in the data units between LIBS and LA-TOF-MS signals, the LIBS emissions and mass signals were auto-scaled using the following factor before combining them for the PLSR algorithm.

$$\text{Auto-scaled factor} = \left(\frac{x_i - x}{SD}\right) \qquad (1)$$

where x_i is original emission or mass signal; x is the averaged signal of all the emission or mass signal, SD is the standard deviation of all the emission or mass measured data. The prediction results are shown in Table 4, which provided better results in terms of lower bias for CWE-1 and SARM-18 compared to those from multivariate calibration using LA-ICP-TOF-MS spectra and univariate calibration.

4. Conclusions

Tandem LIBS/LA-ICP-TOF-MS was demonstrated for simultaneously determining the major, minor and trace elements in coal samples. Quantitative information was obtained from both approaches, while LIBS provided information from the minor elements Si, Al, Mg and Ca; LA-ICP-TOF-MS provided information about the trace elements V, Ba, Pb, U, Ce, and Sc. Univariate calibration showed poor performance when quantification was attempted most likely due to strong matrix effects that could not be corrected or reduced by the use of an internal standard. However, PLSR successfully minimized and compensated for matrix effects in both the emission and mass spectra. The LIBS emission and TOF mass signals were evaluated and demonstrated that correlation exist between TOF-MS and total minor emission acquired from LIBS, for the different coal samples. The combination data of mass spectra and LIBS emission by PLSR showed accuracy and precision improvements compared to those from multivariate calibration using LA-ICP-TOF-MS spectra and the univariate calibration. The tandem capability is based on a relatively nominal modification adding LIBS spectral detection to the existing LA-ICP-TPF-MS system; a valuable added approach for expanding capabilities of routine elemental and isotopic analysis.

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Captions of Figures and Tables

Fig. 1 A schematic system of the tandem LIBS-LA-TOF -MS

Fig. 2 Tandem LIBS-LA-TOF -MS spectra (a) LIBS emission and (b) LA-TOF-MS mass spectra for one coal sample (SAM-20) .

Fig. 3 Comparison of (a) univariate calibration, (b) internal calibration with carbon and (c) multivariable calibration (PLSR) by LIBS for Si and Mg.

Fig. 4 Comparison of (a) univariate calibration and (b) multivariable calibration (PLSR) by LA-TOF-MS for V and Ba.

Fig. 5 Correlation analysis between the emission and mass spectra among different coal samples (a) relationship between each trace element mass signal and carbon emission signal (Ic); (b) relationship between each trace element mass signal and total minor elements emission signal(I_{Ca}+I_{Si}+I_{Mg}+I_{Al}). Black points indicate the calibration samples and the red ones indicate the validation samples.

Table 1 Experimental condition for tandem LIBS-LA-TOF-MS measurements.

Table 2 List of minor and trace elements concentration in coal samples (ppm).

Table 3 Comparison of quantitative analysis of minor elements by LIBS using univariate calibration normalized to carbon and multivariable calibration (PLSR) for the predicted samples.

Table 4 Comparison of quantitative analysis of trace elements using different calibration methods (univariate calibration, PLSR and the combined data of emission and mass spectra by PLSR) for the predicted samples.

Highlights

Tandem LIBS LA-ICP-MS

Simultaneous determination of major and minor elements (C, Si, Ca, Al, Mg), and trace elements (V, Ba, Pb, U, etc) in the coal samples.

Extended Dynamic Range

Correlation between LIBS with LA-ICP-MS demonstrated improved the accuracy and precision for quantitative analysis of trace elements in coal.

Table 1

Experimental conditions

TOF-ICP MS (GBC Scientific)	
Forward power, W	1200
Plasma Ar gas flow rate, l min-1	11.00
Auxiliary Ar gas flow rate, l min-1	0.80
Make-up Ar gas flow rate, l min-1	0.90
Extraction lens, V	-1500
Skimmer, V	-1400
Z1, V	-1000
Y mean, V	-200
Y deflection, V	-3
Z deflection, V	-30
Laser Ablation System J-100 Applied Spectra	
Wavelength, nm	213
Pulse energy, mJ	5
Spot size, µm	30

Repetition rate, Hz	10
Carrier He or Ar gas flow rate, l min-1	0.90
Shot number	20
Spectrometer HP ICCD	
Gate width, µs	3
Gate delay, µs	0.80
Detector Gain	200
Grating	600
Central wavelength, nm	340
Acquisition mode	Accumulated

Table 2

Sample	SARM-18	SARM-19	SARM-20	N1632d	CLB-1	CWE-1
Al	13603.01	42396.93	59652.11	9120	7992.43	**
Ba	78	304	372	40.42	34	201.41
Ca	1291.32	9971.86	13415.38	1440	1578	1663.58
Ce	22	56	87	11.7	10	10.124
Mg	663.3	1206	2592.9	390	283.41	529.66
Mn	22	157	80	13.1	8	6.2664
Pb	**	20	26	3.845	5.1	4.1
Sc	4.3	7.6	10	2.89	2	**
Si	28978.8	70110	82542.84	16500	11731.74	17866.7
U	1.5	5	4	0.517	0.55	0.81

V	23	35	47	23.74	12	7.9822

Table 3

Validation Sample	Element	Reference concentration	Univariate calibration	sd	%Bias	PLSR	sd	%Bias
CWE-1	Si	17866.7	25893	1863	-45	21488.2	2928	-20
	Mg	529.66	504	36	5	520.6	53.2	2
	Al	**	13372	815	--	11462.9	606.7	--
	Ca	1663.58	2018	242	-21	1666.6	217.6	0
SARM-18	Si	28978.8	37621	2040	-30	28218.8	1813	3
	Mg	663.3	706	45	-6	678.3	77.1	-2
	Al	13603.01	17611	1375	-29	13757.9	749.3	-1.1
	Ca	1291.32	2076	299	-61	2668.3	151.7	-107

Validation samples	Element	Report	Univariate calibration	sd	%Bias	TOF PLSR	sd	%Bias	Best range	LIBS+TOFPLSR	sd
CWE-1	V	7.9822	3.22	0.91	60	9.84	1.73	-23	44-56	7.48	1.32
	Ba	201.41	286.6	36.3	-42	196.7	24.8	2	120-145	202.56	27.75
	Pb	4.1	5.61	1.25	-37	5.87	0.34	-43	148-238	4.58	1.06
	U	0.81	0.52	0.21	36	0.78	0.19	4	168-238	0.89	0.16
	Ce	10.124	8.13	1.53	20	10.3	1.5	-2	120-145	9.72	2.61
	Sc	**	6.65	1.47		3.61	0.56		44-95	3.87	0.52
SARM-18	V	23	22.3	2.9	3	22.26	2.25	3	44-56	20.52	1.83
	Ba	78	104.02	11.5	-33	98.91	11.9	-27	120-145	69.41	9.1
	Pb	**	7.27	0.84		9.1	1.1		148-238	3.71	0.71
	U	1.5	1.36	0.24	9	1.46	0.19	3	168-238	1.54	0.19
	Mn	22	27.43	1.36	-25	23.76	2.98	-8	50-90	20.03	1.25
	Ce	22	17.06	3.25	22	18.6	3.1	15	120-145	17.3	3.16
	Sc	4.3	8.76	1.38	-104	4.35	0.43	-1	44-95	4.4	0.47

** No reported

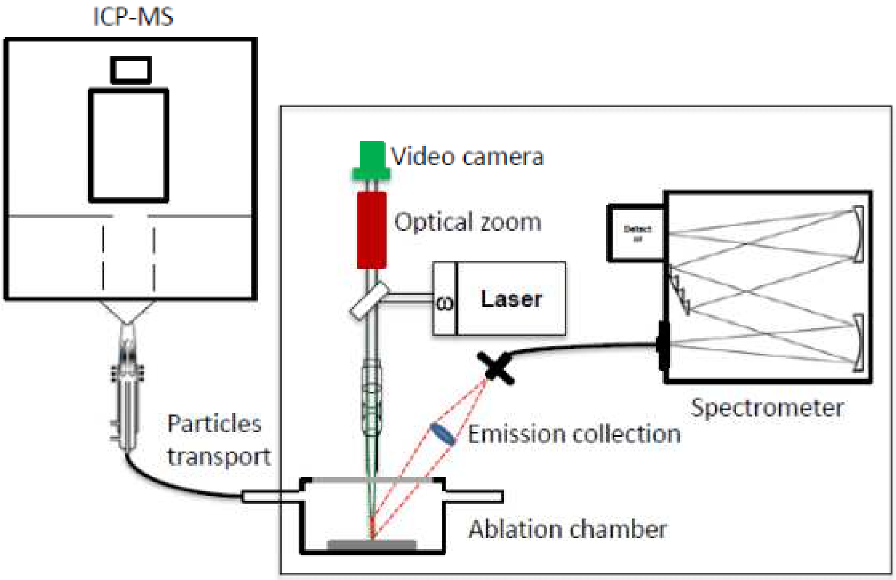

ICP-MS
Video camera
Optical zoom
Laser
Spectrometer
Emission collection
Particles transport
Ablation chamber

Figure 1

Fig. 2a

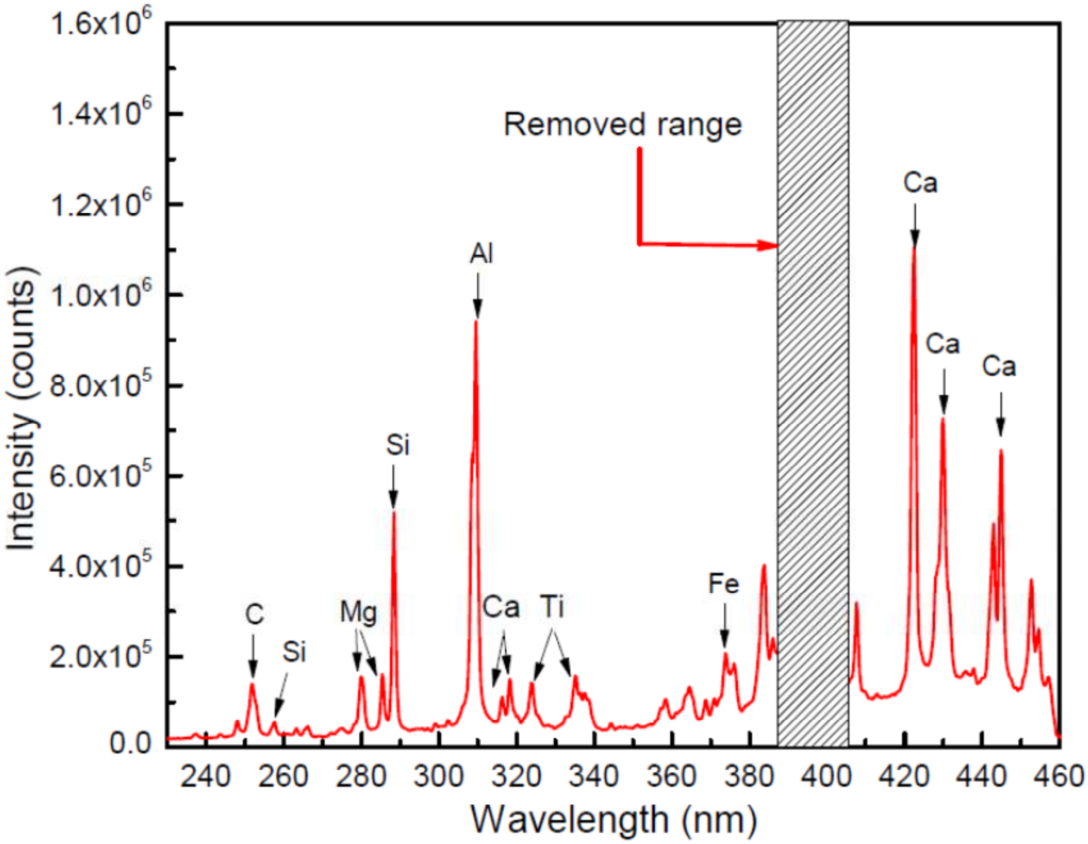

Removed range
C
Si
Mg
Si
Al
Ca
Ti
Fe
Ca
Ca
Ca
Intensity (counts)
1.6x10^6
1.4x10^6
1.2x10^6
1.0x10^6
8.0x10^5
6.0x10^5
4.0x10^5
2.0x10^5
0.0
240
260
280
300
320
340
360
380
400
420
440
460
Wavelength (nm)

Fig. 2b

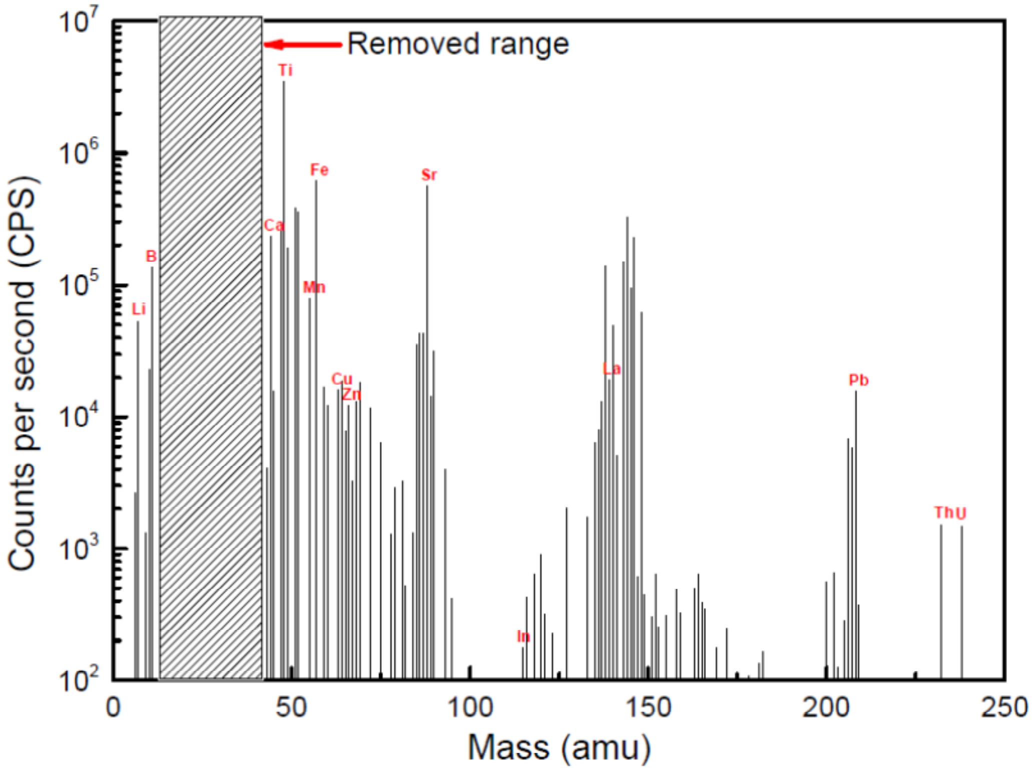

10^7
10^6
10^5
10^4
10^3
10^2
Counts per second (CPS)
Removed range
Li
B
Ca
Ti
Mn
Fe
Cu
Zn
Sr
In
La
Pb
Th
U
0
50
100
150
200
250
Mass (amu)

Fig. 3a

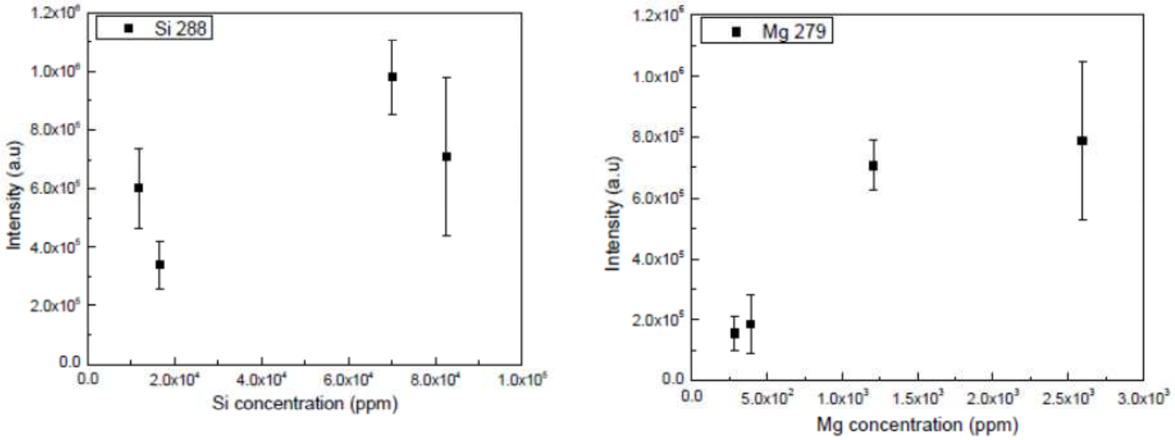

Si 288
Intensity (a.u)
1.2x10^6
1.0x10^6
8.0x10^5
6.0x10^5
4.0x10^5
2.0x10^5
0.0
2.0x10^4
4.0x10^4
6.0x10^4
8.0x10^4
1.0x10^5
Si concentration (ppm)
Mg 279
Intensity (a.u)
5.0x10^2
1.0x10^3
1.5x10^3
2.0x10^3
2.5x10^3
3.0x10^3
Mg concentration (ppm)

Fig. 3b

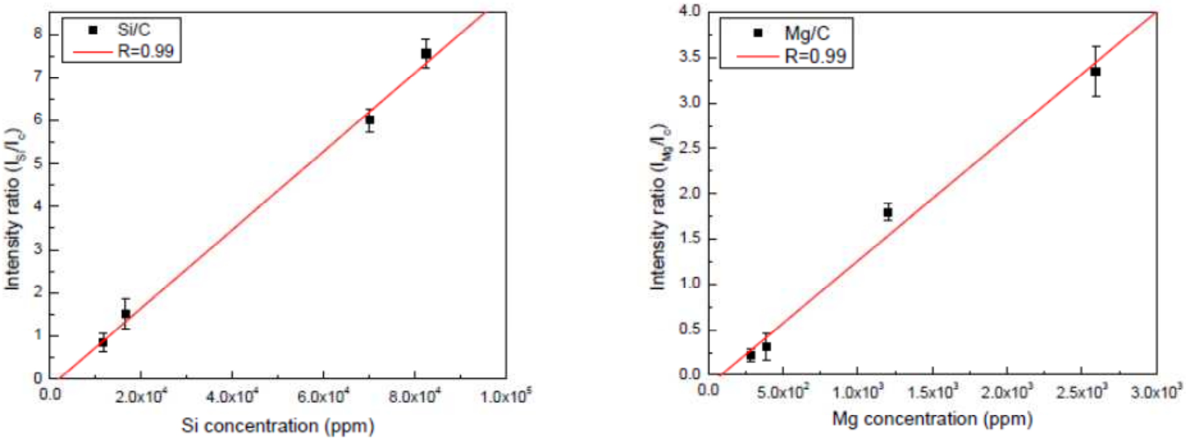

Si/C
R=0.99
Intensity ratio (I_Si/I_C)
0
1
2
3
4
5
6
7
8
0.0
2.0x10^4
4.0x10^4
6.0x10^4
8.0x10^4
1.0x10^5
Si concentration (ppm)
Mg/C
R=0.99
Intensity ratio (I_Mg/I_C)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
5.0x10^2
1.0x10^3
1.5x10^3
2.0x10^3
2.5x10^3
3.0x10^3
Mg concentration (ppm)

Fig. 3c

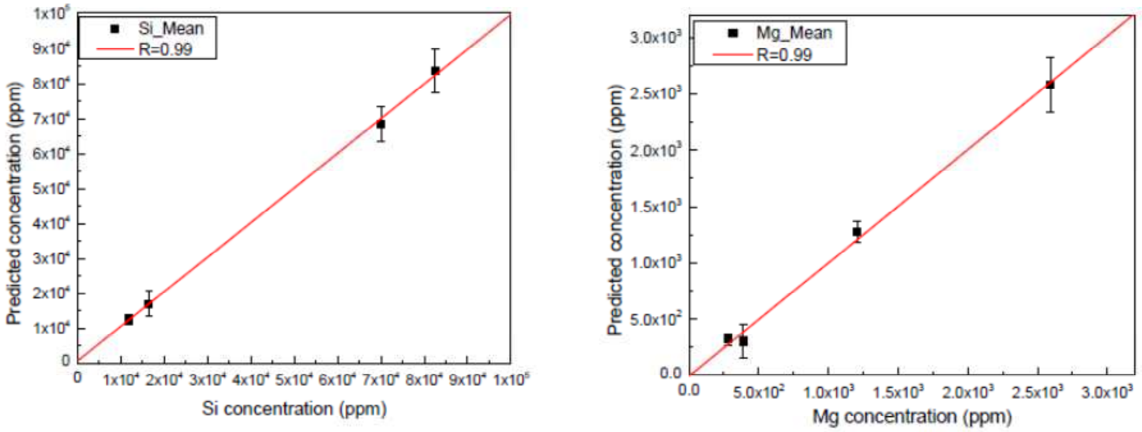

Si_Mean
R=0.99
Predicted concentration (ppm)
Si concentration (ppm)
0
1x10⁴
2x10⁴
3x10⁴
4x10⁴
5x10⁴
6x10⁴
7x10⁴
8x10⁴
9x10⁴
1x10⁵
Mg_Mean
R=0.99
Predicted concentration (ppm)
Mg concentration (ppm)
0.0
5.0x10²
1.0x10³
1.5x10³
2.0x10³
2.5x10³
3.0x10³

Fig. 4a

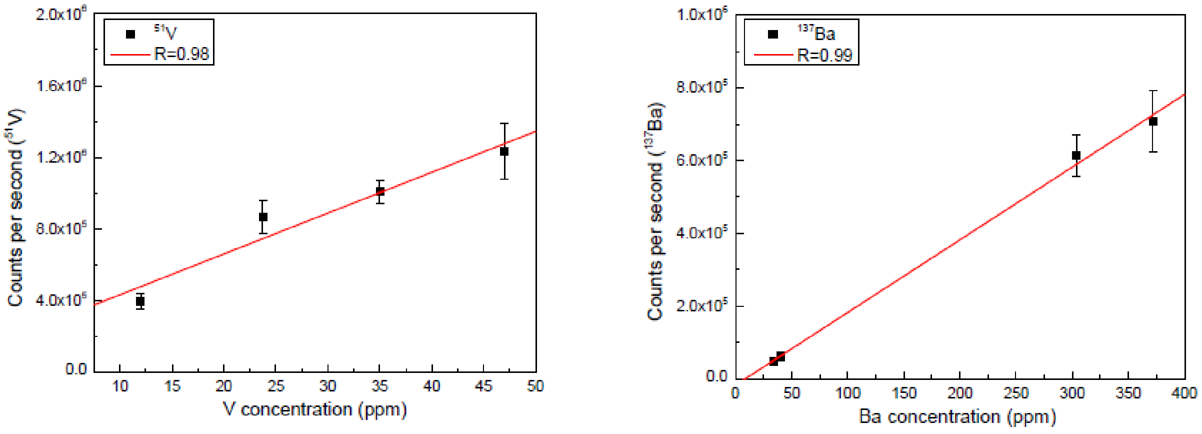

⁵¹V
R=0.98
Counts per second (⁵¹V)
V concentration (ppm)
0.0
4.0x10⁵
8.0x10⁵
1.2x10⁶
1.6x10⁶
2.0x10⁶
10
15
20
25
30
35
40
45
50
¹³⁷Ba
R=0.99
Counts per second (¹³⁷Ba)
Ba concentration (ppm)
0.0
2.0x10⁵
4.0x10⁵
6.0x10⁵
8.0x10⁵
1.0x10⁶
0
50
100
150
200
250
300
350
400

Fig. 4b

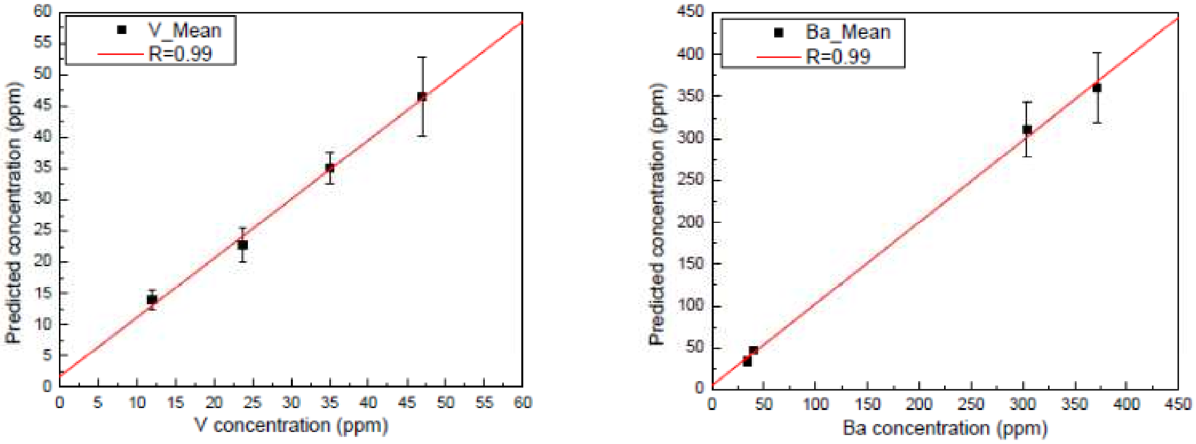
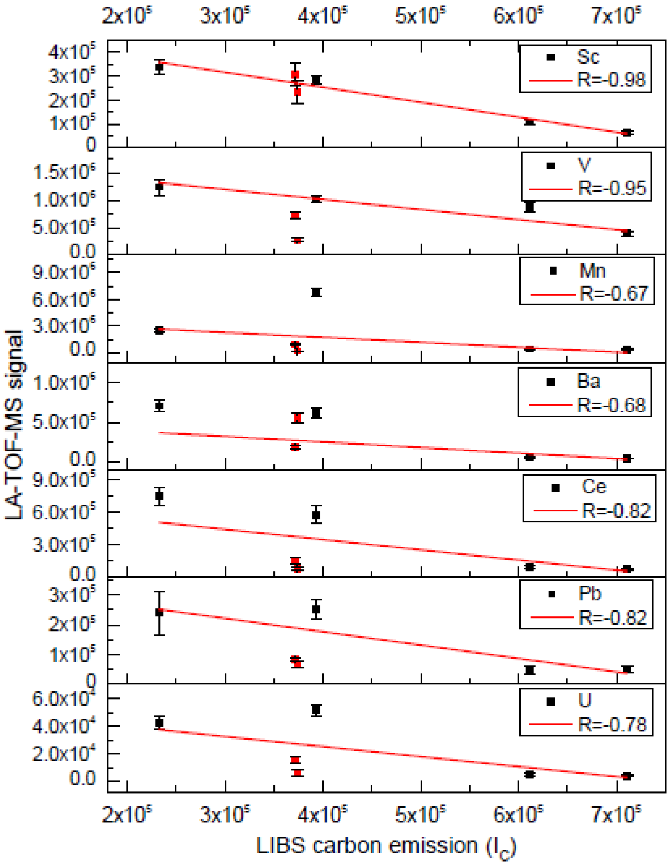
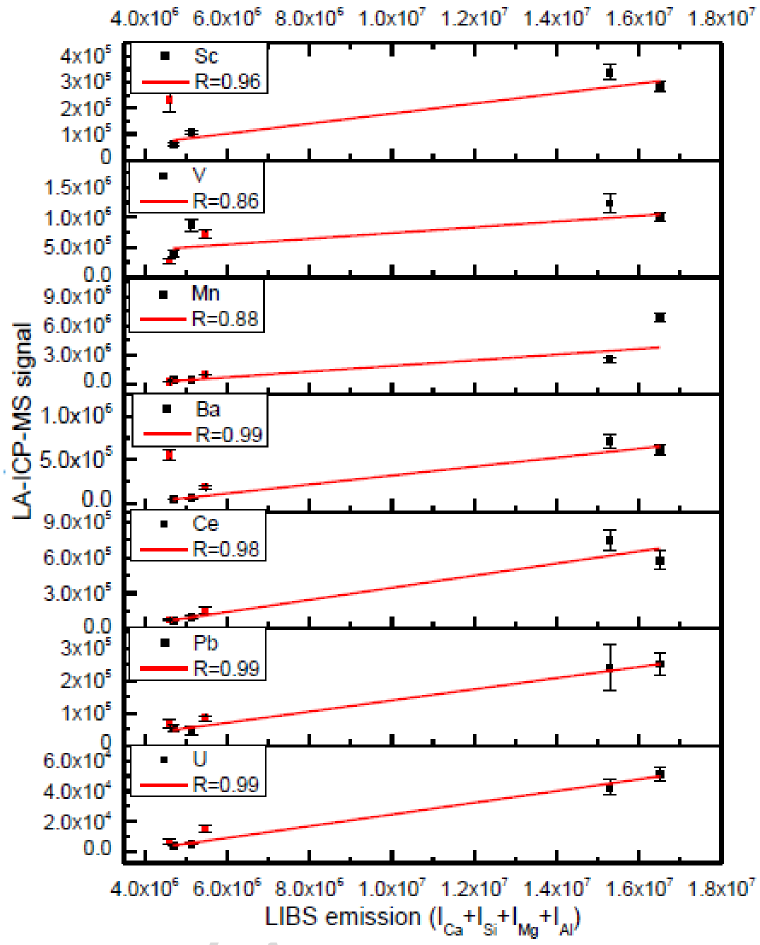

V_Mean
R=0.99
Predicted concentration (ppm)
V concentration (ppm)
0
5
10
15
20
25
30
35
40
45
50
55
60
Ba_Mean
R=0.99
Predicted concentration (ppm)
Ba concentration (ppm)
0
50
100
150
200
250
300
350
400
450

Fig. 5a



2x10⁵
3x10⁵
4x10⁵
5x10⁵
6x10⁵
7x10⁵
Sc
R=-0.98
4x10⁵
3x10⁵
2x10⁵
1x10⁵
0
V
R=-0.95
1.5x10⁶
1.0x10⁶
5.0x10⁵
0.0
Mn
R=-0.67
9.0x10⁵
6.0x10⁵
3.0x10⁵
0.0
Ba
R=-0.68
1.0x10⁶
5.0x10⁵
0.0
Ce
R=-0.82
9.0x10⁵
6.0x10⁵
3.0x10⁵
0.0
Pb
R=-0.82
3x10⁵
2x10⁵
1x10⁵
0
U
R=-0.78
6.0x10⁴
4.0x10⁴
2.0x10⁴
0.0
LA-TOF-MS signal
LIBS carbon emission (I_C)

Fig. 5b


4.0x10⁶ 6.0x10⁶ 8.0x10⁶ 1.0x10⁷ 1.2x10⁷ 1.4x10⁷ 1.6x10⁷ 1.8x10⁷
Sc
R=0.96
4x10⁵
3x10⁵
2x10⁵
1x10⁵
0
V
R=0.86
1.5x10⁶
1.0x10⁶
5.0x10⁵
0.0
Mn
R=0.88
9.0x10⁶
6.0x10⁶
3.0x10⁶
0.0
Ba
R=0.99
1.0x10⁶
5.0x10⁵
0.0
Ce
R=0.98
9.0x10⁵
6.0x10⁵
3.0x10⁵
0.0
Pb
R=0.99
3x10⁵
2x10⁵
1x10⁵
0
U
R=0.99
6.0x10⁴
4.0x10⁴
2.0x10⁴
0.0
LA-ICP-MS signal
4.0x10⁶ 6.0x10⁶ 8.0x10⁶ 1.0x10⁷ 1.2x10⁷ 1.4x10⁷ 1.6x10⁷ 1.8x10⁷
LIBS emission (I_Ca+I_Si+I_Mg+I_Al)

Highlights

Tandem LIBS LA-ICP-MS
Simultaneous determination of major and minor elements (C, Si, Ca, Al, Mg), and trace elements (V, Ba, Pb, U, etc) in the coal samples.
Extended Dynamic Range
Correlation between LIBS with LA-ICP-MS demonstrated improved the accuracy and precision for quantitative analysis of trace elements in coal.