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Elemental analysis of coal by tandem laser induced breakdown spectroscopy and laser ablation inductively coupled plasma time of flight mass spectrometry

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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 213 nm. 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.

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 [2,6 -9]. 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 [10-13]. 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 [14, 15]. Fernandez et al. [14] 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. [16] 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. [17] 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

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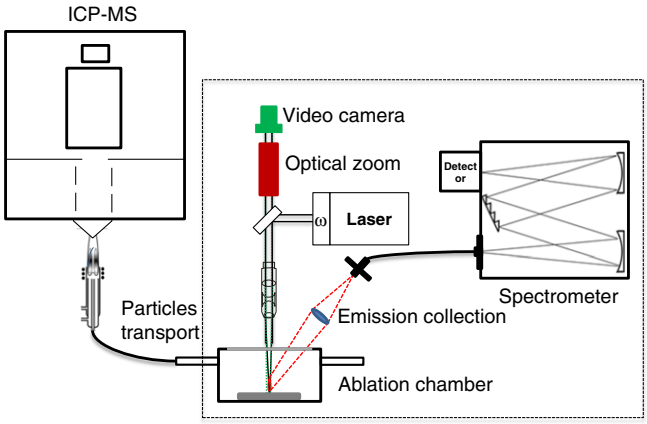

Fig. 1. A schematic system of the tandem LIBS-LA-ICP-TOF-MS.

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. [18, 19] 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. [20] 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 [21, 22], as well as the analysis of volatile matter and ash by using LIBS [23, 24]. Chenery et al. [25] 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. [26] reported on about 50 elements determined by LA-ICP-MS after sample preparation based on mixing powdered coal with binder material. Stankova et al. [27] 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. [28] 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

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

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	
Laser wavelength, nm	213
Pulse energy, mJ	6
Spot size, μm	50
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
List of minor and trace elements concentration in coal samples (ppm).

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

**Not reported.

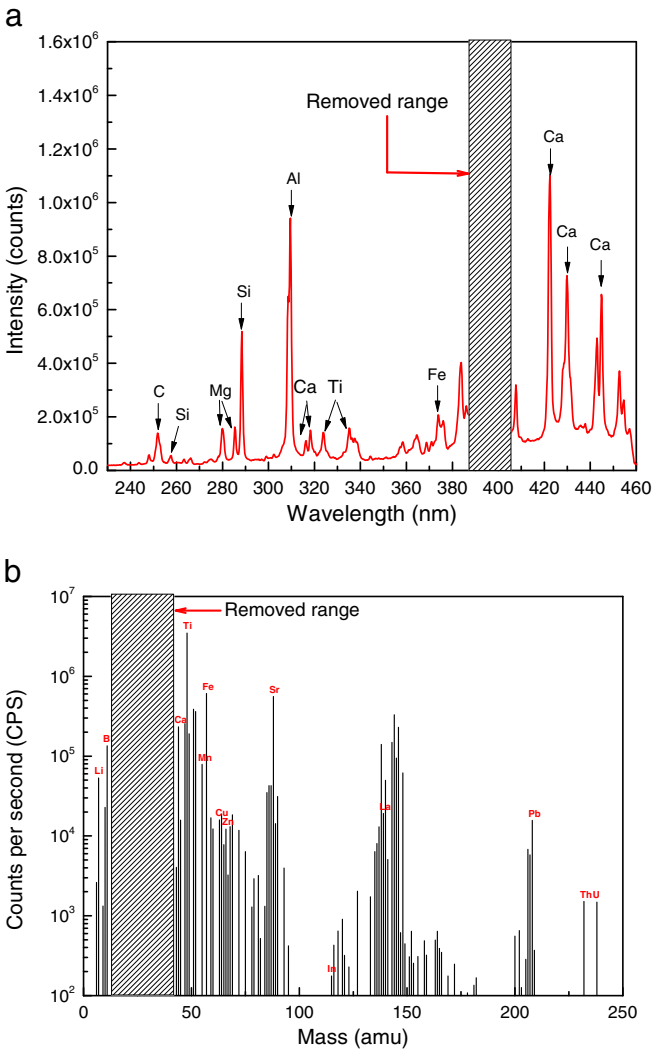

Fig. 2. Tandem LIBS-LA-TOF-MS spectra (a) LIBS emission and (b) LA-TOF-MS mass spectra for one coal sample (SAM-20).