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SIMPLE AND RAPID ANALYSIS OF HEAVY METALS IN SUB-MICRON PARTICULATES IN FLUE GAS

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ABSTRACT

Objective of the present study is to develop a simple and rapid analytical method to monitor heavy metal enrichment in sub-micron particulates. LIBS (Laser Induced Breakdown Spectroscopy) was applied to the elemental composition analysis of dust samples, those were segregated with particle size using an ELPI (Electrical Low Pressure Impactor) in advance. The ELPI equipment is designed for the real-time monitoring of aerosol particle size distributions in the size range from 0.03 to 10 μm, collecting particle samples segregated into 12 different particle sizes. On the other hand, LIBS is one of direct analyses of solid samples, which does not require time-consuming pretreatments of the dust. In this study, simulated ELPI samples were prepared via the evaporation of solutions containing heavy metals on an ELPI impaction plate, and they were utilized as standards to obtain calibration curves for the LIBS signal. Molten fly-ash from waste incineration was selected as an analyte to confirm the analytical method presented in this study. The ash entrained by air at room temperature was segregated by ELPI, and subsequently analyzed for heavy metals by LIBS. Size distributions of particle that contains Pb and Cd were successfully estimated, and enrichment behaviors of them in sub-micron particulates were obviously observed.

INTRODUCTION

In the combustion process of coal and/or waste products, heavy metals such as Pb, Cd and Hg in ash content move to vapor phase in the flue gas due to their high volatilities. Most of them condense into fly-ash through a gas cooling process, and they can be removed by conventional dust collecting equipments, such as a bug filter and an EP. However, a part of these volatile heavy metals tends to be highly concentrated into sub-micron particulates that are too fine to be removed, and as a consequence, they are emitted into the atmosphere in a state of particulate matters. Therefore, in order to control air-borne emissions of toxic heavy metals from various combustion plants, it is very important to understand not only the total emissions but also partitioning behaviors of heavy metals with particle size [1-3].

One of the most convenient equipment to monitor particle size distributions in real-time is an Electrical Low Pressure Impactor (ELPI). It is a type of cascade impactors to segregate dusts with particle sizes, based on the principle of inertial impaction. An ELPI has 12 channels covering the range of particle size from 0.03 to 10μm, and it counts the number of particles electrically in real time on each channel. Sample particles remain trapped on each impaction plate, and they can be individually analyzed for elemental compositions. From the viewpoint of elemental analysis of trapped particles, a normal low pressure impactor (LPI) is better for collecting sample particles than an ELPI, because the larger amount of sample particles can be trapped on each impaction plate at one time. In fact, a normal LPI (e.g. BLPI) has been utilized in some earlier studies on the enrichment behavior of heavy metals and/or alkali metals to fine particles during combustion processes [3-6]. However, a normal LPI is not suitable for the simple and rapid analysis as considered in this study, because it is

incapable of real-time monitoring of particle size distributions. That is the reason why the ELPI came up in the present study.

On the other hand, one of promising methods for direct elemental composition analyses of solid samples is Laser Induced Breakdown Spectroscopy (LIBS). It is a type of atomic emission spectroscopy, and laser breakdown plasma is utilized for the excitation of elements included in analytes [7,8]. Line emissions from excited atoms in plasma are monitored by a spectrometer, and elements in an analyte are not only specified but also quantified. For the LIBS analysis, time-consuming pretreatments, such as the dissolution of particles, are not required, and sample consumption is very small. These facts are major advantages of LIBS, and they make the analytical process more rapid and simple compared with conventional instrumental analyses using AAS and ICP/AES.

The objective of this study is to apply LIBS into the direct analysis of dust samples trapped by ELPI with different particle sizes. If successful, it will only take a few tens of minutes to analyze heavy metals in segregated particles, following the real-time analysis of the particle size distribution carried out by the ELPI. In this paper, to establish calibration and measurement methods, the preparation of simulated ELPI samples was formulated as standards those include known amount of heavy metals. In addtion, to verify the measurement method, PbO powder and molten fly-ash segregated by ELPI was examined to analyze the amount of Pb and other elements by LIBS.

EXPERIMENTAL

Standard Sample for Calibration

Simulated ELPI samples were prepared as standards to calibrate LIBS signals. A standard solution of a measuring element (e.g. Lead Standard Solution, Nacalai Tesque, Inc.) was appropriately diluted by water mixed with a trace amount of yttrium (Yttrium standard solution 1000ppm, KANTO KAGAKU) as an internal reference and PVA (Polyvinyl alcohol 500, KANTO KAGAKU) to fix deposits on an impaction plate surface. The solution of 0.05mL was dropped on a heated impaction plate. The amount of the element condensed on an impaction plate after moisture evaporation can be controlled by the dilution ratio of the original standard solution. Particle sizes of the deposited element on an impaction plate were confirmed to be smaller than 10 μm by SEM observation.

Particle Samples, PbO and Molten Fly-ash

To verify the analytical method to measure the amount of Pb in segregated ash particles, PbO powder (purity: 99.9%, particle size: 8-12μm, Kojundo Chemical Laboratory Co., Ltd.) was selected as simulated ash particulates due to its simple and homogeneous elemental composition. PbO powder was entrained by air at room temperature with a cyclone type particle feeder, and segregated with different particle sizes by ELPI. Figure 1 shows a schematic view of trapped PbO particulates on the photo of an impaction plate. Particulates stick to the impaction plate surface, agglomerated in the shape of nozzles under an upstream channel. Thin aluminum foils were applied for the substrates on impaction plates. They were non-greased to reduce the matrix effect on LIBS. After ELPI sampling, impaction plates with trapped PbO particulates in 12 channels were separated off and treated by the addition of Y and PVA in the same way as the previous section. They are subsequently analyzed for the amount of Pb sticking on an impaction plate by LIBS.

Molten fly-ash was also tested to demonstrate the analytical method presented in this study. The sample ash was extracted from fly-ash collected by a bag filter downstream of an actual gasification and melting process of municipal wastes. Elemental composition of the bulk of the sample ash is summerized in Table 1. It is characterized by high concentrations of volatile heavy metals, such as Pb and Cd. After desiccating at 120 °C in a muffle furnace for

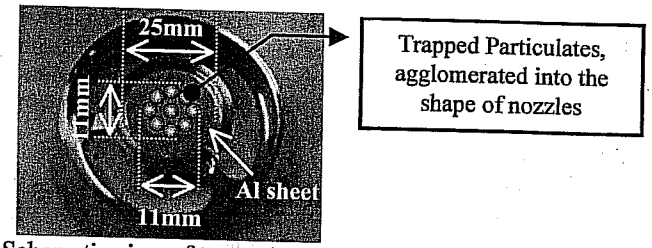

Figure 1 Schematic view of trapped particulates on the photo of an impaction plate

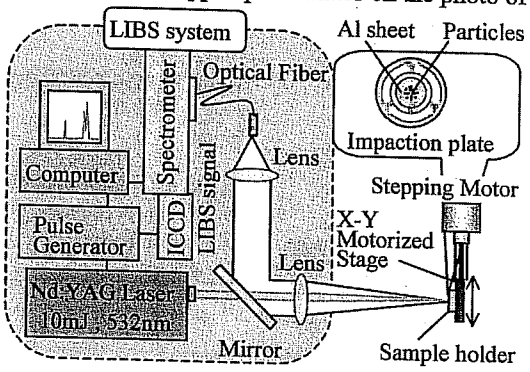

Figure 2 LIBS setup with 2-axis motorized stages for scanning of an impaction plate surface

an hour, the sample ash was entrained by air at room temperature, and segregated with different particle sizes by ELPI as well as PbO powder described above. It is noted that particle size distribution of the sample ash entrained by air might be different from the original at the time when it had been in flue gas, because the sample ash experience an agglomeration when once collected by a bag filter. However, the important thing in the present study is just to produce air-borne ash particulates, and it was not necessarily of interest whether the sample ash was completely dispersed as the original state.

Table 1 Elemental composition of molten fly-ash used in this study

Main element (wt%)		**Trace element (ppm)**	
CaO	31.20	Ba	450
SiO_2	27.34	Sn	370
Na_2O	7.66	Sb	360
Al_2O_3	7.84	Sr	260
K_2O	2.85	Cr	80
MgO	2.90	Cd	75
P_2O_5	0.96	Li	59
Fe_2O_3	1.60	**Other element (wt%)**	
ZnO	1.79	T-Cl	12.50
TiO_2	0.87	T-S	2.04
PbO	0.42	**Ignition loss (wt%)**	7.65
MnO	0.50	**Moisture(wt%)**	2.80
CuO	0.20		Dry base

LIBS Setup with a Surface-Scanning Device

LIBS setup, including the surface-scanning device, is shown in Figure 2. The LIBS system consisted of a YAG laser to ignite the breakdown plasma, a spectrometer equipped with an intensified charge coupled device (ICCD) , an optical fiber system, a digital delay pulse generator for the system synchronization and a PC to control whole system and import

data. An impaction plate with trapped particles is fixed on 2-axis motorized stage, and the area of 11-mm-square on the impaction plate surface can be scanned in 15 seconds corresponding to 150 laser pulses. As a matter of course, this 11-mm-square sufficiently covers particulate sticking area on the impaction plate surface. Specifications of optical and spectroscopic equipments are summarized in Table 2.

Table 2 Specifications of spectroscopic equipment in LIBS setup

Laser	*SL803G (SPECTRON LASER SYSTEMS LTD.)*
Pulse width	6 - 9 nsec
Wavelength	532 nm
Energy used	10 mJ per pulse
Repetition rate	10 Hz (n=150)
Spectrometer	*MS257 (ORIEL INSTRUMENTS)*
Gratings	2400 or 1200 G/mm
Slit width	10 μm
Detection system	
ICCD detector	*InstaSpec V (ORIEL INSTRUMENTS)*
Pixels	1024 x 256
Wavelength range	180 - 850 nm
Gate delay & width	1 μs & 1 μs

RESULTS AND DISCUSSION

Calibration and Detection Limit Estimated

Pb and Y line intensities were measured at the wavelength of 405.8nm and 410.2nm, respectively. Their intensities were estimated as accumulations of signals from 150 pulses, where these intensities represented total amounts of Pb and Y on an impaction plate. As previously described, a specific amount of Y was added as an internal reference element in any cases for both simulated ELPI samples and actual sample particles trapped by ELPI. Figure 3 shows calibration lines of Pb signal obtained with several simulated ELPI samples, where relative intensities of Pb line emission to Y line emission are plotted against the amount of Pb on impaction plates. Sufficient linearity and reproducibility has been confirmed in this calibration line.

Pb Mass Distribution in Segregated PbO Particles with Sizes

PbO powder entrained by air was segregated with different particle sizes by ELPI, being analyzed for the particle size distribution in real time. In this case, the analytical result can be easily converted to Pb mass distribution, because all particles are made of homogeneous PbO regardless of particle sizes. On the other hand, after ELPI analysis, sample particulates separated into 12 channels by sizes were individually analyzed for Pb content sticking on each impaction plates by LIBS. If both analyses are appropriately conducted, they should show the same distribution of Pb mass. And so the comparison between them was carried out.

Figure 4 shows Pb mass distributions in segregated PbO particles with sizes obtained from both ELPI and LIBS analyses. M represents Pb mass in each channels of ELPI, and they are plotted as a form of derivative of particle diameter D_p with logarithmic correction. ELPI and LIBS analytical results were found to be in good agreement with each other. Particulates smaller than 1 μm couldn't be detected by both ELPI and LIBS, because there were little sub-micron particulates in the original PbO powder reagent. However, smaller particulates seem to be easier to analyze for an elemental composition by LIBS, because they can be more easily dissociated and excited without matrix effects than larger particles. Therefore, the validity of the analytical method presented here was confirmed by the agreement between ELPI and LIBS analytical results of larger particles.

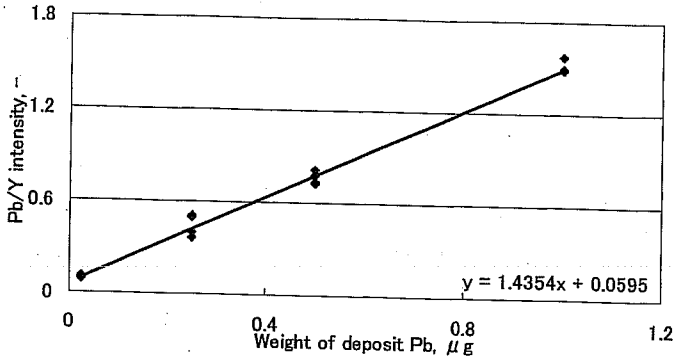

Figure 3 Calibration line of Pb signal obtained from simulated ELPI samples

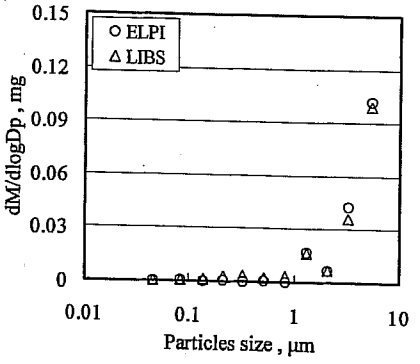

Figure 4 Pb mass distributions in PbO powder with particle sizes obtained from both ELPI and LIBS analyses

Heavy Metal Concentrations in Molten Fly-ash with Different Particle Sizes

As described in previous section, molten fly-ash entrained by air was also analyzed for both particle size distributions and mass distributions of several elements by ELPI and LIBS, respectively. Figures 5(a)~(d) shows particle size distribution of air-entrained fly-ash and mass distributions of Pb, Cd, Ti and Mn. Mass data of 4 elements measured by LIBS are plotted with an error bar corresponding to standard deviations in calibration lines. Points expressed by 'X' in Figure 5(b) represent values below the detection limit in LIBS analysis. Pb and Cd are typical volatile heavy metals in ash content. In LIBS, Pb was measured using visible line spectrum at wavelength of 405.8nm, while Cd measured using ultraviolet line spectrum at 228.8nm. Ti and Mn are nonvolatile minor elements in ash content, and were measured using visible line spectra at wavelength of 399.0nm and 403.1nm. It could be done at the same time of the Pb measurement, because their lines are very close to Pb line.

An element concentration in particulates can be defined by the mass of the element in sample particulates divided by particulate mass themselves. Then, experimental results shown in Figures 5 were converted to concentrations of 4 kinds of elements in ash particles with different particle sizes. Figures 6 (a)~(d) show concentrations of Pb, Cd, Ti and Mn in ash particles segregated by ELPI. Dashed lines in these figures represent the concentration of each element in a bulk of sample ash described in Table 1. In each graph, concentrations higher than a dashed line can be considered as evidence of enrichment behaviors of the element. As shown in Figures 6, Pb, Cd and Mn seemed to be enriched in fine particles smaller than 1μm, while Ti concentration was almost constant independently of particle sizes. Enrichment behaviors of Pb and Cd are quite reasonable, because they are typical volatile heavy metals, as

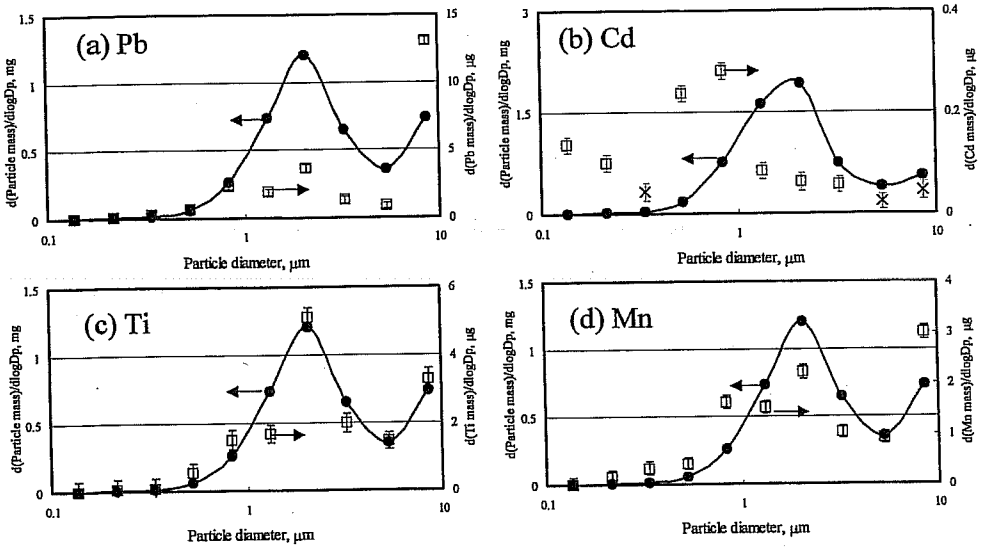

Figure 5 Particle size distribution of air-entrained molten fly-ash and mass distributions of (a) Pb, (b) Cd, (c) Ti and (d) Mn in segregated ash samples

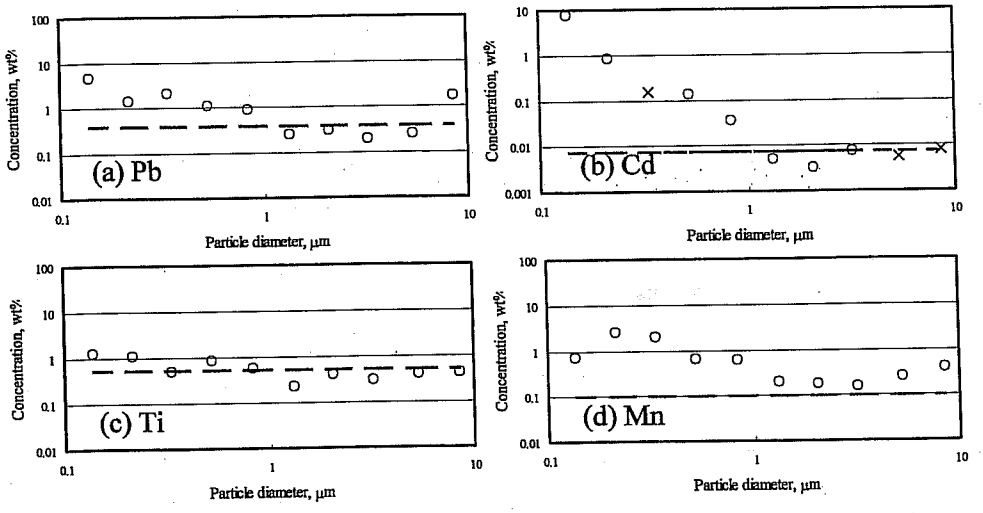

Figure 6 Concentration of of (a) Pb, (b) Cd, (c) Ti and (d) Mn in segregated ash samples. Dashed lines represent concentrations of the element in a bulk sample.

described above. On the other hand, Ti and Mn are regarded as nonvolatile metals in general, and it is unlikely that they condense into fine particulates from vapor phase. Then, the enrichment behavior of Mn was beyond our comprehension.

One of possible explanations is that minor elements like Mn are distributed to fine particulates by their nature without any vaporization processes. For example, they might be dispersed as small excluded particulates in fuel before the combustion. In contrast, large particles are dominated by clusters consisting of major elements like Al, Ca and Si. Another explanation is that a part of Mn can be volatile under chlorine-rich ash melting condition, where many heavy metals can vaporize much more easily than a normal combustion condition.

However, any conclusive evidence for these explanations has not been found. We carefully continue to investigate enrichment behaviors of volatile and nonvolatile elements in fine particulates, taking account of the measurement accuracy and reproducibility.

CONCLUSION

To develop a simple and rapid analytical method to monitor heavy metal enrichment to fine particulates in combustion processes, LIBS was applied to the direct analysis of dust samples segregated with particle size by ELPI. Simulated ELPI samples were prepared via the evaporation of solutions containing analyte elements on an impaction plate, and they were utilized as standards to calibrate LIBS signals. In the experiment using air-entrained PbO powder, LIBS analytical result of Pb mass distribution was confirmed to be consistent with the particle size distribution that was directly measured by ELPI. In the experiment using air-entrained molten fly-ash, concentrations of several elements in particulates segregated with sizes were estimated on trial, and enrichment behaviors of Pb and Cd in sub-micron particulates were obviously observed.

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THE EFFECT OF CHLORINE AND SULFUR ON FINE PARTICLE FORMATION DURING FLUIDIZED BED COMBUSTION OF BIOMASS

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ABSTRACT

Behavior of chlorine and sulfur is critical on the formation of fine particles (particle diameter D_p<1 μm, PM1.0) during combustion. In this investigation, we studied experimentally the effect of adding chlorine and sulfur on fine particle formation in a pilot-scale circulating fluidized bed reactor during combustion of bark, and pulp and paper mill sludge. Chlorine and sulfur were added into the reactor as HCl and SO_2 to keep other fuel ash characteristics than chlorine and sulfur contents constant. The gases were fed into the reactor from two different locations.

The fly ash had two distinct particle types: fine particles (particle diameter smaller than one micrometer) that were formed from volatilized ash compounds, and that were mainly alkali chlorides and sulfates, and coarse fly ash particles. HCl addition was found to increase the concentration of fine particles considerably. The fine particles were almost entirely alkali chlorides. SO_2 addition transformed some of the chlorides into sulfates in the fine particle mode. At the same time, the total fine particle concentration decreased.

BACKGROUND

Fluidized beds are generally suitable for combustion of wide variety of fuels. They have successfully been applied to combustion of biomass as well as such waste materials as sewage sludge, demolition wood, and sawdust. Lately, also refuse derived fuels (REF) have been used in fluidized beds. Waste materials have highly variable compositions, and they sometimes contain high amounts of chlorine and other impurities. Therefore, their use may be limited due to boiler operational issues. Such issues are e.g. bed agglomeration, deposition, corrosion, and emissions to the atmosphere.

Solid fuels, i.e. coal, peat, biomass and different waste materials, contain ash forming inorganic compounds that may transform during combustion. The inorganic elements may be found as included and excluded mineral particles, inorganic salts in the fuel moisture and in association with the hydrocarbon structure of the fuel either as ion-exchangeable elements or by covalent bonding.

The initial occurrence of the inorganic elements in the fuel strongly affects the transformations of these elements during combustion. The inorganic elements that are originally bound in the hydrocarbon structure of the fuel are released when the hydrocarbons decompose. The salts decompose usually in relatively low temperatures, which results in the disproportionate release of their components. The elements that are found as minerals may melt and coalesce with other minerals, and small fraction of the mineral matter may vaporize and be released to the gas phase. Once released, the vaporized species may react chemically inside the fuel particle, be adsorbed to the carbonaceous matter or be released to the gas phase. In the gas phase, they form new particles by nucleation, condense on the pre-existing particles or react chemically with gases and particles. The surface reaction, nucleation and/or condensation result in the enrichment of the vaporized elements in the fine particles [1].

The transformations of the inorganic species during combustion are also affected by the temperature of the fuel particle in the furnace and after the furnace, residence time in the high temperature region, the fuel particle size and other fuel characteristics. The gas atmosphere