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Applicability of XRF and LIBS technologies for on-line characterisation of ashes





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Key words: Ash, on-line, characterisation, XRF, XRT, LIBS

## Summary

The aim of this work was to explore novel on-line methods for ash characterisation to enhance ash recycling and elemental recovery. Reliable and fast methods for ash analysis are needed to recycle ashes in environmentally sustainable and economically profitable way. Basically this means the determination of the concentration of certain elements, such as heavy metals in an online measurement system. X-ray technologies and laser-induced breakdown spectroscopy (LIBS) were researched and demonstrated in fly ash analysis by using laboratory measurement setups.

The X-ray principle can probably be used for indicating that ash contains specific components and making an estimation concerning concentration, too. However, screening the components with any online system is probably too challenging or at least requires more sensor information than spectrometer or X-ray camera can provide individually. There are benefits and drawbacks in both systems (spectral analysis and X-ray camera) but combination of those two could be quite interesting. Spectrometer is more accurate but is not able to detect metals inside the ash whereas the imaging detector can provide indication that "something is there".

The results with LIBS on fly ash characterisation were positive in respect of an online ash analyser. The particle size in fly ash is small enough for LIBS to evaporate most of the particles to achieve a representative sampling. Sample handling needs to be designed carefully to stabilize the distance between the lens and the sample surface. Otherwise the laser focus is not stable at the surface and it causes signal fluctuation. Another challenge is the large amount of elements, and thus high resolution needed in the spectrometer. The high-resolution is well achievable in a narrow spectral region that would mean limiting to a certain element or few elements. Recording the full spectrum with high-resolution is possible, but the instrumentation gets expensive.

Helsinki, December 2015







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## 1 Introduction

Ashes are produced as by-products of thermal conversion processes and are classified as wastes. Their physical and chemical properties together with volume depend on the fuel or fuel mixture, and its quality. The used conversion/combustion technology and process parameters, such as temperature, air-fuel ratio, air staging, retention time and the flue gas cleaning technology have also a strong effect on ash quality. Depending on the fuel, and the environmental and technical properties of the ash, it can be utilised e.g. in earth construction applications, as fertilizer, as raw material in cement production, as a filler in concrete production or in asphalt mixes, and so on. There are also certain criteria for landfilling of ashes if recycling option does not exist.

Determination of the environmental applicability is usually based on the concentration and leachability of harmful substances. Identification of valuable or even critical elements from ashes has also been in focus of the research lately. Thus, chemical characterization of ash is an important criterion to evaluate its value and this information plays an important role for its correct recycling. Further, the content of unburned carbon is related to the efficiency of the incineration process, so the quantitative analysis of carbon plays important role on characterizing the power plant efficiency and for boiler control tasks. In a more general case, when incinerating waste or other heterogeneous fuels, the elemental composition of fly ash may vary and increased amounts harmful elements such as heavy metals is likely.

Elemental composition is usually determined according to the standard methods in laboratories using ICP-OES and ICP-MS when quantitative results are required [1-2]. However, those techniques require time-consuming steps being unable to perform as online measurements.

The aim of this work was to explore novel on-line methods for ash characterisation to enhance ash recycling and elemental recovery. Reliable and fast methods for ash analysis are needed to recycle ashes in environmentally sustainable and economically profitable way. Basically this means the determination of the concentration of certain elements, such as heavy metals in an online measurement system. The thresholds for certain elements and their amount are set. X-ray and laser probing for online ash analysis were studied.

Chapter 2 introduces the X-ray technologies used in ash characterisation and also presents some real-life studies of ash characterization. Then, our laboratory measurement setup and test are introduced together with experimental results.

Chapter 3 describes the background of laser-induced breakdown spectroscopy (LIBS) and its use in ash analysis. Further, the experimental setup to demonstrate the fly ash analysis with LIBS is presented and the results of the experiments are shown. The applicability of LIBS technology for online fly ash analysis is discussed.





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## 2 XRF technologies on ash characterisation

## 2.1 Introduction to X-ray technologies

In this section the different characterization techniques using X-ray are introduced. These descriptions are from S. Eskonniemi's Master's thesis [3] which was done during ARVI project. These technologies are X-ray Fluorescence (XRF) and X-ray Transmission (XRT).

XRF is a quick, non-destructive measuring method being suitable for determining elemental composition of different materials. For this reason it is used widely in different industrial applications, for example in metal, mining and recycling.

The principle of XRF is presented in Figure 1. In XRF the X-ray radiation (with wavelength 0.1 - 10 nm) is directed to the examined sample forcing the electron on atom's inner shell to release. An electron from an outer shell will fill the vacant position releasing energy (0.125 - 125 keV). This energy depends on the energy difference between the atomic shells, i.e. on the structure of the atom. The resulting collection of energy lines is characteristic to every element, thus making determination of material possible. The photons radiated from the sample are collected by a detector which forms a spectrum of energies.



#### Figure 1. Principle behind the X-ray fluorescence.

The XRF measures the sample only from its surface so any dirt or dust on it could cause some erroneous results. Also, anything hidden under the surface is not visible to XRF.

The XRT technology can be used to identify differences between specific atomic densities of materials. As with XRF the XRT does not destroy the sample when measuring. Its advantage to XRF is that information of the internal material compositions is also obtained and not just from the surface. So, the result is independent of surface contaminations.

The principle behind the XRT is that part of the X-radiation is absorbed in the material and part of it penetrates. The passed radiation with reduced intensity is measured, i.e. it is a trans



illumination technology. Material's properties affect how much radiation is absorbed and how much penetrates.



#### Figure 2. Basic idea of the X-ray camera.

To collect the data an X-ray camera is used where intensity from each pixel is converted to electrical signals thus creating a grayscale image. So, basically interesting objects and their location could be determined based on the image.

If objects with different densities and thicknesses are measured, erroneous results may occur. This is because thin particle with high density and thick particle with lower density may have similar results. This can be reduced by using two different wavelengths.

## 2.2 X-ray technologies in ash related applications

In this brief literature review, systems where ashes are measured and characterized online are discussed. The main interest is naturally in systems where X-ray techniques are used but it seems that using X-ray for online measurement is very little studied case. So, offline measurement systems are discussed as well.

Several studies regarding the characterization of ashes using X-ray technologies have been performed. Mainly they concentrate on defining the chemical and elemental compositions of ashes accurately to ensure that it can be further used for example as a raw material in construction industry.

The technologies used for ash characterization were XRF and XRD which seem to be well known and a working set of tools. The ash samples are processed before measuring. Tiwari et al. [4] first sieved the ashes and then mixed them homogeneously with cellulose powder. This mixture was then pressed into pellets which were used in the measurements. Similar methods have also been used by others [5-6]. Provis et al. [7] also used moulds to process their samples which were beforehand mixed with a commercial epoxy binder. For the measurements they demoulded the samples and polished them to make thin specimens.

The elemental ash characterization with X-ray technologies is mostly done in laboratory conditions with a fixed setup. Online and real-time measurements and methods for defining



ash composition are developed but they do not use X-ray for the analysis but other methods. These methods include microwaves absorption, capacity measurement, photoacoustic effect, infrared emission and optical dispersion-reflection technique (listed in [8]). It should be noted that these methods focus on finding the unburned carbon from the coal fly ash thus ignoring all other, possibly interesting materials.

The main motivation in ash characterization studies seems to be the possibility to use the ash entirely as a raw material later on. Apparently, using X-ray techniques to measure ash characteristics online is a unique idea and has not been done before.

## 2.3 Laboratory tests

This section describes the laboratory tests for XRF which were performed at VTT's premises in Tampere in machine vision laboratory. The equipment used is described in the next subsection after which results and conclusions follow.

The main idea in the experiments was to find out if there are some harmful materials in the ash sample and if their amount exceeds predefined limits thus preventing re-use of ash. All this should be done online and continuously so that the eliminated ash can be set aside immediately without eliminating the whole dumb of ash.

#### 2.3.1 Measurement setup

The measurement setup consists mainly of an X-ray source and an imaging detector. A spectrometer is also available but the focus is now on testing how well materials can be detected using the imaging detector.

As an X-ray source Mini-X from Amptek was used (Figure 3). It is a miniature X-ray tube which features a  $50kV/80 \mu A$  power supply, a silver transmission target and a beryllium end window. It is designed for continuous operation in industrial environments. USB is used to communicate and control the tube by computer. [8]



Figure 3. Mini-X, a miniature X-ray tube by Amptek (picture from Amptek's web site [8])





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The imaging detector used in the tests was Advacam's WidePix 1x5 (Figure 4). It has a resolution of 1280x256 pixels which each has an integrated digital counter which counts number of particles. This assures noiseless detection and no added noise caused by image integration or readout. The detector is relatively new; it is introduced two years ago and is not available in the mass markets. However, due to its specified sensitivity this detector was selected keeping on-line industrial production in mind. The continuously sensitive surface is composed of a row of detector tiles. Each tile consists of single Timepix hybrid detector with edgeless silicon sensor making the whole area of WidePix fully sensitive. [10]



#### Figure 4. WidePix 1x5, large area imaging detector by Advacam (picture from Advacam's website [10]).

The Timepix technology allows setting of energy threshold which allows obtaining multichannel radiographs where different materials can be identified. This feature requires getting of several subsequent snapshots with different energy threshold settings.

The detector is connected to computer via USB 2.0 and controlled by using Pixet Lite software.

The setup was constructed such that the WidePix imaging detector was put on the bottom of lead booth horizontally (Figure 5). The Mini-X X-ray tube was then set so that it faces the detector perpendicularly. A large collimator was used in the tube to focus the X-rays to the detector effectively. Without any collimator the source would radiate everywhere forcing to increase the measurement time. Smaller collimator would not have covered the detector area completely thus making the images unevenly illuminated.





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Figure 5. Measurement setup inside lead booth: WidePix 1x5 is situated at the bottom with Mini-X hanging above it.

Even though maximum output from the tube was used the measurement time was somewhat long with frame time being 0.1 seconds and frame count 100 frames. Therefore tests performed were stationary.

The sample was a bag of fly ash and approximately 2 mm thick layer of it was set on a glass Petri dish (Figure 6). The dish was then set right on top of the camera's sensor making the distance from sensor to sample as short as possible.







#### Figure 6. Fly ash sample set in a Petri dish.

VTT Expert Services has earlier made an analysis on the ash sample where they used XRF and X-ray diffraction (XRD) technologies to identify materials and elements from the ash sample [11]. Based on that analysis the major materials in the ash were silicon (Si), calcium (Ca), iron (Fe) and aluminium (Al). Beforehand few elements had been labelled interesting: cobalt (Co), copper (Cu), antimony (Sb), sink (Zn) and aluminium (Al). So based on these two aspects the elements to be identified were chosen.

Unfortunately, the WidePix camera can only measure energies from 5 keV and 60 keV. This means that elements whose characteristic X-rays are below 5 keV and above 60 keV cannot be detected with it but are ignored. Thus Si, Al and Ca are omitted, leaving us with Fe, Co, Cu, Zn and Sb.

#### 2.3.2 Imaging and image analysis

In order to identify an element from the sample the images were taken in such a way that only values around the chosen element's spectrum peak were taken into account. As mentioned earlier, the WidePix detector can be set with different energy threshold values making identification of materials possible. Only one threshold value can be set at a time and values below the threshold are ignored. So, to gather data from a certain spectral band two subsequent images with two different thresholds were taken (Figure 7). In practice two first peaks were covered in one region as they with most elements were so close to each other.







#### Figure 7. Two images with thresholds set around spectral peaks of Fe.

For example, Fe has K lines at 6.40 keV and 7.06 keV so to gather data around both peaks the thresholds were set to 6.0 keV and 7.5 keV (Figure 7). Naturally, some other elements lie on this region as well and will cause false positives. This is the case with Cu and Zn as well as with Co and Fe.

The two threshold images are then subtracted from each other in order to show the data observed between the thresholds.

#### 2.3.3 Results and conclusions

The following five images (Figures 8, 9, 10, 11 and 12) show the subtracted result images. At first it seems that the images are nothing but noise but one should remember that the sample is ash where particles are rather small and scattered evenly.

As mentioned earlier, some of the chosen elements have characteristic X-ray peaks in the same energies and are thus visible in images of another element. This would explain why for example Co whose spectral peaks are in the same region as Fe, has lots of observations in its image even though the earlier analysis shows that its concentration in the sample is only 0.02% whereas Fe has concentration of 5.6% [11]. This also explains why the Sb (concentration of 0.01 %) has fewer observations since no other element found in the sample has its characteristic X-rays in the same region.





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Figure 8. Subtraction image from the Fe spectrum band.



Figure 9. Subtraction image from the Sb spectrum band.



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Figure 10. Subtraction image from the Cu spectrum band.



Figure 11. Subtraction image from the Co spectrum band.





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#### Figure 12. Subtraction image from the Zn spectrum band.

In principle, the different materials can be identified and noticed from the ash sample by using X-rays for transillumination as the elements are clearly visible in the result images above.

The greater is the average value of photo pixels, the better should be the probability to recognise an element by XRF-technology. By taking mean values of the histograms, the following results were obtained which indicates some raise in the values all others except Pb:

- Fe: 16
- Sb: 4
- Cu: 14
- Co: 13
- Zn: 14

In practise due to the nature of ash the positive observations are small points scattered everywhere in the sample. In this case not much more information about the elements is obtained by the imaging detector than when using spectrometer. The spectrometer is also capable of measuring wider spectrum band in one measurement thus making it possible to identify more elements at a time whereas WidePix's X-ray energy range is limited from 5 keV to 60 keV. Of course, with a thicker sample layer the imaging detector would be more useful since the spectrometer measures only the surface of the sample. Also larger particles covered in ash could be identified with the imaging detector.





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For online detection the spectrometer would probably be a better choice as long as the sample layer is thin or other methods (e.g. powder method) for scattering the sample are used. At the moment, the WidePix is not able to take one image with several different energy thresholds simultaneously but requires taking subsequent images with different thresholds for every interesting energy level. This would be troublesome to implement for online measurements. One must also take into account the current energy value restriction of WidePix.

The X-ray principle can probably be used for indicating that ash contains specific components and making an estimation concerning concentration, too. However, screening the components with any online system is probably too challenging or at least requires more sensor information than spectrometer or X-ray camera can provide individually. There are benefits and drawbacks in both systems (spectral analysis and X-ray camera) but combination of those two could be quite interesting. Spectrometer is more accurate but is not able to detect metals inside the ash whereas the imaging detector can provide indication that "something is there". Combination of these indicators - first transillumination analysis and then spectrometer to confirm - could provide quite a good performance.



## 3 Laser-induced breakdown spectroscopy of fly ash

## 3.1 Background

In recent years, laser-induced breakdown spectroscopy (LIBS) has been employed for fly ash chemical composition determination due to its attractive advantages as fast, versatile and multi-elemental analysis [12-15].

Typical ash quantitative analysis is performed by the use of an internal standard and binders for pellet preparation in order to analyse fly ash as a solid sample [13-14]. Other publications describe an "online" methodology to analyse qualitatively the elemental composition of the fly ash by using simple sampling steps [14]. Furthermore, LIBS-based automated devices have been developed for boiler-control systems to monitor in real time unburned carbon in fly ash [16]. However, the sampling remains a challenging task for LIBS online ash measurements due to the fine size and heterogeneous structure of ashes, and required multicomponent analysis.

In this report we present preliminary results on elemental characterisation of fly ash based on LIBS and an "on-tape" sampling approach for ash deposition. The experiments were performed in the laboratory scale as a prerequisite for an online fly ash monitoring.

## 3.2 Principle of analysis

LIBS is based on energetic laser pulse that ablates a small volume of sample material and ionises and heats the ablated material to form high-temperature plasma. Figure 13 shows the process schematically as a function of time. After the laser pulse, the plasma expands and cools down, which makes excited ions and atoms also relax back to their electronic ground state and emit their characteristic luminescence. The luminescence is recorded with an optical spectrometer and the elements can be identified with a detection limit typically around 10-100 mg/kg.



Figure 13. Time series about laser-induced breakdown spectroscopy (LIBS) process.



## 3.3 Experimental setup

A laser was used to ablate small volume of the sample at the time. The laser emitted 5 nsduration pulses at 355 nm wavelength and the light was focused on the sample by planoconvex lens with a focal distance of 50 mm. The energy of the laser pulses was about 15 mJ that was enough to heat the ablated material to form plasma. Light from the induced plasma was collected directly with an optical fiber with a diameter core of 600  $\mu$ m placed 5 cm far from the sample. The fiber was coupled to the entrance slit of a Czerny-Turner spectrograph and to an ICCD camera (iStar, Andor).

The setup allowed detection at spectral region between 260 nm and 900 nm that was covered with several individual spectral windows of approximately 50 nm at the time. For each spectral window, 50 acquisitions were averaged using a repetition rate of 10 Hz, thus the recording of one spectrum took 5 seconds. Sample was moving continuously so that every laser pulse hits a fresh sample surface. That causes pulse-to-pulse variation that is typical to LIBS analysis and can be minimised by averaging multiple spectra (now 50 spectra).



Figure 14. Experimental arrangement. 355 nm wavelength laser pulses are focused on the ash sample surface in order to produce plasma. The emitted light of the plasma is collected by a fiber optic and coupled into a spectrometer for further analysis.

## 3.4 Sample preparation

Ash samples were deposited on commercial and inexpensive carbon tape tabs of 12 mm diameter as shown in Figure 15. The adhesive tabs provide a simple and fast fly ash deposition for further analysis. After deposition, the fly ash sample was pressed uniformly on the carbon tape to produce a more constant lens-to-sample distance in order to reduce the shot-to-shot variation. This simple sampling preparation step increases the shot-to-shot repeatability achieving a more representative signal of the samples by further signal averaging. The "on-tape" sample preparation take no more than few seconds. Signal interference from the tape is not expected since we are continuously moving the sample in order to avoid carbon tape ablation coming from several shots in the same position. The risk





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of tape signal interference can be completely overcome by depositing thicker layer of ash if needed.



Figure 15. Fly ash deposited on an adhesive carbon tape tab. The burnish lines marks are produced after the laser ablation of the sample for LIBS analysis.

The fly ash used in the LIBS experiments was from a BFB boiler. The ash was characterized with an inductively coupled plasma analysis in the certified laboratory to have the following elemental content:

Major components:		Minor components:		
SiO <sub>2</sub>	43.6%	S	4940	mg/kg
$AI_2O_3$	16.8%	Zn	1650	mg/kg
CaO	14.4%	Ba	1460	mg/kg
$Fe_2O_3$	7.8%	Cu	426	mg/kg
$P_2O_5$	3.9%	Pb	380	mg/kg
K <sub>2</sub> O	2.9%	Sr	337	mg/kg
MgO	2.0%	Cr	213	mg/kg
Na <sub>2</sub> O	1.9%	Zr	120	mg/kg
TiO <sub>2</sub>	0.9%	Ni	94.5	mg/kg
MnO	0.5%	V	56.4	mg/kg
		As	27.3	mg/kg
		Sb	26.7	mg/kg
		Y	25.1	mg/kg
		Sn	20.8	mg/kg
		Co	20	mg/kg

The main elemental components Si, Al, Ca, and Fe are expected to dominate the LIBS spectrum. Alkali atoms like K and Na have very strong luminescence, and they should also be easily detectable from the spectra.



## 3.5 Results and conclusions

Recorded spectra were analysed on the spectral range between 260 and 900 nm from the fly ash samples. It was possible to obtain signal peaks from all the mayor species: AI, Ca, Fe, K, Mg, Mn, Na, Si and Ti, except for P. Phosphorus has a weak luminescence peak at the edge of the spectral range where detection efficiency is already relatively low with the spectrometer used in this study. Figure 16 shows an example of the recorded spectra and the elemental analysis performed for the data. The spectral range between 258 nm and 305 nm shows emission lines of Ca, Fe, Mn, Mg, Mg(ion), Na, and Si corresponding to 7 of the 10 major elements in the sample.



Figure 16. Typical LIBS spectrum from fly ash samples. The spectral range between 258 and 305 nm shows emission lines of Ca, Fe, Mn, Mg, Mg(i), Na, and Si corresponding to 7 of the 10 major elements of the sample. Other elements are visible at other parts of the optical spectrum.

It was also possible to obtain signal peaks from some minor elements such as Ba, Pb and Sr. The main limiting factor to detect the minor elements is the strong interference caused by the major elements in the sample. Thus, a high-resolution spectrometer should be used in ash analysis to separate the closely located peaks from each other. In this study, the resolution of the spectrometer was about 0.2 nm as seen from Figure 17. An optical resolution of 0.05 nm or better would greatly help to identify the minor elements from the spectra. Figure 17 also shows almost the full recorded wavelength range from 260 nm to 850 nm. The spectrum is dominated by emission of Fe, Si and Al as expected.

We also identified emission lines from Li on the LIBS spectrum. However, lithium is not present in the reference results, so it is not clear at the present if laboratory analysis has difficulties to detect lithium or if we have made a mistake in spectral analysis.

Regarding the carbon content in fly ash, it is possible to analyse CN molecular emission on LIBS spectra as proposed by Yao et al. [24]. In our experiments, the CN emission band at 388.3 nm can be used for this purpose.

The elements like P and other heavy metals like Hg and As emit their most intense lines below 260 nm, where the sensitivity of our detection system decreases considerably.





However, this is only a technical limitation of the current setup and further analysis of those elements can be performed with different instrumentation if needed.



Figure 17. Recorded LIBS spectrum of fly ash. The spectral range from 260 nm to 850 nm contain several separate recordings to cover to whole spectrum. Zoomed spectrum shows the resolution and quality of the recorded data around the characteristic sodium doublet peaks at 589 nm.

The results with LIBS on fly ash characterisation are positive in respect of an online ash analyser. The particle size in fly ash is small enough for LIBS to evaporate most of the particles to achieve a representative sampling. Sample handling needs to be designed carefully to stabilize the distance between the lens and the sample surface. Otherwise the laser focus is not stable at the surface and it causes signal fluctuation. Another challenge is the large amounts of elements, and thus high resolution needed in the spectrometer. The high-resolution is well achievable in a narrow spectral region that would mean limiting to a certain element or few elements. Recording the full spectrum with high-resolution is possible, but the instrumentation gets expensive.

Figure 18 shows a schematic illustration of an online LIBS analyser of fly ash. The analyser should be placed in a meaningful location in the process to gain online information about the fly ash quality. The sampling for LIBS analysis is possible to arrange with a continuously moving tape or belt, on which the ash is deposited. Furthermore, the surface of the ash sample on the belt should be levelled with a proper mechanism to keep the ash surface at constant distance from the optics. That ensures good focus for all laser pulses on the surface. The required surface accuracy is about 1 mm. The LIBS devices usually record about 10 spectra per second, so with a moving sample, a good signal and sample averaging will be achieved in less than a minute.





Figure 18. Schematic illustration of potential online application of fly ash elemental monitoring with LIBS.





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