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Comparison of Elemental Analysis Techniques for Fly Ash from Municipal Solid Waste Incineration using X-rays and Electron Beams

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Abstract. With the rapid expansion of the waste incineration business both in Europe and globally, there is a growing need for the elemental analysis for fly ash from municipal solid waste incineration. In this work, samples of washed and unwashed ash from municipal solid waste incineration in Sundsvall are evaluated. Qualitative analysis and semi-quantitative analysis are used to compare two elemental analysis methods, scanning electron microscope with energy dispersive spectroscopy (SEM-EDS) and X-ray fluorescence (XRF) measurement. Both methods are used to retrieve the difference in elemental composition between washed and unwashed fly ash. SEM-EDS accurately detects light elements from well-prepared samples in a vacuum environment, while, for online measurements, XRF is a potential method that analyses hazardous metal content in the fly ash.

1 Introduction

Incineration of the municipal solid waste (MSW) is one of the most efficient ways in waste management, because of the large reduction in volume and the high energy recovery. The EU’s rules for waste management, the so-called waste hierarchy, state that the following stages are reuse, material recycling, other recycling – e.g. energy recovery – and finally disposal [1]. In Sweden, a vast majority of this household waste can be recovered or reused, and only four percent is landfilled. Waste incineration provides around 20 percent of all the district heating. The major environmental concern in relation to the short- and long-term impacts of MSW residue disposal is the risk of leaching and subsequent release of potentially harmful substances, particularly inorganic salts and metals trace elements, into the environment [2]. The advantage of municipal solid waste incineration is that many harmful substances break down and the residual substances are bound in ash, which makes them easier to control, handle and recycle. Incineration produces fly ash along with flue gas and heat. The flue gas is cleaned before it is fed out through the chimney, leaving fly ash and sludge from the washing water to be further processed. However, the contents in the fly ash are hazardous to health and the environment, and they thus are commonly stored in storage cells for hazardous waste. Korståverket in Sundsvall is the first power plant in Sweden, which implements a washing process and allows storage of fly ash on a landfill for non-hazardous waste [3]. The washing process generates a mixture of fly ash and sludge that has low leaching of metal content to the surroundings.

X-ray fluorescence (XRF) technique is a non-destructive method for the elemental analysis, which is fast and fully suitable for simultaneous quantitative determinations. Therefore, it presents some
advantages over other spectrometric methods like Neutron Activation Analysis (NAA); which is expensive and not widely available, inductively coupled plasma atomic emission spectroscopy (ICP-AES); which requires dissolution procedures, and are generally time-consuming and can induce losses of some volatile elements [4]. Therefore XRF instrumentation has lower capital cost and is cheaper to use than NAA, is faster than ICP-AES, and is widely available [5], [6].

In this paper, the purpose is to compare two methods to analyse the elemental composition of a random group of fly ash samples: (a) a scanning electron microscope with energy dispersive spectroscopy using electron beams and (b) an X-ray spectrometer using X-rays to irradiate the samples. The fly ash samples are collected both before and after the stabilizing wash process. The major changes affected by the washing process is presented by lowering the Sodium, Potassium, Chloride and Sulfate concentrations. Among the minor constituents increased, e.g. Hg, however, the total concentrations are still low. Final, the washed ash allows to be taken to a class II landfill in Sweden [3].

2 Method

When a material is irradiated by X-rays or highly-focused energetic electron beams, a photon or electron transfers its energy to an inner shell electron in an atom of the material. If the energy of the particle is higher than the binding energy of the electron, it can eject the electron from its atomic orbit. To fill this space, an outer shell electron falls into an empty position of the ejected electron. In this process, the falling electron emits a characteristic fluorescent X-ray photon with an energy which is equal to the difference between the binding energies of those two shells. The energies of the fluorescent photons from a material are characteristic and, therefore, can be used to identify the material [7], [8].

The characteristic X-ray energy lines of the elements of interest are listed in Table 1 [9].

<table>
<thead>
<tr>
<th>Element</th>
<th>Z</th>
<th>Fluorescence $k_\alpha$(keV)</th>
<th>Energy $k_\beta$(keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium (Na)</td>
<td>11</td>
<td>1.040</td>
<td>1.071</td>
</tr>
<tr>
<td>Sulphur (S)</td>
<td>16</td>
<td>2.307</td>
<td>2.464</td>
</tr>
<tr>
<td>Chlorine (Cl)</td>
<td>17</td>
<td>2.622</td>
<td>2.815</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>18</td>
<td>3.314</td>
<td>3.589</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>48</td>
<td>23.173</td>
<td>26.096</td>
</tr>
</tbody>
</table>

To excite the k-shell electrons of a specific element, the X-ray or electron energy in keV needs to be higher than this energy. The X-ray source used in the XRF measurements is capable of 60 keV while the SEM-EDS source was limited to 20 keV.

2.1 Scanning electron microscopy (SEM)

Two samples, the washed ash and unwashed ash, are prepared. The washed ash is dried in the air and ground manually into fine small grains with the dimension of a few hundred micrometers. The unwashed ash is not concreted by the washing process, and it is thus an already fine and powdery material. Therefore, we do not grind the unwashed ash. A portion of fly ash samples is sprinkled onto double-sided carbon tape mounted on an Aluminum stub (1cm diameter), and then it is sputtered with a conductive coating (Iridium) to avoid charging issues with the electron microscope. This grain mounting enables the analyst to determine the particle morphology, external surface structure and external elemental distribution of individual fly ash particles [10].

SEM is one of the techniques for the chemical and physical characterization of fly ash [11].

SEM operates in vacuum environment, which scans the surface of a conductive sample via a highly-focused energetic electron beam to create an image for detailing the topography and collect the information of the composition of the sample. Three common modes of operation are used in an SEM analysis, namely, backscattered electron imaging (BSE), secondary electron imaging (SEI), and EDS [12]. In this study, we use BSE and EDS to characterize the fly ash samples. The BSE consists of high-energy electrons originating in the electron beam that is reflected or back-scattered out of the specimen interaction volume by elastic scattering interactions with specimen atoms. In the EDS, in order to obtain
the precise elemental composition of materials, we use a detector (X-MaxN Silicon Drift Detector, Detector Area: 50 mm², OXFORD instruments) to measure the energy and intensity distribution of X-ray signal generated by a focused electron beam on the specimen.

The elemental analysis is performed in “spot mode”, in which the beam is localized on a single area manually chosen within the field of view. The location is represented on the provided SEM images. The backscatter rates in heavy elements (high atomic number) are higher than in light elements (low atomic number), resulting in brighter spots shown in the image. Thus, the BSE is used to detect contrast between areas with different elemental compositions. The morphology of a fly ash particle is shown in Figure 1. The SEM images present a poor illumination at the peripheries (vignetting), which is caused by the detector sensitivity dropping towards edges of images at low magnification. The size of the washed ash particles (Figure 1 left) is in a range from less than 10 μm to greater than 200 μm. The unwashed ash particles (Figure 1 right) are down to few nanometers.

![Figure 1. Scanning electron microscopy of (left) Washed fly ash; (right) Unwashed fly ash.](image)

2.2 X-ray fluorescence (XRF)

For loose powders samples, the more finely ground the sample the more likely it is to be an even surface and providing for a better analysis. Irregular sample surfaces hamper X-ray performance. Moreover, they also change the distance from the sample to the X-ray source, which introduces air absorption difference. Pressing powder into pellets is a more rigorous sample preparation than loose powders [13]. The process includes grinding a sample into a fine powder, ideally to a grain size of <75 μm, mixing it with a binding aid, and then pressing the mixture in a die at between 20 000 kg and 30 000 kg to produce a homogenous ground sample pellet. However, pellets sample preparation makes it difficult for an online measurement. In this measurement, the washed sample was roughly ground to up to 3 mm. The exposure area is approximate 4-5 cm² since the cone angle of the X-ray beam is 48° in this setup. An XRF setup is thus possible to be mounted above a conveyor belt in a plant ash treatment process.

XRF is an analytical method that determines the elemental composition of all kind of materials. It is also capable of determining materials in varies forms such as solid, liquid, and powder [14]. However, the XRF cannot generally make analyses at the small spot sizes typical of SEM work (about 100 micrometres in this project), so it is typically used for the bulk analyses of larger fractions of materials. Because of the relative ease and low cost of sample preparation as well as stability and ease of use of x-ray spectrometers, XRF is used for analysis of major and trace elements in rocks, minerals, and sediment [15].
An X-ray tube produces a bremsstrahlung continuum extending to low energy, which scatters from the sample. X-rays below the absorption edges do not excite the elements of interest, forming a background that decreases the detection limit of spectrum. If a filter is placed between the tube and sample, X-rays below the K-edge of the filter will be absorbed. It improves the signal to background ratio, improving precision and detection limit [7]. Filters of 0.17 mm Cu and 1 mm Cu are used in this measurements [16]. A 0.3 mm Ge filter also have been considered for these elements below 7 keV.

The XRF measurement setup is shown in Figure 2. An X-ray tube (MOXTEX 60 kV) with Silver (Ag) target is used to irradiate the sample surface. The X-ray fluorescence with discrete energies emitted from the ash sample is detected by an X-ray Spectrometer (Amptek X-123SDD, Detector Area: 25 mm²), which is mounted in an air environment. Due to the large range of fluorescence energies of the materials of interest, two filters and two tube voltages are used to optimize the performance for different elements [17].

3 Results and discussion
The peak area of each element corresponds to a specific element concentration, and it is influenced by fluorescence yield, sensor absorption, source penetration in the sample, and the escape of fluorescence out of the sample. Grammelis [18] notes that the Na, K, P, Cl, Si and Ca contents determine the ash melting behavior – related to the formation of slag and fouling. The importance of the quantification of S, Cl and K elements is related to the corrosion of equipment commonly used in energy recovery plants such as heat exchangers. In combustion processes, S, Cl and K partially vaporize in high temperatures and, after cooling, form HCl, KCl, Cl₂, alkali chlorides and metal sulfides [18]. A dry/wet scrubber is used to spray fine atomized slurry or lime powder into the hot exhaust gas in order to neutralize the acidic gases such as sulfur oxides and hydrogen chloride [19]. Therefore, the washed ash has higher Ca peak than the unwashed ash.

The SEM-EDS spectra of fly ash are presented in Figure 3. For both washed and unwashed samples, the spectra nicely resolve the peaks from interested elements, Na, S, Cl, K and Cd. For the Na peak, the tail at 0.9 keV shows that it overlaps with the escape peak of Cl. For higher energies elements above 10 keV, the spectra present a poor detection due to the maximum beam energy depends on the energy of the incident electrons. It requires an input energy higher than the detectable peak energy by 30-50%. In order to detect Cadmium k\textsubscript{α₁} and k\textsubscript{β₁} peaks, an electron beam with a higher energy is needed, which is not involved in this measurement.
Figure 3. Spectra of washed and unwashed ash sample, SEM-EDS, 20 kV, 5 mins. XRF spectra of ash sample with 0.17 mm Cu filter are presented in Figure 4. A digital filter (one-dimensional filter) is applied to compute averages and smooth noise data. As same as SEM-EDS spectra shown in Figure 3, the Na peak is disturbed by the Cl escape peak, presenting a merged peak. The light elements below 1 keV are easily absorbed by air, thus it is difficult to detect them in the present setup in the air. Ar $k\alpha_1$ peak at 2.958 keV and $k\beta_1$ peak 3.190 keV overlap with Cl $k\beta_1$ 2.815 keV and K $k\alpha_1$ 3.314 keV, respectively. It should be noted that there is no Ar in the ash, but it presents in the spectra, because the normal atmosphere consists of Ar.

Figure 4. Spectra of washed and unwashed ash, XRF, 0.17 mm Cu filter, 15 kV, 10 mins. For detecting Cd, a higher X-ray tube energy 40 kV with 1 mm Cu filter is applied. As shown in Figure 5, the Cd peak at 23.173 keV presents a lower peak in the washed ash compared with the spectra of the unwashed ash. The $k\beta$ energy of Cd at 26.096 keV is disturbed by the $k\alpha$ peak of Sb, but the peak presents at 23.173 keV is able to detect Cd. The Ag peak at 22.163 keV is contributed by the X-ray tube target material rather than the ash.
Figure 5. Spectra of washed and unwashed ash, XRF, 1 mm Cu filter, 40 kV, 60 mins.

In order to compare the SEM-EDS and XRF methods on the performance of elemental analysis, we use the same sample (i.e., the ground sample) for both methods. Tab. 2 shows the comparison between the SEM-EDS and XRF methods for the elements of interest. Each element is presented as its intensity determined by the area of a peak profile (total counts). By employing a semi-quantitative analysis, we present the relative intensity of the elements of interest. Because the escape peak of the Si sensor in the spectrometer is excited by the Cl peak at 2.62 keV, escape photons has lost 1.74 keV of the original photon energy and shows a peak at 0.88 keV adjacent to the Na peak. Thus, the three W/U ratios (the ratio of washed to unwashed) of Na present different values after the washing process. Although the washing process decreased the sulfate content, both methods do not distinguish between sulfur and sulfate. The results thus shows that the S (sulfur and sulfate) is increased by 12-25% after the washing process approximately. Cl and K decrease 17-27% and 42% for the ground ash sample, respectively.

**Table 2.** Comparison between SEM-EDS and XRF for the elements of interest in fly ash. The total counts are normalized for each method.

<table>
<thead>
<tr>
<th>Method</th>
<th>Sample</th>
<th>Na</th>
<th>S</th>
<th>Cl</th>
<th>K</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM-EDS</td>
<td>Washed (Ground sample, Figure 3)</td>
<td>0.316</td>
<td>0.611</td>
<td>0.169</td>
<td>0.143</td>
<td>NULL</td>
</tr>
<tr>
<td></td>
<td>Unwashed</td>
<td>0.569</td>
<td>0.329</td>
<td>1</td>
<td>0.337</td>
<td>NULL</td>
</tr>
<tr>
<td>XRF</td>
<td>Washed (Raw sample, Figure 4 and Figure 5)</td>
<td>3.224e-3</td>
<td>1.857</td>
<td>0.169</td>
<td>0.424</td>
<td>NULL</td>
</tr>
<tr>
<td></td>
<td>Unwashed</td>
<td>3.720e-3</td>
<td>0.094</td>
<td>0.056</td>
<td>0.149</td>
<td>0.312</td>
</tr>
</tbody>
</table>

SEM-EDS is a point measurement method and sensitive to the chosen position since the ash samples are inhomogeneous, while XRF measures a surface average of 0.785 cm² for the ground sample. The effect of the grinding and sample preparation can be evaluated by comparing XRF measurements of raw and ground samples, which is presented in Tab. 3 by comparing ratios of the W/U ratios in Tab. 2.

**Table 3.** Relative comparison of SEM-EDS and XRF methods and of ground- and raw samples using XRF.

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Comparison</th>
<th>Na</th>
<th>S</th>
<th>C</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rc / Ra</td>
<td>Between XRF and SEM-EDS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rc / Rb</td>
<td>Between ground and raw samples</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

When comparing the methods in Tab. 3, Rc/Ra = 0.98 (≈1.0) for K indicates that XRF and SEM-EDS show good agreement for detecting K. For the lighter elements, XRF gives a factor between 1.3 and 1.9 higher content in washed ash. This difference might be due to differences in XRF penetration depth for the lighter elements and must be considered. Tab. 3 further shows that sample preparation affects the
XRF measurement to show higher content of all the evaluated elements after the washing process. Calibration of the XRF analysis must therefore consider the ash preparation.

4 Conclusion

XRF can detect Na, S, Cl, K, Cd and other heavier hazardous elements in fly ash. The provided measurements are semi-quantitative and can be calibrated either using dedicated quantitative analysis software for XRF or with other methods like SEM-EDS. The latter provides good spectral resolution for light elements where air absorption of low energy X-rays disturbs the XRF measurement. In samples containing many different elements, the peaks can distort each other. In these fly ash samples, the Na peak is distorted in both XRF and SEM-EDS measurements due to the Silicon escape peak of Cl. The further process for correcting escape peaks, sum peaks, and background removal must be considered [20].

The XRF method is suitable for online measurements since it requires no specific sample preparation and measuring larger fractions of materials. XRF penetrate relatively deep into the ash sample while the SEM-EDS method mainly measures the surface content. This makes the XRF method sensitive to background noise from the container material. An XRF online measurement method thus needs to be calibrated to consider the effect of surrounding elements. Another conclusion is that the calibration of a measurement system must consider the ash preparation.

We conclude that XRF is a potential method for online measurements of hazardous metal content in fly ash from incineration plants. If the metal composition of the fly ash were known on site, it would be possible to adjust the wash process to optimize the content of the washed/stabilized ash. In the future, it is possible to further develop the washing process into the extraction of metals from the fly ash.

References

Major and Trace Elements on a Single Low Dilution Li-Tetraborate Fused Bead Adv. X-ray anal 41 pp 843-67


