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Distribution of Major and Trace Elements in Ash Particles Determined by Laser Ablation-ICP-MS

Master's Thesis in the International Master's Programme
Applied Environmental Measurement Techniques

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Abstract

Incineration of municipal solid waste has been proven as an effective approach to treat increasing amounts of municipal solid wastes. However, it is necessary to study potential pollution issues related to waste incineration, including the concentration of inorganic contaminants in produced ash material. The aim of this project was to characterise ash particles and determine the mechanisms by which trace elements bind to ash particles. This was done by the analysis of single ash particles using laser ablation-ICP-MS, a technique which enable the direct elemental analysis of solid with high sensitivity and high spatial resolution. Two ash samples from bubbling fluidised bed boilers burning municipal solid waste were used in this study. In order to minimise the measurement uncertainties and be convenient to analyse the experiment data, two data treatment methods, i.e. calibration and normalisation, were performed in this study. Particle groups were identified based on major elements (Al, Si, Ca, Fe) and trace element were compared for the different groups. Comparison between the two ash samples was then performed.

Key words: ash particles, laser ablation-ICP-MS, calibration, normalisation, heavy metals and element distribution.

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Introduction

With the development of society and technology, the living standard of man has dramatically been improved. At the same time, the disposal of waste is an increasing environmental and economic problem. The amount of waste generated every year is growing, in step with economy. It is estimated that each household generates around 1.2 tons of waste each year, and the amount of municipal waste generated by householders and businesses has been increasing by 3-5% every year. If the generation of waste continues to increase at this rate the amount of municipal waste will double over the next 20 years. In order to minimise the amount of waste produced, some management options were introduced to balance waste production, including recycling, composting, landfilling, and waste-to-energy conversion via incineration.

Landfilling is still the dominating method to manage waste worldwide. Enhancement of people's environmental awareness, continuing increments of landfill costs, sharp scarcity of landfill sites and slowness of compost process have led communities and governments to take alternative waste handling methods into consideration. Waste incineration has become more important than before, and the utilisation of this method keeps increasing.

Incineration of waste has many advantages, including significant volume reduction and mass reduction, complete disinfection and energy recovery. (Wey, 2001) Thus, incineration meets the requirements of detoxification, decrement and resource recovery. These methods have been technically proven as an effective waste treatment approach. (Vassilev, 1999) In addition, waste incineration can be seen as a reasonable way to produce energy.

Although waste incineration has many environmental benefits, possible environmental impacts should not be forgotten. There is some concern that pollutants produced during incineration of waste may cause more harm to the environment than in other forms of waste disposal. The incineration of waste can produce three types of pollutants: pollutant emissions to the atmosphere, contaminated wastewater and contaminated ash. Pollutants emissions to atmosphere have received most attention from environmentalists and legislators. The emissions of most concern are total particulate or dust, acidic gases and heavy metals. Water pollution from incinerators is not generally regarded as an important problem because of the limited amount of wastewater generated. However, the wastewater from municipal waste incinerator plants has been shown to be contaminated with heavy metals and inorganic salts and to have high temperatures and high acidities or alkalinities. The production of toxic ash material is a further problem which requires to be investigated.

Produced ash can either be landfilled or reused for different applications. Because combusted ash contains toxic elements, they can exert great effects to environment, especially when hazardous elements can leach into the groundwater. The dominating utilisation of ash is in land development-landfills; ash also can be used in construction as a replacement in concrete sand and in ash based products, such as bricks; furthermore,

ashes can be used as a substitute for aggregate in road base materials, building construction and artificial offshore reefs; underground mines can be stowed with ash; ash can be used for improvement of soil condition for agriculture purpose, because the produced ash contain micro-nutrients, e.g. potassium, phosphorus, zinc, and have therefore soil amendment characteristics.

It is therefore necessary to minimise the content of toxic elements in ash. This can only be achieved with a clear understanding of the mechanisms by which metals bind to ash particles. Produced ash is typically analysed by bulk analytical techniques and studies therefore only report bulk concentrations without distinction between different particles types. Recent developments in microprobes including laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) have opened up the possibility for sensitive individual particle analysis. The study presented here aims at assessing LA-ICP-MS analysis as a tool for single particle analysis to characterise ash samples and provide a better understanding of these mechanisms. Fly ash generated from Municipal Solid Waste by a Bubbling Fluidised Bed boiler was studied using this technique.

Aims and Objectives

The aim of the project is to develop an analytical strategy for the characterisation of single ash particles using LA-ICP-MS and provide a further understand on how potentially toxic trace elements bind to ash particles. The determination of binding mechanisms is important for improvements of incineration processes and could help assessing the leaching of potentially hazardous heavy metals, essentially copper, cadmium, zinc and lead, from produced ash.

The project aims at determining to which type of particles heavy metals are attached to in raw (non-leached) combustion ash and whether their occurrence is systematic or random. The study will primarily be based on two ash samples. Individual ash particles will be analysed and their composition will be determined. Particles groups will be defined based on major element content and trace elements will be studied for the different groups. Approximately 100 ash particles from 2 ash samples (total 200) will be analysed.

Background

Combustion of Municipal Solid Waste
The combustion of waste aims at minimising the volume and quantity of waste while at the same time transfer the waste to energy. The advantage of MSW is that it does not contribute to the greenhouse effect since the household waste consists to a high extent of renewable material.

The term MSW is not transparent and the definitions of MSW differ from country to country. In addition, MSW is different from other traditional fuels. The difference of MSW is characterised by large variety of size of its components (from dust particles to large bulky items), from combustible to non-combustible items, from organic to inorganic origin etc. (Chandler, 1997). This waste stream can be influenced by many factors such as weather conditions and long-term variations associated with society lifestyle changes and so on.

Incineration processes for waste
Incineration of municipal solid waste with energy recovery is a process that involves several stages. The stage of waste delivery, bunker and feeding system is the preparation procedure for incineration of waste. In this stage, which kind of fuel should be used is decided based on the composition and moisture content of waste. The second stage is the combustion of MSW. Different techniques have the different requirements for the temperature and time. After incineration, the combusted waste and bottom ash are removed and collected for disposal or further use. Heat and energy recovery is the third stage of incineration processes. This stage is the utilisation of high temperature gases for the purpose of removing efficiently. The last stage is pollution control. Cooled gases and the airborne fraction of the ash (fly ash) are passed through several procedures to remove a large proportion of particulate and gaseous pollutants, before being released into the atmosphere. (Ares, 2002)

MSW combustion techniques
The combustion stage is the most important stage of the utilisation of MSW. The selection of the different combustion techniques is based on the material that will be fed to the process. The application of a technology developed for a different waste of unsuitable characteristics can often result in poor or unreliable performance. (Draft Reference Document on the Best Available Techniques for Waste Incineration, 2004)

The most commonly used techniques for MSW combustion are the mass burn (MB) techniques. However, in recent years Fluidised Bed Combustion (FBC) has been introduced as an alternative technique. (Rhyner et al., 1995) It is considered to both be an environmentally friendly and offers flexibility over the fuel used.

- Mass Burn Combustors

The fuel burns on a grate in the chamber of mass burn combustor and a refractory lining or water wall heat collection tubes cover the walls of chamber. Excess air is provided to ensure complete combustion. The temperature in the combustion chamber is usually

between 1000 ºC and 1100 ºC. The temperature drops to around 350 ºC as the flue gases reach the air pollution control system. There are different types of mass burn technologies, mainly varying in the design of the combustion chamber, for example, stationary grates, travelling grates (consisting of several overlapping rows of fixed and movable grates), rotating drums grates and grate furnaces with rotary kilns (Van Loo and Koppejan, 2002).

- Fluidised Bed Combustors

A fluidised bed combustor burns solid fuel in a turbulent bed of heated inert material, such as sand. The temperature during combustion is approximately 850 ºC. Air is blown upward from beneath the bed material. Initially, at low velocity, air simply percolates through the empty space between the stationary solid particles; this condition is called "fixed bed". When the airflow rate increase to a certain point, the vertical force exerted by the air on a particle counterbalances the weight per unit area of the bed. In such a condition, the bed of solid particles behaves like a fluid, hence the name "fluidised bed" and the phenomenon is called "fluidisation".

Combustion residues are generated at different locations in the combustor in form of deposits or ashes. The ash fractions are usually named according to the sites they were collected and removed from the system: bottom ash, cyclone ash, filter ash etc.

The fly ash produced in fluidised bed combustor is higher (around 20-50% of total residues) than traditional combustion techniques. And the bottom ash produced in traditional incineration (mass burn) constitutes the major part of the combustion residues (around 80-90%). (Wilewska, 2004)

There are two major types of fluidised bed boilers. The most common are the atmospheric boiler, which operate under atmospheric pressure conditions. The other is the pressurised boiler where combustion takes place under high pressure usually ranging from 1-2 Mpa. Both types can be constructed as stationary (bubbling) or circulating boilers.

o BFB

In Bubbling Fluidised Bed (BFB), the fluidised air has a relatively low fluidisation velocity, typically 1-3 m/s. Thus there is a well-defined boundary between the dense bottom bed and the freeboard, i.e. the area above the bottom bed. The bed medium remains in the chamber (Klein, 2002).

o CFB

A Circulating Fluidised Bed (CFB) Boiler is characterised by relatively high velocity, between 5 and 10 m/s. As a result, a large portion of the solids in the bed is carried further up in the combustion chamber. Most particles carried past the top of furnace are recirculated back to the dense bed (Klein, 2002). This has the effect of increasing gas/solid contact time and subsequently increasing combustion efficiency and of decreasing the emission of pollution.

FBC incineration plant
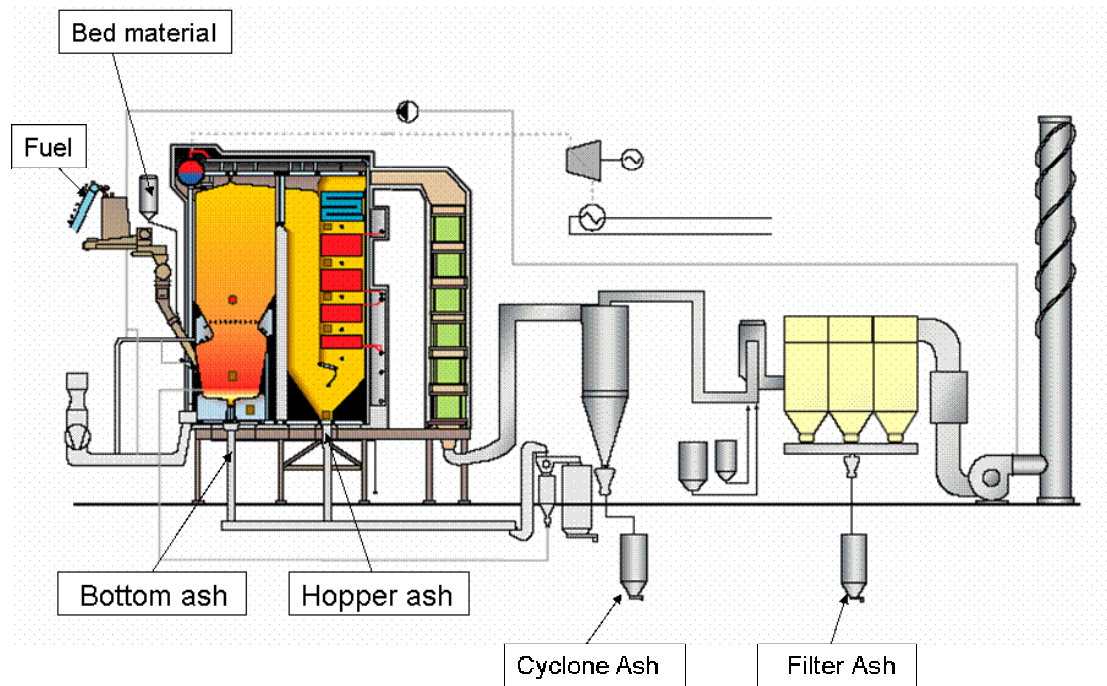
Figure 1: Diagram of BFB incinerator used in this study

Fluidised Bed Waste

Usually, lime, $Ca(OH)_2$ is added in the flue gas channel after the cyclone. So, fluidised bed combustion waste is formed when fine coal is burned in a bed of inert material and crushed lime. The lime reacts with SO_2 released during combustion of the coal to form sulphates. The bed waste product is a granular solid material composed of $CaSO_4$, CaO, other metal oxides, and fly ash. The bed waste forms first hydroxides and then carbonates when they are exposed to moisture and atmospheric air. (Evangelou, 1996)

Technique for the ashes used – Bubbling Fluidised Bed (BFB) Boiler

The ashes used in this study all come from BFB (bubbling fluidised bed) boilers, burning 100% MSW. The operation principle of BFB boiler is showed as following:

The bed of BFB boiler typically operates in a reducing atmosphere of 30% to 40% of theoretical air. This reduces the bed (combustion) temperature, which results in a reduction in nitrogen oxides (NOx). Bed temperature control is imperative to prevent bed agglomeration, good NOx control, and fluidisation. Thermocouples located in the lower furnace help the operator control bed temperature by identifying where rocks may have accumulated or identifying changes in fuel characteristics that require more or less combustion air or flue gas recirculation.

The fluidised-bed is formed by means of a specially sized fired refractory, typically sand, and fuel in the bottom of the furnace. A stream of high-pressure (to 165 bar gauge throttle pressure) fluidising air, which is upwardly flowing, suspends the bed. The high-pressure air can change the characteristics of the bed media in order to make the fuel introduced to the bed to be quickly volatilised. A significant amount of volatiles escape the bed and are burned in the freeboard area above the bed, and the fuel particles are in continuous contact with the bed media in order to burn the particles to completion. To achieve efficient combustion and low emissions, the bed temperature is controlled in the range of 760 ℃ to 870 ℃. The resultant ash becomes fly ash and is caught in the baghouse, precipitator, or scrubber. The superheater outlet temperatures can be controlled up to 510 ℃ according to the requirements.

The BFB fuel can be fired at moisture contents as high as 62% without supplemental fossil fuel firing, assuming reasonable fuel heating value. The BFB fuels include a wide range of conventional fuels and waste fuels with high moisture. (Cronin, 1999)

The BFB boiler has significant operational advantages, including: fuel flexibility, high efficiency, low environmental emissions and reduced capital costs and operating expenses. (B&W BFB Technology, 2005) The advantage of the BFB is its ability to efficiently burn a wide range of fuels including conventional fuels and waste fuels such as wood wastes and sludge, in combination or alone. Significant environmental benefits are also achieved with BFB technology. The BFB produces relatively low levels of nitrogen oxides and carbon monoxide. With the addition of limestone, it can remove high levels of sulphur dioxide without the expense of a flue gas scrubber.

Combusted ash
In BFB boiler two different ash fractions can normally be distinguished and the position of ash collected in the incinerator was showed in Figure 1.

Bottom ash consists of material discharged from the bottom of the furnace and in some cases it also contains the material collected in the grate shifting next to the furnace. (Wiles, 1996) Bottom ash comprises the major portion of the residues generated, depending on the combustion facility design, operating conditions and characteristics of the waste being combusted.

Fly ash is defined as the particulate matter removed from the flue gas stream prior to the addition of any sorbent material, but excludes ash from heat and recovery system (Wiles, 1996). Two kinds of fly ash can be distinguished: *cyclone fly ash* and *filter fly ash* (Chandler, 1997).

Cyclone fly ash consists of fine, mainly inorganic, ash particles carried with the flue gas and precipitated in the cyclones placed after the combustion unit. The ash fraction mainly consists of coarse fly ash particles.

Filter fly ash is the second and finer fly ash fraction precipitated in the electrostatic filters, fibrous filters or as condensation sludge in flue gas condensation units (normally

placed behind the cyclones). A minor part of the fly ash remains in the flue gas anyway and causes dust emissions (depending on the efficiency of the dust precipitation technology used).

Element distribution in bottom and fly ash

The transformation of an element during the combustion process depends on the form in which the element exists in the fuel, the combustion conditions and so on. Consequently these factors affect the distribution of elements between bottom and fly ashes. Volatile elements are evaporated and transported with the gas stream and finally end up in the fly ash or flue gas cleaning residues, whereas the non-evaporative elements remain concentrated in the bottom ash. General trends in distribution of different elements among different ash fraction are showed in Figure 2. (Yan, 2001) The elements are divided into four groups on the basis of their distribution among different ash fractions during combustion. It is concluded that chloride-forming elements are more concentrated in fly ash. On the other hand, the elements that form stable oxides remain in the bottom ash.
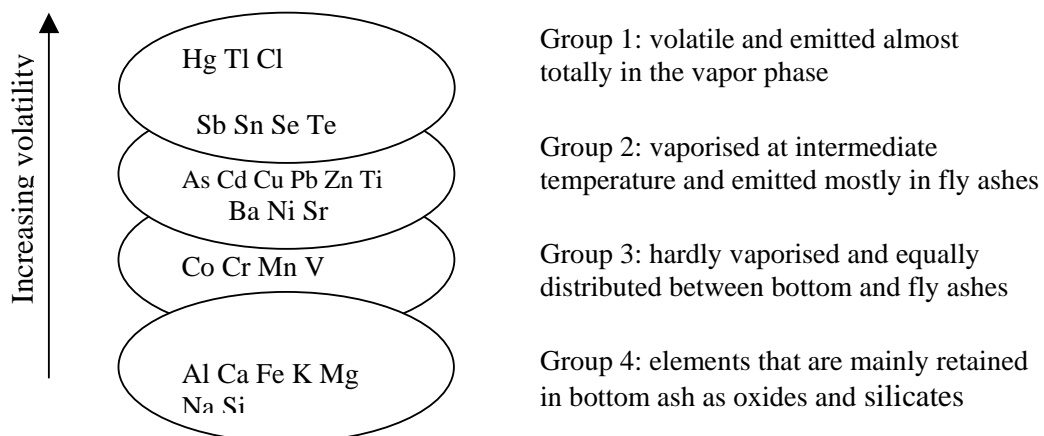
Figure 2: Volatilisation trends of considered elements during combustion

Fly ash

In this study, two fly ash samples will be analysed by LA-ICP-MS. The environmental impacts and utilisations of fly ash are based on the properties of fly ash, so, it is neccesary to study the properties of fly ash.

Generally, fly ash is the finer material (65% to 80%) of the coal ash and its properties vary greatly with coal source, type of coal burned and type of ash collector.

Chemical and Physical Properties

In general, fly ash consists of three groups of solid components. The first group has the characters of low water reactivity but possesses surface electric charge that may adsorb metal cations or oxyanions. These solids are made of SiO_2, Al_2O_3, Fe_2O_3, and TiO_2.

The second group exhibits metals or metalloids adsorbed onto the oxide surfaces. The research proved that heavy metals or oxyanions are mostly found adsorbed on to surfaces of oxides that are represented by the smallest of fly ash particles (largest surface area). The chemical behaviour and release of heavy metals and oxyanions to water is highly interrelated to the surface electric properties of oxides.

The third group includes highly water reactive components. Generally, this group includes oxides of Ca, Mg, K, Na, Ba as well as gypsum ($CaSO_4 \cdot 2H_2O$), a nearly a neutral salt, and sulphite (SO_3).

A great deal of research has been carried out on the properties of fly ash as well as the utilisations of fly ash. The physical and chemical properties of fly ash relating to pollutant reactions must be known before disposal or any other uses. Roy and Griffin proposed a fly ash classification scheme based on the physical and chemical properties, Appendix II. In this study, the groups are decided based on this classification. (Evangelou, 1996)

Environmental impact of fly ash
Fly ash is finer material collected in the stack by various filter systems of an incinerator and is always more highly contaminated than bottom ash. Currently fly ash, which is considered hazardous waste, can be co-disposed of to landfill by mixing with non-hazardous waste, often bottom ash. Hazardous waste will no longer be co-disposed of with non-hazardous waste until July 2004 under the Landfill Directive; instead it will have to go to special hazardous landfill sites.

Although the reasonable measure was taken to dispose the contaminated fly ash, because fly ash contains toxic elements, monitoring of the disposal of fly ash has also become an important issue. A problem that some consider an environmental issue is the movement of heavy metals from fly ash landfills to drainage waters. (Evangelou, 1996) In many disposal sites, the levels of heavy metals or metalloids exceeded EPA's public water supply guidelines. An important consideration is that soils that receive fly ash or ash disposal sites should always have the pH maintained at above 6 in order to keep most heavy metals immobile.

Utilisation of fly ash
Fly ash has been mainly used for landfilling in combination with bottom ash for long periods. However, at present, the biggest market for fly ash is as a replacement for cement in concrete applications. (Hwang, 2005) Dry fly ash can be used as an inert fill material or supplementary cemetitious material to improve cohesion and stability of bituminous concrete binder and soil embankments. In combination with sand, fly ash may be a supplement or substitute for cement to make a flowable fill, or as grout for concrete pavement sub- sealing.

There is also a need to expand fly ash utilisation. It is estimated that only 25% of ash generated annually are currently being utilised. This disposal of millions tons of fly ash may cause a serious environmental problem. Increased ash utilisation will not only solve

this disposal problem, but also bring about other environmental benefits. For example, when a ton of ash is used to replace the cement in concrete, 0.8 ton of CO_2 emissions can be reduced from the production of cement. At present, because of high transportation cost, ash utilisation is generally limited within a 150 miles radius of its generation location. To expand ash utilisation, it is necessary to increase the value of fly ash to allow it to be transported a greater distance.

Five generic areas have been identified as potential markets for utilisation of separated, quality-controlled fly ash products. (Hwang, 2005) They are i) cement and concrete, ii) ceramics and refractories, iii) plastic fillers, iv) metal matrix composites, and v) carbon adsorbents. Each area has the potential to consume a large volume of fly ash and even provide a significant cosy savings and improve workability.

Fly ash can also be used in agriculture. Numerous studies have been carried out which demonstrate that fly ash could be used as source of K, P, Ca, Mg, S and many of the micronutrients. Other agricultural uses of fly ash include liming, improving soil moisture holding capacity and the reclamation of surface mined lands. (Evangelou, 1996)

Studies on metal in ash or ash composition
A study in 1988 by a team of engineers at Rutgers, shows that toxic metals in municipal incinerator ash are more abundant and more soluble, and therefore more dangerous than previously thought (Clapp, 1988).

Therefore, characteristics of heavy metals in ash, behaviour of heavy metals during MSW combustion and conditions that control the fate of heavy metals in waste combustion systems have been studied to a certain extent.

The concentration and distribution of heavy metals in fly ash particles is determined by many factors, including fuel composition, the type of incinerator, conditions during combustion, the efficiency of emission control devices, and so on. Many studies about the influence of these factors on the distribution of heavy metals in ash were performed. Li et al. concluded that the physical and chemical characterisation of solid residues depends on many factors, such as the composition od feed MSW, the type of incinerator, the air pollution control devices, the operating conditions and so on. Their chemical analysis showed that in the solid residues, less volatile elements with high boiling temperatures remained in the bottom ashes and grate sifting, while more volatile elements with low boiling temperature were captured by the fly ashes. (Li et al., 2004) Wey et al. related the waste composition and operating temperature to the metal partition in the sand bed, the fly ash and in the gas pahse. Their findings indicated that the metallic chlorides decrease the absorption efficiency of heavy metals in the sand bed and increase that in the fly ash. (Wey et al., 1998) Hasselriis et al. studied the heavy metal emission data from municipal waste combustion and examined the relationship between particulate matter, emission controls, and emission factors for the heavy metals. Their findings indicated that the waste composition and the combustion and emission control technology employed all contribute to the variability of metals and particulate emissions. (Hasselriis et al., 1996)

Querol et al. studied the trace elements affinities. It is concluded that different elements have different material affinities in the combustion waste. (Querol et al., 1995) Spear showed that the glass is an important location for V, Cr, Cu and Zn and Cr and V are thought to be concentrated in magnetite, although the major source in the ash is the glass. (Spear, 2004)

Toledo et al. explained the behaviour, fate and/or partitioning of some heavy metals in BFB incinerator with a conceptual model. (Toledo et al., 2005) They made the conclusion that the partitioning of heavy metals is governed by the combination of kinetics and diffusion with fluid dynamics in the fluidised bed.

Laser ablation-ICP-MS

Inductively couple plasma-mass spectrometry is widely used for the analysis of trace elements in solution. Solid samples are typically analysed as liquid after extraction or digestion using strong acids. Alternatively, direct analysis of solid can be performed using sample introduction system including laser and spark ablation. Laser ablation-ICP-MS consists of a sample introduction system using a laser beam to ablate a small amount of material at the surface of a sample, and an ICP-MS instrument for the online analysis of sampled material (Günther, 2005). This technique is typically used for the analysis of trace elements in solid samples, but it has also been used for major element analysis as the ICP-MS offers high sensitivity, wide dynamic range and relatively simple spectra for most elements in the periodic table. LA-ICP-MS is interesting because it allows the direct analysis of solid samples with minimal sample treatment. More importantly, LA-ICP-MS opens up the possibility for the spatially resolved analysis of trace elements and the determination of their distribution in a sample (Günther, 2005).

The principle of LA-ICP-MS is relatively simple; solid particles are physically ablated by laser beam with the surface of the sample. The aerosol produced by laser is carried in a stream of argon into the torch of the ICP-MS. In the plasma, the aerosol is vaporised, atomised and ionised, and the produced ions are introduced into a mass spectrometer where they are separated based on their mass-to-charge ratio for subsequent detection. Therefore, the technique provides elemental information.

Figure 3 illustrates the experimental setup for the direct analysis of ash samples by LA-ICP-MS (Günther, 2005).
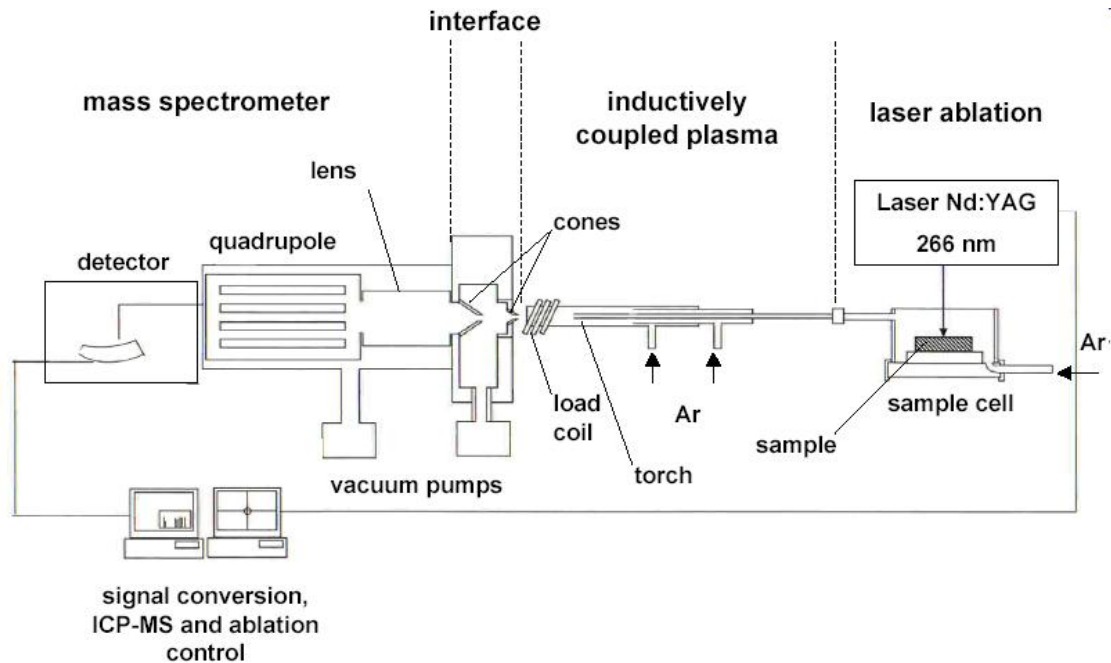
Figure 3: Schematic set-up of LA-ICP-MS (Dussubieux, 2005)

The setup of LA-ICP-MS comprises the following main component.

1. Laser system

For many applications the use of UV wavelengths (266, 213 and 193 nm) for laser ablation is more suitable than longer wavelength radiations (visible and IR) for which the ablation is accompanied by sample melting and which do not allow the ablation of all minerals. Therefore, laser systems used for LA-ICP-MS today are typically based on UV laser beams. The beam is either obtained from an Nd:YAG or an eximer laser source. While eximer lasers directly produce beams in the UV at 193 nm, the beams obtained from Nd:YAG lasers are at higher frequency (IR) and their frequency needs to be changed using optical frequency converters (quadrupling to 266 nm or quintupling to 213).

2. Optics

Optics are used to focus the laser beam onto the sample, homogenise the beam and change the frequency of the laser beam. Various techniques for homogenising the energy density across the beam at the sample surface have been studied and significant improvements have been achieved to ensure an equal energy distribution throughout the ablation spot and obtain reproducible ablation craters.

3. Ablation cells

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The ablation cell is used to accommodate the samples and is designed to maximise transport efficiency and minimise dead volumes which could result in contamination of the cell between analyses of a sample. The volume of the ablation cell also affects the signal as result of dilution in the cell. The ablation cell is placed on a stage which can remotely be moved at micrometer resolution. Using a CCD camera or a microscope, it is possible to precisely select ablation spots or lines on the sample surface.

4. ICP-MS system

The laser ablation unit continuously provides ablated aerosols to the ICP-MS and it is therefore important that the ICP-MS can analyse selected elements at a high time resolution if changes in samples composition have to be determined. Currently, the majority of ICP-MS systems used with LA employ a quadrupole mass filter. This configuration offers a sufficiently fast scanning capability with the possibility to scan over the full mass range in less than a second, even for an extended suite of elements.

Other mass spectrometer configurations available for ICP-MS are time-of-flight and sector field, but they are far less common that quadrupole.

An LSX-200 laser ablation system (Cetac, Omaha, NE, USA) was used together with an Elan 6000 quadrupole ICP-MS instrument (Perkin Elmer Sciex, Canada). The instruments were connected using Tygon tubing.

Experimental

Ash samples
Sample description
The ash samples used in this study are cyclone fly ash and all come from bubbling fluidised bed boilers, burning 100 % municipal solid waste.

The first ash sample in this study, labelled SAMPLE A, was produced in a 20 MW boiler in autumn 2002. Ammonia was added to the combustion zone.

The ash sample labelled SAMPLE B was produced during spring 2000 in a 15 MW boiler. To clean the flue gases sodium bicarbonate $NaHCO_3$ coated with ammonia NH_3 was added to the combustion zone.

In addition, lime $Ca(OH)_2$ was added in the flue gas channel after the cyclone when all ashes were produced.

Chemical characteristics of ash samples
The chemical properties of ashes have been studied by means of ICP-MS analysis after digestion of the samples (Appendix I). Ash composition provided as oxides was transferred to the concentrations of corresponding elements (Table 1). In both samples, the major components are SiO_2, Al_2O_3, CaO and Fe_2O_3. Three major of the components, i.e. Al_2O_3, SiO_2 and Fe_2O_3, do not vary to a great extent. Ash SAMPLE A has slightly higher Al_2O_3 and Fe_2O_3 contents while SAMPLE B has a slightly higher SiO_2 content. The large amount of CaO in fly ashes is due to the presence of residues from the lime flue gas treatment process. The higher Na_2O content in ash SAMPLE B is due to the addition of sodium bicarbonate ($NaHCO_3$) to the combustion zone for the purpose of cleaning the flue gases.

Table 1: Chemical characteristics of fly ashes used in this study: ash composition

Element	Concentration (%TS)	
	SAMPLE A	*SAMPLE B*
Si	17.9	19.3
Al	12.9	10.4
Ca	12.7	12.1
Fe	3.56	2.98
K	1.64	1.84
Mg	1.52	1.57
Mn	0.247	0.183
Na	2.81	4.15
Ti	1.19	0.97

Table 2 provides trace element concentrations in the two ash samples. The variation in element composition between the two samples is generally relatively small. The concentrations of Cu and Zn in ash SAMPLE A are much higher than those of SAMPLE B. This variation is likely to be due to the different boilers used and the different materials that were added to the combustion zone.

Table 2: Chemical characteristics of fly ashes used in this study: trace element composition

Element	Concentration (mg/kg TS)	
	SAMPLE A	SAMPLE B
As	25.8	46
Ba	2710	2950
Cd	11.4	14.3
Co	34.5	19.9
Cr	549	628
Cu	5890	3840
Ni	221	159
Pb	1500	1140
S	6590	7930
Sn	117	72.9
Sr	400	373
V	49.7	61.5
Zn	9010	5930

LA-ICP-MS analysis

Fly ash samples are a heterogeneous mixture of different kinds of particles; hence the average composition of the particulate sample obtained by bulk methods does not necessarily describe well the distribution of elements in the sample. The direct analysis of single particles may provide a further knowledge on the distribution of elements and further understanding of metal binding to ash particles.

Ash particles were dispersed and fixed as far as possible from each other using regular double-side tape. The tape was then fixed onto a PTFE substrate. The particles were examined under a CCD microscope with magnification 400x and particles of interest were identified. Particles were photographed and analysed by LA-ICP-MS.

Analysis of individual particles was performed with an LSX-200 laser ablation system (Cetac, Omaha, NE, USA) coupled to an Elan 6000 quadrupole ICP-MS instrument (Perkin Elmer Sciex, Canada).

Surface analysis was conducted through the ablation of a scan line across the surface of particles. The position of the laser on the surface of the sample is observed using a high-resolution camera attached to a monitor. A pulsating Nd:YAG laser beam operating at 266nm (quadrupled frequency) was used to ablate the ash particles. An aerosol from the sample produced by laser is introduced into ICP-MS and the isotopes of interest are analysed. The scanning speed was kept at a low speed (10 μm s^{-1}) and with a small spot size: 25μm, while energy was optimised to provide a sufficient signal. For the ICP-MS, a short dwell time (5 ms) was used together with a short quadrupole settling time. Argon gas flowing through the sample cell was used as a blank. The laser ablation parameters and ICP-MS acquisition parameters used in this study are showed in Table 3.

Table 3: LA-ICP-MS instrument operating parameters

Laser ablation parameters		ICP-MS acquisition parameters	
Parameter		Analysed isotope	^{23}Na, ^{24}Mg, ^{27}Al, ^{28}Si, ^{34}S, ^{37}Cl, ^{39}K,
Laser type	Nd:YAG		^{44}Ca, ^{48}Ti, ^{51}V, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{58}Ni,
Mode	Q-switched		^{59}Co, ^{63}Cu, ^{64}Zn, ^{75}As, ^{88}Sr, ^{107}Ag,
			^{114}Cd, ^{120}Sn, ^{121}Sb, ^{138}Ba, ^{208}Pb
Wavelength	266nm	RF power	Quadrupole ICP-MS
Ablation pattern	Scan line	Plasma gas	16.0 L min^{-1}
Energy level	0.8 mJ	Auxiliary gas	0.9 L min^{-1}
Spot size	25 µm	Carrier gas	1.0 L min^{-1}
Repetition rate	20Hz	Dwell time	5 ms
Scan speed	10 µm s^{-1}	Sweeps/reading	5

Calibration and normalisation

In order to minimise the measurement uncertainties, two methods – calibration and normalisation were introduced in this study.

Calibration with an external standard

Calibration with an external standard reference material SRM 1633b (National Institute for Standardization and Testing, USA) is used as external standard for the purpose of calibration of the LA-ICP-MS. SRM 1633b is a bituminous coal fly ash that was sieved through a nominal sieve opening of 90 µm (170 mesh) and then blended to assure homogeneity. The concentration of elements in SRM is provided in Appendix V.

The reference material was pressed into a pellet for analysis by laser ablation. The material was first mixed with a binder material (Bornitrid) in a ratio of 7:3 and pressed into a pellet using 8 tons of pressure. The mass of reference material and binder material are 1.4 and 0.6 g respectively. Furthermore, one binder pellet is also prepared to calculate the signal corresponding to the reference material in pellet.

During the lab work, blank (which means the signal of different elements without ablation), pellet with binder, pellet with binder and reference material were analysed before sample analysis by LA-ICP-MS. The analytical sequence comprises; (a) analysis of the argon blank; (b) analysis of the pellet with binder; (c) analysis of the pellet with binder and reference material; (d) analysis of the NIST Soil for normalisation; (e) analysis of ash sample. Calculations are based on average values.

Because the SRM is mixed with a binder, the intensity for the SRM cannot be given directly by LA-ICP-MS, it must be calculated by the following equation:

$$0,30 * Intensity(binder) + 0,70 * Intensity(SRM) = Intensity(binder + SRM)$$

or $\quad Intensity(SRM) = \left[Intensity(binder + SRM) - 0,30 * Intensity(binder)\right] * \dfrac{1}{0,70}$

Then, the intensity of standard is used for calibration of sample. The concentrations of sample particles were calculated by means of the following equations:

$$Sensitivity = \frac{NetIntensity\,of\,analyses\,of\,SRM}{certified\,concentration\,of\,SRM}$$

$$NetIntensity = Intensity\,mean - blank\,mean$$

$$ParticleConcentration(unnormalised) = \frac{NetIntensity\,of\,analysed\,ash\,particle}{Sensitivity}$$

Normalisation

In addition to the calibration using SRM 1633b, normalisation of LA-ICP-MS signals based on internal standardisation was introduced in this project taking into account uncertainties in the calibration. To compensate for between-day variations in sensitivity a routinely analysed NIST soil reference material in the form of pellet was used as the external standard. Furthermore, an internal standard for normalisation was chosen from the elements analysed in the experiment. The sum intensity of Al, Si, Ca, Fe, Na, Mg, K, Ti and S was considered for normalisation as they represent major elements used in particle type determination and their sum should be relatively constant. All signal intensities from particle analysis were normalised against this sum.

Normalisation can be estimated from the following equations:

$$Ratio\,1-\# = \left(\frac{Intensity\,of\,day\,1}{Intensity\,of\,day\,\#}\right)_{NIST}$$

This ratio indicates the difference in sensitivity between different workdays.

$$Intensity(isotope - Ratio) = Intensity(isotope) * Ratio$$

The intensity of elements in different days was corrected by means of multiplying ratio between different workdays, in order to correct the variation of instrument in different days.

$$Intensity(element) = \frac{Intensity(isotope - Ratio)}{relative\,abundance}$$

In order to know the intensity of element of interest, the intensity of isotope was divided by isotopic abundance.

$$NormalisedValue = \frac{Intensity(element)}{Intensity(Sum)}$$

The sum intensity of Al, Si, Ca, Fe, Na, Mg, K, Ti and S was selected for normalisation as the internal standard, all intensity analysed during lab work were normalised against the sum intensity.

$$NormalisedValue = \frac{Intensity(isotope)}{relative\,abundance * Intensity(Sum)} * \left(\frac{Intensity\,of\,day\,1}{Intensity\,of\,day\,\#}\right)_{NIST}$$

Results and discussion

For this thesis, two ash samples were analysed by LA-ICP-MS, i.e. ash SAMPLE A and ash SAMPLE B. Approximately 100 ash particles were analysed from each ash sample (total 200).

According to the fly ash classification scheme proposed by Roy and Griffin (Appendix II), the ash particles were divided into seven groups based on the calibration results. The group are presented in Table 4.

Table 4: Ash particle classification based on major components.

Group	Sialic component (Σ Si + Al+Ti)	Calcic component (Σ Ca + Mg +Na+ K)	Ferric component (Σ Fe + S)
1. Sialic (essentially Al)	>88(%)	0-12	0-12
2. Sialic (essentially Si)	>88(%)	0-12	0-12
3. Fersic (Fe + sialic)	48-77	0-29	23-52
4. Calsialic (Ca + sialic)	48-<77	>29-52	0-23
5. Modic	>48-88	0-29	0-<23
6. Ferric (Fe)	<48	0-29	>23
7. Calcic (Ca)	<48	>29	0-23

The principle to divide group in this study is decided by the number of ash particles in each group. The particles were divided into 7 groups based on the classification proposed by Roy and Griffin firstly. If the number of ash particles was only one or two in one group for both ash samples, this group was be deleted, such as the group 7 in Appendix II. If there were too many ash particles in one group, this group was divided further based on the detail conditions. For example, group 1 in Appendix II was divided into two groups dominated by Al and Si, respectively. The group is divided based on the percentage of the concentration of essential element to the sum concentration of major elements.

In order to minimise the measurement uncertainties and be convenient to analyse the experiment data, calibration and normalisation were performed in this study. The results of calibration and normalisation were analysed based on the principle of fly ash classification.

Comparison between two ash samples was also performed in order to identify the different distribution of heavy metals in different particles.

Ash particle characterisation with calibration

The average concentrations of two ash samples were calculated to compare with the chemical characteristics by ICP-MS (Tables 1 and 2) analysis in order to check the difference between the single particle analysis and bulk analysis. According to the comparison between Table 5 and Tables 1 & 2, the concentrations of most elements by single particle analysis are lower than those by bulk analysis. For major components in ash SAMPLE A, the concentrations of Al, Si and Ca by single particle analysis are lower, but the concentration of Fe is higher compared with those by bulk analysis. Among the other elements in ash SAMPLE A, the concentrations of Ti and Cu by single particle analysis are higher and the concentrations of Ba and Pb are similar for both analysis methods. The possible reason for this is that there are a few abnormal values in these four elements: Ti, Cu, Ba and Pb.

Table 5: Average value for all particles in two ash samples

Element	Average concentration (%)		Element	Average concentration (mg/kg)	
	SAMPLE A	SAMPLE B		SAMPLE A	SAMPLE B
^{23}Na (%)	1.32±1.15	3.70±2.86	^{51}V	20.6±48.0	41.6±79.5
^{24}Mg	1.16±1.83	2.19±2.95	^{53}Cr	111±284	156±474
^{27}Al	9.60±10.4	10.5±9.38	^{55}Mn	903±849	1550±1612
^{28}Si	9.44±7.88	20.8±13.7	^{58}Ni	92.9±179	125±178
^{34}S	0.05±1.05	0.70±3.26	^{59}Co	17.6±24.5	25.6±31.8
^{39}K	1.03±0.84	2.02±1.54	^{63}Cu	7545±43221	2069±3295
^{44}Ca	4.35±7.68	18.4±22.2	^{64}Zn	3964±13664	3696±3957
^{48}Ti	4.32±3.71	1.51±2.29	^{75}As	2.18±7.03	7.79±20.4
^{57}Fe	7.08±17.0	9.23±14.9	^{88}Sr	270±421	582±1373
			^{114}Cd	3.05±8.72	0.15±2.00
			^{138}Ba	2912±20893	2287±5648
			^{208}Pb	1513±10292	730±533

Comparison between single particle analysis and bulk analysis for ash SAMPLE B is different from the comparison for ash SAMPLE A. The concentrations of most elements by single particle analysis are similar with those by bulk analysis. For major components, the concentrations of Al and Si are almost same by both analysis methods. The concentrations of Ca and Fe by single particle analysis are higher than those by bulk analysis; the high value of Ca is because lime was added in the flue gas channel. The concentrations of Co and Sr by single particle analysis are higher. It should be noticed that the concentration of Cd in this ash sample is much lower than that by bulk analysis.

Compared with the results of two ash samples, for most elements, the average concentrations of particles in SAMPLE A are much lower than those in SAMPLE B except for some elements. Elements Ti, Cu, Zn, Cd, Ba and Pb show higher values in ash SAMPLE A. This situation is quite different from the results from ICP-MS analysis (Tables 1 and 2). The reason for this is possible that the particles for analysis are chosen randomly.

Results of ash SAMPLE A

For single particle analysis of ash SAMPLE A, 92 of 102 ash particles were selected to make groups based on the classification in Table 4, the other ten particles do not correspond with the principle. The results are presented in the table 6 and average concentrations for each group are plotted in Figure 4.

It can be seen from the results of SAMPLE A that in Groups 1, 6 and 7, the concentrations of Na and K have lower values than others group. At the same time, the concentrations of Mg, Ca, Ti and Fe in group1 are lower than others as well.
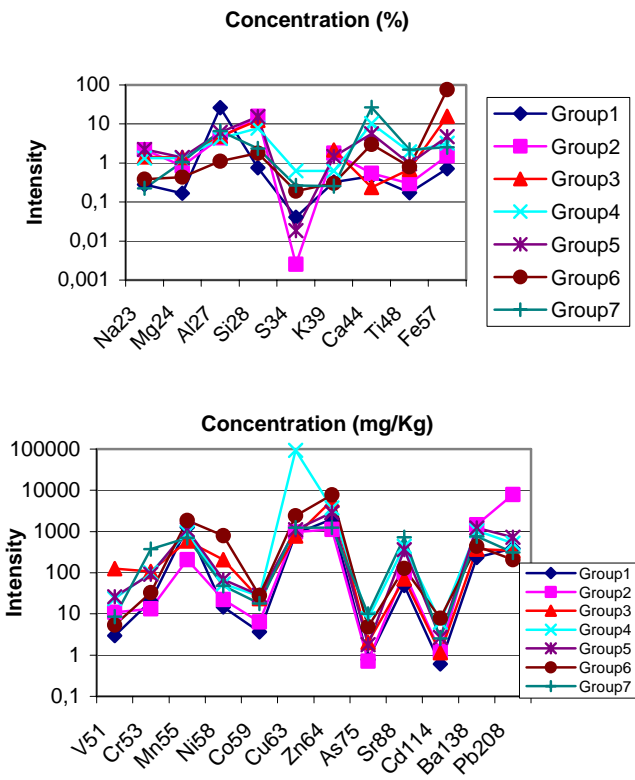

Figure 4: the average concentration of elements in ash SAMPLE A. Top: major elements (concentrations in %); bottom: trace elements (concentrations in mg/kg).

Table 6: the average concentration of elements of ash SAMPLE A

Isotope	*Group1*	*Group2*	*Group3*	*Group4*	*Group5*	*Group6*	*Group7*
	22 particles	14 particles	6 particles	7 particles	32 particles	5 particles	6 particles
^{23}Na (%)	0.28±0.55	2.19±1.33	1.43±1.06	1.34±0.86	2.23±0.67	0.39±0.28	0.22±0.15
^{24}Mg	0.17±0.18	0.85±1.50	1.39±0.79	1.33±0.86	1.40±0.64	0.43±0.66	1.06±1.02
^{27}Al	25.9±9.83	4.43±3.38	4.86±2.02	4.26±2.25	6.11±2.73	1.11±1.75	6.57±11.6
^{28}Si	0.75±1.21	15.7±7.63	12.3±6.57	7.86±5.35	15.4±4.78	1.79±1.96	2.38±3.38
^{34}S	0.04±0.05	0.003±0.006	0	0.63±0.66	0.02±0.05	0.19±0.20	0.27±0.29
^{39}K	0.33±0.49	1.80±0.59	2.16±1.17	0.63±0.45	1.45±0.60	0.30±0.19	0.26±0.16
^{44}Ca	0.46±1.00	0.55±1.11	0.24±0.48	10.3±8.18	5.62±3.56	2.99±6.29	26.4±10.8
^{48}Ti	0.17±0.18	0.30±0.16	0.69±0.67	1.94±1.69	0.97±0.44	0.80±1.21	2.17±3.37
^{57}Fe	0.72±0.69	1.52±1.25	15.6±8.16	3.20±2.22	4.73±2.54	76.5±22.2	2.52±5.33
^{51}V(mg/Kg)	2.98±3.63	11.0±27.2	125±149	23.7±21.2	26.3±20.0	5.33±7.52	8.61±17.8
^{53}Cr	20.7±34.3	13.3±23.8	108±161	100±103	91.2±108	32.7±70.3	376±592
^{55}Mn	1261±929	208±145	590±484	939±527	1111±877	1846±773	708±888
^{58}Ni	14.8±16.3	22.6±20	209±91.9	53.2±36.5	68.6±32.8	793±232	48.1±99.3
^{59}Co	3.68±2.71	6.36±4.45	23.7±9.68	27.0±17.5	28.7±34.7	28.1±17	17.9±32.7
^{63}Cu	883 ±706	985±1398	782±416	93381±148863	1101±687	2408±2506	1247±1575
^{64}Zn	1992 ±4473	1116±1047	5674±9704	3760±2967	2885±2032	7795±1080	1254±1538
^{75}As	0.78±2.38	0.71±2.19	2.05±4.19	7.81±8.34	1.80±2.61	4.81±5.13	10.1±23.5
^{88}Sr	49.3±49.4	99.6±40.4	71.0±50.6	442±198	362±138	128±121	728±654
^{114}Cd	0.61±0.83	1.23±1.67	1.14±1.68	6.31±5.94	2.67±2.45	7.84±11.5	2.53±4.56
^{138}Ba	234±182	1460±3569	376±325	1051±610	1229±1500	436±527	772±990
^{208}Pb	387±405	7892±27769	344±187	522±291	721±454	208±140	308±134

According to the results for SAMPLE A, the lowest values for most trace elements are in group 1 or 2 while the highest values are in group 6 or 7. Vanadium shows the lower content in group 1 and 2 and higher value in group 3. Chromium concentration in groups 1 to 3 is not detected in all particles (minus or zero value); Cr concentrations are higher in group 4 and 5, and group 7 has the highest values. The concentration of Mn in group 2 is lower than the other groups. Group 6 has the highest Ni content. For Cu, the value in group 4 which is more than ninety thousand is much higher than others while the other values are mainly from hundreds to thousands. Average Zn concentrations are similar for all groups with values in the thousands. Arsenic and Cd have higher concentrations in groups 4 to7 with more particles containing these elements. As for Pb, except for an abnormal value in group 2 which is more than twenty thousand, the concentrations in other groups is mainly about hundreds.

Results of ash SAMPLE B
For single particle analysis of ash SAMPLE B, 93 of 100 ash particles were selected to make groups according to the classification in Table 4, the other seven particles did not correspond to any group. The results are provided in the Table 7.

Table 7: the average concentration of elements of ash SAMPLE B

Isotope	Group1	Group2	Group3	Group4	Group5	Group6	Group7
	5 particles	3 particles	5 particles	32 particles	39 particles	3 particles	6 particles
^{23}Na (%)	0.62±0.39	2.09±3.07	1.46±1.30	3.97±2.33	4.85±3.11	2.38±2.26	2.78±3.26
^{24}Mg	0.17±0.11	0.25±0.34	3.43±1.03	2.54±1.94	1.84±2.50	0.64±0.86	2.49±2.78
^{27}Al	32.5±8.72	1.83±2.93	6.91±1.44	9.51±3.38	11.5±10.6	1.65±1.59	3.21±4.52
^{28}Si	2.51±2.23	15.5±15.9	14.2±3.08	21.7±9.70	28.5±13.8	4.68±6.52	5.76±8.27
^{34}S	0	0.21±0.36	0	0.66±1.16	0.48±1.08	0.45±0.44	8.05±10.8
^{39}K	0.29±0.18	0.85±1.17	3.41±1.93	1.76±1.22	2.87±1.48	0.88±0.76	0.69±0.67
^{44}Ca	0.42±94	1.12±1.94	3.13±4.58	28.6±9.61	8.80±6.87	3.84±4.57	83.3±23.8
^{48}Ti	0.27±0.25	0.32±0.45	1.21±0.68	2.08±2.60	1.39±1.85	0.22±0.17	2.41±4.84
^{57}Fe	0.63±0.36	1.28±1.99	22.5±6.15	6.91±5.11	7.40±8.01	79.±19.1	2.80±4.34
^{51}V(mg/Kg)	1.95±4.35	15.6±27.0	102±64.6	51.2±71.8	46.8±89.0	7.34±12.2	15.6±28.0
^{53}Cr	56.2±48.4	33.2±57.5	83.9±101	191±186	92.5±98.4	85.8±65.6	814±1870
^{55}Mn	925±857	206±288	3072±1655	2151±1839	957±754	1825±32.9	1733±2191
^{58}Ni	14.0±8.01	21.6±32.2	249±60.2	127±148	95.6±93.0	866±163	48.4±79.2
^{59}Co	6.19±3.41	14.8±24.6	31.8±6.62	33.4±33.7	24.4±34.6	28.7±3.87	21.1±38.0
^{63}Cu	1320±1260	1226±1331	841±672	1890±1208	2096±1727	11845±17132	1304±795
^{64}Zn	1789±3066	3876±5633	2095±1992	4884±5129	3511±3119	4576±3467	3531±4010
^{75}As	0.021±0.03	2.52±2.21	1.78±3.68	8.70±9.55	5.64±7.25	13.6±21.1	38.0±75.2
^{88}Sr	158±167	98.9±102	91.2±122	557±265	450±768	4379±7345	1081±952
^{114}Cd	0.11±0.24	0.001±0.002	0.80±0.55	0.57±0.85	0.64±1.31	4.43±7.04	0.24±0.46
^{138}Ba	1207±1405	470±521	1132±538	1810±1432	2294±3891	17807±29404	1486±1114
^{208}Pb	211±72.5	787±755	309±321	798±492	894±574	752±687	455±366

Average concentrations for each group are plotted in Figure 5. Individual results in Table 7 and average results for ash SAMPLE B shows that Group1 has the lower concentrations of elements Na, Mg, K, Ca, Ti and Fe compared to the other groups.
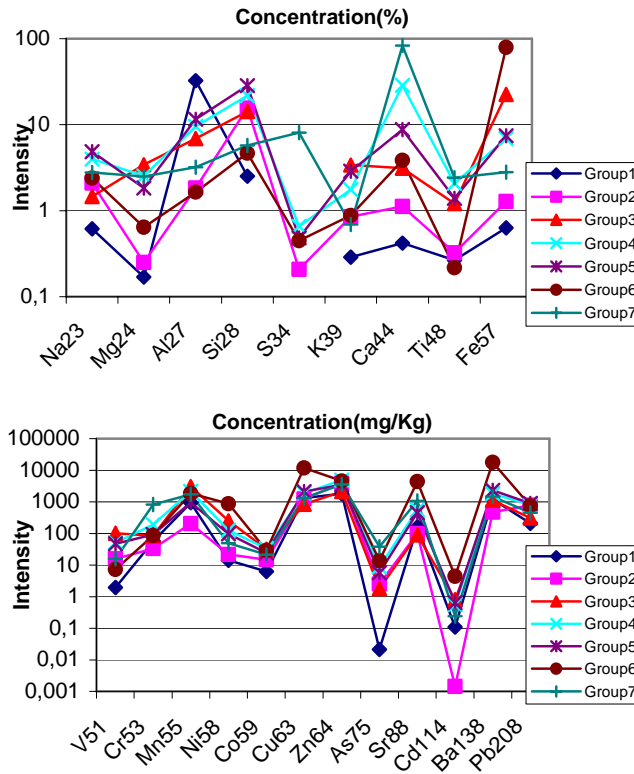

Figure 5: the average concentration of elements in ash SAMPLE B. Top: major elements (concentrations in %); bottom: trace elements (concentrations in mg/kg).

Results for ash SAMPLE B are similar with those for ash SAMPLE A: for most of trace elements, group 1 or 2 have lower concentrations, while groups 6 or 7 have higher concentrations. Vanadium has the lowest content in group 1 and highest value in group 3. The situation for SAMPLE B is almost same as for SAMPLE A: the graph of Cr concentration from group 1 to 3 is not constant and there are many abnormal values (minus or zero value); the values in group 4 and 5 are more continuous and the group 7 has the highest value. Group 2 has lower Mn content compared to the other groups. The concentration of Ni in group 6 is highest in seven groups. For Cu, the value in group 6 which is more than ten thousand is much higher than normal values mainly from hundreds to thousands. The average concentrations of Zn are about thousands. The situations of As and Cd are also similar like that in ash SAMPLE A. About Ba, there is one high value in group 6. The average concentrations of Pb in this sample are reasonable which values are about hundreds.

Comparisons of concentrations in the two ash samples

It can be seen from the comparisons of seven groups between these two ash samples (Appendix III) that: except for some abnormal values, the two ash samples have similar values and trends in the graphs. According to the figures, for major elements (Na, Mg, K and Ca), ash SAMPLE B has a little higher content than SAMPLE A. For all groups, the concentrations of Na in ash SAMPLE B are higher than those in SAMPLE A; the reason for it is that $NaHCO_3$ was added to clean the flue gases in ash SAMPLE B. Furthermore, ash SAMPLE B has lower Cd content than SAMPLE A for most groups, because there are more zero or minus values in ash SAMPL B. The values of Fe and As are similar between two samples; for elements V, Cr and Co, the concentrations of two samples are similar while the values in group 2 of ash SAMPLE B are much higher than those of SAMPLE A; the concentrations of Mn are mainly from hundreds to thousands; the situations of Cu are similar with that of Mn, the values are mainly from hundreds to thousands, except for the abnormal values in group 4 of SAMPLE A and group 6 of SAMPLE B; the values of concentration of Zn are mainly about thousands and the values of Pb are mainly about hundreds, except for the abnormal value in group 2 of SAMPLE A.

Discussion about some abnormal values of ash samples

Minor error caused by instrument uncertainties may occur during analysis. Therefore, there are a few abnormal values in the measurement. Unfortunately, we are not sure that these abnormal values are caused by instrument uncertainties or this is the fact for these particles.

For SAMPLE A, there are many abnormal values in 7 groups, for example, Cu in group 4 and Pb in group 2, shows in Figure 6 and 7.

It can be seen from Figure 6 for Cu concentration graph that there are three particles which are much more than the other values in group 4. In this group, there are seven particles totally; it means there are almost 50% high values appearances. This indicates that the high values for Cu actually are a feature of group 4. According to Figure 7 for Pb concentration graph, one value in group 2 is much higher than others. It is possible to mean there is possibility to have abnormal value in this group.

For SAMPLE B, the Cu and Ba concentrations show abnormal values in group 6, it can be seen from Figure 8 and 9.

There is only one abnormal value for Cu and Ba concentration in group 6 respectively. The reason for it is that there are only three particles in this group. It is possible to mean there is 1/3 possibility to have abnormal value in this group.
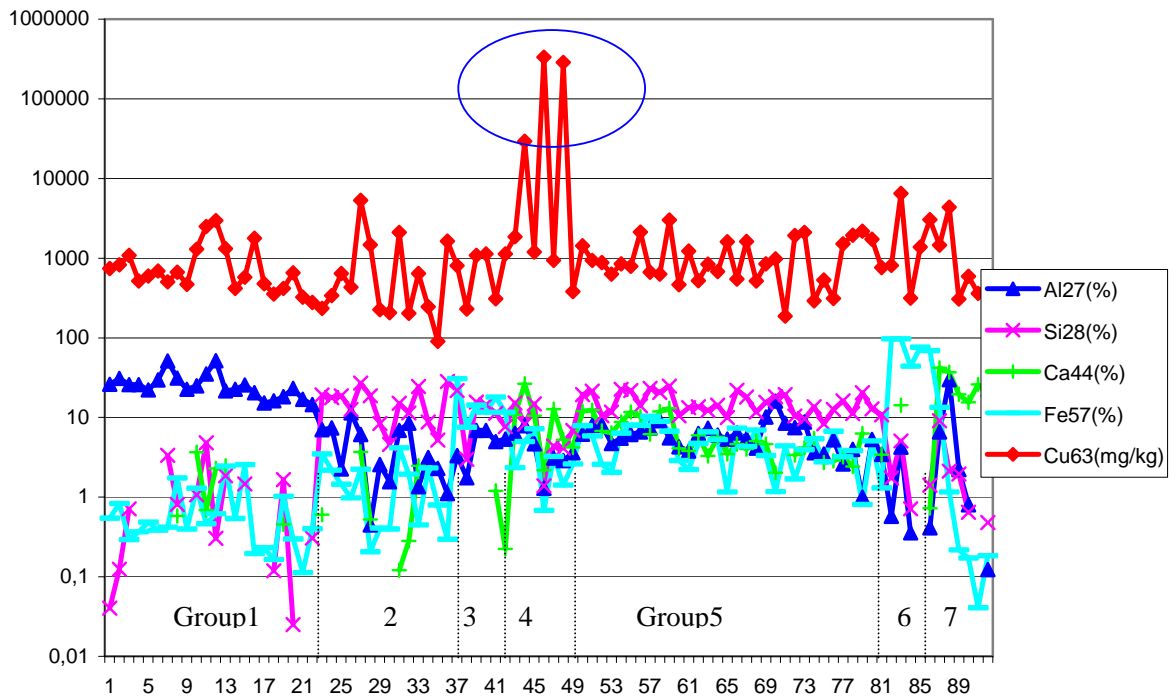
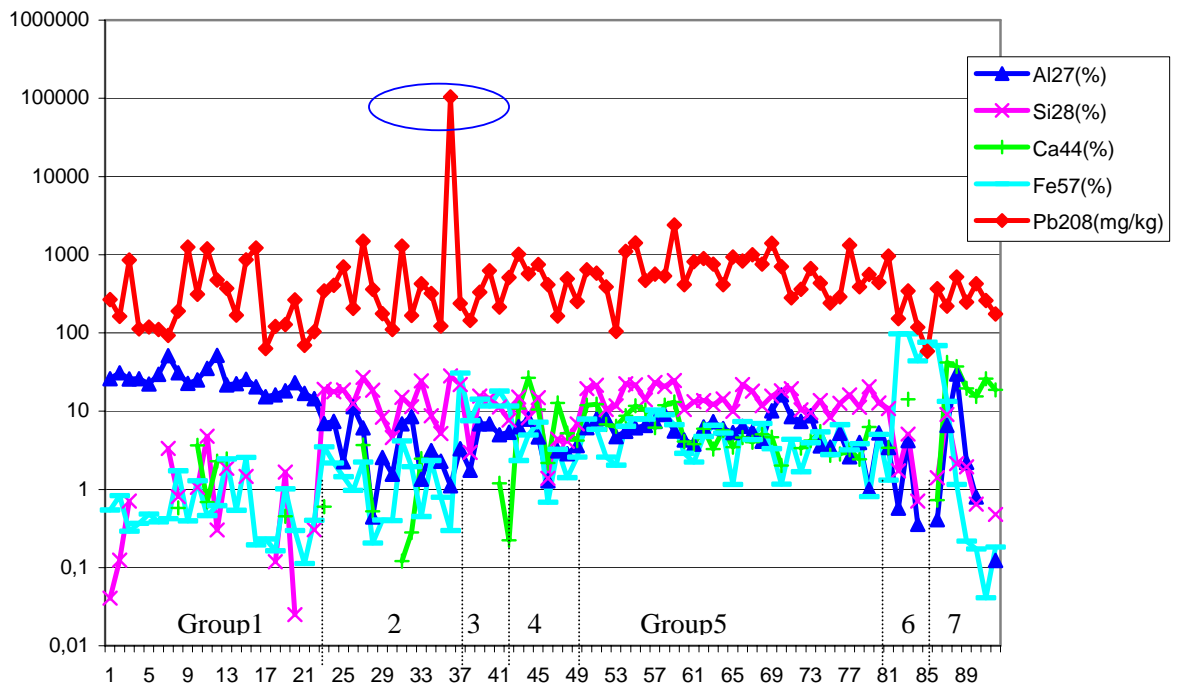**Figure 6: the abnormal value of Cu concentration in SAMPLE A**

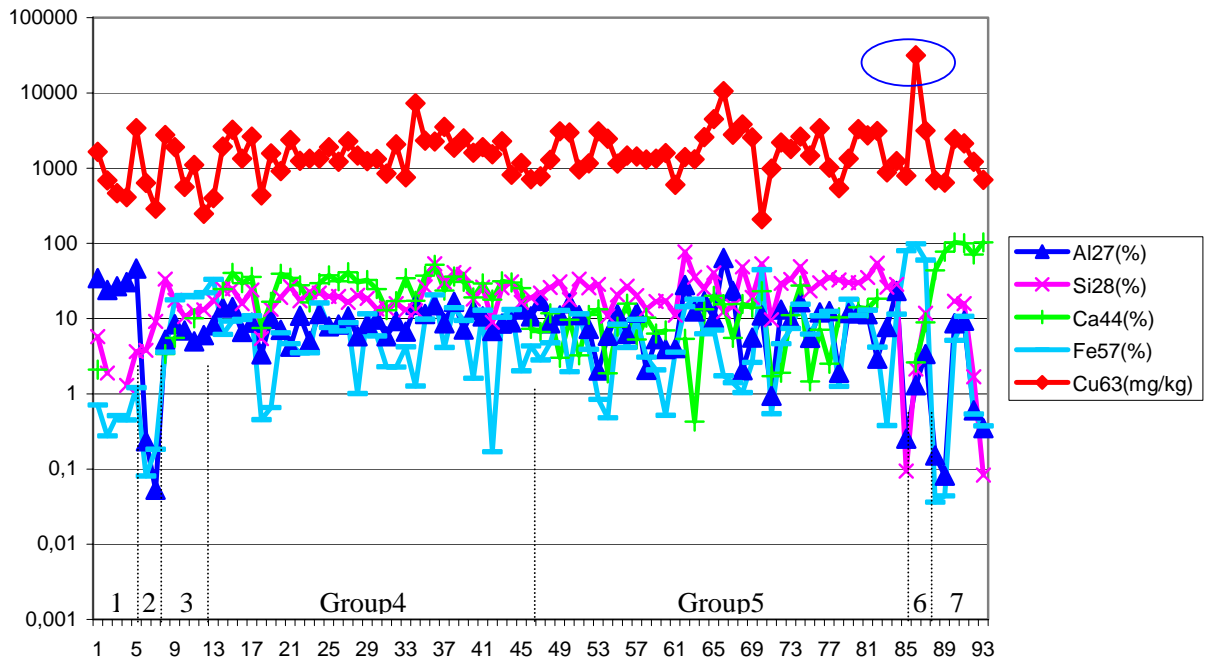**Figure 7: the abnormal value of Pb concentration in SAMPLE A**

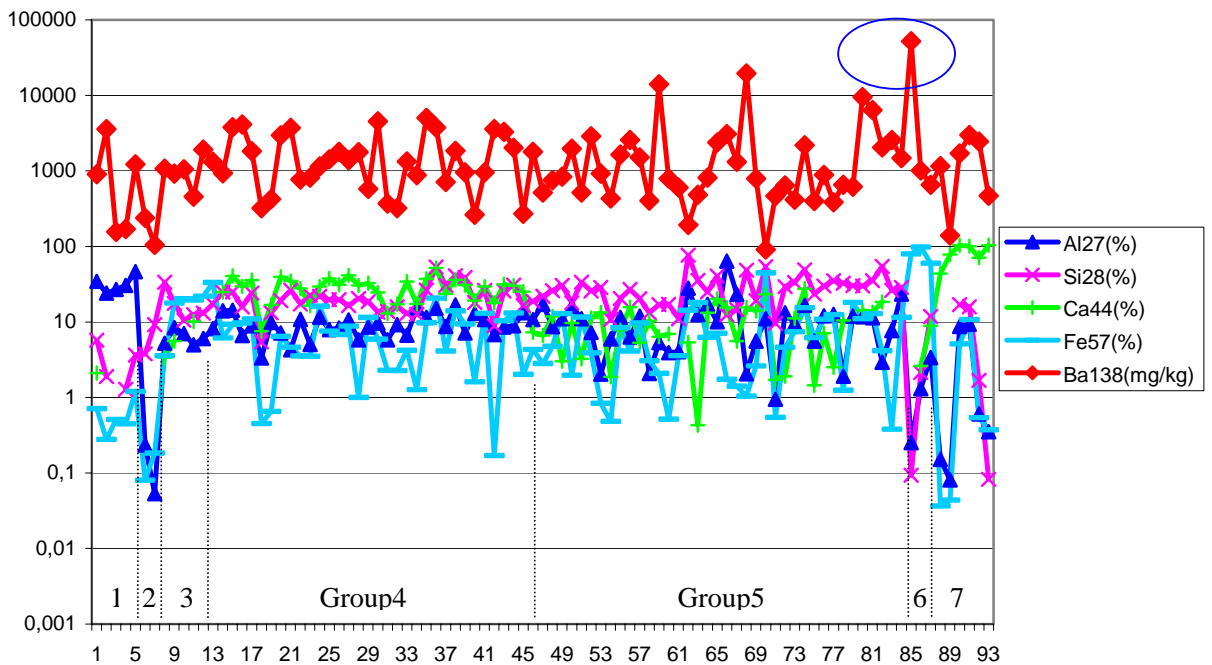**Figure 8: the abnormal value of Cu concentration in SAMPLE B**

Figure 9: the abnormal value of Ba concentration in SAMPLE B

Results of normalisation

Average normalised values for the two ash samples are presented in Table 8. The average values obtained by normalisation are very different from concentrations obtained by calibration. For most elements, the average normalised values in two ash samples are similar. However, the comparison between the two ash samples is similar with the results of ICP-MS analysis except for some elements (Tables 1 and 2). Element S, Cr, Sr and Ba are higher in ash SAMPLE A while the normalised value for Sr is higher in ash SAMPLE B.

Table 8: Average normalised value for all particles in the two ash samples

	SAMPLE A	*SAMPLE B*
^{23}Na	0.089±0.089	0.11±0.09
^{24}Mg	0.035±0.083	0.03±0.03
^{27}Al	0.28±0.33	0.17±0.19
^{28}Si	0.060±0.058	0.078±0.083
^{34}S	0.0006±0.0028	0.0003±0.0006
^{37}Cl	2.28E-05±0.0002	0.0002±0.0008
^{39}K	0.076±0.092	0.088±0.084
^{44}Ca	0.28±0.29	0.37±0.27
^{48}Ti	0.044±0.11	0.040±0.059
^{51}V	0.0002±0.0004	0.0002±0.0003
^{53}Cr	0.001±0.003	0.0006±0.0008
^{55}Mn	0.006±0.006	0.005±0.006
^{57}Fe	0.12±0.20	0.11±0.16
^{58}Ni	0.0008±0.0013	0.0007±0.0008
^{59}Co	6.78E-05±0.0001	4.84E-05±6.23E-05
^{63}Cu	0.066±0.46	0.007±0.008
^{64}Zn	0.008±0.022	0.004±0.004
^{75}As	6.81E-06±1.42E-05	1.53E-05±2.48E-05
^{88}Sr	0.003±0.004	0.005±0.010
^{107}Ag	3.39E-05±4.17E-05	5.88E-05±0.0001
^{114}Cd	8.06E-05±0.0002	2.7E-05±6.15E-05
^{120}Sn	0.004±0.009	0.002±0.004
^{121}Sb	0.001±0.002	0.001±0.001
^{138}Ba	0.051±0.031	0.032±0.071
^{208}Pb	0.095±0.63	0.027±0.036

Normalised values for ash SAMPLE A

Following the same classification method as for concentrations (Table 4), particles were grouped into the same 7 categories as previously. Results for SAMPLE A are presented in Table 9.

Table 9: the normalisation values of ash SAMPLE A

| Isotope	Group1	Group2	Group3	Group4	Group5	Group6	Group7
	22 particles	14 particles	6 particles	7 particles	32 particles	5 particles	6 particles
^{23}Na	0.016±0.020	0.24±0.11	0.094±0.056	0.067±0.036	0.12±0.03	0.012±0.008	0.005±0.004
^{24}Mg	0.006±0.006	0.037±0.057	0.049±0.035	0.026±0.008	0.033±0.015	0.004±0.005	0.009±0.006
^{27}Al	0.86±0.15	0.18±0.11	0.13±0.05	0.069±0.026	0.12±0.06	0.009±0.01	0.041±0.07
^{28}Si	0.005±0.007	0.16±0.05	0.073±0.022	0.031±0.019	0.073±0.021	0.004±0.003	0.004±0.004
^{34}S	0.0003±0.0005	3.35E-5±7.68E-5	0	0.002±0.002	9.67E-05±0.0002	0.0006±0.0006	0.0005±0.0006
^{37}Cl	0	0	0	0	0	0.0004±0.001	0
^{39}K	0.02±0.02	0.22±0.12	0.14±0.06	0.029±0.019	0.073±0.04	0.008±0.005	0.005±0.002
^{44}Ca	0.051±0.11	0.066±0.11	0.031±0.059	0.66±0.08	0.44±0.14	0.068±0.13	0.89±0.11
^{48}Ti	0.011±0.012	0.025±0.013	0.032±0.024	0.061±0.036	0.036±0.014	0.015±0.019	0.028±0.039
^{51}V	3.09E-5±3.95E-5	0.0001±0.0003	0.001±0.002	0.0001±8.47E-05	0.0002±0.0002	1.62E-5±2.5E-5	1.69E-5±3.43E-5
^{53}Cr	0.0003±0.0006	0.0002±0.0004	0.001±0.002	0.0006±0.0004	0.0008±0.0008	0.0001±0.0002	0.001±0.002
^{55}Mn	0.012±0.009	0.002±0.001	0.005±0.004	0.004±0.001	0.006±0.005	0.005±0.002	0.001±0.001
^{57}Fe	0.025±0.021	0.069±0.049	0.45±0.08	0.054±0.024	0.099±0.046	0.88±0.16	0.014±0.028
^{58}Ni	0.0002±0.0002	0.0004±0.0003	0.003±0.001	0.0004±0.0002	0.0006±0.0002	0.004±0.0007	0.0001±0.0002
^{59}Co	2.16E-5±1.5E-5	4.84E-5±3.1E-5	0.0001±2.48E-05	7.48E-05±2.01E-05	0.0001±0.0002	5.07E-5±2.44E-5	1.86E-5±3.11E-5
^{63}Cu	0.007±0.004	0.009±0.009	0.005±0.003	0.87±1.67	0.006±0.004	0.006±0.004	0.002±0.002
^{64}Zn	0.007±0.018	0.005±0.003	0.018±0.033	0.008±0.005	0.006±0.004	0.007±0.008	0.0009±0.001
^{75}As	2.34E-6±5.36E-6	5.8E-06±1.88E-05	1.01E-5±2.12E-5	2.29E-5±2.35E-5	5.52E-6±7.59E-6	7.7E-6±7.25E-6	1.14E-5±2.61E-5
^{88}Sr	0.0009±0.0007	0.003±0.002	0.001±0.001	0.005±0.002	0.005±0.002	0.0008±0.0005	0.004±0.003
^{107}Ag	5.69E-5±3.94E-5	3.95E-5±5.17E-5	2.9 E-05±2.47E-5	5.05E-05±6.05E-05	2.93E-5±4.11E-5	1.73E-5±2.35E-5	7.69E-6±1.22E-5
^{114}Cd	3.24E-5±5.33E-5	6.08E-5±6.97E-5	3.37E-5±4.63E-5	0.0002±0.0001	7.12E-5±5.19E-5	0.0001±0.0002	2.91E-5±5.15E-5
^{120}Sn	0.002±0.003	0.003±0.002	0.002±0.002	0.006±0.004	0.003±0.002	0.003±0.004	0.001±0.002
^{121}Sb	0.0004±0.0003	0.003±0.006	0.0007±0.0008	0.003±0.002	0.0008±0.0004	0.0006±0.0007	0.001±0.002
^{138}Ba	0.007±0.006	0.059±0.12	0.01±0.008	0.018±0.012	0.023±0.035	0.003±0.003	0.005±0.005
^{208}Pb	0.024±0.028	0.48±1.69	0.017±0.009	0.019±0.014	0.025±0.014	0.004±0.002	0.004±0.002
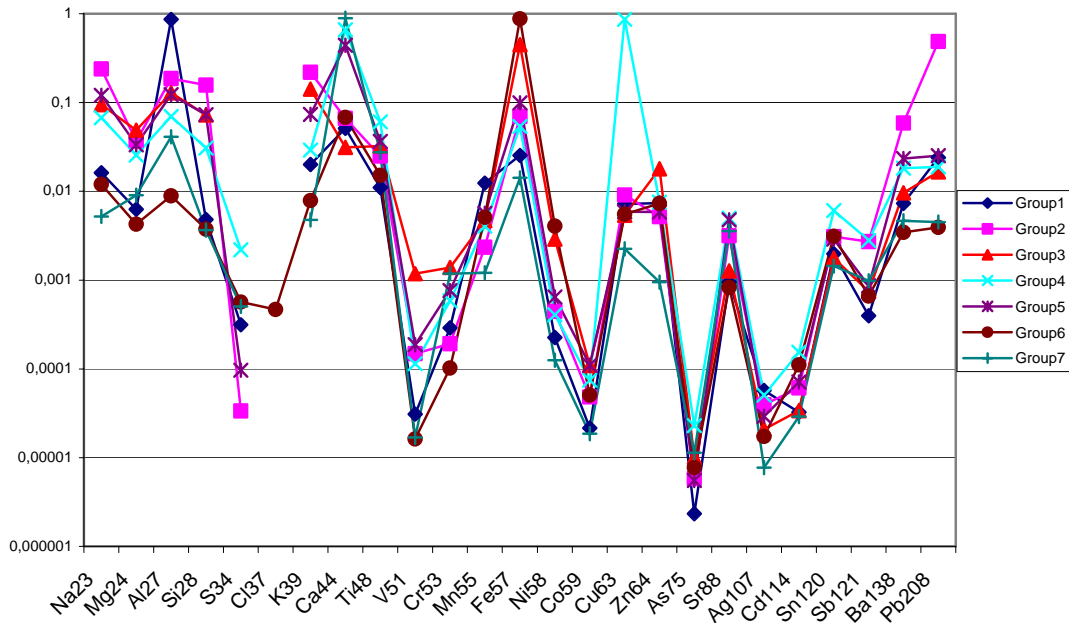
Figure 10: the normalisation of ash SAMPLE A

According to Table 9 and Figure 10 for ash SAMPLE A, average normalised values for heavy metals in groups 6 & 7 are much lower compared with the other groups while the highest normalised values are relatively random. For Na and K, the highest and lowest normalised values are in group 2 and 7, respectively; Mg shows highest value in group 3 and lowest value in group 6; The values of Ti are highest in group 4 and lowest in group 1.

Vanadium shows highest value in group 3 and lowest value in group 1. For Mn and Ag, they have same distribution: highest values in group 1 and lowest values in group 7. Elements Cd and Sn have the same lowest values position while the highest values are in group 4. For elements Ni, Co, Cu and Zn, they show lowest values in group 7 and elements Cr, Sr, Ba and Pb show lowest values in group 6. Group 1 has the lowest As and Sb contents.
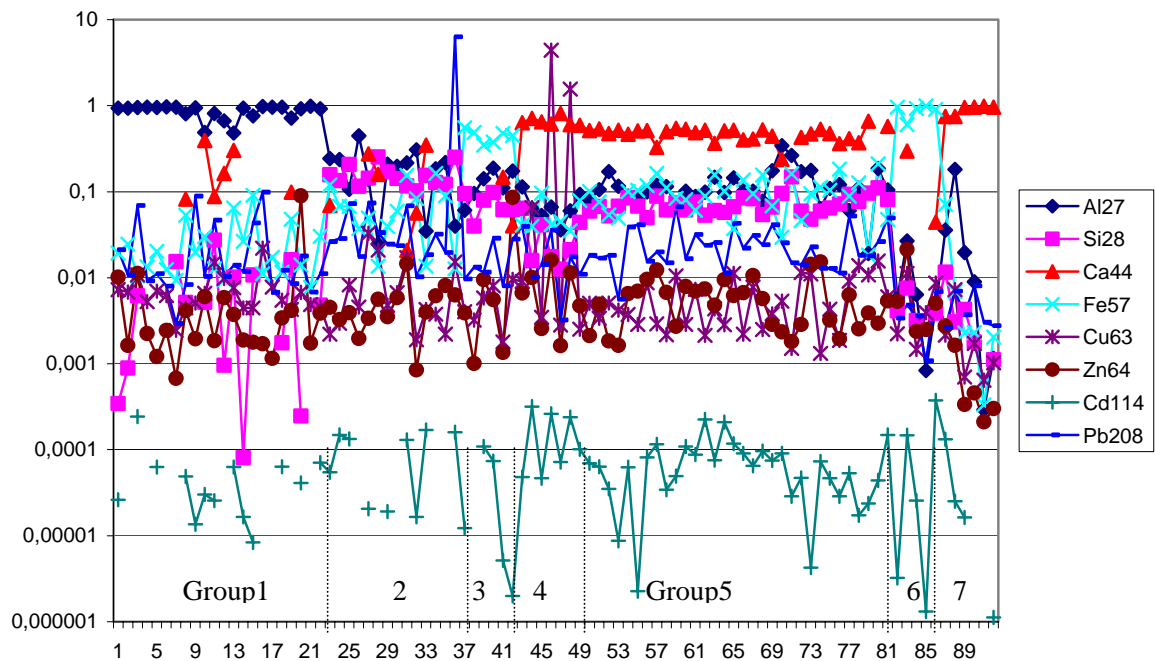
Figure 11: the normalised values of major elements in ash SAMPLE A

It can be seen from the Figure 11 that for four major elements: Cd, Cu, Zn and Pb, the distributions of normalised values of particles are in corresponding with the average normalised values. The normalised values of Cu and Zn are mainly from 0,001 to 0,01 and for the particles in group 7, the values are below 0,001. The variation of normalised values of Pb is relatively high compared with those of Cu and Zn: from 0,001 to 0,1 except for one abnormal value; and values of most particles in groups 6 & 7 are below 0,01. For element Cd, it has relatively high variation and the particles in group 1 to 3 are not constant: there are many zero and minus values in these two groups.

Results of ash SAMPLE B
The results of normalisation of ash SAMPLE B are provided in Table 10.

Table 10: the normalisation values of ash SAMPLE B

| Isotope	Group1	Group2	Group3	Group4	Group5	Group6	Group7
	5 particles	3 particles	5 particles	32 particles	39 particles	3 particles	6 particles
^{23}Na	0.040±0.026	0.23±0.15	0.062±0.055	0.084±0.026	0.16±0.07	0.048±0.044	0.023±0.021
^{24}Mg	0.005±0.002	0.018±0.001	0.073±0.022	0.030±0.024	0.030±0.024	0.008±0.011	0.016±0.020
^{27}Al	0.86±0.07	0.067±0.054	0.12±0.02	0.097±0.042	0.17±0.11	0.016±0.017	0.012±0.016
^{28}Si	0.015±0.012	0.39±0.32	0.056±0.008	0.050±0.012	0.10±0.03	0.010±0.014	0.005±0.006
^{34}S	0	0.0001±0.0002	0	0.0004±0.0008	0.0002±0.0003	0.0002±0.0002	0.0009±0.0011
^{37}Cl	0	0	0	0.0002±0.0007	0.0002±0.001	0	0.0001±0.0003
^{39}K	0.024±0.019	0.14±0.07	0.16±0.08	0.046±0.026	0.13±0.09	0.023±0.021	0.008±0.006
^{44}Ca	0.020±0.045	0.058±0.1	0.10±0.15	0.59±0.06	0.26±0.16	0.085±0.10	0.91±0.08
^{48}Ti	0.015±0.012	0.040±0.036	0.042±0.018	0.043±0.056	0.049±0.075	0.004±0.003	0.018±0.033
^{51}V	1.42E-5±3.18E-5	0.0001±0.0002	0.0007±0.0004	0.0002±0.0002	0.0002±0.0004	2.89E-5±4.85E-5	2.14E-5±3.81E-5
^{53}Cr	0.0007±0.0007	0.0003±0.0005	0.0006±0.0007	0.0007±0.0005	0.0005±0.0006	0.0004±0.0002	0.001±0.002
^{55}Mn	0.007±0.006	0.003±0.0002	0.013±0.007	0.005±0.004	0.004±0.002	0.005±0.0008	0.002±0.003
^{57}Fe	0.017±0.004	0.055±0.029	0.38±0.06	0.061±0.035	0.099±0.076	0.81±0.21	0.010±0.014
^{58}Ni	0.0002±6.37E-05	0.0005±0.0001	0.002±0.0002	0.0005±0.0006	0.0006±0.0004	0.004±0.0009	7.6E-05±0.0001
^{59}Co	2.79E-5±1.39E-5	6.67E-5±6.61E-5	8.93E-5±2.54 E-5	4.85E-5±4.43E-5	5.42E-5±8.61E-5	4.65E-5±5.67E-6	1.17E-5±1.87E-5
^{63}Cu	0.007±0.004	0.024±0.013	0.003±0.002	0.004±0.004	0.007±0.004	0.023±0.032	0.001±0.0005
^{64}Zn	0.002±0.002	0.015±0.011	0.003±0.003	0.003±0.003	0.004±0.003	0.003±0.003	0.0008±0.0009
^{75}As	9.67E-8±1.52E-7	6.01E-5±9.02E-5	5.2E-06±1.09E-05	1.46E-5±1.84E-5	1.49E-5±1.76E-5	2.37E-5±3.71E-5	2.47E-5±4.49E-5
^{88}Sr	0.003±0.002	0.006±0.006	0.001±0.001	0.003±0.001	0.004±0.007	0.032±0.054	0.003±0.003
^{107}Ag	0.0002±0.0004	5.15E-05±4.99E-5	1.5E-5±3.36E-5	5.08E-05±0.0001	6.82E-5±7.56E-5	2.97E-05±5.14E-5	4.79E-6±7.8E-6
^{114}Cd	7.99E-6±1.42E-5	1.48E-5±2.32E-5	1.39E-5±1.91E-5	1.83E-05±1.91E-5	3.89E-05±8.69E-5	0.0001±0.0001	1.77E-5±1.49E-5
^{120}Sn	0.0009±0.0004	0.008±0.0004	0.002±0.002	0.001±0.0007	0.003±0.006	0.0009±0.0004	0.0009±0.001
^{121}Sb	0.0007±0.0003	0.004±0.002	0.0007±0.0006	0.001±0.0009	0.001±0.0009	0.0006±0.0003	0.001±0.002
^{138}Ba	0.036±0.051	0.039±0.018	0.020±0.013	0.017±0.013	0.037±0.067	0.19±0.32	0.008±0.006
^{208}Pb	0.013±0.005	0.17±0.10	0.011±0.011	0.016±0.007	0.032±0.027	0.015±0.014	0.004±0.002
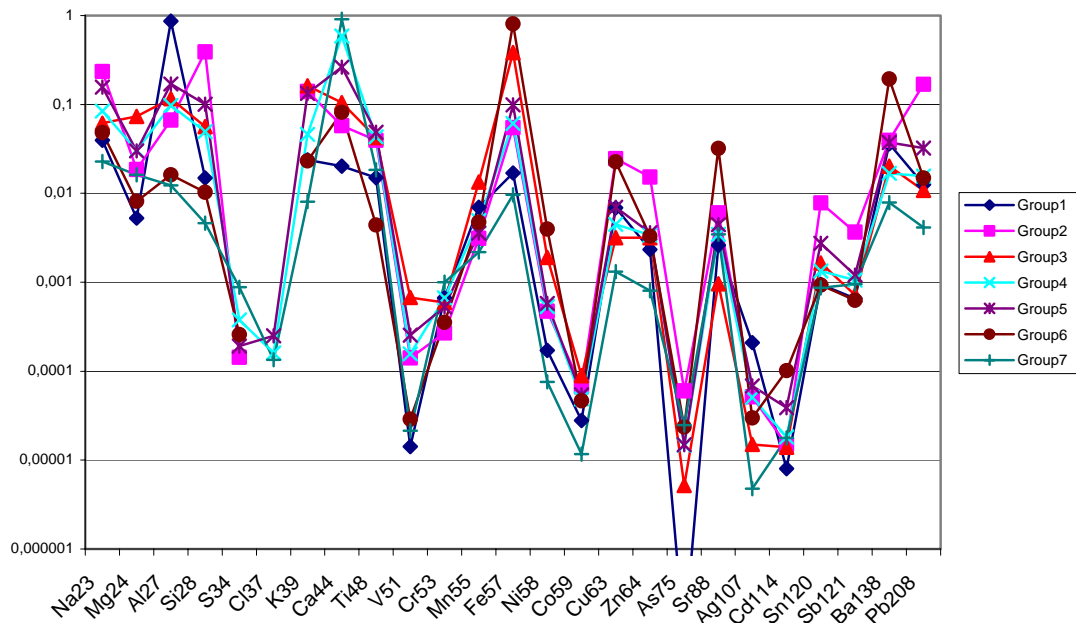
Figure 12: the normalisation of ash SAMPLE B

It can be seen from Table 10 that the results for normalised values of ash SAMPLE B are similar with those of SAMPLE A. For most elements, group 6 & 7 show the lowest values for heavy metals compared with the other groups. For metal element Na, the situation is same as that in ash SAMPLE A: the highest and lowest values are in group 2 and 7 respectively; Mg shows highest value in group 3 but lowest value in group 1; The values of K are the lowest in group 7 but the highest in group 3. Element Ti is totally different: the highest values in group 5 and lowest values in group 6.

Vanadium shows the same situation as for ash SAMPLE A: highest value in group 3 and lowest value in group 1. However, the situation for the other elements is quite different. For elements Mn and Co, the highest values are in group 3 and lowest values are in group 7. Elements Cu, Zn Sn, Ba and Pb have the same distribution: highest values in group2 and lowest values in group 7. For elements Ni and Ag, lowest values are in group 7 and elements Cr and Sb show lowest values in group 6. Group 1 shows the lowest As and Cb contents.
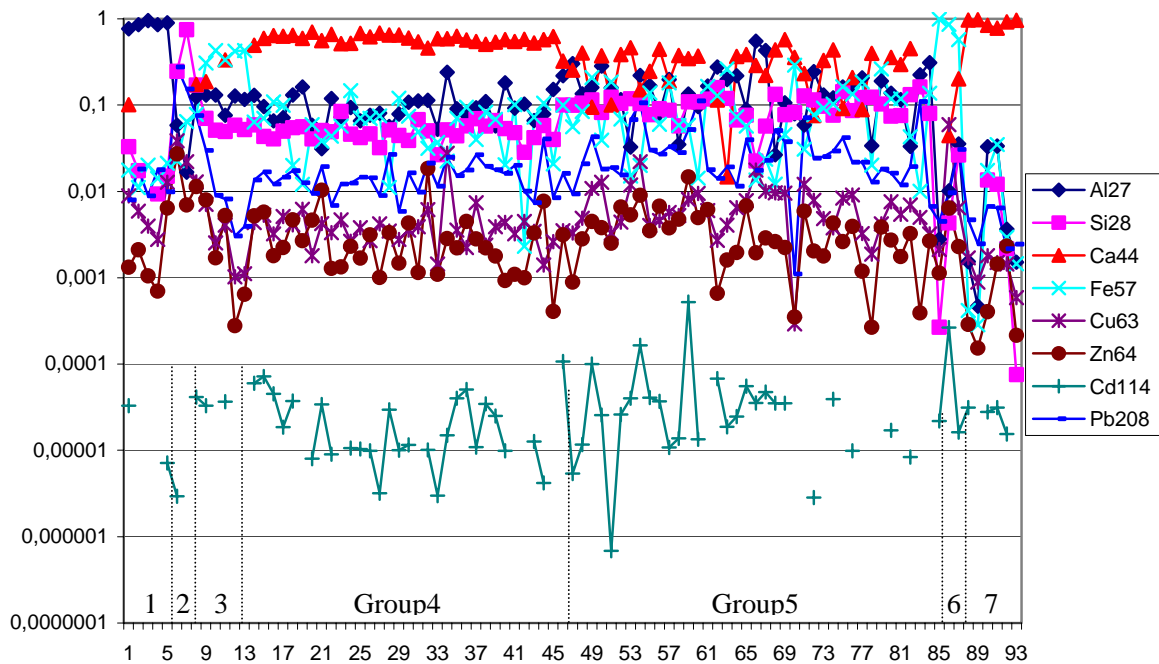
Figure 13: the normalised values of major elements in ash SAMPLE B

According to Figure 13, the situations of Cu, Zn and Pb in SAMPLE B are similar with those in SAMPLE A: the values of Cu and Zn mainly vary from 0,001 to 0,01; the values of Pb are mainly from 0,001 to 0,1 and the values in group 6 & 7 are below 0,01. The situation of Cd is different from that of SAMPLE A: except from group 1 to 3, there are many zero and minus values in other groups.

Comparisons of normalisation values between two ash samples
It can be seen from the results of normalisation and the comparisons between two ash samples based on different group (Appendix IV) that except for some abnormal values, the normalised values of two ash samples are similar. However, the situations of normalisation are quite different from those of calibration. For most elements, values about heavy metals in groups 6 & 7 are much lower compared with the other groups while the highest values are relatively random. It should be noticed that the normalisation value of Cl of most groups show zero. For group 2 which are dominated by SiO_2, there are more elements showing zero normalisation values than other groups.

For major elements, both samples have similar values distribution. Element Na has higher and lower values in group 2 and group 7 respectively. K shows lowest values in group 7 Group 3 has higher Mg content compared with the other groups.

For trace element, V shows highest values in group 3 and lowest values in group 1. Elements Ni, Cu and Ag show lowest values in group 7 while the distributions of highest values for each element are different: Ni is in group 6, Cu is in group 2 and Ag is in

group 1. Element Cr has highest values in group 7 and lower values in group 6. for the other elements, the situation is different. For elements Mn, Co, Zn and Sn, they show lowest values in group 7 and element As show lowest values in group 1. Both elements Sb and Ba have highest values in group 2 but the distributions of lowest values are relatively random.

According to the comparisons between two samples, for elements Cu, Zn and Pb, the normalised values of both samples are similar. For element Cd, there are more zero and minus values in ash SAMPLE B compared with ash SAMPLE A.

Comparison between calibration and normalisation

It can be concluded from the results of calibration and normalisation that most of heavy metals show lower values in groups 1 and 2 and higher values in groups 6 and 7 based on the calibration data treatment method while based on the normalisation data treatment method, the lower values are mainly in groups 6 and 7 and higher values for individual particles are relatively random.

For Na, the lowest values are in group 7 and highest values are different based on different data treatment methods: for calibration, highest values are in group 5 and for normalisation, highest values are in group 2. For element Mg, the situation is quite different: the highest values are in group 3 while the lowest values are different based on different ash samples: for ash SAMPLE A, the lowest values are in group6 and for ash SAMPLE B, the lowest values are in group 1. For K, the situation is much simpler: group 3 shows highest values and group 7 shows lowest values.

For V, the highest value shows in group 3 which is dominated by SiO_2 and Fe and lowest value in group 1 which is dominated by Al_2O_3. Elements Cr show lowest values in group2 that is dominated by SiO_2 and the highest values in group 7. The group 1 has the highest values for Ag and the lowest values of Ag are in group 7. For the other elements, the situations are different according to ash samples or data treatment methods. Elements Ni shows the highest values in group 6 while the lowest values are different based on different data treatment methods: in group 1 and 7 respectively. Element Cu shows the highest and lowest values in group 6 and group 3 respectively based on calibration data treatment method while the highest and lowest values are in group 2 and group 7 respectively based on normalisation data treatment method. For the other elements, only highest or lowest values can be decided. Both of elements Sb and Ba show the highest values in group 2 and elements Cd and Pb show highest values in group 6 and 5 respectively. The lowest values of elements As and Sn are in group 1 and 7 respectively.

The difference between the two methods indicates that there is a problem and that probably one of the methods is better than the other. Because the results of calibration data treatment are not normalised and the normalisation data treatment takes into consideration difference in ablation for different particle type, normalisation is probably the better method.

Discussion of the results of calibration and normalisation

It can be seen from the results of experiments that the concentrations of elements in the two ash samples are similar, although more heavy metals are adsorbed to particles in ash SAMPLE B compared with SAMPLE A. The situation for group 2 is different: for some elements, the concentrations of elements in SAMPLE A are higher than SAMPLE B and for most of similar values between two samples, the concentrations of certain elements are much higher than normal values.

The reason for this is that $NaHCO_3$, coated with ammonia, was added to the combustion zone in order to clean the flue gases in ash SAMPLE B. The concentration of HCl in the gas stream decreased because of reaction with $NaHCO_3$ and metal chlorides were produced. According to the findings of Wey et al., the metallic chlorides can increase the absorption efficiency of heavy metals in the fly ash. (Wey et al., 1998) Meanwhile, lime was added into flue gas scrubber to remove the acid gases of the flue gases. That is the reason why the concentration of Ca in the fly ashes is high.

According to the results of calibration and normalisation, the group1 which are dominated by Al shows higher Ag content and lower V and As content; it means Al rich ash particles adsorb more Ag and less V and As. The higher values of Cu, Sb and Ba and lower values of Cr in group 2 mean glass can adsorb more elements Cu, Sb and Ba and less Cr. The values of elements Mg, K and V are highest in group 3 which are dominated by SiO_2 and Fe, this fact means that glass is an important location for Mg, K and V and these three elements are also concentrated in magnetite. The facts that Fe rich ash particles (group 6) adsorb more Ni and Cd show that there is more possibility for Ni and Cd to be adsorbed by magnetite. Group 7 has higher Cr content and lower Na, K, Mn, Ni, Co, Cu, Zn, Ag and Sn content, it means Ca rich ash particles adsorb more Cr and less Na, K, Mn, Ni, Co, Cu, Zn, Ag and Sn.

The results above were made based on the mean value of calibration and normalisation. However, the standard deviation of those values is high enough to influence the conclusion we made. The high value of standard deviation means that the concentrations of heavy elements in fly ash particles are extremely variable. The reason for this condition is that the concentrations of heavy metals in fly ash depend on many factors, including fuel composition, the type of incinerator, conditions during combustion, the efficiency of emission control devices, and so on.

Conclusion

Economic development and living standard improvement have brought about a great increase in municipal solid waste year after year. The ever-growing MSW load has a great impact on the environment and people's health. Many methods have been utilised for waste treatment; incineration of MSW has been technically proven as an effective waste treatment approach. However, incineration of MSW can also cause some environmental problems: it not only produces significant pollutant flue gases, but also gives rise to considerable amounts of solid residues. Thus, it is necessary to study and better characterise ash particles.

The binding mechanisms of heavy metals to ash particles was studied in this paper by using of LA-ICP-MS in order to have a better understanding of the leaching of potentially hazardous heavy metals. Two data treatment methods: calibration and normalisation were introduced to analyse the experiment results. However, there is a great difference between two methods. According to the comparison between two methods principles, the better method is probably normalisation. Although there are many factors that can affect the accuracy of results, the following conclusions mainly based on normalisation data treatment method can be drawn:

- Al rich ash particles adsorb more Ag but less V and As.
- Glass is an important location for elements Cu, Sb and Ba while Cr is on the contrary.
- Elements Mg, K and V show higher concentration in glass and magnetite particles.
- Elements Ni and Cd have more possibility to be adsorbed by magnetite
- Ca rich ash particles adsorb more Cr and less Na, K, Mn, Ni, Co, Cu, Zn, Ag and Sn.

Further study about factors that can affect the distribution of heavy metals will be needed in order to have a better understanding of the distribution and the potential influence of heavy metals.

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Appendix

Appendix I: Chemical characteristics of fly ashes by ICP-MS analysis after sample digestion

Ash composition

ELEMENT	SAMPLE	SAMPLE A	SAMPLE B
TS	%	99,9	99,8
SiO_2	% TS	38,3	41,4
Al_2O_3	% TS	24,3	19,7
CaO	% TS	17,8	17
Fe_2O_3	% TS	5,08	4,25
K_2O	% TS	1,98	2,22
MgO	% TS	2,53	2,61
MnO	% TS	0,319	0,236
Na_2O	% TS	3,79	5,59
P_2O_5	% TS	2,33	1,93
TiO_2	% TS	1,99	1,61
Summa	% TS	98,4	96,5
LOI	% TS	-2,4	1,2

Trace elements composition

Element (mg/kg TS)	SAMPLE A	SAMPLE B	Element (mg/kg TS)	SAMPLE A	SAMPLE B
As	25,8	46	Ni	221	159
Ba	2710	2950	Pb	1500	1140
Be	1,8	1,63	S	6590	7930
Cd	11,4	14,3	Sc	3,68	3,74
Co	34,5	19,9	Sn	117	72,9
Cr	549	628	Sr	400	373
Cu	5890	3840	V	49,7	61,5
Hg	0,102	0,25	W	<60	<60
La	24,6	28,5	Y	23,2	21
Mo	11,3	14,9	Zn	9010	5930
Nb	19,7	12,2	Zr	287	254

Appendix II: Fly ash groups (Roy and Griffin, 1982)

Group	Sialic component ($\Sigma\ SiO_2 + Al_2O_3 + TiO_2$)	Calcic component ($\Sigma\ CaO + MgO + Na_2O + K_2O$)	Ferric component ($\Sigma\ Fe_2O_3 + SO_2$)
1. Sialic (essentially Si + Al)	>88(%)	0-12	0-12
2. Fersic (Fe + sialic)	48-77	0-29	23-52
3. Calsialic (Ca + sialic)	48-<77	A29-52	0-23
4. Modic (frommodalconcept)	>48-88	0-29	0-<23
5. Ferric (Fe)	<48	0-29	>23
6. Calcic (Ca)	<48	>29	0-23
7. Fercalsic (Fe + Ca)	<48	>29-77	23-71

Appendix III: Comparisons of calibration between two ash samples
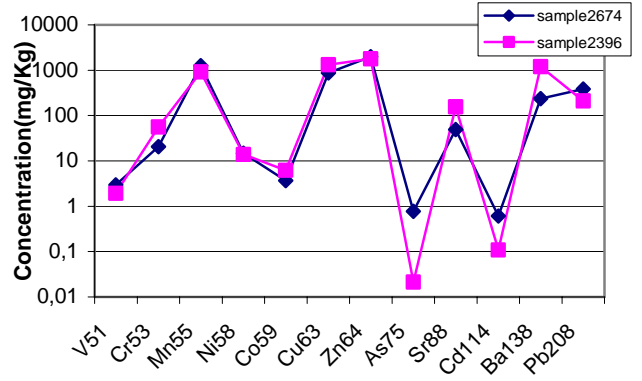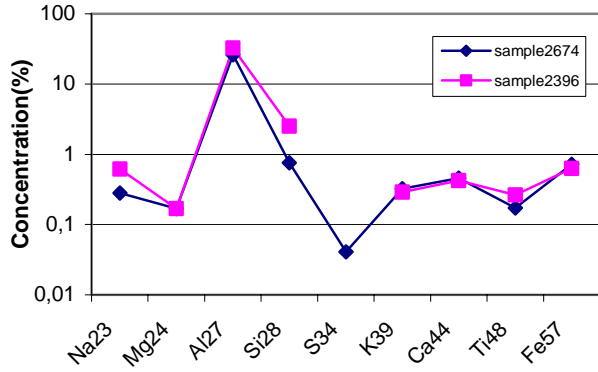
Comparison between two samples - Group1

Comparison between two samples – Group2
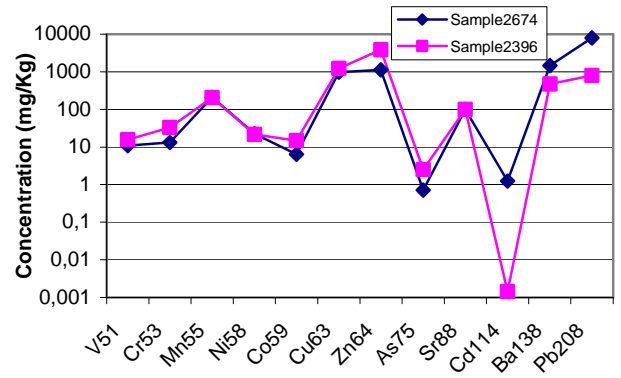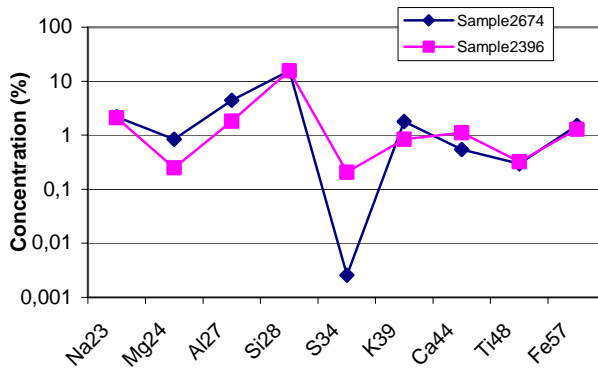
Comparison between two samples – Group3
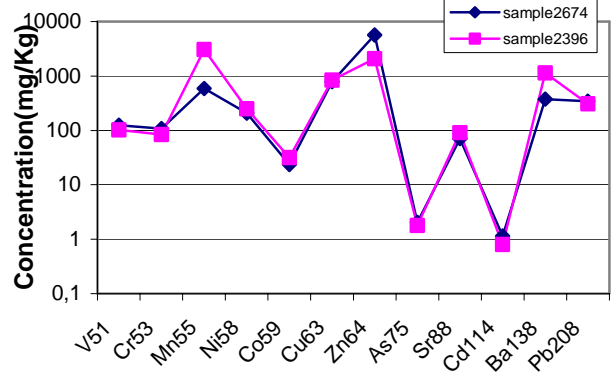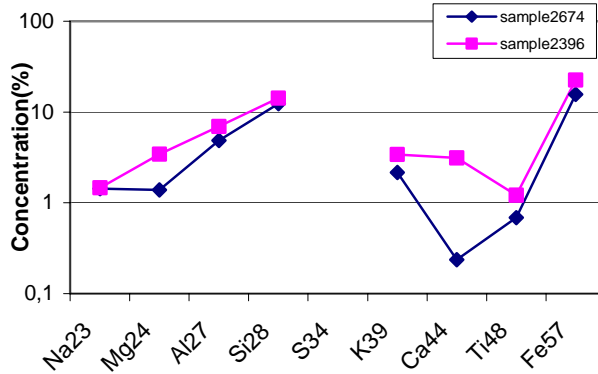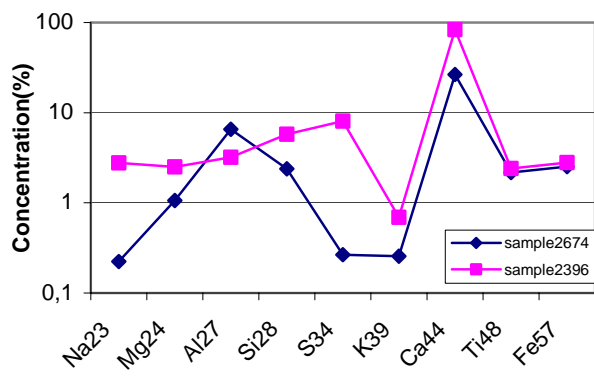
Comparison between two samples – Group4
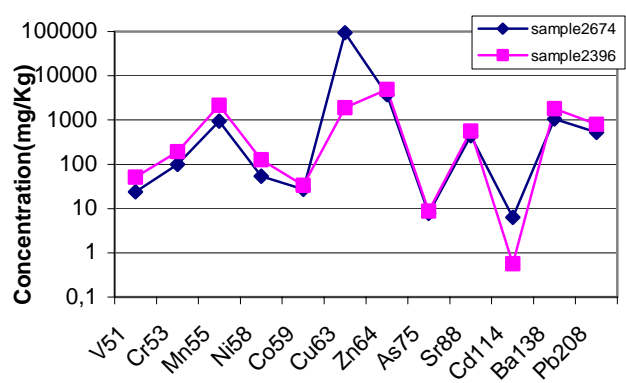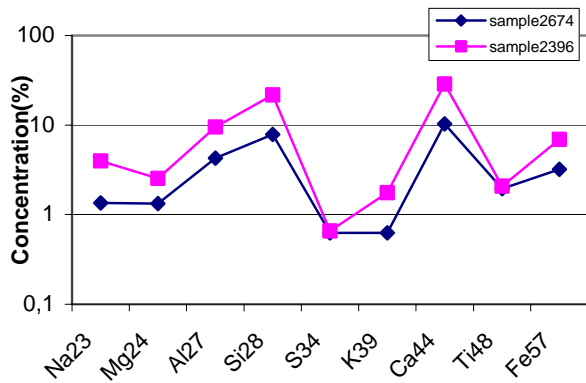
Comparison between two samples – Group5
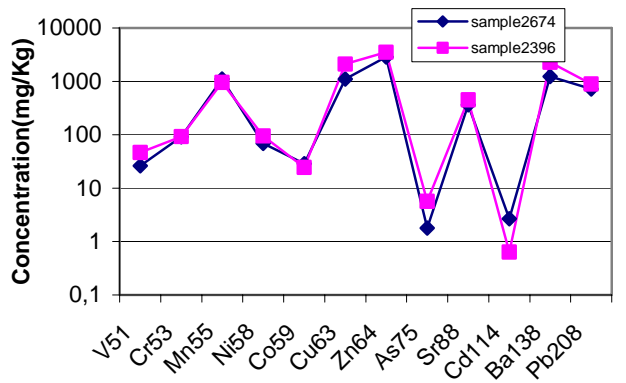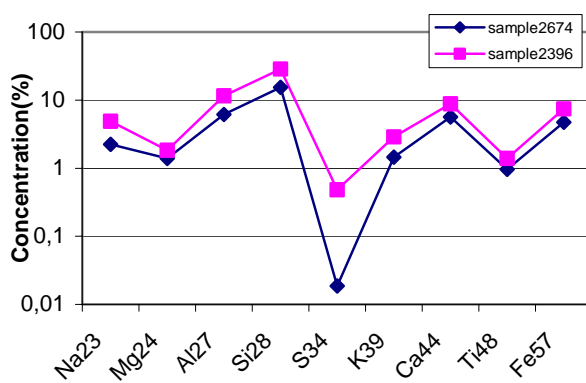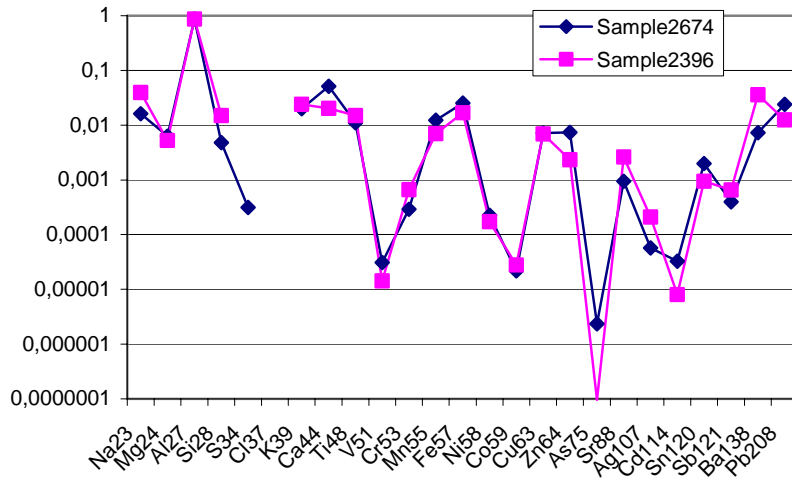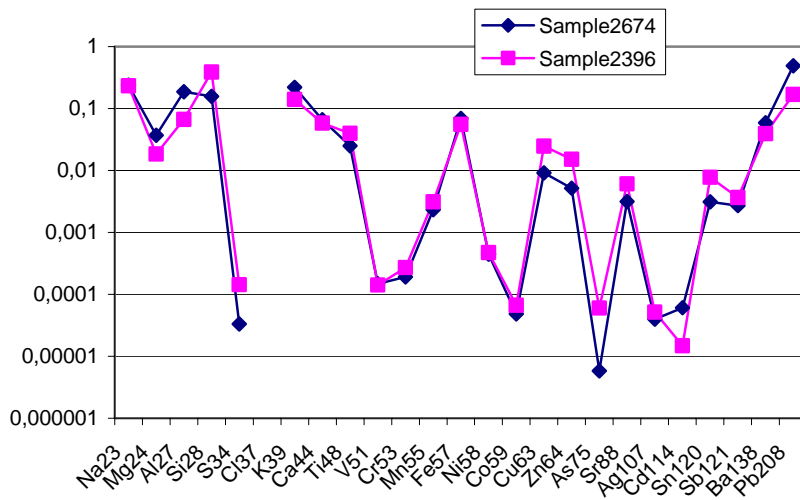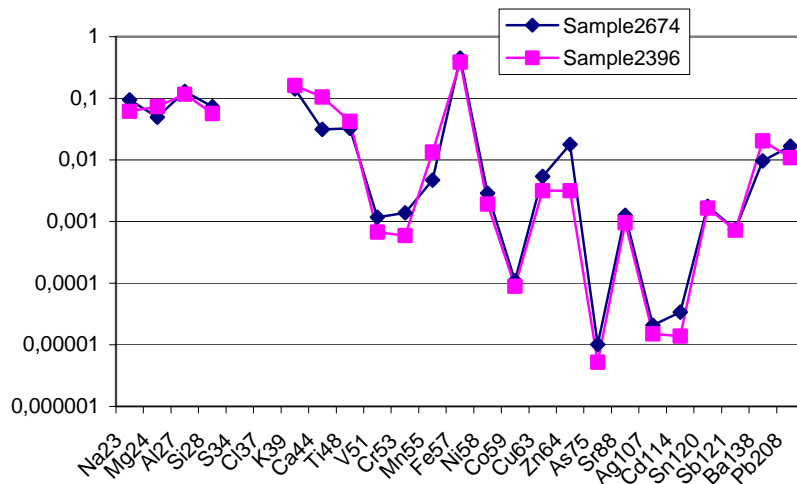

Comparison between two samples – Group6
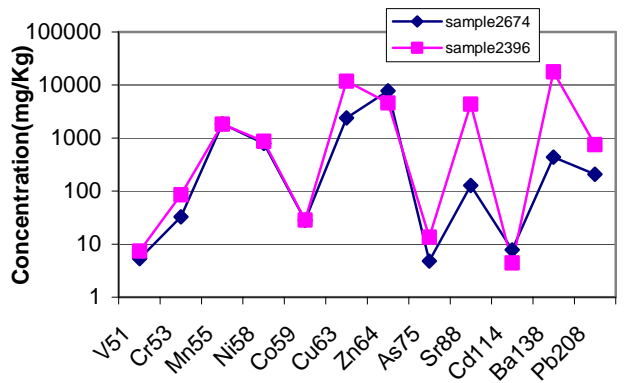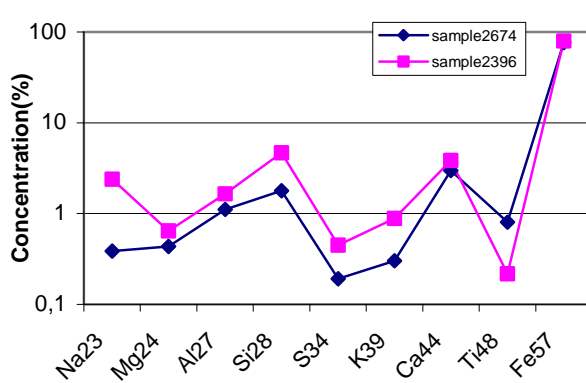
Comparison between two samples – Group7
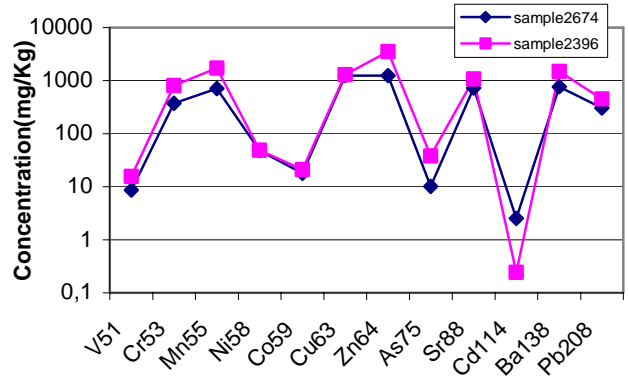
Appendix IV: Comparisons of normalisation values between two ash samples
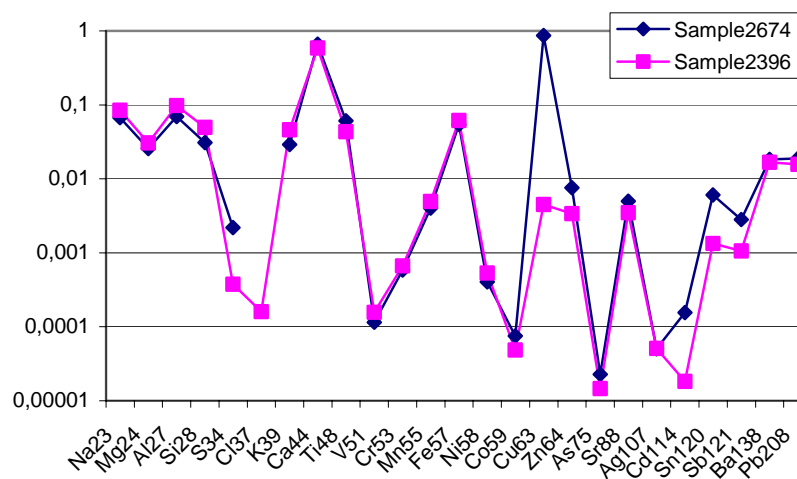
Comparison between two samples - Group1

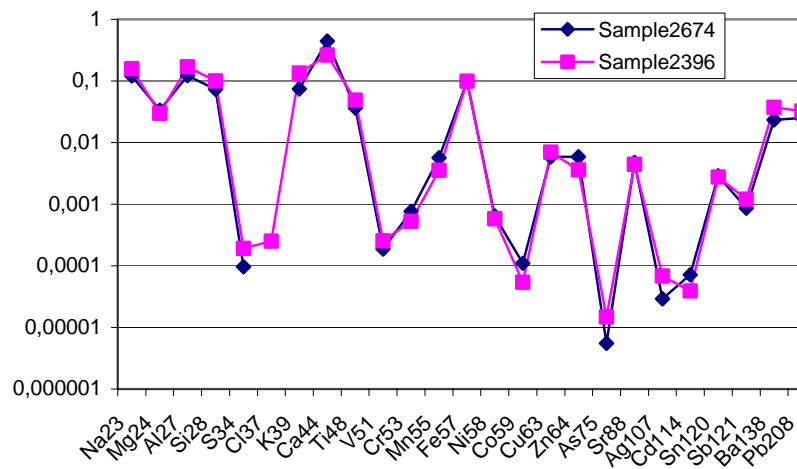Comparison between two samples – Group2
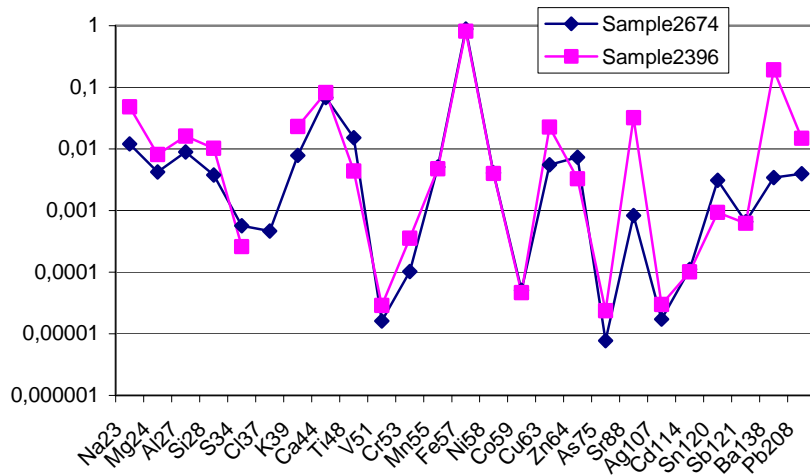
Comparison between two samples – Group3

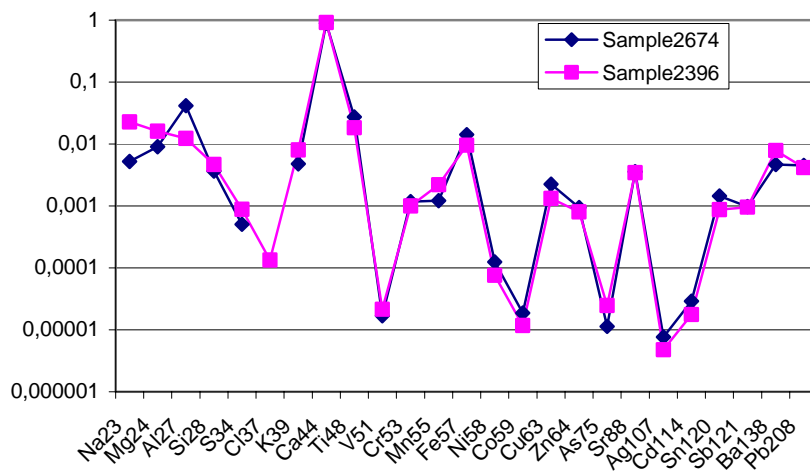Comparison between two samples – Group4

Comparison between two samples – Group5

Comparison between two samples – Group6

Comparison between two samples – Group7

Appendix V: Standard Reference Material 1633b

Table 1. Certified Values

Element	Mass Fraction (%)			Element	Mass Fraction (mg/kg)		
Al	15.05	±	0.27	As	136.2	±	2.6
Ca	1.51	±	0.06	Ba	709	±	27
Fe	7.78	±	0.23	Cd	0.784	±	0.006
Mg	0.482	±	0.008	Cr	198.2	±	4.7
K	1.95	±	0.03	Cu	112.8	±	2.6
Si	23.02	±	0.08	Pb	68.2	±	1.1
Na	0.201	±	0.003	Mn	131.8	±	1.7
S	0.2075	±	0.0011	Hg	0.1431	±	0.0018
Ti	0.791	±	0.014	Ni	120.6	±	1.8
				Se	10.26	±	0.17
				Sr	1041	±	14
				Th	25.7	±	1.3
				U	8.79	±	0.36
				V	295.7	±	3.6

Table 2. Noncertified Values

Element	Mass Fraction (mg/kg)	Element	Mass Fraction (mg/kg)
Sb	6	P	2300
Br	2.9	Rb	140
Ce	190	Sc	41
Co	50	Sm	20
Cs	11	Ta	1.8
Dy	17	Tb	2.6
Eu	4.1	Tl	5.9
Gd	13	Tm	2.1
Hf	6.8	W	5.6
Ho	3.5	Yb	7.6
La	94	Zn	210
Lu	1.2		
Nd	85		