THESIS FOR DEGREE OF DOCTOR OF PHILOSOPHY

Alkali-containing aerosol particles – release during biomass combustion and ambient air concentrations

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Abstract

Air pollution in the form of particles has considerable influence on human health and climate. Atmospheric aerosol particles arise from direct emissions of particles and from the conversion of certain gases to particles in the atmosphere. They are produced by a number of different sources and have a typical lifetime of about a week in the atmosphere. The chemical composition of the atmospheric aerosol is highly variable in time and space, and the different effects of the aerosol can usually not be understood without taking its multi-component nature into account.

The overall aim of this thesis is to contribute to an improved understanding of climate effects and air quality issues related to aerosol particles. The thesis focuses on aerosol particles containing alkali-compounds, and particles produced by biomass combustion are of particular interest. Aerosol mass spectrometer techniques for highly sensitive and selective detection of alkali-containing particles have been further developed and applied in laboratory experiments, in fluidised bed combustion, and in ambient air measurements. The experimental techniques provide the chemical composition of individual aerosol particles with high time resolution and they are well suited for combustion aerosol applications, and for detection of sea salt particles that contain a large fraction of sodium compounds.

Laboratory experiments were performed to study the emission of potassium- and sodium-containing compounds during rapid pyrolysis of birchwood. The alkali emission during the pyrolysis phase and from ash and char formed at high temperatures was characterized. Studies were also carried out during biomass combustion in a 12 MW(thermal) circulating fluidized-bed boiler. The effect of the addition of chlorine and/or sulphur to the fuel on fly ash composition, deposit formation, and superheater corrosion was investigated. Addition of sulphur and chlorine increased the formation of submicron particles and lead to enhanced deposition of potassium sulphate and chloride. The results compared well with results from earlier laboratory-scale experiments concerning the effects of chlorine and sulphur on potassium chemistry. The findings are of importance for actions aimed at minimizing alkali related corrosion and deposition problems during large-scale biomass conversion.

The seasonal variation of the elemental composition of particulate matter in Skopje was studied by chemical analysis of samples collected with impactor technique. Major aerosol components were identified including mineral dust, oil combustion, traffic-related aerosol and secondary sulphate, while a separate biomass burning component could not be identified with the employed methods. Aerosol mass spectrometry was used to study the influence of atmospheric transport patterns and meteorology on alkali concentrations in Gothenburg. The observed potassium and sodium concentrations were concluded to be affected both by emissions from the nearby region and by long-range transport. Sodium-rich sea salt particles were favoured by westerly winds and high wind speeds, and were preferentially observed in air masses originating from the Atlantic. Potassium-rich particles originating from biomass burning were favoured by low temperatures and low wind speeds, and they were most abundant in air masses transported from Eastern and Central Europe.

Keywords: aerosol, alkali metal, sodium, potassium, pyrolysis, combustion, biomass burning, circulating fluidised bed, surface ionisation, aerosol mass spectrometry, air quality

List of Papers

This thesis is based on the work presented in the following papers:

I. K. O. Davidsson, B. J. Stojkova (now B. Kovacevik), and J. B. C. Pettersson
"Alkali emission from birchwood particles during rapid pyrolysis"
Energy and Fuels 16 (2002) 1033-1039.

II. K. O. Davidsson, L.-E. Åmand, B. Leckner, B. Kovacevik, M. Svane, M. Hagström, J. B. C. Pettersson, J. Pettersson, H. Asteman, J.-E. Svensson, and L.-G. Johansson
"Distribution of potassium, chlorine and sulfur between ash, aerosol, and deposits during wood fuel combustion in a circulating fluidized bed boiler"
Energy and Fuels 21 (2007) 71-81.

III. M. Svane, T. L. Gustafsson, B. Kovacevik, J. Noda, P. U. Andersson, E. D. Nilsson, and Jan B. C. Pettersson
"On-line chemical analysis of individual alkali-containing aerosol particles by surface ionization combined with time-of-flight mass spectrometry"
Aerosol Science and Technology (2009), in press.

IV. B. Kovacevik, A. Wagner, J. Boman, J. Laursen, and J. B. C. Pettersson
"The seasonal variation of the elemental composition of particulate matter in Skopje, FYR Macedonia"
Submitted to Science of the Total Environment.

V. B. Kovacevik, T. L. Gustafsson, J. Noda, M. Svane and J. B. C. Pettersson
"Alkali-containing aerosol particles in South-West Sweden: Influence of meteorological conditions and air mass origin"
Manuscript for Atmospheric Environment.

Contents

1. Introduction

By breathing ambient air we are exposed to a number of airborne contaminants including aerosol particles invisible to the eye. The concentrations of contaminants are generally increasing as a result of growing traffic volumes and ever-higher levels of energy conversion, as well as an increasing industrialization of our world.

By definition an aerosol is particulate matter, solid or liquid, suspended in a gas (Baron and Willeke, 2001), and some examples are dust, fog, and smoke. Particles have long been implicated in the deterioration of visibility and the cause of adverse effects on health and the environment (Pope and Dockery, 2006; Schlesinger et al., 2006; WHO 2005). Consequently international organizations like the World Health Organization (WHO) and national environmental agencies have established guidelines and standards for particulate matter concentrations. Aerosols particles are becoming widely recognized due to their significant local, regional, and global impacts. Local impacts are due to industrial processes, traffic emissions, wood burning, and other aerosol sources that may lead to urban air pollution and possible health effects. Regional problems may be due to aerosol transport from areas of high emissions to relatively clean remote regions, while global scale impact includes effects on the radiation budget of the atmosphere and effects on heterogeneous chemistry that may influence the entire planet (Solomon et al., 2007).

Biomass is experiencing an increased interest as a renewable energy source due to concerns regarding global warming, needs to reduce the dependency on fossil fuels, disposal of agricultural residue, and local job employment. Nowadays biomass contributes with more than 10 % to the global energy supply and it is the main renewable energy source (IEA, Task 32). On the other hand, biomass combustion is a significant source of fine particle emissions to ambient air and its environmental impact is an important issue. The amount of formed particles depends on the properties of the fuel and the combustion technology. Compared to other types of fuels, biomass has a relatively high content of inorganic compounds, and especially potassium compounds, that are released during combustion and contribute to particle formation as the flue gases cool down (Nielsen et al., 2000, Jenkins et al., 1998). The resulting particle emissions depend on details of the combustion process, the size distribution and composition of formed particles, as well as on the use of flue gas cleaning techniques (Obernberger, 2005).

One important technique for large scale biomass combustion is Fluidised Bed Combustion (FBC). The behavior of the inorganic constituents originating from the fuel is one of the areas in which FBC development work is concentrated due to the problems caused by them during plant operation. Problems include deposit formation, corrosion and agglomeration of bed material, which may result in high maintenance costs and decreased plant availability (Baxter et al., 1998; Olsson et al., 1997, Oberberger, 2005).

Processes behind formation and behavior of particles during biomass combustion are complex and still not completely understood and solved. There is a need for knowledge and research in order to further develop the utilization of biomass combustion technology, as well as to reduce particulate emissions and to understand their environmental impact.

The overall aim of the present thesis is to contribute to an improved understanding of air quality issues and climate effects related to aerosol particles. The thesis focuses on aerosol particles containing sodium and potassium compounds, and particles produced by biomass combustion are of particular interest. One goal of this work was to study the alkali behavior during combustion and the properties of particles formed during biomass burning. Another goal was to study urban air pollution with particles originating from biomass burning as well as from other sources.

The thesis is based on five enclosed papers. The purpose of the study presented in paper 1 was to characterize the initial alkali emission during wood pyrolysis. Laboratory experiments were performed where single wood particles were rapidly inserted into a preheated furnace and the release of alkali was followed by surface ionization (SI) technique.

Paper 2 presents studies of potassium, chlorine, and sulfur distributions between ash, particles, vapor and deposits during combustion of biofuels in a CFB. The measurements were performed in the 12 MW_{th} CFB boiler at Chalmers University of Technology.

An aerosol mass spectrometer (AMS) dedicated to sensitive and selective detection of particle-bound alkali compounds by SI is described in Paper 3. The instrument was further developed from an earlier version by the use of an orthogonal acceleration time-of-flight mass spectrometer (TOF-MS). The use of the AMS was demonstrated in laboratory experiments and in ambient air measurements.

Field measurement campaigns were performed in Skopje, the capital city of FYR of Macedonia. Particulate matter with diameter less than 2.5μm (PM 2.5) was collected during four measurement campaigns at an urban background site. The aim was to characterize the seasonal variation, the typical concentration of major aerosol components and the impact of different aerosol particles sources on the urban air quality. In this research conventional sampling and analysis methods were applied. The work is presented in Paper 4.

Paper 5 finally presents field studies of alkali-containing aerosol particles using the AMS developed in Paper 3. Measurements were performed at an urban background site in Gothenburg and the concentrations of submicron sodium- and potassium-containing particles were related to changes in meteorological conditions and the origin of the air masses reaching Gothenburg.

2. Background

This chapter provides some basic background information related to the research presented in the thesis. The listed references should be used for more thorough information on the different subjects.

2.1 Aerosol

An aerosol is an assembly of solid or liquid particles of various sizes suspended in a gaseous medium for a long enough time to be observed and measured (Baron and Willeke, 2001). The term aerosol includes both the particles and the suspending gas. Smoke from power generation, salt particles from ocean spray and suspended soil particles are all examples of aerosol particles. The atmospheric aerosol is the particles found in our atmosphere which originate from different natural and anthropogenic sources, and in both cases primary particles are directly emitted and secondary particles are formed by gas-to-particle conversion in the atmosphere. The nature of the source influences the physical properties and the chemical composition of the particles (Hinds, 1999).

Aerosol research is a very important topic in current environmental research because of the effects of aerosol particles on the atmosphere, climate and public health. Aerosol particles scatter and absorb solar and terrestrial radiation, they act as cloud condensation and ice nuclei and are thus involved in the formation of clouds and precipitation, and they affect the distribution of atmospheric trace gases by heterogeneous chemical reactions (Finlayson-Pitts and Pitts, 2000; IPCC, 2007; Seinfeld and Pandis, 1998). They are also involved in the spreading of biological materials like pollen, spores and viruses. Exposures to aerosol particles can cause or enhance respiratory, infectious, cardiovascular and allergic diseases (Pope and Dockery, 2006; Schlensinger et al., 2006; WHO 2005).

On global scale emissions from natural sources including deserts, oceans, and vegetation exceed emissions from anthropogenic sources. The natural sources are well distributed around the planet, and most of the mass of emitted particles comes from these sources. The anthropogenic sources are mainly concentrated in industrialized regions of the world and emissions may there exceed those from natural sources (Hinds, 1999).

Important anthropogenic sources of the primary particles are biomass combustion and incomplete combustion of fossil fuels (WHO, 2006). Primary particles are also emitted from mechanical processes such as construction activities, wind-driven or traffic-related suspension of road, soil and mineral dust, sea salt, and biological materials like pollen, microorganisms and plant fragments (Pöschl, 2005). Secondary particles are formed in the atmosphere through chemical reactions of gaseous precursors. Important anthropogenic producers of secondary aerosols are stationary combustion processes, agriculture, diesel engines and chemical and petrol industry (WHO, 2006).

Aerosol particles will undergo different processes by which they will age and change their particle size, composition and other properties. The lifetime or residence time of aerosol particles in the atmosphere depends on aerosol properties and meteorological conditions and ranges from hours to weeks. There are different mechanisms by which aerosols are removed from the atmosphere and deposit on the Earth's surface or some other surfaces. Particles will deposit by wet deposition when they are scavenged and precipitated with the rain or snow particles on their way to the surface, or by dry deposition when they diffuse, transport, adhere and deposit on some surface (Hinds, 1999).

The concentration, composition, and size of atmospheric aerosol particles are the primary parameters that determine the environmental and health effects. These parameters also affect the retention period and travel distances in the atmosphere (Seinfeld and Pandis, 1998). The particle size is the most important parameter for the characterization of particle behavior. Size distribution spectra give information about atmospheric aerosols and also about the origin and history of the aerosols. Atmospheric aerosol particles range in size over more than four orders of magnitude, from freshly nucleated clusters containing a few molecules to cloud droplets and dust particles up to some hundreds micrometers (McMurry, 2000). This gives a size range from approximately 10^{-9} to10^{-4} m (Baron and Willeke, 2001).

Aerosol particles may be divided into two main groups, coarse particles that have a diameter larger than 2.5 μm and fine particles with a diameter smaller than 2.5 μm. Fine and coarse particles usually have different chemical compositions, sources, and lifetimes in the atmosphere and they exist together as chemically different aerosols. The fine particles are often acidic and contain sulfates, ammonium compounds, hydrocarbons, toxic metals, elemental carbon (soot), and water in the atmosphere (Hinds, 1999). The coarse particles are often basic and contain crystal materials and their oxides, such as silicon, iron, calcium, and also sea salt particles and vegetation debris.

2.2 Urban Aerosol

About half of the world's population lives in urban areas because of the opportunity for a better quality of life. The number of urban dwellers is expected to grow by 2% per year during the coming three decades (Molina and Molina, 2004). The developing world will urbanize even faster and the urban population will double from 2 billion to 3.9 billion. These concentrations of people and their activities have an impact on the urban, regional, and global level.

During recent decades air pollution has become one of the most important problems of the cities, and aerosol particles and their direct effect on human health are of major concern. Urban aerosol is aerosol over large cities in the lowest kilometer of the atmosphere. The urban aerosol contains contributions from nearby and regional sources, both natural and anthropogenic, which have aged in the atmosphere from minutes to days (Hinds, 1999). The anthropogenic sources dominate.

The particle size distribution of urban aerosol is complex since particles are emitted from different sources and affected by size dependent processes of growth, evaporation, and removal. Depending on the physical and chemical processes involved in the particle formation and growth and their behavior, they are divided into three main size fractions, called modes (Finlayson-Pitts and Pitts, 2000; Hinds, 1999). Atmospheric particles in urban air usually have a multimodal size distribution that includes the coarse mode, the accumulation mode and the nuclei mode.

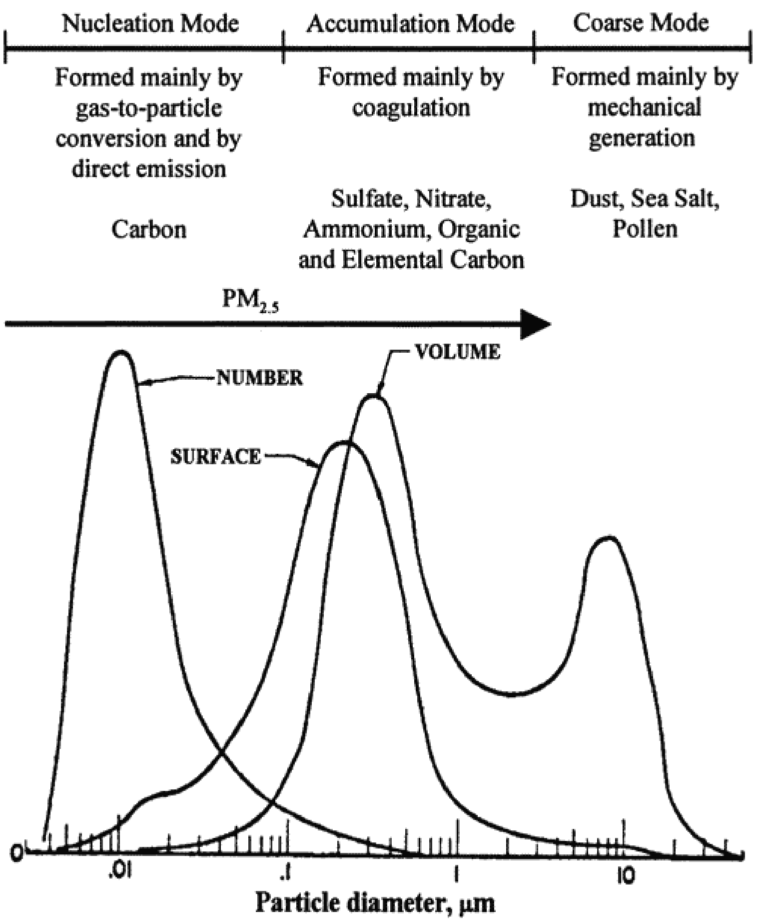

Figure 2.1. Urban aerosol distribution presented in number, surface, and volume distributions. The three common aerosol modes are presented with their main processes of formation, common sources and constituents (adapted from Hinds, 1982).

Figure 2.1 shows examples of the ambient particle distribution that may be found in a city. The coarse mode is characterized by a low number concentration and relatively high mass concentration. They are quickly removed from the atmosphere by sedimentation and precipitation, and their lifetime in the atmosphere is only a few hours or days. Accumulation mode particles range from 0.1 to 1µm in diameter. They include nucleation mode particles that have grown or coagulated to become included in the accumulation mode, or primary particles like soot particles that may be emitted with a size in this range. Particles accumulate in this mode because removal mechanisms are weak (Hinds, 1999). Consequently, they have a long residence time and as a result can be transported over long distances. Nuclei mode particles range under 0.1 µm in diameter and they are recently formed from gas species or emitted directly from combustion processes e.g. by traffic (Kulmala et al., 2004). Their atmospheric lifetime is short because they grow rapidly by coagulation with each other and with particles in the accumulation mode. The expression ultrafine particle is used for particles with a diameter smaller than 0.1µm. Reported concentrations of ultrafine particles in ambient air vary from 100 to 1000/cm^3 in rural and oceanic environments, 10^4/cm^3 in urban areas, and 10^6/cm^3 near an urban freeway (Slama Lighty et al., 2000). In most urban environments, both coarse and fine mode particles are present, but the proportion of particles in these two size ranges varies substantially between cities around the world, depending on local geography, meteorology and specific sources.

2.3 Health effects and Regulations

Studies of urban aerosol particles indicate that there are risks to health at concentrations found in many cities in both developed and developing countries (WHO, 2005). The assessments of WHO show that for particles there is no indication of any threshold of effects, and there are no safe levels of exposure, but risk of adverse health effects increases with exposure. The adverse health effects are found at very low levels of exposure which are not greatly above the background concentrations, which for particles smaller than 2.5 µm has been estimated to be 3-5 $\mu g/m^3$ in both the United States and Western Europe (WHO, 2006).

Epidemiological studies have correlated elevated levels of particles with broad health effects, like effects on pulmonary and cardiovascular system but also increased mortality and cancer (Pope and Dockery, 2006; Schlensinger et al.,2006; WHO 2005). Studies have associated these correlations more with particles less than 2.5 µm as the fine particles can settle in the lungs and may reach the alveolar region, while coarse particles are filtered in the nose and throat (Pope and Dockery, 2006; Schlensinger et al.2006; WHO 2005). The smaller particles may also be more dangerous and more reactive than larger particles because they have a larger surface-to-volume ratio. Ultrafine particles contribute very little to the overall mass, but are very high in number, which in episodic events can reach several hundred thusand/cm3 in the urban air and some studies show that they are causally involved in adverse responses especially in sensitive humans (Oberdörster, 2001).

A typical ambient particle that is inhaled consists of coagulated primary combustion particles or geological particles, coated with some mixture of condensed organic species, secondary $SO_4{}^{2-}$, and NO_3^-, and H_2O at equilibrium with local humidity (Slama Lighty et al., 2000). In some areas the combustion of wood and other biomass fuels may also be an important source of particulate air pollution, especially because combustion particles are largely in the fine mode (Amann et al., 2005).

Most regulatory environmental agencies group particle pollution into two categories: PM_{10} and $PM_{2.5}$ that corresponds to the total mass concentration of all particles with a diameter less than 10 and 2.5 µm, respectively. WHO has published Air Quality Guidelines with limiting values for PM_{10} and $PM_{2.5}$, both for short-term and long-exposures, which aim is to support actions to achieve air quality that protects public health. The guidelines present the concentrations at which increased mortality responses due to particulate matter air pollution are expected based on current scientific findings (WHO, 2006). The recently adopted guidelines for the annual mean particulate matter concentrations are 10 $\mu g/m^3$ and 20 $\mu g/m^3$ for $PM_{2.5}$ and PM_{10}, respectively, while the 24 hour mean concentrations are 25 $\mu g/m^3$ and 50 $\mu g/m^3$ (WHO, 2006).

2.4 Biomass Combustion and Related Problems

2.4.1 Biomass

Biomass consists of organic residues from plants and animals obtained from harvesting and processing of agricultural and forestry crops. Some materials considered as a biomass are straw residues, residues from food production, urban wood waste and waste residues from timber processing operations (Baxter et al., 1998). Woods and wood-derived products represent the most commonly used biomass fuels.

The components of biomass are cellulose, hemicelluloses, lignin, lipids, proteins, simple sugars, starches, water, ash, and other compounds (Jenkins et al, 1998). The concentration of each class of compound varies depending on species, type of plant tissue, stage of growth, and growing conditions. Carbon, the main constituent of biomass, makes up 30-60 wt. % of dry matter, 30 to 40 wt. % of the dry matter in biomass is oxygen, and hydrogen which is the third major constituent comprises 5 to 6% dry matter. Nitrogen, sulfur, and chlorine usually make up less than 1% of dry matter, but occasionally well above this. Nitrogen is a macronutrient for plants and critical to their growth. Also some other inorganic elements can be found in high concentration. Potassium is a macronutrient for plants, and it is a highly mobile element in plants, moves to younger, actively developing tissues and exceeds 1% dry matter in annual growth tissue (Baxter et al., 1998). In some grasses and straws, silica is the third largest inorganic component. There are also other inorganic elements present in the fuels like P, Ca, Mg, Fe, Al, and Ti.

2.4.2 Combustion of Biomass

At a world level biomass combustion covers around 15% of the energy conversion, it is the main source of energy for many developing countries and most of it is non-commercial for small-scale heating and cooking (IEA). In industrialized countries biomass contributes only 3% of the total energy use. In Europe the biomass contribution to the total energy consumption is largest in Finland (18%), Sweden (17%) and Austria (13%) (IEA).

There are different conversion processes for conversion of biomass into energy. The conversion process can be thermochemical (combustion, pyrolysis, gasification), or bio-chemical (biogas or bio-ethanol production). Biomass is mainly used in processes of thermal energy production, electrical energy production and cogeneration of electrical and thermal energy. The thermal utilization of biomass for heat and electricity is becoming very important and it is going to be one of the important ways to reduce greenhouse gas emissions from energy production. Biomass combustion is a proven and widely applied technology in the size range from few kW for household heating to several MW for district heating and up to more than one hundred MW for power stations based on steam cycles.

Combustion means that oxygen is supplied to burn the fuel and it is a complex process that consists of coupled heat and mass transfer with chemical reaction and fluid flow (Jenkins et al., 1998; Nussbaumer, 2003). The main steps of the process are drying, devolatilization, gasification, char combustion, and gas-phase oxidation. The time for each reaction depends on the fuel size and properties, on temperature, and on combustion conditions. The products of those reactions are heat, water, carbon dioxide and ash. In a boiler, the produced heat is transferred to water or steam carried in steel tubes, and the water may be used for district heating and the steam may be used for electricity production.

2.4.3 Technical Problems

Biomass industry has developed rapidly within the last decades, but there are still some obstacles, such as fireside technical problems and pollutant emissions, and there is a need of knowledge and research in order to further develop the biomass combustion technology.

Inorganic species are released during combustion of biomass fuels and transported to surfaces in a boiler by different mechanisms and form deposit in several different forms (Baxter, 1993; Nielsen et al., 2000). Alkali and alkaline earth metals react with silica or sulfur in the high temperature furnace regions and form slag masses. These slag masses can form and accumulate on grates or on walls with high surface temperature. Another problem is agglomeration, which is common in fluidized bed combustors, where reactions in the bed lead to the formation of large aggregated composites of bad material and ash, which can lead to eventual defluidization of the bed and plant shut-down. Fouling deposits can be formed on all heat transfer surfaces, but also at the furnace exit in circulating fluidized beds on particle separation devices.

The undesirable effects of deposits are: they retard heat transfer and lead to decline in boiler efficiency and capacity if they cannot be removed, deposits can grow to the extent that flow through the boiler is restricted and cause mechanical damage, deposits accumulate in quantities unmanageable by the facility leading to early shutdown for maintenance, and deposits may lead to corrosion (Nielsen et al., 2000).

Alkali and alkaline earth metals in combination with other fuel elements such as silica and sulfur, and facilitated by the presence of chlorine, play a major role in the undesirable reactions in combustion facilities (Baxter et al.,1998; Olsson et al.,1997). Alkali compounds may have low melting temperatures close to heat exchanger operating temperatures. Potassium is a major concern and problems are particularly severe when burning straws, grasses and other herbaceous materials, as well as younger tissues of woody species because they contain more potassium than mature wood.

2.4.4 Particle Emissions

Primary pollutants formed in biomass combustion are particulate matter, CO, HC, NO_X, and SO_X, and including volatile organic compounds (VOC) and polycyclic aromatic hydrocarbons (PAH) that are emitted during incomplete combustion (Jenkins et al., 1998). Acid gases, lead and other heavy metals may also be emitted.

Investigations of particle emissions have shown that well designed and properly operated automatic wood combustion plants achieve a high combustion quality and thus result in low emissions of unburned hydrocarbons and soot (Nussbaumer, 2005). Particles from well designed and operated automatic wood combustion consist mainly of inorganic matter such as salts, while particles from wood stoves operated under poor conditions consist mainly of soot and organic substances (Klippel et al., 2007). Under poor conditions the particle size distribution is shifted to larger sizes because of condensation of unburned hydrocarbons on existing particles in the flue gas.

Studies have shown that particles from incomplete combustion have high cell toxicity and carcinogenic potential (Klippel et al., 2007).

Most combustion generated particles have an aerodynamic diameter smaller than 1 µm. Appropriate particle removal device should be applied before the flue gases are emitted through the stack into the atmosphere. These devices may be cyclones, electrostatic precipitators, and baghouse filters. A fraction of the flue particles penetrates the removal equipment and it is emitted into the atmosphere. For example precipitators have a penetration window in the particle size range 0.1 to 1.0µm (Porle, 1995). Application of these devices is not a problem for medium and large scale facilities, since it is economically affordable, but for small-scale biomass combustion systems it is not feasible. Small scale biomass combustion systems are affecting the air quality and they are identified as a major particle emission source together with industry and traffic.

2.4.5 Alkali Metals

Alkali metals are very reactive and are never found in elemental form in nature. They are famous for their vigorous, exothermic reactions with water. In air they quickly oxidize and formed alkali compounds are very stable non reactive substances. Their reactivity is because these elements all have one electron in their outermost shell, and they need to remove it to form a cation and reach preferred stable inert gas configuration. The alkali metals have low melting points and densities and react readily with halogens to form ionic salts, and with water to form alkaline hydroxides.

Generally, salts of sodium and potassium are much more abundant and practically used than salts of the other members of the alkali metal group. Salts of lithium, rubidium and cesium occur in the Earth's crust but are not very common.

Sodium makes up about 2.6% by weight of the Earth's crust, making it the sixth most abundant element overall (CRC Handbook of Chemistry and Physics, 2004) and the most abundant alkali metal. Sodium is present in many different minerals, of which the most common and famous is ordinary salt, sodium chloride. This mineral occurs in solid deposits (halite) and in great quantities dissolved in seawater. Sodium is an essential element for animal life. Sodium ions have important role in many physiological processes such as regulation of blood and body fluids, heart activity, transmission of nerve impulses. On the other hand the ion is not needed by plants, and is generally phytotoxic.

Potassium as various compounds makes up about 1.5% of the weight of the Earth's crust and is the seventh most abundant element (CRC Handbook of Chemistry and Physics, 2004). Potassium and sodium have very different functions in organisms, especially in animal cells. Potassium was first isolated from potash where from comes its name. Potassium is an essential mineral micronutrient in human and animal nutrition because of its important biochemical function and also is an essential component of plant nutrition. The most of the world potassium production is consumed by the fertilizer industry and is found in most soil types.

2.5 Aerosol Measurement Techniques

A wide range of methods can be applied for the physical and chemical analysis of aerosol particles, and the selection and combination of analytical methods depends on the sample type and target parameters.

Measured physical properties of aerosol particles include size, number, mass, density, surface and morphology. The most applied techniques for the physical characterization of atmospheric aerosol particles are: differential mobility analysis (DMA), inertial separation (impaction, time-of-flight), scanning and transmission electron microscopy (SEM, TEM) and light scattering for particle size, structure, and density (McMurry, 2000; Pöshl, 2005). Gravimetry and oscillation of deposition substrates are techniques applied to determine particle mass. Spectrophotometry, spectroscopy, and nephelometry are used to determine absorption and scattering coefficients.

Traditional methods for the sampling and chemical analysis of air particulate matter are off-line and involve the collection of the investigated particles on solid deposition substrates (membrane or fiber filters, inertial impaction plates, thermal or electrostatic precipitation plates) or in a liquid (wetted wall cyclone, washing bottle), and intermediate steps of sample storage, transport, and preparation before chemical analysis (McMurry, 2000). These methods are prone to analytical artefacts caused by evaporation of particle components, adsorption or absorption of additional gas-phase components, and chemical reaction during sample collection, storage, transport, and preparation. Also, off-line techniques do not allow the resolution of the high spatial and temporal variability of atmospheric aerosols.

Combustion particles have a size range from a few nanometers to some tens of micrometers. In order for the whole size range to be measured, combination of measurement methods should be applied. Sampling, pre-treatment and dilution are very important for measurements of combustion aerosols, since particle concentrations are high and they are formed during high temperature processes (Burtscher, 2001). Design of the sampling system is of high importance to obtain reliable results because pre-treatment and dilution can affect particle properties by processes like coagulation, diffusion losses, nucleation or condensation.

The basic method to measure mass concentrations of particles off-line in flue gases is gravimetric sampling on quartz or glass fibre filter. This method gives total mass concentrations and later also allows application of different analysis methods like microscopy and chemical analysis. Disadvantages of filter sampling are possible sampling artefacts, low time resolution and lack of on-line analysis (Nussbaumer et al., 2008). Tapered Element Oscillation Microbalance (TEOM) is an instrument for direct measurement of the total mass concentration of particles. In combustion applications the ambient air model of the instrument may be used together with a dilution system.

There is an increasing interest in the particle size of particulate emissions as well as of particulate matter in the ambient air. For measurements of particle mass size distribution, different types of low pressure cascade impactors (e.g. Dekati Low Pressure Impactor, Berner Low Pressure Impactor) are used (Nussbaumer et al., 2008). Size of the particles measured with this method is ranging from 30 nm to 10-20 μm. The low pressure may lead to evaporation of volatile materials and this problem increases with decreasing lower cut-off diameter. Particle samples collected on the impactor stages are weighed and can be used for subsequent chemical analyses.

There is also an interest in particle number concentrations and particle number size distributions, since a high number of ultrafine particles are assumed to be relevant in certain health issues. A common instrument used for on-line measurements of particle number concentrations and number size distribution is the Scanning Mobility Particle Sizer (SMPS). Different versions of the instrument measures particle size in the range from a few nanometres to 1 µm.

Most of these instruments measure bulk physical parameters of the aerosol without information on the single particle level. Over the past years substantial progress has been made in the development of aerosol mass spectrometers for real-time measurements of size selected (single) particles as a result of progress in instrumental design and technology. These instruments, as the aerosol mass spectrometer (AMS) constructed at University of Gothenburg, provide real time analysis of size and chemical composition of individual particles. The principle of work in most real time detection and analysis instruments of single particle is that aerosol particles are sampled into vacuum system where they are decomposed and the produced fragments are characterized by mass spectrometry.

3. Experimental techniques

This chapter briefly summarizes the experimental techniques used in Papers 1-5. The reader is referred to the individual papers and references therein for details concerning the experimental methods.

3.1 Laboratory Setups for Studies of Alkali Emission from Biomass

Studies of alkali emission during pyrolysis of biomass samples were carried out in the laboratory. This section describes the surface ionization (SI) technique and its application to alkali detection followed by descriptions of the instrumentation used during the laboratory experiments.

3.1.1 Surface Ionization Technique

The SI technique has proven to be very suitable for sensitive alkali measurements. The SI phenomenon is a process where an adsorbed atom or molecule on a surface becomes ionized upon desorption (Zandberg, 1995; Ionov, 1972).

The statistical probability of the ionic flux from the surface is dependent on the surface temperature, the work function of the surface and the ionization potential of the atom. This is described by the Saha- Langmuir equation:

$$\alpha = \frac{n_+}{n_0} = \frac{g_+}{g_0} \exp\left[\frac{e(\phi - IP)}{k_B T}\right], \tag{3.1}$$

where α, or n_+/n_0 is the ratio of desorbed ions and neutrals from the surface, g_+/g_0 is the statistical sum ratio of ions and neutrals, e is the elementary charge, ϕ is the work function of the surface, IP is the ionization potential of the atom, k_B is the Boltzmann constant, and T is the surface temperature.

The probability that an adsorbed species will desorb in ionic form is described by the ionization probability β:

$$\beta = \frac{\alpha}{\alpha + 1}. \tag{3.2}$$

The difference between the work function ϕ and the ionization potential IP has the largest impact on the success of the SI method. For most elements IP is larger than ϕ of the surface and desorption from the surface in neutral form dominates completely. However, the alkali metals have very low IP`s and are therefore able to undergo ionization on a hot surface. It has been found that platinum is a suitable surface material due to its slow oxidation and high melting point (McCabe et al., 1988).

During experiments the temperature of the hot surface was typically 1230°C (1500K), which is necessary for fast dissociation of impinging alkali compounds and desorption of ions. The applied alkali detector in the present study of biofuels consisted of a platinum filament, which constitute the ionizing surface, and an ion collector and it is shown in Figure 3.1. Gaseous alkali compounds first hit the Pt surface and dissociated on the surface. The alkali atoms then desorbed from the hot surface as ions. The filament which was biased at 400-500 V repelled the ions and directed them toward a grounded collector. The current at the collector was proportional to the flux of alkali atoms onto the filament.

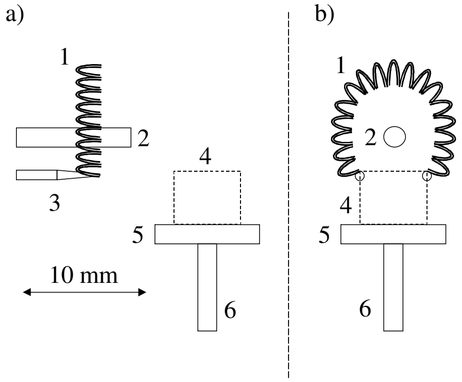

Figure 3.1 The surface ionization detector and sample holder used in Paper 1: a) side view, b) frontal view, 1.Pt filament, 2. ion collector , 3. current feeder, 4. contours of a wood particle, 5. sample plate, and 6. pin connected to the balance.

3.1.2 Single Particle Reactor

Alkali emission studies from biomass samples were carried out in single particle reactor. Vertical and horizontal cross-sections of the experimental set-up are shown in Figure 3.2. The main parts of the reactor are a furnace and a balance. An aluminum oxide sample plate is placed in the middle of the furnace and it is directly connected to the balance. At the same level with the sample plate are placed five entrances, which can be used for different kinds of measurement devices and visual observation. During the alkali emission studies the SI detector and mass spectrometer (Balzers QMG 421C) were connected to the reactor.

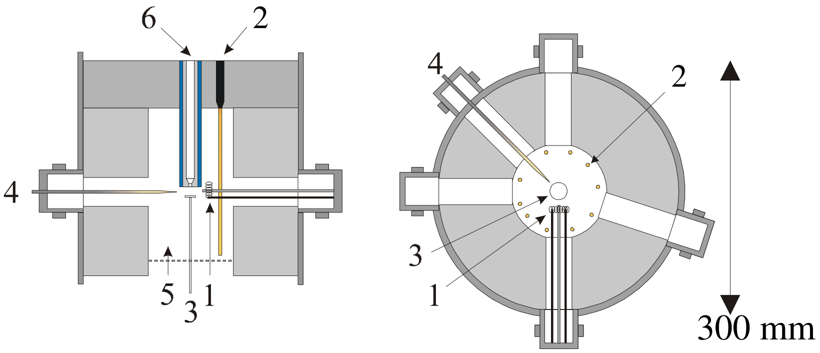

Figure 3.2. The single particle pyrolysis reactor 1. surface ionization detector, 2. heater, 3. sample plate, 4. mass spectrometer capillary, 5. Ar flow, 6. sample insertion tube.

A fuel particle was inserted into the furnace through an insertion tube and landed on a sample plate. The insertion tube may be cooled with air or water in order preventing possible reactions before the particle mass and alkali emission can be measured. The furnace was preheated to a certain temperature, which resulted in rapid heating of the introduced fuel particle. Five u-shaped heaters provide heating and a thermocouple placed near the sample plate measured the temperature of the furnace.

Experiments were carried out by drying the samples at 100°C until they had constant mass and then inserting them into the reactor at different temperature. The alkali emission and particle mass were measured during the subsequent pyrolysis. Some particles were immersed in water until they had gained 50% mass and were then introduced to the reactor. The mass spectrometer was used to measure the water emission during pyrolysis and also to control the oxygen level in order to keep it at 2-4% to avoid the build up of a carbon layer on the platinum surface of the SI detector.

The experimental set-up shown schematically in Figure 3.3 was used for additional experiments where fuel particles were subjected to a constant heating rate of 20 Kmin^{-1}. It consisted of a chamber with a SI detector above a sample crucible in a heater. The SI detector was made of a platinum filament and was kept at 1500K and 500V during experiments. The adjacent ion collector was grounded through an electrometer. A nitrogen flow of 1 l/min was allowed through the chamber during experiments and the alkali emission was sampled with a frequency of 1Hz.

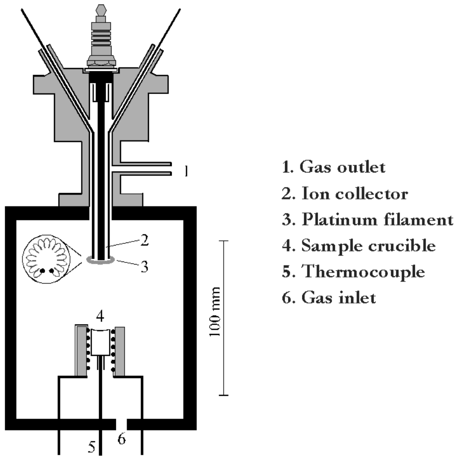

Figure 3.3 Schematic picture of the setup used for pyrolysis of biomass samples using a slow temperature ramp. 1. Gas outlet, 2. Ion collector, 3. Platinum filament of the SI detector, 4. Sample crucible, 5. Thermocouple, and 6. Nitrogen inlet.

3.2 Measurements in a Circulating Fluidized Bed Boiler

In Paper 2 experimental studies of alkali-containing particles were carried out in a commercial-sized CFB boiler. Fuel conversion in a fluidized bed was first introduced by Winkler who patented a gasifier in 1922 (Leckner, 1998). In FBC the primary air is supplied through holes in the bottom of the reactor, and it is flowing upwards in a combustion chamber, with a velocity sufficiently high for the solid particles to be fluidized in the flow, instead of being pulled down by gravity (Valmari, 2000; Kunii et al., 1991).The fuel is fed from different places to achieve an even distribution. The particle suspension is distributed from the dense bottom bed throughout the combustion chamber and continuously carried away with the combustion air (Leckner, 1998). At a certain airflow the bed will behave like a fluid why it is called a fluidized bed, and typical fluidization velocity in circulating fluidized bed combustion (CFBC) is about 5 m/s.

The fluidized bed in a CFBC consists of inert bed material, a low percentage of fuel, and in some cases a sorbent, e.g. limestone. The bed material usually consists of quartz sand particles of 0.3-0.5 mm in diameter. The sand is periodically partially replaced to avoid agglomeration of the bed particles. The bed temperature during CFBC of biomass is controlled by the heat exchanger surfaces on the combustion chamber walls and it is typically about 800 °C. The temperature at the top of the bed is higher by up to ≈ 100 °C than in the bottom bed (Valmari, 2000). Heat produced in combustion is absorbed by bed particles and they distribute the heat throughout the furnace by convection and radiation.

A CFBC is equipped with a cyclone located downstream of the combustor. The airflow in the system is high and some bed particles as well as large char and ash particles will go with the flow, so the cyclone re-circulates particles larger than the cyclone cut-diameter back to the bed. Flue gas together with particles smaller than the cyclone cut-off diameter is directed through the convective pass, its heat is transferred to heat exchanger tubes and the flue gas temperature is decreased below 200°C. Before the flue gas leaves the facility through the stack and continue to the atmosphere, particles are usually collected from the flue gas by an electrostatic precipitator (ESP) or a bag-house.

3.2.1 The 12 MW_{th} CFB at Chalmers University of Technology

During these studies measurements were performed in the 12 MW_{th} CFB at Chalmers University of Technology schematically shown in Figure 3.4. Measurement campaigns were performed during winter time 2002/2003 and 2003/2004, and the boiler was fired with a mixture of wood chips (62-75%) and wood pellets (25-38%). Experiments were performed either with the fuel mixture of wood chips and pellets alone or with addition of chlorine as HCl (aq) and/or sulfur as SO_2 (g). Particles were collected at position B after the exit of the primary cyclone at a gas temperature of 800 °C, and at position F downstream of the secondary cyclone at 160 °C.

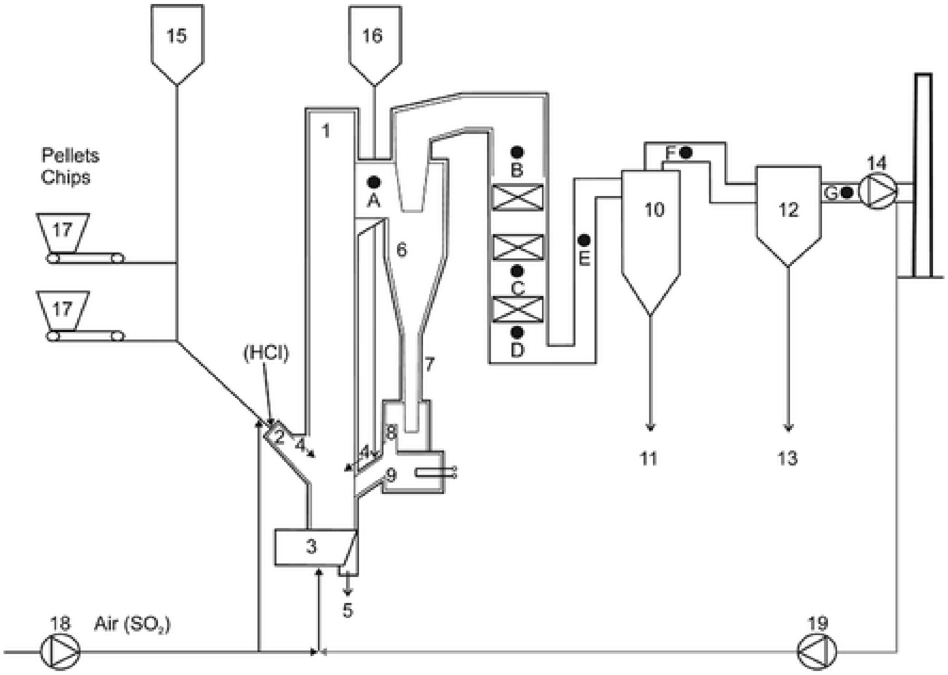

Figure 3.4. Schematic description of the CFB at Chalmers, 1. combustion chamber, 2. fuel feed chute, 3. primary air to air plenum, 4. secondary air inlet at 2.1m, 5 bottom ash removal, 6. hot primary cyclone, 7. particle return leg, 8. particle seal, 9. heat exchanger, 10. cold secondary cyclone, 11. secondary cyclone ash removal, 12 bag filters, 13. filter ash removal, 14. flue gas fan, 15. sand bin, 16. lime bin, 17. fuel bunkers, 18. air fan, 19. flue gas recirculation fan. Measurements positions A, B, C, D, E, F, and G are indicated.

The size of the of combustion particles ranges from a few nanometers to some tens of micrometers (Burtscher, 2001). No single method for particle analysis can cover the whole size range, and methods based on different physical principals have to be applied together.

The instrumental setup for on-line particle sampling used in Paper 2 is illustrated in Figure 3.5. A sampling probe extracted gas at the center of the flue gas duct, and the inlet was oriented perpendicularly to the flue gas flow. The flow rate through the probe was typically 200 dm3/min and the residence time within the probe was < 0.2 s. Particles with a diameter larger than 3 μm were partially removed by a cyclone connected to the probe, whose removal probability increases with particle size. In order to dilute high particle number concentrations, three ejector diluters were connected in series before the measurement instruments resulting in a total dilution factor of 350. The first diluter was heated to 150°C to avoid condensation of water vapor.

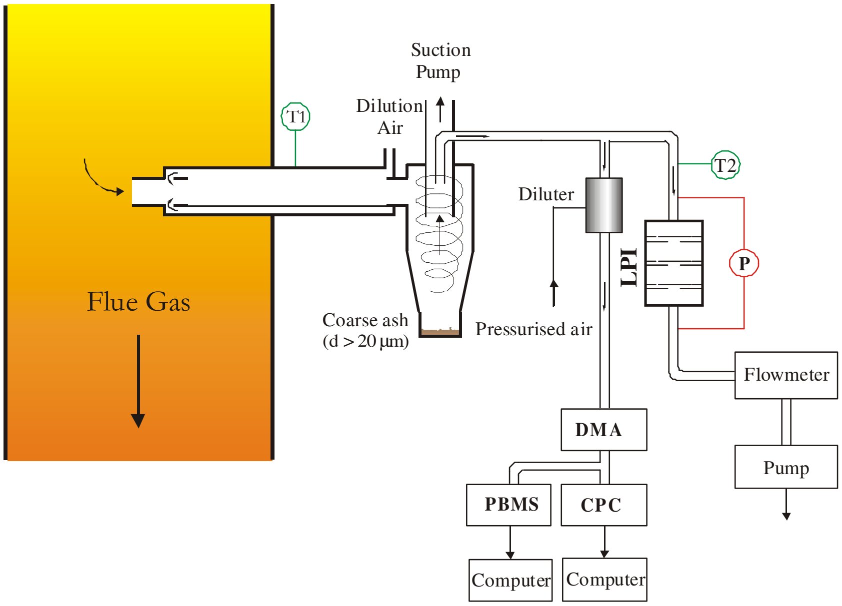

Figure 3.5 The experimental setup. DMA –differential mobility analyzer, CPC- condensation particle counter, PBMS- aerosol mass spectrometer, LPI – low pressure impactor, T1, T2 – thermocouples, P- pressure gauge.

3.2.2 Low Pressure Impactor

During this work a low pressure impactor (LPI), which was constructed at University of Gothenburg was used for collection of particles to obtain information on their mass and chemical composition. The cross section is presented in Figure 3.6. Impactors classify particles according to their aerodynamic diameter, and LPI can be used for collection of particles down to the nanometer size range. The LPI consisted of 11 separated impactor plates, and a jets consisting of particle laden gas was directed towards a collection plate onto which particles impact by inertia.

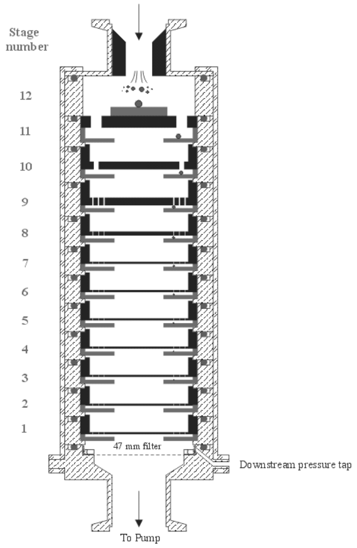

Figure 3.6. The low pressure impactor (LPI) constructed at University of Gothenburg.

Large particles are more inert and unable to follow the gas streamlines and impact on the upper stage plates of the LPI, while the smaller ones will follow the streamlines to lower stage plates until impaction occurs (Baron and Willeke, 2001). The configuration of the separate plates, i.e. the number of holes and their diameter, and the value of pressure drop during sampling, determines the flow rate and cutoff size of each plate.

This sampling method can be followed with application of a large variety of analysis methods, for example gravimetric analysis, microscopy, and chemical analysis. However, in the general case there are drawbacks using a LPI like the long sampling periods before the analysis of the samples. Also a source of error may be volatilization of semivolatile compounds (compounds that are found in both the vapor and particulate phases) (McMurray, 2000). Volatilization can occur because of a pressure drop in the sampler, or due to changes in temperature, relative humidity or composition of the incoming aerosol during sampling. Artifacts associated with sampling transport and storage have also been reported (Chow, 1995). With impactors particle bounce is a problem, but it is largely eliminated by the use of coated substrates on the plates. During this experiment particles were collected on 11 steel plates prepared with vacuum grease dissolved in toluene. The mass from particles collected on each plate was measured, and the particles were later dissolved in 1% HNO_3 and elemental analysis was performed by inductively coupled plasma-mass spectroscopy (ICP-MS).

3.2.3 Scanning Mobility Particle Sizer System

During this work number size distributions were obtained for particles in the size range 0.01-0.35μm with a SMPS (TSI inc., model 3936). The SMPS system includes two parts, a differential mobility analyser (DMA) and a condensation particle counter (CPC). This instrument provides information about the particle size distribution with a time resolution of a few minutes, while chemical composition remains unknown (McMurry, 2000). The instrument is designed in the way that incoming particles are charged, later electrostatic forces of a electric field are used to remove all particles except one limited size fraction, producing at the and monodisperse aerosol.

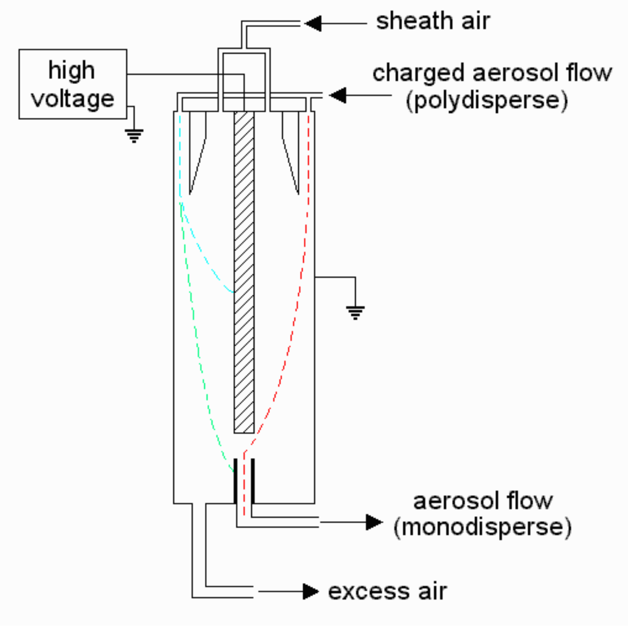

Figure 3.7. Cross section of the Differential Mobility Analyzer (DMA).

The aerosol sample first passes through a bipolar ion neutralizer, which creates a known distribution of positively and negatively charged particles. The charged particles then enter a DMA that is the heart of this system and it classifies particles according to the electrical mobility (McMurray, 2000). A cross section of the DMA is shown in Figure 3.7.

The DMA is consist of two concentric cylinders, an inner electrode, and an outer electrode. The outer electrode is kept at ground potential, while negative voltage (0 to 10 000V) is applied to the inner electrode to create an electric field. A controlled, laminar sheath air flows along the space between the two electrodes, while aerosol particles are introduced into the DMA through a slit at the top of the outer electrode. Particles with negative charges are deflected towards and deposited on outer wall while neutral particles exit the DMA with the excess air. Positively charged particles move towards the negatively charged inner electrode. Only particles within a certain range of electrical mobility have the correct trajectory to pass through a slit near the bottom of the inner electrode. Next, the classified particles enter the detector, the condensation particle counter (CPC), that will give information about the particle number concentration. In this instrument particles pass through a supersaturated vapor of butanol that condenses onto their surfaces and makes them grow into a size that is detectable by light scattering. By ramping the voltage of the inner electrode over selected time, the entire particle size distribution and number concentration can be measured. The Aerosol Instrument Manager software controls the counting process, data collection, calculation and storage.

3.3 Measurements of Ambient Aerosol Concentrations

Ambient air aerosol measurements were performed at two different urban sites, in Skopje, the capital city of FYR of Macedonia, and in Gothenburg, Sweden. The approaches and used instruments were different for the two studies. The measurement campaign in Skopje, at an urban background site, was performed during four periods in order to characterize the seasonal variation and concentrations of aerosol components with equivalent aerodynamic diameter < 2.5μm (PM 2.5). Sampling and analysis was performed with conventional instruments and a detailed description of the used instruments is presented in Paper 4.

During the measurements performed in Gothenburg the key instrument was the Aerosol Mass Spectrometer, which has been developed at Atmospheric Science, University of Gothenburg. This instrument is SI-based for real time analysis of chemical composition of single particles (Svane et al., 2004). The instrument consists of three differentially pumped vacuum chambers containing the aerosol inlet, the surface ionization unit, and the mass spectrometer unit. A schematic picture of the vacuum system of the apparatus is shown in Figure 3.8.

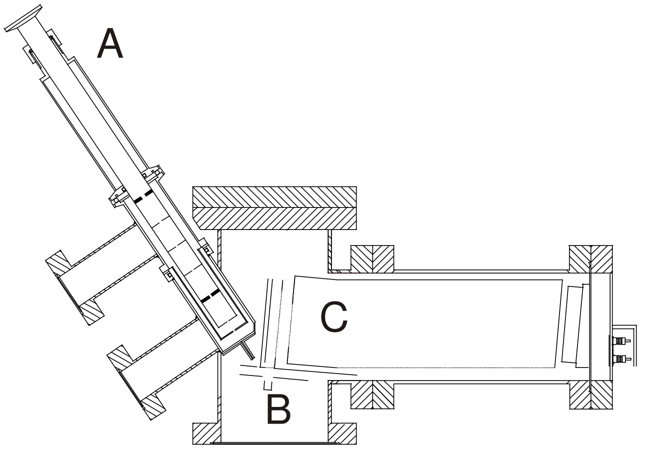

Figure 3.8. Cross-section view of the vacuum system of the AMS: (A) the particle inlet, (B) the ionizing platinum surface and a focusing electrode, and (C) TOF-MS unit.

The vacuum system is pumped by one mechanical pump and two turbomolecular pumps, and a pressure of $1 \cdot 10^{-5}$ mbar is maintained in the main chamber during operation. Aerosol particles are drawn into the AMS through the particle inlet which consists of a critical orifice and an aerodynamic lens system. The critical orifice with a diameter of 100 µm controls the pressure drop and flow rate. The aerodynamic lens system consists of six orifice lenses in a stainless steel tube (Liu at al., 1995a, 1995b). The successive compressions and expansions of the aerosol on its way through the lens system make the particles form a narrow collimated beam. The sharply focused particle beam is directed onto a resistively heated platinum surface in the detection chamber. The Pt surface has been designed as box made from thin platinum foil, which limits problems due to particle bounce effects on the hot surface (Svane et al., 2004). Particles that stick inside the Pt box decompose in contact with the hot surface and the alkali content of the particles is transformed into a burst of alkali ions during typically a few hundreds microseconds.

Paper 3 describes a new version of the AMS instrument that combines SI with an orthogonal acceleration time-of-flight mass spectrometer (oa-TOFMS). In this setup the ions emitted from the Pt surface enter a deflector unit, which at a certain time accelerates them into the flight tube of the oa-TOFMS. The previous version of the AMS used a quadruple mass spectrometer (Svane et al., 2004). The old AMS only measured on one element at the time, while the new version of the instrument produces a mass spectrum for each detected particle. The new oaTOF-AMS was demonstrated in Paper 3 and applied in field measurements in Paper 5.

4. Results

This chapter gives an overview of the results from Papers 1-5 in the thesis. Section 4.1 describes the laboratory studies of alkali emission from biomass samples (Paper 1) and Section 4.2 presents the results from particle measurements during biomass combustion in a commercial scale CFB (Paper 2). Section 4.3 summarizes the results from ambient air measurements in Skopje based on Paper 4, and Section 4.4 finally describes the application of AMS technique in ambient air measurements of alkali-containing particles (Papers 3 and 5).

4.1 Alkali Emission during Wood Pyrolysis

When biomass is fed into a hot environment it will undergo several dramatic changes including drying, pyrolysis, combustion of volatiles and char combustion. The different phases may overlap in time and the rate of change will affect the combustion process. It is important to know when and how combustible gases as well as condensable material such as alkali compounds are released in a combustion facility. The aim of Paper 1 was to study the release of alkali compounds from biomass samples that undergo rapid heating. The laboratory conditions were intended to mimic the rapid heating experienced by fuel particles when introduced to a boiler such as a CFB boiler.

Experiments were initially performed where fuel particles were pyrolysed during slow heating at a heating rate of 20 Kmin^{-1}. Typical results are shown on Figure 4.1. Alkali (Na + K compounds) was first released from the wood during the pyrolysis phase (200-400°C) and then above ~620°C due to evaporation from the ash. Alkali that was released during pyrolysis was referred to as pyrolysis alkali and alkali released from the ash phase was referred to as ash alkali.

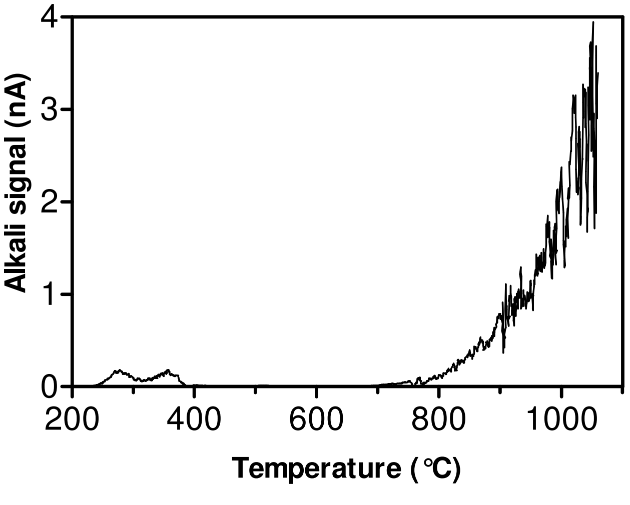

Figure 4.1. Total alkali release from birch wood during pyrolysis at a heating rate 20Kmin^{-1}.

In a next set of experiments wood particles were dropped into a pre-heated reactor, and the mass of the wood particle and the alkali release were followed as a function of time. Typical results from the experiments performed in the single particle reactor are presented in Figure 4.2. At a reactor temperature of 400 °C alkali was emitted during the pyrolysis phase. The alkali emission followed the derivative of the fuel particle mass, and small particles released alkali earlier than large ones because of a faster heating of the small particles. At higher temperatures alkali release was also observed from the char and ash remaining after the pyrolysis phase was completed. At 800°C, large particles released alkali in two phases: the first one is due to pyrolysis alkali and the second one due to ash alkali. For small particles the two phase overlap in time and pyrolysis alkali cannot be distinguished from ash alkali. The difference between different particle masses was likely caused by larger temperature gradients and lower heating rates in the large particles. Small particles released more alkali per unit initial mass and also gave higher alkali signal compared with larger particles.

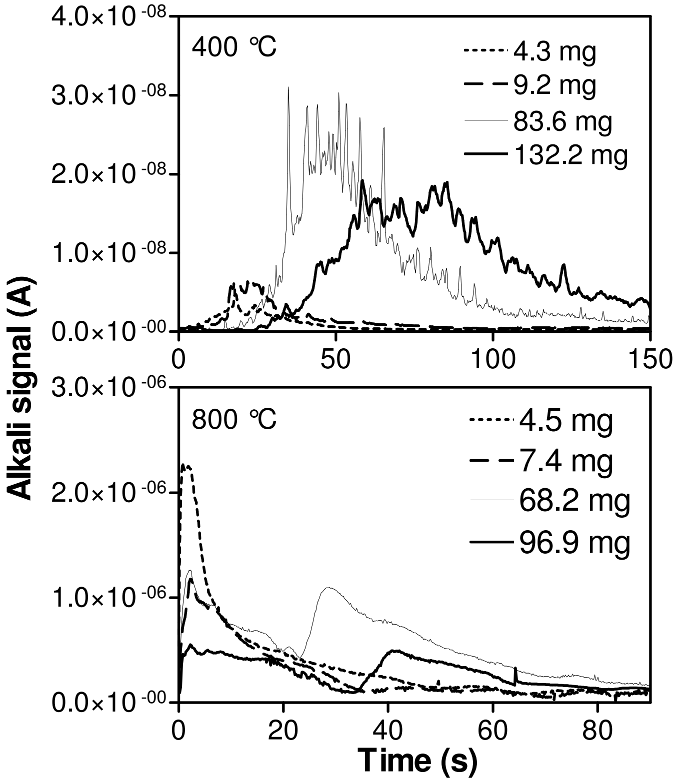

Figure 4.2. Alkali signal as a function of time for different initial particle masses at 400 and 800°C.

Figure 4.3 shows total emitted alkali per unit initial sample mass as a function of initial sample mass. The total alkali emission decreased with increasing sample mass and this is more evident at higher temperatures. The reason for this likely is secondary reactions between alkali and the char. From small particle alkali emission is higher because the gas has a shorter transport through the char layer and less secondary reactions forming stabile alkai compounds will occur.

At higher temperatures the char layer is more porous (Davidsson and Pettersson, 2002) and the gas evolution is faster and builds up a pressure that forces gases out, which lowers the possibilities for secondary reactions. At low temperatures this force will be smaller and alkali will have more opportunities to interact with char surfaces.

From the experiments with the wet particles it is shown that water evaporates upon heating and is also produced during the pyrolysis. The effect of water evaporation is to cool the sample and delay the pyrolysis phase and the related the alkali emission, but the total alkali emission seems not to be affected by addition of water.

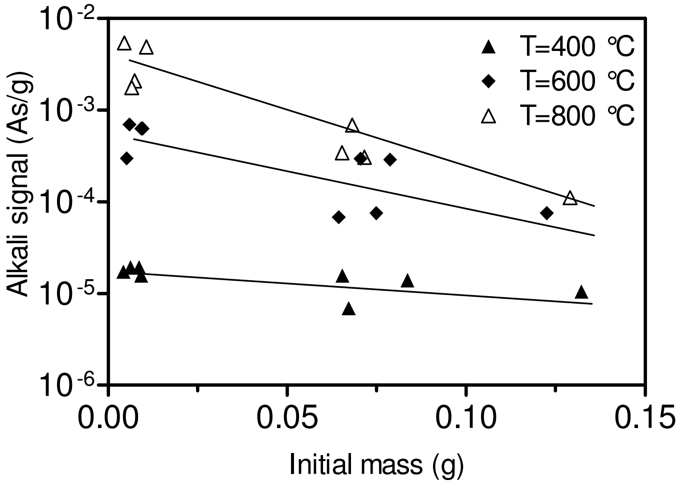

Figure 4.3. Total alkali emission per unit initial sample mass as a function of initial sample mass for different temperatures. Solid lines are trend-lines to guide the eye.

The results of the study described in Paper 1 show that the temperature history of the fuel sample is very important for the understanding of when and where in a reactor alkali is released from the fuel. A wood chip will emit alkali during pyrolysis at 300-400 °C. Large chips will emit less alkali per unit mass than small ones, and the alkali in the char eventually will be emitted during char burning at higher temperatures in the combustion process.

4.2 Wood Combustion in a Circulating Fluidized Bed Boiler

The alkali release from biomass fuels depends on the alkali concentration of the fuel and also on the presence of other compounds. Chlorine has been found to enhance alkali release from biofuels (Olsson et al., 1997) by formation of potassium chloride that has a higher vapor pressure than other common alkali compounds. The relased alkali compounds will condense on particles in the flue gas or on existing surfaces and may form corrosive deposits (Nielsen et al., 2000). It has been shown that addition of sulfur enhances formation of potassium sulfate and thereby hinders formation of potassium chloride (Hansen et al., 2000).

In paper 2 the potassium, chlorine, and sulfur chemistry, and the transport and distribution of these species in a commercial-scale CFB boiler were studied with and without additives to the fuel. Combustion of a mixture of wood chips and wood pellets

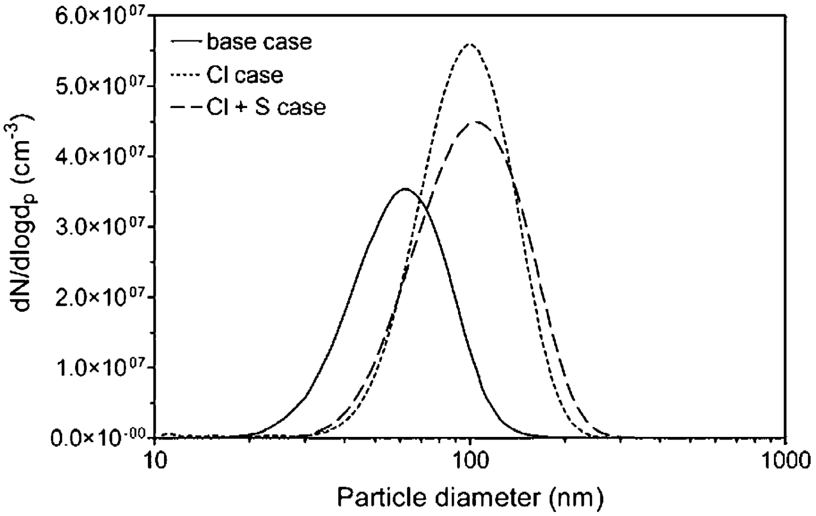

Figure 4.4. The number size distribution shifted from a peak at ~60 nm in the base case to ~100 nm in the addition cases.

without additive was referred to as the "base case", and the additive cases were referred to as the Cl, Cl + S, and S cases.

Number size distributions of submicron particles in the flue gas are shown in Figure 4.4. Sampling was performed at position F and results are displayed for the base case, the Cl case, and the Cl + S case. The particles grew to larger size when HCl and SO_2 was added with the fuel and the particle number concentrations were slightly higher than for the base case. The additions resulted in larger concentrations of volatile compounds, which condensed to form submicron particles when the flue gas was cooled.

Addition of chlorine to the furnace increased the number and mass of submicron particles in the flue gas because the formation of gaseous potassium compounds was enhanced. Also it is concluded from the results that the coarse fly ash component was not strongly influenced by changes in potassium, chlorine and sulfur concentrations. The total mass of the coarse mode particles was higher at position B than at position F because the large particles were removed by the secondary cyclone.

Particle mass distributions for total mass and for selected elements measured at position F in the base case are shown in Figure 4.5. The particles carried by the flue gas had a bimodal size distribution. The submicron particles originated from volatile compounds that nucleated to form new particles or condensed on existing particles when the flue gas was cooled. A large fraction of these particles consists of potassium, sulphur, and chlorine. The particles in the micron size range were mostly ash components from the fuel that had remained in the solid or liquid phase during the combustion process. The coarse particles consisted mainly of non-volatile elements such as calcium, magnesium, aluminium, iron, and phosphor. Elements present in the fine mode are also present in the coarse mode because of the condensation of gaseous components on the surface of large particles.

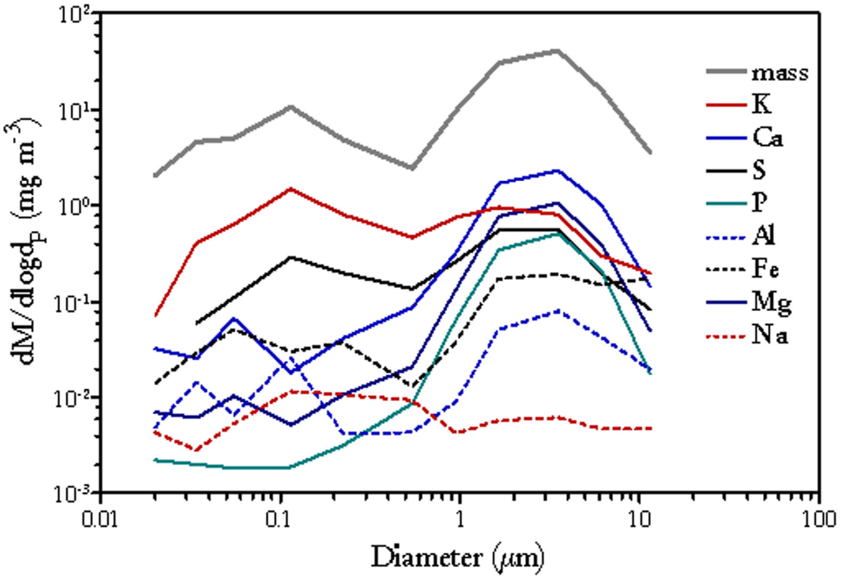

Figure 4.5. Particle mass size distributions for the total mass and selected individual elements measured with an LPI at position F downstream of the secondary cyclone under base case conditions.

It was concluded that addition of sulfur and chlorine increased the formation of submicron particles and also lead to deposition of potassium sulfate and chloride inside the boiler. The results compared well with earlier work based on laboratory-scale experiments concerning effects of chlorine and sulfur on potassium chemistry.

In addition to the results presented in Paper 2, particle number concentrations were also measured before and after the bag-house filters in the CFB facility. Figure 4.6 shows the calculated capture efficiency of the bag-house filters as a function of particle diameter. Most particle sizes are efficiently captured by the filter, but the filter is somewhat less efficient in the accumulation mode range. Particles in this size range are thus more likely to escape from the boiler and be released into the ambient.

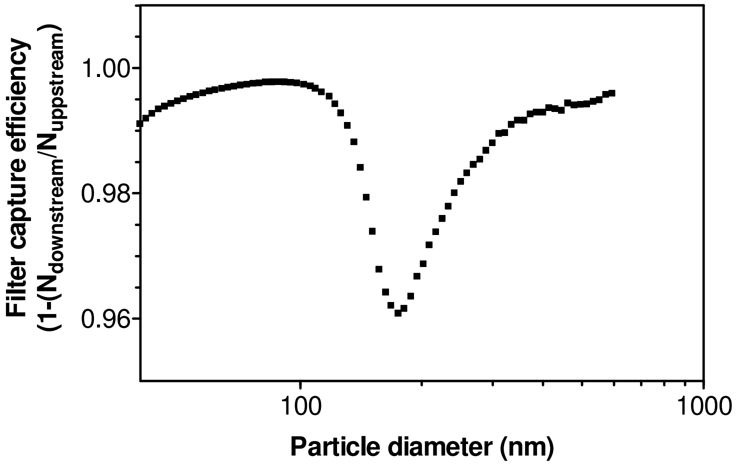

Figure 4.6 Bag filter capture efficiency in the CFB as a function of particle size. The capture efficiency was determined by number concentration measurements upstream and downstream of the filters using a SMPS.

4.3 The Composition of Particulate Matter in Skopje, FYR of Macedonia

Aerosol particle measurements ($PM_{2.5}$) were performed in central Skopje from December 2006 to October 2007. The aim was to characterize the seasonal variation and typical concentrations of major aerosol components and to obtain information about the importance of different pollution sources for the ambient air quality.

Samples were collected with a conventional impactor loaded with polycarbonate filters. The mean $PM_{2.5}$ concentrations for all data varied in the ranges 10.3-142 $\mu g\ m^{-3}$ with a mean of 38 $\mu g\ m^{-3}$, and the mean values for the four seasons varied within a factor of two with the highest values observed during winter and summer.

The samples were analysed for particulate mass, black carbon (BC) and seventeen elements (Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, and Pb). Elemental analysis of the collected samples was performed with an EDXRF spectrometer, and the BC was determined with a visible light reflectometer. The elemental composition data for all measurements was dominated by Si, S, Ca, Fe, and BC, which shows that mineral dust and combustion processes made substantial contributions to the aerosol. Lower concentrations of the other analyzed elements were detected in most samples, with the exception of Cl, V, and Cr that were often below the detection limits. The BC and elemental composition data for the individual seasons showed large variation and there were clear seasonal variations for several elements. The concentrations of the elements Si, K, and Ca associated with mineral dust peaked in the summer, see Figure 4.7a. The concentrations of elements S, K and BC that are associated with biomass and fossil fuel combustion were high during the winter period (Fig. 4.7b). Figure 4.7c illustrates the large variability of the traffic related elements Zn and Pb as well as Mn throughout the different seasons.

The elemental and BC concentrations were highly variable within the relatively short sampling campaigns, and long term measurements will be needed to obtain better estimates of the average concentrations in Skopje. The contribution of the elemental mean concentrations corresponded to 38, 59, 61 and 64% of the total $PM_{2.5}$ mass for winter, spring, summer and autumn, respectively. The remaining unexplained mass likely corresponded to ammonium, nitrate and organic carbon (OC), as well as elements such as Na, Mg and Al that were not measured in the present study.

Aerosol composition was compared to the composition of average crustal rock by calculation of enrichment factors (EFs). The group of Si, K, Ti, Rb and Sr exhibited low and similar EFs indicating a soil dust origin. K and Rb had higher EFs in winter compared to the other seasons, which indicate that one or more additional sources contributed significantly during this season. Obvious sources are biomass burning and oil combustion. The EF for Ni was also close to the expected ratio in mineral dust during the summer and considerably higher during the other seasons, and the dominating Ni source was likely to be heavy oil combustion. The EF for Ca was also relatively low, which suggested a significant contribution from mineral dust to this element. The other elements were considerably enriched implicating emissions of particles bearing these elements from other sources than crustal rock.

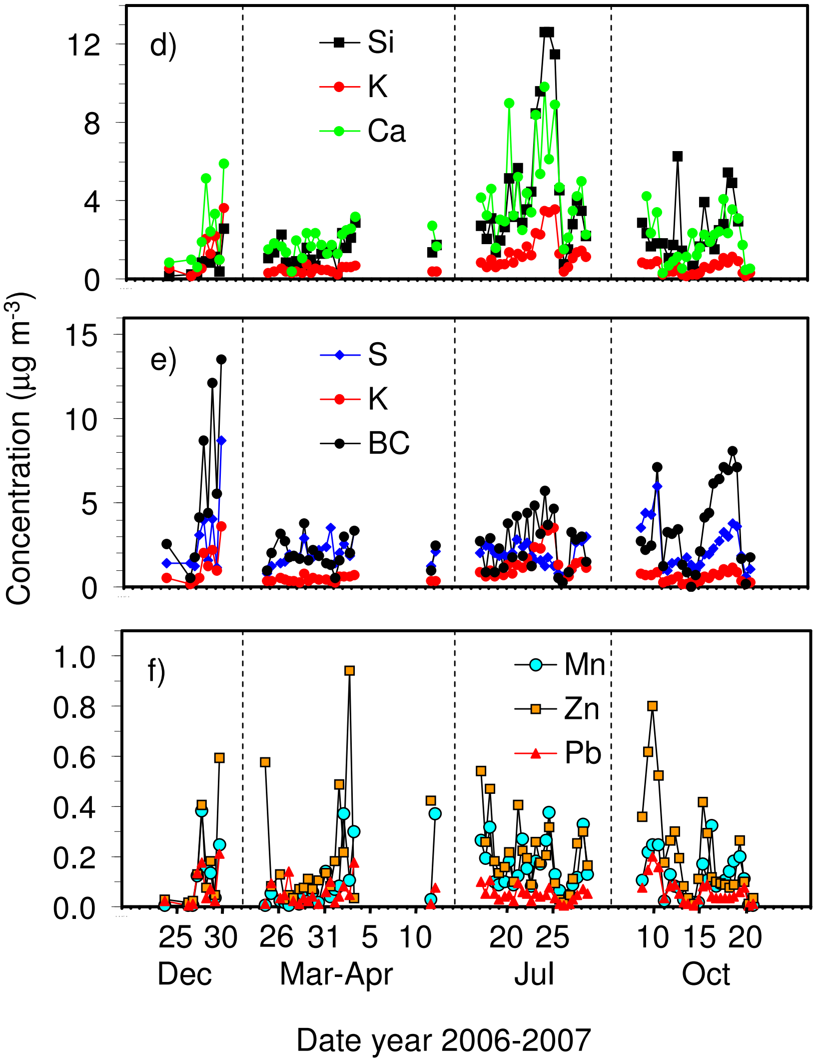

Figure 4.7. Concentrations of selected elements for the four measurement periods in Skopje from December 2006 to October 2007.

Pairwise correlations between the $PM_{2.5}$, BC, and the different elements were calculated, and scatter plots between pairs of elements were constructed. Correlation coefficients for the Si, K, Ca, Ti, Fe, Rb, and Sr group ranged from 0.79 to 0.97, which is an indication of the predominantly crustal origin for these elements. An example of a scatter plot for the Si-Fe pair is shown in Figure 4.8a. Good correlation (r = 0.93) was also obtained between V and Ni concentrations, and a scatter plot for V and Ni is shown in Fig. 4.8b. Heavy oil burning is an important anthropogenic source of both V and Ni and the elements are often found to be well correlated (Jang et al, 2007).

The elements Fe, Zn, Ba and Cu together with BC are often concluded to indicate a vehicular source (Viana, 2008). Pb could also be expected to be found together with these elements since leaded fuel was used in Macedonia until 2006. Zn and Pb had a correlation factor of r = 0.53. Correlation was, however, considerably better under all periods except spring when some data pairs deviated strongly in Zn/Pb ratio suggesting that there was more than one source for these elements during that period.

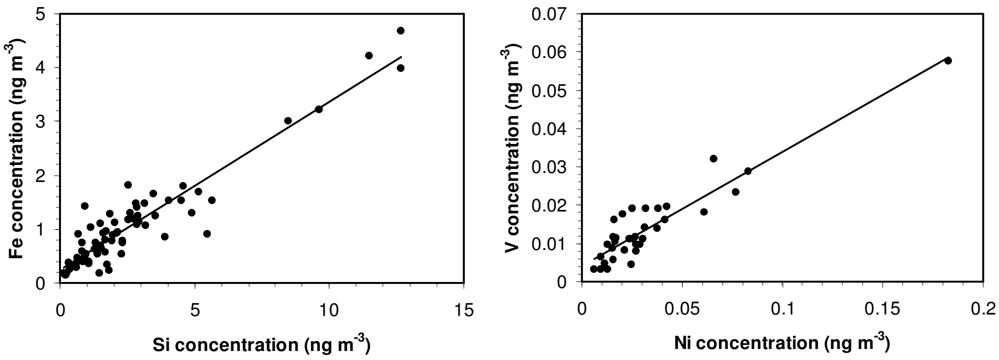

Figure 4.8. Relationships between measured ambient concentrations of pairs of species a) Si and Fe, and b) Ni and V .

Factor analysis (FA) and positive matrix factorization (PMF) of the data set were also applied to obtain a better understanding and quantification of the contributions from different sources.

The dominating factor in the FA analysis was identified with mineral dust based on the correlated data for Si, K, Ca, Ti, Fe, Br, Rb and Sr. A second factor had large S, V, Ni, and BC contributions and was identified with combustion of heavy oil and possibly with biomass burning since Cl had a high and K a moderately high loading. A third factor was attributed to traffic-related emissions, as indicated by Pb and Zn, and it may also have included contributions from industrial activities. The results from PMF confirmed the conclusions from FA. In addition to the three factor obtained by FA, a factor related to regional production of secondary sulfate combined with mineral dust was identified. In addition, back trajectory calculations showed that the highest mineral dust concentrations where associated with air mass transport from the Sahara.

An interesting conclusion was that a separate aerosol component due to biomass burning could not be distinguished. Biomass burning is known to be common in Skopje and the surrounding region, and the problem may be that biomass burning often coincides with the oil combustion. Both factors should be most important during periods that require heating and they may be difficult to separate due to a similar time variation. More data collected during the winter season may have helped to identify the biomass burning component, but it is not certain since the contribution from biomass burning is seldom found as a separate factor in principal component analysis based on filter samples (Viana et al. 2008).

The study confirms that Skopje suffers from serious air pollution. The air quality is comparable to the conditions in other cities in Southern Europe and worldwide that are known to be among the most polluted in the world. A notable result was that the Mn concentrations were substantially higher in Skopje than in the other listed cities. The mean Mn value was also close to the air guideline value of 0.15 µg Mn/m^3 for Europe set by WHO (2001), and with considerably higher concentrations observed during some 12 h periods. The Mn results call for further studies to evaluate the potential treat to human health.

4.4 Alkali-containing Aerosol Particles in Gothenburg, Sweden

The SI technique used for sensitive detection of alkali compounds in the laboratory (Paper 1) and in combustion facilities (Paper 2) has also been applied to ambient air measurements. Paper 3 describes the development of a new AMS instrument based on SI technique that provides simultaneous Na and K measurements in individual submicron aerosol particles. The instrument was applied during a measurement campaign in Gothenburg from February 16 to May 20, 2007. A limited set of single particle data is presented in Paper 3 and time dependent integrated Na and K concentration data for a three month period are described in Paper 5.

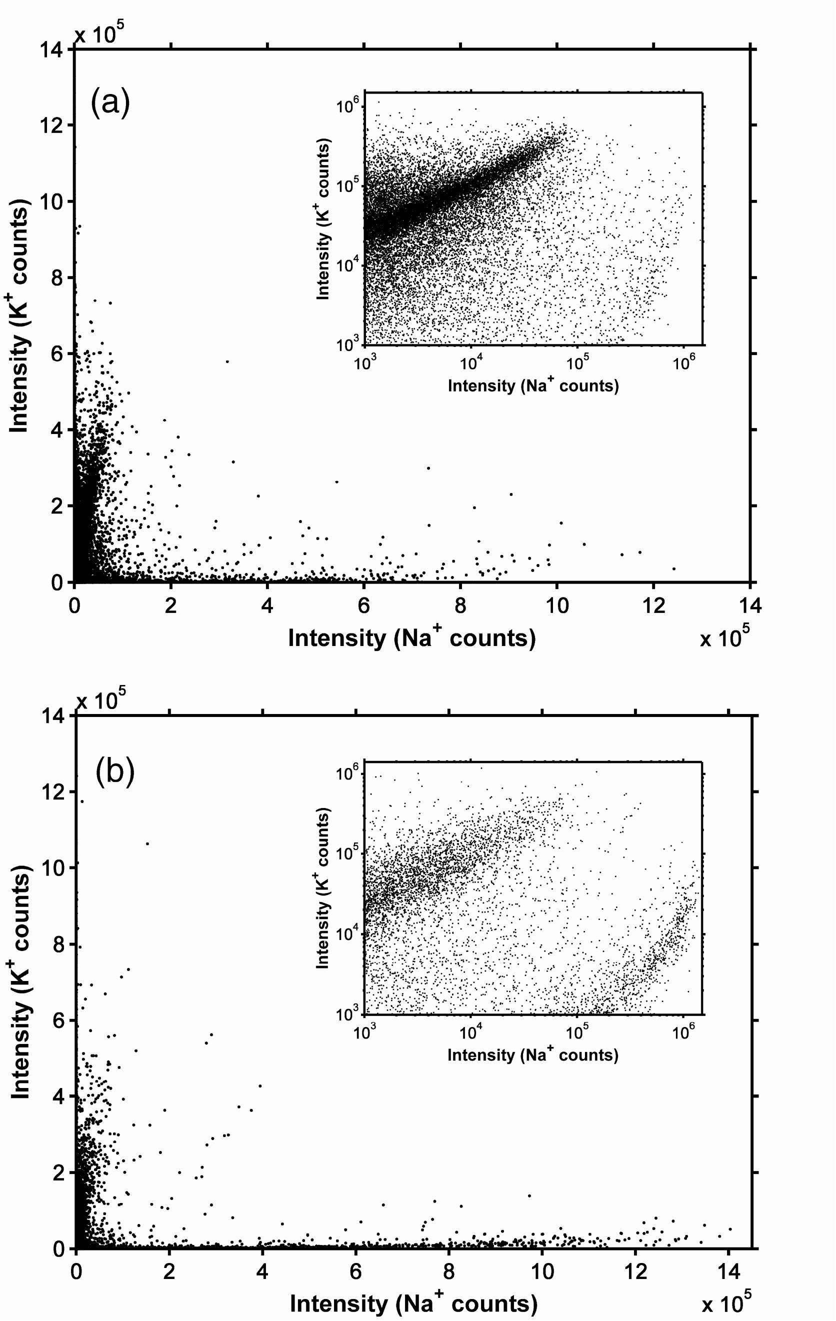

Figure 4.9 The number of Na$^+$ and K$^+$ ion counts in individual particles. a) Sampled from ambient air in Göteborg from 04:00 to 08:00 on February 20, 2007. b) Sampled from ambient air in Göteborg from 15:52 to 19:52 on April 11, 2007. The insets show the same data on a logarithmic scale.

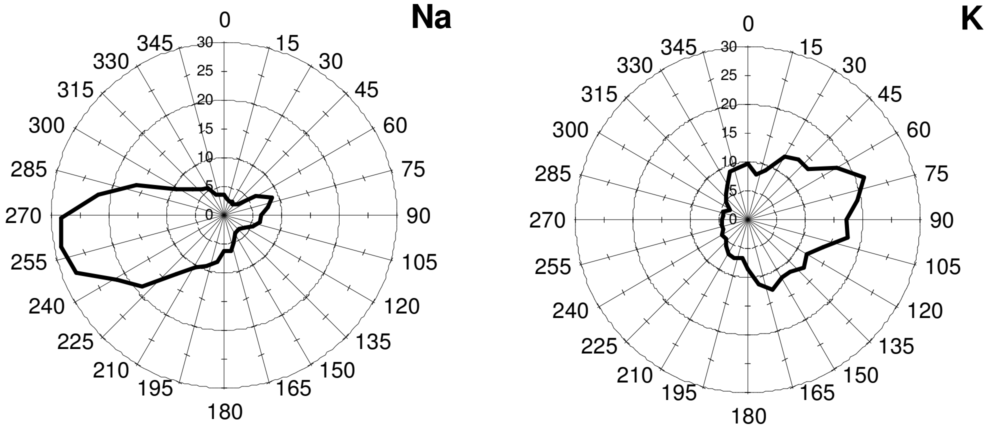

Figure 4.10 Sodium and potassium concentrations in submicron particles as a function of wind direction for all data obtained during the measured campaign in Gothenburg from February 16 to May 20, 2007.

Measurements in the laboratory and in ambient air showed that the instrument was capable of on-line quantitative chemical analysis of individual particles. Sea spray particles and particles originating from biomass burning were identified based on their content of sodium and potassium. This is illustrated by the results shown in Figure 4.9 where clusters of particles with different Na:K ratios may be attributed to combustion aerosol particles and sea spray particles.

The overall aim of the ambient air measurements was to characterize the concentrations of sodium- and potassium-containing particles during a relatively long period including the winter and spring seasons, and to address the importance of local emissions and long range transport for the atmospheric loading in the urban background environment. Typical alkali concentrations were in the range from 1-50 ng m^{-3}, but with large variations in concentrations and Na:K ratio depending on the prevailing conditions. High concentrations of sodium-containing particles were favoured by westerly winds and high wind speeds, and were concluded to be related to sea salt particles in marine air masses. High concentrations of potassium-containing particles correlated with low temperatures and low wind speeds. The influence of the local wind direction on Na and K concentrations is illustrated in Fig. 4.10.

Table 4.1. Back trajectory cluster analysis for six air mass types: air mass category, number of 6 min samples, mean N and K concentrations [ng m^{-3}], Na:K concentration ratio, mean PM_{10} and trace gas concentrations [μg m^{-3}], temperature (T) [°C] and wind speed (WS) [m s^{-1}].

Origin	Samples	Na	K	Na:K	PM_{10}	O_3	NO	NO_x	T	WS
1. Central Eur.	3238	3.9	14	0.27	34.8	46.2	11.5	51.4	7.0	3.5
2. Eastern Eur.	2171	6.2	21	0.29	34.1	53.8	16.6	57.6	2.9	4.7
3. Northern Eur.	5027	6.0	5.6	1.1	20.1	57.6	7.8	36.0	8.3	3.5
4. Western Eur.	1393	4.9	11	0.45	25.3	49.3	4.6	32.0	8.0	3.6
5. Atlantic	4188	33	3.6	9.2	27.2	66.6	2.7	23.3	7.2	5.4
6. Polar	847	8.6	2.7	3.2	20.1	57.1	9.1	36.9	4.9	4.7

Cluster analysis of air mass back trajectories helped to relate the AMS data to the type of air mass reaching Gothenburg during different periods. Table 1 summarizes mean values for the alkali, PM_{10} and trace gas concentrations for different types of air masses. The highest mean Na concentration and the highest Na:K ratio were observed in air masses with an Atlantic origin. The highest mean K concentrations and lowest Na:K ratios were observed when the air masses had an Eastern or Central European origin. The observed Na:K ratios were in these cases consistent with alkali-containing particles originating from solid fuel combustion processes (Svane et al. 2005b, 2006). NO, NOx and PM_{10} concentrations were also high for these air mass types compared to the other cluster types. The air masses originating from Northern and Western Europe, as well as from the Polar region appear to have consisted of polluted air with different degrees of marine character.

Diurnal variations in both potassium and sodium concentrations were also observed during a period with daily ground temperature inversions, see Figure 4.11. Potassium-rich particles were transported from areas with extensive agricultural burns in Eastern Europe during this period, but local emissions also appeared to make a significant contribution. In addition, sodium-rich particles were associated with sea breeze during the same period. The study illustrates the capacity of the developed AMS for selective and sensitive detection of specific types of particles in ambient air.

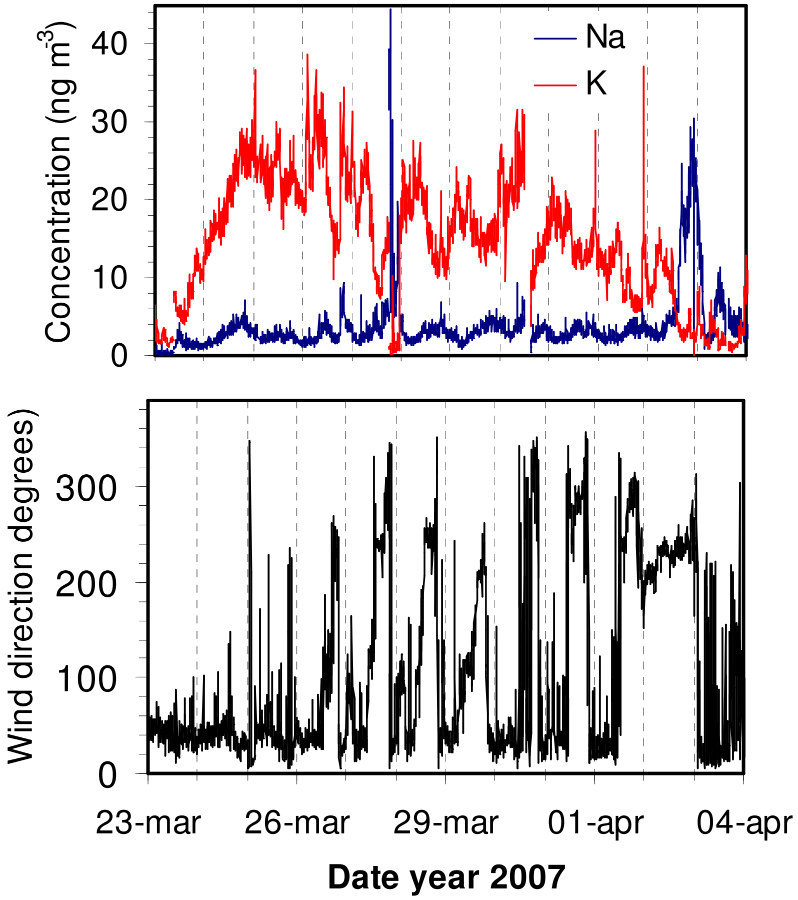

Figure 4.11 Concentrations of sodium and potassium in submicron particles (upper panel) and wind direction (lower panel) during an episode with air mass transport from Eastern Europe. Gothenburg experienced daily temperature inversions during the display time interval. The weakly modulated Na signal is attributed to sea breeze.

5. Concluding Remarks and Outlook

The environmental concerns and limited amounts of fossil fuels are the main reasons for the interest in biofuels. The behavior of the inorganic constituents originating from the fuel is one of the important research areas due to the problems caused by them in power plant operation. Biomass combustion is also a significant source of fine particle emissions and their characterization and reduction is an important issue.

The laboratory studies of alkali emission from wood during pyrolysis together with particle measurements during biomass combustion in a commercial scale CFB boiler have contributed to the understanding of the factors controlling the amount, size, and composition of particles formed during these processes. A wood chip will emit alkali during pyrolysis at 300-400 °C. Large chips will emit less alkali per unit mass than small ones, and the alkali in the char eventually will be emitted during char burning at higher temperatures in the combustion process. Water in the biofuel will delay the pyrolysis process and thereby the alkali emission, but the total alkali emission seems not to be affected.

The particles formed during biomass combustion have a bimodal size distribution. The submicron particles originate from volatilized elements that nucleate to form new particles or condense on existing particles when the flue gas is cooled. A large fraction of these particles consists of potassium, sulphur, and chlorine. The particles above the micron size range are mostly ash components from the fuel that have remained in the solid or liquid phase during the combustion process. The measured number size distributions showed a greater number of particles with larger size during addition of HCl and SO_2 than without addition. The information may be used in computational fluid dynamics simulations of boilers to develop predictive calculations of the particle size distribution, composition as well as emissions.

Studies of particle concentrations performed in Skopje, FYR Macedonia have shown that pollution in smaller cities may be comparable to pollution in megacities, or even worse due to unique local conditions. The conclusion is that Skopje suffers from serious air pollution due to central and residential heating, the transport sector and industrial activities within the city. Major aerosol components were identified as mineral dust (main observed tracers Si, K, Ca, Ti, Fe, Sr, Rb), combustion (BC, S, K, V, Ni), traffic-related aerosol (Pb, Zn), and secondary sulfate combined with mineral dust suggesting a regional origin. Combustion sources have a strong impact on wintertime air quality and contributions from mineral dust increase the $PM_{2.5}$ concentrations substantially under dry summer periods.

In developing countries the research concerning air quality and especially aerosol research is less advanced and data are incomplete. More characterization studies will be needed including measurements, chemical speciation and application of models for ambient particles to determine particle sources and possible health effects of particulate air pollution.

An AMS instrument based on SI technique has been developed at University of Gothenburg. The instrument is capable of on-line chemical analysis and provides simultaneous Na and K measurements in individual submicron particles. Single particle characterization studies were performed in Gothenburg during a relatively long period including the winter and spring seasons. Typical alkali concentrations were in the range from 1-50 ng m^{-3}, but with large variations in concentrations and Na:K ratio depending on the prevailing conditions. High concentrations of sodium-containing particles were favoured by westerly winds and high wind speeds, and were concluded to be related to sea salt particles in marine air masses. High concentrations of potassium-containing particles correlated with low temperatures and low wind speeds, and were mainly related to air masses originating from Eastern and Central Europe. Low Na:K ratios suggested that these particles originated from solid fuel combustion including biomass burning. Future work should focus on analysis of data on the single particle level, and the experimental data should be compared with results from atmospheric models that include emissions and aerosol dynamics for marine and combustion aerosols.

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