Chapter 14
Particulate Matter

**Jun Dong, Yong Chi, Augustina Ephraim, Ange Nzihou
and Lina María Romero Millán**

Abstract Particulate matter (PM), defined as the sum of solid and liquid particles suspended in the air, is often divided into two main groups: the coarse fraction with a size ranging from 2.5 to 10 μm (PM_{10}–$PM_{2.5}$), and the fine fraction with a size smaller than 2.5 μm ($PM_{2.5}$). PM can be generated from various sources such as unpaved roads, vehicles, agricultural processes, uncovered soil, mining operations, as well as burning of fuels. Statistical data show that in Europe, 1378 thousand tonnes of $PM_{2.5}$ are generated in year 2016, accounting for 5% of the total main air pollutants including sulphur oxides (SO_x), nitrogen oxides (NO_x), ammonia (NH_3), and non-methane volatile organic compounds (NMVOCs) [1]. This chapter will focus on the thermochemical process of solid fuels such as biomass and biowaste, because these types of fuels today are increasingly being used for energy purposes and have contributed to PM emission in many regions of the world. The presence of PM is significantly relevant to health problems, smog formations, acid rain issues, and climate changes. Characterization of PM is challenging, because PM is not only made up of a complex group of components (mainly black carbon, organics, sulfate, nitrate, alkalis, trace metals, crustal material and salt), but also comes in a wide range of sizes from nanoparticles (diameter less than 0.05 μm) up to millimeter-sized particles. In addition to this, PM characteristics are also proven to depend on various factors such as fuel type, thermal technology and temperature. Detailed knowledge of PM released during biomass and biowaste thermal conversion is essential for controlling air emissions. Over the last decades, attempts have been made to better understand the mechanisms and pathways of PM formation. Also, techniques are developed for PM sampling, collection and analysis, as well as the understanding of its physical and chemical characteristics. This chapter will thus be structured into four parts dedicated to PM fundamentals, collection techniques, physical and chemical characterizations. Available sampling

J. Dong (✉) · A. Ephraim · A. Nzihou · L. M. Romero Millán
RAPSODEE CNRS, UMR-5302, Université de Toulouse, IMT Mines Albi, Campus Jarlard, 81013 Albi Cedex, 09, France
e-mail: jun.dong@mines-albi.fr

Y. Chi
Department of Energy Engineering, Zhejiang University, Hangzhou 310027, China

devices, standards, analytical methods and techniques will be presented. Advantages, disadvantages, and major applications regarding biomass and waste thermal conversion will also be presented.

14.1 Fundamentals of Particulate Matter

14.1.1 Introduction: Definition, Origin, and Health Impacts

Particulate matter (PM) refers to the sum of solid and liquid particles dispersed in ambient air, which includes both organic- and inorganic-derived particles such as road dust, soot, smoke, and liquid droplets [2]. PM varies greatly in origin, size, and components (Table 14.1). It can be generated from both natural and man-made sources. Wind-blown dust, sea salt, volcanic ash, pollen, fungal spores, soil particles, the products of forest fires and the oxidation of biogenic reactive gases are examples of naturally origin PM. Anthropogenic PM sources constitute fossil fuel

Table 14.1 Classification, source origin, and main components of PM

PM fraction	Source origin	Main components
Coarse fraction ($PM_{2.5}$–PM_{10})	Agricultural activities	Agricultural soil, OC
	Traffic resuspension	Road dust
	Wind-blown dust, construction and mining activities, industrial resuspension	Si, Al, Ti, Fe
	Tyre and brake wear	Cu, Zn
	Combustion in energy and manufacturing industries (coal, coke, heavy oil)	EC
	Wind-land fires and volcanoes	Volcanoes' ashes, burned OC
	Biological sources	Plant debris and fungal spores
	Ocean spray	Na, Cl, Mg
Fine ($PM_{2.5}$) and ultrafine fraction ($PM_{0.1}$)	Diesel-fueled vehicle engines	BC
	Biomass combustion	OC, PAHs
	Maritime traffic	BC, OC, SO_4-2
	Combustion in energy and manufacturing industries	Pb, Cd, As, Cr, V, Ni, Se, SO_4-2
	Processes in non-metallic industries	Si, Al, Fe
	Metal processing activities	Pb, Cd, Cr, Zn

Reproduced with permission from Royal Society of Chemistry [4]
OC Organic carbon; *EC* elemental carbon; *BC* black carbon; *PAHs* polycyclic aromatic hydrocarbons. In general, combustion process has the potential to emit BC, which includes both OC and EC fractions

combustion (especially in vehicles and power plants), industrial processes (producing metals, cement, lime and chemicals), construction work, quarrying and mining activities, cigarette smoking and domestic fuel burning [3]. Particles in air can be either:

Primary particles, which are released directly from their source, for instance fuel burning, traffic, and industry.

Secondary particles, which are indirectly formed within the atmosphere as a result of chemical reactions. Examples include sulphates and nitrates formed from the oxidation of atmospheric SO_2 and NO_2.

In terms of size, PM is often classified into two main groups:

The coarse fraction, with a diameter larger than 2.5 μm;
The fine fraction, with a size up to 2.5 μm ($PM_{2.5}$). The particles which are smaller than 0.1 μm ($PM_{0.1}$) are called ultrafine particles, which includes the nanoparticles.

The size of particles determines primarily how long they will reside in air and how they are transported. Coarse particles tend to settle to the ground within hours, while fine particles can remain in the atmosphere for several weeks [5]. The limits of air quality regulations are typically based on the mass of PM_{10} and/or $PM_{2.5}$, for these fractions are small enough to be inhaled and respired to cause human health impacts [6]. For instance, PM_{10} can reach the upper part of the airways and lung, while $PM_{2.5}$ can perhaps penetrate the lung and reach the alveoli and $PM_{0.1}$ can directly pass into the bloodstream. The inhalation of PM is often associated with increased morbidity and mortality, the collective incidence and severity of which are strongly influenced by the duration and amount of PM exposure [7]. According to the estimation of the World Health Organization (WHO), exposure to PM has caused about 16% of lung cancer deaths, 11% of chronic obstructive pulmonary disease deaths, and more than 20% of ischemic heart disease and stroke [8]. Recent studies report that more than 5 million people in the world suffer from premature death due to indoor and outdoor air pollution [9, 10]. Realizing this fact, PM is currently considered to be one of the important indicators of ambient air pollution and proper characterization of PM has received increasing attention [11, 12].

14.1.2   Source Categories and Apportionment

PM is derived from a wide range of both natural and anthropogenic sources, among which the most significant contributors can be summarized into five categories: traffic, industry, domestic fuel burning, natural sources including soil dust (re-suspended) and sea salt, and unspecified sources of pollution of human origin [11].

Traffic related emissions mainly contain vehicle exhaust emissions and non-exhaust vehicular particle emission. PM from vehicles may be generated directly in the engine during combustion of fuels and lubricants, or, formed in the

air by nucleation and condensation during dilution and cooling of the hot exhaust gaseous emissions from the tailpipe. Non-exhaust particles typically arise from road-tyre interaction and brake wear by mechanical process, followed by re-suspending with organic and inorganic gaseous PM precursors and crustal dust particles.

Industry is one of the major contributors of air pollutants in urban areas. Its sources include mainly combustion emissions in power plants or factories (e.g. coal, oil, municipal waste incineration), and industrial process emissions of various types of industries (petrochemical, metallurgic, ceramic, pharmaceutical, IT hardware, etc.).

Domestic fuel burning includes wood, coal, agricultural straw and gas fuel for cooking or heating, especially in developing countries. PM from cooking and heating emissions is a major source of indoor environment pollution.

Natural sources include soil dust and sea salt. **Soil dust** can be carried by the wind and re-suspended by vehicular traffic. **Sea salt** particles primarily generated from the mechanical disruption of the ocean surface, and secondarily formed by non-sea sulphate and organic species due to gas-to-particle conversion process [13].

The "**unspecified sources of human origin**" category mainly includes secondary particles formed from unspecified pollution sources of human origin. Those particles are secondarily formed within the atmosphere as a result of chemical reactions, which can either be inorganic or organic. For instance, SO_2 emitted from shipping, industry and power generation can combine agricultural NH_3 to form inorganic sulphate PM. A combination of NH_3 with NO_x from traffic, power generation, industrial and residential sources may form inorganic nitrate PM. VOCs are examples of secondary organic PM, which may be formed from industrial activities, combustion processes, and transport emissions.

The global source appointment of urban ambient $PM_{2.5}$ and PM_{10} has currently been reported by Karagulian et al. [11]. The results (Fig. 14.1) of different source contributions suggest that 25% of urban ambient $PM_{2.5}$ was contributed by traffic, 22% from unspecified sources of human origin, 20% from domestic fuel burning, 18% from natural dust and sea salt, and 15% by industrial activities including power generation.

Thermal treatment process is the main focus of this chapter. Regarding fuel combustion, the statistical data in the US show that this sector contributed to about 25% of the total anthropogenic $PM_{2.5}$ emissions in 2011, significantly decreased from about 40% in 1990 (Fig. 14.2) [14]. In China, coal burning contributes to about 3–26% of urban atmospheric $PM_{2.5}$, especially in the northern cities (Fig. 14.3). Biomass burning is likely to be another important source category for controlling China's $PM_{2.5}$, as it has contributed 5–7% of the total $PM_{2.5}$ in the urban atmosphere [15].
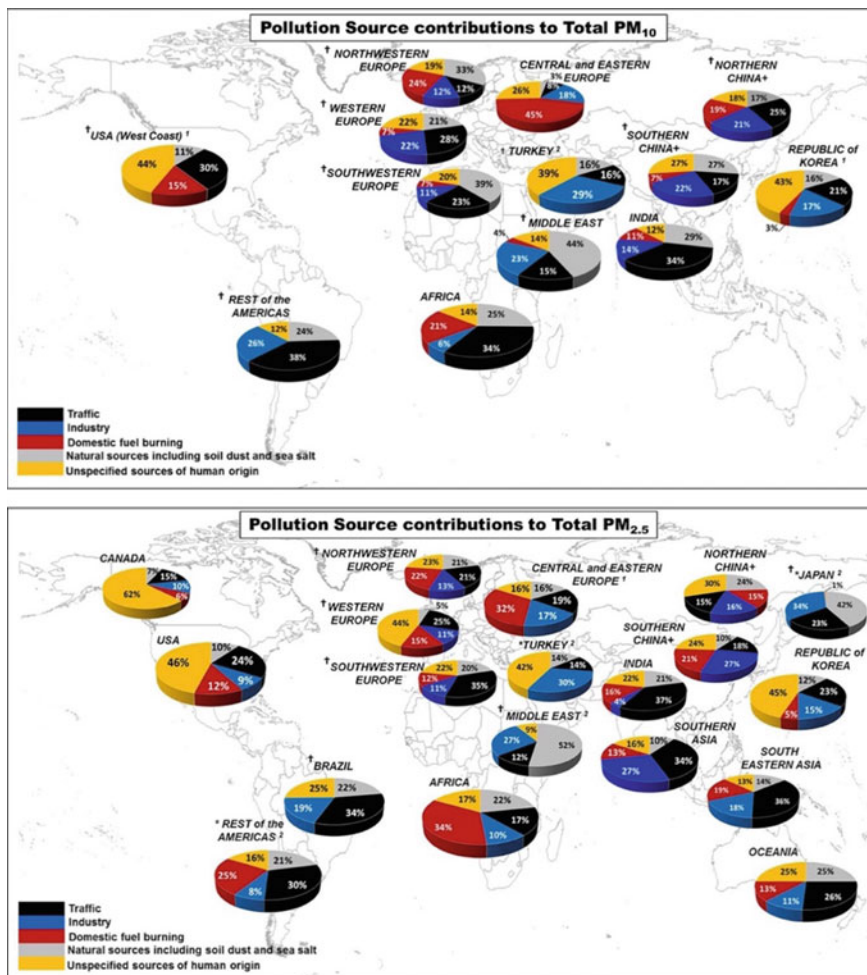
**Fig. 14.1** Population-weighted averages for relative source contributions to total PM_{10} and $PM_{2.5}$ in urban sites. Some data (e.g. PM_{10} in USA, Korea and Turkey; $PM_{2.5}$ in central and eastern Europe, Japan, Middle East, and rest of the Americas) only provide indicative results. More details as well as the meaning of each symbol (e.g. *, +) can be found in the sourced literature. Reprinted with permission from Elsevier [11]

14.1.3   Components of PM

PM comprises a number of complex components including crustal materials (soil, dust), organic matters, metals, acid salts, sulfate, nitrate and ammonium [16]. The composition of PM can vary dramatically, depending on the emission source categories or process conditions.
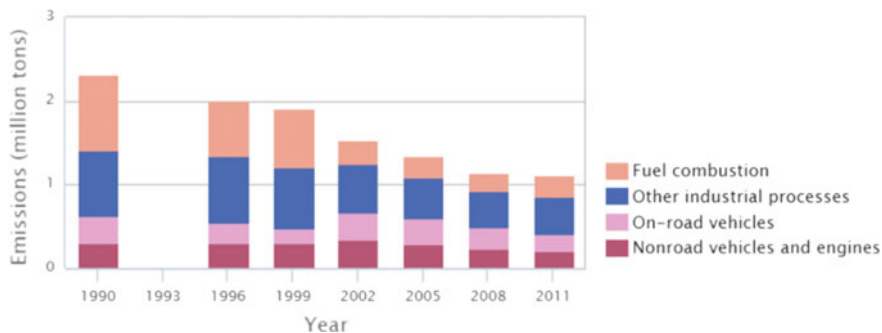
Fig. 14.2 Anthropogenic PM$_{2.5}$ emissions in the US by source category (1990–2011). *Source* US EPA [14]. Data for year 1993 have not been updated by the US EPA, so that they are absent from the figure
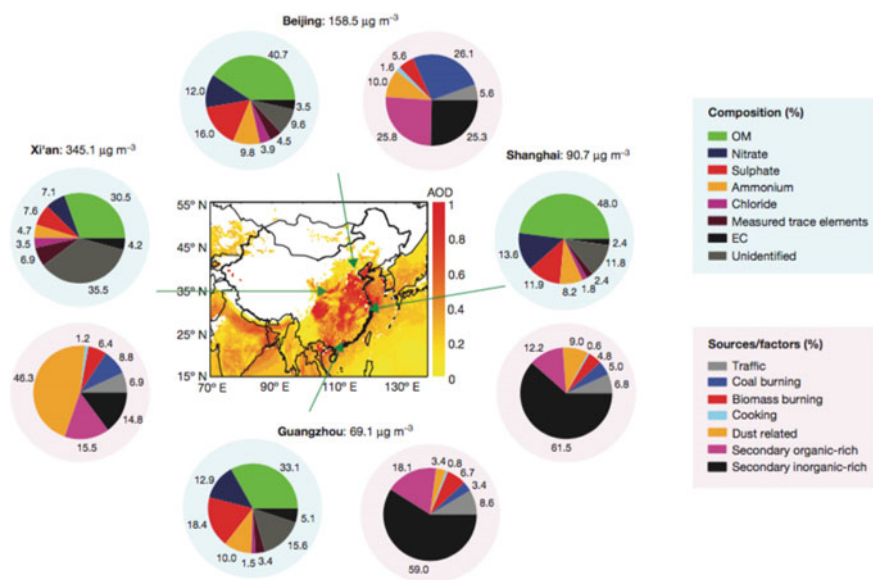
Fig. 14.3 Source apportionment and composition of PM$_{2.5}$ collected during the high pollution events of 5–25 January 2013 at the urban sites of Beijing, Shanghai, Guangzhou and Xi'an in China. Reprinted with permission from Springer Nature [15]

Figure 14.4 shows the composition of an example airborne PM$_{10}$ and PM$_{2.5}$, based on average monitoring data in the UK [17]. The chemical makeup of PM has shown a division between the coarse and fine modes. The coarse fraction (PM$_{10}$) consists mainly of crustal material, i.e., iron rich dust. The dominant components of fine fraction (PM$_{2.5}$) are organic matters, sulfate and nitrate.
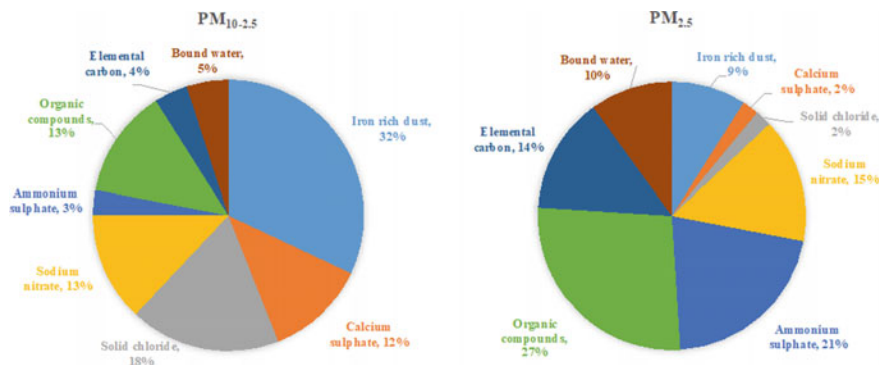
Fig. 14.4 Composition of an example airborne PM_{10} and $PM_{2.5}$ at UK sites

In addition to the size distinction, PM from a gasoline vehicle, diesel vehicle, woodstove, or a coal-fired boiler may have a large difference [18]. PM from solid fuel combustion such as coal, oil, biomass and waste can produce coarse particles from the release of non-combustible materials, i.e. fly ash; fine particles from the condensation of materials vaporized during combustion; as well as secondary formed particles through the atmospheric reactions of sulphur oxides and nitrogen oxides initially released as gases [2]. Organic carbon (OC) includes products of incomplete combustion, such as polycyclic aromatic hydrocarbon (PAHs) and unburned fuel. Elemental carbon (EC) is nonvolatile carbon in graphite like form, found in mainly nanometer size fractions (<56 nm; 56–100 nm; and 100–180 nm) [19]; however, EC is never found in pure form in the atmosphere, because various OC and other compounds are adsorbed onto, and/or mixed with the EC core [20]. EC containing a coating of mixed OC and inorganics, with adsorbed carbonaceous material, is referred to as back carbon (BC), or soot in fuel combustion.

14.1.4   PM Formation Mechanism During Thermal Conversion of Biomass and Biowaste

This chapter will focus mainly on the characteristics of PM formed and emitted during thermochemical process of solid fuels such as biomass and biowaste. Thermal conversion of solid fuels, such as pyrolysis, gasification, incineration or their combination process, mainly produces PM containing soot, spherical organic carbon particles and inorganic ash particles. Figure 14.5 illustrates the possible formation pathways of PM during combustion of typical fuels (coal, biomass, and oil) [21]. The formation of combustion generated PM can be summarized by three mechanisms:
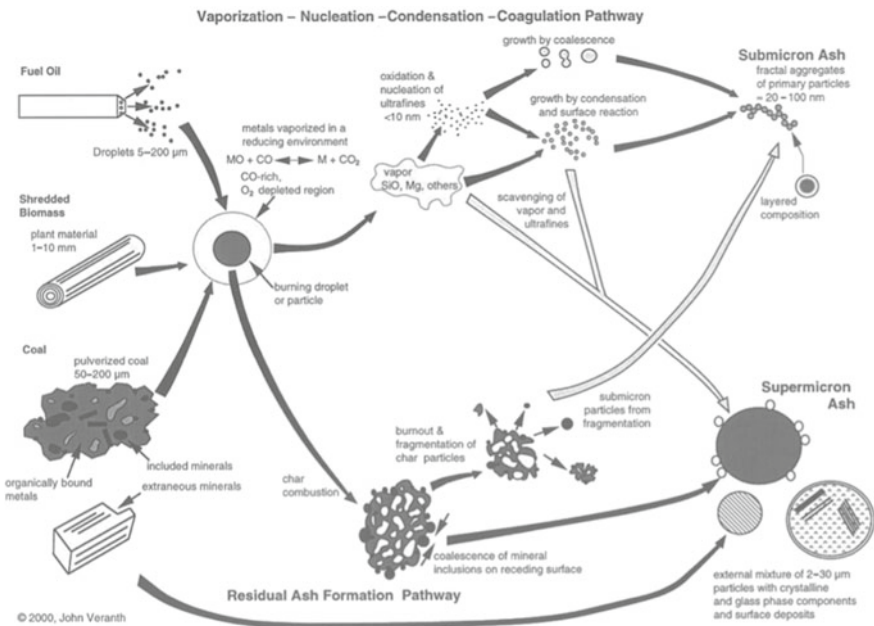
Fig. 14.5 Formation pathway of PM during combustion of solid and liquid fuels. Reprinted with permission from Taylor & Francis [21]

1. Coarse particles formed from residual fly ash particles;
2. Fine fly ash particles produced from the vaporization, condensation, nucleation of easily volatilized ash components;
3. Fine organic particles and soot produced from incomplete combustion.

Solid fuels contain considerable amounts of ash forming inorganic elements. During the thermal conversion process, these inorganic species produce an oxidation product, i.e., ash. The majority of the ashes could be retained inside the furnace, named, bottom ash; however, a small portion could be entrained from the furnace with the flue gas and forms the **coarse fly ashes** (>1 μm). These coarse fly ash emissions can achieve a particle size range from a few μm to about 200 μm [22].

The **fine ash particles** (<1 μm) are mainly formed from the easily volatilized inorganic elements, such as alkali and heavy metals, released from the fuel to the gas phase during combustion. These fine ash particles are formed by nucleation, condensation, surface reactions, coagulation and agglomerations.

Fine organic particles and soot are formed due to incomplete combustion, originating from combustible materials of the fuels. For instance, soot is a complex mixture of amorphous EC and organics, formed mainly inside the flame in the carbon rich area. During devolatilization and combustion of volatiles, the hydrocarbon compounds of fuel particles are likely to form aromatic rings and PAHs. Soot is thereafter formed by further growth of PAHs, which then becomes larger by

surface reactions, coagulation and agglomeration. Organic particles are also one source of PM, which are mainly incomplete combustion products that remain in the flue gas. Organic particles can be present in liquid or gaseous form depending on environmental conditions, as the main part of the organic material of fine particles could usually be condensed at far below 500 °C [23–25]. The incomplete combustion conditions may include poor combustion, or sub-stoichiometric reactions of pyrolysis and gasification. In flue gas conditions, the organic vapors condense mainly on existing fine particles through condensation and/or adsorption [26].

The PM formation depends various factors including the fuel, combustion condition and flame type, etc. Compared with fossil fuels (e.g. coal), biomass fuels, such as wood, straw or biowaste, have several special characteristics: a higher volatile content, a lower ash content, and a higher alkali metals content. Thus, in industrial scale biomass combustion units, the amounts of soot in the emissions are typically negligible owing to the high volatilized components and a high combustion efficiency. However, the incomplete combustion condition in traditional small scale combustion units, especially in household stoves, would cause an important fraction of soot and OC in PM emissions.

The ash forming inorganic elements in biomass fuels can be divided into three categories [22]: (i) non-volatilized elements such as Ca, Si, Mg, Fe, Al, etc.; (ii) easily volatilized elements such as K, Na, S, Cl, etc.; (iii) easily volatilized heavy metals such as Zn, Cd, Ob, etc. Biomass has a lower ash content than coal, typically 0.5–1% for wood and 4–8% for agricultural by-products. However, it is rich in alkali elements. For example, the K content in a range of straws can be as high as 2% of the dry weight according to the study of Christensen et al. [26]. Their S content is found to be fairly constant at 0.1%. For MSW (municipal solid waste), the Cl contained could be even richer than biomass or coal, which is mainly determined by the PVC (polyvinyl chloride) in plastic and the salts (NaCl) in food waste. During thermal conversion, these species undergo gas phase reactions resulting in the formation of alkaline (K, Na) metal chlorides, sulphates, carbonates, and heavy metals oxides [22]. These elements in biomass or biowaste can greatly influence the size distribution and composition of inorganic PMs.

As a result of the aforementioned particle formation mechanisms, PM during thermal conversion of biomass and biowaste typically exhibits a bimodal particle size distribution: a peak of submicron particles (PM_1), and the other peak of coarse mode dominated by PM_{10}. The main constituents of biomass PM are K, Cl, S, Ca, Na, Si, P, Fe and Al [27]. Becidan et al. [28] report that K, S, Cl and Na dominated the PM composition for a number of biomass types, such as wood, demolition wood and coffee wastes. This is confirmed by the study of Jöller et al. [29, 30] that the PM are predominantly K_2SO_4 and other alkali compounds (Na_2SO_4, KCl, NaCl) for clean wood chips. Other studies also verify the abundant existence of Fe, Ca, Al, Zn, etc., in fine particles during waste and biomass combustion [31, 32]. Vaporization and subsequent condensation from the gas phase is the main pathway of PM_1 formation; while entrained non-volatilized ash residuals and fly ash particles are the main compounds of PM_{10}. It is also shown by Gao et al. [33] that the ultrafine PM is produced mostly from the volatiles, rather than during char combustion.

14.1.5 Emission Limits and Regulations in Selected Countries

To keep a clean and healthy air environment, air quality standards concerning PM emission have been gradually built up. However, the development of associated regulations, especially for PM_{10} and $PM_{2.5}$, just started within the latest decade. Those standards regulate the PM emission either in the ambient air, or from specific facilities, such as coal-fired power plants, biomass and waste-to-energy plants and other sources. Generally, the emission standards are established by the governments based on the best available technologies and monitoring emission data.

The World Health Organization (WHO) has produced air quality guidelines with the aim to reduce the health impacts of air pollution worldwide. Its updated version 2005 has regulated thresholds and limits for PM_{10} and $PM_{2.5}$, which should be measured on both a 24-h (short-term) and annual mean (long-term) basis to estimate health effects. Many different countries have regulated a separate emission limit for $PM_{2.5}$ in the ambient air. Table 14.2 summarizes the associated air quality standards of $PM_{2.5}$ in several selected countries [34].

However, the emission limit of $PM_{2.5}$ from coal, biomass or waste combustion is still under development: $PM_{2.5}$ from coal combustion is still regulated as part of PM —no country has a separate emission limit for $PM_{2.5}$ from coal-fired power plants. Additionally, waste-to-energy and biomass-to-energy plants are still not widely applied in most countries, since, the emission limits of PM for biomass or waste thermal plants are far from well-established or regulated worldwide.

The emission limits of PM from coal-fired power plants and waste-to-energy plants in selected countries are listed in Table 14.3 [34]. Different countries base their standards on different time periods, ranging from half-hourly average to 24-h average, or annual averages. The differences also attain at the varying reference conditions and units. For instance, most countries use 0 °C and 101.3 kPa in dry flue gas as the reference condition; but Indonesia and Thailand set their reference temperature at 25 °C. The USA set limits based emissions per unit of electricity produced; but Japan and Thailand use parts per million by volume in flue gas. The EU, Australia, China, Germany, India, Indonesia and South Africa regulate pollutant concentration per cubic meter of flue gas. Currently, China has the strictest limits for coal-fired power plants, although its air quality standards are less strict than those for the WHO and EU. Regarding waste-to-energy plants, EU has the toughest limits.

Table 14.2 International and national air quality standards of $PM_{2.5}$ in selected countries (Unit: $\mu g/m^3$)

Country	WHO	EU	Australia	China	India	Indonesia	Japan	South Africa	Thailand	USA
24 h	25		25	75	60	230	35	40	50	35
Annual	10	25	10	35		90	15	20	25	12

Table 14.3 Emission standards of PM from coal-fired power plants and waste-to-energy plants in selected countries (Unit: mg/m^3)

Country[a]	Coal-fired power plants (24-h average)		Waste-to-energy plants	
	Existing	New	Half-hourly average	24-h average
Australia[*]		80		n.a.[e]
China[*]	30/20[b]	10	30	20
Germany[*]	20	10	30	10
India[*]	100/50[c]	30		50
Indonesia[**]	150	100		350
Japan[*]	100	50		17/19/50[f]
South Africa[*]	100	50		10
Thailand[**]	180	80		320
USA[*]	18.5[d]	12.3[d]		25.2
EU IED[*]	20	10	30	10

[a]Countries with a superscript "[*]" use 0 °C, 101.3 kPa on a dry flue gas basis as the reference conditions; while countries with a superscript "[**]" use 25 °C, 101.3 kPa on a dry flue gas basis as the reference conditions

[b]The first value applies to all plants; the second value applies to plants in key regions

[c]The first value applies to plants installed before 2003; the second value applies to plants installed between 2003 and 2016

[d]The USA set limits based emissions per unit of electricity produced. For conversion into a mg/m^3 basis, data from Zhu et al. [35] is used

[e]Currently Australia does not have national air emissions standards applicable to industrial facilities such as WtE plants

[f]For existing municipal waste combustion plant, limit value of 19 mg/Nm^3 is applied to plants with capacity >250 tpd, limit value of 50 mg/Nm^3 is applied to plants with capacity 35–250 tpd; for new or substantially modified municipal waste combustion plants (after September 2008), limit value of 17 is applied to plants with all sizes; for commercial and industrial waste incineration plants, limit value of 50 mg/Nm^3 is applied to plants with all sizes. Emission standard concentrations are corrected to 7% oxygen

The emission standards for each country and region have been progressively strengthened over the years. The regulated emission limits will become stricter with the developing best available technologies.

14.1.6 PM Characterization

The growing utilization of biomass and biowaste as energy resources highlights the importance of the need for their environmentally sustainable management. PM is one of the major constituents of air pollutants. Gaining better understanding of the characteristics of PM is helpful to design an efficient process for its capture and removal from the flue gas, as well as to develop more effective controlling methods. For example, PM generated from biomass gasification process can be removed

using high temperature filters; however, the filtration efficiency and the operation and dimensioning of the filter could greatly depend on the PM mass concentration and size distribution. The composition of PM could also be crucial, since biomass materials are rich in alkali, which may form silicates with low melting temperatures that may negatively affect the filter operation [36].

Determining the characteristics of PM commonly requires a sampling and collection process beforehand. Collection of PM by filters or sets of impactor substrates are typically used techniques, which can provide detailed information about PM composition and size. The disadvantages of using these techniques are that they can be expensive and time consuming, since the analysis methods require a minimum amount of material, which may take time for collecting sufficient samples. Over the last decades, the development of different PM collection techniques, including both off-line and on-line approaches, have received considerable attention.

Environmental and health effects of PM depend on both the physical and chemical characteristics of PM. Various analytical techniques have thus been developing for PM characterization. Typical properties that are characterized include PM size, shape, morphology, chemical composition, crystalline structure, organic compounds, etc., using instruments such as scanning electron microscope (SEM), x-ray fluorescence (XRF), inductively coupled plasma (ICP), x-ray diffraction (XRD), thermal/optical reflectance and transmittance (TOR/TOT), gas chromatography-mass spectrometry (GC-MS), etc.

Different PM collection techniques are presented in Sect. 14.2. The major sampling devices and standards are also introduced. Sections 14.3 and 14.4 discuss a variety of PM physical and chemical characterization techniques, respectively. Each specific set of PM characteristic is linked to its major applications regarding biomass and biowaste thermal conversion.

14.2 Particulate Matter Collection Techniques

14.2.1 Sampling and Measurement Types

The collection of PM produced from the thermal conversion of biomass and biowaste can be done in two ways: by collecting source samples or ambient samples. For source sampling, the PM is collected directly from the gas conduit such as the flue-gas stack of a combustion process or the product-gas pipeline of a pyrolysis or gasification process. For ambient samples, the PM is collected from the atmosphere away from the exhaust or pipeline of any gas source. In this chapter, we will focus only on source sampling.

How a source is sampled depends on the type of particle measurement of interest. Particle mass or concentration is currently the regulated measurement, although there is growing interest in particle size distribution [22, 37]. For most

Table 14.4 Technical standards for particulate emissions monitoring

Standard	Content
ISO 23210	Stationary source emissions—determination of $PM_{10}/PM_{2.5}$ mass concentration in flue gas—measurement at low concentrations by use of impactors
ISO 9096	Stationary source emissions—manual determination of mass concentration of particulate matter
EN 13284-1	Stationary source emissions—determination of low range mass concentration of dust—part 1: manual gravimetric method
EN 13284-2	Stationary source emissions—determination of low range mass concentration of dust—part 2: automated measuring systems
EN 14181	Stationary source emissions—quality assurance of automated measuring systems

particle analyzers, dilution of the gas sample is required in order to operate within their required ranges. Dilution conditions have been shown to affect measurement of particle size distribution, although they tend to have little effect on overall particulate mass [37, 38]. Hence, special attention must be given to the choice of dilution systems if the particle sizes are to be determined. Examples of dilution systems will be discussed in Sect. 14.2.3.

The relevant standards for sampling and analysis of particulate emissions are shown in Table 14.4 [39]. These standards are qualified by either International Organization for Standardization (ISO 23210, ISO 9096) or European Committee for Standardization (EN 13284-1, EN 13284-2, EN 14181), thus are widely suitable to be used globally.

14.2.2 Examples of Off-Line Collection Techniques

14.2.2.1 Bag Sampling

A bag sampling system is often used to collect a specified volume of PM sample in a bag to be later analyzed at a different location. Thus, the use of this system is ideal when the PM analyzer is far from the source or when the source produces irregular emissions. Nonetheless, a bag sampling system can lead to a loss of PM through adsorption of the particles on the bag wall as well as changes to the particle size distribution due to coagulation [18]. Thus, the samples must be analyzed as quickly as possible to reduce errors in measurements.

Figure 14.6 illustrates a bag sampling system, which is available commercially [18]. This system consists of a stainless steel, airtight container, which is fitted with a sampling bag by means of a clamp-down lid. The Tedlar bag has a twist valve at its inlet and an actuated ball valve is placed in the sampling line connected to this inlet. Furthermore, a vacuum pump removes the gas between the stainless steel container and the sampling bag. When the actuated ball and twist valves are opened, the sample is drawn into the bag until the bag pressure is the same as that

**Fig. 14.6** Bag sampling system. Reprinted with permission from Institute for Clean and Secure Energy [18]
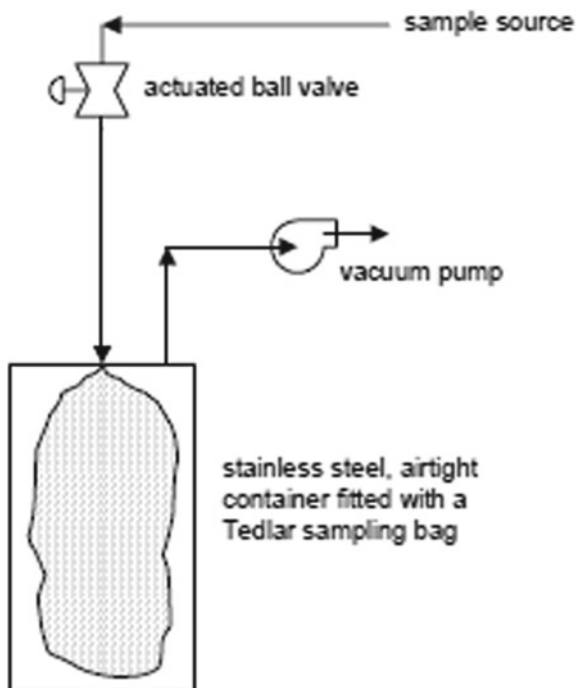
between the stainless steel container and the sampling bag. Once the bag is filled, the ball and twist valves are closed, and the sample bag is removed from the stainless steel container. Then the twist valve inlet can be connected to a dilution system or directly to an analyzer for further analysis.

14.2.2.2 Filter Sampling

PM samples can also be collected on a filter, and afterwards extracted with a solvent, or directly sent into the analyzing equipment, depending on the characterization techniques selected (see detailed physical and chemical characterization techniques in Sects. 14.3 and 14.4). If the particle size distribution is to be measured in addition to particle concentration, the filter samples can be collected on cascade impactors, such as a micro-orifice uniform deposit impactor (MOUDI) [40] or a K-JIST cascade impactor [41]. The MOUDI contains 8–10 stages plus an after filter, with each stage containing a filter. For a K-JIST cascade impactor, 5 stages are present, as shown in Fig. 14.7, which enable the sampling of PM of major concern including PM_{10}, $PM_{2.5}$ and PM_1 [41]. After particle collection, the particles on each filter can be extracted using a solvent, such as hexane, and then analyzed by an advanced analytical method such as gas chromatography/mass spectrometry, in a laboratory.

**Fig. 14.7** A schematic of 5-stage cascade impactor (K-JIST). Reprinted with permission from Elsevier [41]
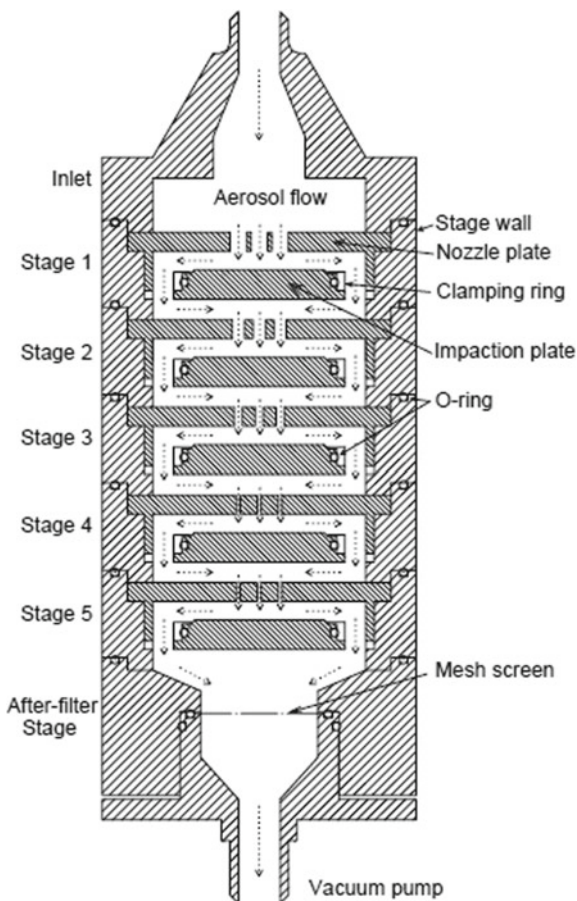
14.2.3 Examples of On-Line Collection Techniques

14.2.3.1 Diluted Sampling

On-line analyzers of PM usually require upstream dilution of the source sample. This is mainly to prevent supersaturation of volatile matter in sample gas (e.g. water, SO_x and VOCs), which may result in condensation, nucleation and coagulation of nanoparticles, and thereby compromise the PM number measurements. Dilution conditions, including humidity, temperature, gas residence time and system size/configuration, could affect the formation of nanoparticles and thus must be controlled. These influences are discussed in detail by Kelly et al. [18]. Another reason for lowering the PM concentration of the source sample is to match the ranges of the analytical instruments used.

Typically, dilution is performed using dry compressed air. Furthermore, in order to avoid adherence of PM to the sampling components or chemical reactions in the

sampling train, it is recommended to use Teflon or stainless steel tubing [42]. Three common types of dilution systems are: Eductor system, Hildemann system and constant-volume dilution sampler, as shown in Fig. 14.8. These types are discussed extensively by Kelly et al. [18].
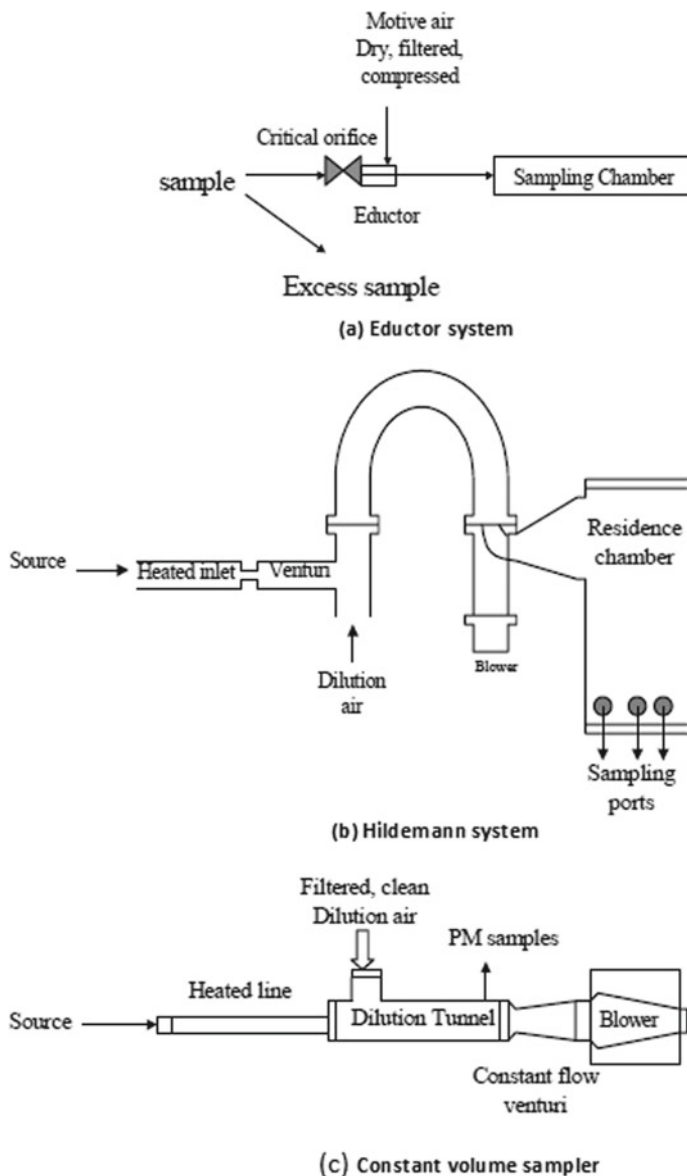
Fig. 14.8 Common types of dilution systems. Reprinted with permission from Institute for Clean and Secure Energy [18]

14.2.3.2   Raw Gas Sampling

Despite what has been discussed above, undiluted or raw gas sampling is also used because of the relative simplicity of the sampling system. However, because of the high concentration of moisture, particulates, and temperature, it is often difficult to obtain reproducible and reliable results. Although permitted for some regulatory applications, it is mainly used for non-regulatory and/or field testing [42].

An example of a commonly used system for raw gas sampling is the GRAVIMAT SHC502 by SICK AG, which is illustrated in Fig. 14.9 [43]. Using a probe, particle matter (or dust) is sampled by extracting a partial gas volume isokinetically, i.e. at the same velocity as the main volume flow. Isokinetic extraction prevents the occurrence of sedimentation in the sample line and ensures that the gas contains the precise representative amount of PM at the source. All dust particles in the extracted partial volume flow are retained in the dust collector filter (GS5 filter head probe).

In addition to the dust or PM collector, the probe head also contains the measuring orifice for the gas velocity, and partial volume flow as well as the measuring sensor for the gas temperature in the duct.

14.2.4   Filter Selection

The above-mentioned PM collection techniques highlight the importance of the use of filters, which are widely applied in most PM collection cases. Currently, different
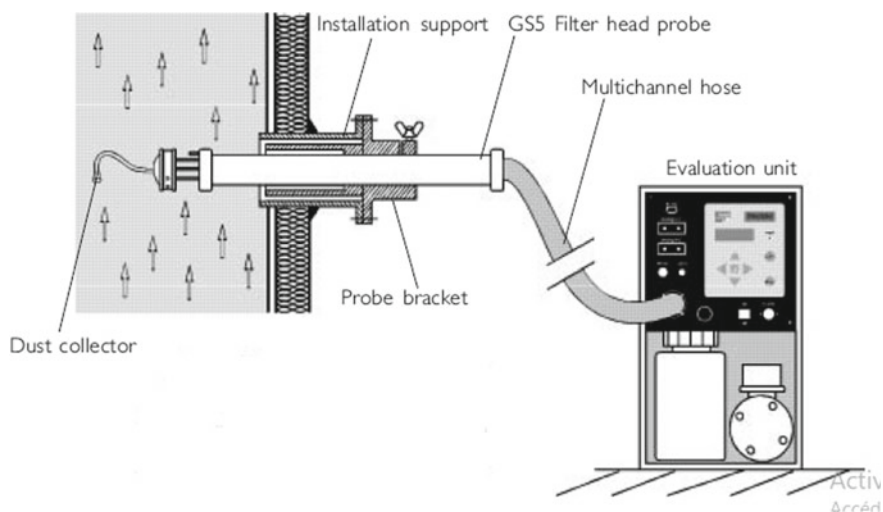

Fig. 14.9 GRAVIMAT SHC 502 System. Reprinted with permission from SICK AG [43]

types of filters are available for PM collection. They can be generally classified into three categories [44]:

- **Fiber filters**, for example glass fiber filter, quartz fiber filter and cellulose fiber filter. They are made of a deep mesh of fibers with random orientations.
- **Membrane filters**, for example polycarbonate membrane filter, Teflon membrane filter and polytetrafluoroethylene (PTFE) filter. They have a tortuous complex structure through the whole filter material.
- **Capillary pore filters**. They are normally composed of a thin, smooth polycarbonate or polyethylene terephthalate film, with some circular pores within the structure.

A scanning electron micrographs (SEM) diagram of these filters is shown in Fig. 14.10.

The appropriate selection of a filter for the collection of PM from biomass and biowaste thermal processes will depend on many key factors, such as sampling systems, filter media, and analysis techniques.
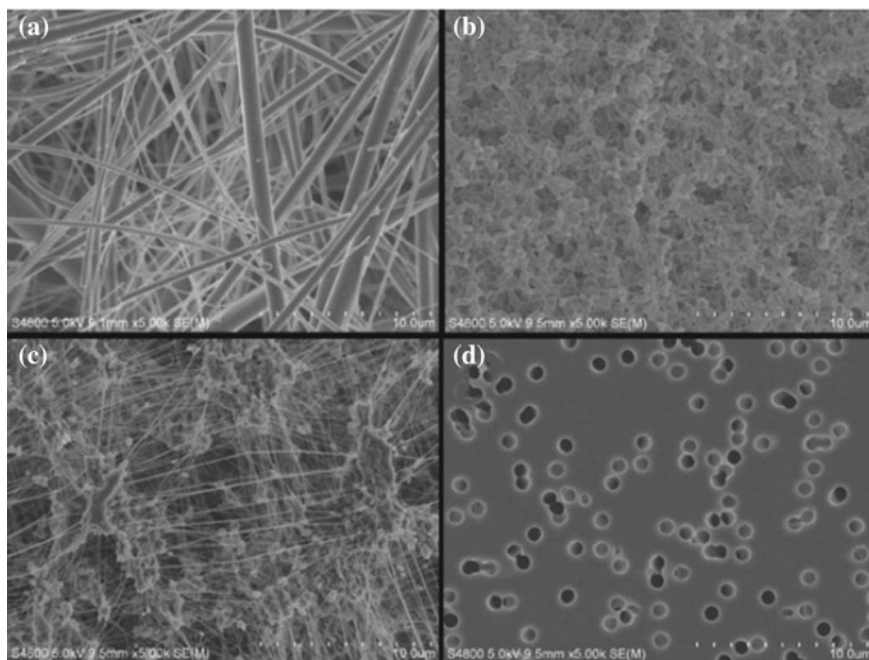
Fig. 14.10 Scanning electron micrographs (SEM) diagram of different types of filters. *Source* Adapted from Lindsley et al. [44]. **a** glass fiber filter with a 1-μm equivalent pore diameter; **b** mixed-cellulose esters filter with 0.8-μm equivalent pore diameter; **c** polytetrafluoroethylene filter with 3-μm equivalent pore diameter; **d** polycarbonate capillary pore filter with 1-μm pore size

The filter pore size and filter efficiency are important characteristics of the filter, which will directly affect the PM collection efficiency. In addition, the intended analyzing techniques are also a determining factor. For example, quartz fiber filter can endure high temperatures without decomposing [45], which makes it an optimal material for thermal analysis techniques, such as thermal/optical reflectance and transmittance (TOR/TOT). A polycarbonate membrane filter is often used when PM samples are to be examined by scanning electron microscopy (SEM), since the particles could be easily distinguished from the flat filter surface. However, no single filter media will be appropriate for all analyses. Different types of filters should be paired with different analysis techniques, including both physical and chemical PM characterization procedures.

14.3   Physical Characterization of Particulate Matter

Understanding the physical characteristics of PM is very important to estimate its effect on human health and the environment. Generally, the physical characteristics of PM could include the mass, size, shape, density, surface properties, microstructure, volatility, hygroscopicity, optical properties, etc. Here the most important parameters associated with thermal conversion of biomass and waste—PM mass, size distribution, and morphology, are discussed.

14.3.1   Weighing Gravimetry for Mass

The mass of PM is determined gravimetrically based on the post-weight and pre-weight difference of a sampling process.

Filters are used in most cases for PM collection. Its mass is determined by an analytical electron-microbalance. The sampling period and gas flow should be recorded, as mentioned in Sect. 14.2, so the PM quantity could be calculated as a function of the air/gas flow (mg/m^3) or the combusted fuel mass (mg/g fuel).

Both the unexposed and exposed filters should be equilibrated in a conditioning environment beforehand to reduce variability to an acceptable level, for example, placed at 15–30 °C for at least 24 h free of acidic or basic gases [46]. Specific conditions should be determined follow the type of filters and the guideline from the manufacturer. The filters should be then taken directly from the conditioning chamber to the balance to minimize the risk of contamination.

To guarantee the accuracy of results, quality control procedures are also regulated. For example, NIST standards [47] specify the recommended frequency of quality control filters for the PM program, as shown in Table 14.5.

Table 14.5 Recommended frequency of quality control filters for the PM program

Type of filter	Description	Acceptance criteria
Lot stability test filters	12 filters are repeatedly weighed to determine the minimum necessary equilibration time for filters from the same manufacturing lot	Weight trend approaches zero
Batch stability test filters	3 filters from a batch are repeatedly weighed during equilibration to verify the stability of the filter shipment batch	Weight loss <5 μg
Laboratory blank filters	1 laboratory blank filter is weighed for every weighing session	Weight loss <15 μg
Field Blank Filters	Unexposed filters from each shipment batch are designated as field blanks by the client	Weight difference <30 μg
Replicate filter weighings	Every filter (pre-weighing) or every third filter (post-weighing) is reweighed	Weight difference <15 μg

14.3.2 Size Distribution

The size of the particle is a key physical parameter that influences the characteristics of PM, for example, determines the deposition in the human respiratory system when inhaled. As has been mentioned in Sect. 14.1, $PM_{2.5}$ and PM_1 are more toxic than PM_{10}, as their smaller diameters allow them to penetrate deep into the lungs. For biomass and biowaste thermal plants, the size of PM determines primarily at which place it could be trapped in flue gas cleaning systems. For instance, the efficient operation of a cyclone requires a minimum particle size of 2.5 μm, and an electrostatic precipitator could remove very fine particles less than 1 μm with 95–99% efficiency [48].

Currently, there are a wide range of techniques available for particle size analysis. Some of the more common methods, and their strengths and limitations, are shown in Table 14.6 [49, 50].

The result of a particle size distribution can be presented in different ways: number size distribution, mass size distribution, volume size distribution, or intensity size distribution. The result will depend on the mechanism of measuring techniques and equipment used. The data could be converted from one type of distribution to another, however several assumptions should be made.

For biomass and biowaste thermal processes, laser diffraction and impactors are the dominant techniques used in PM size distribution determination.

The principle of laser diffraction particle sizing technique has been introduced in Chap. 2. This technique could report the particle size as a volume or number equivalent sphere diameter. The PM samples can be either dry powder or wet dispersed in a liquid. Generally, a larger quantity (a minimum of 20 ml) of the PM sample is required for dry analysis. Wet dispersion is applicable for PM collected on a filter, since PM usually has a very small quantity. For example, Min et al. [48]
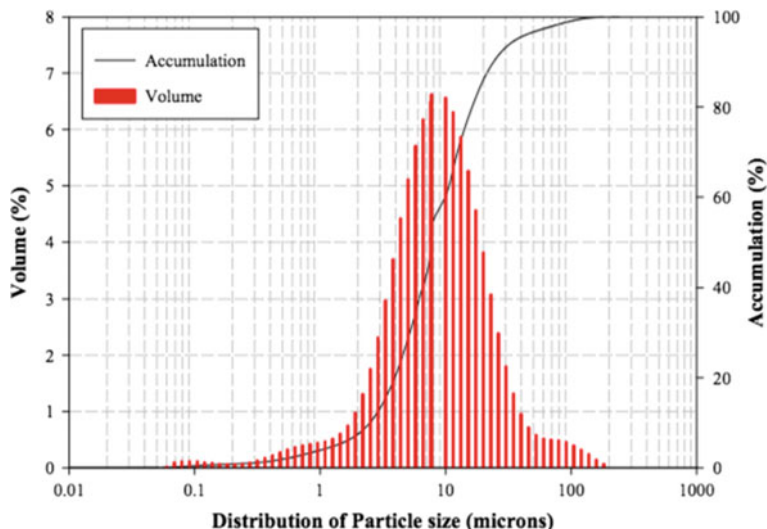
Table 14.6 Particle size distribution techniques

Technique		Strengths and limitations [49, 50]
Sieve analysis	✓	The sample could include a range of different densities, different refractive indices or water-soluble materials, suitable for bulk materials
	✓	The results are a separated size fraction for further study
	✗	Not suitable for fine particles <100 μm
	✗	Not suitable for elongated needle-shape samples
Sedimentation	✓	Determines particle size as a function of settling velocity
	✓	Suitable for particles <10 μm
	✗	Requires careful selection of the dispersion media
	✗	A bulk sample is required, e.g., 2–5 g
Elutriation analysis	✓	Determines particle size as a function of settling velocity
	✓	The technique is non-destructive
	✗	A bulk sample (about 10 g) is necessary
Laser diffraction method	✓	Suitable for measuring sizes between 0.1 and 3000 μm
	✓	Fast, can be performed on very small samples
	✓	Can conduct a continuous measurement for analyzing process streams
Electrical impedance	✓	Suitable for a wide range of sizes 0.4–1200 μm
	✗	Requires dispersing of the sample in a liquid medium
Microscopic sizing and image analysis	✓	Samples can be analyzed without being handled
	✗	Analyzing can be time-consuming
	✗	The results will be tedious and error prone if manually analyzed

used the wet dispersion method to detect the size distribution of PM collected from the gasification syngas and cleaning systems. The results were given in volume size distribution as shown in Fig. 14.11.

Impactors are also widely used to measure PM in the flue gas, which present particle size distribution in mass. The working principle of impactors is based on gravimetrically segregation the particles into different sizes from a particle laden gas stream. Some of the most used impactors include: Low Pressure Cascade Impactors (LPI), Electrical Low Pressure Impactor (ELPI), and Micro-Orifice Uniform Deposit Impactor (MOUDI). The former two could collect PM in the range of 30 nm–10 μm; and the latter is able to trap ultrafine PM smaller than 0.4 μm [51].

As an example, Fig. 14.12 shows the size distribution of PM from wood pellets gasification using a LPI [52]. Three types of gasifier were used: a bubbling fluidized bed (BFB), a circulating fluidized bed (CFB), and an indirect BFB. Results clearly reveal a bimodal particle mass size distribution: a fine mode at a size of around 0.1 μm, and a coarse mode at approximately 3 μm. Note that slightly different particle size distributions are observed for each gasifier, which may be attributed to tar condensation to form new particles.

Fig. 14.11 An example of particle size distribution (volume) of PM from gasifier outlet, using laser diffraction technique. Reprinted with permission from Springer Nature [48]

Fig. 14.12 An example of particle size distribution (mass) of PM from wood pellets gasification at three types of furnace, using a low pressure impactor. Reprinted with permission from Elsevier [52]
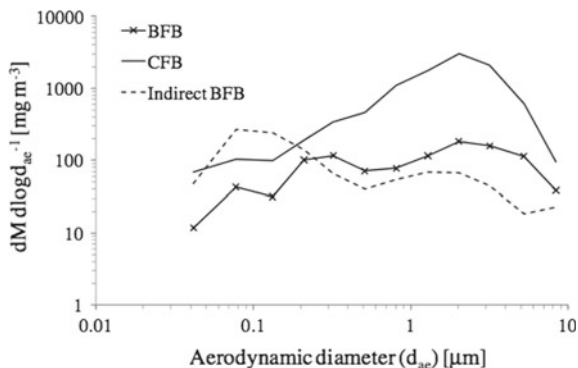

14.3.3 Morphology

Morphology, for example, shape, surface structure and microstructure, is another major physical property of PM. The morphology of PM has proven to significantly affect the chemical properties. Scanning electron microscopy (SEM) is ideally suited and widely used for characterization of PM from biomass and biowaste thermal conversion. The principle of SEM technique is to use electrons to form magnified images, which could provide better feature resolution, a wider range of magnification, and a greater depth-of-field than conventional optical microscopes [45]. The basic information and mechanism of the SEM technique can be found in

Chap. 2. One of the major advantages of SEM applied for biomass and biowaste thermal processes is that the SEM technique can achieve spatial resolution at submicron level, which makes it well-suited for $PM_{2.5}$ and PM_{10} analysis.

SEM technique is able to identify the different particle shapes of both fine and coarse PM fractions. For example, Morgalla et al. [53] characterized the PM collected from different stages of an impactor during wood pellet gasification in an indirect bubbling fluidized bed. As shown in Fig. 14.13, it is found that the fine particles (especially for PM collected in stage 1) seem to be agglomerated; while the coarse particles (stage 9) appear more separated and irregular.

SEM technique is also convenient to characterize the PM samples trapped by fiber filters. An example is given in Fig. 14.14 [54], which identified a high degree of the heterogeneity of PM both in terms of particle size and morphology ranging from nanoscale (ca. 0.04 µm) to micron scale (ca. 22 µm).
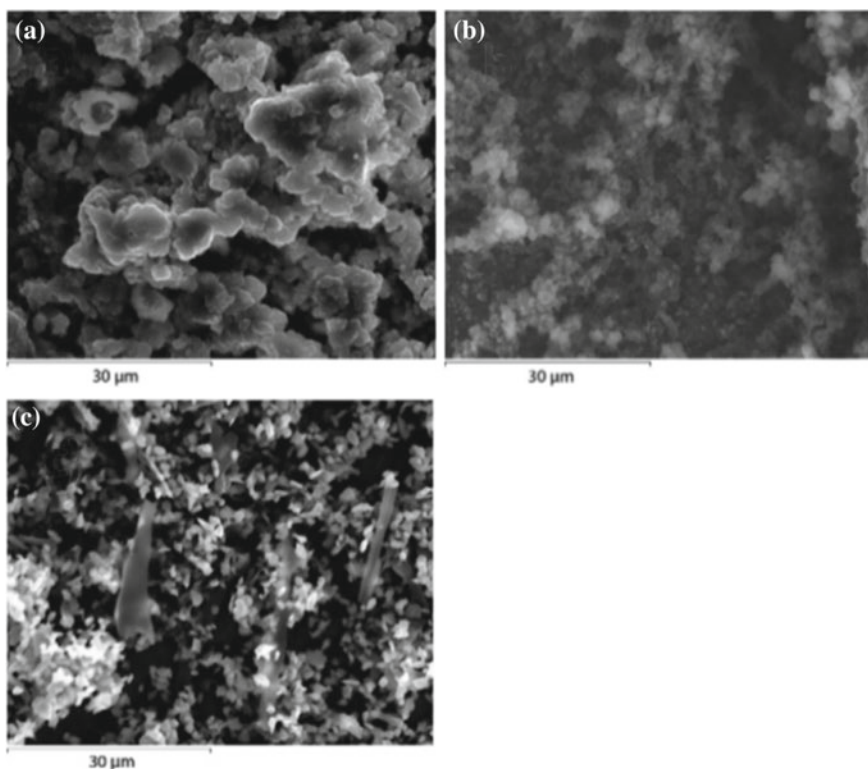
Fig. 14.13 SEM images of PM collected on different low pressure impactor stages corresponding to different geometric mean diameter (dae). **a** Stage 1 (0.04 µm); **b** stage 5 (0.32 µm); **c** stage 9 (2.02 µm). Reprinted with permission from Elsevier [53]
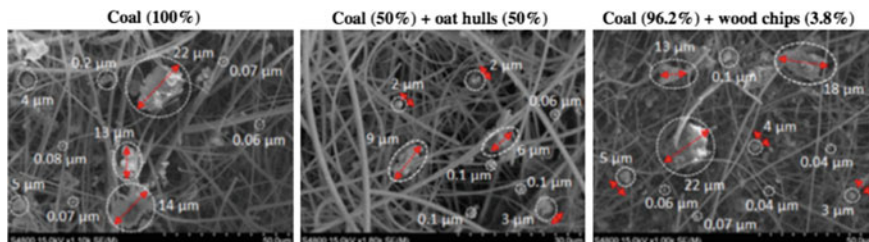
Fig. 14.14 SEM images of PM collected on quartz fiber substrates during biomass and coal co-firing. Reprinted with permission from Elsevier [54]

14.4 Chemical Characterization of Particulate Matter

The chemical characterization of PM is a very important issue due to the harmful effects that it represents for human health [55]. PM chemical characterization is complex, as fine particles are a mixture of different organic and inorganic compounds, and then, the use of several simultaneous analytical techniques is required.

At the present time, the chemical composition of PM produced from the thermochemical transformation of alternative materials like biomass and biowaste is not completely identified. Accordingly, the appropriate characterization of PM can help to understand the impact of raw materials characteristics and transformation process conditions on the chemical patterns of emission, and their associated environmental impacts and risks on human health.

Figure 14.15 briefly illustrates the various techniques which are commonly available for the characterization of both inorganic and organic composition of PM. Several of the most widely used techniques will be introduced in the following parts. Note that the fundamentals, measurement principles, and equipment used for these techniques have been described in detail in Chap. 2. Here the focus will be mainly associated with their applications in PM characterization.

14.4.1 Inorganic Composition Characterization Techniques

14.4.1.1 X-Ray Fluorescence (XRF)

XRF technique is usually used for PM chemical analysis, as it presents major advantages over other analysis techniques like ICP-OES, ICP-MS and AAS. In particular, XRF is a non-destructive technique. The PM samples, usually captured in filters, can be directly analyzed in the XRF apparatus without particular pretreatments, reducing the contamination risks of the samples.

The sampling strategy, e.g. the filter material, flow rate and sampling time should be adapted to the analytical technique and must be selected to obtain
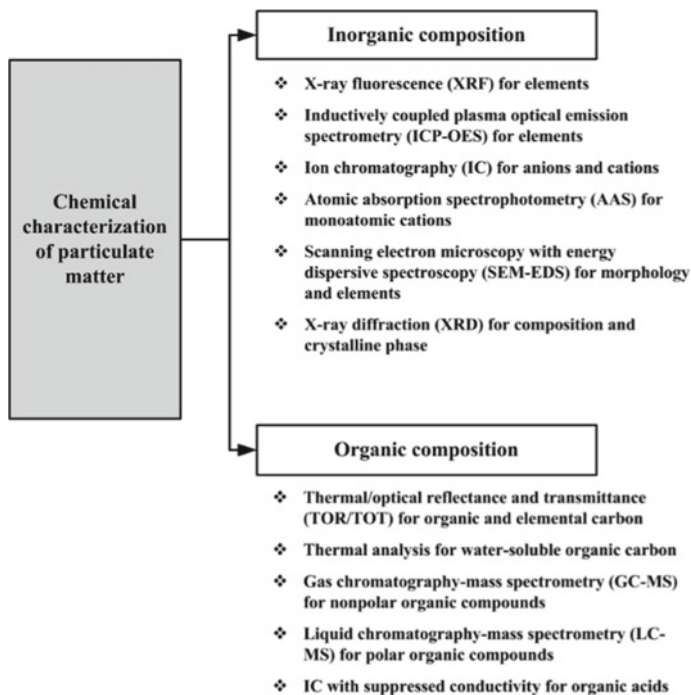
Fig. 14.15 Some of the commonly used techniques for chemical characterization of particulate matter

sufficient material for analysis. According to the PM loading in the air/gas stream, sampling times can go to hours to days [56].

Since both the sampling filter and the collected particles need to be analyzed, the appropriate choice of the filter material is an important issue to avoid interference between them [57]. Also, it is generally recommended to use thin membrane filters instead of thick fiber filters to avoid measurement errors due to the particle penetration in the collecting media [58]. The suitability of different filter materials for inorganic composition analysis using X-ray fluorescence is presented in Table 14.7.

In all cases, the blank analysis of the filter background is necessary to identify its major and minor constituents and accurately determine the collected PM composition. In this regard, it is recommended to analyze 2–5 filters to determine the background variability. It must be pointed out that the method detection limit is determined from the standard deviation of the filter blank analysis [62–64], and then, lower blank values are related to lower detection limits.

After PM sampling, filters must be carefully protected from contamination, since the sample size is small and the levels to be measured are low. Filter contamination can be minimized using samplers that do not expose the filter directly to the atmosphere and reducing the air exposure time before and after sampling [62]. The filters and membranes can be directly analyzed with the XRF instrument without

Table 14.7 Suitable sampling filter materials for XRF analysis of particulate matter

Filter material		Suitability for X-ray fluorescence [59–61]
Glass fiber filter	✗	High and often variable concentration of inorganic element. High blank values
Polycarbonate membranes	✓	Low blank values
	✓	Thin membranes
	✓	Collect particles in the membrane surface only. No corrections for x-ray adsorption have to be taken into account
Cellulose fiber filters	✓	Very low blank values
	✗	Thick filters
	✗	Corrections for x-ray adsorption should be done due to the filter thickness
PTFE filters	✓	Very low blank values
	✓	Thin membrane filters
	✓	The presence of F does not interfere with the analysis

any particular pretreatment or sample preparation, according to the protocols presented in Chap. 2. For accurate quantification, the XRF apparatus should be adequately calibrated using standards i.e. vacuum-deposited thin-film elements and compounds, polymer films and thin glass films [62].

The obtained spectrum from XRF analysis should be corrected by the subtraction of the filter background and adjusted for x-ray adsorption if necessary [62, 65]. If a quantitative analysis is performed, the PM composition can be obtained as a function of the analyzed sample surface area (mg/cm^2). From this value and considering the gas flow and sampling time, the composition can also be expressed as a function of the air/gas flow (mg/m^3) or the combusted fuel mass (mg/g fuel).

14.4.1.2 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

PM analysis can also be performed using ICP-OES, as this technique has a very wide analytical range with detection limits in the ppb range for almost all elements. ICP-OES allows the identification of elements from lithium to uranium excepting halogens. However, carbon, nitrogen, hydrogen and oxygen cannot be identified using this technique and are usually determined according to CHNS analysis.

As presented in Chap. 2, the main challenge of this analytical technique is the adequate digestion of the sample prior to the analysis. Since the PM cannot be easily recovered from the sampling filters and membranes, both filters and collected particles may be digested together completely before ICP-OES analysis. In this regard, the correct selection of the filter materials is of great importance.

The suitability of different filter materials for inorganic composition analysis using ICP-OES technique is presented in Table 14.8. As stated with the XRF technique, it must be pointed out that the method detection limit is determined from

Table 14.8 Suitable sampling filter materials for ICP-OES analysis of particulate matter

Filter material	Suitability for ICP-OES analysis [62, 63, 66]	
Glass fiber filter	✗	High and often variable blank values
Quartz fiber filter	✓	Low and relatively low blank values
	✗	The presence of soluble silicates can interfere with Si quantification
Cellulose filters	✓	Very low blank values
	✓	Easily digested due to their low resistance to acids
PTFE filters	✓	Very low blank values
	✗	Digestion performed with strong acids and high temperatures

the standard deviation of the filter blank analysis, and then, lower blank values are related to lower detection limits.

The filter choice will also depend on many other factors like sampling efficiency, mechanical resistance, chemical stability, cost and availability, and compatibility with the analytical method, as presented in Sect. 14.2.

Regarding the filter and collected particle digestion prior to ICP-OES analysis, highly concentrated acids like HCl, HNO_3, HF, and H_2O_2 are usually used. Reagent quantities are determined according to the sample size and the elements to be analyzed. For unknown samples, it is recommended to develop a digestion method according to the filter and sample size and the elements to be quantified, as presented in 'Digestion method development' section in Chap. 2.

In this regard, the standard EN 14902:2005 related to the measurement of Pb, Cd, As and Ni in the PM_{10} fraction of suspended PM, can be used as a reference for the digestion method development. Even when this standard is focused on the measurement of some particular constituents, it can give valuable insights to the sample preparation procedure for the analysis of a large range of elements.

Most digestion methods use HNO_3 and H_2O_2 to perform the complete digestion of samples and filters; however, if Si needs to be quantified, the use of HF and H_3BO_3 acid is recommended [67]. It is important to note that during the digestion step, it is necessary to ensure the complete submersion of the sampling filter in the digestion vessel, in order to attain the total decomposition of the sample.

When the total digestion of the sample is completed, the resulting solution is diluted volumetrically with demineralized water, according to the requirements of the analysis apparatus. Then, the solution can be analyzed using the ICP-OES protocol, as has been described in detail in Chap. 2.

As presented for XRF analysis, the PM composition can be obtained as a function of the analyzed sample surface area (mg/cm^2) or collected particle mass (mg/g PM). From this value and considering the gas flow and sampling time, the composition can also be expressed as a function of the air/gas flow (mg/m^3) or the combusted fuel mass (mg/g fuel).

14.4.1.3   Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS)

The EDS is a variation of the X-ray fluorescence, which is generally coupled to SEM. The combination of these techniques allows the simultaneous analysis of the morphology and surface structure of a sample, and its elemental composition. The SEM technique of PM has been described previously in Sect. 14.3; hence, the use of EDS will be introduced here. Even if the quantitative analysis is possible for this technique with certain corrections and restraints, SEM-EDS is mostly used to analyze the content and dispersion of metals in the sample.

As described in Chap. 2, energy-dispersive X-ray spectroscopy uses the X-ray spectrum emitted by a sample bombarded by a focused high-energy beam of electrons, to determine a localized chemical composition. Point analysis or element mapping are possible with this technique.

As for the other presented techniques, attention must be paid to the composition of the sampling filter, as it can impact the obtained results. Filters with low concentration of inorganic elements are then recommended, as in the case of the XRF analysis.

The SEM-EDS pictures of PM produced from biomass and biowaste combustion are presented here as a reference.

In Fig. 14.16, the SEM-EDS analysis of a single particle from the co-firing of 50% coal—50% oat hull is presented [54]. It is possible to observe the size, morphology and inorganic composition of the particle, as well as the quartz filter used for the sample collection. It must be noted that the Si signal in the ED spectrum comes from the filter, showing the importance of the appropriate choice of the sampling filter or membrane material.

Coal (50%) + oat hull (50%)
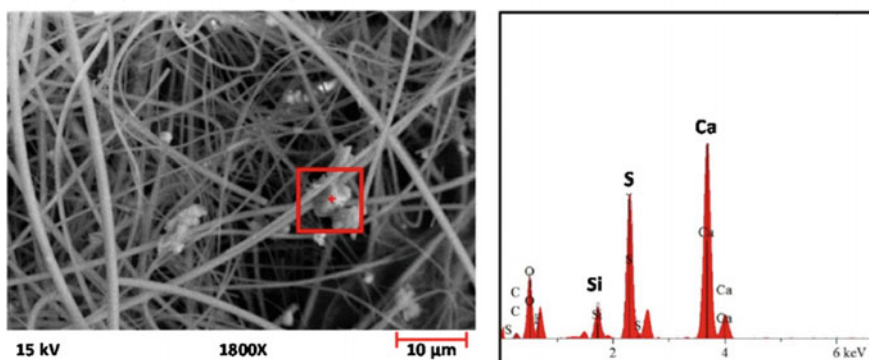
Fig. 14.16 SEM-EDS analysis of an individual particle from the co-firing of coal and oat hull. Reprinted with permission from Elsevier [54]
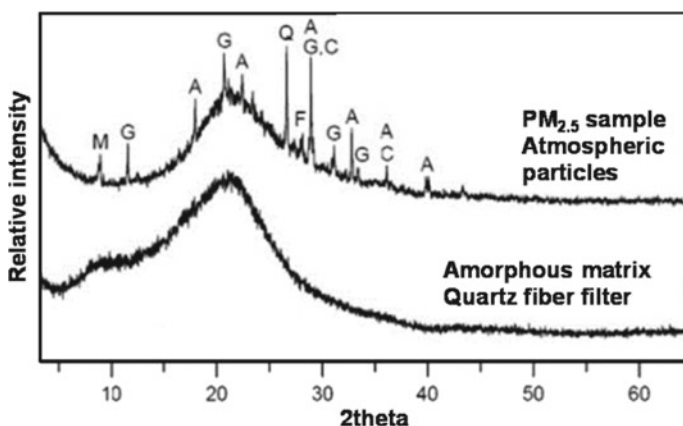
14.4.1.4 X-Ray Diffraction (XRD)

The already presented techniques are all suitable for the analysis of the inorganic content of biowaste combustion PM; however, they are not sufficient to distinguish different compounds and crystalline structures of a given element. In this regard, XRD is an excellent tool for the analysis of inorganic compounds in PM and the identification of their crystalline phases. This information can give insight into the origin and formation mechanisms of the components present in the PM.

One of the major advantages of this technique is the fact that this is a non-destructive analysis, giving the possibility to perform further characterization and analysis.

As for the already presented techniques, the filter material selection is important for the accurate analysis of samples. For XRD, the blank corresponds to the diffraction pattern of the filter material, and then, the filtering media should be chosen according to the crystallographic phases to be analyzed. In practice, the x-ray diffraction peaks of the filter spectra should not overlap with the diffraction peaks of the crystalline species present in the analyzed samples.

In this regard, several authors have studied the XRD patters of different filter materials used for atmospheric particulate matter analysis [68–70]. Accordingly, Teflon, glass fiber, quartz fiber and cellulose acetate are considered as the most suitable materials for particulate matter analysis from biomass and biowaste combustion.

Figure 14.17 shows an example of the impact of the filter material in the sample XRD pattern. It can be observed that the amorphous matrix of the quartz filter used for particle collection is easily distinguished by a broad peak, while the present crystalline phases in the analyzed particles produce sharp peaks. If there is an

Fig. 14.17 Impact of filter material in sample x-ray diffraction pattern. A: ammonium nitrate, C: calcite, F: feldspar group, G: gypsum, M: mica group, Q: quartz. Reprinted with permission from Elsevier [71]
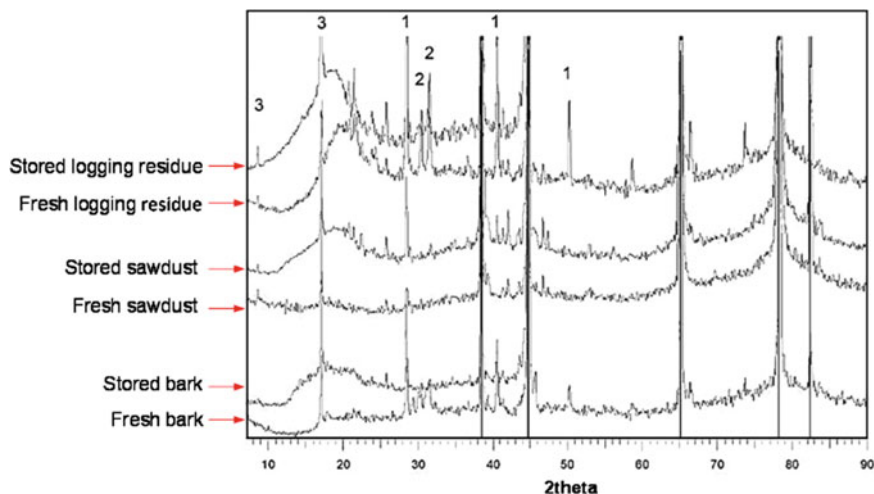
Fig. 14.18 XRD diffractogram of PM from the combustion of different pelletized biofuels. Reprinted with permission from American Chemical Society [72]

overlap of the diffraction pattern of the filter and the sample, it is not possible to precisely identify the crystalline species in the sample.

For its part, Fig. 14.18 shows the XRD diffractogram of the particles collected form the combustion of different pelletized biowaste [72]. The vertical lines indicate the spectra from the collector material (aluminum foil impactor), and the observed peaks are related with the crystalline phases present in the analyzed particles. The authors report the identified phases as KCl (1), $K_3Na(SO_4)_2$ (2), and a possible unidentified Zn phase (3).

As each different phase produces a different combination of peaks, the crystalline compounds in the sample can be identified from the analysis of the x-ray diffraction spectra. It is important to note that the previous knowledge of the inorganic elements present in the sample is required to the correctly identify the phase.

Generally, a qualitative analysis of the crystalline phases present in the sample is adequate for the basic PM chemical characterization. However, in some applications, it would be necessary to perform a quantitative analysis. In this respect, different authors have proposed several methods for quantitative analysis of PM samples using standards [70, 73–75].

14.4.1.5 Examples of Inorganic Characterization of Biomass and Biowaste Combustion PM

The particle formation and chemical composition is influenced by the fuel properties, i.e. biomass or biowaste. From the available characterization techniques, the main inorganic constituents of PM from biomass and biowaste thermochemical conversion processes are presented in Table 14.9.

Table 14.9 Examples for the main inorganic composition of PM generated from biomass and biowaste thermochemical conversion processes

Biomass/ biowaste	Particle size	Sampling method/ material	Main reported inorganic constituents	Analytical technique	References
Wheat straw combustion	PM_1	Low pressure impactor	K, Cl, Si	SEM-EDS	[76]
Wheat straw combustion	PM_{1-10}	Low pressure impactor	K, Mg, Ca, Si, Cl, S	SEM-EDS	[76]
Pine wood bioslurry combustion	PM_{10}	Low pressure impactor	Mg, Ca, Al, Si, Fe, Na, K, S	ICP-OES	[77]
Beech wood combustion	$PM_{2.5}$	Quartz fiber filters	Al, Ca, Cu, Fe, K, Na, Pb, Zn	ICP-OES	[78]
Eucalyptus wood combustion	PM_{10}	Cellulose acetate filters	Ca, Mg, Cr, Fe, Co, Si	ICP-OES XRF	[79]
MSW combustion	$PM_{2.5}$	High temperature and low pressure impactor	Ca, Si, Mg, Al, K, Na, Zn, Cl, Pb, Ti, P, S	ICP-OES SEM-EDS	[80]
Rice straw combustion	$PM_{2.5}$	Cellulose and PTFE filter	Al, Ca, Cr, Cu, K, Si, Mg, S	ICP-OES	[81]
Rice straw combustion	PM_{10}	Quartz filter	Fe, Si, Al, Ca,, Cr, Cu, S, Pb	ICP-OES	[81]
Light diesel oil	$PM_{2.5}$	Teflon filter	As, Fe, Al, Mn, Pb, Cr, Zn, Cu, Ni	ICP-OPS	[82]

Some authors presented the PM composition as a function of the air/gas flow (mg/m^3), while some others, as a function of the fuel mass input (mg/g fuel), or the collected PM mass (mg/g PM). In some cases, only a qualitative analysis is performed. Accordingly, for comparison purposes, it is important to verify the sampling and analysis conditions, as well as the reported units for PM composition. The list of the inorganic composition present in PM is not exhaustive and is based on the reported results of the referred authors. The composition of PM from light diesel oil combustion is presented only for comparison purposes.

14.4.2 Organic Composition Characterization Techniques

14.4.2.1 Thermal/Optical Reflectance and Transmittance (TOR/TOT)

TOR/TOT technique is used to quantify organic and elemental carbon (OC and EC) in PM. OC and EC are typical and important components from thermal conversion of biomass and waste. As has been reported, OC could account for about two-thirds by mass of aerosol produced from biomass burning [83]. The principle of TOR/TOT technique is based on heating the carbon-containing sample to different temperature stages under both inert and oxidizing conditions, and quantifying the converted CO_2 with an infrared absorption detector, or, converting CO_2 to CH_4 by a methanator oven before being measured with a more sensitive flame ionization detector (FID).

Currently, more than 20 methods are available for OC and EC quantification [45]. Generally they provide comparable results of the value of total carbon (TC = OC + EC); the main difference among the methods are specific definition of OC and EC.

For PM analysis, the Interagency Monitoring Protection Visual Environment (IMPROVE) thermal protocol is the most widely applied method. Its recommended procedures are illustrated in Table 14.10 and Fig. 14.19. In the first 1–4 steps, the four OC fractions are thermally desorbed under a flow of non-oxidizing helium carrier gas with controlled temperature ramps. In the second 5–7 steps, the oven is then switched to an oxidizing 2% oxygen/98% helium with another series of temperature ramps to determine the three EC fractions. Special attention should be paid to a pyrolyzed carbon fraction (OP), which is formed during the first non-oxidizing part of the analysis (between step 1–4). The OP fraction is quantified by carbon evolved between the time oxygen is added and the reflected signal returns to its original value. IMPROVE regulates the final OC as the sum of OC1 + OC2 + OC3 + OC4 + OP; and EC as the sum of EC1 + EC2 + EC3 − OP.

Table 14.10 IMPROVE method for TOR/TOT technique

Step	Carbon fraction	Carrier gas	Temperature (°C)
1	OC1	100% He	25 (ambient) −140
2	OC2	100% He	140–280
3	OC3	100% He	280–480
4	OC4	100% He	480–580
5	EC1	98% He/2% O_2	580
6	EC2	98% He/2% O_2	580–740
7	EC3	98% He/2% O_2	740–840
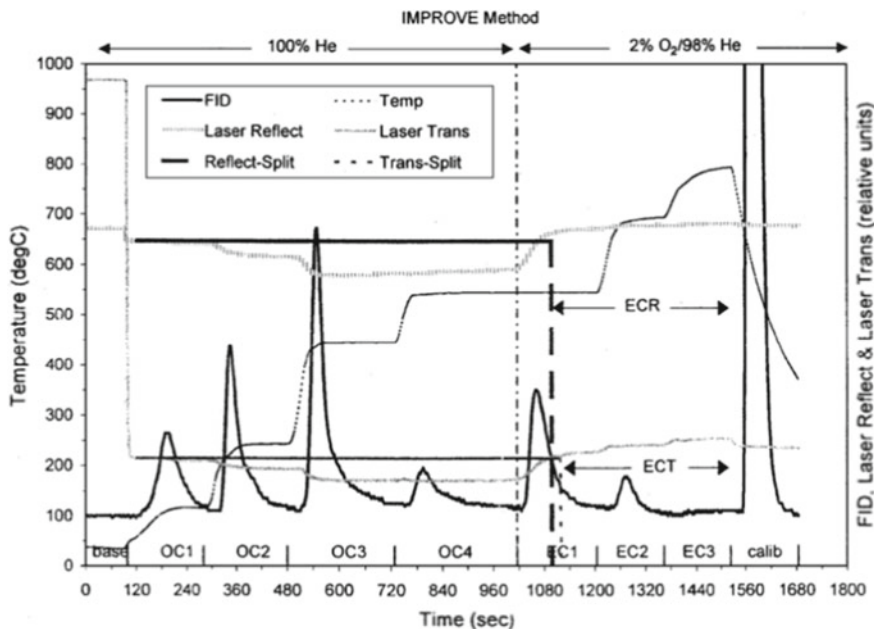
Fig. 14.19 Typical IMPROVE protocol thermogram. Reprinted with permission from Taylor & Francis [84]

Table 14.11 TOR/TOT characteristics of PM$_{2.5}$ samples from three types of biomass burning.

	Unit	Biomass type		
		Rice straw	Pine needles	Sesame stems
PM$_{2.5}$	mg/m^3	41.39 ± 15.01	27.32 ± 13.15	29.47 ± 11.28
OC	mg C/m^3	24.15 ± 9.51	14.22 ± 7.37	13.70 ± 6.13
EC	mg C/m^3	1.42 ± 0.46	2.04 ± 1.01	1.30 ± 0.49
OC/EC	–	16.80 ± 2.81	7.01 ± 0.96	10.15 ± 1.58

Reproduced with permission from Elsevier [85]

To conduct TOR/TOT analysis, PM samples should be collected on quartz-fiber filters that need to be pre-heated at 900 °C for 3 h by the carrier gas before sampling. During analysis, a 0.5 cm^2 punch from each exposed filter is taken and placed in a quartz boat that is inserted into the oven for appropriate analysis.

As an example, Table 14.11 shows the TOR/TOT analysis results from PM$_{2.5}$ samples of three types of biomass burning (rice straw, pine needles, and sesame stems). The results show a high ratio of OC/EC for all types of the biomasses.

14.4.2.2 Gas Chromatography-Mass Spectrometry (GC-MS)

GC-MS is used for qualitative and quantitative determination of nonpolar organic compounds in the PM. In the past years, techniques have been established for appropriate preparation of samples ready for GC-MS analysis, of which a pre-treatment procedure involving solvent extraction and concentration is necessary. Realizing that this pre-treatment is often time-consuming and increases the risk for error, currently, thermal desorption (TD) technique has been coupled with GC-MS as an alternative to the solvent extraction technique [86, 87]. The TD-GC/MS technique does not require sample extraction. Thus, the PM sample preparation procedures are similar as TOR/TOT technique: a small piece of quartz-fiber filter, around 1–2 cm^2 punch, is taken out of a whole filter; 1 μL of internal standard solutions is added to the sample to normalize the MS response before the sample is attached to the analyzing injection tube. However, the use of TD technique should raise attention to procedure conditions, thus affecting the accuracy of final results [88].

The GC-MS technique is typically used to quantify polycyclic aromatic hydrocarbons (PAHs) in PM, since they are reported to contribute the carcinogenicity adverse effects. An example of the various PAHs contained in the PM during the combustion of five agricultural residue-derived biomass fuels (sunflower stalk pellets, straw pellets, buckwheat shells, corn stalk pellets, wheat grain screenings) and two reference fuels (wood, sewage sludge pellets), is illustrated in Fig. 14.20.

Fig. 14.20 PAHs contained in PM during combustion of several biomass fuels (µg/kg). Reprinted with permission from American Chemical Society [89]
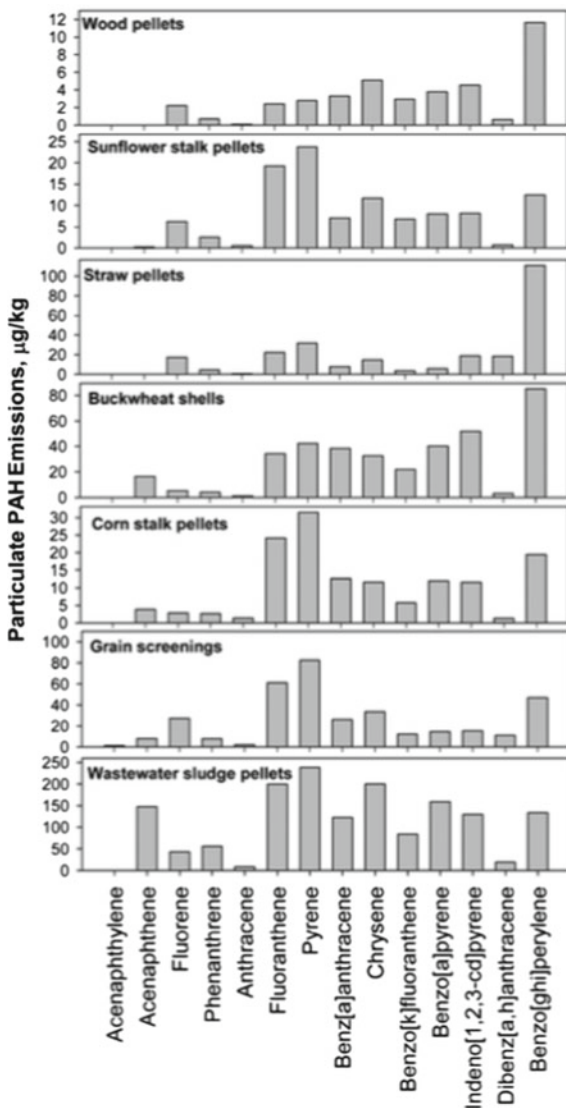
References

1. European Environment Agency (EEA).: National Emissions Reported to the Convention on Long-Range Transboundary Air Pollution (LRTAP Convention). https://www.eea.europa.eu/data-and-maps/data/national-emissions-reported-to-the-convention-on-long-range-transboundary-air-pollution-lrtap-convention-12. Accessed 30 Oct 2018
2. WHO Regional Office for Europe: Health Aspects of Air Pollution with Particulate Matter, Ozone and Nitrogen Dioxide. Bonn, Germany (2003)

3. Kelly, F.J., Fussell, J.C.: Size, source and chemical composition as determinants of toxicity attributable to ambient particulate matter. Atmos. Environ. **60**, 504–526 (2012)

4. Harrison, R.M., Hester, R.E., Querol, X.: Airborne Particulate Matter: Sources, Atmospheric Processes and Health. Royal Society of Chemistry, Cambridge (2016)

5. Nussbaumer, T.: Overview on technologies for biomass combustion and emission levels of particulate matter. Swiss Federal Office for the Environment (FOEN), Zürich, Switzerland (2010)

6. Zereini, F., Wiseman, C.L.S.: Urban Airborne Particulate Matter—Origin, Chemistry, Fate and Health Impacts. Springer, Berlin (2010)

7. Morakinyo, O.M., Mokgobu, M.I., Mukhola, M.S., Hunter, R.P.: Health outcomes of exposure to biological and chemical components of inhalable and respirable particulate matter. Int. J. Environ. Res. Public Health **13**, 592 (2016)

8. Traboulsi, H., Guerrina, N., Iu, M., Maysinger, D., Ariya, P., Baglole, C.J.: Inhaled pollutants: the molecular scene behind respiratory and systemic diseases associated with ultrafine particulate matter. Int. J. Mol. Sci. **18**(2), 243 (2017)

9. Zhang, Y., Cai, J., Wang, S., He, K., Zheng, M.: Review of receptor-based source apportionment research of fine particulate matter and its challenges in China. Sci. Total Environ. **586**, 917–929 (2017)

10. Brauer, M., Freedman, G., Frostad, J., et al.: Ambient air pollution exposure estimation for the global burden of disease 2013. Environ. Sci. Technol. **50**(1), 79–88 (2015)

11. Karagulian, F., Belis, C.A., Dora, C.F.C., Prüss-Ustün, A.M., Bonjour, S., Adair-Rohani, H., Amann, M.: Contributions to cities' ambient particulate matter (PM): a systematic review of local source contributions at global level. Atmos. Environ. **120**, 475–483 (2015)

12. Burnett, R.T., Pope III, C.A., Ezzati, M., et al.: An integrated risk function for estimating the global burden of disease attributable to ambient fine particulate matter exposure. Environ. Health Perspect. **122**(4), 397–403 (2014)

13. Chen, J., Li, C., Ristovski, Z., et al.: A review of biomass burning: Emissions and impacts on air quality, health and climate in China. Sci. Total Environ. **579**, 1000–1034 (2017)

14. United State Environmental Protection Agency (USEPA).: 2011 National Emissions Inventory (NEI) Data. https://www.epa.gov/air-emissions-inventories/2011-national-emissions-inventory-nei-data. Accessed 30 Oct 2018

15. Huang, R.J., Zhang, Y., Bozzetti, C., et al.: High secondary aerosol contribution to particulate pollution during haze events in China. Nature **514**, 218–222 (2014)

16. Sielicki, P., Janik, H., Guzman, A., Namieśnik, J.: The progress in electron microscopy studies of particulate matters to be used as a standard monitoring method for air dust pollution. Crit. Rev. Anal. Chem. **41**, 314–334 (2011)

17. AQEG (Air Quality Expert Group): Particulate Matter in the United Kingdom. Department of Environment, Food and Rural Affairs, UK (2005)

18. Kelly, K.E., Sarofim, A.F., Lighty, J.S., Arnott, W.P., Rogers, C.F., Zielinska, B., Prather, K. A.: User Guide for Characterizing Particulate Matter: Evaluation of Several Real-Time Methods. University of Utah, Institute for Clean and Secure Energy, USA (2003)

19. Mauderly, J.L., Chow, J.C.: Health effects of organic aerosols. Inhal. Toxicol. **20**, 257–288 (2008)

20. Li, N., Nel, A.E.: The cellular impacts of diesel exhaust particles: beyond inflammation and death. Eur. Respir. J. **27**, 667–668 (2006)

21. Lighty, J.S., Veranth, J.M., Sarofim, A.F.: Combustion aerosols: factors governing their size and composition and implications to human health. J. Air Waste Manage. Assoc. **50**, 1565–1618 (2000)

22. Obaidullah, M., Bram, S., Verma, V.K., De Ruyck, J.: A review on particle emissions from small scale biomass combustion. Int. J. Rene. Energ. Res. **2**, 147–159 (2012)

23. Simoneit, B.R.T.: Biomass burning—a review of organic tracers for smoke from incomplete combustion. Appl. Geochem. **17**, 129–162 (2002)

24. Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R.: Sources of fine organic aerosol. 8. Boilers burning No. 2 distillate fuel oil. Environ. Sci. Technol. **31**(10), 2731–2737 (1997)

25. McElroy, M.W., Carr, R.C., Ensor, D.S., Markowski, G.R.: Size distribution of fine particles from coal combustion. Science **215**, 13–19 (1982)
26. Christensen, K.A., Stenholm, M., Livbjerg, H.: The formation of submicron aerosol particles, HCl and SO_2 in straw-fired boilers. J. Aerosol Sci. **29**(4), 421–444 (1998)
27. Nussbaumer, T.: Combustion and co-combustion of biomass: fundamentals, technologies, and primary measures for emission reduction. Energy Fuels **17**(6), 1510–1521 (2003)
28. Becidan, M., Todorovic, D., Skreiberg, Ø., Khalil, R.A., Backman, R., Goile, F., Skreiberg, A., Jovovic, A., Sørum, L.: Ash related behaviour in staged and non-staged combustion of biomass fuels and fuel mixtures. Biomass Bioenerg. **41**, 86–93 (2012)
29. Jöller, M., Brunner, T., Obernberger, I.: Modeling of aerosol formation during biomass combustion in grate furnaces and comparison with measurements. Energy Fuels **19**(1), 311–323 (2005)
30. Jöller, M., Brunner, T., Obernberger, I.: Modeling of aerosol formation during biomass combustion for various furnace and boiler types. Fuel Process. Technol. **88**, 1136–1147 (2007)
31. Wang, G., Deng, J., Ma, Z., Hao, J., Jiang, J.: Characteristics of filterable and condensable particulate matter emitted from two waste incineration power plants in China. Sci. Total Environ. **639**, 695–704 (2018)
32. Uski, O., Jalava, P.I., Happo, M.S., et al.: Effect of fuel zinc content on toxicological responses of particulate matter from pellet combustion in vitro. Sci. Total Environ. **511**, 331–340 (2015)
33. Gao, X., Wu, H.: Combustion of volatiles produced in situ from the fast pyrolysis of woody biomass: direct evidence on its substantial contribution to submicrometer particle (PM_1) emission. Energy Fuels **25**(9), 4172–4181 (2011)
34. Zhang, X.: Emission Standards and Control of $PM_{2.5}$ from Coal-Fired Power Plant. IEA Clean Coal Centre, London, UK (2016)
35. Zhu, F., Wang, L.: Analysis on technology-economy and environment benefit of ultra-low emission from coal-fired power units. Environ. Prot. **42**(21), 28–33 (2014)
36. Gustafsson, E., Strand, M., Sanati, M.: Physical and chemical characterization of aerosol particles formed during the thermochemical conversion of wood pellets using a bubbling fluidized bed gasifier. Energy Fuels **21**(6), 3660–3667 (2007)
37. Mylläri, F., Karjalainen, P., Taipale, R., Aalto, P., Häyrinen, A., Rautiainen, J., Pirjola, L., Hillamo, R., Keskinen, J., Rönkkö, T.: Physical and chemical characteristics of flue-gas particles in a large pulverized fuel-fired power plant boiler during co-combustion of coal and wood pellets. Combust. Flame **176**, 554–566 (2017)
38. Nyström, R.: Particle emissions from residential wood and biodiesel combustion. Doctoral thesis of Umeå University. Umeå, Sweden (2016)
39. Castellani, B., Morini, E., Filipponi, M., Nicolini, A., Palombo, M., Cotana, F., Rossi, F.: Comparative analysis of monitoring devices for particulate content in exhaust gases. Sustainability **6**, 4287–4307 (2014)
40. Marple, V.A., Rubow, K.L., Behm, S.M.: A microorifice uniform deposit impactor (MOUDI): description, calibration, and use. Aerosol Sci. Technol. **14**, 434–446 (1991)
41. Kwon, S.B., Lim, K.S., Jung, J.S., Bae, G.N., Lee, K.W.: Design and calibration of a 5-stage cascade impactor (K-JIST cascade impactor). J. Aerosol Sci. **34**, 289–300 (2003)
42. Hinds, W.C.: Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles. Wiley, New York (1999)
43. SICK AG.: Operating Instructions GRAVIMAT SHC502: Gravimetric Dust Concentration Measuring System. SICK Engineering GmbH, Ottendorf-Okrilla, Germany (2014)
44. Lindsley, W.G.: Filter Pore Size and Aerosol Sample Collection. NIOSH Manual of Analytical Methods, 5th edn. (2015)
45. Ruzer, L.S., Harley, N.H.: Aerosols Handbook: Measurement, Dosimetry, and Health Effects. CRC Press, Boca Raton (2012)
46. United State Environmental Protection Agency (USEPA): APTI Course 435—Atmospheric Sampling: Instructor's Guide. Air Pollution Training Institute, NC, USA (1980)

47. RTI International: Standard Operating Procedure for Particulate Matter (PM) Gravimetric Analysis. North Carolina, USA (2008)
48. Min, J., Nam, S.B., Kim, N.R., Kim, D.J., Yoon, Y.S., Park, S.N., Gu, J.H.: A study on the characteristics of particulate matter in the syngas produced from the waste gasification with cleaning systems for energy utilization. J. Mater. Cycles Waste Manag. **19**, 1155–1165 (2017)
49. Malvern Instruments. A Basic Guide to Particle Characterization. Malvern Instruments Limited, Worcestershire, UK (2012)
50. Epstein, N., Grace, J.R., Otten, L., Fayed, M.: Handbook of Powder Science & Technology. Chapman & Hall, New York (1997)
51. Amaral, S.S., De Carvalho, J.A., Costa, M.A.M., Pinheiro, C.: An overview of particulate matter measurement instruments. Atmosphere **6**(9), 1327–1345 (2015)
52. Gustafsson, E., Lin, L., Strand, M.: Characterization of particulate matter in the hot product gas from atmospheric fluidized bed biomass gasifiers. Biomass Bioenerg. **35**, S71–S78 (2011)
53. Morgalla, M., Lin, L., Seemann, M., Strand, M.: Characterization of particulate matter formed during wood pellet gasification in an indirect bubbling fluidized bed gasifier using aerosol measurement techniques. Fuel Process. Technol. **138**, 578–587 (2015)
54. Al-Naiema, I., Estillore, A.D., Mudunkotuwa, I.A., Grassian, V.H., Stone, E.A.: Impacts of co-firing biomass on emissions of particulate matter to the atmosphere. Fuel **162**, 111–120 (2015)
55. Vasconcellos, P.C., Souza, D.Z., Sanchez-Ccoyllo, O., et al.: Determination of anthropogenic and biogenic compounds on atmospheric aerosol collected in urban, biomass burning and forest areas in São Paulo, Brazil. Sci. Total Environ. **408**, 5836–5844 (2010)
56. Fine, P.M., Cass, G.R., Simoneit, B.R.T.: Chemical characterization of fine particle emissions from fireplace combustion of woods grown in the northeastern United States. Environ. Sci. Technol. **35**(13), 2665–2675 (2001)
57. Austria International Atomic Energy Agency: Sampling, storage and sample preparation procedures for X ray fluorescence analysis of environmental materials—IAEA-TECDOC-9SO. Vienna, Austria (1997)
58. Lodge Jr., J.P.: Methods of Air Sampling and Analysis. CRC Press, Florida (1988)
59. Salazar, A.: Glass-fibre filter for analysis of aerosol particles using energy-dispersive x-ray fluorescence. X-Ray Spectrum. **21**(3), 143–147 (1992)
60. Beckhoff, B., Kanngießer, B., Langhoff, N., Wedell, R., Wolff, H.: Handbook of Practical X-ray Fluorescence Analysis. Springer, Berlin (2006)
61. Adams, F.C., Van Grieken, R.E.: Absorption correction for X-ray fluorescence analysis of aerosol loaded filters. Anal. Chem. **47**(11), 1767–1773 (1975)
62. Landsberger, S., Creatchman, M.: Elemental Analysis of Airborne Particles. Gordon and Breach Science Publishers, Amsterdam (1999)
63. EN 14902:2005: Ambient air quality—Standard method for the measurement of Pb, Cd, As and Ni in the PM_{10} fraction of suspended particulate matter. European Standard (2005)
64. California Environmental Protection Agency: Procedure for the determination of trace elements in particulate matter emitted from motor vehicle exhaust using inductively coupled plasma mass spectrometry (ICP-MS). California, USA (2010)
65. Criss, J.W.: Particle size and composition effects in X-ray fluorescence analysis of pollution samples. Anal. Chem. **48**(1), 179–186 (1976)
66. Buck, C.S., Paytan, A.: Evaluation of commonly used filter substrates for the measurement of aerosol trace element solubility. Limnol. Oceanogr. Methods **10**, 790–806 (2012)
67. Coedo, A.G., Dorado, M.T., Padilla, I., Alguacil, F.J.: Use of boric acid to improve the microwave-assisted dissolution process to determine fluoride forming elements in steels by flow injection inductively coupled plasma mass spectrometry. J. Anal. At. Spectrom. **13**, 1193–1197 (1998)
68. Santos, M.D., Matos, J.R., Carvalho, L.R.F., Sant'Agostino, L.M., Korn, L.M.: An X-ray diffraction study of filters used for atmospheric aerosol sampling. Powder Diffr. **11**(3), 230–234 (1996)

69. Davis, B.L., Johnson, L.R.: On the use of various filter substrates for quantitative particulate analysis by X-ray diffraction. Atmos. Environ. **16**(2), 273–282 (1982)

70. Sturges, W.T., Harrison, R.M.: Semi-quantitative X-ray diffraction analysis of size fractionated atmospheric particles. Atmos. Environ. **23**(5), 1083–1098 (1989)

71. Choung, S., Oh, J., Han, W.S., Chon, C.M., Kwon, Y., Kim, D.Y., Shin, W.: Comparison of physicochemical properties between fine (PM$_{2.5}$) and coarse airborne particles at cold season in Korea. Sci. Total Environ. **541**, 1132–1138 (2016)

72. Boman, C., Nordin, A., Boström, D., Öhman, M.: Characterization of inorganic particulate matter from residential combustion of pelletized biomass fuels. Energy Fuels **18**(2), 338–348 (2004)

73. Esteve, V., Rius, J., Ochando, L.E., Amigó, J.M.: Quantitative X-ray diffraction phase analysis of coarse airborne particulate collected by cascade impactor sampling. Atmos. Environ. **31**(23), 3963–3967 (1997)

74. Esteve, V., Carda, J., Reventos, M.M., Amigó, J.M.: Quantitative X-ray diffraction phase analysis of airborne particulate collected by a cascade impactor sampler using the Rietveld full-pattern fitting method. Powder Diffr. **12**(3), 151–154 (1997)

75. Jordán, M., Alvarez, C., Sanfeliu, T.: A powder diffraction quantification method (ALJOR) for atmospheric particulate matter. Environ. Geol. **42**(7), 810–816 (2002)

76. Wang, X., Hu, Z., Adeosun, A., Liu, B., Ruan, R., Li, S., Tan, H.: Particulate matter emission and K/S/Cl transformation during biomass combustion in an entrained flow reactor. J. Energy Inst. (2017). https://doi.org/10.1016/j.joei.2017.10.005

77. Feng, C., Wu, H.: Synergy on particulate matter emission during the combustion of bio-oil/biochar slurry (bioslurry). Fuel **214**, 546–553 (2018)

78. Czech, H., Miersch, T., Orasche, J., et al.: Chemical composition and speciation of particulate organic matter from modern residential small-scale wood combustion appliances. Sci. Total Environ. **612**, 636–648 (2018)

79. Gonçalves, C., Alves, C., Evtyugina, M., Mirante, F., Pio, C., Caseiro, A., Schmidl, C., Bauer, H., Carvalho, F.: Characterisation of PM$_{10}$ emissions from woodstove combustion of common woods grown in Portugal. Atmos. Environ. **44**(35), 4474–4480 (2010)

80. Brunner, T., Fluch, J., Obernberger, I., Warnecke, R.: Investigations of aerosol formation pathways during MSW combustion based on high-temperature impactor measurements. Fuel Process. Technol. **105**, 154–160 (2013)

81. Oanh, N.T.K., Ly, B.T., Tipayarom, D., Manandhar, B.R., Prapat, P., Simpson, C.D., Liu, L. J.S.: Characterization of particulate matter emission from open burning of rice straw. Atmos. Environ. **45**(2), 493–502 (2011)

82. Wu, D., Zhang, F., Lou, W., Li, D., Chen, J.: Chemical characterization and toxicity assessment of fine particulate matters emitted from the combustion of petrol and diesel fuels. Sci. Total Environ. **605**, 172–179 (2017)

83. Duan, F., Liu, X., Yu, T., Cachier, H.: Identification and estimate of biomass burning contribution to the urban aerosol organic carbon concentrations in Beijing. Atmos. Environ. **38**(9), 1275–1282 (2004)

84. Chow, J.C., Watson, J.G., Crow, D., Lowenthal, D.H., Merrifield, T.: Comparison of IMPROVE and NIOSH carbon measurements. Aerosol Sci. Technol. **34**(1), 23–34 (2001)

85. Park, S.S., Yu, J.: Chemical and light absorption properties of humic-like substances from biomass burning emissions under controlled combustion experiment. Atmos. Environ. **136**, 114–122 (2016)

86. Ono-Ogasawara, M., Myojo, T., Smith, T.J.: A simple direct injection method for GC/MS analysis of PAHs in particulate matter. Ind. Health **46**(6), 582–593 (2008)

87. Chow, J.C., Yu, J.Z., Watson, J.G., Ho, S.S.H., Bohannan, T.L., Hays, M.D., Fung, K.K.: The application of thermal methods for determining chemical composition of carbonaceous aerosols: a review. J. Environ. Sci. Heal. A **42**(11), 1521–1541 (2007)

88. Elorduy, I., Durana, N., García, J.A., Gómez, M.C., Alonso, L.: Optimization and validation of thermal desorption gas chromatography-mass spectrometry for the determination of

polycyclic aromatic hydrocarbons in ambient air. J. Anal. Methods Chem. (2018). https://doi.org/10.1155/2018/8734013

89. Krugly, E., Martuzevicius, D., Puida, E., Buinevicius, K., Stasiulaitiene, I., Radziuniene, I., Minikauskas, A., Kliucininkas, L.: Characterization of gaseous-and particle-phase emissions from the combustion of biomass-residue-derived fuels in a small residential boiler. Energy Fuels **28**(8), 5057–5066 (2014)