Transmission Electron Microscope Study on the Physical and Chemical Characteristics of Atmospheric Particulate Matter PM1.0 in Heavily Polluted Weather

Yingshi Song*  
Chinese Research Academy of Environmental Sciences, Beijing 100012, China  
*Corresponding author (E-mail: keystone2006@163.com)

Yu Tao  
College of Land Management, Nanjing Agricultural University, Nanjing 210095, Jiangsu, China

Abstract  
With the continuous intensification of human activities, atmospheric particulate matter in the air is increasing, causing serious harm to health and ecological environment. Atmospheric particulate matter has attracted increasing attention. Atmospheric particulate matter (PM) is one of the most important pollutants in air pollution. It is of great importance and necessity to study PM because of its wide source, complex composition, huge quantity, diverse nature and great harm. Because PM1.0 particle size is small, can enter the human body directly, the harm to health is more serious. In recent years, with the continuous progress of science and technology, the equipment of high resolution microscope has been constantly updated. The single particle analysis technology based on transmission electron microscope and X-ray energy spectrum analysis has been widely applied, playing an increasingly important role in the study of atmospheric particles. In this paper, transmission electron microscope and X-ray energy spectrometer were used to study the physical and chemical characteristics of atmospheric particulate matter PM1.0 under severe pollution weather, and the structural information, particle size and chemical composition of PM1.0 were obtained. The analysis data showed that there was a strong correlation between the particle morphology of atmospheric particulate matter PM 1.0 and element composition and particle formation process.

Key words: Heavy Pollution, PM 1.0, Physical and Chemical Characteristics, Transmission Electron Microscope, X-Ray Energy Spectroscopy

1. Introduction

Atmospheric environment is a necessary factor for human survival. The quality of atmospheric environment can not only affect the urban ecosystem, but also affect and restrict the sustainable development of urban economy. With the rapid development of industrial scale, the large-scale combustion of oil, coal and other fuels, the density of urban population and the increase of motor vehicles, air pollution is gradually turning from the original soot pollution to compound pollution [1, 2]. Air pollution in cities is worse than in rural areas. Due to the wide sources of atmospheric pollutants, the existence of pollution particles is not only a simple additive relationship [3], but also the interaction and complex physical and chemical reactions. These reactions have caused a series of adverse effects on the atmospheric environment, resulting in frequent occurrence of atmospheric haze, acid rain and photochemical smog pollution, as well as changes in the atmospheric environment in urban areas, thereby causing changes in the urban ecosystem. Air pollutants have a huge impact on the living environment of human beings, which is an important reason for the deterioration of the ecological environment and a huge obstacle to people’s life and the stable development of society [4]. Atmospheric particulate matter (PM) is one of the most complex and harmful components of atmospheric pollutants. It mainly refers to some liquid or solid particles with wide particle size range and different physical and chemical properties scattered in the ambient air. PM1.0, an atmospheric pollutant with small particle size, can enter the human body directly with respiration. Because PM1.0 particle size is small, easy to adsorb some toxic element, and do not break down the metal contamination particle pollution atmosphere, can breathe directly into the body through the human, has serious harm to human health, lead to all sorts of body function disorder, the body grow slowly, and even induce a variety of cancer disease [5, 6]. Therefore, it is of great practical significance and necessity to study the atmospheric particulate matter PM1.0 under severe pollution weather.

In recent years, there has been a lot of research on atmospheric particles. Yue T et al. analyzed and studied the physical and chemical characteristics of atmospheric particulate matter PM2.5, analyzed the seasonal variation of PM2.5 and its causes, and obtained the seasonal regularity of PM2.5 in the Pearl River delta region, providing certain guidance for the prevention and treatment of PM2.5. Yan Y studied the atmospheric particulate matter in Taiyuan City as an example, analyzed and discussed the physical characteristics of atmospheric particulate matter and the distribution characteristics of chemical water-soluble ions, which provided some
guidance for pollution prevention and control in Taiyuan City. Wu D et al. analyzed and studied the particle size distribution of atmospheric particulate matter. Their study showed that there were finer particle size particles in winter, coarser particle size particles in spring, and less fine particle size particles in summer. The concentration of coarse particle size changed little during the day and night, and the concentration of fine particle size was higher at night than during the day. Qi A et al. studied the relationship between atmospheric particulate pollutants and the number of deaths from respiratory diseases, and their study indicated that the increase of deaths from respiratory diseases may be related to the increase of PM2.5 concentration. Sun Y et al. analyzed and studied the atmospheric pollution particles in sipping city, discussed the physical and chemical properties of atmospheric particles, and analyzed the possible sources of atmospheric particle pollutants when pollution weather occurred. Ai H et al. studied the concentration of PM2.5 in the atmosphere and established a PM2.5 prediction simulation model. The experimental results showed that the proposed model had higher accuracy and better prediction effect on PM2.5 concentration. Liu X et al. selected PM2.5 for related research, and used ion chromatograph to analyze the mass concentration of water-soluble inorganic ions in PM2.5, and used model system to simulate the location and source of PM2.5 and ions in sampling period. Yu Y analyzed and studied the physical characteristics and particle sources of PM2.5, and the study showed that the coarse particulate matter rose from the ground during dust weather and traffic and transportation peak periods can reduce the proportion of PM2.5 in PM10. The change of PM2.5 concentration is not only related to seasons, but also closely related to air pressure, air humidity and wind speed.

The six main atmospheric pollutants in urban air environment are carbon monoxide, ozone, sulfur dioxide, particulate matter, nitrogen oxide, and lead pollution, among which the generation of atmospheric particulate matter is the most complex and the most harmful to the environment. Atmospheric particulate pollutants are the primary pollutants in the urban air environment at present. They have a huge impact on human health and can enter the human body directly through breathing. They are the key to the prevention and control of urban pollution. Among the atmospheric particulates, the particulates with small particle size are the most harmful. Especially for PM1.0, the harm to health and air environment is more serious [7]. Therefore, it is of great significance to study the physical and chemical characteristics of PM1.0 for improving atmospheric air quality, improving atmospheric visibility and reducing the impact of polluted weather on human health [8]. PM 1.0, also known as submicron particulate matter, is atmospheric particulate matter with diameter less than 1.0 micron [9]. At present, TEM technology is mainly used to study the atmospheric particles, mainly on the morphological characteristics, physical and chemical characteristics of particles and other information, according to the physical and chemical characteristics to determine the source of particles. A large number of experimental studies have shown that there are many kinds of PM 1.0, and the generation mechanism of particles of different kinds is a complex and indefinite physical and chemical process [10]. Due to the limitations of existing research methods, so far, experts and scholars have not reached a complete unified result on the source and generation process of PM 1.0 of atmospheric particulate matter and submicron particulate matter.

In this paper, 59 PM1.0 single particle samples collected under severe pollution (haze) weather conditions were studied [11], and an analytical method based on transmission electron microscopy energy spectrum analysis was proposed, and particulate matter was analyzed by TEM and EDS. By severe pollution weather conditions to PM 1.0 experiment research, obtained the PM1.0 particle morphology, particle size and chemical composition elements such as physical and chemical characteristics, microscopic analysis discussed the source of PM1.0, manual discharge of pollutants in the severe pollution weather is the main mechanism in the process of formation, provide certain guidance for prevention and control of pollution in the weather.

2. Method
2.1. Particle Sampling

In this study, the TH-3150 single-particle sampler was used for the collection of atmospheric aerosol single particles [12]. The nozzle diameter of the sampling head was 0.5 mm, and the sampling flow rate was 1.0 L/min, which prevented the sampling membrane from being destroyed by excessive sampling flow. A copper mesh film having a diameter of 3 mm was used as a film for aerosol particle collection, and covered with a carbon support film. When it is sampling set the height of the sampler to about 2m from the ground. The working mechanism of the sampler: the atmosphere maintains a flow rate of 1.0 L/min through the 0.5 mm nozzle, and the aerosol fine particles in the air will remain on the copper mesh membrane under the influence of the impactor; when sampling, the sampler needs to be stabilized first. Ensure that the sampling head position is above the vertical direction; the sampling time is moderately corrected according to the degree of atmospheric pollution and the concentration of aerosol particles to prevent excessive aerosol particles from being collected on the copper mesh membrane [13]. The particles on the copper mesh are dispersed and uniform.

After the sampling is finished, the collected particles are firstly observed by an optical microscope to determine whether the collected atmospheric particles are uniformly dispersed on the sampled copper mesh film. In general, the number of atmospheric particulates collected on the copper mesh membrane is characterized by a
dense distribution of the copper mesh membrane and a thin edge distribution [14]. The particle size of the particles is also in accordance with the coarse distribution of the intermediate particles of the copper mesh membrane and the fine distribution of the edge particulate matter. If the sample is initially observed, it is determined that the collected particles are uniformly dispersed and can be subjected to transmission electron microscopy. Prior to transmission electron microscopy experiments, the particle sample needs to be placed in a prepared sample box and stored in a desiccant of suitable humidity and temperature. This is mainly to avoid the sample being affected by the environment and causing interference to the experimental results. If the sampling flow rate is too large, the carbon film covered on the copper mesh film is damaged, or the particles collected on the copper mesh film are unevenly dispersed, which affects the TEM analysis, and the particle sampling is directly performed again.

2.2. Transmission Electron Microscopy

In this study, the analysis of PM1.0 samples was carried out using a transmission electron microscope and an X-ray energy spectrometer combined with the research method TEM-EDS. Transmission electron microscopy is an electron optical device with high resolution. At present, the resolution of transmission electron microscope has reached 0.2 nm. Transmission electron microscopy is very different from ordinary optical microscopy. Its light source is an electron beam with a relatively short wavelength. In general, the wavelength of the electron beam of a transmission electron microscope is much shorter than the wavelength of visible light. TEM-EDS technology can not only analyze the physical characteristics such as the shape and size of single particles, but also the chemical characteristics of chemical composition analysis.

The working principle of transmission electron microscopy is to irradiate the electron beam accelerated by the device on the thin particle sample. The electrons in the electron beam collide with the atoms in the experimental sample, and the electrons generate stereoscopic angle scattering. The size of the scattering angle is affected by many factors (such as the material type, thickness, density, etc. of the experimental sample), so that images with different brightness and darkness can be generated. The image is magnified and focused and displayed on imaging instruments such as fluorescent screens, film, and photographic coupling components.

Transmission electron microscopy generally consists of five systems: illumination system, imaging system, vacuum system, recording system, and power system. The illumination system generally includes two main components, an electron gun and a condensing mirror. Its function is to provide a constant wavelength and stable brightness electron beam for the transmission electron microscope. It is an essential condition for the imaging system to observe the sample. It is a transmission electron microscope that can amplify the key to observation. Transmission electron microscopy generally consists of five systems: illumination system, imaging system, vacuum system, recording system, and power system. The illumination system generally consists of two main components, an electron gun and a condenser. Its function is to provide a constant wavelength and stable brightness electron beam for the transmission electron microscope. It is a necessary condition for the imaging system to observe the sample. The imaging system generally consists of three lenses: an objective lens, a middle mirror and a projection lens. The lens is the most critical component of the transmission electron microscope. It determines the resolution level of a transmission electron microscope and can be regarded as the heart of a transmission electron microscope. The vacuum system provides a vacuum environment for the electron beam passage to prevent the electron beam from colliding with residual air molecules to generate ionized discharge and scattered electrons, ensuring the stability of the electron beam and reducing sample contamination. The recording system can reliably record some data information during the experiment. The power system is designed to provide a stable accelerating voltage and electromagnetic lens current.

The analysis of the sample is generally carried out at an accelerating voltage of 200 kV. The transmission electron microscope is mainly used to observe the particle size and morphology of the particles. To ensure that the analyzed particles are representative, we typically select 3 or 4 grids from the center to the edge region for analysis. These particles basically cover all particle size segments, and generally about 20 low magnification microscope images can be obtained in one sample, containing hundreds of particles; after preliminary observation, TEM-EDS was used for high-resolution analysis, and the elemental composition of the particles was analyzed by an energy spectrometer. The spectrometer is mainly used to analyze the chemical composition of a single particle. It can detect elements with an atomic number above C (atomic number Z is greater than or equal to 6), and can analyze the elemental composition and content of the particle. At the same time, because the particles are collected on the copper network, we do not analyze the Cu elements. Similarly, EDX does not detect the N element, and the peak of the C element contained in the particles such as organic matter is very strong, which is significantly higher than the C peak contained in the carbon film, so that the C element in the organic substance can be detected. In order to reduce the human body from the radiation damage of the instrument and the electrolytic damage of the particles, the general EDS spectrum is collected in only 15s. Analysis of the chemical composition of the mixed particles helps to identify the type of particles that are mixed and their source.

In order to quantitatively describe the structure of the internal mixed particles, we imported the
high-resolution image of the TEM preliminary analysis into the item software system to statistically analyze the area of the atmospheric particles and the equivalent circle diameter [15]. The relative concentration of the elements contained in each particle is automatically calculated by the system. According to the morphological characteristics and elemental composition of each particle, the type of the particles is counted, the number of each type of particles is counted, the morphology of the particles is observed, and the morphological characteristics and number of different types of particles are statistically analyzed. The detailed steps of software image analysis are as follows

(1) Importing the electron microscope image to be analyzed into the item software;
(2) adjust the correct ratio so that the particles appearing in the field of view are clearly distinguishable;
(3) Use the magic wand and the circle tool to circle all the particles that appear in the image;
(4) Combine the topographical features of the particles with the energy spectrum analysis, determine the name, and input on the image;
(5) The system automatically generates the equivalent circle diameter and other data of each circled particle;
(6) Loop analysis, processing all the images.

3. Experiments

3.1. Experiment Apparatus

The experimental analysis used H-800 transmission electron microscope and integrated X-ray energy spectrometer. The morphology and chemical composition of submicron particle’s PM 1.0 were analyzed by TEM and EDS to determine the source of the particles.

3.2. Experimental Sample

59 single particle samples collected according to the above sampling method.

4. Results

The source of particulate matter was analyzed by TEM and EDS for 59 single-particle samples collected under severe pollution (smog weather) weather conditions. During the sampling period, PM 1.0 is mainly composed of soot particles, sulfate particles, composite acid condensation particles, metal oxide particles, mineral particles and the like. The types of particles from different sources were analyzed by TEM, and the number was counted. The detection rate was calculated as shown in Figure 1.

![Particle detection rate](image)

**Figure 1.** Detection rate of each component of sample particles

The relative quantitative data of chemical elements in soot particles were analyzed by EDS multi-element element mode. Because the sample environment changes with time, this times only the experimental analysis of the soot particles of the case, the results shown in Figure 2.
5. Discussion

5.1. Change Characteristics of Particle Mode and Particle Formation Process

The particle size of atmospheric particulate matter varies greatly. The diameter of the particle directly determines the atmospheric lifetime of the particulate matter and the final entry into the human body, and the physical, chemical and optical properties of the atmospheric particulate matter are closely related to the particle size [16]. At present, the most widely used particle size division method in atmospheric particle research is to divide the granularity into four modes. The atmospheric particle size is defined by the particle diameter range as the nuclear mode (particle diameter less than 20 nm), the Aitken core mode (particle diameter between 20 nm and 100 nm), and the accumulation mode (particle diameter is 0.1 μm to Four modes, such as between 1 micron) and coarse particle mode (particle diameter greater than 1 micron). Due to the different sources of modal particles, the degree of impact on the atmospheric environment varies. Using transmission electron microscopy, we can observe the size and shape of PM1.0, and also directly analyze the change process between particle modes. The results show that the modal change characteristics of PM1.0 are closely related to the formation process of particles.

The sample data indicates that PM 1.0 is mainly composed of soot particles, composite acid condensation particles, sulfate particles, mineral particles, metal oxide particles, etc. during the sampling period. Among them, the proportion of soot is the largest, up to 60.5%, which is the main particulate matter of air pollution. Soot is a solid particulate matter emitted from coal-fired and industrial production processes and is an important component of atmospheric particulate matter PM1.0 under severely polluted weather conditions. In the observation of TEM and SEM, soot particles are the most detectable particle types. Of the 59 single-particle samples, only three soot particles with chain, dendritic, and cluster-like aggregate morphological characteristics were counted in this experiment. The reasons for the different morphological characteristics of soot particles are mainly due to different sources of combustion, and their sources may correspond to combustion sources such as industrial smelting, coal burning, automobile exhaust and biomass burning. Analytical observation of the TEM image, for the chain assembly, it is speculated that the possible formation process is: the particles are first combined into nuclear mode particles by condensation; the nuclear mode particles form the Aitken core mode particles by condensation; a chain of modal aggregates is accumulated. For the dendritic and cluster-like aggregates in the soot particles, only the formation process from the Aitken nuclear mode to the accumulation mode can be found. Only a few Aitken nucleus granules are onion layered structures, and most of the Aitken nucleus modal particles are disordered and there are tiny crystalline regions inside. In the dendritic and cluster-like structures, there is an adhesion relationship between the particle chains, which is favorable for the steady state and growth of the particle chains, and their particle diameters are larger than that of the chain aggregates.

The detection rate of the composite acid condensed particles was 11.3%, and the detection rate ranked second. In the experimental sample data, a large number of stacked polymer particles composed of spherical ultrafine particles were detected, and the number of accumulations was random. The diameter of the polymer is mostly between 0.7 and 2.2 microns. After the electron beam irradiation damage experiment was continued for
50s, the boundary of the polymer particles merged and the shape became an approximate ellipsoid. It can be seen that the thermal stability of the composite acid condensed particles is relatively poor. It can be seen from experiments that the mode of the composite acid condensed particles is changed from the Aitken nucleus mode through a series of atmospheric physicochemical reactions to an accumulation mode. Its structural form is mainly heterogeneous structure.

The detection rate of sulfate particles was 9.1%. The experiment mainly determined the existence form of sulfate by the molar ratio of (Na+K)/2S and Ca/S. The experimental results of TEM and EDS were analyzed. The sulfate particles of the experimental sample were mainly mixed phase particles composed of calcium sulfate, potassium sulfate and ammonium sulfate. And particles generally contain traces of soot particles, mineral dust, metal oxides and the like. The sulfate particles are classified into two types of stable particles and condensed particles according to the stability of the sulfate particles under electron beam irradiation. Potassium sulphate, ammonium sulphate and some calcium sulphate particles are condensed granules and the condensed particles of potassium sulphate and calcium sulphate are mostly in the form of long-shaped bundle-shaped aggregates, and the shape of ammonium sulphate particles is not fixed. In addition, some of the calcium sulfate crystal particles are stable particles whose particle shape is a polygonal accumulation mode and the surface is covered with an amorphous substance.

5.2. Single Particle Element Composition

The chemical composition of one of the individual particles is analyzed by an energy spectrometer to obtain the elemental composition characteristics of the particulate matter. The single particles mainly include the following elemental components: C, O, Mg, Al, Si, P, S, Cl, K, Ca, Mn, Fe, Zn, etc.

Soot aggregates, the main elements are C, O, Si, etc.; at the same time contain a certain amount of trace elements, such as Fe, S, Fe, Mg, Ca, Al, and O and so on. The chemical characteristics of soot particles from different sources may be different. In this study, there are three types of soot, cluster and chain aggregates, and their constituent elements are different.

The main mineral particles in the atmosphere are ground dust and secondary atmospheric chemical reactants. The number of mineral particles in this sample is small, usually showing regular rectangular and irregular shapes. Mineral particles mainly contain elements such as Fe, S, and O, and also contain certain elements such as Ca, Si, and Al.

The most important metal oxides are Fe-rich, Zn-rich and Pb-rich particles. The Fe-rich particles are mainly circular. The Zn-rich and Pb-rich particles are usually internally mixed with sulfur-rich particles and exhibit an irregular shape. It has been found that most of the Zn-rich particles contain Pb, which means that the Zn-rich Pb particles present in the mixture may be from the same anthropogenic source. At the same time, some other metal elements such as Mn, Ba, Ti, and Sn are also detected.

The main elements of the composite acid condensation particles are S, C, O, etc., and also contain trace amounts of elements such as Cl, Zn, Pb, Fe, Ca, Al, Na, and K.

Sulfate particles generally exhibit a foamy appearance, mainly due to the weak decomposition of sulfate particles under the irradiation of electron beams, leaving a residue of foam conversion. The energy spectrum results show that the main elements are S, Ca, O, etc., and the secondary elements are Ba, Si, Al, Ti, O, and the like.

According to the experimental results of TEM and EDS, the sources of PM1.0 in the sample sampling area are mainly coal combustion, industrial waste gas, motor vehicle exhaust and biomass combustion. Under the condition that the pollution source remains unchanged, the rapid increase of fine particles in the atmosphere is the main cause of severely polluted weather.

6. Conclusions

In recent years, in order to understand the impact of air pollution particles on the ecological environment and human health, more and more experts and scholars have invested in the study of atmospheric particles. Atmospheric particle research has become a research hotspot in the field of environmental science and atmospheric science. The study of atmospheric particle physicochemical characteristics plays a key role in the prevention and control of atmospheric pollution. It can directly understand its source according to the physicochemical properties of particulate matter, and fundamentally solve the atmospheric pollution. PM1.0 particles in the atmosphere often carry some toxic metal substances. Because PM1.0 has a small particle size, it can directly enter the human body through people breathing, which causes toxic substances to harm the human body and seriously threatens human life and health.

The atmospheric particulate matter is PM 1. 0 is mainly composed of soot particles, metal oxide particles, composite acid condensation particles, mineral particles, sulfate particles and the like. Among the samples collected the main component of PM 1. 0 is soot aggregate. According to the analysis, the key pollutant in heavy polluted weather is composite acid condensation particles. In this paper, through TEM and EDS, the modal
changes of PM 1.0 particles, the formation process of particles, and the composition of particle elements are systematically analyzed. The analytical data show that the morphological characteristics of PM 1.0 particles and the physicochemical characteristics of chemical constituents and the formation process of particulate matter have a great correlation.

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