Polycyclic Aromatic Hydrocarbons and Heavy Metals in the Atmosphere-A Review

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Abstract: Atmospheric particulate matter is one of the major air pollutants. Because of its wide range of pollution, heavy pollution, and great health hazards, it has attracted widespread attention worldwide. This article summarizes the current status of chemical speciation analysis of heavy metal components of atmospheric particulate pollutants and Health effects characterization methods, and expounds the sources and hazards of polycyclic aromatic hydrocarbons, and the extraction and detection methods of polycyclic aromatic hydrocarbons.

Keywords: Polycyclic Aromatic Hydrocarbons; PM2.5; Heavy Metals

1. The concept, source and hazards of PM2.5

1. 1 The concept of PM2.5

PM2.5 refers to particulate matter with an aerodynamic equivalent diameter of less than or equal to 2.5 microns in the atmosphere, also known as lung particulate matter. Although the content of PM2.5 in the atmosphere is very small, because it carries viruses and harmful substances for a long time, and has multiple transmission routes, and it is far away from the human body, it is more harmful to the human body.

1.2 The source of PM2.5

It mainly has natural sources and human sources, but the latter is more harmful. Natural sources include soil dust (including oxide minerals and other components), sea salt (the second largest source of particulate matter, whose components are like sea water), plant pollen, spores, bacteria, etc. Volcanic eruptions release large amounts of volcanic ash into the atmosphere, and forest fires or exposed coal fires and sandstorms will provide a large amount of fine particles to the atmosphere. Artificial sources, includes fixed sources and sports sources. Stationary sources include various fuel combustion sources, such as power generation, metallurgy, petroleum, chemistry, textile printing and other industrial processes, heating and cooking. When various vehicles use fuel during operation, the flow source is mainly exhaust gas in the atmosphere.

1.3 The hazards of PM2.5

Epidemiological investigations have found that PAHs in urban air particulates are related to the incidence and mortality of lung cancer among residents. In the process of PAHs entering the human body, the fine particles act as a rider. Most PAHs are adsorbed on the surface of particles, especially particles with a diameter of less than 5 mm, while PAHs are adsorbed on large particles, rarely. In other words, the more PM2.5 in the air is, the greater the chance that we will be exposed to carcinogens and polycyclic aromatic hydrocarbons.

2. The concept and source hazards of polycyclic aromatic hydrocarbons

2.1 The concept of polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) refer to hydrocarbons containing more than two benzene rings in the molecule. These compounds are chemically stable. As a persistent organic pollutant, polycyclic aromatic hydrocarbons are widely present in the environment. [1]

2.2 The source of polycyclic aromatic hydrocarbons

Similar to the sources of atmospheric PM2.5, the main sources of PAHs and their derivatives in the atmosphere include natural sources and man-made sources. Compared with man-made sources, natural resources make less contribution to PAHs and their derivatives, and human activities related to fuel combustion dominate the contribution of PAHs and their derivatives. [2-4] Man-made emission sources mainly include industrial production emissions, motor vehicle emissions and human life emissions. Industrial production consumes a lot of fossil fuels. Incomplete combustion of fossil fuels will produce many polycyclic aromatic hydrocarbons. In addition, many industrial activities related to the petrochemical industry also contain a large amount of polycyclic aromatic hydrocarbons in the exhaust gas. In recent years, with the rapid increase in the number of motor vehicles, the contribution of motor vehicle emissions to PAHs and their derivatives has increased significantly. Studies have shown that the exhaust gas emitted by motor vehicles contains a variety of PAHs, and the mileage of motor vehicles has a greater impact on the concentration of PAHs. In addition to the above sources, secondary sources also help increase the concentration of nitro groups and oxygenated polycyclic aromatic hydrocarbons. [5-10]

2.3 The hazards of polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons are a class of global pollutants [11]. They are widely distributed, have carcinogenic, teratogenic and mutagenic effects, and are harmful to human health. Polycyclic aromatic hydrocarbons and their derivatives attached to atmospheric PM2.5 may cause damage to human health after being inhaled into the human body. Studies have shown that long-term exposure to severe PAH pollution will cause greater damage to liver and kidney function. In addition, polycyclic aromatic hydrocarbons can greatly increase the risk of skin cancer and gastrointestinal cancer. [12-16]

3. Extraction and detection of polycyclic aromatic hydrocarbons

3.1 Extraction of polycyclic aromatic hydrocarbons

The content of PAHs in actual environmental samples is very low and cannot be directly measured by the instrument. Therefore, pre-processing is required before measurement. The pretreatment of PAHs includes three processes: extraction, concentration and purification. Concentration generally uses rotary evaporation, nitrogen blowing, etc.; purification is used for samples with complex matrices, mainly using silica gel or Florisilica gel columns. The extraction process is the top priority of pretreatment technology. PAHs extraction technology includes more traditional Soxhlet extraction, liquid-liquid extraction, solid phase extraction, etc. and with the development of new materials and new technologies, researchers have improved on traditional technologies. New extraction techniques, such as solid phase microextraction, liquid phase microextraction, magnetic solid phase extraction, supercritical fluid extraction, etc. as well as extraction methods that use auxiliary technologies such as ultrasound and pressure, such as ultrasonic extraction, pressurized solvent extraction, etc.[17]

3.2 Detection of polycyclic aromatic hydrocarbons

3.2.1 GC

GC analysis method is a classic and widely used analysis method. It has the advantages of simple operation, high sensitivity, low detection limit and fast analysis speed. The current report is to use FID detector to test PAH. Zhang Maosheng

[18] used gas chromatography to determine 12 kinds of PAHs in environmental water samples, and the detector was FID. The detection limit of this method was 0.001~0.01μg/L, and the recovery rate of addition was 95.0%~124.4%.

3.2.1 GC-MS

This method effectively solves the problem that gas chromatography is difficult to separate several isomers, and has the advantages of small volume, low detection limit and high selectivity. Liu et al. [19] sampled GC-MS to determine the PAHs in atmospheric particulates in Beijing. The mass spectrometer selects the SIM mode, the injection temperature is 260°C, the detector temperature is 280°C, and the gradient temperature program is used, that is, 90°C, for 1 minute. The average concentration of PAHs in atmospheric particulates in Beijing urban area is 28.53-362.15 ng/m^3, and the average concentration of PAHs in atmospheric particulates in Beijing urban area is 28.53-362.15 ng/m^3. In addition, it is analyzed by mass spectrometry which shows the type and content of PAH in each season.

4. Research status of heavy metals in atmospheric particulates

In recent years, atmospheric heavy metals related to atmospheric particulate matter, especially PM2.5, have attracted considerable attention. These metals not only promote the formation of secondary aerosols, leading to deterioration of air quality, but also have adverse effects on human health through inhalation, digestion, and skin contact [20, 21]. Epidemiological analysis and toxicological studies have confirmed that due to the strong fluidity and non-biodegradability of heavy metals combined with PM2.5, it will lead to an increase in cardiovascular mortality and morbidity, and cause chronic diseases in various organs of the human body. Poisoning, and may cause lung cancer or nasal cancer due to its long-term accumulation [22, 23]. Studies have shown that exposure to excessive amounts of Cd, Cu, Zn or Mn can also cause renal dysfunction [24], damage to the reproductive system, weakened immune and nervous systems in young children [25], and even accelerate brain aging [26]. Oxidative damage and inflammation caused by heavy metals (such as Cu, Mn, and Co) in PM2.5 in winter have been observed in the epithelial cells of human lungs [27]. Because heavy metals in atmospheric particulates have a serious impact on human health and the ecological environment, scholars at home and abroad have conducted extensive research on them.

5. Using Chromatography-Mass Spectrometry Technology to Determine

Heavy Metals in the Air

High performance liquid chromatography (HPLC) and gas chromatography (GC) can effectively separate heavy metal elements in different forms. ICP-MS has the advantages of high sensitivity, less interference, and simple connection to the separation and detection system. Therefore, HPLC/GC-ICP- MS is widely used in heavy metal speciation analysis [28]. Heavy metal speciation analysis methods based on chromatography-mass spectrometry technology usually require the preparation of atmospheric particulate matter samples into liquid samples. Therefore, finding a suitable extraction or digestion method without causing loss is very important to achieve high recovery rate in the case of conversion [29]. The US EPA 3060A alkaline digestion method proposed by the US Environmental Protection Agency for the determination of Cr(Ⅵ) in the solid phase has been applied to the analysis of Cr speciation in atmospheric particulate matter samples. [30-32] Huang et al. [33] optimized the alkaline digestion method and determined the soluble Cr(Ⅵ) and total Cr in atmospheric particulates in New Jersey. In recent years, the methods for determining the organic and Inorganic speciation of as in atmospheric particulates have been summarized [28,34]. These methods usually use solutions such as nitric acid, phosphoric acid, hydroxylamine hydrochloride, ascorbic acid or citric acid buffer solution for acid extraction or acid digestion, shaking, microwave or ultrasonic assisted extraction to prepare solution samples for determination of As form. For example, Huang et al. used phosphoric acid solution-assisted microwave extraction method for atmospheric particulate matter Various forms of as can be extracted in the medium, and the recovery rate can reach more than 90% [35]. The extraction methods of Hg speciation analysis in solid phase include acid leaching, alkali extraction and distillation [36]. The distillation method has good effect on the extraction of organic mercury and less background interference, but the extraction process is easy to produce the transformation between forms, which is suitable for the samples with less inorganic mercury [37]; acid leaching method is widely used and optimized due to its high recovery rate and less human interference. Method optimization is not only the use of microwave and ultrasonic assisted extraction to improve the extraction rate and efficiency [38], and the use of organic solvents also has good results [39].

Conclusion

Therefore, future research work in related fields should focus on two aspects:

In view of the complex composition of atmospheric particulate matter and the low content of heavy metal elements in environmental samples, based on the advanced analysis and characterization methods in the field of materials science, the detection method is optimized and multiple methods are used to improve the sensitivity and accuracy of the analysis method.

Polycyclic aromatic hydrocarbons are a kind of persistent organic pollutants, which pose a serious threat to human living environment and health. It is especially important to accurately and quantitatively analyze the content of PAH in the environmental matrix. Therefore, the requirements for the pretreatment and analysis technology of environmental samples are getting higher and higher. While classic sample pretreatment and analysis techniques continue to improve, new techniques have also emerged. It can be seen from a large amount of literature that fast, energy-saving, environmentally friendly and efficient pretreatment technologies have been widely used. Analytical technology detection technology will also develop in the direction of high sensitivity, high selectivity, intelligence and rapid online determination. In addition, many advanced cutting-edge methods, especially pretreatment methods, are mostly in the laboratory research stage, and there is still a certain distance between domestic and foreign standard methods. [17]

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