The determination of PAHs in PM10 of different open-source

Yuanyuan Liu *
Shandong Xiehe University, Jinan, China

*Corresponding author e-mail: liuyuan0906@126.com

Abstract. Orthogonal experimental is designed to determine using of L12 (6 * 22) orthogonal, the time is 12 hours and the temperature is 55 ℃, dichloromethane amount of 200 ml to extract the best conditions, the best extraction conditions were eight of Jinan City A typical open-source Soxhlet extraction, the extract of the rotary Evaporation, chromatography purification after blowing nitrogen; using GC-MS determination of the content of polycyclic aromatic hydrocarbons. Through the eight kinds of samples of data comparison, the steel dust found in samples of the highest content of polycyclic aromatic hydrocarbons. With the strong carcinogen Dibenzo (a, h) anthracene, 16 in the highest levels of polycyclic aromatic hydrocarbons.

1. Introduction
Open source is a kind of compound source class, which has the characteristics of source strength uncertainty [1], emission randomness and emission location uncertainty. at present, there is no clear and unified definition of open source, which is generally defined as a variety of sources that do not pass through irregular discharge, such as line source, industrial material pile placed in open air, solid garbage dump placed in open air, construction site, bare land, road, farmland, barren mountain and so on. studies have shown that open sources in northern cities contribute more to ambient air TSP and PM10 concentrations than fixed and mobile sources [2].

Polycyclic aromatic hydrocarbons (PAHs), a class of aromatic organic compounds with more than two benzene rings, is one of the earliest environmental pollutants found to have "carcinogenic, teratogenic, mutagenic ", which has important effects on human health and the environment [3]. The research on polycyclic aromatic hydrocarbons (PAHs) in foreign countries started earlier and began systematic research as early as 1970s. The research in this field started late in China, and the research on PAHs in different open source particles was less. This paper studies the distribution of polycyclic aromatic hydrocarbons (PAHs) in different open source PM10 of Jinan city by Soxhlet extraction and Temperament Joint Inspection (GC/MS) method, and studies the distribution of PAHs in different open source PM10.
2. Experimental section

2.1. Sample collection and extraction of polycyclic aromatic hydrocarbons

2.1.1. Sample collection by source. Eight typical open sources in Jinan were selected as the research object.

(1) Collection of soil dust samples
The four suburbs of the city evenly distributed, in the east, south, west west and north direction, about 20 km from the urban area to take 2 samples, in the urban dominant wind direction: northeast, southwest direction from the urban area 20-40 km, respectively, take 3 samples, a total of 14 samples, each sample is more than 2 kg, the above samples are surface soil (surface 20 cm).

(2) Collection of dust samples
Area collection of building windowsill dust, sampling height of 3-15 m, in each district of the city evenly set up 2 sampling points, a total of 10 points.

(3) Collection of fly ash samples
Select typical normal combustion of 75 t/h, 130t/h and 410 t/h and other tonnage, different combustion modes (circulating fluidized bed, pulverized coal furnace, etc.), different dust removal mode of coal burning industrial boiler (electrostatic precipitator and cyclone precipitator)3; collect dust hopper download ash about 1-2 kg / bag.

(4) Collection of sand samples from the Yellow River
On the exposed Yellow River beach near the Yellow River embankment near Luokou floating bridge, a sampling point is set up every 1 km along the Yellow River bank, and a total of 4 sampling points are set up to take the Yellow River sand, which is more than 500 g respectively.

(5) Collection of demolition waste samples
At Jichai and Construction University school-based demolition waste and demolition site dust swept up mixed, in these three building demolition site collection demolition waste three, each sampling site to collect samples more than 2 kg.

(6) Collection of building dust samples
The dust and construction waste swept around the construction site near Yanshan Interchange and Shanshi, Cultural East Road, are mixed together, and three building dust are collected around 100 m of the three construction sites, each sampling point collects more than 2 kg of samples, representing the source of building dust in Jinan.

(7) Collection of steel dust samples
A dust sample was collected from the head and tail of the sintering furnace and the ash hopper of the electrostatic precipitator.

(8) Collection of road dust samples
Thirty-two large, medium and small roads in Jinan were selected,1-3 were sampled on each road, and 35 samples were set up. Absorb with vacuum cleaner, after mixing sampling, each sampling point sampling about 500 grams, sampling with filter membrane vacuum cleaner.

2.1.2. Treatment of samples from various sources. The powder source samples were dried naturally in the laboratory, and the particulate matter samples below 10 microns were obtained by using a vibrating screen machine.

2.1.3. Sample pretreatment. A classical Soxhlet extraction method was used to extract polycyclic aromatic hydrocarbons (PAHs) from the sample with dichloromethane as extractant. L12(6*22) orthogonal table was selected to optimize the experimental conditions. Through the analysis of a large number of references, select extraction time, water bath pot temperature, solvent addition as the analysis factors, extraction time selected 12 h, 16h, 20h, 24h, 36h, 48h six levels, water bath pot temperature selected 55℃,60℃ two levels, solution dose selected 150 ml, 200ml two levels.
The sample was placed in a soxhlet extractor for extraction. The extract was distilled and concentrated on a rotary evaporator. Finally, the PAHs in the extract were separated and purified by silica gel column chromatography.

| No | Extraction Time | Water bath pot temperature | Dissolved dose | $\sum$PAHs(ng/g) |
|----|-----------------|-----------------------------|---------------|------------------|
| 1  | 12              | 55                          | 150           | 3075.57          |
| 2  | 16              | 55                          | 200           | 2652.59          |
| 3  | 12              | 60                          | 200           | 2745.60          |
| 4  | 16              | 60                          | 150           | 2395.70          |
| 5  | 20              | 55                          | 200           | 1665.71          |
| 6  | 24              | 55                          | 150           | 1754.80          |
| 7  | 20              | 60                          | 150           | 2494.19          |
| 8  | 24              | 60                          | 200           | 2245.86          |
| 9  | 36              | 55                          | 150           | 2569.62          |
| 10 | 48              | 55                          | 200           | 3143.97          |
| 11 | 36              | 60                          | 200           | 3053.95          |
| 12 | 48              | 60                          | 150           | 1859.13          |

Table 2. Mean response table

| Level  | C1(Extraction Time) | C2(Water bath pot temperature) | C3(Solvent) |
|--------|---------------------|--------------------------------|--------------|
| 1      | 2911                | 2477                           | 2358         |
| 2      | 2524                | 2466                           | 2585         |
| 3      | 2080                |                                |              |
| 4      | 2000                |                                |              |
| 5      | 2812                |                                |              |
| 6      | 2502                |                                |              |
| Detail | 910                 | 11                             | 226          |
| Rank rank | 1                    | 3                             | 2            |

The main influencing factors of extraction efficiency are: extraction time > dissolved dose > water bath pot temperature. The optimum experimental conditions were determined as follows: when the sample was weighed 1.0 g, the extraction time was 12 h, the temperature of the water bath pot was 55 degrees (the reflux rate was 3-4 times / hour), and the amount of dichloromethane added was 200 ml.

2.2. GC/MS Instrument analysis conditions

Gas chromatography-mass spectrometry (GC-MS) is GC/MS used to analyze polycyclic aromatic hydrocarbons (PAHs) in the sample. It can provide mass spectrometry, which can reduce the effect of chemical noise by mass spectrometry, accurate mass of molecular ion peak, strength ratio of fragment ion field, isotope ion peak, ion mass spectrometry of selected ion, etc. In GC-MS, high-resolution mass spectrometers can detect accurate mass numbers, tandem mass spectrometry, time series or space series, and so on.

In this study, 16 kinds of PAHs need to be separated and determined. The number of rings is from two rings to five rings. Because the content of some PAHs components is low and the response factor is small, the sample is injected without shunt, and the injection quantity is increased to ensure that each PAHs can reach the detection limit and ensure the validity of the analysis results.

Chromatographic conditions: injection port temperature 290℃, interface temperature 290℃; column type: TR-5MS (30 m × 0.32 mm × 0.25 um)

Temperature programmed: 70(2 min) → 10℃/min → 260℃(8 min); 5℃/300(5)
Carrier gas: helium gas, flow rate 1.0 ml/min; injection mode: no shunt injection (splitless)
Mass Spectrometry Conditions: Ion Source Temperature 200°C, Electron Multiplier Voltage 1.0 kv.

3. Experimental results and discussion

3.1. Qualitative and quantitative analysis PAHs experimental sample PM10

3.1.1. Qualitative analysis. EPA 16 PAHs with priority monitoring is NaP, AcP, AcPA, Flu, PhA, AnT, FluA, Pyr, BaA, Chr, BbF, BkF, BaP, InP, DbA, BghiP.

The standard sample of the PAHs was determined, and the qualitative spectrum was obtained. According to the obtained spectrum, the qualitative and quantitative ions of the 16 samples were determined, and the time group was determined. The sample volume was 2 microliters. By SCAN method, the mass scanning range of mass spectrum was 50 to 350, and the chromatogram was shown in figure 1.

3.1.2. Quantitative analysis. The standard curve is to take 400 µg/L, 800µg/L, 1000µg/L, 2000µg/L, 4000µg/L of PAHs standard samples for GC/MS analysis, using selective ion detection method (SIM) determination. All the correlation coefficients of 16 PAHs were above 0.99.

3.1.3. Comparison of data analysis. The content of polycyclic aromatic hydrocarbons (PAHs) in 8 typical open sources in Jinan were compared and analyzed according to the results.

A comparative analysis of the total amount of PAHs in 8 open sources is given in Table 1

| name | Removal of waste | Road dust | Steel dust | Dust dust | Soil dust | Building dust | Yellow River Sands | Coal soot |
|------|------------------|-----------|------------|-----------|-----------|---------------|-------------------|----------|
| ∑PAHs ng/g | 6344.65 | 4670.43 | 13154.26 | 13154.26 | 2634.33 | 3792.95 | 3507.33 | 710.13 |

PAHs components of 8 open source particles are shown in Table 2
### Table 4. PAHs component spectrum of Eight open-source particles

| name of waste | Road dust | Steel dust | Yellow River Sands | Building dust | Coal soot of waste | Soil dust | Dust dust | ∑ |
|---------------|-----------|------------|--------------------|---------------|--------------------|-----------|----------|----|
| NaP           | 140.38    | 169.11     | 351.70             | 79.27         | 138.91             | 585.42    | 75.89    | 165.28 | 1705.96 |
| AcPA          | 0.00      | 0.00       | 0.00               | 0.00          | 0.00               | 0.00      | 0.00     | 0.00   | 0.00    |
| AcP           | 0.00      | 0.00       | 0.00               | 0.00          | 0.00               | 0.00      | 0.00     | 0.00   | 0.00    |
| Flu           | 48.21     | 0.00       | 0.00               | 0.00          | 0.00               | 0.00      | 0.00     | 0.00   | 56.22   |
| PhA           | 681.95    | 307.54     | 1580.39            | 47.57         | 149.46             | 54.82     | 4.74     | 107.74 | 203.31  |
| AnT           | 63.20     | 0.00       | 148.20             | 0.00          | 0.00               | 0.00      | 0.00     | 0.00   | 211.40  |
| FluN          | 346.29    | 17.12      | 2464.67            | 0.00          | 0.00               | 0.00      | 0.00     | 0.00   | 2828.08 |
| Pyr           | 341.12    | 128.69     | 1699.95            | 15.51         | 36.15              | 1.45      | 24.34    | 234.34 | 2402.31 |
| BaA           | 112.95    | 242.08     | 618.81             | 9.69          | 5.27               | 1.37      | 255.26   | 21.19  | 1266.60 |
| Chr           | 199.17    | 88.81      | 1185.13            | 9.78          | 24.39              | 0.00      | 10.96    | 126.43 | 1644.70 |
| BBF           | 298.36    | 125.75     | 1198.55            | 10.67         | 47.58              | 2.40      | 6.24     | 140.88 | 1828.42 |
| BKF           | 348.20    | 148.94     | 109.96             | 16.09         | 58.71              | 6.55      | 10.98    | 9.70   | 709.14  |
| BaP           | 71.78     | 16.89      | 221.31             | 8.32          | 16.08              | 1.52      | 1.91     | 35.00  | 372.82  |
| InP           | 1272.37   | 1207.12    | 1265.15            | 1152.09       | 1156.92            | N/F       | N/F      | 2134.12| 7261.65 |
| DaB           | 2229.82   | 2148.83    | 2177.65            | 2134.04       | 2133.26            | N/F       | N/F      | 2147.30| 15105.83|
| BghiP         | 190.76    | 71.33      | 134.80             | 2.96          | 7.69               | 0.38      | 1.35     | 69.70  | 478.96  |

A total of 8 kinds of source samples of demolition waste, road dust, steel dust, Yellow River sand, building dust, fly ash, soil dust and dust were collected and PM were established in this study. Table 5 shows that the PAHs components have the following characteristics:

1. Of the eight open sources, the ∑PAHs difference is nearly two orders of magnitude, the highest is steel dust, 13154.26 ng/g, the lowest is fly ash, only 710.13 ng/g. The order of ∑PAHs from high to bottom is: iron and steel dust > demolition waste > road dust > building dust > Yellow River sand, soil dust > fly ash, which indicates that the most important contribution to the environment is the pollution source of iron and steel industry, followed by traffic pollution sources, and the contribution of natural sources is relatively small. The main reason is that in the pollution sources of iron and steel industry, the combustion of fossil fuels and some industrial raw materials will produce a large number of PAHs. In nature, although there are residues of pahs in pesticides and fertilizers, the content is relatively low, and the biochemical degradation of microorganisms in nature can remove a part of pahs, so the pahs in nature are relatively small.

2. None of the eight open sources contained AcP > (1,2, pyrene > phenanthrene > pyrene > benzo (b) fluoranthene > naphthalene > benz (a) anthracene, benz (k) fluoranthene, benzo (ghi) pyrene, benzopyrene, anthracene. The results show that the concentrations of PAHs in Jinan are very different.

3. The proportion of each source, represented by benz (a) pyrene, benzo (k)anthracene (page 491 above), dibenzo (a,h) anthracene, was calculated from large to small, followed by soil dust > Yellow River sand > building dust, road dust > steel dust > fly ash, indicating that the greatest contribution to carcinogenic activity is soil dust.

### 4. Conclusion

The optimum conditions of Soxhlet extraction: extraction time is 12 h, water bath pot temperature is 55℃, extraction solvent is 200 mL.

Eight typical open sources PM. in Jinan The highest content of 16 PAHs was found in iron and steel dust (13 154.26 ng/g) and the lowest in fly ash (710.13 ng/g).

The highest containing carcinogen benzo (a) pyrene, benzo (ghi)\57542;\57542;\57542;\57542;\57542;\57542; anthracene is soil dust and the lowest is fly ash. The experimental results provide basic data for the control and source analysis of PAHs in Jinan atmosphere.

### Acknowledgments

This work was financially supported by Shandong Province Scientific research plan project of colleges and universities.
References

[1] Yang Fei, Yang Lingxiao, Meng Chuanping, Zhu Yanhong, Yao Lan, Lu Yaling, Yuan Qi, Sui Xiao, Wang Wenxing. Seasonal variation characteristics and health risk assessment of polycyclic aromatic hydrocarbons (PAHs) in PM2.5 in Jinan [J]. Journal of the University of the Chinese Academy of Sciences. 2014 (03): 389-396.

[2] Chen Fei. Study on the source analysis of inhalable particles and the formation of secondary organic aerosols in cities [D]. Nanjing: Nanjing University of Science and Technology, 2014.

[3] Gao Kangning, Cao Huoyong, Consuma, and Xu Man. Study on the Characteristics of the Change of the Ambient Air PM2.5 and PM10 in Shijiazhuang City[J]. Energy Environmental Protection.2015 (04):62-64.

[4] Chen Bo. The influence of the typical urban green space on the concentration and chemical composition of PM2.5 and the like in Beijing area[D]. Beijing: Beijing University of Technology,2016.