Study on the Determination of Free Formaldehyde in Carbon-Coated Air Purifying Material by Water Extraction Method

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Abstract. The free formaldehyde in carbon-coated air purifying material was determined by water extraction method. The effects of solid-liquid ratio, extraction time and extraction temperature on the content of free formaldehyde in carbon-coated air purifying material were studied. In this paper, orthogonal tests and single factor tests were designed, and the optimal extraction conditions were 1:40 solid-liquid ratio, 90 min extraction time and 40 °C extraction temperature. Under this extraction condition, the relative standard deviation (n=8) of the repeated test is 0.80%, and the recovery rate is 90%-100%, which indicates that the analytical method for determining the free formaldehyde in carbon-coated air purifying material by water extraction method is feasible.

1. Introduction
Formaldehyde [1-3] is a colorless, strongly irritating gas and also a protoplasmic poison. Formaldehyde has intense stimulation effect to human body organ. Excessive formaldehyde can cause irritation to the eyes, nasal cavity and respiratory tract, which may cause itching, inflammation, etc., and even cause serious diseases such as tumors and leukemia, because of the degree of harm to the human body is extremely serious. At present, formaldehyde has been recognized as a carcinogenic and teratogenic substance by the World Health Organization. It is a recognized source of allergic reactions, and long-term exposure will lead to genetic mutations.

With the rapid development of the social economy and the improvement of people's living standards, the more interior decoration materials, office equipment and household appliances using, the more formaldehyde probably produced. Therefore, the air purifier has become one of the important tools to remove indoor formaldehyde. Carbon-coated air purifying material is a common filter material in the air purification industry. It is formed by uniformly spreading the broken activated carbon between two non-woven fabrics to form a carbon cloth, and then folded and fixed to combine the effect of the HEPA filter and the activated carbon filter, which can effectively filter PM2.5 particles and gaseous pollutants such as formaldehyde [4]. However, formaldehyde and its derivatives, as the basic chemical materials, are inevitable in the production process of carbon-coated air purifying material. There are safety risks caused by the volatile formaldehyde in carbon-coated air purifying material. The presence of free formaldehyde in the carbon-bonded cloth is easily volatilized and poses a safety risk. Therefore, it is necessary to strictly limit the content of formaldehyde in the carbon-coated air purifying material.

In this paper, the free formaldehyde in carbon-coated air purifying material was determined by water extraction method [6-8]. The optimal extraction conditions were determined by orthogonal tests and single factor tests, which provided a reference for the control and detection of formaldehyde in
carbon-coated air purifying materials.

2. Experimental

2.1. Materials and Instruments

2.1.1. Materials. Ammonium acetate (analytically pure AR), Sinopharm Chemical Reagent Co., Ltd.; glacial acetic acid (analytically pure AR), Sinopharm Chemical Reagent Co., Ltd.; formaldehyde standard solution (10.4mg/ml), Shanghai Anpu Experimental Technology Co., Ltd.; Acetone (analytically pure AR), Sinopharm Chemical Reagent Co., Ltd.; deionized water, 18 MΩ⋅cm, laboratory-made.

2.1.2. Instruments. Water phase needle filter (0.45μm), Shanghai Anpu Experimental Technology Co., Ltd.; precision electronic balance ME203E/02, METTLER TOLEDO instrument (Shanghai) Co., Ltd.; UV-visible spectrophotometer UV-1780, shimadzu Japan; constant temperature water bath oscillator SHZ-C, Laizhou Yuanmao Instrument Co., Ltd.

2.2. Preparation of Standard Curve Working Fluid

Pipette 1 ml of formaldehyde standard solution into a 100 ml volumetric flask, dilute to the mark with deionized water, shake well, and prepare a formaldehyde intermediate solution with a concentration of 104 mg/L. And the pipette 1 ml of formaldehyde solution from the formaldehyde intermediate solution into a 100 ml volumetric flask, dilute to volume, shake well, and prepare a working solution of 1.04 mg/L. Then pipette formaldehyde working solution 0, 2.0, 4.0, 6.0, 8.0, 10.0 ml to 10 ml colorimetric tubes separately, dilute to the mark with deionized water, add 2 ml acetylacetone solution, shake and heat the mixture was in a boiling water bath for 3 min, taken out and cooled to room temperature. And the absorbance was measured at a wavelength of 413 nm using a 1 cm absorption cell with water as a reference. The absorbance A value measured in the above series of standard solutions is subtracted from A0 value of reagent blank (zero concentration) to obtain the calibrated absorbance y value. The calibrated absorbance y is the ordinate and the formaldehyde concentration x (g) is the abscissa to draw the standard curve. After linear regression, the standard curve equation of concentration and absorbance of standard solution was obtained: y=0.0200x−1.3810, R²= 0.9991. Y is the absorbance, and x is the concentration, which are shown in Figure 1.

![Figure 1. Standard curve](image-url)
2.3. Experimental Method
The sample of the carbon-coated air purifying material was cut into a sample to be tested with an area of 10±1 cm². The samples with a certain quality of cut were weighed as M g and put directly into 250 ml bottle with plug triangle. Add V ml deionized water according to the different solid-liquid ratio, close the lids, and put it into the constant temperature water bath oscillator at the set temperature, oscillate for a certain time, and filter it with filter to another flask for analysis. After cooling to room temperature, remove 10 ml filtrate into 25 ml colorimetric tube, add 2 ml acetone solution and cover the plug. After being heated in boiling water bath for 3 min and cooled in the dark condition, the deionized and 2 ml acetone solution mixed under the same oscillation condition were taken as a blank. The absorbance value was measured at 412 nm and the formaldehyde concentration C (indicated by the formaldehyde standard curve) was calculated. Then the free formaldehyde content is calculated as follows:

\[
\text{Free formaldehyde extraction (μg/g)} = \frac{C \times V}{10 \times M}
\]  

C, formaldehyde concentration value calculated according to the standard curve of formaldehyde, μg;  
V, Extraction volume, ml;  
10, conversion factor of solution volume of extraction liquid volume removed from the extraction solution, color reaction, ml;  
M, the mass of the sample, g.

2.4. Orthogonal Experimental Design of Free Formaldehyde Extraction in Carbon-Coated Air Purifying Material [5]

| Table 1. Factors and levels | Factors |
|----------------------------|---------|
|                            | Levels  |
|                            | A       |
| Solid-liquid ratio         | 1:10    |
|                            | 1:20    |
|                            | 1:30    |
|                            | 1:40    |
|                            | B       |
| Extraction time /min       | 30      |
|                            | 60      |
|                            | 90      |
|                            | 120     |
|                            | C       |
| Extraction temperature /°C | 30      |
|                            | 40      |
|                            | 50      |
|                            | 60      |

In order to further study the effects of solid-liquid ratio, extraction time and extraction temperature on the amount of free formaldehyde extracted from carbon-coated air purifying materials, three factors and four levels test were selected, according to the orthogonal design method on table L16 (4³) to find the most suitable conditions, and the free formaldehyde extraction amount was taken as the investigation index. The factor level arrangement is shown in Table 1.

3. Results and Discussion

3.1. Orthogonal Test Results
The results of the orthogonal test are shown in Table 2. In the table, \( \bar{K}_i \), \( \bar{K}_2 \), \( \bar{K}_3 \) and \( \bar{K}_4 \) are the average values of free formaldehyde extractions obtained from the corresponding levels, and the calculated value larger the level conditions better. It can be seen from Table 2: (A) \( \bar{K}_i > \bar{K}_j > \bar{K}_k > \bar{K}_l \), (B) \( \bar{K}_i > \bar{K}_j > \bar{K}_l > \bar{K}_k \), (C) \( \bar{K}_i > \bar{K}_k > \bar{K}_j > \bar{K}_l \). Therefore, the optimum combination extraction condition of free formaldehyde in the carbon-coated air purifying material is A4B3C2, that is, the solid-liquid ratio is 1:40, the extraction time is 90 min, and the extraction temperature is 40 °C. R is the extreme difference, which indicates the primary and secondary order and the larger the R value, the better the main effect. It can be seen from the variance in Table 2 that R1>R3>R2, which shows that the solid-liquid ratio in the test range has a significant effect on the extraction amount of free formaldehyde in the carbon-coated air purifying materials, and the extraction temperature is significant for the free formaldehyde extraction, while the extraction time has less impact.
Table 2. Results of orthogonal experiment

| No. | Factor | Free formaldehyde extraction(μg /g) |
|-----|--------|-------------------------------------|
| 1   | A 1 B 1 C 1 | 0.263 |
| 2   | A 1 B 2 C 2 | 0.728 |
| 3   | A 1 B 3 C 3 | 0.429 |
| 4   | A 1 B 4 C 4 | 0.536 |
| 5   | A 2 B 1 C 2 | 0.321 |
| 6   | A 2 B 2 C 1 | 1.190 |
| 7   | A 2 B 3 C 4 | 0.930 |
| 8   | A 2 B 4 C 3 | 1.184 |
| 9   | A 3 B 1 C 3 | 0.520 |
| 10  | A 3 B 2 C 4 | 0.874 |
| 11  | A 3 B 3 C 1 | 0.897 |
| 12  | A 3 B 4 C 2 | 1.108 |
| 13  | A 4 B 1 C 4 | 0.421 |
| 14  | A 4 B 2 C 3 | 0.878 |
| 15  | A 4 B 3 C 2 | 0.924 |
| 16  | A 4 B 4 C 1 | 0.412 |

\[
\begin{align*}
K_1 & = 0.381 \\
K_2 & = 0.917 \\
K_3 & = 0.795 \\
K_4 & = 0.960 \\
R & = 0.579 \\
\end{align*}
\]

Optimal level: A_4, B_3, C_2

3.2. Single Factor Test

3.2.1. Effect of Different Solid-Liquid Ratio on Free Formaldehyde Extraction in Carbon-Coated Air Purifying Material. The solid-liquid ratio was set to 1:10, 1:20, 1:30, 1:40, 1:50, 1:60 at the optimum level of orthogonal test, which the extraction time was 90 min, and the extraction temperature was at 40 °C. The effect of solid-liquid ratio on the amount of free formaldehyde extracted from the carbon-coated air purifying material was studied, and the optimal leaching ratio was selected. The results are shown in Figure 2.

![Figure 2. Variation of free formaldehyde extraction at different solid-liquid ratios](image)
It can be seen from Figure 2 that the extraction amount of free formaldehyde in the carbon-coated air purifying material increases with the increase of the solid-liquid ratio of the extraction. When the solid-liquid ratio of the extraction does not exceed 1:40, the amount of free formaldehyde extracted increases with the increase of the ratio. When the ratio of leaching to solid-liquid ratio exceeds 1:40, the extraction amount tends to be stable. Therefore, the optimum solid-liquid ratio of the single factor test design is 1:40.

3.2.2. Effect of different extraction time on the amount of free formaldehyde extracted from carbon-coated air purifying material. The extraction time was set to 30 min, 60 min, 90 min, 120 min, 150 min, and 180 min at the optimum level of orthogonal test, which the solid-liquid ratio was 1:40, and the extraction temperature was at 40 °C. The effect of the extraction amount of free formaldehyde in the carbon-coated air purifying material was studied, and the optimal extraction time is selected.

![Figure 3. Variation of free formaldehyde extraction at different extraction times](image)

It can be seen from Figure 3 that the extraction amount of free formaldehyde in the carbon-coated air purifying material increases with the increase of extraction time. When the extraction time does not exceed 90 min, the amount of free formaldehyde extraction increases with time, and the extraction amount decreases gradually after the time exceeds 90 min. Therefore, the optimal extraction time for the single factor test design is 90 min.

3.2.3. Effect of different extraction temperatures on the free formaldehyde extraction from carbon-coated air purifying material. The extraction temperature was set to 30°C, 40°C, 50°C, 60°C, 70°C, 80°C at the optimum level of orthogonal test, which solid-liquid ratio was 1:40, and the extraction time was 90 min. The effect of temperature on the amount of formaldehyde extracted from the air-cleaning material in the carbon cloth is selected to optimize the extraction temperature.

It can be seen from Figure 4 that when the extraction temperature is lower than 40°C, the free formaldehyde extraction in the carbon-coated air purifying material increases with the increase of temperature, and when the extraction temperature exceeds 40°C, the formaldehyde extraction amount decreases as the temperature increases. Therefore, the optimum extraction temperature for the single factor test design is 40°C.
3.3. Verification Test

3.3.1 Precision Verification. According to the results of orthogonal test and single factor test, the optimum conditions for the determination of free formaldehyde in carbon-coated air purifying material by water extraction method were as follows: the solid-liquid ratio was 1:40, the extraction time was 90 min, and the extraction temperature was 40 °C. The best test conditions were tested in parallel for 8 replicates.

Table 3. Results of precision of method

| No. | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | Average value | RSD% |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|---------------|------|
|     | Free formaldehyde extraction (μg/g) |     |     |     |     |     |     |     |               |      |
| 1   | 0.954 | 0.950 | 0.962 | 0.966 | 0.952 | 0.950 | 0.971 | 0.959 | 0.958         | 0.80  |

3.3.2 Recovery Verification. The determination of recovery is used to assess the suitability of the experimental method. The test was carried out by adding a known concentration of formaldehyde solution to the sample solution and then performing the measurement. Using the existing three carbon-coated air purifying material samples, each sample was taken from two erlenmeyer flasks respectively, adding 3.0 g sample, 120 ml of deionized water, and then adding a certain amount of formaldehyde solution of known concentration to one of the samples. And then the condition of extraction was the extraction time of 90 min and the extraction temperature of 40 °C. The free formaldehyde extraction amount of the samples in the two bottles was determined according to the test method, and finally the recovery rate was calculated by the following formula. The results are shown in Table 4.

\[ K = \frac{A-B}{C} \times 100\% \]  

(2)

K, recovery rate;
A, the formaldehyde extraction after adding a known concentration of formaldehyde solution; B, the free formaldehyde extraction from the sample;
C, the formaldehyde extraction solution known to be added.
Table 4. Result of the recovery rate of method

| Sample | \( B (\mu g/g) \) | \( C (\mu g/g) \) | \( A (\mu g/g) \) | Recovery rate \( K(\%) \) |
|--------|------------------|------------------|------------------|------------------|
| 1      | 0.958            | 1.667            | 2.587            | 97.7             |
| 2      | 0.795            | 0.667            | 1.457            | 99.3             |
| 3      | 0.489            | 0.333            | 0.817            | 98.5             |

It has been proved by experiments that the recovery rate of the free formaldehyde content in the carbon-coated air purifying material by water extraction method is between 90% and 100%.

4. Conclusion

The orthogonal parameters and single factor experiments show that the optimal parameters for the determination of free formaldehyde in the carbon-coated air purifying material by water extraction method are: solid-liquid ratio 1:40, extraction time 90min, and extraction temperature 40 °C. Through precision experiments and recovery experiments, it is shown that this method is feasible for determining the free formaldehyde content in carbon-coated air purifying material.

Acknowledgement

This article is founded by the “National Key R&D Program of china”. This paper belongs to “The Research on Key Performance and Safety Testing Technology of Household Environmental Purification Products (Project No.: 2017YFF02099)” and “The Fundamental Research on Purification Performance and Safety Testing Technology of Air Purification Materials and core components (Question No.: 2017YFF0209901)”.

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