Study on the pollution level and source analysis of aldehydes and ketones in indoor environment based on HPLC platform

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Abstract: The pollution level of aldehydes and ketones in indoor air, floor, coating, and furniture samples was analyzed by using high-performance liquid chromatography(HPLC). The study showed that 30 rooms were detected with different concentrations of aldehydes and ketones, with an average value of 0.432 mg/m^3, mainly including formaldehyde, acetaldehyde, and acrolein/acetone. The average concentrations of aldehydes and ketones in floor, furniture and coating samples were 0.648 mg/m^3, 0.590 mg/m^3 and 0.341 mg/m^3, respectively. Factor analysis and multiple linear regression analysis were used to determine that the contribution rate of aldehydes and ketones pollution caused by floor, coating and furniture samples accounted for 75.4% of indoor pollution. The least square method was used to fit the concentrations of aldehydes and ketones in indoor air and corresponding decorated materials in 10 rooms. The results showed that the pollution of aldehydes and ketones in these 10 rooms was mainly caused by coating, as well as floor and furniture materials dominated by wood products.

1.Introduction

Indoor air pollution has become one of the most concerned hot issues in today's society [1]. Currently, formaldehyde pollution has attracted extensive attention, but in recent years, research has found that there are a large number of other types of aldehydes and ketones in residential environments. These compounds are not well-known but are common air pollutants and pose a serious threat to human health. Therefore, the study of aldehydes and ketones pollution in indoor air is particularly urgent.

Aldehydes and ketones are primary and secondary pollutants produced by photochemical reactions and major components of photochemical smog, having a significant impact on the atmospheric environment [2-3]. Most of the small-molecule aldehydes and ketones are highly volatile, irritating and toxic, posing negative effects on human health [4]. Short-term exposure to high concentrations of aldehydes and ketones can cause symptoms such as dizziness, vertigo, and nausea [5], while long-term exposure increases the risk of respiratory diseases such as asthma. Furthermore, research has shown that aldehydes and ketones are associated with childhood malformations and leukemia [6-11]. Additionally, studies have revealed that commonly used decorative materials, furniture, and coating can emit or release aldehydes and ketones pollutants [12-15], with more severe pollution in newly renovated homes [15]. The methods for determining aldehydes and ketones in air mainly include spectrophotometry, gas chromatography(GC), HPLC, etc. HPLC due to its detection principle of different analytes having different adsorption capacities and distribution coefficients in the liquid phase, can effectively distinguish aldehydes as the time for the mobile phase to detach from the stationary phase varies. This method has a low detection limit, simple operation and lower cost, making it the mainstream method for detecting aldehydes and ketones today.

Currently, there are no regulations or standard limit requirements for aldehydes and ketones in indoor environments in China, and there are also no relevant product standards for related building materials and decorative materials. Compared to formaldehyde pollution, research on other types of aldehydes and ketones in indoor air is relatively insufficient, leading to a lack of awareness of prevention among residents. This study can enable consumers to have a clear understanding of the sources of aldehydes and ketones pollution caused by decoration, and thus make reasonable planning during the design stage.

2. Experimental materials and methods

2.1 Equipment and reagents

1 m^3 environmental test chamber (Jinan Hainate Tech. Co., Ltd.); Constant flow sampler (Jinan Keju Instrument Equipment Co., Ltd.); Waters e2695 high-performance liquid chromatography instrument (Waters); Ultra-pure water machine (WIGGENS); 13 aldehyde and ketone (DNPH) compound reference standard (BePure); DNPH sampling tubes; Chromatographically pure acetonitrile

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2.2 Experimental methods

Based on preliminary research results, the top three predominant building materials in bedrooms were identified as flooring, furniture and coating. Therefore, this study investigated the pollution levels of aldehydes and ketones in indoor air, flooring, coating, and furniture samples from 30 rooms. Among them, 10 sets of flooring, coating and furniture samples were the same type and batch as those used in the corresponding rooms. Indoor air samples were tested according to the test method specified in GB/T 18883-2022 "Standards for indoor air quality", with reference to the summer temperature range requirements, the middle value of 25 ℃ was taken, and the doors and windows were closed for 12 hours before sampling. The dimensions of the flooring and furniture samples were (500×500) mm, with four pieces in each category, sealed with inert materials on all sides and the back. The coating samples were applied to (500×500) mm glass plates, with four pieces in total, and cured for 3 days in an environment with a temperature of 23.0 ℃ and relative humidity of 50.0%. The material samples were tested in a climate chamber with a temperature of 25.0 ℃, relative humidity of 50%, and ventilation rate of 0. After being placed in the climate chamber for 12 hours, the samples were collected using a sampling flow rate of 0.5 L/min for a sampling volume of 10 L. After completion of the collection, add acetonitrile to the sampling tube for elution. Collect the eluent in a 5 mL volumetric flask and dilute it with acetonitrile. Use a syringe to extract the eluent, filter it through a filter, and transfer it to a 2 mL sample bottle for testing.

2.3 HPLC injection conditions

Mobile phase: acetonitrile/water; gradient elution with 60% acetonitrile maintained for 20 min, linear increase from 60% to 100% acetonitrile within (20-30) min, followed by a decrease to 60% acetonitrile within (30-32) min, and maintained for 8 min. Detection wavelength: 360 nm. Flow rate: 1.0 mL/min. Injection volume: 20 μL. Column: C18.

3. Results and Discussion

3.1 Pollution levels and composition characteristics of aldehydes and ketones in indoor air

The concentrations of 13 aldehydes and ketones in the bedrooms of 30 households were analyzed, as shown in Figure 1. Aldehydes and ketones were detected in all 30 rooms at different concentration levels, ranging of 0.160-0.911 mg/m^3 (mean: 0.432 mg/m^3). It can be seen that the main components of aldehydes and ketones in these rooms were formaldehyde, acetaldehyde and acrolein/acetone, with concentration ranges of 0.011-0.446 mg/m^3 (mean: 0.117 mg/m^3), 0.028-0.235 mg/m^3 (mean: 0.079 mg/m^3) and 0.039-0.331 mg/m^3 (mean: 0.107 mg/m^3), respectively. In addition to formaldehyde, which is well-known, there were other aldehydes and ketones present in the indoor air. According to the limit requirement in GB/T 18883-2022, the formaldehyde limit is ≤0.08 mg/m^3. It can be observed that the concentrations of various aldehydes and ketones in the indoor air of these rooms, apart from formaldehyde, were also at relatively high levels.

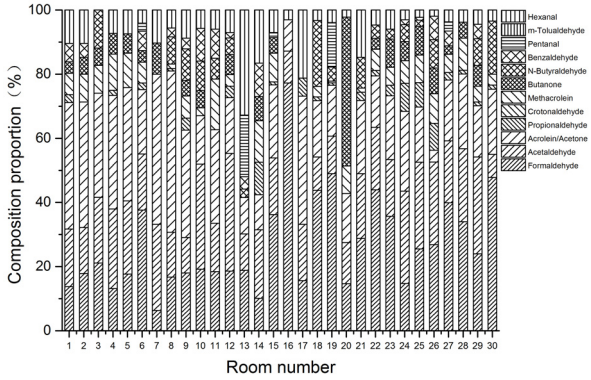

Figure. 1 Composition proportion of aldehydes and ketones in indoor air

The Spearman correlation analysis was conducted on the aldehydes and ketones that exceeded the detection limit in all 30 rooms, as shown in Table 1. It can be seen that there were significant correlations ($p<0.01$, $r>0.57$) between acetaldehyde and acrolein/acetone, as well as between acetaldehyde and propionaldehyde, indicating possible common sources of these three compounds. Similarly, significant correlations ($p<0.01$, $r>0.55$) were found between formaldehyde and acetaldehyde, between crotonaldehyde and butanone ($p< 0.01$, $r> 0.65$), and between pentanal and hexanal ($p<0.05$, $r>0.40$), suggesting potential common sources. There were no significant correlations observed among most other aldehydes and ketones, indicating a lower likelihood of common sources.

Table 1 Spearman's rank correlation coefficients among 11 aldehydes and ketones in indoor air

	Formal dehyde	Acetal - dehyde	Acrolein/A cetone	Propiona l dehyde	Methyla- crolein	Butano ne	N-Butylald ehyde	Benzal dehyde	Pentana l
Acetaldehyde	0.554[b]								
Acrolein/acetone	0.242	0.675[b]							
Propionaldehyde	0.272	0.574[b]	0.461[a]						
Methylacrolein	0.11	0.432[a]	0.354	0.323					
Butanone	-0.155	0.189	0.081	0.130	0.670[b]				
N-butylaldehyde	0.330	0.349	0.377[a]	0.226	-0.154	-0.279			
Benzaldehyde	-0.112	0.202	0.348	0.221	0.307	0.124	0.138		
Pentanal	0.288	0.337	0.147	0.060	-0.070	0.002	-0.004	0.139	
Hexanal	0.113	0.277	0.261	0.451[a]	-0.159	-0.172	0.191	0.360	0.412[a]

[a]$p < 0.05$; [b]$p < 0.01$

3.2 Pollution levels and composition characteristics of aldehydes and ketones in decorative materials

This study analyzed the pollution characteristics of aldehydes and ketones in commonly available flooring, furniture and coating samples. Each material category contained 30 sets of samples, totaling 90 sets of samples. Among them, 10 sets of flooring, coating and furniture samples were the same type and batch as those used in the corresponding rooms. Aldehydes and ketones were detected in different concentrations in all three categories of materials. The concentrations of aldehydes and ketones in the flooring and furniture samples were relatively high, ranging of 0.155-1.286 mg/m^3 (mean: 0.648 mg/m^3) and 0.195-0.967 mg/m^3 (mean: 0.590 mg/m^3), respectively. The Mann-Whitney U test showed that there was no significant difference in the concentrations of aldehydes and ketones between these two materials ($p>0.05$). The concentration of aldehydes and ketones in the coating samples was 0.208-0.533 mg/m^3 (mean: 0.341 mg/m^3). The Mann-Whitney U test showed that there was a significant difference in the concentrations of aldehydes and ketones between the coating samples and the other two types of materials ($p<0.05$). It can be seen that the concentration of aldehydes and ketones in the flooring and furniture samples made from wood as raw material is significantly higher than that in the coating samples. This is because compared to solid wood flooring and furniture, which are expensive, flooring and furniture made from raw materials such as veneer plywood panel and particle board are more popular due to their low price. However, the content of aldehydes and ketones in these flooring and furniture products will be higher, because although the main component is wood, it is all made by pressing and fixing wood chips with adhesives, and there are a large number of aldehydes and ketones in the adhesives, as shown in Figure 2.

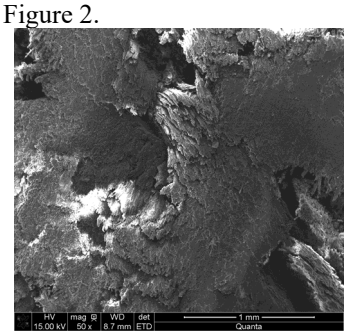

Figure 2 Scanning electron microscopy (SEM) image of veneer plywood panel

At the same time, the composition proportion of aldehydes and ketones in different materials was studied, as shown in Figure 3. The aldehydes and ketones composition proportion of the flooring samples is shown in Figure a), and most of the flooring samples were mainly composed of acrolein/acetone, acetaldehyde and propionaldehyde, with average proportion of 35.7%, 31.1% and 17.3%, respectively. The composition proportion of the coating samples is shown in Figure b), and it can be seen that the coating samples basically presented a characteristic composition dominated by formaldehyde, with an average proportion of 46.0%, followed by acetaldehyde, with an average proportion of 26.2%. The composition proportion of the furniture samples is shown in Figure c), and the main components were acetaldehyde and formaldehyde, with average proportion of 34.7% and 22.7%, respectively.

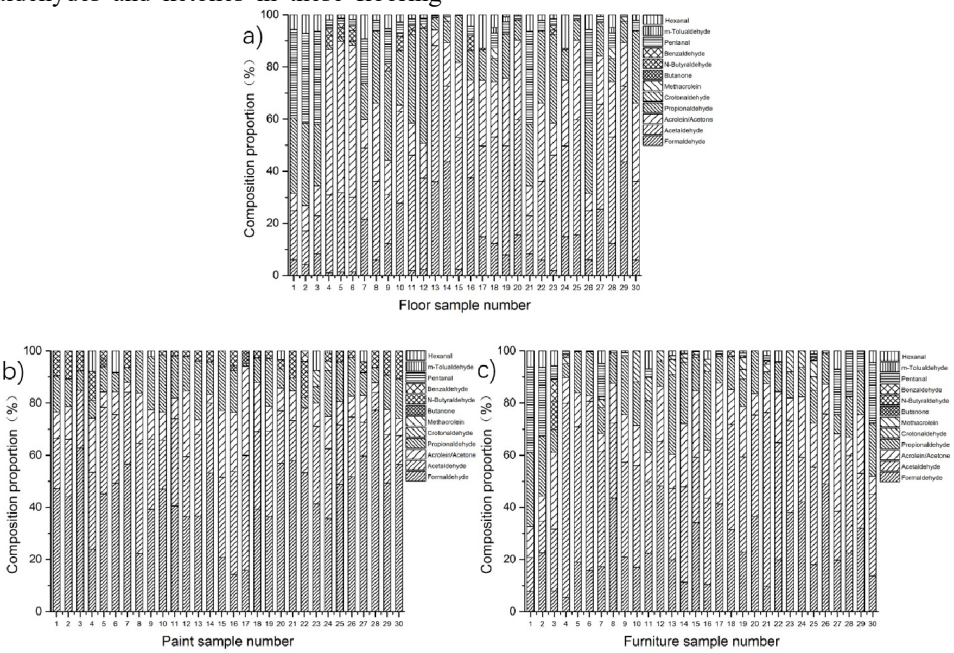

Figure. 3 Composition proportion of aldehydes and ketones compounds in three types of decoration materials
a) Floor; b) Coating; c) Furniture

3.3 Source analysis of aldehydes and ketones

This study used factor analysis to analyze the sources of aldehydes and ketones pollution. The method extracted four factors with eigenvalues greater than 1 (Factor 1 to Factor 4), and the cumulative variance contribution rate is 74.8%. Table 2 lists the load values of aldehydes and ketones on the four factors, and the closer the value is to

1, the greater the contribution of the compound to that factor. The values greater than 0.5 on different factors are displayed in bold. From Table 2, it can be seen that Factor 1 has a variance contribution rate of 25.3%, and the components with larger loads are acetaldehyde, acrolein/acetone and propionaldehyde. As mentioned in section 3.2, the composition of most flooring samples is mainly composed of these three components, so it is speculated that Factor 1 is related to the flooring. In addition, furniture samples showed a characteristic dominated by acetaldehyde. Therefore, aldehydes and ketones in Factor 1 may come from both flooring and furniture samples. In summary, Factor 1 is speculated to be a mixed source of flooring and furniture samples. The variance contribution rate of Factor 2 is 20.7%, and the major loadings are methylacrolein and butanone. Currently, no strong correlations have been found between these two components, indicating that Factor 2 is an unknown source. The variance contribution rate of Factor 3 is 17.8%, with major loadings being pentanal and hexanal. Research by Wang et al. [16], Zhang et al. [17] and Wang et al. [18] suggests that pentanal and hexanal originate from the degradation of wood itself, indicating that Factor 3 represents self-degradation sources of wood-based decorative materials. The variance contribution rate of Factor 4 is 10.7%, with formaldehyde being the major loading. Studies by Zhang, et al. [19] and Wang et al. [20] indicate that formaldehyde may come from coating samples. The research in section 3.2 also found that formaldehyde is the main aldehydes and ketones compound in the coating samples. Additionally, studies have shown that formaldehyde is associated with the use of urea-formaldehyde resin in board and laminated wood materials, as urea-formaldehyde resin is widely used as an adhesive in the production of engineered wood products [21]. Moreover, section 3.2 found that formaldehyde is the main aldehydes and ketones compound in 5 floor samples and most furniture samples. Therefore, it is speculated that Factor 4 represents the sources of adhesives in coating, flooring, and furniture samples.

Table 2 Factor loading table of aldehydes and ketones in indoor air

Aldehydes and ketones	Factor 1	Factor 2	Factor 3	Factor 4
Formaldehyde	0.128	-0.017	-0.007	**0.898**
Acetaldehyde	**0.816**	-0.076	0.006	0.277
Acrolein/acetone	**0.665**	-0.217	-0.120	-0.217
Propionaldehyde	**0.785**	0.083	0.004	0.088
Methylacrolein	0.548	**0.695**	-0.170	0.048
Butanone	-0.019	**0.895**	-0.055	-0.096
N-Butylaldehyde	0.465	-0.364	-0.089	-0.029
Benzaldehyde	0.482	0.343	0.332	-0.404
Pentanal	-0.175	0.052	**0.894**	0.060
Hexanal	0.089	-0.129	**0.899**	-0.097

Multiple linear regression (MLR) analysis was used to quantify the relative contribution rates of different aldehydes and ketones to indoor air pollution. The standardized total amount of aldehydes and ketones was taken as the dependent variable, and the factor scores of the decomposition sources were used as independent variables for MLR analysis. The equation obtained was:

$$Y_{\Sigma aldehydes/ketones}=0.745Factor1+0.385Factor2+0.080Factor3+0.352Factor4 \quad (1)$$

（R^2=0.996，p＜0.001）

Based on the equation above, Factor 1 (flooring and furniture source) contributes 47.7% to aldehydes and ketones in indoor air, Factor 2 (unknown source) contributes 24.6%, Factor 3 (self-degradation source of wood) contributes 5.1%, and Factor 4 (source of adhesives in coating, flooring and furniture) contributes 22.6%, as shown in Figure 4. Factors 1, 2 and 3 can be collectively considered as sources of indoor decorative materials. Therefore, the contribution rate of flooring, coating and furniture samples to aldehydes and ketones in indoor air is 75.4%.

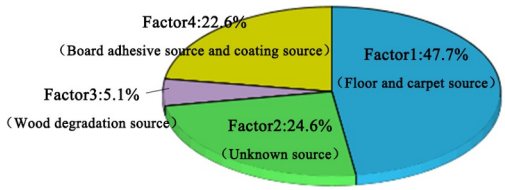

Figure. 4 Relative contribution of each source to total aldehydes and ketones in indoor air

The aldehydes and ketones concentrations in 10 rooms and corresponding flooring, coating, and furniture samples were studied using the least square method. Under the conditions of the climatic chamber method mentioned in section 2.3, the concentrations of aldehydes and ketones in the three types of decorative materials were measured at loading rates of 0.25, 0.5, 0.75, and 1.0 m^2/m^3, and the pollution equilibrium release amounts at the four loading rates were fitted by the least square exponential method.

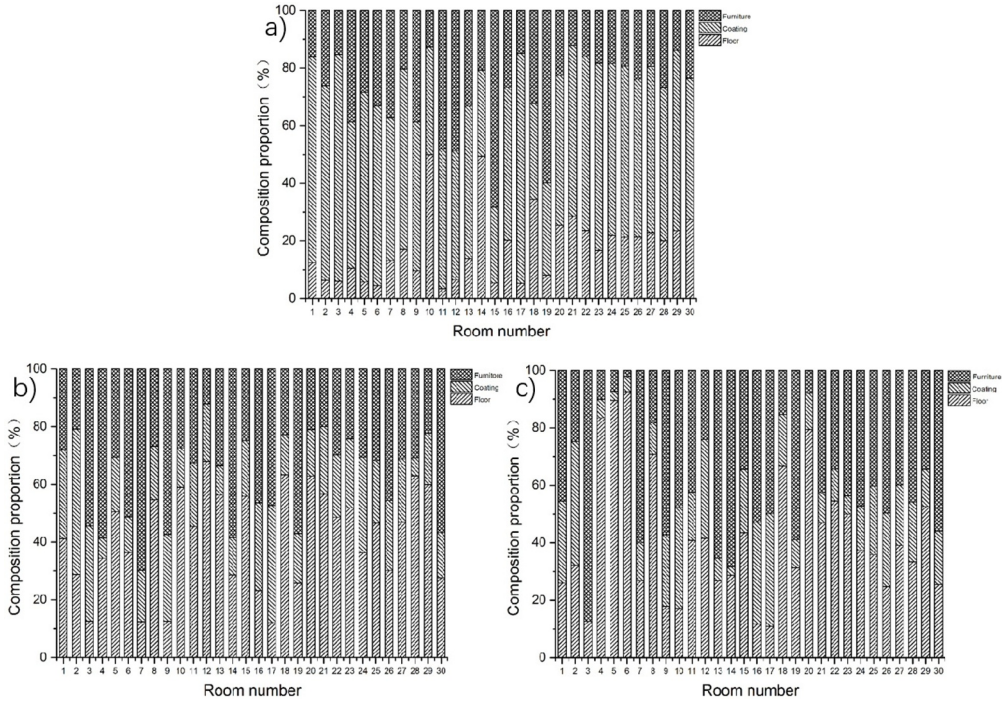

Figure. 5 Predicted composition proportion of aldehydes and ketones in three types of decoration materials
a) Formaldehyde; b) Acetaldehyde; c) Acrolein/Acetone

The three aldehydes and ketones with the highest concentrations in these rooms, namely formaldehyde, acetaldehyde and acrolein/acetone, were selected for the analysis mentioned above. The predicted values of formaldehyde concentrations in these rooms averaged 93.8% of the actual values after removing extreme cases with large deviations due to low actual values. The percentages for acetaldehyde and acrolein/acetone were 87.7% and 90.6%, respectively. The proportions of formaldehyde, acetaldehyde and acrolein/acetone in the predicted values were also studied, as shown in Figure 5. It can be seen that the main source of formaldehyde in these rooms is the coating samples, with an average proportion of 54.4%. Acetaldehyde and acrolein/acetone mainly originate from the flooring and furniture samples, with average proportions of 78.5% and 82.1%, respectively. It can be concluded that the aldehydes and ketones pollutants in these rooms mainly come from coating and flooring/furniture made of wood-based materials. Therefore, by properly controlling the decorative materials of these major pollution sources, the degree of aldehydes and ketones pollution in the rooms can be adjusted and controlled.

4 Conclusions

This study investigated the levels of aldehydes and ketones in the indoor air, flooring, coating and furniture samples. The results showed that aldehydes and ketones at different concentrations were detected in all 30 rooms, with an average value of 0.432 mg/m^3. The main components were formaldehyde, acetaldehyde and acrolein/acetone. The average concentration of aldehydes and ketones in the flooring samples was 0.648 mg/m^3, with the main components being acrylonitrile/acetone, acetaldehyde and propionaldehyde accounting for 35.7%, 31.1% and 17.3%, respectively. The average concentrations of aldehydes and ketones in furniture samples were 0.590 mg/m^3, with the main components being acetaldehyde and formaldehyde accounting for 34.7% and 22.7%, respectively. The average concentrations of aldehydes and ketones in coating samples were 0.341 mg/m^3, with the main components being formaldehyde and acetaldehyde accounting for 46.0% and 26.2%, respectively. Mann-Whitney U test results showed no significant difference in the concentrations of aldehydes and ketones between floor and furniture samples ($p>0.05$), but there was a significant difference in concentrations between coating and floor/furniture samples ($p<0.05$).

Factor analysis and multiple linear regression were used to determine that the contribution rate of indoor aldehydes and ketones pollution caused by flooring, coating and furniture samples was 75.4%. Then, the contributions of flooring, coating and furniture samples to air quality in 10 rooms were verified using least square method, indicating that aldehydes and ketones pollution in these rooms mainly originated from coating, flooring and furniture, especially wood-based decoration materials. Therefore, as long as the main sources of pollution controlled reasonably, it was possible to adjust and control the degree of aldehydes and ketones pollution in the rooms. At the same time, this study can also provide a theoretical basis for tracing the sources of other pollutants in indoor air.

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