

A New HPLC Method to Determine Carbonyl Compounds in Air

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Abstract: In this paper, a new HPLC method was established to determine the carbonyl compounds in air. As the absorbent, 2, 4-dinitrophenylhydrazine (2, 4-DNPH) reacted with carbonyls specifically, which form the corresponding 2,4-dinitrophenylhydrazones, then analyzed by HPLC. The chromatographic conditions, the recovery rate, stability of samples, reagent blank, sampling efficiency were all studied systematically. The results showed that this established method had high sensitivity and good selectivity compared with other analytical methods, and it can determine ten carbonyl compounds in air in 26 min simultaneously.

Keywords: Carbonyl compounds, HPLC, 2,4-dinitrophenylhydrazine.

In recent years, aldehydes and ketones have been the pollutants constantly in air with the development of the chemical industry. Most of aldehydes and ketones are toxic or carcinogenic. Therefore, it is extremely necessary to study the sampling process and analytical method of aldehydes and ketones. At present, the main domestic analytical methods are colorimetric and titrimetric method. In addition, ion chromatography and gas chromatography are also adopted¹. These methods can only be used for the analysis of one or two kinds of aldehydes and ketones, and the selectivity and sensitivity of these methods are often low. Thus, the application of these methods in analysis of actual samples are limited greatly. In this paper, a new HPLC method for simultaneous analysis of ten kinds carbonyl compounds in ambient and polluted air was established with high sensitivity and selectivity.

Basic Principle

In acidic condition, 2,4-dinitrophenylhydrazine(2,4-DNPH) acting as absorbent reacts with carbonyl compounds in air specifically, to form the corresponding 2,4-dinitrophenylhydrazones derivatives, which can be determined by HPLC.

Experimental

Instrument and reagents

The HPLC system consists of LC-4A liquid pump of Shimadzu Corp. of Japan, SIL-6B automatic sample injector, SPD-2AS ultraviolet-visible spectrophotometer detector and

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Chromatopac C-R 6A data processor.

Formaldehyde, acetaldehyde, acraldehyde, butyraldehyde, benzaldehyde, valeric aldehyde, acetone, butanone, acetophenone, methylisobutyl ketone (MIBK), *n*-hexane, methylene dichloride, 2, 4-dinitrophenylhydrazine were all A.R. grade too. 2, 4-Dinitro-phenylhydrazone derivatives were made according to reference², which were used as the standard samples of HPLC analysis.

2, 4-Dinitrophenylhydrazine absorbent should be prepared 48 h before sampling, by dissolving 2,4-dinitrophenylhydrazine solid in 2 mol/L HCl and extracted with *n*-hexane/methylene dichloride (7:3).

Gas sampling

Two fritted glass disc bubblers were connected, and 10 mL 2,4-dinitrophenylhydrazine absorbent and 5 mL *n*-hexane / methylene dichloride (7:3) were added. The air samplers were used and the sampling velocity was 0.5~1.0 mL/min, the sampling time was 10~60 min.

Pretreatment of samples

The carbonyl compound samples in air collected were transferred quantitatively into 100 mL separating funnel, then extracted by 3×10 mL *n*-hexane/methylene dichloride (7:3). The organic layers extracted three times were combined and transferred into 50 mL colorimetric tube with plug. The organic phase was volatilized completely with protection of nitrogen on 40°C water bath. The residue was dissolved with methanol, then transferred into a 10 mL volumetric flask and made up to the volume with methanol. An aliquot of 20 µL was injected to the HPLC system for analysis.

Sample analysis

The samples were analyzed qualitatively by the relative retention times of the 2,4-dinitrophenylhydrazone standard samples and analyzed quantitatively by the external standard method through the same HPLC system.

Results and Discussion

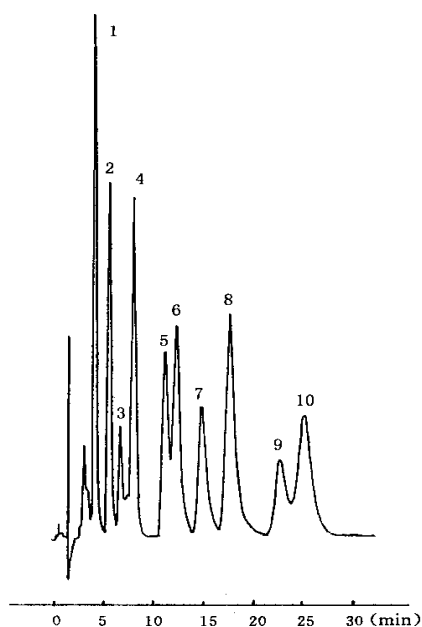
Chromatographic conditions

Zorbax-C₈ column (4.6 mm ID × 250 mm) was selected. The mobile phase was methanol/water (60:40) and the flow rate was 1.5 mL/min. The detection wavelength was 350 nm, and injected volume 20 µL. Ten kinds of carbonyl compounds were studied including formaldehyde, acetaldehyde, acraldehyde, butyraldehyde, valeric aldehyde, benzaldehyde, acetone, butanone, methy-isobutyl ketone(MIBK) and acetophenone. Their 2,4-dinitrophenylhydrazone derivatives could be separated completely in 26 min under the chromatographic conditions, and the chromatogram is given in **Figure 1**. The detection limits of these 2,4-dinitrophenylhydrazone at a signal/noise ratio of 3 were 1 ng to 5 ng, and the linear range was wide from 1 ng to 1000 ng.

Extraction recovery rate

Different concentrations of the standard samples of ten kinds of 2,4-dinitrophenylhydrazones were added quantitatively into 10 mL 2,4-dinitrophenylhydrazine absorbent for 5 min, then extracted according to section “*Pretreatment of samples*”. The results showed that the average recovery rate was 91%~97%. So our method could assure the quantitative recovery of 2,4-dinitrophenylhydrazones from carbonyl compounds.

Figure 1 The chromatogram of ten kinds of carbonyl compounds



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|----------------------|--------------------------|----------------------|
| 1. Formaldehyde-DNPH | 2. Acetaldehyde-DNPH | 3. Acraldehyde-DNPH |
| 4. Acetone-DNPH | 5. Butyraldehyde-DNPH | 6. Butanone-DNPH |
| 7. Benzaldehyde-DNPH | 8. Valeric aldehyde-DNPH | 9. Acetophenone-DNPH |
| 10. MIBK-DNPH | | |

Stability of samples

The stability of samples were studied as follows: the 2,4-dinitrophenylhydrazone derivatives formed by the reaction on absorbent were sealed in tubes and kept in refrigerator(0~4°C) for 12d. Then it was extracted according to section “*Pretreatment of samples*”. The result showed that the 2,4-dinitrophenylhydrazone derivatives in 2,4-dinitrophenylhydrazine absorbent was stable for at least 12 d under the above conditions.

The 2,4-dinitrophenylhydrazone derivatives formed were extracted by 3×10 mL *n*-hexane/methylene dichloride (7:3), and the organic phase was volatilized completely with protection of nitrogen on 40°C water bath. The residue was preserved in sealing and protected from light at room temperature for 30 d, then dissolved in methanol and

determined by HPLC. The result showed that the 2,4-dinitrophenylhydrazone derivatives preserved under this conditions could be stable for at least 30 d.

Reagent blank

Our result showed that in 10 mL absorbent solution, the blank value of formaldehyde-D-NPH was 0.4 μ g, that of acetone--DNPH was 0.2 μ g. And the other carbonyl compound-DNPH could not be detected. The reagent blank values were so low that they did not have any effect on environmental monitoring.

Sampling efficiency

Three fritted glass disc bubblers were connected in series to sample samples of the formaldehyde and acetone of simulated air. The result demonstrated that the sampling efficiency of the first bubbler was >88%, and that of the combined series of the first and the second bubblers was >97%. Therefore, it was applicable to use two fritted glass disc bubblers in series in actual sampling.

Determination of simulated gas mixture

We simulated the gas mixture including five carbonyl compounds: formaldehyde, acetaldehyde, butyraldehyde, valeric aldehyde and acetone. The simulated gas was sampled and analyzed according to section “**Experimental**”. The five carbonyl compounds could be separated completely by HPLC. The relative standard deviation of the five carbonyl compounds were all <10%.

Determination of actual samples

We sampled and analyzed the workshop air of an organic chemical factory and a paint factory. The experiments showed that the carbonyl compounds had good separation by HPLC method, there were no interfering peaks. The added standard recovery rate was 90%~99%, and the relative standard deviation of carbonyl compounds were all <10%.

Conclusion

Compared to other analytical methods for carbonyl compounds, the new HPLC method possesses high sensitivity and good selectivity, and can determine ten kinds of carbonyl compounds in air simultaneously in 26 min. This method is simple, efficient and can be expected to have wide application.

References

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