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The Analysis of VOCs by GC/MS with Whole Column Coldtrapping on a Fused Silica Capillary Column in Indoor Environment

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Abstract: Whole column coldtrapping(WCC) on a fused silica capillary (FSCC)combined with GC/MS analysis was evaluated for use in the investigation of volatile organic compounds(VOCs) in indoor air. Research had indicated that a temperature of -80℃ is optimal for WCC. Samples were analyzed on a 50m × 0.2mm cross-linked 5% phenylmethylsilicone fused silica column. Liquid nitrogen was used as the coolant for the peak resolution significantly. The analysis can be performed quickly and conveniently. More than 112 of VOCs were determined in the samples from three typical indoor environment including: (1) a room which had just been decorated involving building materials and paints; (2)a kitchen used for Chinese cooking, and(3) a room had tobacco smoke. The method is could be readily applied to rapid sample screening for VOCs contamination surveys or initial investigations with its valid and simple sampling and analytical technique.

Keywords: VOCs, GC/MS, Indoor environment, Whole column coldtrapping, Analysis

1. Introduction

The method of purge and trap with whole column coldtrapping(WCC), as developed by PanKow and Rosen(1), is used to analyze volatile compounds in water and wastewater. The benefits of WCC include simplicity,high sensitivity as a result of the splitless analysis, and excellent relative retention time reproducibility. Interest in analytical methods for the determination of volatile organic compounds(VOCs) in specific consumer products such as petroleum-based solvents, deodorizers, and air fresheners, cigarettes, paints, lacquers, varnishes, etc.(11-12).

The choice of the analytical method of VOCs in indoor air is determined by several factors such as collection efficiency of sampling, chemical and thermal stability of sampler sorbent (if need it) during sampling, storage and desorption, low blank levels of solvent and sorbent (if need it).

The method of WCC/GC/MS do not need any of solvents and sorbents. No sample preparation prior to analysis is required. It is the lowest blank levels comparing with some of other analytical methods.

Characteristic ions for "postrun" selected ion monitoring(SIM) were chosen for each target compounds based upon relative abundance. SIM was employed to increase instrument sensitivity, essential in the low level indoor air pollutants range. Typically three ions per compound were chosen for data acquisition and were usually the major ions designated in USEPA method(2).

Table 3 shows the recovery and mean relative standard deviation(RSD) of target VOCs of the five runs at 100ng/ μ L. A chromatogram obtained from the WCC/GC/MS of the standard is presented in Figure 1.

The peaks are uniformly sharp. All exhibit peak widths which are less than 6s wide at the base. Cryogenic focusing increases the peak resolution significantly and is highly amenable to use with capillary columns. The system is easily operated; with the minimal sample preparation and short retention times, analysis can be performed quickly and conveniently.

Figure 2,3 presents a WCC chromatogram of a "decorated" room indoor air sample(sample Indoor1#) and "smoking" room indoor air sample(sample Indoor3#),respectively. As expected, benzene, toluene, ethyl benzene, xylene, naphthalene, and some alkanes as major compounds in Environmental Tobacco Smoke (ETS) of indoor air.

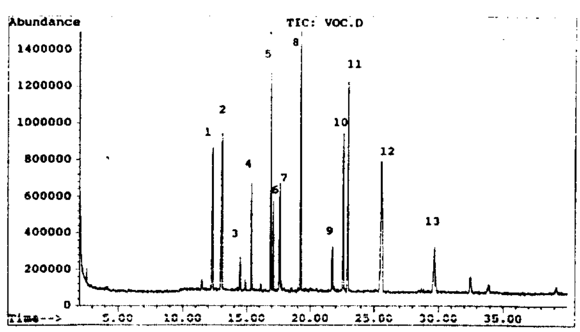

Figure 1 The chromatogram of the standard target VOCs

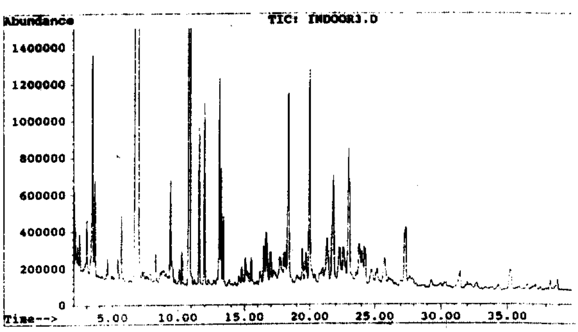

Figure 3 The chromatogram of a "smoking room" indoor air sample (sample Indoor 3#)

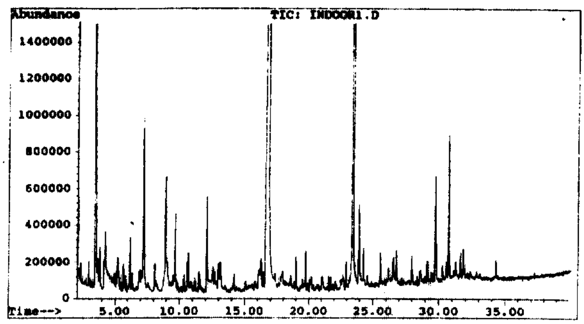

Figure 2 The chromatogram of a "decorated room" indoor air sample (sample Indoor 1#)

Table 3 Recovery and RSD of Target VOCs

Target VOCs	Recovery(%)	RSD(%)
benzene	96.2	5.29
toluene	97.4	4.32
ethyl benzene	102.3	7.87
m-+p-xylene	98.9	8.81
o-xylene	96.0	6.13
octane	94.2	3.42
nonane	92.1	5.33
decane	93.7	7.42
carbon tetrachloride	107.2	6.41
tetrachloroethene	95.5	6.87
chlorobenzene	100.1	8.95
cyclohexane	93.8	6.26
methylcyclohexane	96.2	4.09

Lower-boiling-point compounds are quite difficult to cryo-focus in a bore glass or metal tube because of the very low temperatures needed. The cryo-focussing of these compounds can be enhanced by the use of coated capillary tubes. The inner wall of the tube may be coated with any substance which shows retention toward the compounds of interest. Solid, adsorbent coatings may be most useful because of their high affinities for the nonindustrial indoor air environments has increased dramatically in the last 5 years. The US Environmental Protection Agency's recommended method for analysis of VOCs in indoor air utilizes Tenax solid adsorbent/thermal desorption technology(2). But it has been shown that the resolution of VOCs can be improved further with the use of cold trapping,which involves freezing either part(3) or all of the column—WCC(1,4) in water and wastewater. VOCs represent a wide-spread threat to indoor environment. These materials, some of which are carcinogenic, mutagenic or highly toxic even at very low concentrations(5), are often found in indoor air(6). As a result, the analytical chemistry of VOCs is of great interest. Gas chromatography in conjunction with mass spectrometry (GC/MS) often is the analytical method of choice for VOCs because of its ability to obtain complete compositional analysis over a very wide range of numbers and concentrations(7). However, GC is a very slow technique and often represents the rate-limiting step in the analysis-remediation loop(8).

In this paper, a new method, whole column coldtrapping/ gas chromatography/ mass selective detection(WCC/GC/MS) for analysis and identification of more than 112 VOCs isolated from samples of typical indoor air is reported in detail. Especially, the discussion was emphasized in the methodology employed in this study.

2. Experimental methods

2.1 Apparatus and Materials

A Hewlett-Packard 5890 II GC/5971A MSD with G1030A MS ChemStation (DOS series) was used. The GC column was a HP-5 fused-silica capillary column(50m × 0.2mm, 0.33 μm film thickness, Hewlett-Packard Co.). All chemicals for preparation of analytical standards were obtained commercially and solvents were glass distilled. The target VOCs standard gas were prepared by dynamic method, ranging nominally from 10 to 400 ng/μL.

2.2 Analytical conditions

Table 1 lists chromatographic and mass spectrometric conditions used throughout the investigation. The long injection time allows for the complete transfer of the 10-1000 ml samples from the syringe or gas-bag to the column head.

Table 1 GC/MS analytical conditions

Instrument or Conditions	Description
Gas chromatography	
Temperature program	
column:	-80℃,2min; -80℃ to 40℃ at 50℃/min; hold 2min at 40℃; 40℃ to 100℃ at 4℃/min; 100℃ to 250℃ at 10℃/min
inject port:	ambient temperature
GC/MS transferline:	280℃
coldtrapping:	-80℃
Carrier flow rate:	1 ml/min (Helium)

Mass spectrometer	
Scan mode:	
identification of VOCs scan mode:	30-450 amu
quantitation of VOCs selected ion monitoring(SIM)mode:	characteristic ions designated in USEPA Method
Ion source mode:	electron impact ion source(EI)
MS tuning compound:	perfluorotributylamine(PFTBA)
MS library:	NBS49K(US)

2.3 Sampling

The air samples were collected from three types of indoor environment, which are listed in Table 2.

10-100 ml syringe used as sampler were washed and rinsed with water, methanol, and acetone and then stored at 300 ℃ for 2hr. After sampling, the syringe were capped with silicone rubber caps, and sealed with Teflon seal tape again. All syringes were double sealed in order to prevent contamination prior to use. If gas-bag was used as air sampler it was sealed tightly and carried to laboratory. They were refrigerated at low temperature before analysis.

Table 2 Conditions of sampling sites

Sampling sites	Conditions of indoor environment
Indoor 1#	a room(16.8m2 × 2.75m) which had just been decorated involving building materials and paints obtained commercially, indoor air temperature: 16℃
Indoor 2#	a kitchen(in residential buildings)(5.6m2 × 2.70m) used for Chinese cooking, indoor air temperature:24℃
Indoor 3#	a room(14.7m2 × 3.10m) had tobacco smoke, indoor air temperature: 20℃

3. Results and Discussion

Ideally, any methods for VOCs determinations should include calibration for all compounds present in indoor air. However, it would be prohibitively time consuming and expensive. For this work, a representative list of target VOCs for routine analysis was selected. The target VOCs are the prevalence of compounds in indoor air and frequently have been used as target analyte by other investigators(9-10). They are the potential for a compound to act as a tracer for low-molecular-mass organic target compounds. Adsorption of the compounds of interest on active adsorption sites is the basis for affinity(retention) and selectivity of these materials. For adsorbent-coated cold traps, efficient cryo-focussing and large concentration enhancements can be obtained at the compounds. This can greatly reduce the cooling requirement for these devices.

4. Conclusions

This study shows that quantitative sample collection over extended periods of time can be achieved for virtually all VOCs of indoor environmental significance. The high chromatographic efficiency of WCC has much to offer air analysis, as in the analysis of samples contaminated with complex mixtures, such as cigarettes, paints etc. The method of WCC/GC/MS may be well suited for indoor air analysis where very limited sampling volume require significantly valid analytical technique. The method is also could be readily applied to rapid sample screening for contamination surveys or initial investigations with its valid and simple sampling and analytical technique. Overall, the technique is highly successful and should prove very useful for trace volatile organic analysis in indoor air.

Acknowledgment

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