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Assay of some volatile compounds in human exhalation

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Abstract—The assay of trace volatile low molecular weight(MW) compounds in human breath or in ambient atmosphere typically involves gas chromatography with flame ionization detection (FID). This paper introduced a direct assay which can overcome the difficulties of collection low concentration samples. In order to pre-concentrate the trace low MW compounds, a small trapping column filled with absorbent must be used before thermal desorption of the collected samples onto chromatographic column(packed with Porapak Q) for separation. It has been proved that the characteristic of absorbent mainly influence the recoveries and the linear range of this method is from 0.05 ng to 5200 ng for pentane, methanol, ethanol and acetone.

Keywords: trapping column; low molecular weight compounds; human exhalation.

1 Introduction

The analytical application of gas chromatography (GC) for detecting trace volatile complex organic mixtures was well known for over a half century(Ioffe, 1977; Kaji, 1978; Person, 1989; Christman, 1982). Nowadays, GC is generally used to determine ambient air pollutants, and in clinic investigations to characterize some chemical compounds which indicate or predict certain kinds of diseased or malfunctions of the human body(Teranishi, 1972; Gearhart, 1976; Castello, 1987; Peinado, 1987; Phillips, 1987; Zlatkis, 1973). Some papers have mentioned the pre-concentration methods based on an enrichment step employing solid adsorbent and the thermal desorption(Fabbri, 1987; Namiesnik, 1988; Yang, 1987).

In this paper, the method for determination of low MW compounds in human exhalation and in corresponding environment is described. At first, the components are trapped in an adsorption tube which is filled with charcoal, and then, they are desorbed thermally and separated on a GC column packed with Porapak Q. The trapping tube filled with charcoal can be effective not only as an adsorption tube but also as desorption one.

2 Experimental

2.1 Apparatus

The instrumentation system used is made up with a CHROM 4 (made in Czechoslovakia) gas

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chromatography equipped with FID and sampling. This system is modified according to the reference that was used previously for the automatic determination of selected C_2-C_5 hydrocarbons in ambient samples(Person, 1989).

2.2 Procedure and sampling

Using a CHROM GC with double injector, the analysis was performed successfully. To bring the samples into the GC, a 6-port valve and three 3-port valves were involved for switching over the carrying gas N_2 to pass through the adsorption tube. They also took part in pre-treatment of the enriching tube before usage. Meanwhile they can also ensure the GC for efficient performances. The adsorbent tube was first located at out of GC, the pure N_2 heated by first injection port of GC was passing through the tube to remove contaminant, otherwise the pure N_2 flow-rate controlled by a valve is carrying the standard trapped on the pre-concentration tube after the standard injected at room temperature. When the adsorbent tube is located inside the second injection port, the temperature of desorption is controlled by adjusting the temperature controller of the injector. The sampling system described in detail in another paper (Qin, 1997) was connected onto GC with a stainless steel capillary tube, which should be as short as possible and partly located inside the GC column oven.

2.3 Standard

The gas standards can be prepared according to the volumetric method by using the following equation:

$$C_i = V_i d_i / V_v,$$

where, C_i is the concentration of analytically pure standard i (mg/L); V_i is the volume of pure liquid volatile compound (μl); V_v is the volume of the container (L); d_i is the density of standard i (mg/μl)). By, adding appropriate amounts of volatile liquid compounds with a micro-syringe into a container of known volume, we could obtain the gas standards or their mixtures of specified concentrations.

2.4 Determination and conditions

The pre-concentration tube is used to transfer either standards or realistic samples into GC via a capillary tube connector. Prior to use, the tube must be purged by a passing pure heated nitrogen (approx. 250℃) at a flow-rate of 25ml/min for about 20 minutes in order to remove all contaminants.

For calibration the gas standards (<0.5ml) are introduced with a gas-tight syringe from the injection port. They are carried through the tube by pure nitrogen and trapped by the adsorbent at room temperature (approx. 25℃). The calibration curves are obtained from the injection of the standards on GC analysis.

A definite volume (200—600 ml) of breath or air sample for analysis was directly drawn through the adsorbent at room temperature for 10—30 minutes by a portable pump after calibration. The sampling flow-rate was adjusted at 20—50ml/min by a needle valve. The volume of samples collected was dependent on their concentration. The sampling tube must have sealed by silicone rubber after removal from the collecting or sampling system, and the GC analysis should be performed immediately.

Chromatographic separation was accomplished on Porapak Q (80—100 mesh), packed in a stainless steel column (1.2m×0.3cm id). The temperature for desorption of the samples from the adsorbent is controlled at 250℃. During thermal desorption, the carrier gas N_2 with flow rate of 25 ml/min passes through the pre-concentration tube and transfers the desorpted components onto the analytical column at 143℃. The retention times of methanol, ethanol, pentane and acetone are all within 10 minutes. The qualitative and quantitative analysis are carried out according to their respective peak heights and retention times.

3 Results and discussion

3.1 Desorption and recovery

The relationships between the recoveries and desorption conditions of various compounds in our experiments are shown in Fig. 1 and Fig. 2. Obviously the recoveries are effected by the carrier gas flow-rate. The optimum recoveries of methanol, ethanol, acetone and pentane are 100%, 85%, 75% and 70% respectively, while the carrier gas flow-rate during adsorption is 25 ml/min. Using a constant flow-rate, recoveries of the trap can be kept at a certain level, even when the injector temperature is changed from 248—340℃ as shown in Fig. 2 in which 100 μl of 26 μg/ml gas standard is injected.

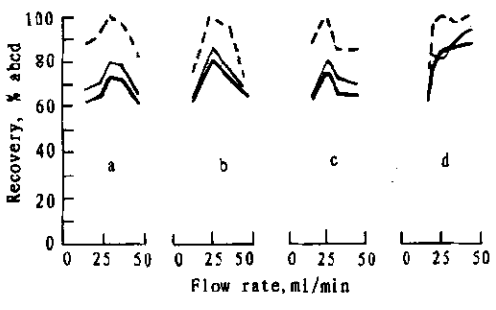

Fig. 1 The relationship between recoveries at different desorption temperatures and carrier gas flow-rates for adsorption
Desorption temperature (℃: a=258, b=288, c=315, d=340)- - - - Methanol ——Ethanol —— Acetone

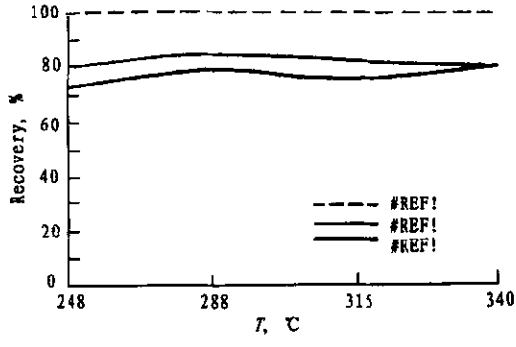

Fig. 2 The relationship of recoveries and desorption temperatures using a carrier gas flow-rate of 25 ml/min

3.2 Breakthrough volume V_g

A quartz glass capillary is used to determine the breakthrough volumes of the charcoal at different column temperatures. It is a specific column at its middle part (10cm×1.5mm id) filled with 0.059g active carbon (0.06—0.08cm) and at the remainder of the glass column filled with glass beads. After installing the column into the oven of the GC, the retention times are measured at different column temperatures. The breakthrough volumes V_g can be obtained according to the following equation:

$$V_g(\text{ml/g}) = \frac{237(t_R - t_M)F_c 3/2\{[(P_i/P_o)^2 - 1]/[(P_i/P_o)^3 - 1]\}}{T_c W_s},$$

where, F_c is the carrier gas flow-rate (ml/min); P_i is the inlet pressure (Pa); P_o is the outlet pressure (Pa); T_c is the column temperature (K); W_s is the weight of the active carbon (g); t_R is the retention time (min); t_M is the dead time(min).

The results of V_g are shown in Table 1.

Table 1 Breakthrouth volume V_g of the volatile compounds at various temperatures and V_g(ml/g) at 35℃

T_c, ℃	V_g(ml/g) × 10^3			
	Methanol	Ethanol	Acetone	*n*-Pentane
102	0.052	0.355	0.708	
125	0.034	0.151	0.234	
150				1.479
152	0.023	0.071	0.078	
160				1.122
170				0.549
35	0.213	5.37	29.9	6290

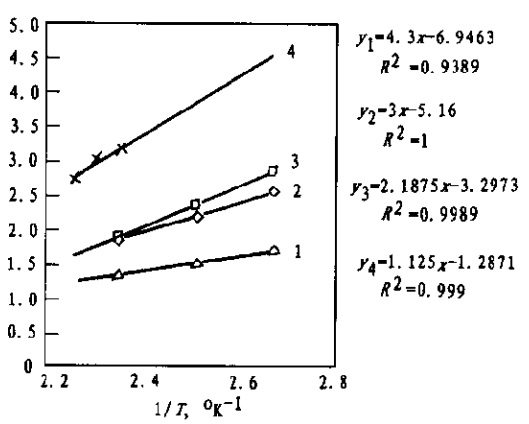

Fig.3 The relationship between logarithm V_g of the breakthrough volumes (V_g) of volatile compounds on charcoal column and the reciprocal of the column temperature (K)
1. methanol; 2. ethanol; 3. acetone; 4. *n*-pentane

Fig. 3 shows the relevance of $\log V_g$ to $1/T_c$. The V_g of the components on charcoal (at 35℃) is calculated with the extrapolation method according to the data of $\log V_g$ of methanol, ethanol, acetone and pentane against the corresponding column temperatures. It is demonstrated that V_g(35℃) if pentane is the largest among these compounds. The results have been obtained seem to be consistent with our recovery data: higher V_g corresponds to stronger absorbability and lower recovery. While the order of experimental recovery is methanol > ethanol > acetone > *n*-pentane.

3.3 Analysis

After being purged with pure N_2 heated at 250℃, the charcoal tube is kept unsealed for more than 20 minutes at room temperature. Then it is examined to determine if there are any components adsorbed from the ambient atmosphere. The blank test shows that nothing is adsorbed if without a stream of gas passing through the tube.

The calibration curves were constructed according to the results of the peak heights on the GC chromatograms by injecting 50-300μl each of 1.58μg/ml gas standard with a gas-tight syringe on sampling of GC shown in Fig. 4.

The calibration curves are linear over the concentration range of interest, at least in the range of 0.05—5200 ng with linear regressive coefficients > 0.98. Higher doses were not analyzed

because the level in human exhalation could not be that high.

The minimum detection limits for the four compounds were 20—60 ng.

The reproducibility was ± 5% ($n = 8$) for 5200 ng with syringe of max. volume 500μl; ± 5%—15% ($n = 8$) for 50—160 ng with syringe of max. volume 10μl.

3.4 Practical example

The analyses of human breath have become more and more conspicuous recently. Especially they were used in the early medical diagnoses to find out what disease a person possibly had. They were used in toxicology to understand the effect of the environmental contaminants on human beings (Flakensson, 1989), or to monitor cancer and diabetes.

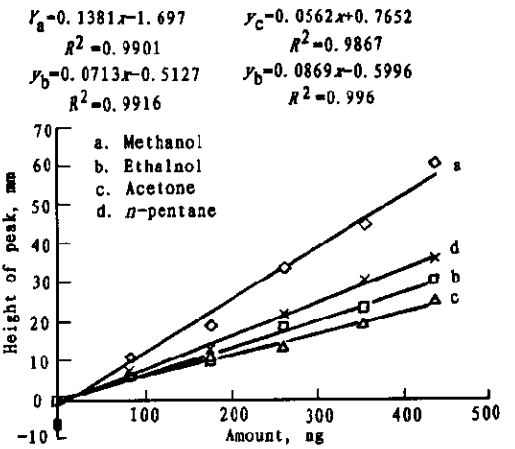

Fig. 4 The calibration curves made by using pre-column with charcoal on GC CHROM 4

a. methanol; b. ethanol; c. acetone; d. *n*-pentane

The results of realistic samples presented in Table 2 show that the amounts of compounds in human exhalation may be influenced by the respective environmental concentration, but not significantly. The concentrations of acetone and pentane in exhalation may reflect the individual health condition.

Table 2 The concentration of ambient air and human exhalation at different places and times

Sample	Sampling site	Concentration, ng/ml			
		Methanol	Ethanol	Acetone	*n*-pentane
Air	Chem. lab.	0.4—22	0.5—23	1—7	0.2—0.3
	Corridor	7.6	5.1		
Breath	Chem. lab	0.3, 2.2	0.4, 1.9	0.8	0.1—0.3
	Outside of chem. lab				
	1 h later	0.05	0.2	0.5	0.2
	2.5 h later	0.09	0.7	0.5	0.3
	15 h later	0.1	0.3	0.4	0.3

4 Conclusions

A rapid, sensitive and practical analytical technique for some volatile low molecular weight compounds in human exhalation taking methanol, ethanol, pentane and acetone as examples is discussed in this paper. The results may be considered as bio-markers to reveal the effect of environmental pollutants on human breath. In case that there is an obvious difference of the concentration of some target compounds, such as acetone and pentane in exhalation respired between healthy and sick persons, it may be possible to disclose some diseases or to part monitor the exposure to certain contaminant. In summary, this assay is an easier and more sensitive method

compared with those using mouth-cap and sample bags, because of the analytical range 0.05—5200 ng with linear regressive coefficient >0.98, the recoveries of methanol, ethanol, acetone and *n*-pentane respectively 100%, 85%, 75% and 70% and the detection limits 20—60 ng with precision ±5%—15% ($n=8$).

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