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SIMPLE INTERFACE FOR TRANSFERRING HIGH-BOILING COMPOUNDS FROM SAMPLE ADSORPTION TUBES ONTO CAPILLARY GAS CHROMATOGRAPHIC COLUMNS

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SUMMARY

The description and performance of a simple and easily made interface for transferring high-boiling compounds from sample adsorption tubes onto capillary columns is described. Results obtained with diphenylamine, fenitrothion, cocaine, halogenated pesticides and polychlorinated biphenyls are presented. The quality of injection obtained with this interface is equal to that obtained using conventional injection and splitless systems. Use of the interface with on-adsorber derivatization of amphetamine, followed by capillary gas chromatography–mass spectrometric analysis is also reported.

INTRODUCTION

Samplers for monitoring indoor and outdoor air have been extensively developed during the last decade. They consist, in part, of tubes (*ca.* 75 mm × 6.4 mm O.D.) made of glass or stainless steel. The tubes are filled with a solid adsorbent packing material, such as charcoal, Tenax, molecular sieve, silica gel, etc. During monitoring, the tube sampler is connected to a suction pump. A controlled flow of ambient air is drawn through the tube, and contaminant vapours and gases are adsorbed onto the packing material. This allows "spot" sampling or measurement of very low vapour concentration. The tubes may also be used to adsorb vapour phase samples by diffusion.

Once the air sampling has been completed, the collected contaminants are quantitatively displaced from the packing, either thermally or by leaching with a suitable solvent, and analyzed by gas chromatography (GC). Analysis by thermal desorption directly into the gas chromatograph is much faster and more sensitive than that obtained through solvent extraction.

Satisfactory single stage[1] and two stage[2] thermal desorption techniques to transfer trace organic vapours from sample adsorption tubes onto packed GC columns have been available for sometime. Raschdorf[3] reported on the use of a syringe needle filled with Tenax for trapping and injection of vapour samples into packed GC columns.

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However, in attempting to utilize the much greater resolution obtained by capillary chromatographic columns, a major problem arises with the thermal desorption of sample adsorption tubes: for proper desorption a carrier gas flow-rate of about 30 ml/min is required, whereas the optimum flow for capillary column operation is 1–5 ml/min.

A number of sample adsorption tubes–capillary column interfaces have been developed. Some are integrated in the GC and require a hardware modification of the injector system of the instrument[3,4]; others are stand alone units and require a heated transfer line between the adsorption tube and the GC oven[5].

We have developed a thermal desorption apparatus for transferring high-boiling compounds from sample adsorption tubes onto capillary columns. It is also suitable for on-adsorber derivatization of organic compounds. The interface is simple and can be easily constructed from readily available materials. The description and evaluation of the interface is the subject of this article.

EXPERIMENTAL

Adsorption tubes

The adsorption tubes used in this study were constructed of glass tubing (7.5 cm × 6.3 mm O.D. × 4 mm I.D.) with a small restriction in the middle, and contained a small amount of Tenax-GC (35–60 mesh), *ca.* 30 mg. The adsorbent material was held in place with plugs of silanized glass wool. Prior to use, the tubes were conditioned for 30 min by heating to 250°C in a helium stream at a flow-rate of 30 ml/min. The adsorption tubes were used for injection of both liquid and vapour samples.

For vapour sampling, a trace vapour generator employing dynamic dilution of vapours and a "pumped" sampling method were used[2]. In a typical liquid injection, 1 μl of a standard solution is deposited with a syringe on the solid adsorbent, and after evaporating the solvent by passage of a carrier gas flow for a few seconds, the sample is analyzed in the same manner as an air sample.

Standard solutions of diphenylamine, fenitrothion, cocaine, amphetamine and acetylamphetamine were prepared in *n*-hexane, while the solvent for Silvex methyl ester, Aldrin and the Aroclor mixture was 2,2,4-trimethylpentane. Solvents were distilled-in-glass grade from Caledon.

Chemicals injected or collected on the Tenax adsorbent were analyzed by capillary GC as described below.

Description and operation of sample desorption apparatus

The sample desorption apparatus[6] is shown schematically in Fig. 1. It makes use of the inner walls of a syringe needle as a trapping interface between the main sample tube and the capillary column. During the desorption cycle, the sample tube (F) is enclosed between two perforated PTFE caps (B and G). A helium gas stream (H) is allowed to flow through the sample tube. The needle of a gas-tight syringe (Hamilton 1801 N) is inserted about 1 cm in the PTFE cap (B) (vapour tight conditions are insured), the plunger being removed as shown in Fig. 1. The aluminium heating block (D) is then rested on the adsorption tube (250°C for 2–3 min). The deposited or collected chemicals are vapourized by the action of heat and flushed

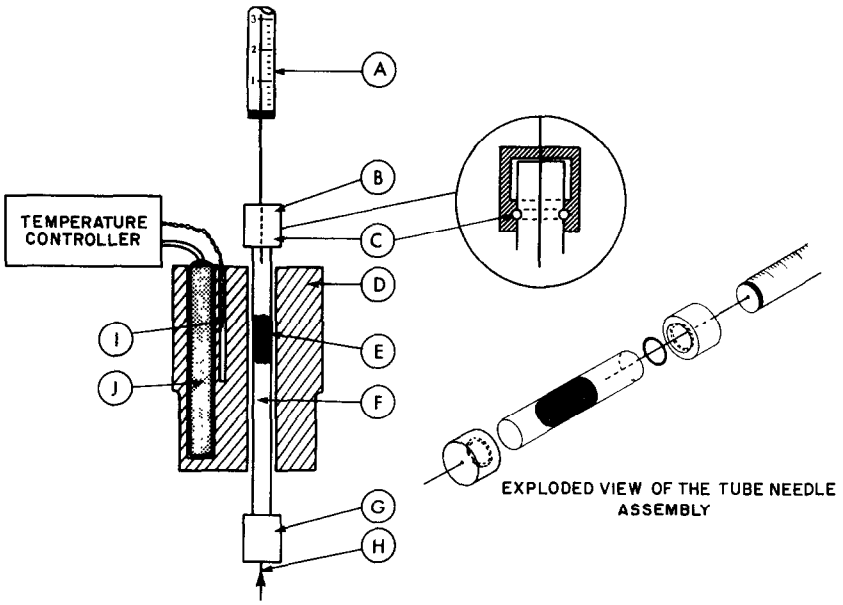

Fig. 1. Schematic drawings (exploded view and vertical cut) of the sample adsorption tube-capillary column interface. A = gas-tight syringe (plunger removed); B and G = perforated PTFE caps; C = O-ring; D = aluminium block; E = adsorbent; F = sample tube; H = carrier gas; I = thermocouple; J = heater.

with the carrier gas stream (30 ml/min) to the inner cold walls of the syringe needle, where they are trapped, while the carrier stream is vented through the barrel bore. No special cooling is applied to the exposed portion of the needle; due to the little mass flow of the carrier stream, the stainless-steel walls of the needle stay relatively cool.

For injection, the needle is withdrawn from the PTFE cap (B). The plunger is inserted in the syringe down to the midpoint and a conventional septum injection into the GC is performed. The heated injector port vapourizes the chemicals trapped in the needle of the syringe upon insertion through the septum; simultaneously, the plunger is fully depressed driving the vapours into the carrier stream of the GC (*ca.* 1 ml/min).

Chromatographic analysis

Two GC instruments were used, a Tracor 570 and a Hewlett-Packard HP 5790A, each fitted for capillary operation in the splitless mode, and with capacity for integration.

The Tracor gas chromatograph was equipped with a nitrogen-phosphorus detector and an electron-capture detector. The HP 5790A gas chromatograph was coupled to an HP 5970A mass selective detector. The experimental parameters and GC conditions are presented in Tables I and III.

Polychlorinated biphenyl vapour source

A continuous stream of polychlorinated biphenyl (PCB) vapours in air was

generated by passage of a low flow of nitrogen through a U-tube containing glass beads wet with Aroclors 1254 and 1260. This vapour stream was mixed with a larger flow of air[7] to achieve a controlled dilution ratio of the equilibrium vapour pressure of the PCBs in the test stream. With the U-tube thermostated at 0°C and a dilution ratio of 1/500, PCB concentrations of the order of 100 ng/m^3 were obtained. In sampling the test stream, adsorption tubes were maintained at room temperature, sampling time was 10 min and the sampling flow-rate was 500 ml/min.

On-adsorber derivatization of amphetamine

Amphetamine (1 μl, containing 50 ng/μl) was deposited with a syringe on the adsorbent material in the sampling cartridge. After evaporating the solvent by passage of a carrier gas flow for a few seconds, 1.5 μl of acetic anhydride were deposited

TABLE I

CONDITIONS AND PRECISION OF THE CHROMATOGRAPHIC SYSTEM: CAPILLARY GC APPLICATIONS

*Compound and amount injected**	*GC conditions*	*Average*** t_R *(min)*	*R.S.D. (%)*	*Average amount (area units)*	*R.S.D. (%)*
Diphenylamine (2 ng)	Tracor 570 GC–NPD***, column, DB-1 15 × 0.25 mm I.D. Fused silica. Carrier gas, helium (p = 10 p.s.i.); make-up gas, helium, 30 ml/min; column oven temperature, 60°C (30 s), then at 6°C/min to 130°C. Injector and detector temperature, 200°C.	9.59	0.1	141450	7.0
Fenitrothion (5 ng)	Same as above. Column oven temperature, 60°C (60 s), then at 20°C/min to 150°C and at 6°C/min to 235°C. Injector and detector temperature, 250°C.	9.01	0.2	366300	5.8
Cocaine (10 ng)	Same as fenitrothion	12.33	0.19	312090	7.7
Silvex methyl ester (500 pg)	Tracor 570 GC–ECD; Column, SE-54, 15 m × 0.25 mm I.D. fused silica. Carrier gas, nitrogen (p = 10 p.s.i.); make-up gas, nitrogen, 30 ml/min; column oven temperature, 100°C (1 min), then at 20°C/min to 150°C (0.1 min) and at 5°C/min to 200°C (20 min); injector temperature 225°C detector temperature 350°C.	9.59	0.09	119480	2.2
Aldrin (200 pg)	Same as Silvex methyl ester	13.23	0.08	54648	4.9

* 1 μl sample solutions were deposited on the adsorbent.
** Number of determinations, n = 5.
*** Fuel gas for NPD, hydrogen, 2.5 ml/min, air 150 ml/min.

on the same end of the Tenax adsorbent às that of the preceding drug sample. The adsorption tube was installed in the sample desorption apparatus, the end where the chemicals were deposited facing the carrier stream, and purged with a stream of helium for 5–6 s at 250°C, *i.e.*, PTFE cap (G) is on; PTFE cap (B) is off. On-adsorber acetylation took place and Tenax acted as a short chromatographic column. It retained the acetylated derivative while allowing the excess reagent to be vented to ambient. The block heater was removed and purging with the carrier gas was contained for 2 min. After evaporating the unreacted acetic anhydride, the adsorption tube was capped with PTFE plug (B), the needle inserted in the cap as shown in Fig. 1 and the amphetamine derivative transferred to the inner walls of the needle by thermal desorption. Heating time was 2 min at 250°C, and the carrier flow-rate was 15 ml/min.

RESULTS AND DISCUSSION

The performance of the interface was evaluated using a number of relatively non-volatile compounds and with a mixture of PCBs. Nanogram and picogram quantities of nitrogenous and halogenated compounds, respectively, were deposited on the absorbent, transferred to the needle by thermal desorption and subsequently injected and analyzed by capillary GC under temperature programmed conditions; the results are presented in Table I. The retention times (t_R) varied by less than 0.3%. With all compounds investigated, the quality of injection obtained with this interface was equal to that obtained, under the same conditions, using conventional splitless injection of a 1-μl solution of the same compound. The results of some initial quantitative measurements are also presented in Table I.

Injection of PCBs

Fig. 2 shows representative chromatograms of (a) direct liquid injections and (b) vapour source analyses of the same Aroclor mixture obtained under identical capillary GC–electron capture detection (ECD) conditions. Vapour samples collected on the Tenax adsorbent were transferred to the needle, and subsequently injected into the gas chromatograph. In Fig. 2 differences between the vapour and liquid signatures are evident, and attest to the fact that the partial pressure of a particular component in the vapour phase (t_R = 6.96, 9.21 and 9.53 min) may far exceed the mole fraction in solution, and that low-boiling chlorinated organic compounds (t_R = 2.93 and 3.22 min) are not effectively trapped on the inner walls of the needle; however, no differences in peak shapes and separation are observed. The reproducibility was tested by depositing with a syringe 2-μl portions of PCB mixture on the Tenax adsorbent, evaporating the solvent prior to thermal desorption and transfer of the PCBs to the needle, and analyzing by capillary GC as described above. The data in Table II show adequate reproducibility of peak areas and excellent reproducibility of retention times. The interface can be used for monitoring the presence of PCBs in the flue stack of industrial incinerators. It is more appropriate to threshold sensing of target chemicals rather than to quantitative trace analytical applications.

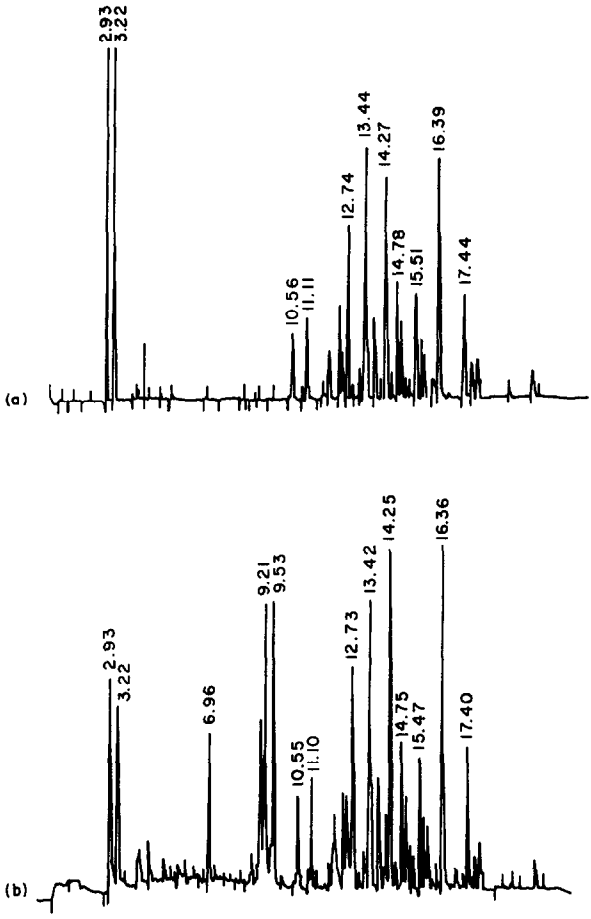

Fig. 2. Comparison of chromatograms from (a) direct liquid injection (b) vapour source sample of 1:1 mixture of Aroclors 1254 and 1260. Chromatographic conditions: Tracor 570 GC–ECD; SE-54, 15 m × 0.25 mm I.D. fused silica. Column oven temperature, 100°C (1 min), then at 20°C/min to 200°C (0.1 min), then at 5°C/min to 225°C (20 min). Carrier gas, nitrogen (10 p.s.i.), make-up gas, nitrogen (30 ml/min).

TABLE II

REPRODUCIBILITY OF RETENTION TIMES AND PEAK AREAS OF POLYCHLORINATED BIPHENYL MIXTURE

*Average** t_R *(min)*	*R.S.D. (%)*	*Average amount (area units)*	*R.S.D. (%)*
10.56	0.1	25835	7.4
11.11	0.12	31731	3.4
12.74	0.08	75293	5.9
13.43	0.08	90067	8.6
14 25	0.07	88779	10.8
14.77	0.1	39412	10.3
15.49	0.07	28347	8.6
16.38	0.08	64051	12.4
17.43	0.07	18763	9.3

* Number of determinations, $n = 5$.

On-adsorber derivatization of amphetamine and GC–mass spectrometry (MS) applications

We have recently reported on the detection of amphetamine in air by solid adsorbent preconcentration and packed column GC analysis[8]. In an attempt to utilize the much greater resolution obtained by capillary GC columns, the transfer–injection procedure described above was used with amphetamine. Initial results from GC and GC–MS analyses of standard solutions of the drug (50–500 ng) were not satisfactory. Although the retention time reproducibility was very good, significant sample loss and variable recoveries for the amine were observed. The most likely explanation is that the sample was not effectively trapped onto the needle inner walls, the carrier gas may have carried large amounts of the more volatile amphetamine into the cooler upper part of the syringe barrel where condensation occurred.

Numerous derivatization procedures for amphetamine have been developed[9]. On-column and injector port derivatization schemes have also been reported[10,11];

TABLE III

CONDITIONS AND PRECISION OF THE CHROMATOGRAPHIC SYSTEM: ON-ADSORBER DERIVATIZATION OF AMPHETAMINE/GC–MS ANALYSIS

Compound and amount injected	*GC–MS conditions*	*Average* t_R (min)*	*R.S.D. (%)*	*Total abundance (arbitrary units)*	*R.S.D. (%)*
Amphetamine (150 ng)	Column, OV-101, 12 m × 0.25 mm I.D. fused silica. Carrier gas, helium (p = 8 p.s.i.); interface temperature 275°C; column oven tempeerature, 80°C (1 min), then at 5°C/min to 115°C. Injector temperature 280°C. Mass spectrometer conditions: initial mass, 30 a.m.u.; final mass, 200 a.m.u.; scanning rate, 690 a.m.u./s; and peak detection threshold, 250 units.	5.90	0.2	Erratic results	–
Amphetamine (50 ng) + acetic anhydride (1 5 μl)	Column, same as above; oven temperature, 100°C (1 min), then at 10°C/min to 180°C. Mass spectrometer conditions for scanning analyses: initial mass, 30 a.m.u.; final mass, 250 a.m.u.; scanning rate 690 a.m.u./s; and peak detection threshold, 250 units. SIM analyses: ions monitored 43, 44, 86, 91, 118 and 117 a.m.u.; selected ion window size 0.5 a.m.u.	8.02	0.22	16081	13.3
Amphetamine acetate derivative (50 ng)	Same as above	8.02	0.14	15114	9.8

* Number of determinations, n = 5.

they are based on the coinjection of the drug and excess reagent into the gas chromatograph.

It is possible, however, to use the interface reported here for on-adsorber derivatization of organic compounds prior to transfer and injection into the capillary GC system. It provides a simple mechanism for the separation of excess reagent and other low-boiling interfering compounds from the newly formed derivative.

When amphetamine was reacted with acetic anhydride, and the less volatile acetylamphetamine transferred to the needle and subsequently injected and analyzed, satisfactory recoveries were obtained (Table III). GC–MS analysis showed a peak retention time and a mass spectrum identical with those for amphetamine acetate derivative prepared in solution. Since the application at our laboratory only requires the detection of the presence of amphetamine, derivatization yields were not thoroughly investigated; however, an amount of 1.5 μl acetic anhydride was satisfactory for levels of amphetamine of 100 ng and less.

The acetyl derivative of the amine was chosen for study because of its chemical simplicity. The acetylation procedure is simple, rapid and economical. The excess acetic anhydride is readily removed by purging with a carrier gas stream and is not released in the chromatographic system. Furthermore, the acetyl derivative can be effectively trapped in the needle. This area of research is still largely unexplored and work is in progress to study similar and different chemical reactions for their potential application to on-adsorber derivatization techniques.

On the basis of these initial studies it is concluded that the interface described herein is suitable for qualitative and semiquantitative trace analysis of high-boiling organic compounds. It provides a simple means of transferring these chemicals from sample adsorption tubes onto capillary GC columns. It is especially suitable for injection of large volume liquid samples and on-absorber derivatization, since the solvent or excess reagent, respectively, is purged and does not enter the column. It is anticipated that the system can also be used for medium and low-boiling compounds by suitably coating the inner walls of the needle with a sorbent material.

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