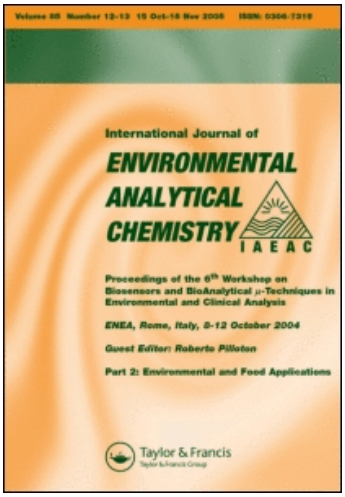

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Direct Coupling of a Gas-Phase Enrichment Column with the Liquid Chromatograph

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An on-line transfer from an enrichment column into a column of the liquid chromatograph was solved for solutes enriched in a gas-solid system. A procedure permitting the separation of some groups of organic compounds significant for the characterisation of components with offensive odour from exhaust gases of diesel engines was verified.

Hydrophobic copolymers were applied to the enrichment of the components under analysis. The influence of the volume of the passed sample on the shape of the desorption peak was investigated with the use of a hydrocarbon phase as the strongest mobile phase for a given type of sorbent in the enrichment column. The desorption course showed the necessity of using a pre-concentration column for which the hydrocarbon is a weak mobile phase and the necessity of applying a binary mobile phase to the separation of oxygen containing compounds in the liquid chromatograph.

KEY WORDS: Odour analysis, enrichment technique, on-line GC-LC.

INTRODUCTION

With growing interest of chemists in the components present in various mixtures in ever decreasing concentrations also grows the complexity of mixtures of substances subjected to analysis. A total identification of all components in the mixtures is impossible under these circumstances and is generally not required. For both detailed identification and good characterisation of the mixtures a group separation of components is often necessary. The application of liquid chromatography is known to be the most advantageous for the purposes of group separation.

A problem of the group separation of the components concentrated from the gaseous phase in an enrichment column was faced when components with offensive odour were studied in exhaust gases of diesel engines. On the basis of an adopted standard method[1] the components of the exhaust gases should be classified into three groups, i.e., a non-recorded fraction of paraffinic hydrocarbons, an evaluated fraction of aromatic hydrocarbons and a fraction of oxygen-containing organic compounds. The last fraction, representing the most significant component of the offensive odour, can further be separated by the method suggested in the present paper.

PROBLEM ANALYSIS

The group separation of the components adsorbed in the enrichment column from the gas—in the present case from the exhaust gases of a diesel engine—is associated with a number of complications. Thermal desorption of the components from the enrichment column is out of the question because of the presence of high-boiling components in the mixture under analysis and a risk of thermal decomposition of the applied organic macroporous sorbent. Extraction with a liquid and subsequent analysis in the liquid chromatograph is possible; however, it is associated with certain disadvantages. The sample taken for the purpose of the group separation is considerably diluted, and the process cannot be automated and necessitates longer time.

The authors therefore decided to apply a direct coupling of the enrichment column for the gaseous phase to the liquid chromatograph. Some technical questions and problems associated with chromatographic system had to be solved. In the course of the desorption of substances from the enrichment column with a liquid, gas bubbles are generated in the desorption liquid used, making detection impossible and, simultaneously, the risk is run of the possibility of disturbing the layer of the sorbent in the analytical column. Washing with a gas that is highly soluble in the solvent (the mobile phase of the liquid chromatograph) was therefore used prior to the introduction of the liquid solvent. This system, e.g., *n*-butane as a scavenging gas and *n*-heptane as a mobile phase, does not give rise to bubble formation in spite of a considerable pressure drop in the detector cell and detection is thus not disturbed.

The principle of the application of the enrichment technique to the atmosphere or to significant emissions makes demands on the properties of the sorbent used in the enrichment column and determines thus also the range of the solvents that can be used. The situation can be characterised schematically as follows:

Properties of the sorbent used in the enrichment column with the fluid phase:

the gas phase	the liquid phase
small adsorption of water	"reversed" phase
great permeability	great variance of peaks
(large diameter of the	(small number of
sorbent grain, large	theoretical plates that
diameter of the column)	can be obtained)

The use of a hydrophobic sorbent in the enrichment column[2] is unavoidable since in the majority of samples of both atmosphere and gaseous emissions, significant from the view-point of environmental protection, water vapour is present, mostly in a considerable excess in relation to the components under determination. The hydrophobic sorbent in the enrichment column, which is called the "reversed" phase in liquid chromatography, practically eliminates the application of the reversed phase in the separation system of the liquid chromatograph. In order to desorb the components from the enrichment column in a sufficiently small volume, a solvent must be used that behaves towards the sorbent in the enrichment column as a very strong mobile phase.[3] From the above mentioned facts it follows further that no stationary phase of analogous character can be exploited in the separation system since the solvent used will always be rather a strong mobile phase for it. In consequence of this neither a step-wise gradient nor a displacement technique will be usable in the separation system, which is usually important in the case of trace analysis. On the contrary, for a polar sorbent (sigel) used in the analytical column, the solvent used in the enrichment column will represent too weak a mobile phase to permit the separation of the mixture during an acceptable time period. This is why the authors considered it necessary to use the solvent with a moderator that would increase the strength of the mobile phase towards the sorbent of the analytical column.

For the group separation of aromatic and oxygen-containing organic substances which are desorbed from the enrichment column simultaneously, the use of a short column with silica gel—a so-called concentration column is advantageous. In this column the desorption of aromatic compounds proceeds practically without any retention with the hydrocarbon mobile phase while oxygen-containing compounds are displaced from the column only by the mobile phase strengthened with the moderator and transferred into the analytical column in a sufficiently small volume.

EXPERIMENTAL

The experimental equipment was assembled from principal parts of the liquid chromatograph with accessory multiway valves which made it possible to change the flow direction of the mobile phase on the one hand and to change the mobile phase itself on the other. The selection of various parts permitted the equipment to be adapted easily to different measurements.

A MC 300 (Mikrotechna, Prague, Czechoslovakia) and an VLD 300 (Development Workshops, the Czechoslovak Academy of Sciences, Prague, Czechoslovakia) pumps were used as sources of the mobile-phase flow. A differential UV detector with the wavelength of 254 nm and the cell volume of 10 μl (Development Workshops, the Czechoslovak Academy of Sciences) was used for detection, in some measurements also an RB-1 differential refractometer (Development Workshops, the Czechoslovak Academy of Sciences). A TZ 4208 recorder with the range of 10 mV or an EZ-11 recorder with the range of 5 mV (both manufactured by Laboratory Instruments, N.E., Prague, Czechoslovakia) was used to record the peaks. A damper of pressure pulses and a manometer were connected to the MC 300 pump.

The following columns were applied in the measurements:

The enrichment column was made of stainless steel. Its inside diameter was 10 mm and the length was 70 mm. It was equipped on both ends with PTFE seals with holes for the connection to inlet capillaries.[4] It was packed with Chromosorb 102, 60–80 mesh (John Manville, Celite Div., U.S.A.). It was connected to the instrument with the aid of metal capillaries (equipped with recesses for cup nuts) having an inside diameter of 1 mm and additional coupling by means of PTFE hoses.

The concentration column was made of stainless steel tube with an inside diameter of 2 mm and length of 100 mm. The mobile phase inlet was realised via the injection port equipped with an injection septum. The column was packed with either Porasil B, 37–75 μm (Water Ass., Framingham, U.S.A.) or glass beads, 70–90 μm, or silica gel CH, 50–63 μm (LACHEMA, N. E., Brno, Czechoslovakia). The column was placed in a bath in which it could be activated at a temperature of ca. 360 K.

The analytical column was made of stainless steel tubes in two versions. One of them had an inside diameter of 4 mm, the other 6 mm; the length of both of them was 100 mm and both were packed with Silasorb 330 with particle diameter of 10 μm (LACHEMA).

The arrangement of the instrument is illustrated schematically in Fig. 1. It makes possible the following operations:

1) Switching on and off of the enrichment column [1] in the course of

the flow of the mobile phase (*n*-heptane) from the pump [10] through the valve [3] and the concentration column [5].

2) Washing of the enrichment column [1] with *n*-butane through the valves [3] and [2], again [3] to the flask [4] with *n*-heptane.

3) Intake of *n*-heptane from the flask [4] through the valve [3] into the enrichment column [1] up to the valve [2].

4) Simultaneously with the operations mentioned under points 1 and 3 *n*-heptane passes from the pump [10] through the valve [3] into the

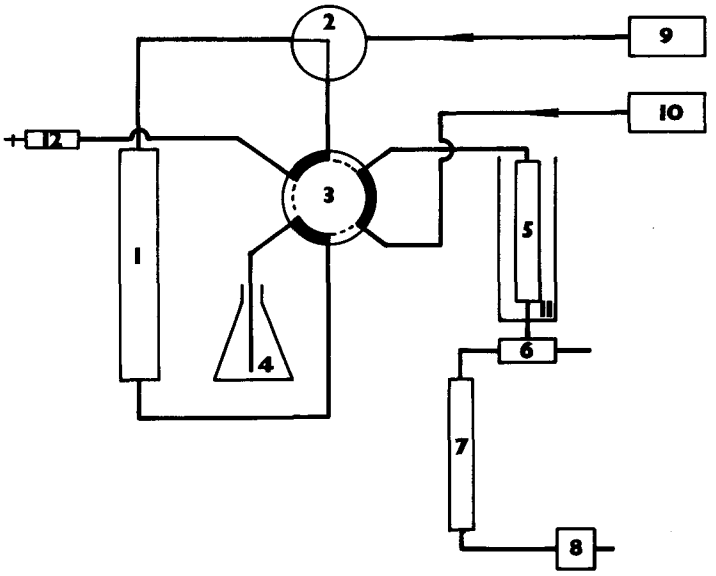

FIGURE 1 Schematic of the apparatus. 1-enrichment column, 2-three-way stopcock, 3-six-way stopcock, 4-mobile phase reservoir (n-C_7H_{16}), 5-concentration column, 6-column switching, 7-analytical column, 8-UV detector, 9-pump with *n*-heptane + *i*-propanol, 10-pump with *n*-heptane, 11-water bath, 12-injection syringe (50 ml).

column [5] from there either directly into the waste (at the activation of the column or washing with the mobile phase) or into the column [7].

5) By switching the valve [3] into the second position (dashed line in Fig. 1) the mobile phase passes via the valve [3] to the enrichment column [1], the valve [2], again the valve [3] into the concentration column [5] and from there to waste or into the column [7] and into the detector [8].

6) The valve [2] switched into the second position (dashed line in Fig. 1), the mobile phase with the moderator passes from the pump [9] via the

valves [2] and [3] into the concentration column [5] and from there into the column [7] and into the detector [8] or from the column [5] directly to waste.

Chemicals

n-Heptane (VEB Labor Chem. Apolda, GDR) was purified with activated alumina. *i*-Propanol (LACHEMA) was of normal quality. Testing substances, *m*-xylene, benzydiphenyl, acetophenone, fural, 2-methyl-4-ethylphenol and *m*-cresol were of technical grade.

RESULTS AND DISCUSSION

In order to analyse exhaust gases 3–7 l of emissions from diesel engines were taken at a speed of ca. 1 l/min. In the course of washing of the enrichment column with *n*-butane no desorption of the components under analysis occurred, as was verified experimentally.

In the enrichment column packed with Chromosorb 102 with a particle diameter of 0.1–0.2 mm an efficiency of 100–200 theoretical plates only can theoretically be obtained at a very low flow-rate of the mobile phase. A number of theoretical plates $n = 89$ was obtained experimentally at a flow-rate of *n*-heptane of 0.05 mm/s. The desorption was performed in practice at a flow-rate of 0.4 mm/s, when the efficiency was $n = 45$ only. Under these circumstances the inlet concentration pulse entering the separation section of the chromatography will obviously take up an inacceptably large volume. Retention volumes of oxygen-containing compounds on Chromosorb 102 can be diminished by either increasing the temperature or using a mixed mobile phase, as shown in Table I. For technical reasons it is not convenient to work at an increased temperature of the enrichment column. The application of a mixed phase is impossible since the separation of oxygen-containing compounds takes place in the concentration and the analytical columns. A high adsorption capacity of Chromosorb 102 causes the majority of the compounds under analysis to be adsorbed at the end of the enrichment column through which the gaseous phase with the sample entered. As a consequence of this it is important which end of the column will be used for the introduction of the liquid mobile phase in order to perform the desorption from the enrichment column. The volumes of the mobile phase required for the elution of the components that were obtained using different types of connection of the enrichment column to the liquid chromatograph are given in Table II. The outlet sample volume from the enrichment column represents a potential inlet of the sample into the separation section of the liquid chromatograph, i.e., the inlet of the separation column.

The effluent from the enrichment column is composed of the mixture of the compounds under analysis and the mobile phase which is a very weak mobile phase towards the adsorption packings of both concentration and analytical column. As a result of this only the fraction of paraffinic and aromatic hydrocarbons is eluted from the concentration column. Both of

TABLE I

Retention volumes of compounds on the enrichment column measured at different temperatures using mobile phases of different composition

	Mobile phase and temperature (ml, °C)								
Compound	n-C_7 25	n-C_7 55	n-C_7 70	n-C_7 89	n-C_7^+ 25	n-C_7^{++} 25	c-C_6^{+++} 25	c-C_6^{+++} 55	c-C_6^{+++} 70
m-Xylene	4.1	3.8	3.5	3.3	4.1	4.1	4.1	3.3	3.0
Benzyldiphenyl	6.3	5.0	4.6	3.7	6.5	6.4	5.0	3.8	3.2
Acetophenone	7.2	5.5	4.8	4.0	7.5	6.3	7.2	5.0	4.2
2-Methyl-4-ethylphenol	10.0	6.3	5.4	4.5	9.9	6.3	9.4	5.1	4.2
Fural	12.5	7.1	6.0	4.5	10.7	7.4	11.2	5.8	5.0
m-Cresol	16.0	8.4	7.0	4.8	13.9	6.6	14.3	6.1	5.0

n-C_7, n-heptane
n-C_7^+ n-heptane + 0.1 vol.% of i-propanol
n-C_7^{++}, n-heptane + 1.0 vol.% of i-propanol
c-C_6^{+++}, cyclohexane.

TABLE II

Elution of compounds from the enrichment column for different types of connection to the apparatus

	Peak width at half height (ml)	
Compound	A	B
m-Xylene	0.63	2.3
Acetophenone	0.70	5.5
m-Cresol	0.96	12.6

A, connection: gas inlet = solvent outlet
B, connection: gas inlet = solvent inlet.

them can be led—by means of column switching—directly into an UV detector, outside the analytical column, where the aromatic hydrocarbons only are detected. The portion of the sample containing oxygen compounds is strongly adsorbed on the silica gel of the concentration column and their retention volumes would be too large to be acceptable from the view-point of both analysis time and efficiency of the analytical

column on which the oxygen fraction is to be further separated. The stepwise gradient technique was therefore selected for the desorption of oxygen compounds from the concentration column and a mobile phase containing a moderator (*i*-propanol) was applied. The elution power of this mobile phase was determined for selected components and such a concentration of *i*-propanol was selected that made it possible to desorb all the components in a sufficiently small volume, while simultaneously using to advantage the separation capability of the concentration column.

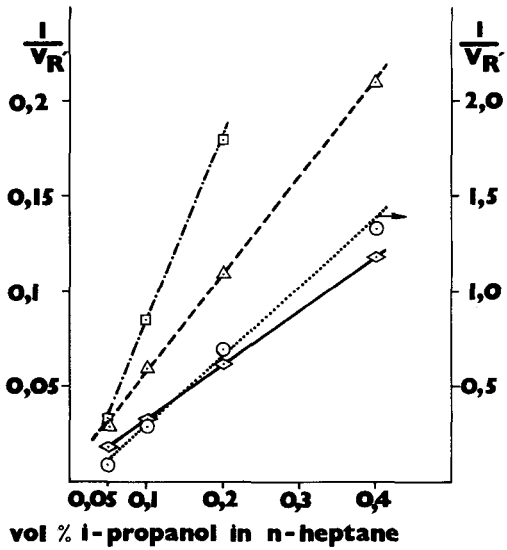

FIGURE 2 Reciprocal value of the retention volume correlated to the composition of the mobile phase. Solutes: ⊙, acetophenone; △, 2-methyl-4-ethyphenol; ⊡, fural; ◇, cresol.

Figure 2 shows retention volumes of some selected oxygen compounds depending on the concentration of the moderator in the mobile phase. The column switching between the concentration and the analytical columns provides at the same time isocratic conditions in the analytical column. The first volume of the effluent from the enrichment column is led through the concentration column outside the analytical column into the detector. The mobile phase in the analytical column, which consists of *n*-heptane containing 0.2–0.4 vol. % of *i*-propanol is thus not affected by the entrance of *n*-heptane from the concentration column and operates in the course of the separation of oxygen compounds in the isocratic regime. If the pure hydrocarbon mobile phase passed through the analytical column

the desorption of *i*-propanol from the analytical column would occur and an opposite concentration gradient would be established in the column for the separation of oxygen compounds proper. This phenomenon would occur even at an initial passage of the modified mobile phase through the concentration column when *i*-propanol from the mobile phase is adsorbed by the packing of the concentration column and it would enter the analytical column only in the moment of the frontal penetration from the concentration column. The use of the mobile phase containing the moderator, which is simultaneously the mobile phase for the analytical

TABLE III

Influence of the sampling system on retention and separation efficiency in the analytical column for the components of technical-grade *m*-cresol

Parameter	Peak no.	A	B	C	D
Relative retention time	1	0.194	0.209	0.351	0.297
	2	0.489	0.502	0.561	0.524
	3	0.596	0.595	0.640	0.619
	4	1.000	1.000	1.000	1.000
Number of theoretical plates	3	1421	1286	1995	1770
	4	872	888	1127	885

A, direct injection of the sample into the analytical column.

B, direct injection of the sample into the concentration column coupled to the analytical column (in isocratic regime).

C, sampling from the enrichment column—separation without the washing of the enrichment column with the modified mobile phase.

D, sampling from the enrichment column—separation of components after the washing of the concentration column with 2 ml of the modified mobile phase.

column, diminishes the volume of the mobile phase in which the solute enters the analytical column since conditions are established in the concentration column which are suitable for the step-wise gradient technique.

In the applied analytical column, packed with particles with a diameter of 10 μm, ca. 4100 theoretical plates can theoretically be obtained for a non-sorbed component with the ideal pulse solute inlet. Up to 1420 theoretical plates were obtained in practice for the component with capacity ratio $k = 9$.

Table III and Figure 3 demonstrate the influence of the entire applied system on the retention and the separation efficiency of the analytical column for selected components. The efficiencies obviously are not

influenced by the enrichment and the concentration columns. In case "C" somewhat higher retentions are caused by the absence of the moderator in the initial volume of the effluent from the concentration column. Since under these circumstances the effect of the gradient of the mobile phase appears, the apparent efficiency is somewhat greater in this case than in cases "A", "B" and "D". Cases "C" and "D" demonstrate the application of the entire procedure of the analysis, including sampling by means of the enrichment column.

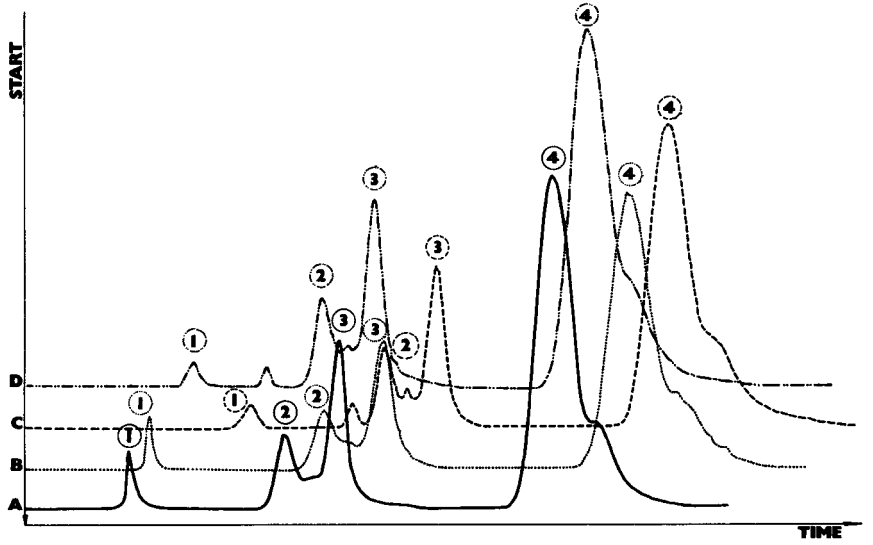

FIGURE 3 Chromatograms demonstrating the influence of the entire applied system on the retention and the separation efficiency. For symbols A, B, C, D, see Table III.

The procedure suggested above can thus be applied to the separation of principal significant groups of compounds in the sample under analysis, i.e., to the aromatic and the oxygen containing fraction. An additional separation of the oxygen fraction can simultaneously be obtained, which is significant for the purposes of the determination of the components with offensive odour.

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