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ENRICHMENT OF TRACE COMPONENTS FROM LIQUIDS BY DISPLACEMENT COLUMN LIQUID CHROMATOGRAPHY

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SUMMARY

In trace analysis an enrichment has to be carried out in general. In order to achieve an enrichment the trace components have to be transferred to a volume which is orders of magnitude smaller than the original one. Such a process is displacement chromatography which has not yet been investigated systematically as enrichment procedure.

In the present paper the fundamentals of enrichment by means of adsorption chromatography are discussed theoretically and investigated experimentally. The relationship between the enrichment factor and the change of the distribution coefficient is discussed for gradient elution and displacement chromatography. The limiting volume to which a trace component can be condensed is shown to be dependent on the mixing characteristics of the column. It is demonstrated that enrichment factors of the order of ten thousand can be obtained for polar as well as non-polar compounds using adsorbents with hydrophilic and hydrophobic surfaces, respectively.

INTRODUCTION

In trace analysis, very often an enrichment has to be carried out, otherwise the signals attainable from the initial trace concentrations would remain below the base-line noise level of the measuring instrument. In enrichment from liquids, the trace compounds are finally concentrated in a volume of solution that is aimed to be several orders of magnitude smaller than the original volume. Evaporation, extraction and adsorption followed by extraction of the adsorbent are the most widely used enrichment techniques. The most efficient means of exploiting the distribution between two phases for the enrichment of components would be expected to be chromatography.

Chromatographic enrichment techniques of trace species have been applied in the past to liquids[1–8] as well as to gases[9], but no systematic investigation or optimization of the procedure has been undertaken. The following characteristics have to be considered in the design of enrichment techniques: magnitude of the enrichment factor, degree and reproducibility of the yield, speed of operation, reliability of the apparatus, capability of automation and cost.

An enrichment of components by chromatographic techniques can be achieved in principle by non-isocratic elution methods as well as by the displacement method. The most commonly used enrichment techniques in elution chromatography are based on the increase in temperature in gas chromatography and the generation of a suitable

solvent gradient in liquid chromatography. In the chromatographic enrichment of trace components from liquids, the highest enrichment factors may be expected with the displacement technique, and this method was chosen therefore to be studied systematically.

THEORETICAL

In chromatography, the isocratic elution technique with pulse injection of the sample is usually used. In this technique, in principle the components of the sample mixture can be completely separated from each other but at the same time they are diluted with the eluent and, at the end, the concentration of the sample component has decreased.

In order to obtain an increase in the concentration of the sample components in chromatography, non-isocratic techniques have to be applied. Generally in gas chromatography the temperature of the column is increased during the separation in order to obtain an enrichment of sample components. In liquid chromatography the composition of the liquid phase fed to the column is changed in such a way that the sorption of the sample components by the stationary phase decreases. The change in the composition of the influent to the chromatographic column can result in two modes of chromatography: gradient elution and displacement, the latter being a limiting case of the first.

In Fig. 1, isocratic elution, gradient elution and displacement chromatography are shown schematically for a single component assuming a square-wave sample input and a step-wise change of the composition of the solvent.

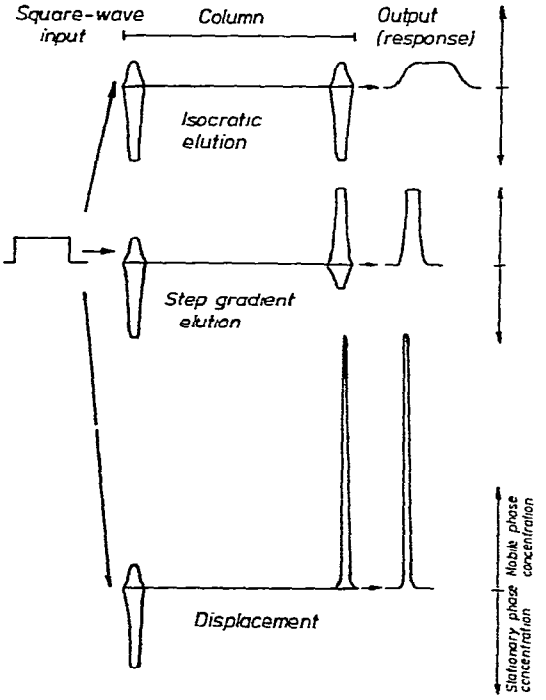

Fig. 1. Schematic representation of different types of chromatography.

In isocratic elution, the composition of the solvent is constant and the volume of the sample is compressed at the beginning of the column because of the sorption of the sample by the stationary phase. On the way through the column, the sharp flanks of the input square-wave become more diffuse owing to the chromatographic process. At the end of the column, the volume of the sample is increased again owing to desorption from the stationary phase according to the distribution ratio. As a final result, the sample is somewhat diluted at the flanks but is contained in nearly the same volume.

In step-gradient elution the process starts as in isocratic elution. After a given time, however, the composition of the column influent is changed in such a way that the sorption of the sample decreases. When the step gradient has passed the sample zone, the sample will occupy about the same column volume but a larger fraction will be present in the mobile phase. At the end of the column the sample volume is increased according to the decreased distribution ratio of the sample. As a result, the sample is taken up by a solvent volume which is smaller than the original sample volume, *i.e.*, the sample has been enriched.

Displacement chromatography also starts as in isocratic elution. After the sample has entered the column, however, the composition of the column influent is changed step-wise by adding a solvent or solvent component (the displacer), the front of which moves faster than that of the sample component and which reduces the distribution ratio of the sample to such an extent that it is forced to move together with the displacer front at the same velocity. In this manner the displacer front compresses the sample as the sample front moves more slowly than the displacer front. After a certain time, depending on the initial zone length of the sample, a steady state is achieved. The compression action of the displacer and the dispersion phenomena balance each other. Contrary to the step-gradient elution technique, the column volume taken up by the sample and also the distribution ratio are decreased. This results in a particularly high enrichment of the sample.

The mathematical description of displacement chromatography is difficult because of the non-linear character of the process. In the first theoretical approaches extensive simplifications were made[10,11]. A more rigorous treatment has been given recently[12], but so far it has not been possible to derive a theory that includes both the thermodynamic and kinetic effects. Limiting the theory to the steady state of displacement, a simple approach[10,11] can be used, which considers only the thermodynamic effects but is satisfactory for the discussion of the sample enrichment.

Displacement is observed in adsorption and ion-exchange chromatography for convex adsorption isotherms. In this case the front boundary of a component is self-sharpening. According to the theory of isothermal non-linear chromatography, the concentration velocity is determined by the first derivative of the distribution isotherm. For a convex distribution isotherm, therefore, the concentration velocity decreases with the concentration. On the other hand, broadening of the boundary occurs due to the kinetic phenomena. As a final result, thermodynamic and kinetic effects will balance each other when a particular sharp shape of the boundary is reached and a steady state will result.

The migration velocity of such a final boundary is determined by the mass distribution ratio of the component:

$$u_i = \frac{v}{1 + \kappa_i} \tag{1}$$

where

u_i = migration velocity of the stable front boundary of component i;
v = flow velocity of the mobile phase;

$$\kappa_i = \left(\frac{\text{amount of } i \text{ in the stationary phase}}{\text{amount of } i \text{ in the mobile phase}}\right) \text{ in equilibrium}$$

= mass distribution ratio, capacity factor.

After a certain time, the composition of the column influent is changed stepwise by feeding the displacer to the column. As for the trace species, a self-sharpening boundary of the displacer is formed. This front of the displacer moves faster than the front of the trace species. As a final result, the trace species is compressed to a narrow zone which moves with the displacer front at the same velocity, remaining at a constant width:

$$u_i = u_d \tag{2}$$

where

u_i = migration velocity of the final stable zone of the trace species i;
u_d = migration velocity of the stable front of the displacer.

Considering that both the distribution ratio of the trace species and the displacer depend on the concentration from eqns. 1 and 2 an expression is derived that gives implicitly the concentration of the trace species:

$$\kappa(c)_i = \kappa(c)_d \tag{3}$$

Eqn. 3 indicates that the trace compound is enriched up to the concentration at which its distribution ratio becomes equal to that of the displacer.

In order to develop the steady state, a minimum column length is needed. The front of the trace species must not leave the column before the displacer front has caught up. According to eqn. 1, the minimum length fraction of the column to be left for the development of the steady state is given by the expression

$$\frac{(\Delta z)_{\min}}{L} = \frac{1 + \kappa(c)_d}{1 + \kappa(c)_{i0}} \tag{4}$$

where

$(\Delta z)_{\min}$ = minimum column length needed to reach the steady state;
L = total length of the column;
$\kappa(c)_{i0}$ = distribution ratio of the initial concentration, c_{i0}, of the trace species.

In general, the displacer is either a pure solvent or a solvent component of high concentration. Under these conditions, the distribution ratio of the displacer approaches zero and only a small fraction of the column is needed for the development of the steady state.

EXPERIMENTAL

Apparatus

The chromatographic equipment used for the enrichment experiments included a high-pressure liquid chromatograph (Siemens S100) with a step gradient device (Siemens) containing two reservoir loops of 220 ml each, a multi-wavelength UV absorption detector (Waters 440) and a potentiometric recorder (Siemens, Kompensograph III). For the enrichment of trace components from volumes larger than 220 ml, a reciprocating diaphragm pump (Orlita DMP-AE) with a low-volume pulse damper (Orlita PD3-500) was used instead of the liquid chromatograph with a step gradient. The enrichment columns were constructed from stainless-steel tubing of length 250 mm and I.D. 3 mm and packed with hydrophilic or hydrophobic adsorbents.

For off-line UV absorbance measurements of effluent fractions collected at the outlet of the liquid chromatograph, a UV spectrophotometer (Beckman Acta V) was used with a cell of 3 ml.

Chemicals

The column packings used for the enrichment study were silica (LiChrosorb SI-60, Merck, Darmstadt, G.F.R.), 5 or 30 μm, for solutions in hydrocarbons, and octadecylsilica (LiChrosorb RP-18, Merck), 5 μm, for aqueous solutions.

The enrichment experiments were carried out with the following test samples: 1,2,5,6-dibenzanthracene (DBA) (purum, Koch-Light, Colnbrook, Great Britain) dissolved in 2,2,4-trimethylpentane (LiChrosolv, Merck), cyclohexane (LiChrosolv, Merck) or water (doubly distilled); and *p*-cresol (Austranal purum, Loba Chemie, Vienna, Austria) dissolved in cyclohexane (LiChrosolv, Merck).

The displacer solvents used were: dichloromethane (LiChrosolv, Merck) for LiChrosorb SI-60 columns and dioxane (LiChrosolv, Merck) for LiChrosorb RP-18 and LiChrosorb SI-60 columns.

Procedures

The liquid sample (aqueous solutions of trace compounds or solutions in hydrocarbons) is placed in the first reservoir loop of the step-gradient device, and the second loop is filled with the displacer liquid. Then the sample liquid is forced through the enrichment column by means of the pump of the liquid chromatograph using the solvent of the test solution as the pumping medium. During this period the trace components are stored in the stationary bed of the column. After a given volume of the sample has passed through the column, the pump is switched over to the displacer reservoir loop and the displacer starts to push the trace components to the end of the column. The effluent in the breakthrough area of the front of the displacer is collected and contains the enriched trace components.

If the sample volume is larger than the storage volume of the reservoir loop of the gradient device, the enrichment column is loaded directly from the sample container via a pump. After completion of the loading the sample container is replaced with a reservoir with the displacer solvent and the enrichment process starts. In this procedure the dead volume from the pump inlet to the column inlet must be small in order to avoid a significant dispersion of the front of the displacer.

If the concentration is not too high, the output curve of the trace species is determined by on-line measurement of the light absorbance of the column effluent at a given wavelength by means of a flow-through detector. At higher concentrations the column effluent is collected in fractions, diluted with solvent in a given ratio, and measured off-line batch by batch with a spectrophotometer. A fraction volume of a single drop of about 20 μl was used in order to approach the requirements[14] for an accurate representation of the output profile.

RESULTS AND DISCUSSION

Mechanism of chromatographic enrichment (displacement versus gradient elution)

In principle, displacement chromatography is the limiting case of gradient elution chromatography. In gradient elution chromatography, the composition of the eluent is changes in such a way that the capacity factors of the sample components decrease with time. As a result, their migration velocities as well as their zone heights increase whereas their zone widths decrease. The change in the solvent composition can be performed smoothly (*e.g.*, linear gradient) or abruptly (step gradient). In order to influence the migration of a sample component, the solvent gradient has to move faster than the sample component. When the solvent gradient runs over a sample component, part of the amount of it present in the stationary phase is expelled to the mobile phase. At the end of the column it is eluted in a smaller volume, which results in an enrichment.

In addition to the effect of the overall decrease in the capacity factor due to the change in solvent composition, a further zone compression occurs. This effect results from the fact that during the overriding of the solvent gradient the rear boundary of the sample component zone moves faster than the front boundary as the capacity factor of the sample component in front of the gradient is higher than that behind it. The zone compression and therefore the enrichment depend on the extent of the decrease in the capacity factor caused by the change in the solvent composition.

For a step gradient of the solvent composition, a limiting case exists in which the capacity factor of the sample component is decreased to such an extent that it moves with the same migration velocity as the step gradient, which means that the sample is accumulated in the region of the gradient. The steepness of the gradient determines the volume in which the sample is accumulated.

In Fig. 2 the transition from isocratic elution via step-gradient elution to displacement chromatography is demonstrated experimentally. The data corresponding to Fig. 2 are given in Table I. On dosing a large volume of the solution of a solute in the eluent into the column under isocratic conditions (Fig. 2a), the solute is eluted in a volume which is only slightly increased compared with the original sample volume owing to the dispersion of the flanks. The concentration plateau corresponds to the original concentration in the sample. If a solvent step gradient is introduced after dosing the sample, it can be seen that the solute is eluted in a volume which is smaller than the original sample volume and its concentration has been increased (Fig. 2b). It can be recognized that the decrease in volume and increase in concentration depend on the decrease in the capacity factor of the solute by the change in eluent composition (Figs. 2b and 2c). The shapes of the flanks of the output profiles are related to the shapes of the corresponding distribution isotherms[15]. If the change in

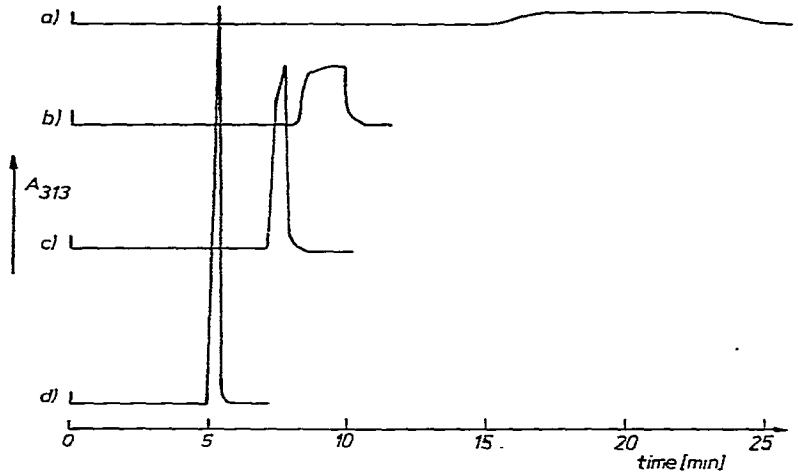

Fig. 2. Transition from isocratic elution to displacement chromatography. Column, LiChrosorb SI-60 (5 μm); sample, 2.5 ml of DBA solution in 2,2,4-trimethylpentane, 1 mg/l; flow velocity, 0.8 mm/sec. Column influent: (a) 2,2,4-trimethylpentane; (b) 2,2,4-trimethylpentane–dichloromethane (9:1, v/v); (c) 2,2,4-trimethylpentane–dichloromethane (8:2, v/v); (d) dichloromethane.

TABLE I

COMPARISON OF ENRICHMENT BY GRADIENT ELUTION AND DISPLACEMENT CHROMATOGRAPHY

Sample, 2.5 ml of DBA solution in 2,2,4-trimethylpentane (1 mg/l); column, LiChrosorb SI-60 (5 μm); column influent, flow velocity 0.8 mm/sec.

Composition of column influent, step gradient from 2,2,4-trimethylpentane to	κ_t	*Output peak height (absorbance units)*	*Output peak width (ml)*	*Enrichment factor*
2,2,4-Trimethylpentane	2.7	0.030	2.9	1
2,2,4-Trimethylpentane–dichloromethane (9:1, v/v)	0.64	0.115	0.65	3.8
2,2,4-Trimethylpentane–dichloromethane (8:2, v/v)	0.43	0.370	0.26	12.3
Dichloromethane	0	0.800	0.14	26.7

solvent composition reduces the capacity factor of the solute to the point where its migration velocity increases to that of the step gradient, then the total solute is accumulated in the region of the step gradient and its concentration reaches a maximum, as can be seen in Fig. 2d. The volume in which the solute is condensed depends exclusively on the diffusiveness of the composition step of the solvent.

Fig. 3 shows that in displacement chromatography the sample is indeed accumulated in a very small volume in the area of the displacer front.

Limits of enrichment

Elution volume. The maximum condensation of a trace component by chromatographic techniques is obtained in the displacement mode. As long as the con-

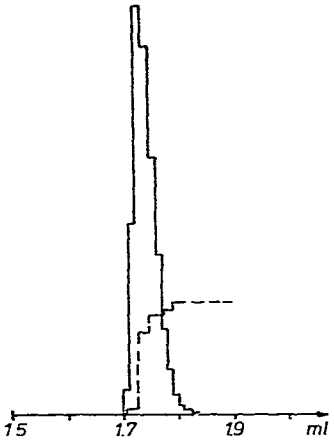

Fig. 3. Accumulation of the trace species in the region of the breakthrough curve of the displacer. Solid line, light absorbance at 280 nm corresponding to *p*-cresol; broken line, refractive index corresponding to the change from cyclohexane to dioxane. Column, LiChrosorb SI-60 (5 μm); sample, 200 ml of *p*-cresol solution in cyclohexane (10 mg/l); displacer, dioxane; flow velocity, 0.28 mm/sec.

centration is not limited, the final volume into which the trace compound can be compressed depends only on the elution volume in which the accumulation step of the displacer takes place. This volume depends on the dispersion phenomena in the chromatographic column. Owing to these dispersion phenomena, the column response to an input pulse is an output peak, the shape of which depends on the shape of the distribution function of the solute in the chromatographic phase system. The column response to an input step is an output curve which is the integral of the peak obtained as the pulse response. A wide square-wave input function as applied in the chromatographic enrichment can be considered as a positive input step followed by a negative one. The width of the response of the column to an input pulse or input step depends, amongst other factors, on the particle size and the flow velocity[16]. In Table II the influence of the particle size is shown and in Table III the influence of the flow velocity. It can be seen that the proper design and operation of the enrichment column results in a decrease in the elution volume by a factor of five. Independent of the original volume of the sample, the trace components can be concentrated in this manner in a volume of about 0.1 ml.

TABLE II

INFLUENCE OF PARTICLE SIZE ON THE PEAK WIDTH OF THE DISPLACED COMPONENT

Sample, 200 ml of *p*-cresol in cyclohexane; column, LiChrosorb SI-60; displacement solvent, dioxane.

Particle size (μm)	*Theoretical plate number*	*Output peak width (ml)*
30	500	0.5
5	3000	0.2

TABLE III

INFLUENCE OF FLOW VELOCITY ON THE PEAK WIDTH OF THE DISPLACED COMPOUND

Sample, 2.5 ml of DBA in cyclohexane; column, LiChrosorb SI-60 (5 μm); displacement solvent, dioxane.

Flow velocity (mm/sec)	*Output peak width (ml)*
0.14	0.11
0.28	0.14
0.48	0.18

Concentration. The absolute limit of enrichment is given by the solubility of the trace compounds in the mobile phase. A lower limit, however, can be given by the basic requirement for displacement chromatography. When the distribution isotherm of the solute is convex, as is normal in adsorption, the migration velocity increases with concentration. Therefore, in displacement chromatography the concentration can increase only up to the point where the migration velocity of the solute equals that of the displacer.

A larger loading of the column does not increase the concentration beyond the limiting point but results in an increase in the zone width. As long as this point is not reached the enrichment increases with the column load. Both effects are shown in Fig. 4.

Load capacity. Each column has a certain maximum load which can be utilized for enrichment (see eqn. 4). If the sample volume loaded becomes too large, then the fraction of the length of the column occupied by the sample will become too large. In this instance the remaining length is not sufficient to complete the enrichment process and to achieve the steady state. The front of the solute zone breaks through before the front of the displacer has reached it.

Fig. 5 shows an example of column overloading. Under these circumstances, the solute can be only partially concentrated in front of the displacer. Table IV demonstrates the linear increase in the solute concentration in the breakthrough volume of the displacer front with increasing loading volume up to the point where part of the solute is eluted before it can be overtaken by the displacer front.

Application of enrichment by displacement chromatography

For the enrichment of trace species from solution by displacement chromatography, an adequate adsorbent and a suitable displacer have to be chosen. A high initial adsorption of the solute and a strong reduction in the adsorption by the displacer are pre-conditions for a high enrichment factor. The choice of the adsorbent and displacer will depend on the chemical natures of the trace components and the solvent. A high enrichment factor can be expected only if the solvent and solute are chemically considerably different. The displacer must be adsorbed more strongly than the solute, it must be miscible with the solvent of the sample and the trace component should be fairly soluble in it.

Polynuclear aromatic hydrocarbons in water. As an example, the enrichment of 1,2,5,6-dibenzanthracene (DBA) from aqueous solution is described. LiChrosorb

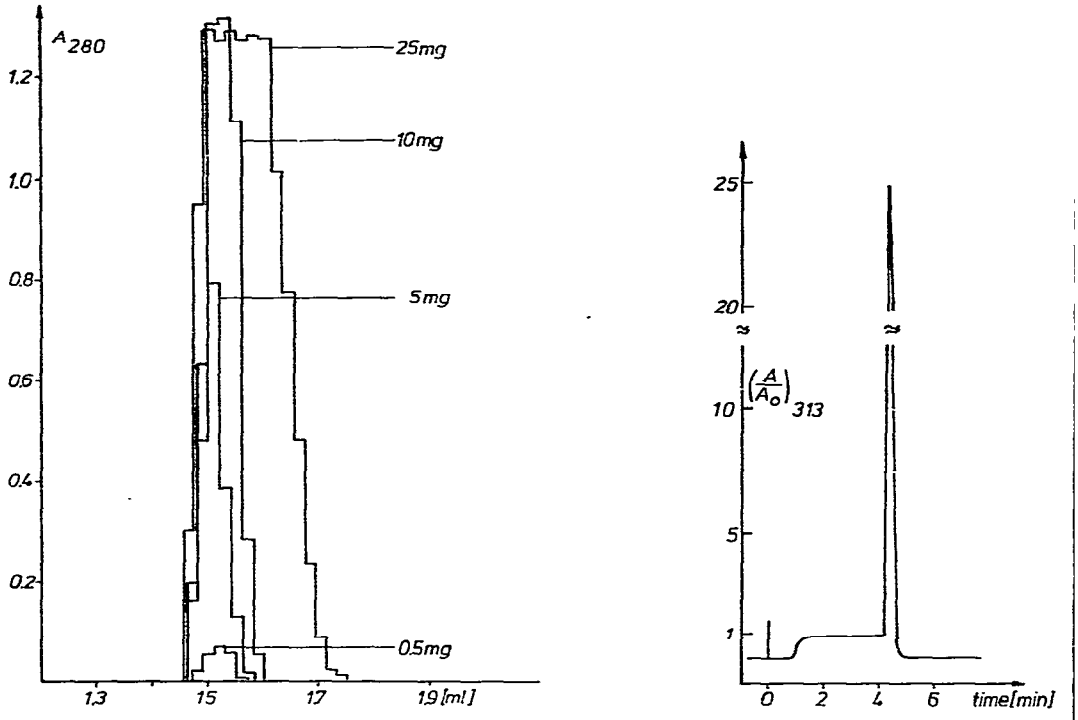

Fig. 4. Influence of the amount of trace species on its final concentration. Column, LiChrosorb SI-60 (5 μm); sample, 50 ml of *p*-cresol solutions in cyclohexane containing different amounts of *p*-cresol; displacer, dioxane; flow velocity, 0.6 mm/sec.

Fig. 5. Displacement chromatography on an overloaded column. Column, LiChrosorb SI-60 (5 μm); sample, 6.25 ml of DBA dissolved in 2,2,4-trimethylpentane, concentration 1 mg/l; displacer, dichloromethane; flow velocity, 1 mm/sec.

TABLE IV

LOAD CAPACITY OF THE COLUMN

Column, LiChrosorb SI-60 (5 μm); void volume, 1.84 ml; sample, 2.5 ml of DBA solution in 2,2,4-trimethylpentane; breakthrough volume, 6.79 ml; displacer, dichloromethane.

Load volume (ml)	*Light absorption (absorbance units)*	*Absorption/volume (absorbance units/ml)*	*Difference of absorption (absorbance units)*
1.25	0.026	0.021	
2.5	0.057	0.023	0.031
3.75	0.085	0.023	0.028
5.0	0.115	0.023	0.030
6.3	0.122	0.019	0.007

RP-18 (5 μm) was chosen as column packing material and dioxane as the displacer. The column was loaded with 250 ml of an aqueous solution saturated with DBA. After the displacement, DBA was found to be concentrated quantitatively in 0.2 ml, corresponding to an enrichment factor of 1250.

Phenols in hydrocarbons. The enrichment is demonstrated for a solution of *p*-cresol in cyclohexane. LiChrosorb SI-60 (5 μm) was chosen as the column packing material and dioxane as the displacer. The column was loaded with 520 ml of a test solution containing 10 mg/l of *p*-cresol. As a result of the displacement, *p*-cresol was concentrated quantitatively in a volume of 0.1 ml, which corresponds to an enrichment factor of 5200.

Enrichment from below the detection limit. The detection of a constituent which cannot be directly measured because of its low concentration is shown in Table V. A highly diluted solution of DBA in water was prepared and the UV absorbance at 298 nm was measured before and after enrichment by displacement chromatography. Although the fraction from the chromatographic displacement column had to be diluted because of the cell volume of the spectrophotometer, the trace component could be easily detected after chromatographic enrichment, which was not possible before.

TABLE V

ENRICHMENT OF A POLYNUCLEAR AROMATIC HYDROCARBON TRACE SPECIES IN WATER OF A CONCENTRATION BELOW THE DETECTION LIMIT

Column, LiChrosorb RP-18 (5 μm); displacer, dioxane.

Sample enrichment	*Absorbance (298 nm)*
Original sample: 500 ml of water containing 225 ng/l of DBA	0.000
Sample enriched by displacement: 0.3-ml fraction collected and diluted to 3 ml	0.020

Storage time. In the practice of trace analysis, often the sampling has to be undertaken in the field and the analysis is carried out some time later in the laboratory. If a large sample volume has to be taken, it will be convenient to reduce the volume at the sampling site and to store the sample in a small container. This aim can be achieved by using a storage column to which the trace compounds are transferred by pumping through the large sample volume. It is important that the trace compounds are held in the storage column for some time without significant dispersion. Table VI shows the result of the enrichment by displacement chromatography applied after different storage times. It can be concluded that trace compounds can be stored for several days without significantly reducing the enrichment effect.

TABLE VI

INFLUENCE OF STORAGE TIME IN THE COLUMN ON THE PEAK WIDTH OF THE DISPLACED COMPOUND

Sample, 200 ml of *p*-cresol in cyclohexane; column, LiChrosorb SI-60 (5 μm); displacement solvent, dioxane.

Storage time in column	*Output peak width (ml)*
1 h	0.2
1 day	0.2
3 days	0.2 (slight tailing)

Column regeneration. In practice, not only the time for a single analysis is important but also the time required to prepare the system for the next analysis. In displacement chromatography, the regeneration of the column requires the replacement of the displacer solvent with the sample solvent. Sometimes the regeneration succeeds more rapidly by using an intermediate solvent between the displacer and sample solvent. The regeneration of a LiChrosorb SI-60 column operated with dioxane as displacer can be performed with cyclohexane or 2,2,4-trimethylpentane directly using about 10 times the column void volume. A LiChrosorb RP-18 column operated with dioxane as displacer can be regenerated with water with about 10 column void volumes if methanol is used as an intermediate solvent; otherwise the regeneration volume would be significantly higher. These examples show that the regeneration volume and regeneration time, with proper execution of the regeneration, are only small fractions of the loading volume and loading time in enrichment displacement chromatography.

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