GRADIENT ELUTION ADSORPTION CHROMATOGRAPHY OF AROMATIC HYDROCARBONS

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SUMMARY

Elution adsorption chromatography of higher aromatic substances on alumina was improved by using a programmed gradient of pentane–ether which shortened the time of analysis and increased the sharpness of the separation.

The suitability of the method was demonstrated in a qualitative and quantitative analysis of creosote oils. A sensitive photometric detection method permitted work with sample amounts smaller than 1 mg.

INTRODUCTION

When separating aromatic substances boiling within a wide distillation range by elution adsorption chromatography on high activity adsorbents, the time necessary for eluting the heaviest compounds, for example the tetraaromatic hydrocarbons, is rather long, and the width of the peaks so large that often they disappear in the noise of the base line. When adsorbents with a lower activity are used, the compounds eluted at the beginning are often not completely separated, or are not separated at all and eluted in a single peak.

These difficulties may be overcome by using gradient elution adsorption chromatography (GEAC), for gradually increasing solvent strength significantly shortens the time necessary for eluting the heaviest compounds, and furthermore, the width of the peaks of these compounds is not much different from those eluted at the beginning. This method was theoretically developed by SNYDER[1], with a special view to the linear gradient elution chromatography.

Mixtures of aromatic substances boiling within a wide distillation range are very often present in commercial products (creosote oil, wash oils, anthracene oil), and it is often important to know their composition, especially in the case of the creosote oil and the other oils for wood protection. Some of these aromatic hydrocarbons even have different fungicidal effects and, therefore, it is often important to have more detailed knowledge about the compositions of these oils, not only from the point of view of research but even for their commercial applications.

Until now, the physico-chemical constants of these oils have been mostly used

for their evaluation, but recently, gas chromatography and mass spectrometry have been tried for their analyses.

The applicability of gas chromatography is limited by the presence of high-boiling aromatic hydrocarbons (chrysene and higher). The determination of the latter is difficult and demands a special adjustment[2] and, furthermore, the sample is exposed to high temperatures for a considerable time which has a deleterious effect upon thermally unstable or easily polymerising substances.

Mass spectrometry can be used for the analysis of mixtures containing tetra-aromatic hydrocarbons such as chrysene, benzanthracene and others, but not more than seven hydrocarbon groups may be determined simultaneously which means that a mixture containing substances from the alkylbenzenes up to the pyrenes and chrysenes has to be preliminarily separated by means of other methods, for example, by distillation, adsorption chromatography etc. The presence of substances containing nitrogen, oxygen, or sulphur considerably complicates the analysis, for example, benzothiophenes have the same nominal value of m/e as alkylbenzenes, and the derivatives of biphenyloxide are identical with the homologues of biphenyl and acenaphthene. It is not possible to differentiate, by the means of mass spectrometry, substances with an identical nominal value of m/e such as fluoranthene–pyrene or chrysene–1,2-benzanthracene–triphenylene–tetracene. It is also necessary, therefore, as in the case of gas chromatography, to use special treatment in mass spectrometry, especially when the sample contains mechanical impurities, deposits and such like.

In this work, GEAC on alumina in combination with UV-spectrometry was found, to be a suitable method for the analysis of higher-boiling aromatic hydrocarbons, and aromatic mixtures with a wide distillation range.

The analysis of creosote oil, which is a mixture of aromatic hydrocarbons from coal tar having boiling points within the range of 200–400° and containing small amounts of nitrogen, oxygen and sulphur compounds, is reported as an example. No preliminary treatment of the sample was given and the aromatic fraction was divided into eight hydrocarbon types which were quantitatively determined.

EXPERIMENTAL

Materials

Alumina Woelm Eschwege Neutral was used as the adsorbent. The surface area of the activated adsorbent was about 100 m²/g. The adsorbent was first activated at 400° for 8 h and then deactivated by addition of 2 % water. The standardisation[3] was carried out by measuring the equivalent retention volumes of some aromatic hydrocarbons on elution with *n*-pentane. The results of these measurements are shown in Table I.

One meter long glass columns with an inner diameter of 4 mm, possessing a device for introducing the sample were used.

The pump was a programmed gradient pump, Dialagrad Model 190, manu-factured by the firm ISCO.

A UV spectrophotometer SP 800 B (Pye-Unicam) with a flow-through quartz cell, 1 mm path length and a volume of 0.13 ml, was used for the detection.

TABLE I

EQUIVALENT RETENTION VOLUMES R^0 OF AROMATIC HYDROCARBONS

Adsorbent: alumina–2.0% H_2O. Eluent: n-pentane.

Compound	R^0 (ml/g)
Indane	0.51
Naphthalene	1.55
Acenaphthene	2.88
Fluorene	9.80
Phenanthrene	13.40

Procedure

0.5 mg of a mixture of standards (indane, naphthalene, acenaphthene, fluorene, phenanthrene, pyrene, chrysene, and carbazole), dissolved in iso-octane, was introduced into the column containing 16 g of the adsorbent, previously wetted with pure pentane, and then the program of the gradient of pentane–ether, lasting 2 h, was started. The flow rate of the eluents through the column was 45 ml/h. The detection was realised by measuring the extinction, using a constant wavelength of 260 nm. The chromatogram demonstrating the separation of the mixture of standards, and
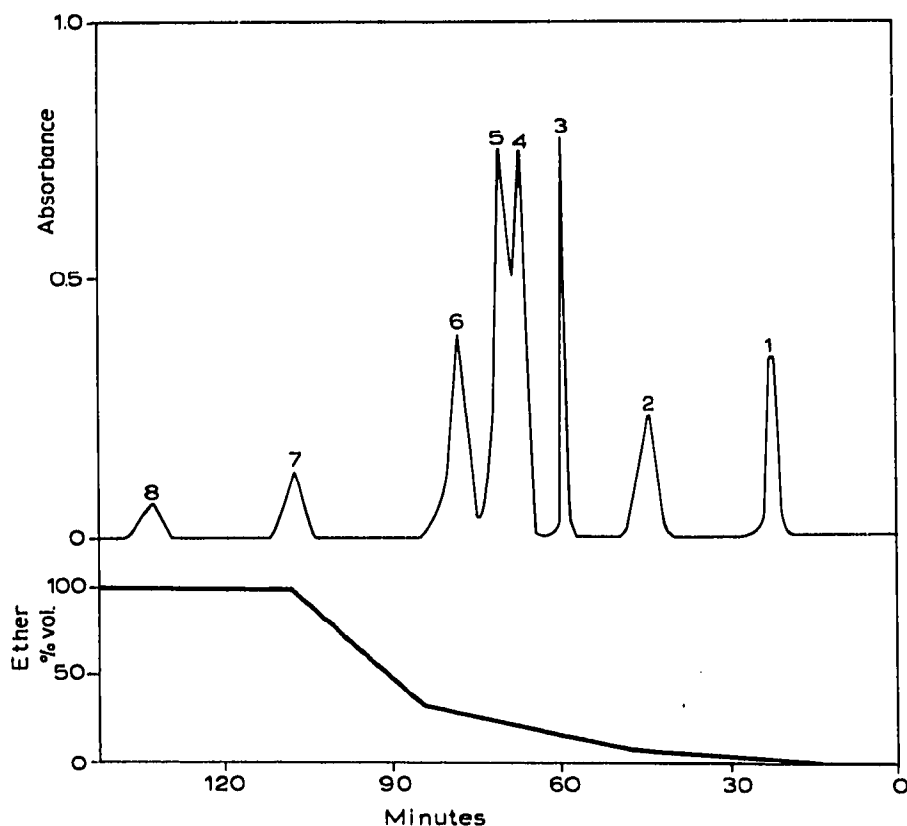

Fig. 1. GEAC separation of the mixture of standards and the course of the gradient. Adsorbent: alumina–2% H_2O. Eluent: Pentane–ether. 1 = Indane; 2 = naphthalene; 3 = acenaphthene; 4 = fluorene; 5 = phenanthrene; 6 = pyrene; 7 = chrysene; 8 = carbazole.
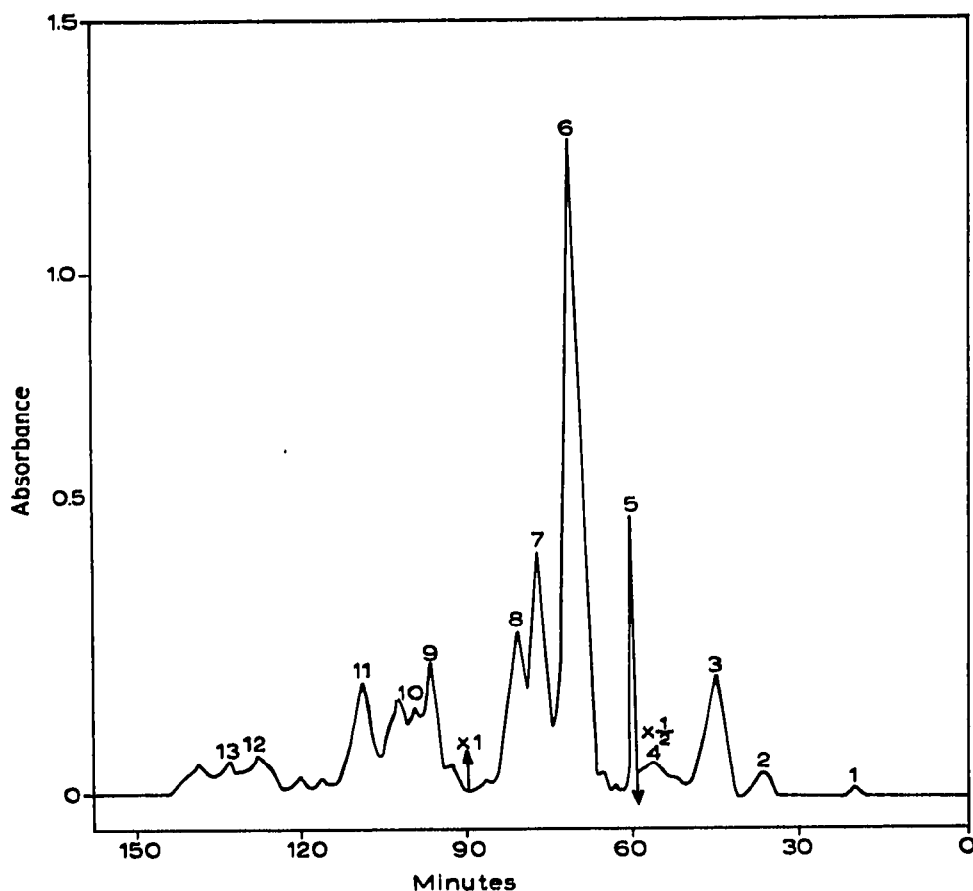
Fig. 2. GEAC separation of creosote oil. Adsorbent: alumina-2% H_2O. Eluent: Pentane–ether. 1 = Alkylbenzenes, indanes, tetralins; 2 = indenes, dihydronaphthalenes; 3 = naphthalene, benzothiophene; 4 = alkylnaphthalenes; 5 = acenaphthene, biphenyl; 6 = phenanthrene, anthracene; 7 = pyrene; 8 = fluoranthene; 9 = triphenylene; 10 = 1,2-benzanthracene; 11 = chrysene; 12 = indole; 13 = carbazole.

also the flow of the gradient, are shown on Fig. 1. The analysis of 1 μl of creosote oil was done under identical conditions, and the chromatogram is shown on Fig. 2.

The qualitative determination of single compounds was carried out by comparing the retention volumes of single peaks of the analysed mixture with those given by the mixture of standards, on one hand, or by adding pure standards directly to the mixture being analysed, on the other hand. In addition, the single eluted compounds were collected, and their UV-spectra were measured and compared with published data.

The quantitative determination of single groups was carried out by measuring the peak areas by means of a planimeter. These groups of substances were then calculated using the following relation:

$$A_j = \frac{P_j \cdot k_j \cdot 100}{\sum\limits_{i=1}^{\infty} P_i \cdot k_i}$$

where A_j represents the percentage weight of compounds of the j-group, P_j is the

TABLE II

GROUPS OF AROMATIC HYDROCARBONS DETERMINED AND THEIR k-FACTORS

Group	Components	k-factor
I	Alkylbenzenes, indanes, tetralins	44.0
II	Indenes, dihydronaphthalenes	6.9
III	Naphthalene, benzothiophene	8.2
IV	Alkylnaphthalenes	12.3
V	Biphenyl, acenaphthene	12.5
VI	Fluorene, phenanthrene, anthracene	1.8
VII	Pyrene, fluoranthene	1.3
VIII	Chrysene, triphenylene, benzanthracene	1.0

peak area of the j-group and k_j is a factor for the said group. The denominator consists of the sum of the products of the peak areas and their k-factors. The partition into groups and k-factors are shown in Table II.

RESULTS AND DISCUSSION

It is necessary, for the successful separation of a mixture of aromatic hydrocarbons, to choose a suitable method of detection. Spectrophotometric detection is suitable for all kinds of aromatic hydrocarbons, especially for polycondensed ones, which are often present in small amounts only. Detection at a constant wavelength 260 nm is very satisfactory, because it permits a reliable determination of these substances even when they are present as only 0.5 % of a complicated mixture of aromatic hydrocarbons.

With the regard to the character of a mixture to be separated, another wavelength could be used when measuring the extinction of the eluted compounds. It is not advantageous, however, to work with a wavelength shorter than 230 nm because the gradient itself causes a change of extinction in the eluent.

Interference of saturated hydrocarbons and olefins may be excluded by using a detector measuring the light absorption in the UV-region at a suitable wavelength. The high sensitivity of the detector allows one to work with an extremely small amount of a sample (0.5–1.0 μl of creosote oil) assuring that the analytical run is in the linear part of the adsorption isotherm. By this means, not only an optimum separation of the mixture, but even good reproducibility, is achieved.

Analysis of creosote oil by the means of elution adsorption chromatography, with a single solvent, e.g., pentane, does not appear to be satisfactory, as the retention volumes of the heaviest compounds are extremely large. As shown in Fig. 2, GEAC not only results in a good separation, but, at the same time, substantially shortens the analysis time. Whilst the analysis of similar mixtures by elution adsorption chromatography took 7–10 h[4], this time was shortened to about 2.5 h in our case. A very good separation of the basic groups of mono-, di-, tri- and tetraaromatic hydrocarbons was obtained and it was even possible to determine other parts of these groups with good accuracy, for e.g. acenaphthene biphenyl; pyrene, fluoranthene; and occasionally some further compounds, such as benzpyrenes, indole, carbazole and others which, in this case, were not taken into consideration and their quantitative evaluation was not provided for.

The reproducibility of the separation achieved, was very good, especially in the region from fluorene onwards. In the part, where naphthalene, alkylnaphthalenes, biphenyl and acenaphthene are eluted, the system is very sensitive to any deviation of the gradient, the purity of the eluent, the room temperature etc. Most of the time this may be obviated by determining the sum of the diaromatic hydrocarbons, *i.e.* groups III, IV and V are determined as a whole. When it is desired to obtain these groups separately, and when accurate conditions cannot be guaranted, it is better, to carry out a second chromatogram on 2% $H_2O-Al_2O_3$, eluting the sample with pure pentane and finishing the experiment at the time when acenaphthene and biphenyl are eluted completely. By means of this chromatogram, the distribution of the diaromatic hydrocarbons can easily be determined.

The presence of phenols which are not eluted until after the nitrogen compounds, does not matter, when gradient elution chromatography is used. An advantage of the said method even consists in the possibility of separating the non-basic types of nitrogen substances. In the system Al_2O_3-pentane the values of the retention volumes for indole and carbazole are approximately the same as those for benzpyrene and dibenzofluorene[5]. With the increase of the solvent strength, the values of retention volumes decrease. This change, however, is not identical as for the nitrogen compounds, as it is for aromatic hydrocarbons. The change of the retention volume caused by a change of the solvent strength, is smaller for the substances containing nitrogen than for the aromatic hydrocarbons[6] and these nitrogen substances are therefore eluted later than the aromatic hydrocarbons.

Coal tar products are characterised by a small percentage of polyalkylated aromatic hydrocarbons. The greater part of these consist of the parent aromatic hydrocarbons and their monomethyl isomers. This fact facilitates the quantitative evaluation, when no similar mixture with a known composition is available. It is possible, in such case, to prepare a calibration mixture of the basic hydrocarbons and, by evaluating its chromatogram, to determine the appropriate *k*-factors needed. Such measurements just give semi-quantitative results, because, for a more accurate analysis, further data should be known, such as, for example, the relative participation of anthracene and phenanthrene and other information about the composition of the mixture analysed. In our case, we tested several samples of creosote oil, the compositions of which were determined by the means of mass spectrometry. These samples were analysed by the GEAC method and the chromatograms obtained were evaluated. From these samples the *k*-factors, shown in Table II, were calculated. The applicability of the *k*-factors to the quantitative evaluation of the mixture being analysed, is conditioned by the fact that identical conditions of the analysis must be maintained, *e.g.* a constant flow rate of the eluent, a constant wavelength and path length of the cell. It is important, too, to maintain an identical system of gradient concentrations, because it is necessary to achieve a separation for which the *k*-factors have been calculated. It also has to be pointed out that the applicability of the *k*-factors introduced is limited to those coal tar products having an approximately uniform distillation range. When analysis of aromatic hydrocarbons with a considerably different composition is carried out, it is necessary to check up the respective *k*-factors experimentally.

The analyses of two creosote oil samples divided into eight groups (see Table II) are reported in Table III. The results of the mass spectrometry analysis are also shown in the same table for comparison. If a creosote oil sample contains more sulphur, *i.e.*

TABLE III

COMPARISON OF MASS-SPECTROMETRIC (MS) AND GEAC ANALYSES (% WT.) OF CREOSOTE OILS

Group	Sample 1[a]		Sample 2[b]	
	MS	GEAC	MS	GEAC
I	9.9	1.3	5.4	3.8
II	2.4	1.1	2.9	2.1
III	26.0	36.5	12.8	14.2
IV	25.9	24.1	17.3	15.3
V	13.3	12.7	14.5	18.1
VI	16.1	12.6	29.6	29.5
VII	5.4	8.1	15.6	12.0
VIII	1.0	3.6	1.9	5.0
Total[c]	100.0	100.0	100.0	100.0

[a] Sulphur content 2.1 % wt.
[b] Sulphur content 0.42 % wt.
[c] Aromatic hydrocarbons = 100 % wt.

benzothiophene and its homologues are present, then a difference between the analysis by mass spectrometry and by GEAC appears, resulting from the fact that the first method includes benzothiophenes among the alkylbenzenes, while the latter determines it as naphthalene or an alkylnaphthalene. This is illustrated in the case of sample 1 shown in Table III. As is evident from this table, the quantitative analysis of creosote oil by GEAC affords good results, even when the analysed samples have quite different compositions. However, only the relative concentrations of single aromatic hydrocarbon types may be obtained, not the absolute values; furthermore, GEAC gives, in general, higher results for the tetraaromatic hydrocarbons. These higher results are more probable than the lower ones by the mass spectrometry, where some distortion may occur, caused by the preliminary treatment of the sample and by an insufficient evaporation of the heaviest fractions in the evaporator of the mass spectrometer.

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