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Analysis of Polycyclic Aromatics

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Polycyclic aromatic hydrocarbons (PAH), among them carcinogenic compounds, have been found to be widely distributed in the human environment. The formation of PAH in processes relevant to environmental pollution will be described (pyrolysis or incomplete combustion of aliphatic and aromatic material, formation in higher plants). The application of the following methods to the analysis of PAH mixtures will be discussed: gas chromatography (capillary columns, use of liquid crystals and inorganic salts such as LiCl or CaCl₂ as stationary phases in packed columns, selective detectors); luminescence spectroscopy (use of phosphorescence in paper and thin-layer chromatography, Shpol'skii spectra, quenchofluorimetry); mass spectroscopy.

The combination of benzene nuclei to form polycyclic aromatic hydrocarbons (PAH) is formally possible in very many ways. The great majority of the conceivable structural principles for PAH's have now been experimentally verified, and a considerable number of compounds are known for nearly every one of these principles.

The many interesting properties of this class of substances are of great current interest, and are consequently being investigated in research laboratories throughout the world. To the theoretical chemist, the PAH's are still interesting subjects for the application of new quantum-chemical models. Physicists and physical chemists are interested in this class of substances because of their remarkable electrical and spectroscopic properties. The diverse relationships between structural principle and chemical reactivity in the PAH's are being intensively studied. Many PAH's are strong carcinogens, and that is why biochemists, hygienists, and doctors, as well as government departments, are so interested in these substances at present. This is

the aspect that comes to mind first when PAH's are to be discussed at a symposium on environmental analysis.

PAH's have been found nearly everywhere in man's surroundings. There are two reasons for this: firstly, very sensitive methods have been developed over the years for the detection of PAH's, and secondly, PAH's are formed in many processes that take place all around us. Some examples of the occurrence of PAH's are given in Table I.

PAH's are found, e.g., in the atmosphere, concentrated in urban air. Table I shows quantitative data for the carcinogen benzo[a]pyrene based on a report by Hettche¹ for the cities of Los Angeles, London, and Bonn. The concentrations given were measured in the winter months. Lower values are found in summer. The lower summer values can be attributed in part to the

TABLE I
Examples for the occurrence of carcinogenic PAH in the human environment

<u>Benzo[a]pyrene in town air (mcg/1000 m³ of air)</u>	
Los Angeles	5
London	68
Bonn	133
<u>Carcinogenic aromatic hydrocarbons in water (mcg/m³ of water)</u>	
Groundwater	1-10
Effluents	approx. 100,000
<u>Benzo[a]pyrene in vegetables (mcg/kg of vegetables)</u>	
Kale	16
Spinach	7
<u>Benzo[a]pyrene in cigarette smoke</u>	
1 mcg in the smoke from	40 cigarettes

absence of emissions from heating installations. Another reason for the lower values in summer is probably the accelerated breakdown of benzo[a]pyrene under the influence of sunlight.

PAH's are found in water. Borneff's research group in Germany has examined this problem particularly thoroughly. The values given in Table I for carcinogens in effluents and in groundwater were taken from a report by Borneff,² and give the total quantity of benz[a]anthracene, benzo[j]- and benzo[b]fluoranthene, indeno [1.2.3-cd]pyrene, and benzo[a]pyrene. Boundary lines of this nature are naturally always rather arbitrary, and depend on both the analytical and the toxicological knowledge that exists at the particular time.

Another example of products that contain PAH's and that are consumed daily by man is food. As an example, Table I shows the benzo[a]pyrene

contents in two types of vegetables according to investigations by Grimmer.³

Finally, the most popular source of PAH's, including carcinogenic types, is cigarette smoke: 1 mcg of benzo[a]pyrene has been found in the smoke from 40 cigarettes.³

It may be mentioned in passing that PAH's are also assumed to occur in interstellar material. In particular, it is thought that PAH's of the type known as "condensed polyphenyls", hydrocarbons such as triphenylene and hexabenzocoronene, are probably present.⁴ These hydrocarbons are characterized by very great thermal and photochemical stability.

PAH's are formed in more or less large quantities in all pyrolytic processes in material containing carbon and hydrogen. Since processes of this type are common in industry, it is not surprising that PAH's occur everywhere in our environment. In the 'fifties and 'sixties, the pyrolytic formation of PAH's from simpler hydrocarbons was studied in particular by Badger's⁵ research group in Australia and by Lang *et al.*⁶ in Germany. Only a few results from these investigations will be briefly described here.

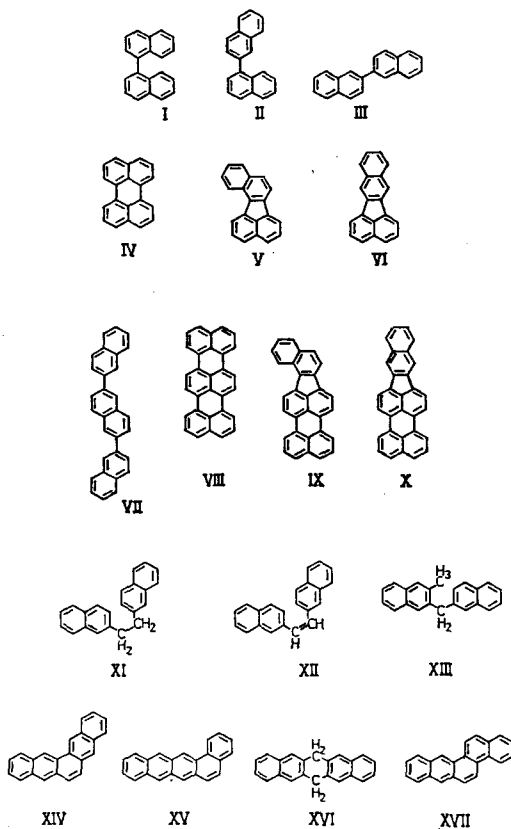
The conversion of paraffins into aromatic hydrocarbons at high temperatures has been known for a long time. In 1886, Norton and Andrews⁷ obtained benzene by passing hexane through a hot pipe. Toluene can be formed from *n*-heptane, and *ortho*-, *meta*- and *para*-xylene and ethylbenzene from *n*-octane, in a similar manner. The formation of naphthalene and its homologs in processes of this type is also known. As was shown by the investigations of Badger and Lang, a large number of PAH's are formed from simple aromatic compounds at high temperatures. The experiments were mainly carried out at 700–800°C in a flow system. Some examples will be discussed in more detail.

On pyrolysis of naphthalene,⁶ the isomeric binaphthyls I, II, and III are formed; of these, III predominates, since it is unable to enter into ring closure reactions. Perylene IV and the benzofluoranthenes V and VI, probably formed by cyclodehydrogenation of the binaphthyls I and II, are also found in the reaction product. In addition to these compounds formed from two naphthalene nuclei, there are smaller quantities of hydrocarbons containing three naphthalene nuclei. These are ternaphthyl VII, terylene VIII, and the naphthoperylene IX and X.

In the pyrolysis of alkylaromatic hydrocarbons, direct condensation of the nuclei such as occurs in the case of naphthalene takes place only to a minor extent, if at all. The hydrocarbon molecules are preferentially linked via the alkyl groups. Thus dinaphthylethane XI and dinaphthylethylene XII are formed on pyrolysis of 2-methylnaphthalene.⁶ The pentaphene XIV that is also found could be formed from dinaphthylethylene XII by cyclization. Benzo[a]tetracene XV and dihydropentacene XVI are also formed, probably by ring closure from the dinaphthylmethane derivative XIII. The formation

of benzo[b]chrysene XVII is surprising, and must be assumed to involve an intermediate migration of a methyl group on the naphthalene nucleus.

In addition to the mechanisms discussed above, diene syntheses and ring expansions also take place during the pyrolysis of aromatic hydrocarbons. A mechanism for the pyrolytic formation of benzo[a]pyrene has been proposed by Badger⁸ on the basis of extensive experimental studies. According to Badger, tetraline XVIII is first thermally alkylated with *n*-butyl-

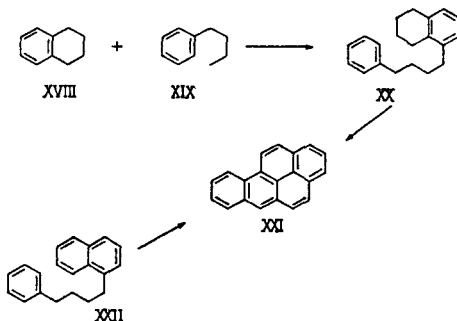


benzene XIX to form XX. This is followed by cyclization and aromatization to give benzo[a]pyrene XXI. Experimental evidence of the transition from XX to XXI includes the fact that the pyrolysis of 1,4'-phenylbutylnaphthalene XXII, the dehydrogenated analog of XX, yields a complex mixture of products, which contains benzo[a]pyrene as well as 1,1'-binaphthyl, perylene, and other hydrocarbons. It should be pointed out that the precursors XVIII and XIX postulated in Badger's mechanism can be formed from many C₂

to C_{10} fragments under pyrolysis conditions. The formation of PAH's on pyrolysis of material containing carbon and hydrogen probably proceeds by free-radical mechanisms in every case.

It is certain that processes of the type discussed here also take place under the conditions of the incomplete combustion of hydrocarbons. This extends the spectrum of possible sources for PAH's in our environment. The occurrence of PAH's in foods, particularly fruit and vegetables, has been attributed to contamination by dust from the atmosphere. Comparative studies have in fact shown that grain samples from German industrial areas contain about 10 times as much PAH as samples from areas with no industry.³

Although the PAH's to which man is exposed are mainly due to sources connected with our modern industrial world, it is now certain that PAH's



existed before there was any form of industry. Knorr⁹ pointed out in 1957 that natural products such as petroleum and coal, the remains of fossil plants and animals, contain PAH's, some of which are carcinogenic, and that the natural occurrence of these substances must therefore be taken into account in considerations on exogenous carcinogenesis. Gräf¹⁰ showed in 1965 that carcinogenic PAH's are present in plants, e.g. grain, even if surface contamination by atmospheric emission can be strictly ruled out. It has been shown that plants produce PAH's, including benzo[a]pyrene, under physiological conditions. In a crucial experiment, rye grains were allowed to grow in a nutrient solution that was known to be free from PAH's. After 8 days the rye plants, which were about 20 cm long, were dried, together with the roots, and extracted. Exactly the same number of ungerminated rye grains were also extracted. The result was convincing, since the rye seedlings, after growing for only 8 days, contained carcinogenic PAH's in relatively large quantities, whereas the ungerminated grains were practically free from these

substances. The PAH's must therefore have been synthesized during the growth of the rye plants. Gräff's investigations also show that the carcinogenic PAH's function as auxins in the plant metabolism. There is evidently a direct relationship with the carcinogenic PAH's acting on human and animal cells.

Various occurrences of PAH in our environment were discussed above: air, water, plants, and so on. There is no end to the list. Very special investigations have been carried out. The scope covered by the analytical information varies widely from one investigation to another. Many authors confine themselves to the determination of benzo[a]pyrene, while 10 to 20 different PAH's were quantitatively determined in other studies. Lao *et al.*¹¹ analyzed 150 different PAH's in town air. We are faced with the question of what information is required to enable us to reach relevant conclusions about the possible danger to man from PAH in his environment. Is it enough to determine the benzo[a]pyrene or should one determine as many different PAH's as possible? The largely unclarified situation when various PAH's act together in carcinogenesis clearly favors the second alternative. It will generally be desirable for the analytical information to be as comprehensive as possible. To achieve this aim, an efficient gas chromatography-mass spectroscopy-computer combination will be the method of choice in many cases. However, there are also less expensive methods for the analysis of PAH's that are of great value, in particular the combination of TLC with luminescence.

The first investigations of the use of gas chromatography for the analysis of complex PAH mixtures came from the field of coal-tar chemistry. These early measurements had all the disadvantages of isothermal operation for mixtures with wide boiling ranges. A decisive advance in this field was the introduction of temperature-programmed gas chromatography.¹² Further progress resulted from the use of capillary columns and of packed high-efficiency columns with selective stationary phases. There is now an extensive literature on the gas chromatography of PAH mixtures.

There are a number of critical separations in the GLC of complex PAH mixtures. Examples are the separation of anthracene and phenanthrene, the separation of the five isomeric 4-ring aromatic hydrocarbons, and the separation of benzo[a]pyrene and benzo[e]pyrene. This last separation is particularly important in connection with the problem in which we are interested, since out of these two isomeric benzopyrenes, only benzo[a]pyrene is carcinogenic. The situation is further complicated by the many alkylaromatic compounds that can occur in natural mixtures.

Most of these separation problems can be solved with efficient capillary columns. As an example, a recent investigation by Grimmer *et al.*¹³ will be discussed in some detail. Grimmer *et al.* examined the exhaust gases from motor vehicles for PAH's. Before the actual GC analysis, a PAH concentrate was obtained from the exhaust gases and broken down into two fractions.

The methods used were liquid-liquid partition and chromatography on silica gel, as well as gel chromatography. The first fraction contained the PAH's from naphthalene to fluoranthene, and the second fraction the PAH's up to the dibenzopyrenes. For the GLC Grimmer *et al.* used capillary columns 50 m long with polydimethylsiloxane OV 101 and polyphenylmethylsiloxane OV 17 as stationary phases. The efficiency of the columns for benzo[a]pyrene was about 70,000 HETP. As an example, Figure 1 shows the isothermal gas chromatogram of a motor vehicle exhaust gas in the boiling range pyrene to benzo[ghi]perylene. The boiling point of benzo[ghi]perylene at normal pressure is 500°C.

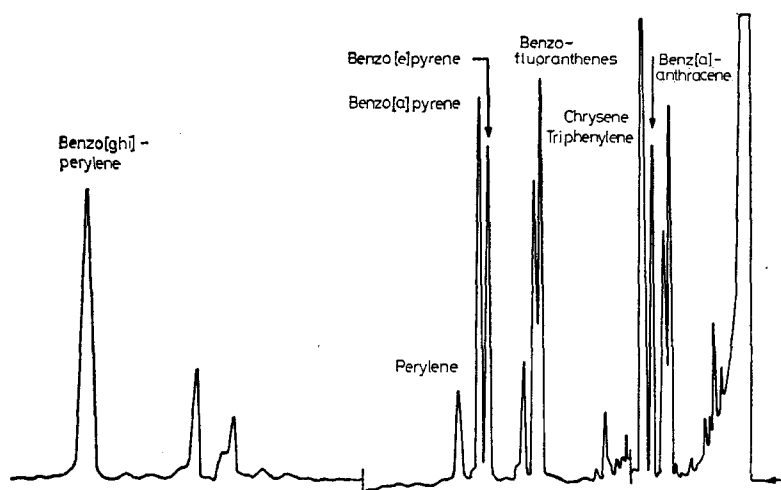


FIGURE 1 Capillary gas chromatogram of a PAH mixture (for details see text and ref.¹³).

An excellent separation was achieved in the region of the catafused 4-ring aromatic hydrocarbons. The weakly carcinogenic benzo[a]anthracene is clearly separated. No separation was achieved between chrysene and triphenylene. It should be mentioned that triphenylene in complex PAH mixtures can be detected with very high selectivity and sensitivity by phosphorescence spectroscopy.¹⁴

A very extensive separation was also achieved in the region of the peri-condensed 5-ring aromatic hydrocarbons. Special mention should be made of the excellent separation between benzo[a]pyrene and benzo[e]pyrene. It should be added that the separation between the two isomeric benzopyrenes has also been achieved in a few cases on packed columns of medium length. Thus Bhatia¹⁵ obtained a very good separation on a 6-m column with silicone OV 7 on glass spheres pretreated with dimethylchlorosilane. The last peak

in the chromatogram is due to benzo[ghi]perylene. Under slightly modified conditions, the chromatography can be extended to coronene.

The usefulness of GLC for PAH's seems to end in the coronene region. However, there are many PAH's with higher molecular weights than coronene that can quite easily occur in our environment, though only in very low concentrations because of their low volatility. As things stand at present, other analytical methods must be used or developed for the determination of these compounds.

It is well known that capillary columns have the advantage of a small pressure drop, so that very long columns with correspondingly high numbers

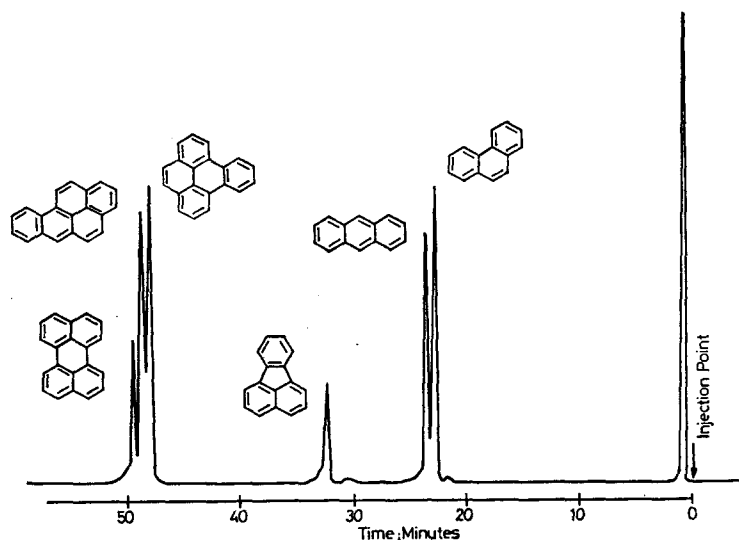


FIGURE 2 Capillary gas chromatogram of a PAH mixture (for details see text and ref.¹⁸).

of theoretical plates can be used. Columns with lengths of up to 1000 m and several million theoretical plates have been described.¹⁶ On the other hand, investigations by Grob and Grob¹⁷ have shown that the efficiency of a capillary column per unit length increases with decreasing column length. Gouw and his co-workers¹⁸ made use of this fact and used short capillary columns only 10 m long for the rapid separation of PAH mixtures with wide boiling ranges. They used silicone OV 101 as the stationary phase. An example is shown in Figure 2.

Figure 2 is the gas chromatogram of a test mixture. The separation between anthracene and phenanthrene is excellent. The running time before anthracene appears is about 23 min. The separation of perylene from the benzopyrenes

is also good. The separation of benzo[a]pyrene and benzo[e]pyrene should be sufficient for some purposes.

In connection with the possibilities offered by long capillary columns in GLC, one must not forget the use of selective stationary phases. Among other things, liquid crystals have proved very useful as stationary phases in the GLC of aromatic hydrocarbons (see Figure 3).

Figure 3 is a gas chromatogram of a technical phenanthrene-anthracene-carbazole mixture. The chromatogram was obtained using a packed column 1 m long, with liquid crystals as the stationary phase.¹⁹ As one can see, an excellent separation between anthracene and phenanthrene was achieved on this very short column. The running time up to and including anthracene was 15 min.

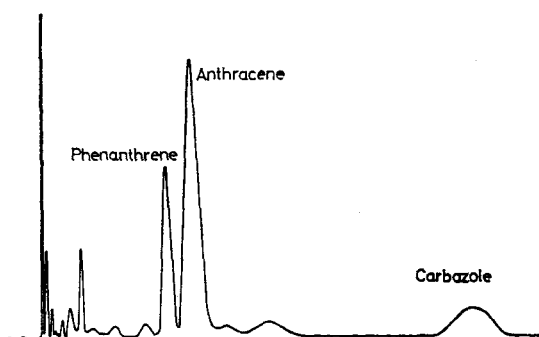


FIGURE 3 Gas chromatogram of a PAH mixture (for details see text and ref.¹⁹).

Columns containing inorganic salts such as lithium chloride or calcium chloride on conventional supports have also proved useful in the gas chromatography of PAH mixtures. Since the column temperatures are below the melting points of the salts, the conditions prevailing here are those of gas-solid chromatography. Columns of this type have the advantage that they can be used at high temperatures. They also exhibit interesting selective effects.

In 1964, Sauerland²⁰ reported an excellent separation of anthracene and phenanthrene on calcium chloride. Chortyk and his co-workers,²¹ in an article published in 1965, reported investigations on the separation of complex PAH mixtures on lithium chloride. The mixtures studied covered the boiling range from naphthalene to coronene. Under suitable conditions, it was even possible to achieve a partial separation of the two isomeric benzopyrenes. Figure 4 gives an example for the great selectivity of such columns. This figure shows the gas chromatogram of a mixture of naphthalene homologs.²² Calcium chloride on Chromosorb was used as the column packing. The

separation was carried out with temperature programming and with a flame ionization detector. The boiling points of the naphthalene homologs investigated at normal pressure are shown on the left of the figure. It is interesting to note that 1-methylnaphthalene appears before 2-methylnaphthalene, contrary to the order of their boiling points. The next pair, 1,4- and 1,5-dimethylnaphthalene, appear in order of their boiling points. Although the difference in boiling point between these compounds is about 4°C, the separation is by no means good. On the other hand, the separation between 1,5- and 2,3-dimethylnaphthalene is complete, although the difference in boiling points is only about 0.1°C here. A weak separation is also found for 2,3,5- and 2,3,6-trimethylnaphthalene, with a boiling point difference of

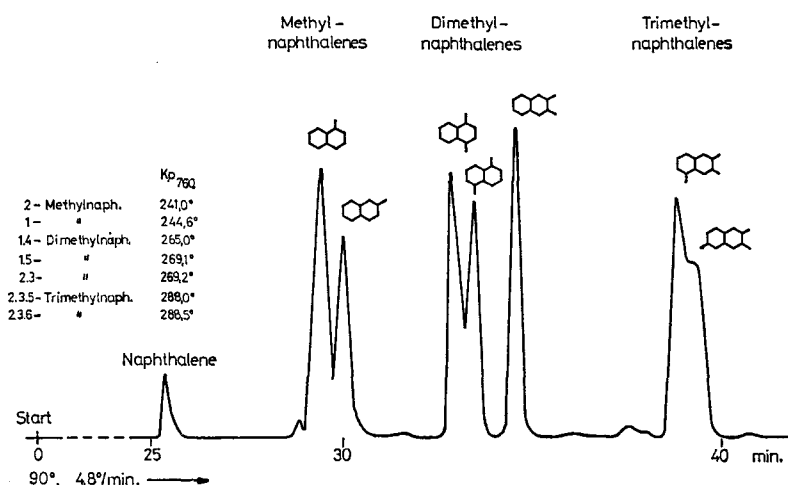


FIGURE 4 Gas chromatogram of a mixture of naphthalene homologs (for details see text and ref.²²).

0.5°C. From this and a whole series of other examples, we can deduce the following. The calcium chloride column retains naphthalene homologs in which positions 2 are occupied considerably longer than corresponding 1-derivatives, regardless of the boiling points. This explains, for example, the good separation of 1,5- and 2,3-dimethylnaphthalene, which cannot be achieved on organic phases (with the exception of liquid crystals¹⁹), and is difficult even with capillary columns.²³ It may be assumed that calcium chloride columns will exhibit similar selectivities for the methyl derivatives of other aromatic systems.

One may occasionally be faced with the analytical task of determining very small quantities of PAH's in large quantities of aliphatic material. For example, it is required by law that petroleum waxes used as food additives

or in the drug industry be practically free from PAH's. The determination of PAH's in trace concentrations in a wax is very difficult by GLC with non-selective detectors. Successful use can be made here of the electron capture detector,²⁴ which is highly sensitive to aromatic compounds, whereas it does not record aliphatic and alicyclic compounds.

Selective GLC detectors are also useful for other problems in environmental analysis. So far only the analysis of polycyclic hydrocarbons has been discussed. However, polycyclic systems with hetero atoms obviously also occur in our environment, for example in the dust present in the air. Compounds containing nitrogen in complex mixtures can often be determined very simply by gas chromatography with a nitrogen-selective detector.

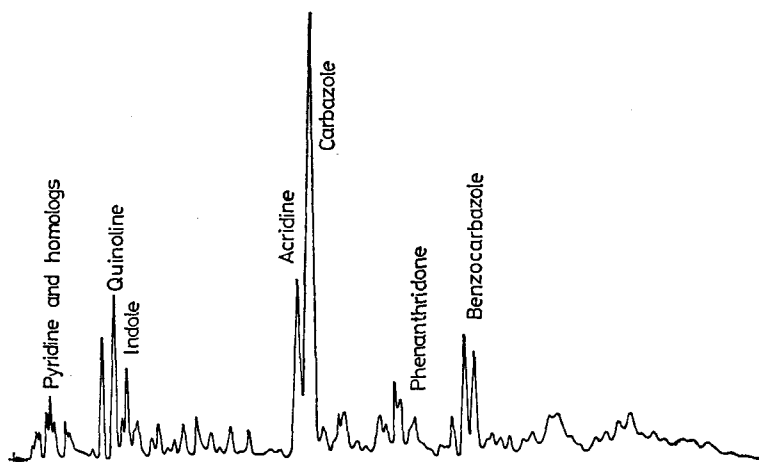


FIGURE 5 Gas chromatogram of a coal tar with the nitrogen detector (for details see text and ref.¹⁹).

Figure 5 shows an example. This is the temperature-programmed gas chromatogram of a coal tar, recorded with the Hewlett-Packard nitrogen flame ionization detector.¹⁹ As thorough test measurements showed, practically nothing but the coal-tar components containing nitrogen is recorded. The recording of hydrocarbons, phenols, etc., is completely suppressed by correct adjustment. Carbazole is recognized as the most abundant N compound in the coal tar. A number of other compounds are assigned, as can be seen from the diagram. The same technique can also be useful for other analytical problems, for example in the investigation of atmospheric dust samples.

Probably the most frequently used separation methods for the analysis of PAH mixtures until now have been paper chromatography (PC) and TLC.

The PC of PAH's requires the use of hydrophobic paper. The decisive breakthrough into this field was achieved in 1952 by Micheel and Schweppe,²⁵ who were the first to use acetylated paper for the chromatography of PAH's. TLC, the faster method giving sharper separations, has also gained growing importance in the analysis of PAH's. There is an extensive literature on the PC and TLC of PAH's and the application of these methods to natural samples from man's environment. We shall consider here only one aspect of these methods in more detail, namely the visualizing and characterisation of the spots by fluorescence and phosphorescence.

Even in the first investigations on the PC of PAH's, fluorescence was used to visualize the spots. The observation of phosphorescence as a complementary method has been introduced in 1958.²⁶ It is a good idea to use both methods, since it is usually the weakly fluorescent PAH's that exhibit intense phosphorescence, whereas the weakly phosphorescent PAH's generally fluoresce strongly. Poorly separated substances whose spots overlap in the chromatogram can thus be localized in some cases by the observation of fluorescence and phosphorescence. For further characterisation of the separated substances, the phosphorescence spectra of the PAH's can be determined directly on the paper with the aid of a phosphorescence spectrometer. This method has been developed further in particular by Pfaff and Sawicki.²⁷ The mean phosphorescence lifetimes of the separated PAH's can also be determined directly on the paper. These times largely agree with the phosphorescence lifetimes found in solid solution, and can be used together with the spectra to identify the substances. All that has been said here about the phosphorescence evaluation of paper chromatograms also applies to thin layer chromatograms.

Fluorescence and phosphorescence spectroscopy play an important part in the analysis of PAH's, mainly because of the very great sensitivity of these methods. They are also superior to u.v. spectroscopy in their selectivity. A comparison of u.v., fluorescence, and phosphorescence spectroscopy as methods for the analysis of PAH's is shown in Table II. The methods are compared here for selectivity, sensitivity, and reproducibility. One plus denotes "average", two plusses "good", and three plusses "excellent". It should be mentioned that the introduction of the rotating cell into phosphorescence spectroscopy by Hollifield and Winefordner²⁸ led to a substantial improvement in the reproducibility of phosphorescence intensity measurements (for further recent advances in phosphorimetry see²⁹).

The fluorescence spectra of most PAH's in liquid solution at room temperature consist of relatively few bands. Shpol'skii³⁰ has shown that very characteristic fluorescence spectra with an extremely large number of bands are obtained for PAH's if the measurements are carried out at low temperatures in a solid paraffin matrix. *n*-Alkanes from *n*-pentane to *n*-decane

and cyclohexane have been found particularly suitable for use as the matrix. Eichhoff and Köhler³¹ were among the first to investigate the use of Shpol'skii spectra in the trace analysis of PAH's. The Shpol'skii spectra of anthracene, benzo[a]pyrene, dibenz[a,h]anthracene, and 20-methylcholanthrene were investigated in *n*-heptane at 79°K. They exhibit characteristic differences and allow the detection of all four compounds in the same mixture. For a measuring volume of 0.06 ml, the detection limit for benzo[a]pyrene was 4.10^{-11} g. The methods have been used, in combination with PC, for the determination of benzo[a]pyrene in atmospheric dust. But it should be mentioned that the usefulness of Shpol'skii spectra in fluorescence and phosphorescence analysis is not unambiguous.³²

TABLE II
Comparison of UV, fluorescence and phosphorescence spectroscopy as analytical methods for PAH.

	<u>Selectivity</u>	<u>Sensitivity</u>	<u>Reproducibility</u>
UV spectroscopy	+	+	++
Fluorescence	++	+++	++
Phosphorescence	+++	+++	++

The selectivity of fluorimetry can be significantly increased in many cases by the use of special fluorescence quenching effects. This method was introduced by Sawicki *et al.*,³³ who called it "quenchofluorimetry". In the quenchofluorimetric analysis of multicomponent systems, use is made of the observation that certain quenching substances weaken the fluorescence of different compounds to different degrees. In the limiting case, the fluorescence of all the substances in a mixture are quenched, except that of the compounds to be determined.

With nitromethane as the quencher, it is possible to distinguish PAH's with the fluoranthene skeleton from all other PAH's. Whereas the fluorescence of PAH's with the fluoranthene skeleton is not quenched in the presence of nitromethane, quenching is observed for all other structures. The effect can be verified both in solution and on thin layer chromatograms. This structure-

specific quenching effect is of great value for the recognition and determination of fluoranthenes in complex PAH mixtures.

We have carried out extensive studies on the fluorescence quenching effect of methyl iodide on a large number of aromatic and heteroaromatic systems.³⁴ A mixture of 1 part by volume of benzene and 4 parts by volume of methyl iodide was used as the solvent. On excitation with wavelengths greater than 400 nm, the fluorescence quenching effect in this solvent is due to the external heavy-atom spin-orbit coupling effect of methyl iodide. With exciting wavelengths smaller than 400 nm, both the heavy-atom perturbation and the inner filter effect of the methyl iodide are effective. Out of 50 PAH's and corresponding heteroaromatic systems examined, practically complete quenching of the fluorescence was observed for 44 compounds, whereas the fluorescence of the other 6 compounds suffered practically no quenching. These compounds can be recognized with very high selectivity in complex PAH mixtures and quantitatively determined by fluorescence spectroscopy. The method has been evolved into a highly specific procedure for the determination of perylene in complex PAH mixtures. The range of application of the method can be increased, with some loss of specificity, by variation of the methyl iodide content in the solvent. In this way, it is possible in many cases to recognize PAH's with the perylene skeleton in PAH mixtures, and this provides a valuable complement to Sawicki's method for the detection of PAH's having the fluoranthene skeleton.

A discussion of the analysis of PAH's would be incomplete without a mention of mass spectroscopy. Reference has already been made to the combination of GC and mass spectroscopy, which is one of the most impressive new analytical methods. When mass spectroscopy is applied to complex PAH mixtures without previous separation, methods that give mainly the molecule peaks are more suitable than electron impact. The method of electron addition mass spectroscopy introduced by von Ardenne *et al.*³⁵ should be mentioned here; in this method, the ionization is achieved by addition of thermal or almost thermal electrons. Another method is field ionization, in which electrons are removed from the molecules by very high electric fields.

Much has been said already about carcinogenic aromatic compounds and their occurrence. This is an analytical aspect. However, even reliable analytical information has little relevance to the problem of the danger to life through chemicals in the environment, unless it is combined with corresponding reliable toxicological information. The situation at present seems to be characterized by a serious disparity in our knowledge of environmental analysis and of environmental toxicology. For example, Henschler³⁶ suggested that the presumed toxic effects of chemicals in the environment far outnumber the effects that have been verified. The situation with regard to

the environmental toxicology of the PAH's is also by no means free from contradictions. However, because of the uncertainty of judgment that characterizes environmental toxicology, it is impossible to rule out any toxic risk in cases where an effect is suspected. This makes the great efforts of scientists in the field of environmental analysis essential.

References

1. H. O. Hettche, *Schriftenreihe der Landesanstalt für Immissions- und Bodennutzungsschutz des Landes Nordrhein-Westfalen (BRD)* **12**, 92 (1968).
2. J. Borneff, *Gas- und Wasserfach* **108**, 1072 (1967).
3. G. Grimmer, *Erdöl Kohle* **19**, 578 (1966).
4. B. Donn, *Astrophys. J.* **152**, 129 (1968).
5. G. M. Badger, *Proc. Roy. Soc.* **1956**, 87.
6. K. F. Lang, H. Buffleb, and M. Zander, *Erdöl Kohle* **16**, 944 (1963).
7. L. M. Norton and C. Andrews, *Amer. Chem. J.* **8**, 1 (1886).
8. G. M. Badger, *Symposium on the Analysis of Carcinogenic Air Pollutants* (Cincinnati, Ohio, August 29–31, 1961).
9. M. Knorr, *Schweiz. Z. Hydrol.* **19**, 283 (1957).
10. W. Gräf, *Med. Klinik* **15**, 561 (1965).
11. R. C. Lao, H. Oja, R. S. Thomas, and J. L. Monkman, *Presented at the Symposium on Recent Advances in the Analytical Chemistry of Pollutants* (Halifax, N.S., August 23–25, 1972).
12. H. D. Sauerland, *Brennst.-Chem.* **44**, 37 (1963).
13. G. Grimmer, A. Hildebrandt, and H. Böhnke, *Erdöl Kohle* **25**, 442, 531 (1972).
14. M. Zander, *Angew. Chem. Int. Ed.* **4**, 930 (1965).
15. K. Bhatia, *Anal. Chem.* **43**, 609 (1971).
16. R. P. W. Scott, *Gas Chromatography 1964*, edited by A. Goldup (The Institute of Petroleum, London, 1965).
17. K. Grob and G. Grob, *J. Chromatogr. Sci.* **7**, 515 (1969).
18. T. H. Gouw, I. M. Whitmore, and R. E. Jentoft, *Anal. Chem.* **42**, 1394 (1970).
19. H. D. Sauerland and M. Zander, *Erdöl Kohle* **25**, 526 (1972).
20. H. D. Sauerland, *Brennst.-Chem.* **45**, 55 (1964).
21. O. T. Chortyk, W. S. Schlotzhauer, and R. L. Stedman, *J. Gas Chromatogr.* **1965**, 394.
22. H. D. Sauerland and M. Zander, *Erdöl Kohle* **19**, 502 (1966).
23. J. Q. Walker and D. L. Ahlberg, *Anal. Chem.* **35**, 2028 (1963).
24. W. Lijinsky, I. I. Domskey, and J. Ward, *J. Gas Chromatogr.* **1965**, 152.
25. F. Micheel and H. Schweppe, *Naturwissenschaften* **39**, 380 (1952).
26. M. Zander and U. Schimpf, *Angew. Chem.* **70**, 503 (1958).
27. J. D. Pfaff and E. Sawicki, *Anal. Chim. Acta* **32**, 521 (1965).
28. H. C. Hollifield and J. D. Winefordner, *Anal. Chem.* **42**, 1759 (1968); R. Zweidinger and J. D. Winefordner, *Anal. Chem.* **42**, 639 (1970).
29. M. Zander, *Intern. J. Environ. Anal. Chem.* **1973**, Vol. 3, 29.
30. E. V. Shpol'skii, *Usp. Fiz. Nauk* **71**, 215 (1960); *ibid* **80**, 255 (1963).
31. H. J. Eichhoff and M. Köhler, *Z. Anal. Chem.* **197**, 271 (1963).
32. R. J. Lucasiewicz and J. D. Winefordner, *Talanta* **19**, 381 (1972).
33. E. Sawicki, T. W. Stanley, and W. C. Elbert, *Talanta* **11**, 1433 (1964).
34. M. Zander, *Z. Anal. Chem.* **263**, 19 (1973).
35. M. von Ardenne, K. Steinfeldt, and R. Tümmler, *Angew. Chem.* **73**, 136 (1961).
36. D. Henschler, *Angew. Chem.* **85**, 317 (1973).