

COMMUNICATION

TADEUSZ DUTKIEWICZ, STEFANIA RYBORZ, JACEK MASŁOWSKI*

ON METHODOLOGY OF POLYNUCLEAR AROMATIC
HYDROCARBONS DETERMINATION IN WATER

1. INTRODUCTION

Considering an ever increasing occurrence of neoplastic diseases, a large number of studies on carcinogenic compounds such as, e.g. PAH have been performed during the last 40 years. The most important feature of carcinogenic substances of the PAH group is the cyclic structure of benzo(a) anthracene with carbon substituent in the active position — meso. Substantial amounts of PAH are found in airborne particulates, soil, water and biological materials including also some of the foodstuffs [5]. PAH are formed in pyrolytic processes occurring during incomplete combustion of carbonic feels, petrol or mineral oil. They are also produced by grinding tyres, or in the course of pitch and asphalt production. These compounds penetrate water in various ways. Raw municipal sewage may contain large amounts of PAH, in general, however, the higher the contribution of industrial wastewater the higher is the PAH level [2].

According to Berneff and Kunte the asphalt pavement road run-off contains high PAH concentrations. This has been stated from the increased concentrations of these compounds in combined sewage municipal wastewater observed during rain. Environmental pollution over the highly industrialized and urbanized area of Upper Silesian Industrial Region (USIR) due to the presence of PAH has not been sufficiently examined yet. Hence of complex studies on the presence, transportation and changes of concentration of PAH in natural environment should be undertaken in order to determine their pathways and possible effects on human healths, as well as to develop effective methods for PAH elimination from environment.

2. REVIEW OF ANALYTICAL METHODS

The works aiming at PAH determination are the subject of numerous studies both in this country and abroad. So far, however, there are no universal and precise methods allowing the determination of PAH in various components of the environment.

All the methods developed employ chromatographic distribution of hydrocarbons eluted from the sample, and spectrometric or fluorometric measurement of adsorption within the ultraviolet range.

A number of studies [4] suggest that to determine PAH in water hydrocarbons, should be eluted using the method of direct extraction by ultrasonic field. The extracts obtained are purified in a chromatographic column filled with basic aluminium oxide. Distribution of PAH is performed by using thin layer technique

* Centre of Environmental Development, Katowice Division of the Research Institute for Environmental Development, Katowice, Poland.

with bidirectional development of chromatogram. Six hydrocarbons have been determined by direct measurements of fluorescence in the solution. This method is time-consuming, moreover, when purifying the extract some losses in PAH may be expected.

ACHESON et al. [1] compared the thin layer method of PAH separation with the method of gas chromatography. They found that for a number of substances the range of PAH identification by gas chromatography was wider than that in the thin layer technique; the latter, however, produced a better separation of PAH.

The comparison of continuous and periodic extraction techniques used for the separation of PAH from water gives preference to extraction performed under simultaneous action of ultrasonic field.

KOMERS et al. [3] employed column chromatography determination of PAH in airborne particulates.

Column was packed with neutral alumina and the cyclohexane-ethyl ether system being used as an eluent. From each of 35 fractions flowing out of the column, a 3 cm³ sample was collected and subjected to spectrophotometric analysis. With this method a precise quantitative determination of concentrations is for some hydrocarbons difficult, because of the overlapping of absorption bands representing various fractions.

Of the studies performed in Poland the methods developed in the State Institute of Hygiene deserve a special attention. A method of PAH separation in chromatographic column using alumina as a carrier was published by WYSZYŃSKA [6]. The system of cyclohexane-benzene with a gradual increase of benzene concentrations in cyclohexane is taken as the eluent. This method of PAH determination is considered inconvenient since its preparation requires a number of time-consuming steps.

For the above reasons the authors started to work on the improvement of PAH determination method based on the Komers' method. PAH concentrations have been determined in airborne particulates, water and soil, and further on in biological materials too. Analytical procedure for extraction of PAH from water, and conditions for chromatographic separation and identification of the compounds are presented in the sequel.

3. EXPERIMENTAL

3.1. PAH EXTRACTION FROM WATER

This process has been conducted using the periodic extraction method; its efficiency was tested on the following solvents: benzene, cyclohexane, and chloroform. As cyclohexane is practically insoluble in water, does not produce any stable emulsion, and it is more selective for PAH than benzene and chloroform; it has been selected for further experiment. This resulted in the reduction of ballast substances in the extract, thus facilitating a better separation of components in question. Sample volume, selected depending on water pollution level, ranged from 1 to 10 dm³; i.e., 50 cm³ of cyclohexane was added to 1 dm³ of sample and mixed for 1 hour with magnetic stirrer.

Extraction has been performed twice for each sample. The obtained extracts were filtered through anhydrous sodium sulphate and dried in the jet of compressed air. A full quantitative extraction is one of the difficulties encountered while examining water. In the experiments the extraction efficiency for various water samples ranged from 40 to 90 per cent.

Considering the fact that the extraction efficiency cannot be determined a priori, an internal standard of benzo (a) pyrene has been applied; it allowed to determine the percentage of PAH transferred to the solvent phase. A number of tests carried out, according to the described procedure, allowed to determine the concentrations of PAH in the water analyzed. Low concentrations of PAH were found in samples of settled water; much higher levels observed in unclarified samples have indicated adsorption of PAH on the suspended matter. The results inclined the authors to assume the possibility of co-precipitation of water dissolved PAH with ferric hydroxide and calcium oxalate precipitates. In order to develop more efficient and more adequate methods of extraction of PAH from water the investigations were first performed on

the adsorption of PAH on granulated activated carbon Z-4, and the desorption by elution with cyclohexane. Efficiencies of hydrocarbon adsorption on activated carbon reached almost 100% but the method of desorption requires refining. Experiments were aimed at increasing extraction efficiency by ultrasonic means and freeze drying of water samples.

It has been found that PAH extracts are unstable and decomposed when stored. Losses in PAH after 1 week, depending on storage conditions are the following:

Storage conditions	PAH losses (%)
darkness, room temperature	about 36,
darkness, temperature 270 K	about 50,
daylight, room temperature	about 70.

3.2. SEPARATION OF PAH BY COLUMN CHROMATOGRAPHY

Flub's neutral alumina deactivated to 68% of its former activity constituted the filling of chromatographic column. This carrier was wet formed into a column 12 cm long over which 2 cm³ of PAH extract were placed. Thereupon hydrocarbons were washed out first with cyclohexane, and starting from the 14-th fraction — with the mixture of cyclohexane and ethyl ether given in voluminal ratio 97:3. Finally from each of 25 fractions a 3 cm³ sample was collected. The complete outflow of all the fractions tested was about 1.5 h. The efficiency of the column was 95%.

3.3. IDENTIFICATION AND DETERMINATION OF PAH

The fractions collected were analyzed with the spectrophotometer Pye Unicam 1800 in the wavelength range of 220–520 nm.

The interpretation was based on zero-line with the selection of a narrow band. This method produced satisfactory separations of pyrene, benzo(a)anthracene, fluoranthene, anthracene, chrysene, benzo(e)pyrene, benzo(a)pyrene, antranthrene, benzo(ghi)perylene and coronene.

All the above listed hydrocarbons have been found in water samples taken from the Bytomka River near its outfall to Klodnica, e.g. benzo(a)pyrene concentrations ranged from 2.25 to 9.65 µg/dm³.

The chief advantage of the method that it is labour and time saving; the determination period for one sample is about 4 hours. Excellent separations have been obtained for 10 hydrocarbons belonging to the PAH group. At present the research is aimed at the most effective technique of PAH extraction and at the application of domestic neutral alumina to the separation of their components.

4. CONCLUSIONS

Because of its selectivity and quickness the chromatography using spectrophotometric techniques to separate and identify individual hydrocarbons is the most useful method of PAH determination, under various environmental conditions.

Sensitivity of the method is adequate for determining PAH concentrations in water, air and soil, provided sufficient care is taken during storage and processing of the samples to avoid the losses of these compounds.

REFERENCES

- [1] ACHESON M. A., *Factors affecting the extraction and analysis of polynuclear aromatic hydrocarbons in water*, Water Research **10**, 3, 1976.
- [2] HARRISON R. M., *Polynuclear aromatic hydrocarbons in raw, potable and wastewaters*, Water Research **4**, 333–343, 1975.

- [3] KOMERS W., *Polycyclic hydrocarbons. Determination of polycyclic hydrocarbons in air*, Research Institute for Environmental Hygiene Raport G 689, Delft, Holland, 1976.
- [4] KUNTE H., *Nachweisen für polycyclische aromatische Kochlenwasserstoffe in Wasser*, Wasser Abwasser Forschung **1**, 35-38, 1976.
- [5] SOKOŁOWSKA R., *Studies on some foodstuffs for benzo(a)pyrene contents* (in Polish), Roczniki PZH **3**, 245-259, 1974.
- [6] WYSZYŃSKA H., *Benzo(a)pyrene in environment and human body*, (in Polish) Gaz, woda, Techn. Sanit. **1**, 2-4, 1972.