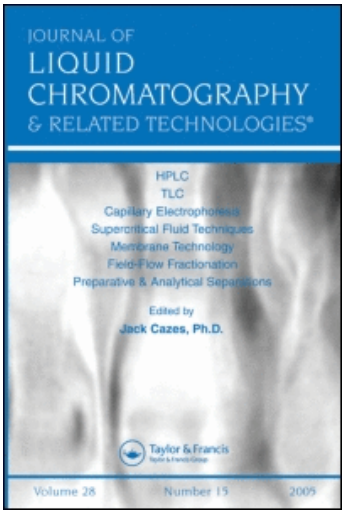

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Lehotay, J. , Halmo, F. , Brandšteterová, E. and Oktavec, D.(1993) 'HPLC-DAD Determination of Benzo(a)Pyrene in Waste Gas', Journal of Liquid Chromatography & Related Technologies, 16: 16, 3575 — 3584
To link to this Article: DOI: 10.1080/10826079308019710
URL: http://dx.doi.org/10.1080/10826079308019710

JOURNAL OF LIQUID CHROMATOGRAPHY, 16(16), 3575-3584 (1993)

HPLC-DAD DETERMINATION OF BENZO(A)PYRENE IN WASTE GAS

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ABSTRACT

Diode array detection (DAD) was used in HPLC trace determination of benzo(a)pyrene in gas emission. The lienarity and detection limit was calculated. It was found that DAD - HPLC combination is selective and sensitive enough to be used for the monitoring of the benzo(a)pyrene concentration in gas emission where its presence is presumed. The limit of the determination of the suggested method is 1 $\mu g/m^3$.

INTRODUCTION

Polyaromatic compounds are often formed because of the incomplete combustion of organic materials or in pyrolysis processes. (To the most frequent sources belong the refinery units used in oil processing and the high temperature pyrolysis processes). The polyaromatic substances represent a group of noxious organic compounds and from the carcinogenity point of view mainly benzo(a)pyrene shows a most toxic character /1/. For this reason the development of an analytical

method is very important for the determination of very low concentrations of benzo(a)pyrene in the emissions. The qualitative criteria for polyaromatic substances in the atmosphere are described in several articles /1, 2/. HPLC is often used for the separation of polyaromatic compounds mainly in the case of very low concentrations /3/. The determination of benzo(a)pyrene in imissions in the surroundings of big cities requires the sample of a bigger air volume - up to 860 m^3 /4/. The correlation between the polyaromatic substances in the atmosphere and waters was also determined /4/. HPLC with a precolumn system can be used for the on-line preconcentration of polyaromatic hydrocarbons. In this way a lower limit to the determination can be achieved /5, 6/.

A new separation technique for polyaromatic hydrocarbon determination is the micellar electrokinetic capillary chromatography /7/. While benzo(a)pyrene belongs to toxic substances its concentration is being followed in biological materials too /8, 9/.

EXPERIMENTAL

A right result of benzo(a)pyrene determination depends on the sampling technique and on the method used for the quantitative analysis. In sampling the highest effectivity of the benzo(a)pyrene trapping from the waste gas using a sorption equipment is required. There is a possibility of the presence of some other organic substances with similar physical-chemical properties in the emission as benzo(a)pyrene shows, for this reason the use of an separation method is necessary. So the use of the high performance liquid chromatography with selective detection is of great advantage as it can be seen from the discussion in the next section.

The boiling point of benzo(a)pyrene is 495.5 ^{o}C and for this reason it is obvious that it is present in the emission in the form of aerosols, or it is sorbed on the particles. The temperature of the emission gases containing benzo-

(a)pyrene moves in a wide interval of from 50 to 300 ^{o}C in dependence on the process followed. This fact must be taken into account in the construction of the sampler. At a temperature of the emission gases up to 100 ^{o}C cellulose filters can be used /2/. In the most cases there are used filters from glas fibres, or their combination with sorption tubes and polyurethane foam /10/. Glass filter impregnated with paraffine oil can be used, too /2/.

The sampling train consists of the sampling probe from stainless steel (inside diameter of 10 mm). The suction tube is heated to such a degree that the temperature of the aspirated gas stream corresponds to that in the waste gas channel; this prevents any change in the state of aggregation of the sample gas components. The heat output of the suction tube was 250 W per meter. The filtration head consisted of a flat filter from glass fibres (GF/A Whatman) and a polyurethane foam layer. The flowmeter (PUMA PS) was used for the measurement of the waste gas volume. For the measurement of the temperature of the gas in front of the filter a thermocouple was used. An oil diffusion pump (LP-VK 2-5) was used as a suction aggregate. The sampling filter must be protected from UV radiation and sealed in airtight polyethylene bags and stored under cool conditions in the dark until required for sample preparation.

For the benzo(a)pyrene determination by HPLC there was used a chromatographic column Separon SGX C18 with 5 μm particles (Tessek Prague) with an inside diameter of 3.3 mm, the lenght of the column was 150 mm. A high pressure liquid chromatograph consisted of the following parts :

high pressure pump Model 501 (Waters-USA)
6-way valve (VALCO - USA)
spectrophotometric detector Model 484 (Waters - USA)
diode array detector Model 990 (Waters - USA)
PC computer NEC (Work Station).

The benzo(a)pyrene extraction was performed in an ultrasonic bath, the preconcentration was realized by means of

Kuderna-Danish evaporator. All solvents used in this work were redistilled. A standard benzo(a)pyrene with p.a. purity was used for the determination (Supelco - USA).

Before the start of the sampling process the temperature and pressure of the emission gases, the velocity profile of the flowing gas must be measured in order that the isokinetic sampling can be realized. The emission gas was passing through 2 filters ordered one after the other in order that the quantity of the benzo(a)pyrene sampling could be tested. The sample gas volume moved in an interval of about 0.5 - 1 m^3.

The filters were extracted with 2x 10 ml of hexane in an ultrasonic bath (15 minutes). The extract was transferred into a 25 ml calibrated vessel that has been refilled with hexane up to the mark. 10 ml of hexane was evaporated on Kuderna-Danish evaporator. The rest was solubled in 1 ml of methanol and the solution was injected into the liquid chromatograph. The purity of the filters and solvents used is checked by the analysis of chemical blank value solutions including the working up of the blank filter.

The separation and determination of benzo(a)pyrene were carried out with the chromatographic column Separon SGX C18. A mixture of 90 % methanol in water was the mobile phase, the flow rate of the mobile phase was 0.5 ml/min. The determination of benzo(a)pyrene was carried out by UV detector at 364 nm. There was also used a diode array detector in the range from 210 to 400 nm to confirm that there was no interference with the other substances.

RESULTS AND DISCUSSION

Care must be taken to optimize HPLC conditions for retention time of benzo(a)pyrene sensitivity and selectivity of the separation process. Using a diode array detector the determination can be carried out if there is eluted another component in the place of the elution of benzo(a)pyrene and a suitable

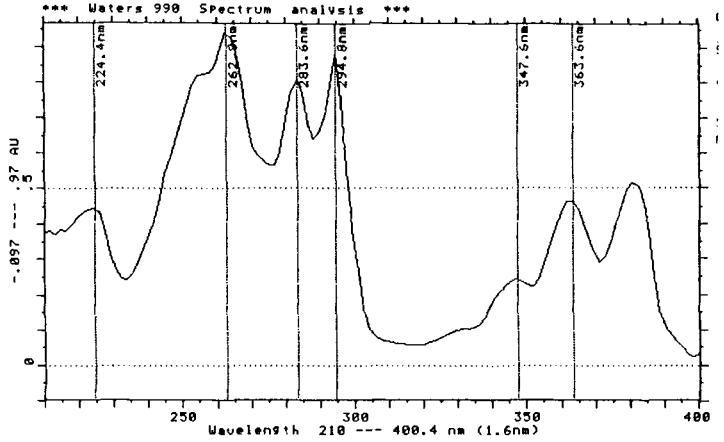

Fig.1 UV spectrum of benzo(a)pyrene in the range from 210 to 400 nm in the mobile phase of 90 % methanol in water.

wave lenght for detection can be found. Some absorption maxima of benzo(a)pyrene can be seen in Fig.1, from which the maximum at 264.4 nm would be most advantegously used as the limit of the determination would have the least value. On the other hand many organic substances absorb at this wave lenght and an interference can be occured. It can be seen from the contour chromatographic records (Figs.2 and 3) that there is an absorption maximum at 364 nm in the time of benzo(a)pyrene elution as it is obvious from the contour chromatogram of the standard (Fig.4). For this reason the detection will be selective at this wave lenght for benzo(a)pyrene and the possibility of the interference with other substances is considerably lower.

The conditions of the separation were chosen so that in the place of elution of benzo(a)pyrene there were eluated no substances with similar optical properties as the determined substance. It is obvious from the contour chromatograms (Figs.2 and 3) that no other substances are eluted at the elution time of about 18 minutes which have the absorption maximum in the

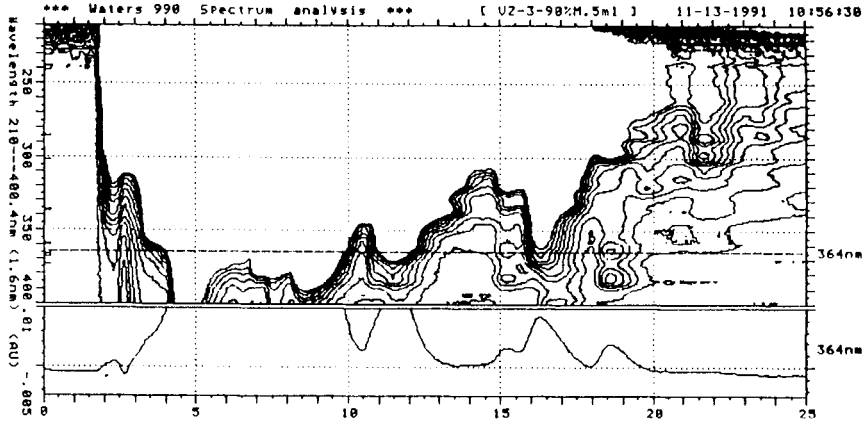

Fig.2 Contour chromatographic record and chromatogram at 364 nm of the sample 1.
Injection 10 µl, column Separon SGX C18 (5 µm particles), mobile phase 90 % methanol in water, flow rate 0.5 ml/min.

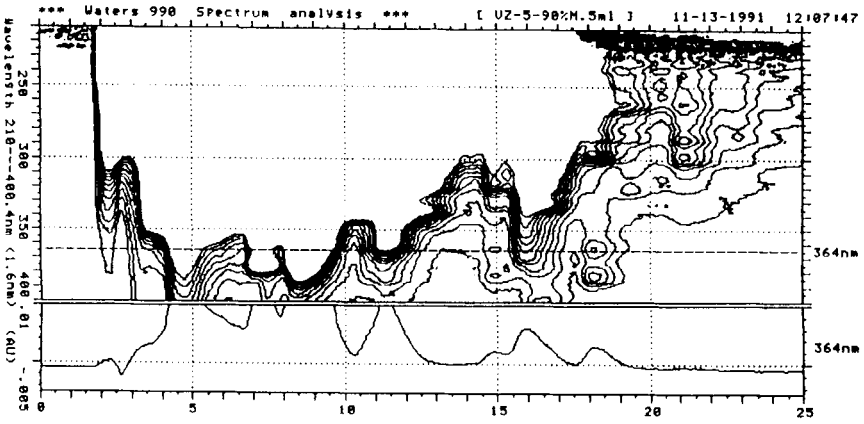

Fig.3 Contour chromatographic record and chromatogram at 364 nm of the sample 2
Separation conditions as in Fig.2

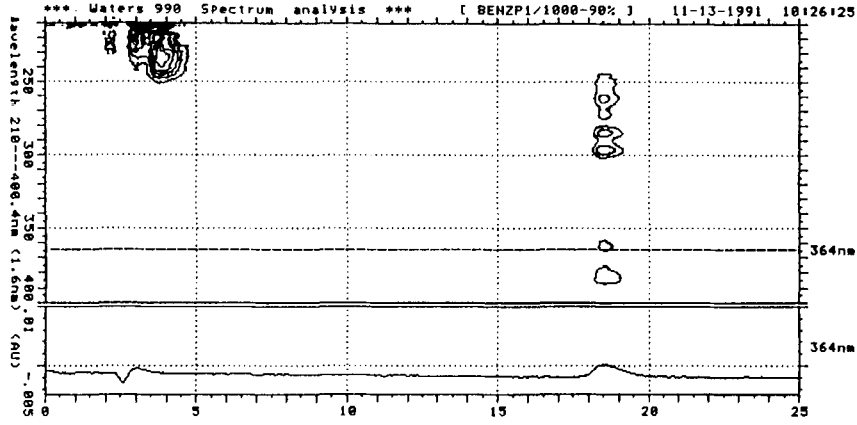

Fig.4 Contour chromatographic record and chromatogram at 364 nm of standard benzo(a)pyrene (concentration 1 ppm in the solution) Separation conditions as Fig.2. Elution time of benzo(a)pyrene 18.7 min.

range of 300-362 nm except benzo(a)pyrene. From the chromatograms can be seen that with benzo(a)pyrene also other substances are eluted, but their absorption maxima are below 300 nm and they have no effect on the detection at higher wave lenght.

The qualitative evaluation was carried out on the basis of a comparison of the elution time of the standard and the sample and on the basis of the absorption maximum at 364 nm that is characteristic for benzo(a) pyrene as well. The quantitative evaluation was made on the basis of the regression analysis where the dependence between the areas of benzo(a)-pyrene peaks and the quantity determined. The concentration range was from 1 ppm to 10 ppm. The value of the correlation coefficient is proven. In Fig.5 is the chromatographic record of the sample 4 when a spectrophotometric detector at 364 nm was used.

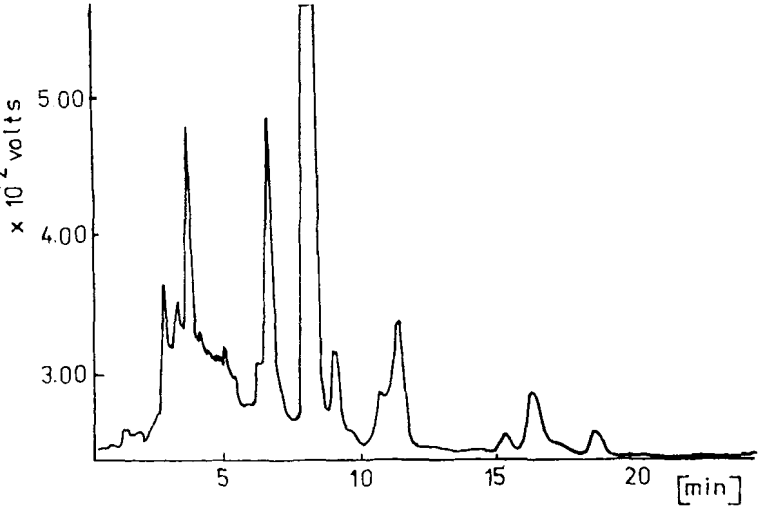

Fig.5 Chromatographic record of the sample 4.
Detection at 364 nm.
Separation conditions as Fig.2.

Tab.1 Determination of benzo(a)pyrene in the samples

No of the sample	Sampling volume m^3	Benzo(a)pyrene concentration //ug/m^3/	Relative standard deviation
1	0.640	10.9	± 8.6
2	0.974	2.8	± 12.4
3	0.500	10.0	± 7.6
4	0.500	3.5	± 10.9

Mean of benzo(a)pyrene concentrations is based on sample gas volume under standard conditions.

The results of the determination of benzo(a)pyrene in the samples are given in Tab.1. From the values of the standard deviations can be seen that the value is increasing with the decreasing of the benzo(a)pyrene content in the sample. The optimum concentration interval is in the range of 1/ug - 10/ug in 1 ml of methanol. The value of the relative standard deviation can be decreased by sampling a greater volume of emission but on the other hand the probability of an interference can increase. The limit of the determination depends on the aspirated waste gas volume. The concentration of benzo(a)-pyrene in the emissions of $1/ug/m^3$ can be determined that is in the agreement to the requirements given in the norm for Germany /2/. The absolute limit of the determination - the amount, that can be determined in the injected solution (10/ul) is 0.5/ug (detection at 364 nm). At this amount the height of the chromatographic peak was five time higher than the noise of the basic line.

Simultaneously with the extract of the first filter the extract of the second filter was analysed. It was found that the amount of benzo(a)pyrene was below the limit of the determination. It can be pointed out that the use of one filter for the determination is sufficient in trapping of benzo(a)-pyrene from the emission.

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Received: January 22, 1993
Accepted: June 12, 1993