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# Some Aspects of the Measurement of Polycyclic Aromatic Hydrocarbons in Aqueous Solution†

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Polycyclic aromatic hydrocarbons (PAH) are formed during pyrolysis or incomplete combustion of organic materials. As a result of an increasing public concern about the contamination of the environment, polycyclic aromatic hydrocarbons are extensively studied compounds. Because PAH are present in effluents from coal firing and advanced coal conversion processes, methods are studied in our laboratory to quantify PAH-emissions.

It is known that during sample collection, sample storage, sample clean-up, trace enrichment and detection irreproducible losses, caused by the chemical reactivity and irreversible adsorption of PAH complicate a quantitative analysis.

In model experiments to study the adsorption of PAH from aqueous solution onto a variety of substrates, the results with pyrene onto silica and coal ash are described. HPLC was used as detection method.

**KEY WORDS:** High performance liquid chromatography, polycyclic aromatic hydrocarbons, adsorption, coal.

## INTRODUCTION

As a result of an increasing public concern about the contamination of the environment, polycyclic aromatic hydrocarbons (PAH) are extensively studied compounds. The PAH are present in effluents from coal firing facilities and advanced coal conversion processes. It is known that during

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sample collection, sample storage, sample clean-up, trace enrichment and detection, irreproducible losses, due to photo-oxygenation,<sup>1</sup> photodecomposition<sup>2</sup> and sorption<sup>3-5</sup> complicate PAH analysis.

Also the *in situ* decomposition of PAH and the reaction of PAH with compounds as NO<sub>x</sub> and SO<sub>x</sub> have hardly been studied. Condensation and sorption of PAH on the walls of stacks and pipes make it very difficult to choose the "right" sampling place and sampling equipment.

However, the adsorption phenomenon can be used for trapping PAH using solid matrices such as carbon, Tenax GC, XAD-resins, polyurethane foams or C<sub>18</sub> bonded phases. In this case the main problem is the desorption efficiency, which is not 100%. The complexity of the analytical chemistry of PAH necessitates to split the study of it into two parts; the first part (this paper) describes the problems associated with the sampling of PAH in water effluent streams and the second part the sampling technique of PAH in the gas phase.<sup>6</sup>

In order to decide which materials should be used for the sampling train and the analytical procedures, the adsorption characteristics of a variety of solids have to be known. Because of the relatively high solubility (135 µg/kg) and stability<sup>7</sup> of pyrene in water we choose this compound as model compound in our adsorption study. The solubility of benzo(α)pyrene is too low to determine its concentration without sample enrichment; so without introducing errors, due to sample handling. Very little is known about the adsorption properties of PAH from the water phase onto solid matrices.

Means *et al.*<sup>4</sup> studied the sorption of pyrene on 14 sediments and soil substrates. They found linear equilibrium isotherms and coverage of 7.9% and also a correlation between partition coefficient and organic carbon content.

May *et al.*<sup>8</sup> developed the so-called dynamic coupled column liquid chromatographic technique and evaluated this method in terms of the saturated PAH solution preparation, solution transfer and extraction, and quantitative analysis processes. They studied the adsorptive properties of three PAH, phenanthrene, chrysene and benzo(α)pyrene on four different surfaces, namely: glass, silanized glass, platinum and aluminum.

Their results showed that losses of PAH from static solutions to surfaces occur in short periods of time and also that stirring such solutions only slightly reduces such losses.

In the present investigation HPLC was used to monitor *in situ* the adsorption of PAH, on silica, alumina, coal slag and three polymers; PVC, PTFE and PE.

## EXPERIMENTAL

### Reagents

Pyrene (Fluka AG) was used as received from the supplier.

Water. HPLC-quality, deoxygenated with helium gas.

Methanol. HPLC-quality.

### Glassware

The glassware and PTFE tubing were rinsed with methanol, acetone and dried with nitrogen gas.

### Procedure

A saturated aqueous pyrene reference solution is prepared according to a method, described by May *et al.*<sup>8</sup> By means of a metering pump (type 312 Isco Inc., Lincoln, Nebr., U.S.A.) with a flow rate of 1.6 ml/min the solution is introduced under continuous magnetic stirring via PTFE-tubing into a 250 ml three-necked glass flask filled with 100 ml water. The temperature is  $22 \pm 2^\circ\text{C}$ . To prevent photo-oxidation of pyrene the flask is wrapped in metal foil and flushed with oxygen-free nitrogen with a flow rate of about 30 ml/min.

The adsorbing material is added to the solution and samples are drawn through a filter tube to an injection valve at regular time intervals. The filter consists of a necked quartz tube (length 5 cm, o.d. 3 mm, i.d. 1 mm), containing about 2 mg of quartz wool. The connection between the filter tube and the injection valve consists of a reducing union (1/8"  $\times$  1/16") and PTFE-tubing (o.d. 1/16", i.d. 0.8 mm). The sample is transported to the injection valve by means of a water filter pump.

### High performance liquid chromatography

HPLC was conducted using a Waters Assoc. (Bedford, Mass., U.S.A.) Model 6000 A solvent delivery pump, a Valco Instr. (Houston, Texas, U.S.A.) 6-port manual sample injection valve, provided with a 100  $\mu\text{l}$  sample loop, a guard column and a Waters Radial PAK A (C18 reverse phase) column. The mobile phase was methanol-water (95:5).

Detection of the 100  $\mu\text{l}$  samples was accomplished via a Waters Model 420 Fluorescence Detector with a 254 nm excitation filter and a 375 nm emission filter. The volume of the quartz flow cell was less than 20  $\mu\text{l}$ .

## RESULTS AND DISCUSSION

The concentration of a saturated aqueous pyrene solution is  $135 \mu\text{g}/\text{kg H}_2\text{O}$  at  $22.0^\circ\text{C}$ .<sup>8</sup> In our experiments the initial pyrene concentration is about  $65 \mu\text{g}/\text{l}$ . The peak in the corresponding chromatogram, given in Figure 1 represents  $6.5 \text{ ng}$  of pyrene in a  $100 \mu\text{l}$  sample volume; the detection limit at  $k' = 1.83$  is  $0.7 \text{ ng}$ .

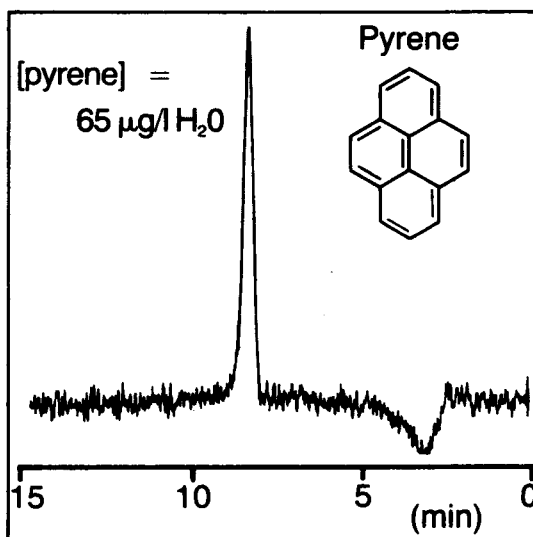


FIGURE 1 Chromatogram of pyrene.

During 70 hours the peak height of pyrene was measured. The average height, expressed as a percentage of the initial pyrene concentration was 95.8% with a standard deviation of 3.8%. This is in agreement with results of Sorrell *et al.*<sup>7</sup> concerning the stability of aqueous pyrene solutions.

The results of the measurement of the concentration decrease of pyrene, starting with a  $65 \mu\text{g}/\text{l}$  aqueous pyrene solution are given in Figures 2 and 3; the adsorbing materials studied are specified in Table I.

Under the prevailing conditions the decrease of the pyrene concentration in the solution can be described as an exponential function of time. In Table II the values of the half-lives and the coefficients of determination are given.

Silica and Alumina H.P.V. give no significant decrease of the pyrene concentration within 70 hours. However, Silica C18 and coal slag adsorb pyrene relatively fast. The difference in behaviour between the two

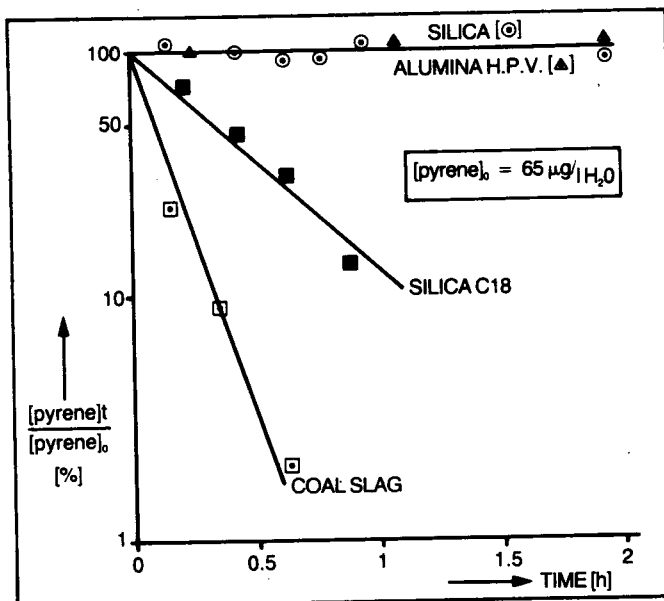


FIGURE 2 Relative concentration of pyrene versus time: inorganic substrates.

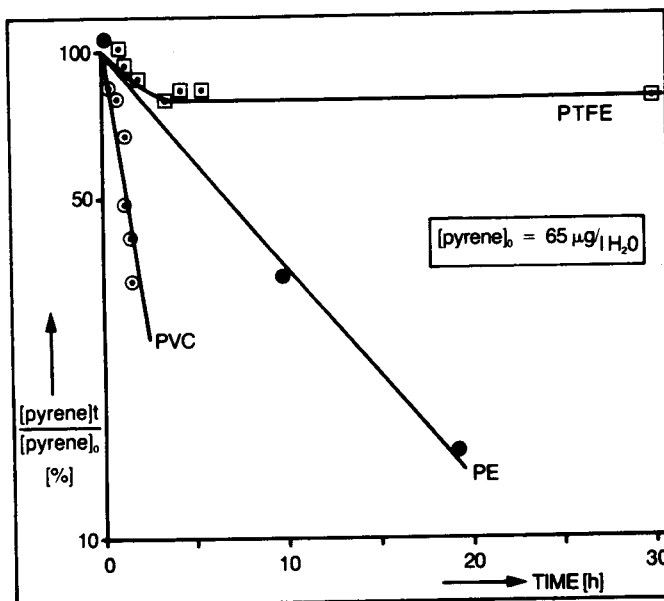


FIGURE 3 Relative concentration of pyrene versus time: polymer substrates.

TABLE I

Survey of substrates studied.

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1	Silica, Li Chrosorb Si-60-10 (Merck), 500 m <sup>2</sup> /g
2	Alumina H.P.V. (Akzo), Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> , 25:75, 524 m <sup>2</sup> /g
3	Nucleosil 10C18 (Machery-Nagel), Silicasilica with chemically bonded C18-groups, carbon content 14.6%, w/w, 190 m <sup>2</sup> /g
4	Coal slag, Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> , 25:50 (avg), carbon content 31.5%, w/w, 75 m <sup>2</sup> /g
5	Polyethylene beads (3 mm), density 0.96 g/cm <sup>3</sup> , melting point 129–133°C, 20 cm <sup>2</sup> /g
6	Polyvinylchloride, slices 3 × 5 × 5 mm, density 1.19 g/cm <sup>3</sup> , glass transition temperature about –60°C, 23 cm <sup>2</sup> /g
7	Polytetrafluorethylene, tubing (o.d. 6 mm, i.d. 4 mm), slices (3 mm thickness), density 2.2 g/cm <sup>3</sup> , 13 cm <sup>2</sup> /g

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materials might be caused by the difference in total carbon content of Silica C18 and coal slag, namely 14.6 and 31.5%, w/w, respectively.

With respect to the polymers studied, one would expect an increasing half-life in the order PVC-PTFE-PE on structural considerations. However, the experimental order is PVC-PE-PTFE. A possible explanation is that the fluorine atom in PTFE with its high electronegativity repels the  $\Pi$ -electron system of pyrene, thereby hampering the diffusion of pyrene into the polymer structure more than in PE and PVC. It is noted that the presence of plasticizer in PVC might also influence the pyrene adsorption process significantly.

Assuming that pyrene molecules with an area of 91 Å<sup>2</sup><sup>9</sup> adsorb flat on the surface it can be seen from Table II that the theoretical coverage is independent of the B.E.T. surface area. Therefore, the sorption process of pyrene onto Silica C18 and coal slag is probably an adsorption; onto PE and PVC an absorption.

## CONCLUSIONS

In the absence of light and oxygen the rate of adsorption of pyrene from water onto certain materials can be described as an exponential function of time. For the inorganic materials studied the rate of adsorption is also correlated with the total carbon content of the adsorbing material.

A significant difference in the rate and mechanism of the sorption process onto inorganic (Silica C18 and coal slag) and polymer (PE and PVC) substrates was observed.

The difference in behaviour between PTFE, PE and PVC can be explained in terms of electronic and steric effects.

Silica, alumina H.P.V. and PTFE, showing no adsorption, are preferred materials to be used in sampling and storage devices.

TABLE II  
Sorption of pyrene from aqueous solution onto various materials.

Material	Mass [g]	Surface area [m <sup>2</sup> ]	Coverage (theoretical) at $t = t_h$ [%]	Half-life [h]	Coefficient of determination
1 Silica	0.2440	122	0	≥ 70	—
2 Alumina H.P.V.	0.1843	96	0	≥ 70	—
3 Silica C18	0.2014	38	$52 \cdot 10^{-3}$	0.33	0.996
4 Coal slag	0.1872	75	$26 \cdot 10^{-3}$	0.11	0.989
5 PE	0.6630	$13 \cdot 10^{-4}$	> 100	6.7	0.997
6 PVC	1.8197	$42 \cdot 10^{-4}$	> 100	1.12	0.967
7. PTFE	1.1672	$28 \cdot 10^{-4}$	0	≥ 70	—



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