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EXTRACTION AND DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS FROM DOMESTIC STOVE AEROSOL

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INTRODUCTION

Polycyclic aromatic compounds (PAC) is a collective noun of compounds, of which many have mutagenic and carcinogenic properties (Bjorseth, 1983; Lee et al., 1981). Like the parent polycyclic aromatic hydrocarbons (PAH), PAC may be divided into a number of subclasses; amino, nitro, cyano polycyclic aromatic hydrocarbons, etc.

To study the effects of stove emission of PAC and other components on the environment and health, and to support new stove design, reliable analytical procedures must be available. Because of the high toxic properties of PAH, the development of extraction and analytical procedures in domestic stove smoke aerosol was of first interest.

For these samples the analytical procedure generally includes an extraction and a clean-up or pre-fractionation step, followed by the proper analytical stage.

In this paper we concentrate on the problems encountered in the development of extraction techniques for PAH from aerosol samples of stove smoke.

The organic part of the collected aerosol samples, which contain PAH, is generally separated from the inorganic part by solvent extraction procedures. PAH are soluble in many organic solvents like acetone, methanol, dichloromethane, cyclohexane, toluene, dimethylsulfoxide, etc. Many of these solvents or mixtures are advocated for the extraction of the organic part of the aerosol (Pitts et al., 1978; Barton et al., 1979).

The extractions are generally carried out by a Soxhlet procedure or as an attractive alternative by ultrasonic agitation. The efficiency of the various available procedures depends on the chemical and physical structure of the sample, properties of the extraction solvent and extraction conditions such as time and temperature. The physical and chemical nature of the collected aerosol sample play an important role in extraction efficiencies (Fitc and Smith, 1979; Griest et al., 1980). Domestic stove smoke aerosol partly consists of carbonaceous particles of small size ranges (<10 μm), so exposing a large adsorption area. This may strongly adsorb PAH and other components and decrease extraction efficiency considerably, as will be shown later.

An attractive alternative for the Soxhlet extraction method is the ultrasonic agitation technique as the latter is less time-consuming and offers the opportunity to extract samples at ambient or other temperatures. In our investigations we favoured low-boiling, non-UV-adsorbing extracting liquids. This allows the extracting agent to be evaporated easily in order to raise PAH concentrations to facilitate the detectability. Moreover, UV-adsorbing liquids interfere with the proper UV-detection of PAH components in the sample.

In this work a number of extraction liquids were tested, applying both the Soxhlet method and ultrasonic agitation as extraction techniques. The extraction procedures were applied to blank, real and spiked aerosol samples and the results were compared.

The analytical procedure to determine PAH after extraction of the aerosol exhaust is based on high-performance liquid chromatography (HPLC) for both the clean-up and analysis step.

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Fluorescence and UV techniques are used for the detection of the separated PAH. The analytical procedure is applied routinely in our laboratory. A detailed discussion of these methods is beyond the scope of this paper. Figure 1 shows a chromatogram of the separation of a standard solution of the 16 PAH under investigation by HPLC.

EXPERIMENTAL METHOD

All chemicals and solvents were of analytical grade (Merck, Darmstadt, F.R.G.) except petroleumether (Shell Rotterdam, The Netherlands). Standards of the 16 Priority Pollutant PAH were from Serco Inc. Roseville Minn., U.S.A., and include: 1 = naphtalene, 2 = acenaphtalene, 3 = acenaphtene, 4 = fluorene, 5 = phenanthrene, 6 = anthracene, 7 = fluoranthene, 8 = pyrene, 9 = benzo(a)anthracene, 10 = chrysens, 11 = benzo(b)-fluoranthene, 12 = benzo(k)fluoranthene, 13 = benzo(a)pyrene, 14 = benzo(g,h,i)-perylene, 15 = dibenzo(a,h)anthracene and 16 = indeno(1,2,3-c,d)pyrene.

Extractions were carried out in standard laboratory glassware. The HPLC equipment for the pre-fractionation and analytical steps was constructed of several manufactured parts.

Domestic stove smoke aerosol from hard wood as fuel was sampled by the filter collection technique on glass fiber filters, of which a representative part was subjected to the extraction procedure. Samples were stored in the dark in closed vessels at a temperature of −16°C and extracted and analyzed within a few days.

Three low-boiling extraction liquids: diethylether, dichloromethane and petroleumether, were tested. The relatively high-boiling dimethylsulfoxide (DMSO) was also applied as an extractant.

Both the Soxhlet extraction technique and ultrasonic agitation were investigated. Typical extraction time for the Soxhlet procedure was 16 h; the extraction was carried out under nitrogen and protected from light to avoid PAH losses from the sample. Under the ultrasonic agitation technique the sample was sequentially treated four times for 10 min with the extractant and afterwards the extracts were collected. For both techniques the extract was then evaporated under a gentle N₂-stream prior to the pre-fractionation.

Fig. 1. Isocratic separation of a standard solution of the 16 PAH under investigation. Eluent: water-acetonitrile, 22:78 v/v; Column: 200 × 3.0 mm with Vydac 201 TP as stationary phase; Detection: fluorescence and ultra-violet; Temperature: 25°C.
Five extraction procedures were tested:

I. Ultrasonic agitation with diethylether at ambient temperature,
II. Ultrasonic agitation with dichloromethane at ambient temperature,
III. Soxhlet extraction with petroleumether,
IV. Soxhlet extraction with dichloromethane,
V. Ultrasonic extraction with dimethylsulfoxide at 100°C.

From the chromatographic data such as retention times, peak height and area, qualitative and quantitative information of PAH in the sample could be obtained.

RESULTS

To test the recoveries of the five selected extraction procedures, blank filters spiked with known quantities of the 16 PAH were extracted and analyzed. For the five extraction methods reproducible recoveries of at least 95 % for the 16 PAH were estimated. For the whole procedure of extraction and analysis, reproducible results of 90 % were determined for all PAH components.

A number of identical aerosol samples were then extracted according to procedures I–V and analyzed.

To compare the different extraction procedures the recovery data were calculated taking the results of method I as unity. These results are summarized in Table 1.

For these types of samples, it is questionable what percentage of the adsorbed and encapsulated PAH material is extracted by a certain extraction procedure. Therefore, a number of aerosol samples were spiked with known amounts of PAH and immediately afterwards extracted and analyzed. For methods I, II and V the results are summarized in Table 2.

Table 1. PAH recoveries of aerosol samples from five selected extraction procedures; results refer to extraction method I. – = Not detected with ether extraction in that typical sample; 0.0 = not detectable with the corresponding extractant

<table>
<thead>
<tr>
<th>Component</th>
<th>Extraction method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>1.0</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>1.0</td>
</tr>
<tr>
<td>Benzo[a]anthracene</td>
<td>1.0</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene</td>
<td>1.0</td>
</tr>
<tr>
<td>Benzo[k]fluoranthene</td>
<td>1.0</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>1.0</td>
</tr>
<tr>
<td>Benzo[g,h,i]perylene</td>
<td>1.0</td>
</tr>
<tr>
<td>Indeno[1,2,3-cd]pyrene</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 2. Recoveries of PAH spiked aerosol samples in percentages of added PAH amounts

<table>
<thead>
<tr>
<th>Component (%)</th>
<th>Extraction method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
</tr>
<tr>
<td>Naphtalene</td>
<td>0</td>
</tr>
<tr>
<td>Acenaphthalene</td>
<td>0</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>137</td>
</tr>
<tr>
<td>Anthracene</td>
<td>87</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>66</td>
</tr>
<tr>
<td>Pyrene</td>
<td>46</td>
</tr>
<tr>
<td>Benzo[a]anthracene</td>
<td>60</td>
</tr>
<tr>
<td>Chrysene</td>
<td>56</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene</td>
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<tr>
<td>Benzo[k]fluoranthene</td>
<td>66</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>63</td>
</tr>
<tr>
<td>Dibenzo[a,h]anthracene</td>
<td>54</td>
</tr>
<tr>
<td>Benzo[g,h,i]perylene</td>
<td>32</td>
</tr>
<tr>
<td>Indeno[1,2,3-cd]pyrene</td>
<td>40</td>
</tr>
</tbody>
</table>
From these results it can be concluded that the recoveries of the spiked material are poor.

DISCUSSION AND CONCLUSIONS

From the experiments and results on PAH spiked blank filters it appears that reliable extraction and analysis procedures are available for simple non-adsorbing sample matrices.

For the aerosol samples under investigation the relative efficiencies for the different PAH and extraction methods are questionable.

The results of Table 1, in which a large number of identical aerosol samples are treated, show different recoveries for the several PAH components. This might be due to the different molecular structures of PAH, as there are linear and angular annulated ring systems. Efficiency variations from one-to-one correlation to 60% deviation between the several extraction procedures are observed. From these data it is hard to decide which percentage of PAH material is extracted.

Besides working with labeled PAH another approach to gain further insight in this subject is the spiking of known amounts of PAH on aerosol samples, and the determination of PAH after equilibrium. The results for the extraction methods I, II and V are summarized in Table 2, indicating poor efficiencies for the methods I and II, while method V tends to produce better results, especially for the 4 and higher aromatic ring systems. But with this approach it is uncertain whether the spiked PAH material behaves the same as the original PAH aerosol deposited during sampling.

From these results it can be concluded that extraction efficiencies may differ strongly for several extraction procedures within one type of sample.

This study has shown that extraction procedures of PAH and related compounds should be selected and evaluated carefully depending on the type of sample under investigation.

Further investigation on this subject in our laboratory will include a.o. a study of what processes control the strong adsorption of PAH and related components by taking an insight into the physical and chemical nature of the aerosol sample, so allowing the development of proper extraction strategies for these types of samples.

REFERENCES


