COMPARATIVE EVALUATION OF PROCEDURES FOR THE DETERMINATION OF PAH IN LOW-VOLUME SAMPLES

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(Received May 1990)

Abstract. The aim of this investigation was to evaluate a simplified version of an HPLC method for the determination of PAH in suspended particles collected from small air volumes indoors, outdoors or in personal exposure measurements. The simplification consisted in: (a) collecting PAH by low-volume samplers; (b) extracting PAH ultrasonically; and (c) omitting separation of interfering substances before analysis by HPLC. The results show that the introduction of these modifications affords a considerable reduction in analysis time and solvent expenditure, without affecting the quality of measurement.

1. Introduction

Airborne polycyclic aromatic hydrocarbons (PAH) are predominantly bound to particles of 1–3 μm MMD (Pierce and Katz 1975, Van Vaeck et al. 1980, De Wiest 1978). Therefore samples of suspended particulate matter (SPM) are used for PAH determination. In outdoor air samples collected from 1000 to 2000 m³ of air during 24 hours were analysed for PAH. Glass fiber filters 20×25 cm placed in a filter holder of a high-volume (HV) sampler usually serve as a collection surface.

HV samplers, being unwieldy, noisy and having too high an air flow, cannot be used indoors. Therefore silent medium volume samplers (36 m³/24 h) have been designed for stationary indoor PAH sampling (Bake and Laskus 1978). For personal monitoring, however, only low-volume personal samplers (2–4 m³/24 h) can be used. Miguel and Friedlander (1978) used a low-volume impactor during 72 h to study the size distribution of benzo-a-pyrene and coronene associated with particles.

Since high sensitivity has been achieved in PAH analysis by means of a high performance liquid chromatograph (HPLC) coupled with a fluorescence detector (May and Wise 1984, Dong et al. 1976), the possibility of using daily low-volume samples was considered.

Preparation of HV samples for analysis comprises Soxhlet extraction, separation of interfering compounds (clean-up) and concentration. All these steps are time consuming and require large volumes of solvent. In place of the Soxhlet method, ultrasonic extraction has been applied successfully by Seifert and Steinbach (1977) in the determination of BaP in SPM by thin-layer chromatography. The efficiency was about 96%.

According to Lee (1981) the clean-up step may not be necessary if a selective analytical method is applied.

May and Wise (1984) have shown that the omission of the clean-up step should not
influence the results of analysis for selected PAH (but may shorten the life of the analytical column).

As we intended to analyse small samples (primarily for benzo-\(\alpha\)-pyrene), the substitution of Soxhlet by ultrasonic extraction and the omission of a clean-up procedure were considered to be appropriate.

2. Comparative Evaluation of Procedures

2.1. SAMPLING

In order to establish whether low-volume, personal SPM samples may contain sufficient PAH for analysis, we inspected PAH concentrations previously measured in the Zagreb air using HV samples. Taking the benzo-\(\alpha\)-pyrene concentration as an indicator of PAH levels we found that it varied from 3 to 50 ng m\(^{-3}\) in winter and down to 0.5 ng m\(^{-3}\) in summer. According to literature data indoor BaP concentrations vary from 0.1 to 8 ng m\(^{-3}\) (Moschandreas et al. 1982) depending on the fuel used for heating and cooking and on the presence of tobacco smokers.

Thus it had to be established whether about 0.2 ng BaP in a sample obtained from 2 m\(^3\) of air may be determined with sufficient accuracy and precision. A mixture of standard PAH solutions containing 5.68 ng fluoranthene (Flu), 0.94 ng benzo-\(b\)-fluoranthene (BbF), 0.27 ng benzo-\(k\)-fluoranthene (BkF), 0.26 ng benzo-\(\alpha\)-pyrene (BaP), 0.48 ng benzo-\(b\)-chrysene (BbChr), 2.24 ng benzo-ghi-perylene (BghiPer), 0.41 ng anthanthrene (Ant) and 4.60 ng coronene (Cor) in 10 \(\mu\)L of acetonitrile was injected nine times into the HPLC apparatus and analysed. The results of the analyses showed that there was no statistically significant difference between the expected and measured concentrations. The coefficient of variation (\(V\%\)) for repeated measurements ranged from 2.6 to 3.8% for the eight compounds, proving that at the given concentration levels the repeatability of the method was acceptable for all compounds measured.

In order to check the repeatability of the whole procedure (extraction, clean-up, evaporation, dissolution and analysis) six equal parts were cut out from an HV sample and analysed, each corresponding in its SPM load to low-volume samples (area through which about 2 m\(^2\) of air has passed). The results are shown in Table I.

The variability coefficients for the PAH present in the sample in quantities equal to or larger than in the standard mixture were 1.5–2.0 times higher, which is still acceptable

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Flu</th>
<th>BbF</th>
<th>BkF</th>
<th>BaP</th>
<th>BbChr</th>
<th>BghiPer</th>
<th>Ant</th>
<th>Cor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\bar{x})</td>
<td>0.8965</td>
<td>1.8001</td>
<td>0.4257</td>
<td>0.6255</td>
<td>0.1228</td>
<td>2.8294</td>
<td>0.1105</td>
<td>n.d.</td>
</tr>
<tr>
<td>(s)</td>
<td>0.1169</td>
<td>0.1213</td>
<td>0.0287</td>
<td>0.03518</td>
<td>0.0236</td>
<td>0.1332</td>
<td>0.0279</td>
<td></td>
</tr>
<tr>
<td>(s_%)</td>
<td>0.0477</td>
<td>0.0495</td>
<td>0.0117</td>
<td>0.01436</td>
<td>0.0096</td>
<td>0.0544</td>
<td>0.0114</td>
<td></td>
</tr>
<tr>
<td>(V%)</td>
<td>13.04</td>
<td>6.740</td>
<td>6.753</td>
<td>5.625</td>
<td>19.2</td>
<td>4.71</td>
<td>25.29</td>
<td></td>
</tr>
</tbody>
</table>

The variability coefficients for the PAH present in the sample in quantities equal to or larger than in the standard mixture were 1.5–2.0 times higher, which is still acceptable.