Quantification of Polycyclic Aromatic Hydrocarbons in the NIST Standard Reference Material (SRM1649A) Urban Dust Using Thermal Desorption GC/MS

Daniel Waterman, Brian Horsfield,¹ Franz Leistner,¹ Keith Hall,³ and Steve Smith*

Division of Life Sciences, King’s College London, Franklin-Wilkins Building, 150 Stamford Street, London, SE1 8WA, U.K.

A thermal desorption GC/MS technique has been developed for the quantification of polycyclic aromatic hydrocarbons (PAHs) in airborne particulate matter using the NIST Standard Reference Material (SRM1649a) Urban Dust. The technique was developed using standard linearity tests in order to establish optimum sample weights and optimum desorption and chromatographic parameters. This direct analysis technique eliminates the use of solvents in the sample preparation (reducing volatile component losses) and also significantly reduces the sample preparation time (no extraction procedure). The technique has been shown to give linearity in terms of the overall TIC response as well as for a prominent series of n-alkanes (C₂₀–C₃₃) and 10 NIST priority PAHs, 8 of which have been quantified. The technique is reported to be uniquely sensitive (PAH concentrations 2–6 mg kg⁻¹) and reproducible (MW = 178–228 SD ≤ 0.228 mg kg⁻¹, ≤7% MW = 252 SD ≤ 0.922 mg kg⁻¹, ≤33%) over the range of sample weights (1–5 mg). Such sample weights illustrate that the technique can be equally applied to the analysis of airborne particulate samples collected over short time periods (24–48 h) using only commonly used low-volume collection devices.

The adverse health effects of airborne particulates are well recognized, and correlation between particulate concentration and incidents of respiratory problems, in particular, have been well illustrated in epidemiological studies, e.g., refs 1 and 2. Such studies have raised concerns regarding the concentration and nature of airborne particulate pollution and although inroads have been made in understanding the chemical, biological, and physical properties of airborne particulates, such work has also succeeded in defining the problem as an extremely complex one.

Airborne particulate matter consists of particles of variable size and composition and is often referred to as PM 10 (particles of mean aerodynamic diameter of 10 μm). A greater understanding of how particles are deposited within the respiratory system³ has meant interest, particularly in understanding the toxicity mechanism, has moved toward smaller fractions of PM 2.5, PM 1, and ultrafine fractions (<0.1 μm).

Chemical characterization is important in adding to the understanding of the toxicity mechanism as well as being vital in assessing the sources of airborne particulate matter (source apportionment) and, therefore, is key to implementation of environmental policies for the reduction of major sources of particulates. As interest moves toward smaller particles, there is an increasing need for highly sensitive chemical characterization techniques that are capable of working with extremely small samples of particulate matter composed of complex mixtures of chemical species in low concentrations.

Multiple and variable source factors mean that particulate composition is extremely complex and variable.⁴ Mетодs for the analysis of the inorganic fraction of particles (elemental analysis, metals analysis, soluble ions analysis) are well established, e.g., ref 5 whereas organic analysis has relied mainly on solvent extraction techniques (Soxhlet), followed by GC/HPLC analysis.⁶ When coupled to organic geochemical techniques such as biomarker analysis and source/emission profiling, the technique has proved a useful tool for source apportionment work (for a recent review, see ref 7).

Although the Soxhlet extraction has been the primary tool of organic analysis, it can be considered to suffer from a number of limitations. The efficiency of a Soxhlet extraction depends on the solubility of the individual organic components in the selected solvent and the ability of the solvent to penetrate the matrix. Extraction is often maximized by the utilization of lengthy multiple-stage extractions, multiple solvent extractions, or physical agitation such as refluxation or ultrasonication. Furthermore, the relatively

---

¹ To whom correspondence should be addressed: (e-mail) steve.smith@kcl.ac.uk; (fax) 44 (0)20 7848 4500.
² Current address: Institute of Petroleum and Organic Geochemistry, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany.
³ Current address: Hall Analytical Laboratories Ltd., Unit A, Millbrook Business Centre, Floats Rd., Manchester M23 9YJ, U.K.
⁵ In source of Petroleum. Determination of soluble organic fraction (SOF) of each particulate on filters—Soxhlet extraction method. IP PM CA/96.
large weights of deposit required (typically 8–10 mg) often necessitates the bulking of samples or high-volume sampling equipment. Soxhlet extraction also suffers from being inappropriate for low molecular weight, volatile compounds, because they are either lost in the solvent reduction stage of sample preparation or are masked by the solvent itself during subsequent gas chromatographic analysis.

Improved extraction techniques have more recently been developed such as microwave digestion and supercritical fluid chromatographic analysis. However, both techniques still require a separate extraction stage prior to analysis and relatively large weights of deposit.

Thermal desorption eliminates the long extraction stage, has been shown to give reproducible organic fingerprints (including more volatile compounds), and requires considerably smaller samples. It was with these factors in mind that we evaluated thermal desorption as a technique for quantifiable organic analysis of airborne particulates.

Thermal desorption has already proved to be a valuable tool in the earth science and energy sectors when coupled with online gas chromatography analysis. Environmental applications of the technique have tended to involve absorption of organics onto solid supports such as Tenax or SPM E fibers prior to desorption and analysis (see ref 12 for a recent review). Typically contaminants from water (studies of wastewater and contaminated soils) or volatile organics in air have been studied by these methods.

The technique of direct thermal desorption with on-line GC is used in the oil industry for analyzing particulates collected directly from engine exhausts. The technique is not established as a quantifiable method but is used to examine the unresolved, broad fuel and lubricant peaks observed using a wide-bore GC column in order to assess the fuel mix performance.

Pyrolysis GC/MS is significantly more energetic technique involving considerable breakdown and fragmentation of large molecules and the solid matrix has started to be used in environmental analysis but has tended to concern studies of biomarkers in contaminated soils and potential applications in bioremediation work.

**EXPERIMENTAL SECTION**

**Thermal Desorption GC/MS Hardware.** The thermal desorption system (illustrated in Figure 1) utilizes a Quantum BTOV-2 thermal analysis port (Q2 Chromatography and EGO)

![Figure 1. Thermal desorption GC/MS system.](image-url)
Analytical Procedure. The GC split ratio is set (15:1) with a column flow rate of 0.8 mL min\(^{-1}\) prior to the liner being placed in the ambient temperature purge extension of the desorption unit, and the sample is purged for 1 min. The dewar of the cryogenic trap is then filled with liquid nitrogen and the trap submerged. The data acquisition and the GC temperature programs are started simultaneously, and the liner is lowered into the body of the desorption oven which is then ramped from 175 to 300 °C at 50 °C min\(^{-1}\). On vaporization, the desorbants are swept by the carrier gas from the heated zone, minimizing potential thermal decomposition, and are focused on the trap for the 10-min desorption period. The trap is then lowered and almost simultaneously flash heated from \(-196\) to 300 °C in 20 s, flushing the desorbants held on the trap onto the GC column for analysis. The GC oven is set at 40 °C for 13 min (including desorption time) and then ramped at 5 °C min\(^{-1}\) to 300 °C and held for 25 min (total analysis time 90 min).

Carrier gas flows are allowed to equilibrate for \(\sim 5\) min between each stage of the process and confirmed by monitoring flow rates on a Humonics Veri-Flow 500 precision low-volume flow meter. On completion of the GC program, the system is cooled, the liner is removed, and the inlet system is cleaned of fragments of glass wool and dust particles by back-flushing with a 2 bar pressure of nitrogen through the purge outlet valve. All equipment is handled using cotton gloves, and all implements used in the preparation are first cleaned with solvent and then in an oven at 350 °C.

Linearity was confirmed using different weight samples of the SRM and plotting integrated areas of the total chromatographic area (relative to a blank run under identical conditions) versus total sample weight (Figure 3). The plot indicates good linearity (\(R^2 = 0.948\)) within the range of weights used, \(1\)–\(5\) mg. As well as the TIC linearity, a series of \(n\)-alkanes (\(C_{20}\)–\(C_{33}\)) labeled in Figure 2, were identified and the chromatographic areas plotted against sample weight illustrating good linearity in the microgram range (Figure 4).

Ten NIST priority PAHs were identified (phenanthrene, pyrene, fluoranthene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, benzo[g,h,i]perylene, indeno[1,2,3-cd]pyrene) covering molecular weights 178–276 and selected from the chromatograms and the integrated areas plotted against total sample weight (Figure 5). The plots indicate that within the range of \(1\)–\(5\) mg of urban dust a linear response for the 10 PAHs is seen. The linearity ranges closely follow that of the total chromatographic linearity range. If then the total urban dust sample weight (\(1\)–\(5\) mg) is converted to PAH weight utilizing the certified values for each PAH, then the linearity range for observing PAHs is seen. The linearity ranges closely follow that of the total chromatographic linearity range. If then the total urban dust sample weight (\(1\)–\(5\) mg) is converted to PAH weight utilizing the certified values for each PAH, then the linearity range for observing PAHs is equivalent to 20–200 ng. The linearity of the PAHs is seen to have similar gradients illustrating comparable response-to-weight ratios and therefore the PAHs are directly comparable at all weights of urban dust along the linearity.

RESULTS AND DISCUSSION

Linearity Tests. Chromatograms (example in Figure 2) were obtained from different weights of samples (\(1\)–\(5\) mg) of SRM run under identical conditions. The chromatograms showed a general progression from high mass—high response to low mass—low response, and all peaks were present in the relative amounts in all chromatograms. Linearity was confirmed in the plot of total chromatographic area, relative to a blank run under identical conditions, versus total sample weight (Figure 3). The plot indicates good linearity (\(R^2 = 0.948\)) within the range of weights used, \(1\)–\(5\) mg. As well as the TIC linearity, a series of \(n\)-alkanes (\(C_{20}\)–\(C_{33}\)) labeled in Figure 2, were identified and the chromatographic areas plotted against sample weight illustrating good linearity in the microgram range (Figure 4).

Ten NIST priority PAHs were identified (phenanthrene, pyrene, fluoranthene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, benzo[g,h,i]perylene, indeno[1,2,3-cd]pyrene) covering molecular weights 178–276 and selected from the chromatograms and the integrated areas plotted against total sample weight (Figure 5). The plots indicate that within the range of \(1\)–\(5\) mg of urban dust a linear response for the 10 PAHs is seen. The linearity ranges closely follow that of the total chromatographic linearity range. If then the total urban dust sample weight (\(1\)–\(5\) mg) is converted to PAH weight utilizing the certified values for each PAH, then the linearity range for observing PAHs is equivalent to 20–200 ng. The linearity of the PAHs is seen to have similar gradients illustrating comparable response-to-weight ratios and therefore the PAHs are directly comparable at all weights of urban dust along the linearity. The high molecular weight PAHs benzo[g,h,i]perylene and indeno[1,2,3-
In order that the PAHs measured in the urban dust SRM can be quantified, an internal deuterated standard, phenanthrene-d_{10}, for the lower volatility certified PAHs phenanthrene, pyrene, fluoranthene, benz[a]anthracene and chrysene, was utilized. The higher molecular weight PAHs were also quantified relative to the phenanthrene-d_{10} standard by utilizing a NIST PAH standard in DCM run with a phenanthrene-d_{10} standard, and response factors were calculated. Prior to spiking the urban dust SRM samples with phenanthrene-d_{10}, a series of 1-μL samples of phenanthrene-d_{10} of differing concentrations in DCM were thermally desorbed from blank liners. A plot of chromatographic area of phenanthrene-d_{10} against phenanthrene-d_{10} sample weight is shown in Figure 6. Good linearity is again seen in the phenanthrene-d_{10} series (R^2 = 0.963) over a range of weights comparable to the weighed samples.
CONCLUSIONS

We have shown thermal desorption GC/MS to be a technique that can accurately quantify polycyclic aromatic hydrocarbons in an airborne particulate standard reference material using small amounts (1–5 mg) of material.

We have shown the following: (1) very good linearity for the total chromatographic response of the SRM (R² = 0.948) over the range of sample weights (1–5 mg) as well as for a series of n-alkanes (C₂₀–C₃₃, R² ≥ 0.931) in the microgram range and 10 PAHs (M_W = 178–276, R² ≥ 0.971) in the nanogram range. The linearity plots of the PAHs showed similar gradients illustrating comparability of all PAHs relative to a standard at all sample weights within the range. The higher PAHs could be quantified by applying response factors relative to the phenanthrene-d₁₀ standard; (2) a rough calculation of the total desorbable organic fraction (3.7%) is comparable to the extractable (Soxhlet) fraction certified as (4.6 ± 0.4%); (3) calculated concentrations of the eight PAHs with 95% confidence limits coincide with the certified ranges apart from chrysene, which falls close to, but just outside of, the narrow certified range; (4) highly reproducible PAH concentrations (M_W = 178–228, SD ≤ 0.228 mg kg⁻¹, ≤ 7% M_W = 252 SD ≤ 0.922 mg kg⁻¹, ≤ 33% over five separate determinations using sample weights in the middle of the linearity range.

A simple calculation using the average deposit weights collected using low-volume sampling equipment in the London Air Quality Network (LAQN) and total organic carbon (TOC) calculations, carried out in conjunction with LECO Instruments (UK) Ltd., show that short sampling periods of 24–48 h provide sufficient material to fall within the linearity of the technique (range from 30 to 60% TOC–SRM calculated as 13–16% (certified as 16 ± 5%).

The technique is at present being used for the routine determination of PAHs and other organic compounds in PM 10 at sites in London, providing much needed information on spatial and temporal trends in organic composition of airborne particulate matter, insight into potentially toxic compounds, and estimates of the major contributing factors.

ACKNOWLEDGMENT

The authors thank the NERC URGENT project for the funding to do this work and also South East Institute of Public Health (SEIPH), the City of Westminster Council, the London Borough of Greenwich Council, Pembrokeshire County Council, and Dianne Hall (BP) for their continued support of this work. We also thank LECO Instruments (UK) for their help in the TOC analysis work.

Received for review November 29, 1999. Accepted May 17, 2000.

AC991372X

Table 1. Comparison of Calculated Concentrations (mg kg⁻¹) of Eight PAHs over Five Runs, Each Using Approximately 3 mg of Urban Dust

<table>
<thead>
<tr>
<th>PAH</th>
<th>run 1</th>
<th>run 2</th>
<th>run 3</th>
<th>run 4</th>
<th>run 5</th>
<th>mean ± SD</th>
<th>certified value ± 95% confidence</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenanthrene</td>
<td>4.658</td>
<td>4.502</td>
<td>4.815</td>
<td>4.657</td>
<td>4.472</td>
<td>4.621</td>
<td>0.124 0.109 0.14 0.37</td>
</tr>
<tr>
<td>fluoranthene</td>
<td>6.378</td>
<td>6.828</td>
<td>6.688</td>
<td>6.576</td>
<td>6.868</td>
<td>6.668</td>
<td>0.178 0.156 6.45 0.18</td>
</tr>
<tr>
<td>pyrene</td>
<td>5.438</td>
<td>4.898</td>
<td>5.008</td>
<td>4.938</td>
<td>4.945</td>
<td>5.055</td>
<td>0.199 0.175 5.29 0.25</td>
</tr>
<tr>
<td>benzo[a]anthracene</td>
<td>2.523</td>
<td>2.238</td>
<td>2.142</td>
<td>3.478</td>
<td>2.956</td>
<td>2.859</td>
<td>0.191 0.167 2.21 0.073</td>
</tr>
<tr>
<td>chrysene</td>
<td>3.455</td>
<td>3.318</td>
<td>3.925</td>
<td>3.365</td>
<td>3.700</td>
<td>3.655</td>
<td>0.228 0.200 3.049 0.06</td>
</tr>
<tr>
<td>benzo[b]fluoranthene</td>
<td>6.030</td>
<td>5.410</td>
<td>5.656</td>
<td>7.372</td>
<td>6.536</td>
<td>6.201</td>
<td>0.780 0.684 6.450 0.640</td>
</tr>
<tr>
<td>benzo[e]pyrene</td>
<td>3.913</td>
<td>3.322</td>
<td>3.992</td>
<td>2.671</td>
<td>4.061</td>
<td>3.592</td>
<td>0.652 0.571 3.090 0.190</td>
</tr>
<tr>
<td>benzo[a]pyrene</td>
<td>2.830</td>
<td>2.103</td>
<td>2.480</td>
<td>2.392</td>
<td>4.141</td>
<td>2.789</td>
<td>0.922 0.809 2.509 0.087</td>
</tr>
</tbody>
</table>

Figure 6. Chromatographic linearity (R² = 0.963) of phenanthrene-d₁₀ in DCM thermally desorbed after injection into a blank liner.

to that of the PAHs in the urban dust (0.05–0.25 µg; Figure 6). Selection of a weight of phenanthrene-d₁₀ within this linearity could now be employed as an internal standard for the quantification of the PAHs.

Quantification of PAHs in the Urban Dust SRM. Five samples of ~3 mg of urban dust were prepared and spiked with 1 µL of 150 ppm (0.15 µg) samples of phenanthrene-d₁₀ in DCM and then thermally desorbed in the usual way. The PAH peaks were then integrated and quantified relative to the phenanthrene-d₁₀ peak. The quantified values are shown along with the certified values in Table 1. The calculated values are extremely good, and all of the certified ranges (95% confidence) overlap with the certified ranges except for chrysene. Calculated 95%-confidence limits are largest the greater the A_Rt (= Rₜ(target) − Rₜ(phenanthrene-d₁₀)) as system responses vary across the chromatograms. Applying a response factor adjusts for decrease in response between the standard and the target PAH, but these higher PAHs also suffered from variable molecular ion percentages over five quantification runs. This is due to low concentrations being measured, the reduction in response toward the high end of the chromatogram as well as increased background interference from the UCM of the chromatogram. Therefore, the PAHs of M_W 276 have not been quantified.

Figure 6. Chromatographic linearity (R² = 0.963) of phenanthrene-d₁₀ in DCM thermally desorbed after injection into a blank liner.

Approximately 3 mg of Urban Dust