



ELSEVIER

Journal of Chromatography A, 912 (2001) 143–150

JOURNAL OF
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Application of micro-scale sealed vessel thermal desorption–gas chromatography–mass spectrometry for the organic analysis of airborne particulate matter: linearity, reproducibility and quantification

Daniel Waterman^a, Brian Horsfield^b, Keith Hall^c, Steve Smith^{a,*}

^aDivision of Life Sciences, King's College London, Franklin-Wilkins Building, 150 Stamford Street, London SE1 9NN, UK

^bInstitute of Petroleum and Organic Geochemistry, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

^cHall Analytical Laboratories Ltd., Unit A, Millbrook Business Centre, Floats Road, Manchester M23 9YJ, UK

Received 24 October 2000; received in revised form 28 December 2000; accepted 3 January 2001

Abstract

Micro-scale sealed vessel thermal desorption–gas chromatography–mass spectrometry (MSSV-TD–GC–MS) has been applied to the analysis of airborne particulate matter using the US NIST Standard Reference Material (SRM1649a) urban dust. We make qualitative comparisons with open system desorption and illustrate that caution should be used when using the technique without an open system comparison. We report linear responses over the same particulate mass range (1–5 mg) and good reproducibility [$SD \leq 0.62 \text{ mg kg}^{-1}$ ($\leq 11\%$)]. We show linearity for a series of 10 *n*-alkanes and 10 polycyclic aromatic hydrocarbons (PAHs) in the SRM. The technique is also shown to be quantifiable (PAH concentrations typically 4–6 mg kg⁻¹). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Micro-scale sealed vessel thermal desorption; Thermal desorption; Airborne particulate matter; *n*-Alkanes; Polycyclic aromatic hydrocarbons

1. Introduction

We have previously shown [1] open system thermal desorption with on-line gas chromatography–mass spectrometry (GC–MS) to be a powerful and sensitive technique for desorbing organic constituents from particulate matter and for quantifying components (e.g., polycyclic aromatic hydrocarbons, PAHs) therein. The method eliminates the need for

an extraction stage therefore reducing the use of solvents and cutting lengthy extraction procedures. The technique retains volatile components, and provides a highly reproducible and quantifiable organic fingerprint while minimising thermal decomposition. The technique requires only small amounts of sample, approximately 3 mg of US National Institute of Standards (NIST) Standard Reference Material (SRM1649a), airborne particulate matter (APM) that is considered to be low in total organic carbon (TOC) compared to typical values measured in, for example, London (16% compared to 30–70% from London). This then compares favourably with sample

*Corresponding author. Tel.: +44-20-7848-4446; fax: +44-20-7848-4500.

E-mail address: steve.smith@kcl.ac.uk (S. Smith).

masses needed for extraction techniques such as Soxhlet extraction [2] and is therefore seen as a potentially powerful technique for organic characterisation of APM and source apportionment.

Open system thermal desorption minimises potential thermal decomposition processes as desorbed components are flushed away from the heated zone onto a cryogenic trap and as heating is not undertaken at high pressure, non-volatile component breakdown is also minimised. Closed system micro-scale sealed vessel (MSSV) GC–MS was developed for geochemical applications such that by varying temperature and using extended heating times the technique has proved useful for simulating maturation of source rocks [3]. We have previously reported a qualitative approach to MSSV thermal desorption by comparing 30 min heating of the standard reference material SRM1649a at 300°C against extended heating of 72 h [4]. Extended heating was reported to increase the amount of low molecular mass compounds compared to the 30 min heating programme due to additional thermal processes occurring similar to that seen in the simulation of geological systems. As well as the thermal desorption (TD) of volatilisable components from the matrix, the predominant process in open system desorption, 72 h heating results in the thermal decomposition of resolvable peaks as well as otherwise unresolved peaks, indicated by a reduced unresolved complex mixture (UCM) hump. The UCM fraction cannot be studied by open thermal desorption. These two processes could be further complicated by a degree of thermal decomposition of non-volatile components that would have remained in the particulate matrix after a 300°C open system desorption. These components could otherwise be analysed using open system thermal desorption by taking the matrix remaining after a 300°C desorption up to elevated temperatures seen in pyrolysis ($\leq 600^\circ\text{C}$) [5].

It is suggested that open and closed systems can be complimentary in that if the closed system can be shown to be linear and reproducible, and any thermal decomposition can be controlled, then useful information about the otherwise unresolvable components may be gleaned. It is the aim of this paper to illustrate that although closed system thermal desorption may lead to additional thermal processes to that of open thermal desorption, the processes are re-

producible and quantifiable and therefore adding a useful element to thermal desorption techniques. We test total chromatographic linearity as well as component linearity and quantify eight PAHs certified in the reference material. We also illustrate that the differences between open and closed systems are not random but are proportional to the mass of sample and therefore potentially controllable and quantifiable processes.

2. Experimental

2.1. MSSV-TD–GC–MS hardware

The MSSV-TD system (illustrated in Fig. 1) utilises a Quantum MSSV-2 thermal analysis port (GC2 Chromatography and EGO). The unit comprises a desorption double oven mounted to a Hewlett-Packard 5890 gas chromatograph, connected to a short path interface and a direct heated cryogenic trap filled with glass beads. The interface has a purge outlet and a nitrogen back flush facility for cleaning debris from the system. The control panel has fully programmable temperature facilities allowing separate control of the oven, the interface and the cryogenic trap as well as programmable temperature ramping and control of the carrier gas flow-rate. The cryogenic trap is cooled using a liquid nitrogen dewar internal to the GC oven that is lowered on completion of the desorption. The timing of the trap heating is integral to the GC temperature programme and is monitored by the control panel.

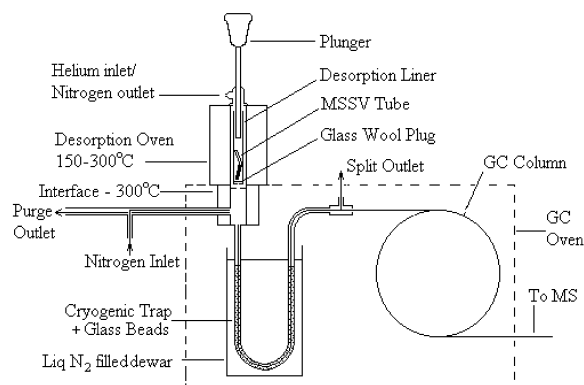


Fig. 1. The MSSV-TD–GC–MS system.

The desorption liner is glass lined steel and sits at the base of the desorption oven. The oven has a plunger attached to the inlet that slides inside the liner and is used to break open the sealed vessels. The GC split is positioned after the cryogenic trap prior to its connection with the GC capillary column (Phenomenex ZB-5, 25 m×0.25 mm I.D., 0.25 µm film thickness). The GC instrument is interfaced to a Fisons MD800 mass spectrometer run in electron impact (EI) mode and scanned from m/z 40 to 520.

2.2. Sample preparation

The NIST standard reference material SRM1649a urban dust was collected using a baghouse method near to Washington, DC, USA, and was purchased through the Laboratory of the Government Chemist (Teddington, UK). The material is certified for a number of component species including PAHs, as well as for total organic content and extractable (Soxhlet) organic content.

MSSV glass tubes are approximately 3 cm×1.3 mm I.D. and have a 40-µl internal volume. The tubes have a bend in the middle forming an internal angle of approximately 170° to aid the breaking of the tubes. MSSV tubes are cleaned in an oven at 350°C for 30 min. The tubes were then 1/4 filled with similarly cleaned 120 mesh glass beads (Alltech) in order to aid retention of liquid standard. A 1-µl volume of 150 ppm D₁₀-phenanthrene in dichloromethane (DCM) was injected onto the beads using a 10-µl GC syringe and the needle carefully withdrawn. The tubes were then left in a clean environment for approximately 30 min in order to allow the DCM to evaporate.

Samples of the urban dust (1–5 mg) were then weighed into the glass tubes on top of the glass beads and deuterated standard. The void space in the tubes was then filled with more glass beads up to within 1 mm from the tube opening which was subsequently sealed in a flame. The sealed MSSV tubes were heated at 300°C for 30 min prior to analysis.

2.3. Analytical procedure

The purge valve of the GC system is opened and the plunger on the thermal desorption oven is

removed to allow an MSSV tube to be dropped into the GC liner, containing a small plug of quartz wool, within the desorption oven at 300°C. The plunger is replaced and the outside of the tube is purged in the flow of the carrier gas for 2 min, cleaning any contaminants from the tube (handled with cotton gloves) prior to closing the purge valve. Carrier gas flows are allowed to equilibrate for approximately 5 min between each stage of the process and monitored on a Humonics Veri-flow 500, low-volume-flow meter. The split ratio is set to 15:1 with a column flow-rate of 0.8 ml min⁻¹. The dewar of the cryogenic trap is then filled with liquid nitrogen and raised to submerge the trap. The data collection is started simultaneously with the GC programme, the MSSV tube is broken open with the plunger, releasing the desorbants into the flow of helium carrier gas, flushing them onto the cryogenic trap. After 2 min of focusing the dewar is lowered and the trap is flash heated to 300°C in 20 s. The GC column remains isothermal (40°C) for a further 3 min before ramping to 300°C at 5°C min⁻¹ and held for 33 min (total analysis time 90 min).

On completion of the temperature programme the GC system is allowed to cool, the purge valve is then opened allowing the liner to be removed. The inlet system is cleaned of fragments of glass wool, MSSV tube and dust particles by back flushing with a 2 bar pressure of nitrogen through the purge outlet valve. The glass wool is replaced in the liner and the liner returned to the desorption oven. Blanks have been run after every three runs to ensure no memory effects occur. Long term elimination of memory effects is ensured by baking out the desorption oven (600°C), interface (340°C) and trap (340°C) overnight with a low flow (5 ml min⁻¹) of helium with the GC column detached.

All equipment is handled using cotton gloves and all implements used in the preparation are firstly cleaned with solvent and then in an oven at 350°C.

3. Results and discussion

3.1. Comparisons of chromatograms of open and closed systems

The chromatographic fingerprints of approximate-

ly 3.0 mg of sample, accurately weighed (± 0.03 mg) obtained by closed system thermal desorption were compared to that of open system thermal desorption previously obtained (Fig. 2). The chromatographic profile was seen to match reasonably well with the open system chromatogram of a similar mass, and very well at retention times (t_R) of >55 min, though clearly differences are apparent below this. For example, the peak at $t_R=50.18$ min prominent in the open system chromatogram (Fig. 2a) is reduced in the closed system chromatogram. A library search (NIST) on this peak indicates that it is carboxylic in nature [hexadecanoic acid, Rev=930 (Reverse Fit Factor – Masslab 3.1, Micromass, UK)]. The peak that is seen to increase most markedly in the closed thermal desorption (Fig. 2b) is the peak at $t_R=48.50$ min and is matched closely to hexadecanitrile (Rev=898). It is suggested then that the carboxylic acid is converted, at least in part, to its analogous nitrile. Such a process could follow a mechanism whereby

the carboxylic acid reacts with ammonia, and forms a nitrile via an amide intermediate. Presence of an ammonia source in the system is therefore assumed. Simoneit [6] uses this mechanism to explain the presence of ambient nitriles formed from biomass under smouldering conditions ($<300^\circ\text{C}$) and is therefore classic of a high temperature system. This process is also seen with the prominent peak in the closed system (Fig. 2b) at $t_R=52.65$ min that is again assigned as a nitrile (Rev=870). This peak is actually present in the open system (Fig. 2a) but to a lesser amount.

At the low end of the closed system chromatogram, an increase in volatile components such as benzene, *p*-xylene, toluene, phenol and alkylbenzenes are seen. It was shown previously [4] that overall total ion current (TIC) counts do not increase over a 72 h period of closed system heating and therefore “new” peaks being observed at longer heating times will have come from a subsequently

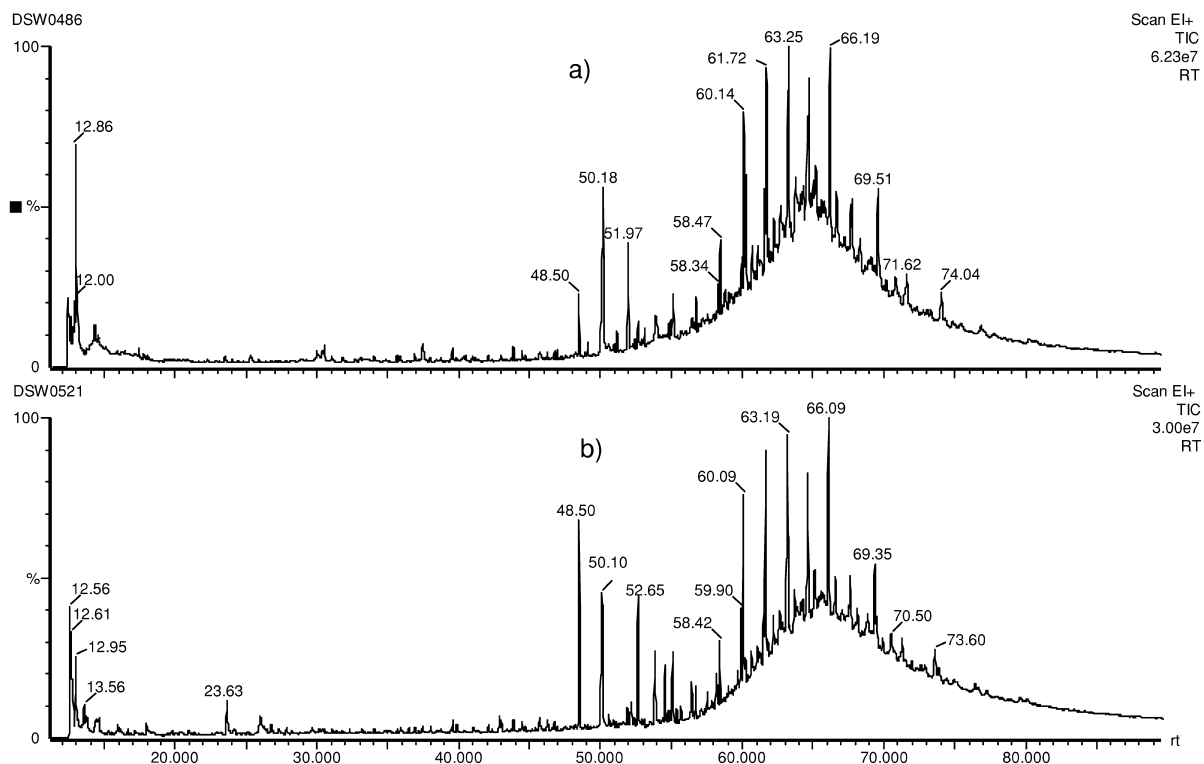


Fig. 2. Comparison of a chromatogram of 3.0 mg of SRM1649a urban dust obtained by open system thermal desorption (a) and a chromatogram of a 3.0 mg sample obtained by closed system thermal desorption (b).

reduced UCM or from breakdown of otherwise resolved peaks. The increase in these compounds is not large and cannot therefore be assigned specifically to either of these processes but may be as a consequence of a small amount of both.

Comparison of three chromatograms from three different masses of SRM show a degree of proportionality to sample mass irrespective of the decomposition mechanisms occurring. Fig. 3a shows that the degree of decomposition of the carboxylic acid, though not complete, is consistent and that the carboxylic acid and the nitrile peaks have a degree of proportionality to the sample mass. Fig. 3b shows that formation of the very volatile components, benzene, *p*-xylene, toluene and phenol are also being

formed in amounts proportional to sample mass. This indicates a degree of linearity and reproducibility of decomposition indicating that decomposition is not purely artifactual. Although this poses the question of studying temperature profiles, we have found that shorter time periods have produced identical chromatographic profiles indicating timescale for reaction is considerably shorter than the time scale for desorption used in this work.

3.2. Linearity tests

A series of chromatograms corresponding to different sample masses of urban dust run under identical conditions were obtained. A plot of total

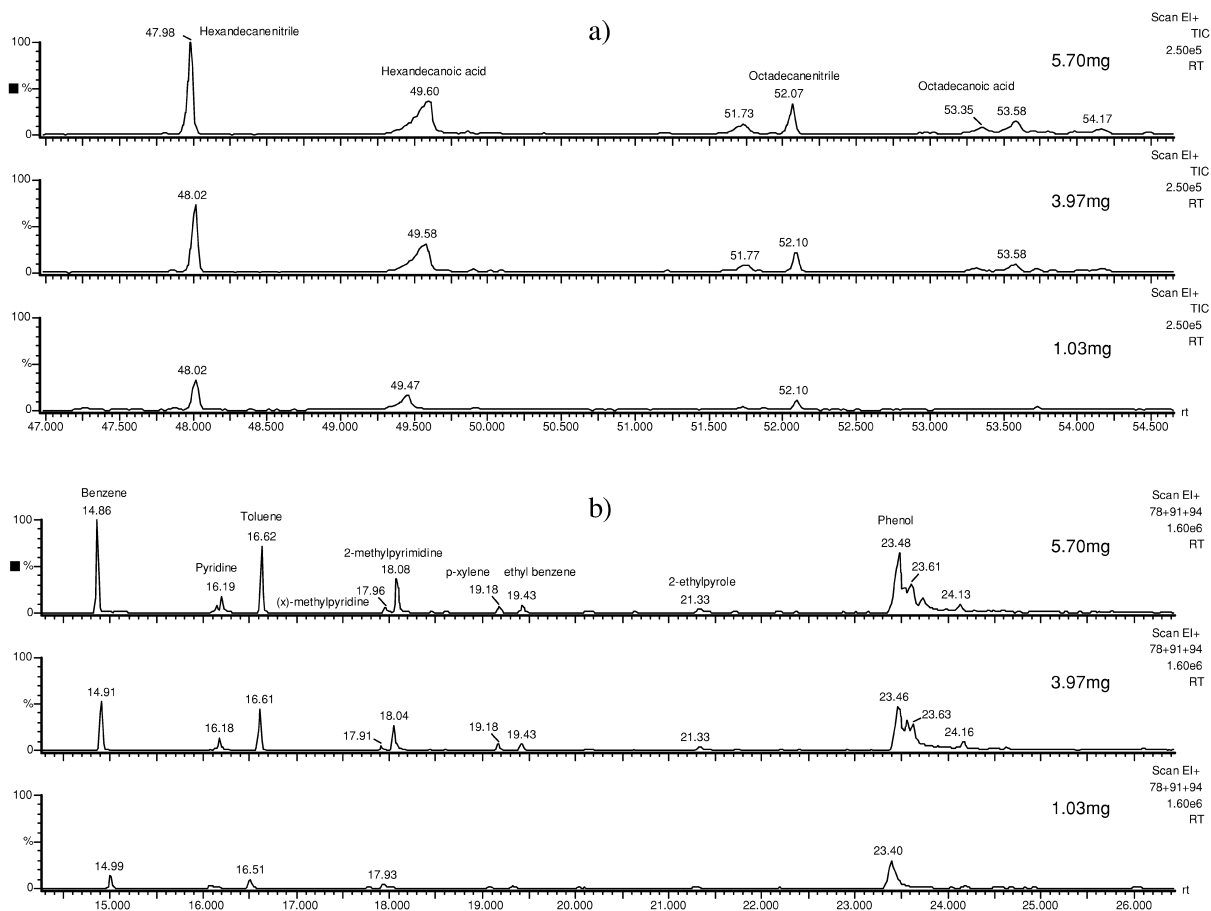


Fig. 3. Expanded chromatograms showing 5.7 mg, 3.97 mg and 1.03 mg (top to bottom) of (a) TIC indicating carboxylic acid peak ($t_R \sim 49.60$ min) and corresponding nitrile peak ($t_R \sim 47.98$ min) and (b) molecular ion chromatograms $m/z = 78+91+94$ showing compounds from benzene to phenol.

chromatographic area (relative to a D₁₀-phenanthrene internal standard) versus total sample mass showed good linearity [slope=3·10¹² counts mg⁻¹, intercepts $x=0$, $y=0$, $R^2=0.993$, observations=5 (5.70 mg, 3.97 mg, 2.92 mg, 1.88 mg, 1.03 mg)]. Therefore in all samples run, a proportional quantity of organic species are being desorbed and detected.

Linearity is demonstrated at a lower mass level when the 12 prominent *n*-alkane (C₂₀–C₃₁) peaks are identified, integrated and plotted against total sample mass in Fig. 4 ($R^2 \geq 0.963$). This plot shows that the technique has a linear response on a homologous series in the μg range, of different concentrations over a wide molecular mass range ($m/z=282$ –436). Likewise 10 NIST priority PAH peaks (phenanthrene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benz[*e*]pyrene, benz[*a*]pyrene, benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene) were identified in the closed system chromatograms and their integrated areas were plotted against total sample mass in Fig. 5 ($R^2 \geq 0.978$). The plots indicate linearity for the 10 PAHs of different concentrations in the ng range corresponding to approximately 2–35 ng of PAH per

compound per sample over a molecular mass range ($m/z=178$ –276).

3.3. Quantification of PAHs in the urban dust SRM

Five samples of approximately 3 mg of urban dust were prepared and spiked with 1 μl of 150 ppm (50 ng) samples of D₁₀-phenanthrene in DCM and then sealed and thermally desorbed from MSSV tubes. Recoveries of D₁₀-phenanthrene were calculated by comparing responses from desorbing D₁₀-phenanthrene from a blank liner at 300°C with responses obtained on subsequent blank runs at 340°C and were calculated to be 99.76% in the initial thermal desorption stage. Eight prominent PAH peaks were then integrated and quantified relative to the D₁₀-phenanthrene peak (larger PAHs had a response factor applied by comparing the response of D₁₀-phenanthrene with the responses of 16 PAHs in the Ultra Scientific Standard, US-106). The quantified values are shown along with the certified values in Table 1. The quantified values are close to certified values and all of the calculated ranges (95% confi-

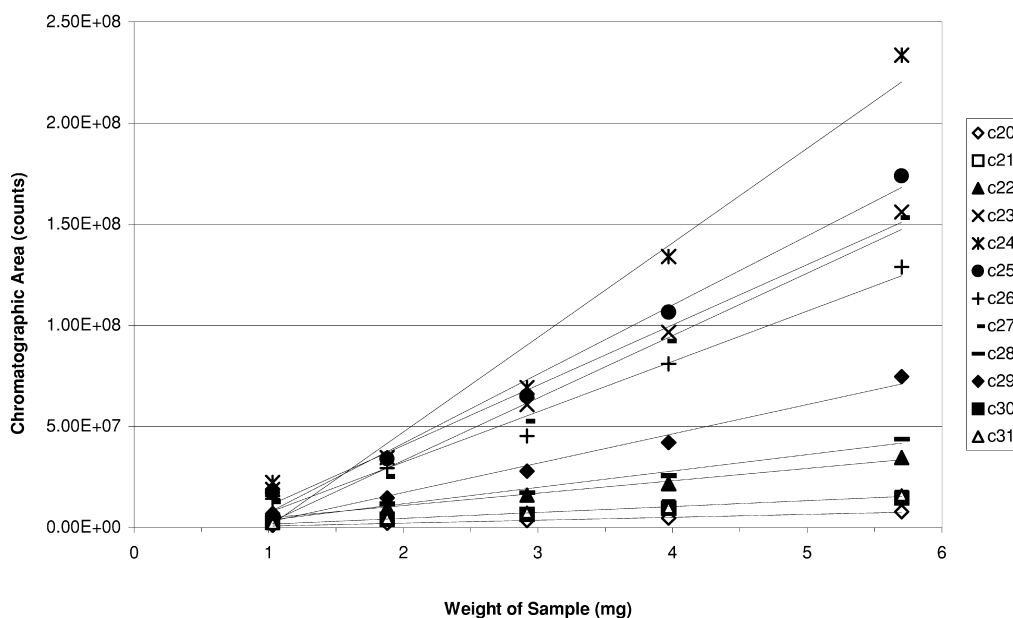


Fig. 4. Chromatographic linearity of 12 *n*-alkanes from C₂₀–C₃₁. (C₂₀ $R^2=0.993$, C₂₁ $R^2=0.993$, C₂₂ $R^2=0.990$, C₂₃ $R^2=0.988$, C₂₄ $R^2=0.963$, C₂₅ $R^2=0.988$, C₂₆ $R^2=0.982$, C₂₇ $R^2=0.982$, C₂₈ $R^2=0.984$, C₂₉ $R^2=0.982$, C₃₀ $R^2=0.990$, C₃₁ $R^2=0.995$).

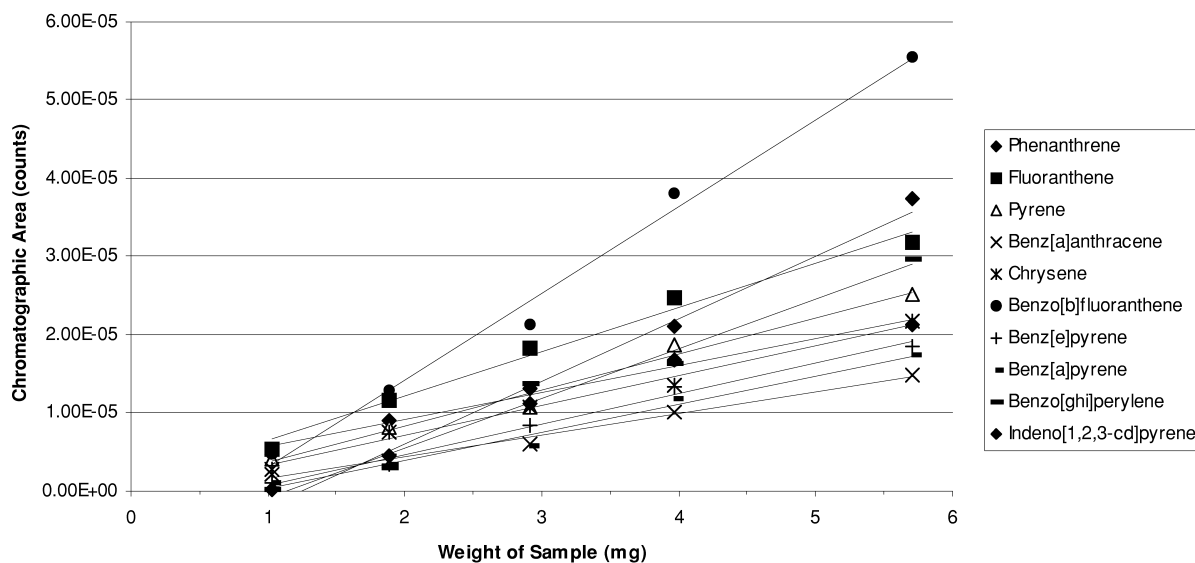


Fig. 5. Chromatographic linearity of 10 PAHs (phenanthrene $R^2=0.983$, fluoranthene $R^2=0.987$, pyrene $R^2=0.983$, benz[a]anthracene $R^2=0.987$, chrysene $R^2=0.988$, benzo[b]fluoranthene $R^2=0.990$, benz[e]pyrene $R^2=0.990$, benz[a]pyrene $R^2=0.980$, benzo[ghi]perylene $R^2=0.978$ and indeno[1,2,3-cd]pyrene $R^2=0.986$).

dence) overlap with the certified ranges. Higher-molecular-mass PAHs have a greater standard deviation due to increased co-elution due to the UCM.

It is clear then that the thermal treatment of the particulate is a technique that behaves in a linear manner and is reproducible to a high degree. It is also apparent that although similar to open system thermal desorption the treatment is more harsh even for the shortest desorption times used in this work so caution should be exercised when considering components that could thermally decompose. It is sug-

gested then that closed system thermal desorption be used in conjunction with open system in order to gain a picture of the “starting point” prior to any decomposition. Decomposition may then be useful as a tool in itself as we have illustrated it shows strong signs of linearity and reproducibility.

4. Conclusions

MSSV-TD-GC-MS is a technique that can accu-

Table 1

Comparison of calculated concentrations (mg kg^{-1}) of the eight PAHs over five runs, each using approximately 3 mg of urban dust

	Calculated concentration (mg kg^{-1})					Mean	SD	$\pm(95\%)$	Certified	$\pm(95\%)$
	Run 1	Run 2	Run 3	Run 4	Run 5					
Phenanthrene	4.486	4.801	4.287	4.827	4.383	4.557	0.245	0.240	4.140	0.370
Fluoranthene	6.238	6.282	6.876	6.161	6.445	6.400	0.285	0.228	6.450	0.180
Pyrene	3.703	4.546	5.383	4.336	4.843	4.562	0.621	0.608	5.290	0.250
Benz[a]anthracene	2.066	2.524	2.685	2.036	2.635	2.389	0.314	0.436	2.210	0.073
Chrysene	3.690	3.098	3.931	4.026	3.538	3.657	0.367	0.415	3.049	0.060
Benzo[b]fluoranthene	5.113	6.335	7.226	5.710	7.777	6.432	1.085	0.868	6.450	0.640
Benz[e]pyrene	2.749	3.931	4.863	3.379	4.617	3.908	0.872	0.986	3.090	0.190
Benz[a]pyrene	1.875	2.045	3.487	2.073	2.877	2.471	0.688	0.953	2.509	0.087

rately quantify PAHs in an airborne particulate SRM using small amounts of material (1.0–5.0 mg). The main advantages of such a technique are that no solvents are used for extraction, there is no need for clean up procedures and therefore analysis time is greatly reduced.

The technique could be greatly enhanced by adapting procedures for collecting airborne particulate matter directly into MSSV tubes as opposed to collection onto bulky filter papers, effectively concentrating particulate material into a smaller volume. The method is ideal however, for the analysis of soils and sediments and is currently being applied in this area.

Acknowledgements

The authors would like to thank the NERC URGENT project for the funding to do this work and

also South East Institute of Public Health (SEIPH), Westminster City Council, London Borough of Greenwich, Pembrokeshire County Council and Dianne Hall (BP) for their continued support of this work.

References

- [1] D. Waterman, B. Horsfield, F. Leistner, K. Hall, S. Smith, *Anal. Chem.* 72 (2000) 3563.
- [2] Determination Of The Soluble Organic Fraction (SOF) Of Diesel Particulates On Filters – Soxhlet Extraction Gravimetric Method, Institute of Petroleum, 1996, IP PM CA/96.
- [3] B. Horsfield, U. Disko, F. Leistner, *Geol. Rund.* 78 (1989) 361.
- [4] P.A. Hall, A.F.R. Watson, G.V. Garner, K. Hall, S. Smith, D. Waterman, B. Horsfield, *Sci. Total Environ.* 235 (1999) 269.
- [5] K.J. Voorhees, W.D. Schulz, L.A. Currie, G. Klouda, *J. Anal. Appl. Pyrol.* 14 (1988) 83.
- [6] B.R.T. Simoneit, *Environ. Sci. Pollut. Res.* 6 (1999) 159.