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Journal of Chromatography A, 791 (1997) 203–211

JOURNAL OF CHROMATOGRAPHY A

Improved detection of polycyclic aromatic compounds in complex mixtures by liquid chromatographic fractionation on poly(divinylbenzene) prior to gas chromatography–mass spectrometry
Application to the analysis of diesel particulates

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Received 29 October 1996; received in revised form 9 April 1997; accepted 4 August 1997

Abstract

Polycyclic aromatic compounds (PACs) are preferentially retained over other compound classes during high-performance liquid chromatography (HPLC) on poly(divinylbenzene) (PDVB) columns with a dichloromethane mobile phase. PAC retention during HPLC with PDVB/CH_2Cl_2 is governed by a multi-mode mechanism that has been previously described. This enhanced retention of PACs makes PDVB columns useful for isolating a PAC fraction from highly complex mixtures such as the emissions from fossil-fuels combustion. The cleaned-up PAC fraction yields a simple chromatogram with easily identified and quantified peaks without significant compound loss or danger of contamination. We illustrate the use of this clean-up method for the isolation of the PAC fraction from a standard reference diesel particulate sample. © 1997 Elsevier Science B.V.

Keywords: Clean-up methods; Polynuclear aromatic hydrocarbons

1. Introduction

Solute retention in high-performance liquid chromatography (HPLC) with poly(divinylbenzene) (PDVB) columns is controlled by a combination of factors ranging from simple molecular size to complex polymer–solute interactions, with the dominant effect depending largely on the solvent strength of the mobile phase for the solute of interest. In earlier studies of the HPLC retention behavior of polycyclic aromatic compounds (PACs) on PDVB columns, we observed that PACs were preferentially retained over other compound classes, particularly when dichloromethane is used as the mobile phase [1–5], while under the same HPLC conditions, alkanes and alkane-rich molecules, (e.g., polystyrenes, nitroalkanes and phthalate esters) underwent size-dependent elution. Indeed, the principal application for PDVB columns is the size-dependent separation of polymers and other large molecules. In this respect, they are similar to the more common polystyrene (PS) packings that are produced with varying amounts of DVB

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0021-9673/97/$17.00
PII S0021-9673(97)00844-3

as a cross-linking agent. The application of HPLC with PS columns to the analysis of macromolecules is well known and has yielded an extensive literature [6,7]. The work reported here does not simply involve the removal of polymeric compounds from a sample, a technique that can be useful in its own right [8], but describes a mixed-mode separation that yields a fraction highly enriched in PACs. Separation with PDVB/CH_2Cl_2 has been employed to advantage in our laboratories for the separation of complex mixtures of PACs resulting from fossil fuels pyrolysis [2,5] and for the isolation of PAC fractions from pond sediment. [9] This report evaluates the use of HPLC with PDVB/CH_2Cl_2 for the clean-up of a complex PAC mixture prior to gas chromatography–mass spectrometry (GC–MS) analysis through the use of an National Institute of Standards and Technology (NIST) standard reference diesel particulate sample.

The soluble organic fraction of diesel exhaust particulates has been shown to be mutagenic in both bacteria and human cells [10–15]. Concern over the potential for human exposure to components responsible for this mutagenicity has prompted many attempts to separate, identify, and quantify the components in the diesel extracts. Many analytical techniques, including GC, HPLC and GC–MS, have been used to analyze diesel extracts, but the complexity of the mixtures make it difficult to satisfactorily separate individual compounds from the matrix. In general the chromatograms feature large undifferentiated envelopes of co-eluting, alkanes, phenyl alkanes and alkyl naphthalenes, originating largely from unburned fuel, on which some individual PACs appear as superimposed peaks. Both the identification and quantification of individual compounds are difficult in these samples. Computerized GC–MS systems are routinely operated in the selected ion mode (SIM) to analyze complex mixtures of PACs and to quantify individual components [16], but unwanted contributions from the more abundant aliphatics and phenyl alkanes in some combustion samples has been reported as an impediment to quantitation [17]. A number of fractionation and clean-up procedures employing both solvent partitioning and column chromatography have been successfully employed to reduce the complexity of the diesel sample matrix prior to analysis [18–22]. Although standard HPLC fractionation procedures do not match the simplicity of the method described in this study, they do demonstrate the value of sample clean-up by yielding an improvement in chromatographic resolution, and consequently, improved detection and quantification [23]. Our goal was not to find a replacement for normal-phase HPLC fractionation, but to determine what level of sample clean-up and what degree of improvement in PAC analysis can be obtained using a method as simple as the one described in this study.

2. Experimental

2.1. High-performance liquid chromatography

The HPLC system consisted of a Perkin-Elmer Series 200 HPLC pump and Model 235 C diode array detection system (Perkin-Elmer, Analytical Instruments, Norwalk, CT, USA). The column consisted of a 500×10 mm Jordi-Gel-500 PDVB column (Jordi, Bellingham, MA, USA). The system was controlled by Perkin-Elmer Turbochrom 4.1 software running on a DEC 486/66 computer (Digital, Merrimac, NH, USA). A Rheodyne manual injector was used with either a 50-μl or a 500-μl sample loop.

2.2. Gas chromatography–mass spectrometry

The GC–MS system consisted of a Hewlett-Packard 5890 Series II gas chromatograph coupled with a Model 5972 mass-selective detection system (Hewlett-Packard, Palo Alto, CA, USA). The GC column was an HP-5 (30 m×0.25 mm, film thickness of 0.25 μm) fused-silica capillary column. Data acquisition and analysis was accomplished using MS Chemstation software running on a HP Vectra 486/66 computer (Hewlett-Packard, Avondale, PA, USA).

2.3. Chemicals and reagents

Dichloromethane was obtained from EM Science (Gibbstown, NJ, USA). Individual standards of dioctyl isophthalate, diundecyl phthalate, ditridecyl phthalate, dibutyl phthalate, dicapryl phthalate, di-iso-decyl phthalate, dinonyl phthalate, butyl-iso-decyl phthalate, diamyl phthalate, iso-octyl-iso-decyl

phthalate, biphenyl, *m*-terphenyl, *m*-quaterphenyl and *m*-quinquephenyl were purchased from Chem. Service (West Chester, PA, USA). A reference standard containing sixteen polycyclic aromatic hydrocarbons (PAHs) targeted by the US Environmental Protection Agency (EPA) was purchased from AccuStandard (New Haven, CT, USA). Standard Reference Material SRM 1650 (diesel particulates) was obtained from the US NIST. A surrogate sample was prepared by adding the EPA sixteen PAH reference standard into a mixture containing the phthalates and polyphenyls listed above. Final concentrations were 10 μg/ml. Deuterated PACs, used for quantitation, were naphthalene-d_8, pyrene-d_{10} and dibenz[*a,h*]anthracene-d_{14}, (obtained from Aldrich, Milwaukee, WI, USA).

2.4. Sample preparation

A 100 mg sample of the diesel particulate sample (SRM 1650) was extracted with 200 ml of dichloromethane for about 24 h in a Soxhlet apparatus with a cycle time of 10 to 15 min. The Soxhlet extract was concentrated to about 2 ml using a Kuderna–Danish concentrator. The concentrated extract was filtered through a 0.2 μm fluorocarbon filter (Gelman Sciences, Ann Arbor, MI, USA). The filter was rinsed with 2 ml dichloromethane three times. The extract was concentrated to 2.0 ml under the N_2. The sample was ready for HPLC fractionation. The Soxhlet extraction apparatus and the Kuderna–Danish concentrator were obtained from ACE Glass (Vineland, NJ, USA).

2.5. Fractionation procedure

Before the PDVB/CH_2Cl_2 system was used to fractionate the diesel particulate sample extract, several injections of (50 μl of 10 ng/μl) the fraction marker, cyclopenta[*def*]phenanthrene (CPHE), were made to determine the fractionation point for PAC. Next 500 μl of the recovery mixture or sample extract was injected into the HPLC and eluted with dichloromethane at 1.5 ml/min. The PAC fraction was collected and concentrated under N_2 to 500 μl before analysis by GC–MS.

3. Results and discussion

As stated earlier, a multi-mode mechanism is involved in the separation of PACs from a complex matrix on a PDVB column using dichloromethane as mobile phase [1–5]. The separation of components that are predominantly aliphatic in nature is governed by steric factors (shape and stereochemistry), thus aliphatics elute in order of decreasing molecular size. On the other hand, the retention for planar, unsubstituted PACs is governed by non-size effects (partition, adsorption, and other distribution effects), therefore PACs are retained on the column well after the aliphatics elute. Components that exhibit both aliphatic and aromatic characteristics (alkyl-arenes) elute in the interval between the pure aliphatics and the planar PAC.

When we first investigated the HPLC retention of PACs on PDVB/CH_2Cl_2 it appeared that the abundance in fossil-fuels combustion samples of myriad types of alkyl-arene isomers might hinder the isolation of combustion-generated PACs of human-health interest. However, our work with a wide range of combustion samples showed that fossil-fuels components tend to be exhaustively alkylated while combustion-generated PACs are predominantly unsubstituted, thus the separation of the two different types in complex mixtures using PDVB/CH_2Cl_2 can be simple and straightforward [2,5].

3.1. Surrogate sample

Earlier studies have shown that the elution volume (V_e) for CPHE, serves as a suitable marker for the onset of the unsubstituted PAC fraction [5]. It is an methylene-bridged PAH that elutes slightly ahead of the unsubstituted PAHs. To illustrate the use of CPHE as a marker and to validate the PDVB column's performance, a surrogate sample was first characterized. The surrogate sample used here consisted of a matrix of alkyl phthalates and polyphenyls, shown to elute predominantly by size [1], was spiked with an aliquot of a reference standard consisting of sixteen PAHs targeted by the US EPA.

This matrix simulates the undifferentiated envelope of aliphatics and alkyl-arenes typically found in fossil fuels and, unlike pure aliphatics, absorbs in the UV and can be detected by common HPLC–UV

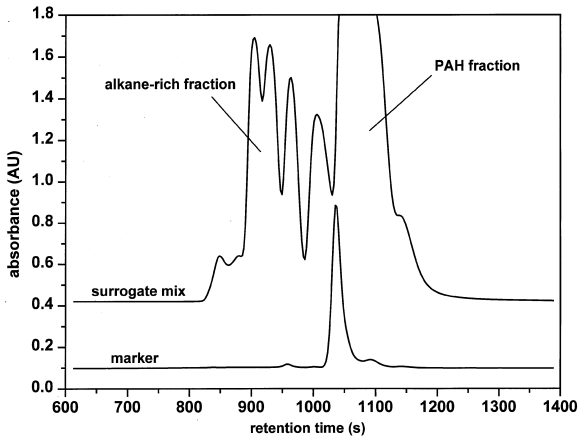

Fig. 1. HPLC chromatograms obtained using a poly(divinylbenzene) column and dichloromethane mobile phase for a surrogate sample and for the fraction marker, cyclopenta[*def*]phenanthrene (CPHE).

detection at low levels. Using surrogate samples of this type, we have found that for a range of environmental and combustion samples, the preponderance of aliphatics, alkyl-arenes and phthalates elute ahead of our retention marker, CPHE, while the PACs of interest elute with or after CPHE. The V_e value for CPHE therefore has served as a convenient marker to aid in the collection of the PAC fraction. Fig. 1 shows data for an HPLC chromatogram of the surrogate mixture together with a chromatogram of pure CPHE. The surrogate sample was also used to determine recovery for the sixteen PAH standard. The mean recovery, determined in triplicate, for all sixteen PAHs was 93% with a relative standard deviation (R.S.D.) of 10%.

3.2. Diesel particulate sample

A 100 mg sample of standard reference diesel particulate sample SRM 1650 was extracted with dichloromethane in a Soxhlet apparatus as described in Section 2.4. In Fig. 2, a GC–MS total ion chromatogram (TIC) of the unfractionated extract is compared with one obtained for the same sample after undergoing clean-up with PDVB/CH_2Cl_2. The trace for the unfractionated sample features a prominent aliphatic envelope with peaks corresponding to dominant components superimposed on it, and the presence of the envelope makes the identification of

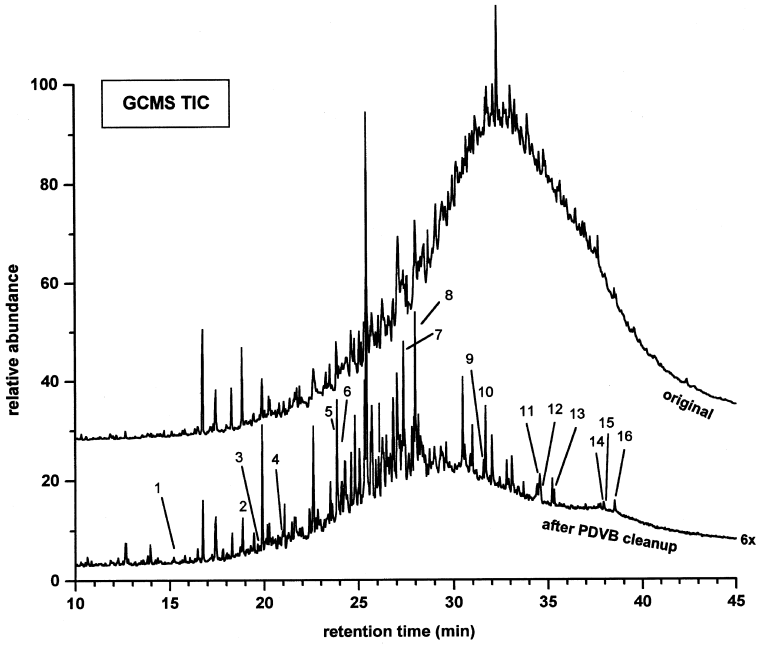

Fig. 2. GC–MS total ion chromatograms (TICs) of a dichloromethane extract of a diesel particulate sample (NIST SRM 1650) before (upper trace) and after (lower trace) fractionation on poly(divinylbenzene). The numbers refer to the PAHs listed in Table 1.

sample components impracticable in many cases. The trace for the PAC fraction, on the other hand, contains only a small undifferentiated envelope with the PACs resolved into clearly separated peaks. Peaks labeled 1–16 correspond to the sixteen PAH target compounds listed in Table 1.

Although this sample clean-up process revealed the great abundance of alkylated species, we observed that some of the sixteen target compounds, notably the abundant fluoranthene and pyrene, could be identified in the original, unfractionated sample by further processing of the data (e.g., by generating mass chromatograms), although, the lower the concentration in the sample, the more difficult it became to identify and quantify a component. A comparison of mass chromatograms obtained before and after clean-up is shown in Fig. 3 for m/z 252 corresponding to the $C_{20}H_{12}$ isomer group including the benzofluoranthenes and benzopyrenes. The upper trace corresponding to the mass chromatogram obtained from the fractionated sample has been offset in both axes for clarity. It can be seen in Fig. 3 that the chromatograms obtained before and after clean-up are similar with the notable exception that an increase in separation between the benzo[*b*]fluoranthene (BbF) and benzo[*k*]fluoranthene (BkF) peaks is seen in the PAC fraction obtained after HPLC with PDVB. This improvement in resolution is seen consistently for the BbF/BbF cluster even though the GC conditions are the same for both cases. This finding is consistent with improvements in resolution observed for other PAC complex mixtures after clean-up with normal-phase HPLC [22]. The well-resolved benzo[*e*]pyrene (BeP) and benzo[*a*]pyrene (BaP) peaks are practically identical in both cases.

Table 1
Results for the determination of sixteen PAHs in a diesel particulate sample

SRM 1650[a] components		Concentration±S.D.[c] (μg/g)		
		NIST[b]	This study	Ref. [15]
1	Naphthalene	NR[d]	5.4±0.2	NR
2	Aacenaphthylene	NR	0.4±0.1	NR
3	Acenaphthene	NR	0.2±0.1	NR
4	Fluorene	NR	0.5±0.3	NR
5	Phenanthrene	79±1	70±10	45±1.9
6	Anthracene	NR	4.4±0.7	NR
7	Fluoranthene	51±4*	62±2	35±1
8	Pyrene	48±4*	54±1	27±0.1
9	Benzo[*a*]anthracene	6.5±1.1*	6.3±0.3	NR
10	Chrysene	22±1	34±2	34±3
11	Benzo[*b*]fluoranthene	NR	5.6±1.0	12±0.3
12	Benzo[*k*]fluoranthene	2.1±0.2	3.7±0.5	8.7±0.4
13	Benzo[*a*]pyrene	1.2±0.3*	0.8±0.1	NR
14	Indeno[1,2,3-*cd*]pyrene	1.8±0.1	4.2±0.5	NR
15	Dibenzo[*a,h*]anthracene	NR	0.9±0.1	NR
16	Benzo[*ghi*]perylene	2.4±0.6*	3.6±0.2	NR

[a] US National Institutes of Standards and Technology, Standard Reference Material 1650, Diesel Particulate Matter. Numbers refer to peaks in Fig. 2.
[b] Values reported by NIST for electron impact GC–MS or HPLC with fluorescence detection. *certified values derived from a composite of analytical methods.
[c] Standard deviation; this work, $n=3$.
[d] Not reported.

Although the m/z 252 mass chromatograms are similar before and after clean-up, the mass spectra of their components show marked differences. This is illustrated in Fig. 4 where the mass spectrum for BeP is shown before and after PDVB clean-up. The mass spectrum obtained after clean-up is much more characteristic of an unsubstituted PAC, being nearly devoid of fragment ions with only the molecular ion dominating. It should be noted that the PAC molecular ions all have an even mass number, being molecular ions, while the co-eluting alkanes and alkyl-arenes create predominantly odd-mass fragment ions upon electron impact. It is perhaps for this reason that many PACs can be quantified with only limited difficulty even in the presence of a significant excess of alkylated components. PAC identification, however, was clearly improved by sample clean-up with PDVB.

Fig. 5 shows mass chromatograms for $C_{24}H_{14}$ PAC (m/z 302), present in the sample at only trace levels. With the instrument used for this work, these components are just barely detectable, however, a significant improvement in detectability can be seen after PDVB clean-up. Peak A is the most abundant isomer cluster while the Peak B cluster is barely discernible. In other samples where the $C_{24}H_{14}$ PACs are more abundant, dibenzofluoranthenes have been identified in Peak A while dibenzopyrenes predominate in Peak B, although other isomers are also likely to be present. Not surprisingly, the $C_{24}H_{14}$ GC–MS elution profile resembles that of the $C_{20}H_{12}$ PACs (benzofluoranthenes and benzopyrenes) having one fewer *ortho*-fused benzene ring. No mass spectra

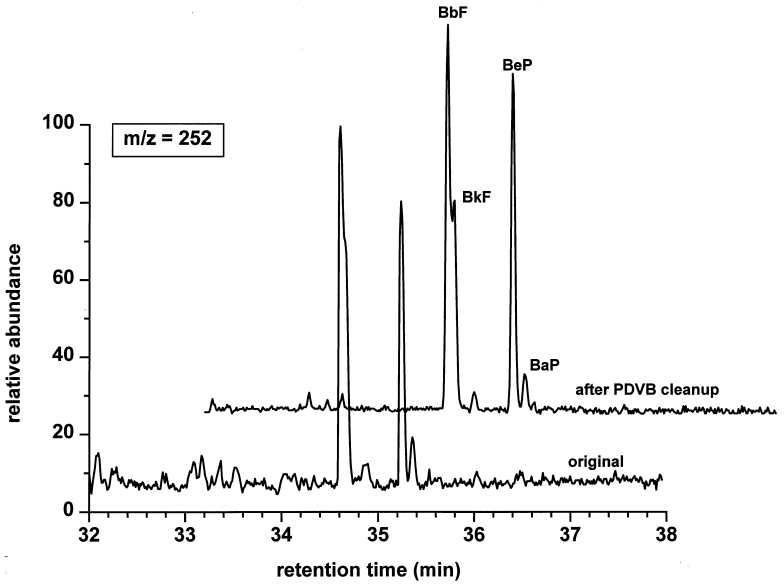

Fig. 3. GC–MS mass chromatograms for m/z 252 obtained for a dichloromethane extract of a diesel particulate sample (NIST SRM 1650) before (lower trace) and after (upper trace) fractionation on poly(divinylbenzene). Abbreviations: BbF=benzo[*b*]fluoranthene, BkF=benzo[*k*]fluoranthene, BeP=benzo[*e*]pyrene, BaP=benzo[*a*]pyrene.

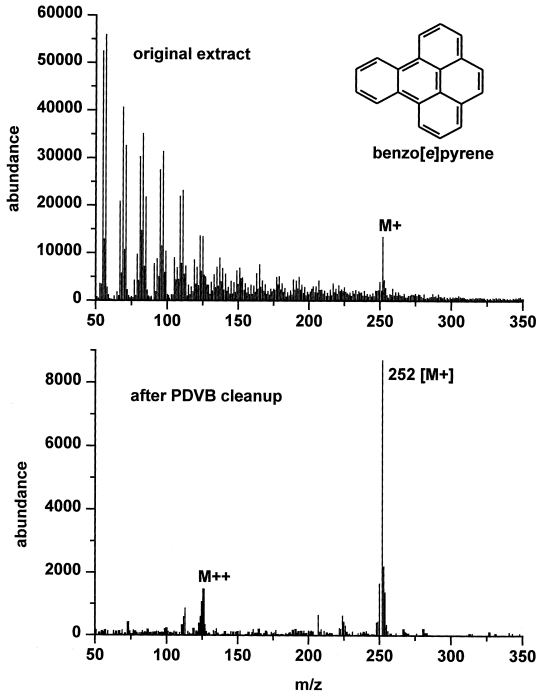

Fig. 4. Mass spectra obtained from the benzo[*e*]pyrene peaks shown in Fig. 3. Note the absence of hydrocarbon fragments in the mass spectrum obtained after PDVB clean-up.

characteristic of PAC could be obtained in either case. The high GC temperatures necessary for the elution of $C_{24}H_{14}$ PACs, combined with their low abundance, often results in uncharacteristic mass spectra dominated by siloxane column-bleed.

Because the unwanted alkylated species produce predominantly odd-mass ions in their mass spectra, another experiment was done to see what level of improvement could be seen in the detection of odd-mass PACs as compared with the standard even-mass target PACs. The presence of a detectable amount of 1-nitropyrene in the SRM 1650 diesel sample afforded us an opportunity to perform this experiment. Fig. 6 shows mass chromatograms for m/z 247, the molecular ion of 1-nitropyrene (1NP), before and after clean-up. The background noise reduction is significantly better than that observed for the even-mass 252 u mass chromatogram in Fig. 3, but the absence of partially-resolved 247 u isomers prevents comparison of resolving-power improvements of the type seen with the BbF/BkF peak, for example. The PDVB clean-up procedure yielded a great improvement in the information content of the mass spectrum of 1NP, however, as seen in Fig. 7. After clean-up, structures can be assigned with confidence to all

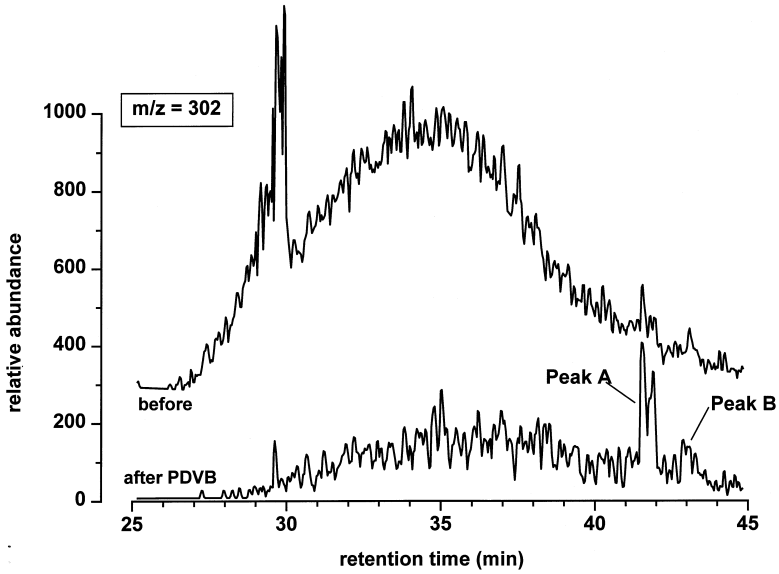

Fig. 5. GC–MS mass chromatograms for m/z 302 obtained for a dichloromethane extract of a diesel particulate sample (NIST SRM 1650) before (upper trace) and after (lower trace) fractionation on poly(divinylbenzene). Peak A and Peak B represent incompletely-resolved clusters of $C_{24}H_{14}$ isomers.

major ions in the 1NP mass spectrum, while in the original mass spectrum, an unequivocal identification cannot be made.

3.3. Quantitative results

We also quantified the PAC fraction obtained by

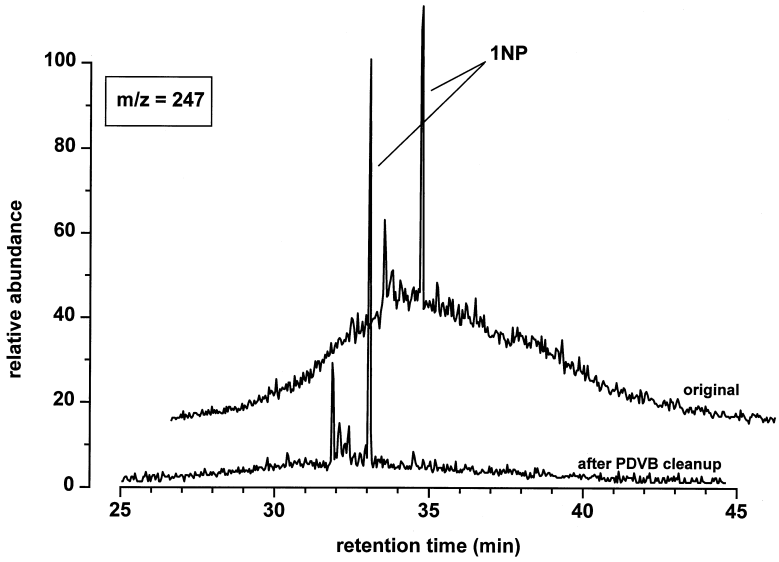

Fig. 6. GC–MS mass chromatograms for m/z 247 obtained for a dichloromethane extract of a diesel particulate sample (NIST SRM 1650) before (upper trace) and after (lower trace) fractionation on poly(divinylbenzene). Peak 1NP is 1-nitropyrene while the other resolved peaks originate from fragment ions of alkylated PAH. The chromatograms are offset 10% for clarity.

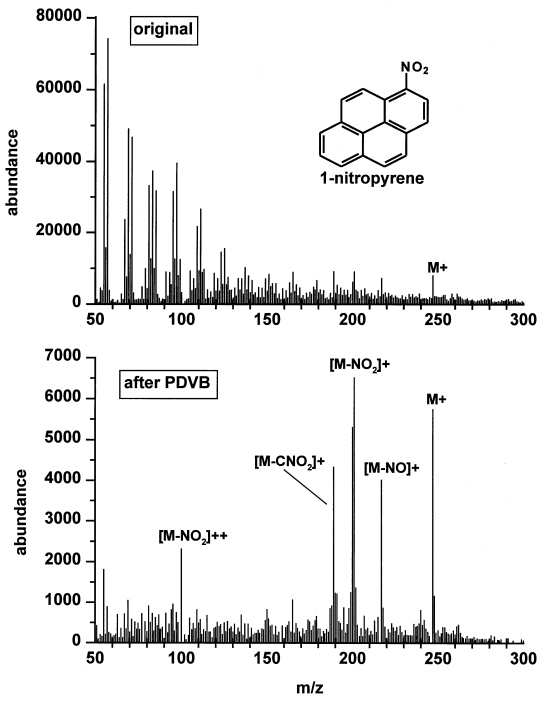

Fig. 7. Mass spectra obtained from the m/z 247 peaks shown in Fig. 6. Structural assignment as 1-nitropyrene is readily confirmed in the mass spectrum obtained after PDVB clean-up.

HPLC with PDVB/CH_2Cl_2 so that we could verify that the clean-up procedure did not result in significant losses of any of the sixteen PAH target compounds. Our results are listed in Table 1. The numbers 1–16 in the first column refer to the corresponding peaks in the chromatogram shown in Fig. 2. The concentration values listed by NIST are taken from the Certificate of Analysis [23] for standard reference material SRM 1650. Concentrations for the certified values were derived from at least two of three analytical methods that included electron impact GC–MS, HPLC with fluorescence detection (FD) and negative-ion chemical ionization (NICI) MS. Additionally, two different sample preparation techniques were used. Regarding the $C_{20}H_{12}$ PAH isomers, the value for BbF was not reported by NIST while that for BkF was determined by HPLC–FD. A look at Fig. 3 reveals that BbF and BkF are poorly resolved in the original sample and their determination would require higher GC resolution or a more selective technique such as HPLC–FD.

The values that we obtained in this study were all determined by exclusive use of GC–MS using the method detailed in Section 2.2. Mean concentrations along with the standard deviation from three analyses are compared with the NIST SRM values [23]. Also, for comparison, we list values previously reported by Savard et al. [15]. We feel that our results compare favorably with the standard values certified for SRM 1650, although they were not statistically equivalent for most analytes; however, this is to be expected when different instruments, methodologies, and sample preparation techniques are compared. Other published results obtained with a different sample preparation scheme are included for comparison [15]. The NIST values were obtained under much more rigorous conditions and were obtained using two different extraction methods and three different analytical methods. Few laboratories are equipped to duplicate the NIST standard values. Our major concern was whether the PDVB/CH_2Cl_2 clean-up procedure could be used as part of an improved method for the quantitative determination of sixteen PAH target compounds, and the data strongly suggest that a satisfactory result can be obtained with this method. An additional benefit obtained using the PDVB/CH_2Cl_2 clean-up procedure was the ability to identify and quantify some less abundant PAC with the result that all 16 of the target compounds could be determined.

4. Conclusions

We conclude from this study that the PDVB/CH_2Cl_2 clean-up method yields a simplified PAC fraction from a highly complex mixture so that PACs are well-resolved and readily quantifiable by GC–MS analysis. The greatest benefit is the improvement in the ease and confidence with which PACs can be identified from their mass spectral signatures after alkylated species are removed from the sample. Some improvement was also obtained in the ability to quantify less abundant PACs. An improvement in the ability to identify and quantify PACs has also been reported to result from the fractionation of complex samples using other HPLC methods, as mentioned earlier [18–22]. The PDVB/CH_2Cl_2 method described here does not result in the degree of separation that can be obtained using normal-

phase HPLC with silica sorbents [22], however, the PAC-enriched fraction obtained using PDVB/CH_2Cl_2 is sufficiently simple to require no additional purification for the determination of a range of PAC analytes, including the EPA sixteen PAH target compounds evaluated in this work. The PDVB/CH_2Cl_2 method has some advantages over silica-based methods, however. Because it is an isocratic method, no time-consuming column equilibration step is required as in the case of silica columns. In addition, the PDVB material is hydrophobic and impervious to the detrimental retention effects caused by the presence of water in the mobile phase as are silica sorbents, with their reactive surface silanol groups. A study of the retention stability of a PDVB/CH_2Cl_2 system yielded the following result: a total of 39 measurements for a benzene retention standard done over a period of approximately six months yielded a mean retention time of 16.01 ml with a standard deviation of 0.090 ml and relative standard deviation of 0.56%.

Many improvements in methodology are possible, especially in the choice of mobile phase. Dichloromethane proved to be satisfactory and enabled us to use a single solvent for extraction, purification and chemical analysis; but we did not attempt to optimize the mobile phase composition to obtain the best separation. We are now experimenting with the use of the PDVB/CH_2Cl_2 HPLC clean-up procedure as a prelude to normal-phase HPLC fractionation and have recently applied the method to the high-efficiency separation of nanogram levels of PAC from milligrams of dibutyl phthalate used to coat impactor stages in size-segregating aerosol samplers [24]. The PDVB clean-up technique could also be used to remove the nearly ubiquitous phthalate and adipate ester contaminants from many types of samples. Other applications can also be envisioned.

Acknowledgements

This research was supported by National Institute of Environmental Health Sciences Center Grant NIH-P30-ESO2109 and Program Project Grant NIH-P01-ESO7168.

References

[1] A.L. Lafleur, M.J. Wornat, Anal. Chem. 60 (1988) 1096–1102.
[2] M.J. Wornat, A.F. Sarofim, J.P. Longwell, Energy Fuels 1 (1987) 431–437.
[3] A.L. Lafleur, M.J. Wornat, Anal. Lett. 22 (1989) 493–506.
[4] A.L. Lafleur, E.F. Plummer, J. Chromatogr. Sci. 29 (1991) 532–537.
[5] A.L. Lafleur, M.J. Wornat, A.F. Sarofim, Energy Fuels 7 (1993) 357–361.
[6] L.R. Snyder and J.J. Kirkland, Introduction to Modern Liquid Chromatography, Wiley, New York, 2nd ed., 1979.
[7] W.W. Yau, J.J. Kirkland and D.D. Bly, Modern Size-Exclusion Liquid Chromatography, Wiley, New York, 1979.
[8] P. Fernandez, J.M. Bayona, J. Chromatogr. 625 (1992) 141–149.
[9] J.L. Durant, W.G. Thilly, H.F. Hemond, A.L. Lafleur, Environ. Sci. Technol. 28 (1994) 2033–2044.
[10] H.L. Liber, B.M. Andon, R.A. Hites, W.G. Thilly, Environ. Int. 5 (1981) 281–284.
[11] S.T. Bagley, S.L. Stoltz, D.M. Becker, R.E. Keen, Mutat. Res. 276 (1992) 81–86.
[12] C.N. Montreuil, J.C. Ball, R.A. Gorse Jr., W.C. Young, Mutat. Res. 282 (1992) 89–92.
[13] J.C. Ball, W.C. Young, Environ. Sci. Technol. 26 (1992) 2181–2186.
[14] D. Schuetzle, F.S.-C. Lee, T.J. Prater, Int. J. Environ. Anal. Chem. 9 (1981) 93–144.
[15] S. Savard, R. Otson, G.R. Douglas, Mutat. Res. 276 (1992) 101–115.
[16] D.H. Lowenthal, B. Zielinska, J.C. Chow, J.G. Watson, Atmos. Environ. 28 (1994) 731–743.
[17] J.R. Farrar-Khan, G.E. Andrews, R. Ishaq, K.D. Bartle, J. Power Energy 207 (1993) 95–106.
[18] M.L. Lee, M.V. Novotny and K.D. Bartle, Analytical Chemistry of Polycyclic Aromatic Compounds, Academic Press, New York, 1981.
[19] M.-L. Yu, R.A. Hites, Anal. Chem. 53 (1981) 951–954.
[20] T.E. Jensen, R.A. Hites, Anal. Chem. 55 (1983) 594–599.
[21] H.Y. Tong, F.W. Karasek, Anal. Chem. 56 (1984) 2129–2134.
[22] G.W. Kelly, K.D. Bartle, A.A. Clifford, D.J. Scammells, Chromatogr. Sci. 31 (1993) 73–76.
[23] Certificate of Analysis, Standard Reference Material 1650, National Institutes of Standards and Technology, Gaithersburg, MD; December 12, 1991.
[24] J.O. Allen, N.M. Dookeran, K.A. Smith, A.L. Lafleur, A.F. Sarofim, Environ. Sci. Technol. 30 (1996) 1023–1031.