Solid Phase Extraction Cleanup for Non-Polar and Moderately Polar Molecular Markers of $PM_{2.5}$ Sources

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Abstract

A solid phase extraction cleanup step substantially improved analytical efficiency and data quality for measurements of non-polar and moderately polar organic molecular marker concentrations in airborne particulate matter. Rapid gas chromatography column deterioration was evident after very few samples in the absence of a cleanup step, resulting in the need for frequent recalibration. High molecular weight polycyclic aromatic hydrocarbons, were among the species most strongly impacted by the deterioration, exhibiting deviations as high as 30 to 40% from expected calibration verification standard values after only a few injections. Column deterioration and calibration verification failure were eliminated by introducing a solid phase extraction step prior to analysis and a total of 58 samples were analyzed with no unacceptable deviation of calibration verification standards from target values

1. Introduction

Whether or not to include a solid phase extraction (SPE) or similar cleanup step for PM organic analysis is an important consideration in maintaining a balance between gas chromatography (GC) data quality and analytical efficiency. Organic analysis of airborne particulate matter (PM) usually includes either separation by solid phase extraction (SPE) or column chromatography into sequential fractions (e.g. Brook et al. 2007) or division into parallel fractions without SPE or column cleanup (e.g. Li et al. 2005). In their pioneering work, Cautreels and Van Cauwenberghe (1977) described injection of the crude sample extract onto the gas chromatographic column without extensive fractionation or sample cleanup as a major advantage for providing a fast, quantitative method for analysis of a large number of compounds over a wide range of polarities present in airborne particulate matter. However, the need for a SPE or similar cleanup step to avoid rapid deterioration of chromatography columns has been widely recognized and thoroughly investigated for a variety of matrices and compounds (Lopez-Avila et al. 1990), and applied to the analysis of non-polar molecular markers in PM (Zielinska et al. 2004).

The Detroit Exposure and Aerosol Research Study (Williams et al. 2008) provided a unique opportunity for directly comparing analytical performance for samples with and without SPE sample cleanup. To process a large number of samples, we initially implemented the simplest possible method

without SPE cleanup for the entire first season of samples. After evaluating method performance during the first season, we reconsidered this approach and developed a SPE step. This paper compares method performance for the GC analysis of hopanes and polycyclic aromatic hydrocarbons (PAHs) with and without a SPE cleanup.

2. Method

Figure 1 compares the sampling and analysis method with and without SPE. PM samples were collected on quartz fiber filters for 24 hours at 113 liters per minute using a Tisch TE-1202 sampler at the Michigan Department of Environmental Protection air monitoring site at Allen Park in Detroit, Michigan during summer 2004 (n=34) and winter 2005 (n=40). Samples were extracted in a 1:1:1 hexane, methanol, and dichloromethane mixture, by volume using a Dionex ASE 200 Accelerated Solvent Extractor, concentrated under nitrogen, and analyzed by gas chromatography/mass spectrometry (GC/MS) with an Agilent 6890 gas chromatograph and Agilent 5973 MSD equipped with a high temperature, inert ion source upgrade. The chromatographic method used splitless injection with a deactivated, single-taper inlet liner and 30 m, 0.25 mm id, 0.25 μm film thickness J&W DB5-MS column.

Concentrated sample extracts were spiked with internal standards benz[a]anthracene-d12, benzo[e]pyrene-d12, dibenz[a,h]anthracene-d14, and n-dotriacontane-d66 immediately prior to GC/MS analysis, an approach that is widely used in environmental analysis (Budde 2001). Samples were spiked with surrogate standards chrysene-d12, benzo[b]fluoranthene-d12, indeno[1,2,3-cd]pyrene-d12, and n-triacontane-d62 immediately prior to extraction to monitor loss during sample extraction and cleanup.

The summer 2004 samples were analyzed without SPE cleanup. For the winter 2005 samples, a SPE cleanup step was added before GC/MS injection using a Supelco Visiprep DL SPE Vacuum Manifold and custom 3 mL glass Teflon-fritted SPE tubes containing 500 mg silica. Except for the additional SPE step, sample processing was identical between the two seasons. Method performance using the SPE cleanup procedure has been thoroughly evaluated resulting in good precision, recoveries,

method detection limits, blanks levels, and agreement with certified reference materials for PAHs and hopanes (Turlington et al. 2009).

3. Results

3.1 Sample Injection Without Solid Phase Extraction Cleanup

A total of 34 samples from Season 1 (Summer 2004) were injected without using a SPE cleanup. Almost immediately, column degradation and loss of calibration occurred, resulting in frequent maintenance and low sample throughput. Table 1 describes pre-sample and post-sample calibration verification results and Figures 2a and 2b compare chromatograms of a pre-sample and post-sample 100 pg/μL calibration standard showing pyrene. The post-sample chromatogram followed the analysis of three samples and clearly shows substantial peak tailing and intensity loss in comparison to the pre-sample chromatogram. Calculated concentrations of most targets in the post-sample 100 pg/μL calibration standard were substantially lower than in the pre-sample calibration analysis. As reported in Table 1, an initial comparison between the pre-sample standard and its prepared concentration show percent deviations of less than 3% for all PAHs. Following the injection of three samples, all PAH concentrations in the post-sample standard deviated from their prepared concentrations by approximately 20% to 40%. For benzo[ghi]perylene and indeno[1,2,3-cd]pyrene alone, this represented a drop in concentration of approximately 45% and 70%, respectively, from prepared values.

Restoring chromatography quality by clipping a portion of the inlet end of the column re-established good peak shape (as verified with pyrene), but most PAH components still deviated by approximately 20% to 30% from target levels. With continued operation, chromatography deteriorated even more rapidly. As a result, even after restoring good peak shape, a time consuming recalibration was still required approximately every three samples for a total of 12 recalibrations to complete all 34 samples.

Some of the most important molecular markers were the most sensitive to peak distortion and poor calibration control. For example, post-sample deviations greater than 30% were observed for

benzo[ghi]perylene and indeno[1,2,3-cd]pyrene, which are potentially useful for distinguishing gasoline from diesel exhaust particulate matter (Zielinska et al. 2004, Chow et al. 2007). In contrast, hopanes, which are less polar than PAHs, were largely unaffected, as shown in Table 1.

3.2 Extraction Solvent Effects

The effect of various extraction solvents on column deterioration in combination with SPE eluent modification was investigated and summarized in Table 2. In each case a sample filter was extracted, evaporated to 100 µL, and passed through the SPE cartridge with 5 × 1 mL aliquots of eluent. Pyrene was monitored for chromatography changes. SPE cleanup with dichloromethane as the eluent failed to improve column performance when the hexane, methanol, and dichloromethane extraction mixture was used. Tailing of pyrene was apparent after only one sample injection and considerably worse after five sample injections. While all hopane targets showed less than 5% deviation from the pre-sample calibration, significant deviations ranging from approximately 10% - 50% resulted for most PAHs. Extraction in pure dichloromethane improved performance only slightly, with maintenance and recalibration still necessary after 10 sample injections. In contrast, no apparent change in chromatography was observed either extracting with hexane and using dichloromethane as the SPE eluent or extracting in 1:1:1 hexane, methanol, and dichloromethane and using hexane as the SPE eluent after 12 injections. To that end, it appeared that either extraction or SPE elution with a pure non-polar solvent eliminated the column deterioration problem, suggesting the contaminant material to be of a polar nature.

3.3 Eluent Optimization

Table 3 compares recoveries of eluents investigated in optimizing the SPE procedure. The SPE cartridges were spiked with all target analytes to produce a concentration level approximating 1 ng/m^3. Using pure hexane, hopane components resulted in > 95% recovery, but PAH recoveries were more variable, ranging from approximately 30% to 80%, and showing a general decline with increasing molecular weight. SPE recoveries greater than 90% were observed for PAHs and hopanes using eluents

of 10% dichloromethane in hexane, 10% acetone in hexane, and 5% dichloromethane/5% acetone in hexane. Additional testing and optimization of the eluent reduced the dichloromethane and acetone levels from 5% to 1% with similar target recoveries and no column deterioration. SPE recoveries for hopanes and PAHs using 1% dichloromethane and 1% acetone in hexane are shown in Table 4.

3.4 Basis for Improved Chromatography with SPE

The improved performance using non-polar hexane as either an extraction solvent or SPE eluent suggests a polar contaminant. Peak distortion was not observed after injecting either a similar number of standard solutions or blank filters spiked with target analytes, suggesting that the contaminants are indigenous to the collected particulate matter, rather than solvent or filter related. Several potentially destructive polar contaminants are present in PM. Water damages chromatography columns (Jennings 1975) and substantial amounts are associated with organic matter in atmospheric aerosols (Speer et al. 2002). Inorganic ions can account for more than 50% of extracted mass in polar solvents like methanol (Grosjean 1975) and inorganic, water soluble PM components can be very acidic (Spengler et al. 1989). Also highly polar organic acids often contribute more to organic aerosol mass than other classes (Li et al. 2005, Rinehart et al. 2006). Any or all of these could play a role in impairing chromatographic performance for PAHs, even when non-polar species like hopanes are unaffected. Remarkably, even extraction or elution with a moderately polar solvent such as dichloromethane apparently extracted enough damaging material to require maintenance and recalibration after a few samples if calibration verification procedures were strictly followed.

3.5 Method Performance

Figures 2c and 2d compare the pre-sample pyrene peak with the post-sample pyrene peak following injection of all 58 samples. With the addition of the SPE step, no deterioration in peak quality was detected, no significant deviation for calibration verification standards was observed, and no GC/MS maintenance was required. The apparent difference in peak height between 2c and 2d is most likely due

to injection volume variability since the ratio between pyrene and its internal standard, benz[a]anthracene-d12, shows a difference of only 1.5% between the pre-sample and post-sample injections. Because secondary organic aerosol is typically more polar than primary organic aerosol, it is likely that the summer samples from the first season contained more polar organic material than samples from the second winter season. However, subsequent analysis of summer samples from the third season has now been completed without the need for recalibration. Calibration control results for 26 evaluations at 2 pg/μL and 9 evaluations at 200 pg/μL are reported in Table 5 and demonstrate good agreement with the prepared concentration and a high degree of precision. The percent difference between the prepared value and average concentration for all compounds is under 10% with corresponding RSD values also less than 10%.

4. Conclusion

The results clearly demonstrate that for typical ambient PM samples, reasonable quality control requirements for calibration verification for all target analytes cannot be met without sample cleanup by SPE or similar procedures, even if routine maintenance procedures such as column-cutting and injector cleaning are frequently carried out. This is an important observation for laboratories faced with decisions on how to best balance data quality with timeliness and resource needs because sample cleanup is costly and time consuming. Using a simple SPE cleanup, it was possible to meet calibration verification checks without GC maintenance throughout the analysis of more than 50 samples.

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5. References

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Figure 1. Comparison of sampling and analytical procedures with and without solid phase extraction.

Figure 2. Quality of chromatography as illustrated by pyrene standard peak a) before sample analysis without solid phase extraction, b) after 3 samples without solid phase extraction, c) before sample analysis with solid phase extraction, d) after analysis of 58 samples with solid phase extraction

Figure 1 Revised

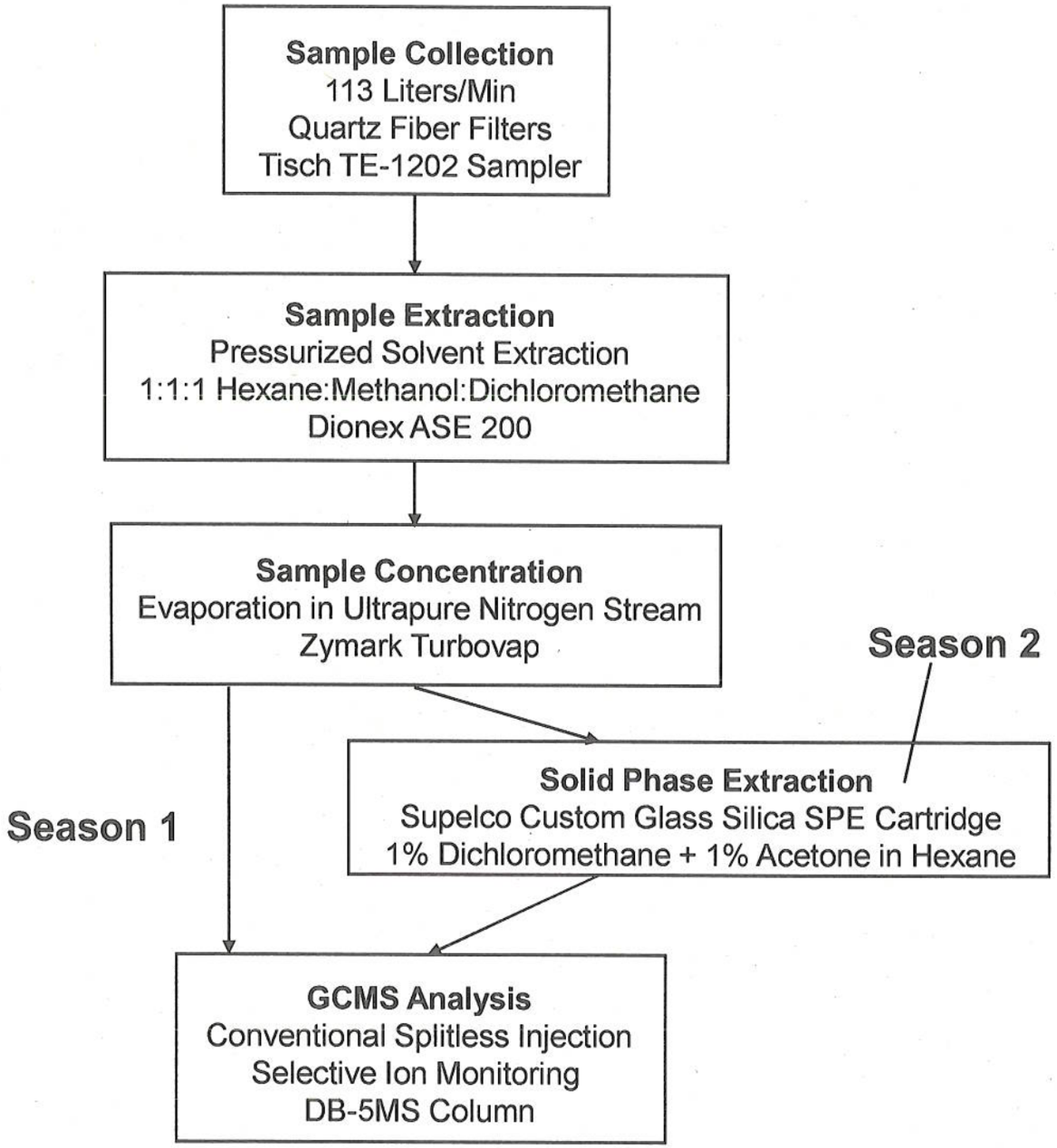

Figure 2 Revised

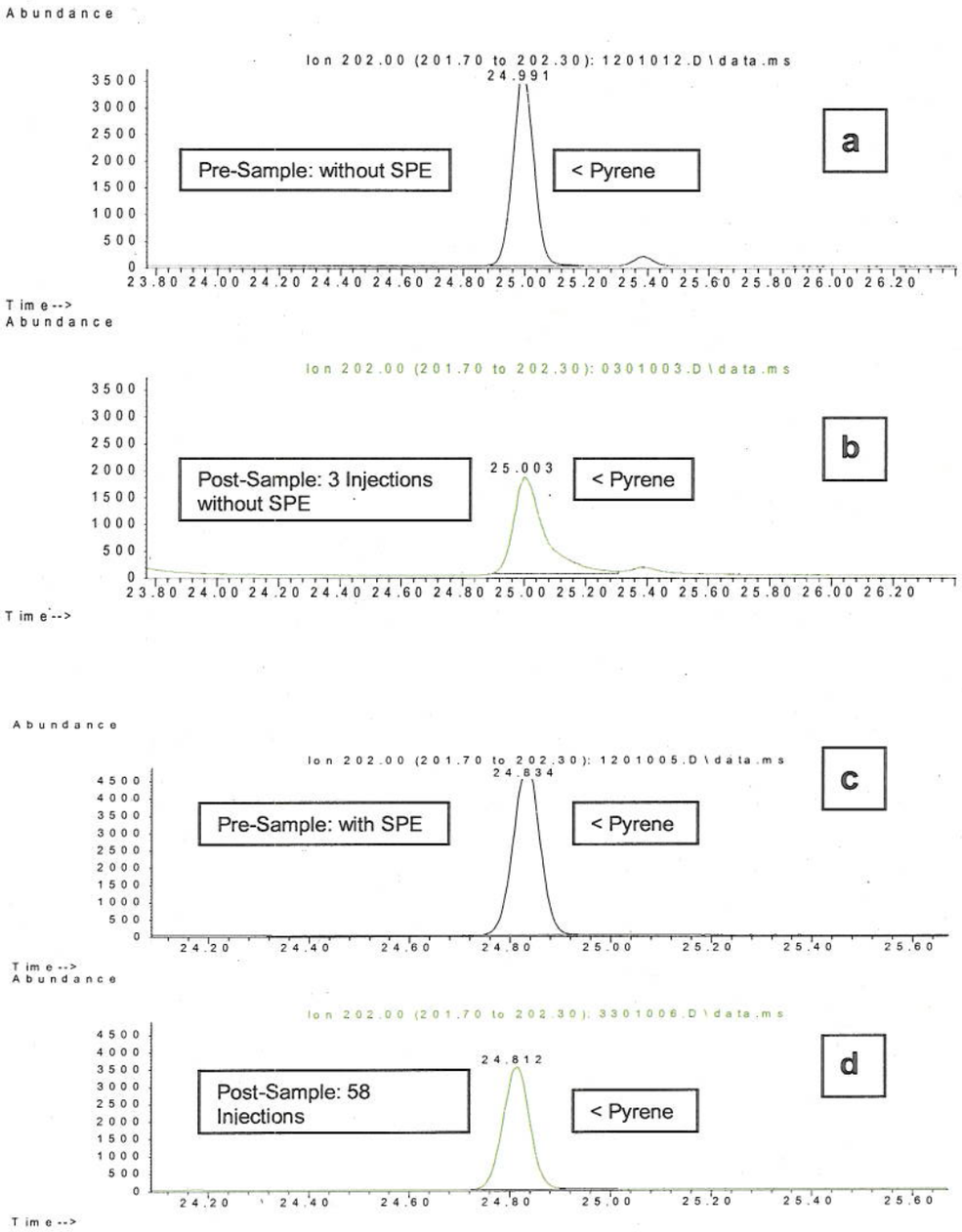

Table 1
Pre-sample vs. post-sample calibration verification without SPE

Component	100 pg/µL Standard Prepared (pg/µL)	Pre-Sample Calculated (pg/µL)	Prepared vs. Pre-Sample % Deviation	Post-Sample Calculated (pg/µL)	Prepared vs. Post-Sample % Deviation
Pyrene	98.7	97.3	1.4%	76.0	23.0%
Chrysene	98.4	96.5	1.9%	73.7	25.1%
Benzo[b]fluoranthene	1.00×10^2	98.6	1.6%	67.0	33.0%
Benzo[k]fluoranthene	99.1	98.0	1.1%	75.6	23.7%
Benzo[a]pyrene	1.00×10^2	97.6	2.5%	63.8	36.3%
Indeno[1,2,3-cd]pyrene	1.00×10^2	102	1%	59.0	41.1%
Benzo[ghi]perylene	98.5	98.7	0.2%	67.5	31.4%
17α(H),21β(H)-30-Norhopane	1.0×10^2	97	3%	1.0×10^2	0%
17α(H),21β(H)-Hopane	1.0×10^2	97	3%	99	1%
17α(H),21β(H)-22S-Homohopane	1.0×10^2	96	4%	1.0×10^2	0%

Table 2
Extraction solvent and SPE eluent effects

Extraction Solvent	Eluent	#Injections	Peak Shape	Comments
Hexane, Methanol, DCM[1]	DCM[1]	5	Tailing	No improvement
DCM[1]	DCM[1]	10	Tailing	Tailing slowed
Hexane	DCM[1]	6	No Tailing	Polar contaminant
Hexane, Methanol, DCM[1]	Hexane	12	No Tailing	Polar contaminant

[1] DCM: Dichloromethane

Table 3
Recovery optimization of silica SPE eluent, 1.10 ng/m^3 equivalent.

Eluent	PAHs	Hopanes
Hexane	30% - 80%	> 95%
10% DCM[1] in Hexane	> 90%	> 90%
10% Acetone in Hexane	> 90%	> 90%
5% DCM[1] + 5% Acetone in Hexane	> 90%	> 90%

[1] DCM: Dichloromethane

Table 4
SPE Percent Recoveries (± %RSD) with 1% dichloromethane + 1% acetone in hexane, 1.10 ng/m^3 equivalent.

Component	Recovery (%) n=3
Pyrene	98.1 ± 1.7%
Chrysene	102 ± 2%
Benzo[b]fluoranthene	103 ± 2%
Benzo[k]fluoranthene	104 ± 2%
Benzo[a]pyrene	102 ± 2%
Indeno[1,2,3-cd]pyrene	102 ± 3%
Benzo[g,h,i]perylene	101 ± 2%
17α(H),21β(H)-30-Norhopane	1.0×10^2 ± 1%
17α(H),21β(H)-Hopane	1.0×10^2 ± 2%
17α(H),21β(H)-22S-Homohopane	99 ± 2%

Table 5
Calibration solution verification and precision at two calibration levels

Prepared Calibration Verification	2 pg/uL (nominal)			200 pg/uL (nominal)		
n replicates	26			9		
Target	**Avg.**	**%RSD[1]**	**%Diff.[2]**	**Avg.**	**%RSD[1]**	**%Diff.[2]**
Pyrene	2.10	4.7	4.9	202	2	0.9
Chrysene	2.05	3.9	2.6	199	1	0.9
Benzo[b]fluoranthene	2.07	4.7	3	196	2	3
Benzo[k]fluoranthene	1.90	6.3	5.2	1.90×10^{2}	3	5.6
Benzo[a]pyrene	2.00	6.8	0.1	194	2	3
Indeno[1,2,3-cd]pyrene	2.03	5	2	198	1	1
Benzo[g,h,i]perylene	1.98	4	0.8	199	1	1
17α(H),21β(H)-30-Norhopane	*	*	*	2.1×10^{2}	4	4
17α(H),21β(H)-Hopane	*	*	*	2.0×10^{2}	3	0.5
17α(H),21β(H)-22S-Homohopane	*	*	*	2.0×10^{2}	3	1

[1] %RSD: relative standard deviation of average calibration verification solution concentration for n replicates
[2] %Difference: difference between average concentration for n replicates and prepared calibration verification solution
* hopanes are below limits of quantitation at this level