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Supercritical fluid extraction of nitrated polycyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbons from diesel exhaust particulate matter

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) and nitrated PAHs (nitro-PAHs) were extracted from diesel exhaust particulates and diesel soot using supercritical $CHClF_2$ (freon-22), CO_2, and CO_2 with added modifiers. Pure CO_2 was able to extract 1-nitropyrene spiked on air sampling filters, but did not yield quantitative extractions from diesel exhaust particulates [standard reference material (SRM) 1650 of the National Institute of Standards and Technology (Gaithersburg, MD, USA)]. 1-Nitropyrene could be quantitatively extracted in 45 min using either pure $CHClF_2$ or 10% toluene in CO_2 as a modifier, whereas 10% mixtures of $CHClF_2$ or methanol in CO_2 yielded only moderate recoveries. Supercritical $CHClF_2$ also yielded quantitative extraction of PAHs from SRM 1650. Various nitro-PAHs could be determined in soot collected from the exhaust pipe of a bus after extraction with CO_2 modified with $CHClF_2$ or toluene.

INTRODUCTION

Diesel exhaust particulate matter contains a wide variety of nitrated polycyclic aromatic hydrocarbons (nitro-PAHs), of which 1-nitropyrene is by far the most abundant [1,2]. Tests with the Ames short-term bioassay for detection of chemical mutagens prove that 1-nitropyrene is a direct mutagen causing spontaneous mutations in *Salmonella typhimurium* bacteria [3–6]. For the determination of nitro-PAHs, diesel particulates are usually extracted for 24 h with methylene chloride with a Soxhlet apparatus [4]. The use of a supercritical fluid could reduce the extraction time to less than an hour while greatly reducing the amount of liquid solvent required. It has been shown previously that PAHs can be quantitatively extracted with pure CO_2 or CO_2–methanol (95:5) [7] using relatively long (*e.g.* 90 min) extraction times, and the extraction of nitro-PAHs from sorbents has been reported [8,9]. However, little is known about the extraction behavior of nitro-PAHs from complex matrices such as diesel exhaust particulates. Under many supercritical fluid extraction (SFE) conditions, supercritical extractions of polar compounds from a complex matrix like diesel exhaust particulates often yields poor recoveries when pure CO_2 is used. Experiments with incinerator fly ash and sediment samples indicate that of-

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TABLE I

COMPARISON OF PROPERTIES OF SUPERCRITICAL FLUIDS

Compound	Critical temperature, T_c (°C)	Critical pressure P_c (atm)	Dipole moment (Debye)
CO_2	31.3	72.9	0.0
Methanol	239.5	81.0	1.7
Methanol–CO_2 (10:90)[a]	51.5	74.2	–
$CHClF_2$	96.1	49.1	1.4
$CHClF_2$–CO_2 (10:90)[a]	38.2	69.6	–
Toluene	318.8	41.4	0.4
Toluene–CO_2 (10:90)[a]	67.2	67.9	–

[a] The critical data of the 10% mixtures were calculated with SF-Solver by ISCO, Lincoln, NE, USA.

ten the solubility of the analyte is not the limiting factor for quantitative extractions [10–13]. Instead, it appears that strong interactions between the analyte and the matrix exist which must be overcome by a stronger solvent than CO_2 [10–13].

The most common way to increase the solvent strength of CO_2 is the use of methanol as a modifier. Because of its high critical temperature of 240°C, pure methanol is not a suitable solvent for supercritical extractions under mild conditions. $CHClF_2$ provides a dipole moment similar to methanol, but has more moderate critical data (Table I). $CHClF_2$ (freon-22) has been used by Li and coworkers [14,15] as a mobile phase for supercritical fluid chromatography (SFC) of steroids and phenols and for the extraction of steroids. Compared to CO_2, $CHClF_2$ showed much shorter retention times for these polar compounds. ($CHClF_2$ is also much more desirable from the environmental standpoint than fully-halogenated freons because it degrades more rapidly in the lower atmosphere and therefore has a low potential for ozone destruction and global warming. In addition, $CHClF_2$ is being suggested as the future coolant in home air conditioning systems [16].) Besides $CHClF_2$ and methanol-modified CO_2, which are expected to yield better extraction results than CO_2 because of their higher dipole moment, toluene was also used as a modifier. Toluene-modified CO_2 has been reported to increase the extraction of dioxins from fly ash, presumably because of its aromatic character [13].

This study compares pure CO_2, pure $CHClF_2$, and CO_2 modified with 10% toluene, methanol, and $CHClF_2$ for their ability to extract nitro-PAHs from diesel exhaust particulates and soot.

EXPERIMENTAL

Samples

The diesel exhaust particulate sample (standard reference material, SRM 1650) was supplied by NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA), and is considered to be representative for cumulative sampling of heavy-duty engines for shorter periods of time [4]. SRM 1650 contains 19 ± 2 μg/g 1-nitropyrene according to NIST based on Soxhlet extractions. The diesel soot sample was collected from the exhaust pipe of a bus which had a 6.9-l International diesel engine (1985). All samples were stored in the dark at 4°C until used.

Supercritical fluid extractions

Supercritical extractions were performed with ISCO 260D or 100D syringe pumps (ISCO, Lincoln, NE, USA) using SFC-grade CO_2 or >99.9% purity $CHClF_2$ (Scott Specialty Gases, Plumsteadville, PA, USA). For generating modified CO_2 two pumps were connected with a mixing tee and two backpressure control valves following the manufacturer's instructions (Fig. 1). SRM 1650 diesel exhaust particulate (25 mg) or diesel exhaust pipe soot (250 mg) were extracted in 0.5 ml or 2.2 ml extraction cells, respectively (Keystone Scientific, Bellefonte, PA, USA). The extraction pressure was 400 atm (405 bar) during all extractions. The extraction

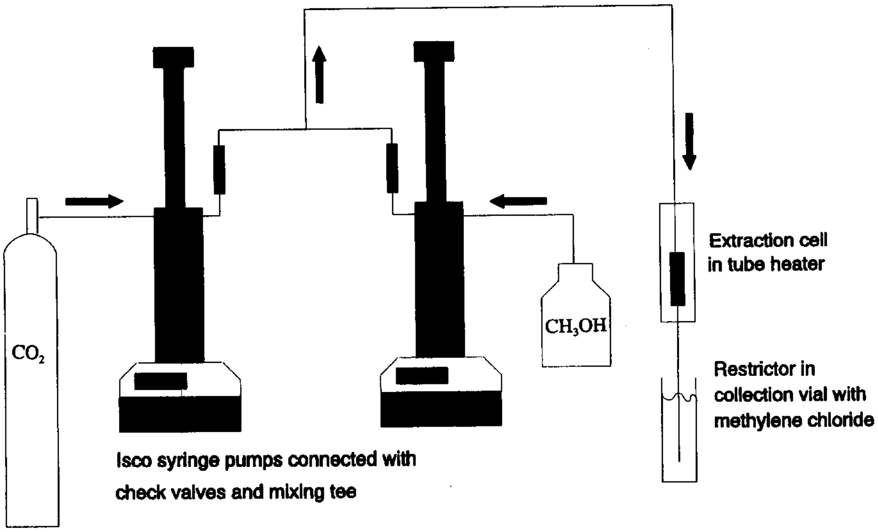

Fig. 1. Schematic diagram of the SFE system using CO_2 with an organic modifier (*e.g.*, methanol). Arrows indicate the direction of extraction fluid flow. Details on the individual system components are given in the text.

temperature was maintained by placing the cell in a thermostatically controlled tube heater. Because of the different critical temperatures of the various pure and modified fluids used, the extraction temperature was 40°C with pure CO_2, 100°C with pure $CHClF_2$, 80°C with CO_2–methanol, 60°C with CO_2–$CHClF_2$ modifier, and 100°C with CO_2–toluene.

Supercritical fluid flow rates were maintained at *ca.* 0.3 ml/min (measured as liquid at the pump) using capillary restrictors with an internal diameter of 19-23 μm (Polymicro Technologies, Phoenix, AZ, USA). Plugging of the restrictor occurred occasionally when CO_2–methanol or pure $CHClF_2$ were used, because of freezing water at the outlet of the restrictor or precipitated analytes inside the restrictor. In these cases, the restrictor was briefly heated with a heat gun to maintain flow. When $CHClF_2$ was the supercritical fluid, restrictors tended to break more frequently and were, therefore, replaced after every extraction.

All extracts were collected in 5 ml methylene chloride placed in a 70 mm long × 18 mm I.D. glass vial. During extraction, methylene chloride had to be added from time to time because of evaporation losses. After the extraction, the solvent was evaporated with nitrogen to a volume of 1 ml. The sample was then transferred into an autosampler vial and the internal standard (deuterated chrysene) was added. HPLC-grade methanol used as a modifier was briefly sonicated for degasification before use. All other organic solvents were pesticide grade ("Optima"; Fisher Scientific, USA).

In order to determine the trapping efficiency of the extracted analytes in the 5 ml methylene chloride, air particulate sampling filters (10 × 40 mm pieces of Whatman QM-A quartz microbore filters) were spiked with 0.2 ml of a solution containing 50 to 90 μg/g each of phenanthrene, 1-nitronaphthalene and 1-nitropyrene in methanol. The solvent was evaporated for 10 min, the filter was transferred immediately into an extraction cell, and extracted with CO_2.

Gas chromatographic analysis

The extracts from the spiked samples were analyzed by gas chromatography with flame ionization detection (GC–FID) using a Hewlett-Packard Model 5890 equipped with an HP 7673 automatic sampler, an HP 3396A integrator, and an HP-5 capillary column (25 m × 320 μm I.D., 0.17 μm film thickness). Hydrogen was used as the carrier gas. Samples were injected at a split ratio of 1:30. The GC oven temperature for all analyses was 60°C followed by a temperature ramp at 8°C/min to 330°C.

All diesel particulate extracts were analyzed by GC–MS (HP 5988) in the selected ion monitoring mode using the molecular ion for each species and the same capillary column that was used for the FID analyses. The carrier gas was helium. Because of limited sample availability, only 25-mg amounts of SRM 1650 were extracted and the samples had to be injected splitless to achieve the required sensitivity. Diesel particulate extracts contained a high amount of nonvolatile organic compounds, so the injection port liner had to be changed daily. Extracts from the diesel bus exhaust pipe soot were injected at a split ratio of 1:40 because larger (250 mg) samples were extracted and nitro-PAH concentrations in this soot sample were significantly higher than in the SRM sample. Certified standards of nitro-PAHs in methanol (NIST SRM 1587) were used for quantitative standards and to confirm the retention times of the individual nitro-PAHs. Each sample extract and quantitative standard was spiked with 90 ng of [$^2H_{12}$]chrysene as an internal standard, and all quantitations were based on the ratios of the individual peak areas to those of the internal standard.

RESULTS AND DISCUSSION

Extractions from spiked filters

As shown in Table II, 1-nitropyrene was quantitatively extracted in 30 min from spiked quartz filters with pure supercritical CO_2 at a pressure of 400 atm and a temperature of 40°C. In addition to demonstrating that 1-nitropyrene has sufficient solubility in CO_2 to be efficiently extracted, these results demonstrate that the chosen trapping conditions allowed recoveries better than 95% for 1-nitropyrene as well as for the more volatile compounds 1-nitronaphthalene and phenanthrene.

TABLE II

SFE RECOVERIES FROM SPIKED QUARTZ FIBER FILTERS WITH PURE CO_2

Compound	Recovery (%)	SD[a] (%)
Phenanthrene	97.4	4
1-Nitronaphthalene	95.4	2
1-Nitropyrene	98.9	2

[a] Standard deviations are based on 5 extractions.

GC-MS analysis of diesel exhaust particulate extracts

Extracts from diesel particulates contain such a broad variety of organic compounds that neither FID nor electron-capture detection were selective enough to analyze these extracts for nitro-PAHs without additional sample treatment. With GC–MS, the most intense peaks in the total ion current chromatogram of the unfractionated diesel exhaust particulate extracts were identified as high-molecular-mass (*ca.* C_{18} to C_{28}) alkanes. When the GC–MS is operated in the selected ion monitoring (SIM) mode, the selectivity was sufficient to quantitate the nitro-PAHs, the PAHs (except for those with *m/z*

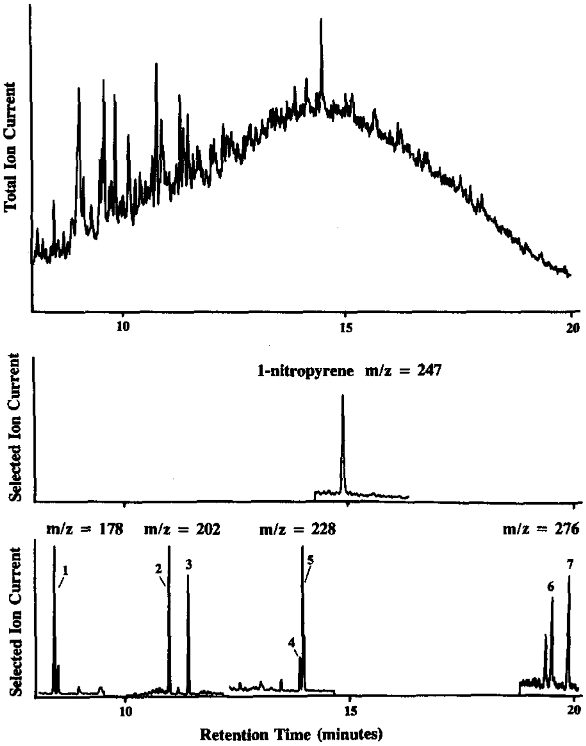

Fig. 2. Comparison of the total ion current chromatogram (scan range 50–350 amu) of an unfractionated $CHClF_2$ extract of diesel exhaust particulate with the selected ion current chromatograms for 1-nitropyrene and phenanthrene (peak 1), fluoranthene (peak 2), pyrene (peak 3), benz[*a*]anthracene (peak 4), chrysene (peak 5), indeno[1,2,3-*cd*]pyrene (peak 6), and benzo[*ghi*]perylene (peak 7).

252 because of interfering ions), and the internal standard (deuterated chrysene) as shown in Fig. 2 by a comparison between a total ion and a selected ion chromatogram of an unfractionated extract. With the extraction of a 25-mg sample, concentration of the extract to 1 ml, and a splitless injection of 1 µl, the method detection limit was *ca.* 1 ng of 1-nitropyrene per mg of soot using SIM.

Extraction kinetics of 1-nitropyrene from bus soot

To determine a reasonable extraction time, preliminary extractions of the bus soot with CO_2–methanol (90:10) were performed and fractions were collected after 5, 10, 15, 25, 35, 45, 60, 90 and 120 min. As shown in Fig. 3, more than 95% of the extractable 1-nitropyrene was extracted after 45 min. Based on these results, the extraction time for all subsequent extractions was set to 45 min.

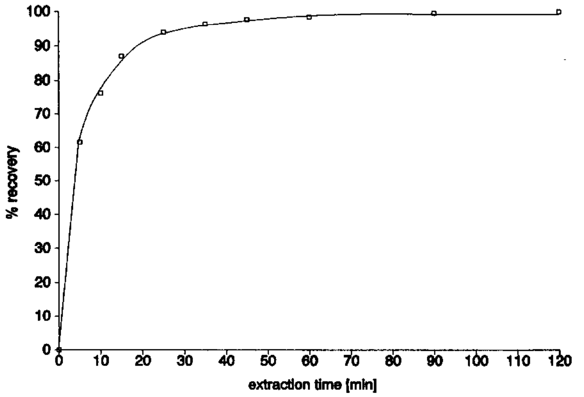

Fig. 3. SFE extraction kinetics of 1-nitropyrene from 250 mg of diesel bus exhaust pipe soot using CO_2 modified with 10% methanol. Fractions were collected after 5, 10, 15, 45, 60, 90, and 120 min of extraction and analyzed as described in the text. The extraction yield was normalized to the final value obtained after 120 min of extraction.

TABLE III

EXTRACTION EFFICIENCIES OF 1-NITROPYRENE FROM NIST DIESEL EXHAUST PARTICULATES USING VARIOUS SUPERCRITICAL FLUIDS

Supercritical fluid	Concentration (µg/g)	Recovery[a] (%)	Average recovery[a] ± S.D. (%)
CO_2	3.3	18	25 ± 9
	3.3	17	
	6.2	32	
	6.3	33	
CO_2–methanol (90:10), set 1	5.8	31	28 ± 3
	5.4	28	
	4.6	24	
	5.9	31	
CO_2–methanol (90:10), set 2	5.1	27	32 ± 8
	5.5	29	
	5.4	28	
	8.3	44	
$CHClF_2$	22.0	116	117 ± 7
	20.9	110	
	23.6	124	
CO_2–$CHClF_2$ (90:10)	7.2	38	43 ± 7
	7.8	41	
	7.2	38	
	10.1	53	
CO_2–toluene (90:10)	19.8	104	97 ± 8
	18.4	97	
	16.9	89	

[a] Recoveries compared to 19 ± 2 µg/g 1-nitropyrene based on Soxhlet extractions as certified by NIST.

Extractions from Standard Reference Material 1650

The first extraction of the diesel exhaust particulates (SRM 1650) was performed with the most common supercritical fluid, CO_2. After 45 min at 400 atm and 40°C, only 25% of the 1-nitropyrene reported by NIST was extracted (Table III). These results indicate that solubility is not the limiting factor for supercritical extraction of nitro-PAHs from exhaust particulate samples, since 1-nitropyrene could easily be extracted from spiked filters (Table II). Extraction with CO_2 containing 10% methanol modifier did not increase the recovery considerably, and only *ca.* 30% of the 1-nitropyrene was extracted. Since methanol modifier has previously been reported to increase the recoveries of moderately polar analytes, these results were somewhat surprising. To verify these low recoveries, a second set of samples were extracted under identical conditions and yielded similar recoveries (Table III).

In contrast to the extraction with pure CO_2 and methanol-modified CO_2, SFE with pure $CHClF_2$ yielded excellent recoveries (117%) *versus* the Soxhlet extraction value (19 ± 2 μg/g) certified by NIST, possibly because of its high dipole moment (1.4 Debye). Since the capillary restrictors sometimes broke when using pure $CHClF_2$ as the extraction fluid (and because of possible environmental objections to using freons as extraction fluids), $CHClF_2$ was also used as a modifier in CO_2 in the hopes of maintaining the high extraction efficiencies while reducing the total amount of $CHClF_2$ used. With CO_2–$CHClF_2$ (90:10), extraction efficiencies were only slightly better than the CO_2 and CO_2–methanol (90:10) results, *i.e.*, only 43% of the 1-nitropyrene was extracted.

Because of the potential of toluene to break π-bonding interactions between the diesel exhaust particulate matrix and the nitro-PAHs, toluene-modified CO_2 was also tested as an extraction fluid. As shown in Table III, CO_2–toluene (90:10) yielded good recoveries (97%). The ability of toluene modifier to extract nitro-PAHs from diesel exhaust particulate is likely a result of its aromatic character rather than its low dipole moment of only 0.4 Debye.

Extractions from the bus exhaust pipe soot

1-Nitropyrene is the only nitro-PAH in the SRM sample that is reported with a certified value. Other nitro-PAHs are present in considerably lower concentrations, but, because of limited sample availability, quantitations of additional nitro-PAHs could not be performed. Much larger quantities of the bus soot were available, which allowed additional nitro-PAHs to be quantitated from the extraction of 250-mg samples. The extractions were performed with CO_2–$CHClF_2$ (90:10) and CO_2–toluene (90:10) as supercritical fluids, which gave the best recoveries from the SRM sample (with the exception of pure $CHClF_2$).

As shown in Table IV, several additional nitro-PAHs besides 1-nitropyrene were extracted from diesel soot using either $CHClF_2$ or toluene as modifiers in CO_2. A comparison of the diesel exhaust particulate extracts (Table III) and the diesel soot (Table IV) shows two interesting differences. First,

TABLE IV

NITRO-PAHs EXTRACTED FROM BUS SOOT

Compounds	Extracted with CO_2–$CHClF_2$ (90:10)		Extracted with CO_2–toluene (90:10)	
	μg/g	SD[a] (μg/g)	μg/g	SD[a] (μg/g)
2-Nitrofluorene	27	7	28	2
9-Nitroanthracene	63	12	62	7
3-Nitrofluoranthene	10	1	11	2
1-Nitropyrene	450	70	540	50
7-Nitrobenz[*a*]anthracene	10	2	12	1
6-Nitrochrysene	4	2	4	1

[a] Standard deviations based on 4 extractions.

the bus soot contains much higher concentrations of 1-nitropyrene. Additionally, the amount of each nitro-PAH extracted from the bus soot using CO_2–$CHClF_2$ (90:10), was nearly identical to that extracted using CO_2–toluene (90–10). While CO_2–$CHClF_2$ (90:10) only extracted 44% as much of the 1-nitropyrene from the diesel exhaust particulate sample (compared to the CO_2–toluene (90:10) extraction, Table III), the extraction of the bus soot sample with CO_2–$CHClF_2$ (90:10) yielded 83% as much 1-nitropyrene as the CO_2–toluene extraction (Table IV).

The large differences in 1-nitropyrene concentrations found in the exhaust particulates and the exhaust pipe soot samples might be explained by the differences in the sources and collection of the two samples. The NIST diesel exhaust particulate sample was collected from the exhaust stream in the heat exchangers of a dilution tube facility, while the diesel soot sample was collected directly from the exhaust pipe of a bus. If it is assumed that the nitro-PAHs were formed at the same time when the particle growth took place, nitro-PAHs would be found inside the NIST-particles as well as on the surface. For quantitative extractions, the supercritical fluid must extract the analyte not only from the surface, but from the inside of a particle as well. Based on the recoveries shown in Table III, this was possible with pure $CHClF_2$ or CO_2–toluene modifier (90:10), whereas $CHClF_2$-modifier was too weak as a solvent. Since all of the fluids tested in Table II [except pure $CHClF_2$ and CO_2–toluene (90:10)] yielded similar amounts of extracted 1-nitropyrene from the NIST diesel exhaust particulate sample, it appears that *ca.* 30% of the 1-nitropyrene was located in "easier" (*e.g.*, surface) sites for extraction. In contrast, the bus soot was present in the exhaust pipe for an extended period of time. During operation of the bus, nitro-PAHs from the exhaust stream could have been adsorbed on the surface of the soot, or it is also possible that the soot acted as a catalyst for the formation of additional nitro-PAHs from PAHs and nitrogen oxides. As a result, the bus soot is more likely to contain high concentrations of nitro-PAHs adsorbed on the surface than the NIST exhaust particulate sample and, therefore, the bus soot has a higher proportion of the nitro-PAHs which are easier to extract than the NIST exhaust particulate sample. While no additional direct evidence exists for this explanation, the results shown in Tables III and IV clearly indicate that even relatively small changes in sample matrix can have significant effects on the extraction efficiencies obtained when the extraction conditions are not sufficiently strong.

Recoveries of PAHs from NIST diesel exhaust particulate

Although the major emphasis of this paper was to develop SFE conditions for the quantitative recovery of nitro-PAHs, the NIST diesel exhaust particulate extracts generated using pure $CHClF_2$,

TABLE V

RECOVERIES OF PAHs FROM NIST DIESEL EXHAUST PARTICULATE

	NIST (μg/g)[b]	% Recovery *versus* NIST Values[a]		
		$CHClF_2$	CO_2–$CHClF_2$	CO_2–toluene
Phenanthrene	71	82 ± 12	61 ± 12	68 ± 4
Fluoranthene	51 ± 4	92 ± 11	66 ± 13	81 ± 3
Pyrene	48 ± 4	89 ± 9	61 ± 13	79 ± 2
Benz[*a*]anthracene	6.5 ± 1.1	106 ± 8	38 ± 9	97 ± 2
Chrysene	22	115 ± 11	41 ± 10	101 ± 1
Indeno[1,2,3-*cd*]pyrene	2.3	105 ± 27	7 ± 5	40 ± 9
Benzo[*ghi*]perylene	2.4 ± 0.6	104 ± 16	5 ± 4	70 ± 9

[a] Percent recoveries *versus* the NIST values ± one standard deviation unit based on triplicate extractions for the $CHClF_2$ and CO_2–toluene (90:10), and quadruplicate extractions for the CO_2–$CHClF_2$ (90:10).

[b] Concentrations reported by NIST based on Soxhlet extraction. The values for phenanthrene, chrysene, and indeno[1,2,3-*cd*]pyrene are given by NIST as informational values without standard deviations. All other values are certified by NIST.

CO_2–$CHClF_2$ (90:10), and CO_2–toluene (90:10) were also analyzed for PAHs to determine if similar trends in extraction efficiencies were obtained. As shown in Table V, the PAH recoveries were similar to those shown in Table III for the 1-nitropyrene from the same sample. Extraction with pure $CHClF_2$ yielded the best recoveries of the PAHs compared to the Soxhlet extraction values reported by NIST, while toluene-modified CO_2 also yielded reasonably good recoveries. As was the case for the 1-nitropyrene, the use of $CHClF_2$ as a modifier in CO_2 did not yield as high recoveries of the PAHs as either pure $CHClF_2$ or toluene-modified CO_2.

CONCLUSIONS

SFE with pure $CHClF_2$ yielded the highest recoveries of both nitro-PAHs and PAHs from diesel exhaust particulates, although CO_2 modified with toluene also yielded good extraction efficiencies. Even though extraction with pure CO_2 yielded quantitative recoveries of nitro-PAHs from spiked air sampling filters, only 30% recoveries of 1-nitropyrene were achieved from diesel exhaust particulates. These results demonstrate that quantitative extraction of nitro-PAHs from diesel exhaust particulates requires extraction fluids that can overcome matrix–analyte interactions as well as simply solvate the analyte.

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