

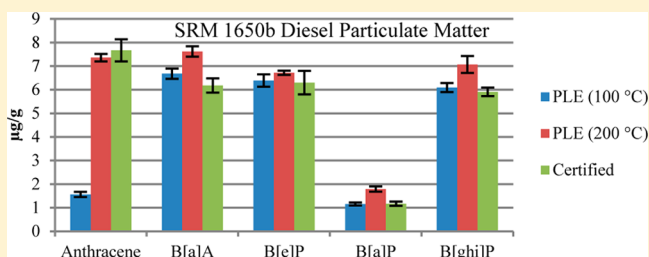
# Pressurized Liquid Extraction of Diesel and Air Particulate Standard Reference Materials: Effect of Extraction Temperature and Pressure

Michele M. Schantz,\* Elizabeth McGaw,<sup>†</sup> and Stephen A. Wise

Analytical Chemistry Division, National Institute of Standards and Technology (NIST), 100 Bureau Drive, Gaithersburg, Maryland 20899, United States

## Supporting Information

**ABSTRACT:** Four particulate matter Standard Reference Materials (SRMs) available from the National Institute of Standards and Technology (NIST) were used to evaluate the effect of solvent, number of static cycles and static times, pressure, and temperature when using pressurized liquid extraction (PLE) for the extraction of polycyclic aromatic hydrocarbons (PAHs) and nitrated-PAHs. The four materials used in the study were SRM 1648a Urban Particulate Matter, SRM 1649b Urban Dust, SRM 1650b Diesel Particulate Matter, and SRM 2975 Diesel Particulate Matter (Industrial Forklift). The results from the study indicate that the choice of solvent, dichloromethane compared to toluene and toluene/methanol mixtures, had little effect on the extraction efficiency. With three to five extraction cycles, increasing the extraction time for each cycle from 5 to 30 min had no significant effect on the extraction efficiency. The differences in extraction efficiency were not significant (with over 95% of the differences being <10%) when the pressure was increased from 13.8 to 20.7 MPa. The largest increase in extraction efficiency occurred for selected PAHs when the temperature of extraction was increased from 100 to 200 °C. At 200 °C naphthalene, biphenyl, fluorene, dibenzothiophene, and anthracene show substantially higher mass fractions (>30%) than when extracted at 100 °C in all the SRMs studied. For SRM 2975, large increases (>100%) are also observed for some other PAHs including benz[a]anthracene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, benzo[ghi]perylene, and benzo[b]chrysene when extracted at the higher temperatures; however, similar trends were not observed for the other diesel particulate sample, SRM 1650b. The results are discussed in relation to the use of the SRMs for evaluating analytical methods.



Analytical chemists, toxicologists, atmospheric chemists, and combustion engineers have extensively studied diesel particulate matter and airborne particulate matter particularly to assess the health risks to humans exposed to atmospheric emissions.<sup>1–3</sup> Diesel particulate matter forms during incomplete combustion of fuels and contains potentially high levels of polycyclic aromatic hydrocarbons (PAHs) and nitrated-PAHs,<sup>4–10</sup> along with a large number of other organic and inorganic components.<sup>11</sup> Diesel particulate matter is one of many constituents in airborne particulate matter and in some locations, particularly urban areas, may be the primary component.<sup>12</sup>

The National Institute of Standards and Technology (NIST) has two urban particulate matter Standard Reference Materials (SRMs) available, SRM 1648a Urban Particulate Matter<sup>13</sup> and SRM 1649b Urban Dust,<sup>14,15</sup> and two diesel particulate matter SRMs, SRM 1650b Diesel Particulate Matter<sup>4</sup> and SRM 2975 Diesel Particulate Matter (Industrial Forklift).<sup>5</sup> The three materials with either an “a” or “b” added to the SRM number had been released previously as SRM 1648, SRM 1649, SRM 1649a, SRM 1650, or SRM 1650a. Because sufficient bulk material remained for each of the materials, the current materials were prepared from the same bulk collections as the previous materials; hence, in some discussions the previous releases are mentioned. These SRMs have been characterized for PAHs and nitrated-PAHs as well as trace elements and/or additional trace

organic contaminants in the case of the two urban particulate matter materials.<sup>4,5,14,15</sup> For these materials, the values on the Certificate of Analysis for the PAHs and nitrated-PAHs (note that there are only trace element values on the Certificate of Analysis for SRM 1648a) are based on the use of Soxhlet extraction and/or pressurized liquid extraction (PLE) using dichloromethane, toluene, or toluene–methanol (1:1, v:v) as the extraction solvents.

One use of Certified Reference Materials (of which SRMs are a subset produced by the NIST) is to evaluate new analytical methods. As pointed out by Schantz,<sup>16</sup> investigators should use natural matrix materials to evaluate extraction methods because spiked materials may not adequately mimic a “real world” sample during the analytical procedure. During the original evaluation of PLE for its effectiveness in the determination of PAHs as part of the certification of particulate matter SRMs,<sup>17</sup> a sediment material, SRM 1944 New York/New Jersey Waterway Sediment, was used to evaluate the effect of the variables used for PLE, particularly temperature and pressure. Varying the pressure between 12.4 and 15.2 MPa and varying the temperature

Received: June 1, 2012

Accepted: September 11, 2012

Published: September 11, 2012

Table 1. PFE Conditions Used for Each SRM

method no.	SRM	$n^a$	solvent	preheat (min)	heat (min)	temperature (°C)	pressure (MPa)	no. static cycles	time (min) for each static cycle
1	1648a	3	dichloromethane	5	5	100	13.8	3	5
2	1648a	3	dichloromethane	5	9	200	13.8	3	5
3	1649b	3	dichloromethane	5	5	100	13.8	3	5
4	1649b	3	dichloromethane	5	9	200	13.8	3	5
5	1649b	3	toluene	1	5	100	13.8	3	30
6	1649b	3	toluene	1	7	150	13.8	3	30
7	1649b	3	toluene	1	9	200	13.8	3	30
8	1649b	3	toluene	1	9	200	20.7	3	30
9	1650b	3	toluene	1	5	100	13.8	3	30
10	1650b	3	toluene	1	5	100	20.7	3	30
11	1650b	3	toluene	1	9	200	13.8	3	30
12	1650b	3	toluene	1	9	200	20.7	3	30
13	2975	3	toluene	1	5	100	13.8	3	30
14	2975	3	toluene	1	5	100	20.7	3	30
15	2975	3	toluene	1	9	200	13.8	3	30
16	2975	3	toluene	1	9	200	20.7	3	30
17	1650b	3	toluene–methanol (9:1)	1	9	200	20.7	5	30
18	2975	3	toluene–methanol (9:1)	1	9	200	20.7	5	30

<sup>a</sup> $n$  = number of samples analyzed.

between 100 and 150 °C had very little effect on the extraction efficiency for PAHs in the sediment. On the basis of these data, 100 °C and 13.8 MPa were chosen as the PLE conditions used to extract PAHs from the air particulate and diesel particulate materials. The conclusion from the study<sup>17</sup> was that PLE at those conditions showed extraction efficiency similar to Soxhlet extraction for most PAHs and slightly enhanced extraction efficiency for the higher molecular mass PAHs (>252 Da) in the diesel particulate matter.

One or more of the air particulate and diesel particulate SRMs mentioned above have been used by a number of researchers to evaluate different extraction methods, including ultrasound-assisted extraction,<sup>18–20</sup> focused microwave-assisted extraction (MAE),<sup>21,22</sup> supercritical fluid extraction (SFE),<sup>23</sup> subcritical water extraction (SWE),<sup>24</sup> direct sample introduction thermal desorption (TD) gas chromatography/mass spectrometry (GC/MS),<sup>25</sup> stir bar sorptive extraction,<sup>26</sup> and additional studies using PLE.<sup>27–32</sup> Ultrasound-assisted extraction<sup>18–20</sup> resulted in values that were in reasonable agreement with the certified values for SRM 1649a, SRM 1650, and SRM 2975. The recovery of PAHs from the urban dust SRM 1649a using focused MAE<sup>21,22</sup> was similar to that from Soxhlet extraction. SFE<sup>23</sup> was evaluated for two sediment materials as well as SRM 1649a and SRM 1650. Lower recoveries than Soxhlet extraction were noted using SFE for the molecular mass of the PAHs  $\geq 228$  Da. It was noted that as the temperature of the extraction was increased from 60 to 200 °C, there was an enhancement of the amount of PAHs extracted from SRM 1649a and SRM 1650, particularly for anthracene. Because anthracene was the only PAH with a completely linear structure investigated, Benner<sup>23</sup> postulated that there was a greater interaction between the linear structure of anthracene and the diesel particles slowing desorption from the matrix.

SWE<sup>24</sup> worked well for the urban dust matrix; however, when applied to the diesel particulate materials, recoveries of only a few percent were obtained for the PAHs. A TD method<sup>25</sup> gave values similar to the certified values for PAHs in SRM 1649a. The stir bar sorptive extraction<sup>26</sup> recoveries (compared to the certified values) ranged from 61% for benzo[ghi]perylene to 125% for benzo[b]fluoranthene in SRM 1649a. Jonker and Koelmans<sup>10</sup>

investigated the choice of extraction solvent for the Soxhlet extraction of a wide range of soot and sediment particles concluding that the overall best solvent for Soxhlet extraction of these materials was toluene–methanol (1:6, v:v) although the solvent choice was matrix- and compound-dependent.

PLE was investigated for the extraction of PAHs and nitrated-PAHs from diesel particulate matter SRM 1650 by Turri-Baldassarri et al.<sup>27</sup> Using PLE with toluene as the extraction solvent at 195 °C and 15.2 MPa (2200 psi) with two 20 min static cycles, the authors<sup>27</sup> noted higher values in SRM 1650 compared to the certified values for several higher molecular mass PAHs as well as 1-nitropyrene. Bergvall and Westerholm<sup>29</sup> found that increasing the number of extraction cycles and static extraction times increased extraction efficiencies for SRM 1649a, SRM 1650b, and SRM 2975. The optimal PLE conditions for their study<sup>29</sup> were toluene as the extraction solvent at 200 °C and 20.7 MPa with five 30 min static cycles for SRMs 1650 and 2975 and four 5 min static cycles for SRM 1649. Using these conditions, they reported higher mass fraction values compared to the certified values for several of the PAHs of molecular mass 252 and higher. Masala et al.<sup>30</sup> did additional studies using SRM 2975 and found optimal conditions to be a toluene–methanol mixture (9:1, v:v) at 200 °C and 20.7 MPa with five 30 min static cycles.

Because of several reports of higher extraction recoveries for selected PAHs in SRM 1649a, SRM 1650b, and SRM 2975 using PLE,<sup>4,17,27,29,30</sup> the current study was undertaken as a more extensive investigation of the different PLE parameters. The potential for obtaining higher extraction efficiencies at higher temperatures and pressures has implications for assigning certified mass fraction values to these particulate matrix SRMs. This study was designed to investigate the effect of solvent, number of static cycles and static times, pressure, and temperature when using PLE for the extraction of PAHs and nitrated-PAHs from two urban particulate matter SRMs (SRM 1648a and SRM 1649b) and two diesel particulate matter SRMs (SRM 1650b and SRM 2975).

**Table 2. Mass Fractions (ng/g) of Selected PAHs in SRM 1649b Urban Dust (Organics) as a Function of PLE Temperature and Pressure**

PLE conditions	this study	this study	this study	this study	% difference between ng/g	ref29 <sup>a</sup>	certificate of analysis <sup>14</sup>		
	100 °C/ 2000 psi (13.8 MPa)	150 °C/ 2000 psi (13.8 MPa)	200 °C/ 2000 psi (13.8 MPa)	200 °C/ 3000 psi (20.7 MPa)		200 °C/ 3000 psi (20.7 MPa)	<b>Certified; Reference</b>	ref (100 °C/ 13.8 MPa)	ref (200 °C/ 13.8 MPa)
	method 5	method 6	method 7	method 8		determined			
	mean (std dev) <i>n</i> = 3	mean (std dev) <i>n</i> = 3	mean (std dev) <i>n</i> = 3	mean (std dev) <i>n</i> = 3		at 200 and 100 °C (2000 psi)			
naphthalene	1052 (52)	1063 (45)	2776 (44)	2477 (16)	160%			1120 ± 420	2890 ± 40
1-methylnaphthalene	891 (31)	881 (28)	898 (60)	899 (26)	46%				
2-methylnaphthalene	942 (44)	941 (32)	1376 (141)	1336 (124)	0.8%				
biphenyl	195 (9)	312 (12)	686 (72)	711 (62)	250%			198 ± 27	640 ± 40
acenaphthene	174 (5)	197 (10)	237 (22)	256 (10)	36%		192 ± 36		
acenaphthylene	201 (5)	192 (9)	252 (22)	275 (18)	25%		184 ± 26		
fluorene	255 (6)	308 (24)	426 (20)	512 (9)	67%			222 ± 16	303 ± 3
dibenzothiophene	192 (1)	412 (22)	628 (25)	572 (27)	230%			183 ± 10	560 ± 10
phenanthrene	4030 (210)	4100 (160)	4328 (24)	4354 (41)	7.4%		3941 ± 47		
anthracene	390 (33)	593 (25)	989 (47)	965 (8)	150%			403 ± 2	920 ± 40
1-methylphenanthrene	426 (12)	566 (35)	536 (22)	549 (28)	26%		346 ± 63		
2-methylphenanthrene	802 (54)	849 (41)	986 (53)	920 (73)	23%		790 ± 110		
3-methylphenanthrene	535 (15)	631 (25)	627 (33)	640 (45)	17%			508 ± 55	650 ± 70
9-methylphenanthrene	369 (26)	405 (15)	385 (34)	373 (37)	4.5%		351 ± 97		
1,7- dimethylphenanthrene	199 (4)	228 (10)	357 (50)	331 (47)	79%		225 ± 18		
fluoranthene	6220 (130)	6290 (160)	6505 (27)	6571 (79)	4.6%		6140 ± 120		
pyrene	5019 (25)	5090 (200)	5029 (28)	4969 (48)	0.2%		4784 ± 29		
3-methylfluoranthene	321 (8)	322 (11)	309 (22)	286 (18)	−3.7%		326 ± 44		
1-methylfluoranthene	108 (1)	119 (9)	133 (5)	115 (9)	23%		132 ± 17		
1-methylpyrene	357 (1)	425 (12)	374 (26)	343 (27)	4.7%		347 ± 41		
retene	230 (92)	233 (8)	273 (40)	239 (3)	19%		251 ± 38		
benzo[ghi]fluoranthene	919 (15)	924 (25)	954 (44)	945 (31)	3.8%		885 ± 15		
benzo[c]phenanthrene	437 (5)	491 (7)	452 (30)	433 (19)	3.4%		449 ± 14		
benz[a]anthracene	2140 (52)	2180 (100)	2391 (26)	2268 (20)	12%		2092 ± 48		
chrysene	2920 (55)	3080 (160)	3099 (49)	2988 (38)	6.1%		3008 ± 44		
triphenylene	1304 (10)	1300 (100)	1344 (52)	1327 (39)	3.1%		1244 ± 52		
3-methylchrysene	251 (21)	226 (10)	263 (20)	279 (14)	5.0%		229 ± 3		
6-methylchrysene	157 (6)	165 (5)	162 (8)	159 (2)	3.0%		153 ± 7		
benzo[b+j]fluoranthene	7650 (160)	7500 (350)	7640 (130)	7760 (220)	−0.1%	<i>b</i>	<i>c</i>		
benzo[k]fluoranthene	1847 (49)	1990 (110)	1860 (160)	1870 (100)	0.5%	2960 (398)	1748 ± 83		
benzo[a]fluoranthene	395 (6)	386 (25)	499(19)	495 (18)	26%			372 ± 32	510 ± 50
benzo[e]pyrene	3130 (120)	3250 (110)	3040 (210)	2898 (99)	−2.9%	4520 (509)	2970 ± 43		
benzo[a]pyrene	2510 (130)	2770 (200)	3100 (190)	2970 (110)	24%	3650 (778)	2470 ± 170		
perylene	637 (20)	606 (34)	607 (25)	624 (28)	−4.7%	900 (206)	606 ± 13		
benzo[ghi]perylene	3890 (160)	4020 (110)	4299 (51)	4220 (41)	10%	6070 (539)	3937 ± 52		
indeno[1,2,3- <i>cd</i> ]pyrene	2616 (22)	2622 (98)	2752 (45)	2678 (28)	5.2%	4390 (306)	2960 ± 170		
dibenz[ <i>a,j</i> ]anthracene	307 (15)	318 (26)	299 (26)	306 (21)	−2.7%		321 ± 44		
dibenz[ <i>a,c+a,h</i> ] anthracene	461 (44)	488 (21)	581 (13)	573 (13)	26%	<i>d</i>	<i>e</i>		
benzo[ <i>b</i> ]chrysene	343 (12)	320 (12)	451 (27)	414 (23)	32%		332 ± 46		
picene	380 (15)	406 (14)	371 (35)	380 (2)	−2.3%	736 (142)	390 ± 28		
corenene	2720 (100)	3010 (100)	3370 (280)	3290 (180)	24%	10500 (907)	2830 ± 460		
dibenzo[ <i>a,e</i> ]pyrene	655 (45)	638 (24)	654 (16)	622 (40)	−0.1%	563 (97)	538 ± 24		
dibenzo[ <i>b,k</i> ] fluoranthene	789 (85)	801 (56)	798 (58)	782 (36)	1.1%		655 ± 35		

<sup>a</sup>The sample used in ref 29 is SRM 1649a. SRM 1649b is from the same bulk material as SRM 1649a, but a smaller particle size was used (123 μm for SRM 1649a vs 63 μm for SRM 1649b). <sup>b</sup>Reference 29 reported a value for benzo[b]fluoranthene of 7980 ng/g with a standard deviation of 659 ng/g. <sup>c</sup>The certified values for benzo[b]fluoranthene and benzo[j]fluoranthene are (5990 ± 200) ng/g and (1731 ± 83) ng/g, respectively. <sup>d</sup>Reference 29 reported a value for dibenz[a,h]anthracene of 567 ng/g with a standard deviation of 55 ng/g. <sup>e</sup>The certified values for dibenz[a,c]anthracene and dibenz[a,h]anthracene are (212 ± 17) ng/g and (290 ± 4) ng/g, respectively.

## EXPERIMENTAL SECTION

SRM 1648a was collected in the St. Louis, MO area in the mid-1970s,<sup>13</sup> while SRM 1649b was collected in the Washington, DC area during the late 1970s.<sup>14</sup> SRM 1650b was collected from the

heat exchangers of a dilution tube facility in which several direct injection four-cycle diesel engines were used,<sup>4</sup> and SRM 2975 was collected from a filtering system designed specifically for diesel-powered forklifts.<sup>5</sup>

The PLE conditions are summarized in Table 1. Additional experimental details related to the calibration, extraction, and analysis methods are summarized in the Supporting Information.

## RESULTS AND DISCUSSION

As stated in the introduction, a recommended use of natural matrix SRM is for the evaluation and comparison of new analytical methods. In the case of evaluating extraction efficiency, the air particulate and diesel particulate matter SRMs are excellent samples for evaluation and offer different and challenging matrixes for comparison. In this study, the mass fractions of PAHs and nitrated-PAHs determined in the various experiments with different extraction parameters (see Table 1) were compared to each other and to the certified and reference values on the current Certificate of Analysis (COA) for each of the SRMs.

On the basis of the PLE studies of Schantz et al.<sup>17</sup> showing that PLE was more effective than Soxhlet extraction in removing PAHs of molecular mass  $\geq 252$  Da from the diesel particulate matter (SRM 1650a), only PLE with toluene was used for the assignment of certified values in SRM 1650b. Results were obtained using PLE at 100 or 200 °C, both at 13.8 MPa, and for the majority of the PAHs, the mass fraction results at the two temperatures were similar. However, significant increases (factors of 2–10) in mass fraction were noted for selected PAHs (i.e., biphenyl, acenaphthylene, fluorene, anthracene, 2-methylanthracene, and dibenzothiophene), and different reference values are indicated on the COA for SRM 1650b for the two extraction temperatures for these particular PAHs.<sup>4</sup> With the reports of Turrio-Baldassarri et al.,<sup>27</sup> Bergvall and Westerholm,<sup>29</sup> and Masala et al.<sup>30</sup> of higher recoveries using higher temperatures and pressures for extraction of the air and diesel particulate matter SRMs, more extensive investigations were warranted.

**Effect of Solvent and Extraction Cycles.** The user-controlled parameters in PLE include choice of solvent, the number of static cycles and the time for each static cycle, the pressure limit of extraction, and the temperature of extraction.<sup>16,17</sup> The parameters used in this study for each material are summarized in Table 1. Note that the heating time is set by the instrument depending on the temperature being used for extraction (in Table 1, for example, 9 min heating time for an oven set at 200 °C). The effect of changing one or more of these parameters has been examined in many of the studies mentioned above<sup>17,27–31</sup> as well as other studies for other applications.<sup>16</sup> Starting with the choice of extraction solvent, two criteria for solvent selection were identified by Jonker and Koelmans<sup>10</sup> for Soxhlet extraction, and these criteria are also applicable for PLE: (1) aromatic solvents may displace the PAHs from the adsorption sites more effectively than aliphatic solvents, and (2) a nonpolar solvent combined with a polar solvent may be more effective than either solvent alone in removing the PAHs. In an earlier study, Schantz et al.<sup>17</sup> did not observe a significant difference among the PAH mass fraction values determined for the diesel particulate materials, SRM 1650 and SRM 2975, using PLE with dichloromethane, toluene, or a toluene–methanol (1:1, v:v) mixture or among the PAH mass fraction values determined for SRM 1649a using PLE with dichloromethane, acetonitrile, or a hexane–acetone mixture (1:1, v:v). Therefore, in the current study, only two solvents, toluene and dichloromethane, were compared for one of the air particulate materials, SRM 1649b (for conditions see methods 3–8 in Table 1). As in the previous study, no significant differences in the PAH or nitrated-PAH mass fractions determined were noted between the

two solvents when all other parameters remained the same (results not shown). On the basis of the work of Masala et al.,<sup>30</sup> a toluene–methanol mixture (9:1, v:v) was also investigated for the diesel particulate materials (methods 17 and 18 in Table 1) with no significant differences noted in the PAH mass fractions determined (Tables S-1 and S-2 in the Supporting Information for SRM 1650b and SRM 2975, respectively).

Previous work with the diesel particulate SRMs by Schantz et al.<sup>17</sup> showed that using more than three static cycles did not increase the amount of PAHs extracted. To confirm that observation with the solvent mixture toluene–methanol (9:1, v:v) found to be optimum by Masala et al.<sup>30</sup> for the diesel particulate SRMs, five static cycles at 30 min each were investigated with the results shown in Tables S-1 and S-2 in the Supporting Information for SRM 1650b and SRM 2975, respectively. Since the results were comparable (with the standard deviations of the measurements) to those obtained using three static cycles, three static cycles were used for the majority of the extractions in the current study with a variation of the static time between 5 and 30 min for SRM 1649b (methods 3–8 in Table 1). As with the solvent selection, no significant differences in the PAH or nitrated-PAH mass fractions determined were observed by increasing the static time from 5 to 30 min (results not shown). A 30 min static time, however, was used for the investigation of the pressure effects because Bergvall and Westerholm<sup>29</sup> had found 30 min to be the optimal static time for the higher temperatures and pressures.

**Effect of Pressure and Temperature on Extraction Efficiency.** The effects of temperature and pressure on the mass fractions of selected PAHs determined in SRM 1649b, SRM 1648a, SRM 1650b, and SRM 2975 are summarized in Tables 2–5, respectively. Similar comparisons are provided in Tables S-3–S-5 in the Supporting Information for nitrated-PAHs in SRM 1649b, SRM 1650b, and SRM 2975, respectively. Comparing the data for extraction at 13.8 MPa vs 20.7 MPa, the pressure used for extraction does not appear to affect the extraction efficiency for the PAHs or nitrated-PAHs (compare methods 7 and 8 in Table 2 and Table S-3 in the Supporting Information, methods 9 and 10 and 11 and 12 in Table 4 and Table S-4 in the Supporting Information, and methods 13 and 14 and 15 and 16 in Table 5 and Table S-5 in the Supporting Information). Comparing the percent differences in the mean mass fractions determined for the PAHs and nitrated-PAHs using 20.7 MPa vs 13.8 MPa with both at 200 °C, the largest difference noted is for acenaphthene in SRM 1650b where the mass fraction determined at 20.7 MPa is 24% lower than that determined at 13.8 MPa. There is no explanation for why this one compound decreased. When using the higher pressure for extraction, the largest increase in mass fraction is for fluorene in SRM 1649b (20%). The differences observed with the use of increased pressure for extraction are not significant (with over 95% of the differences being <10%), and there are no trends in the mass fraction changes with pressure.

The effects of changing the extraction temperature are more dramatic as shown in Tables 2–5 for PAHs in the four SRMs. (Results for SRM 1649b are also presented as bar graphs in Figures S-1–S-3 in the Supporting Information.) When comparing the extraction efficiencies at 200 °C vs 100 °C, both at 13.8 MPa, for the PAHs and nitrated-PAHs (see the percent difference column in Tables 2–5 and Tables S-3–S-5 in the Supporting Information), there are some general trends in the differences. For the majority of the PAHs determined, the differences in the mass fractions measured at the two temperatures were similar. However, for selected PAHs,



**Table 3. Mass Fractions (ng/g) of Selected PAHs in SRM 1648a Urban Particulate Matter as a Function of PLE Temperature and Pressure**

compound	this study	this study	% difference between ng/g determined at 200 and 100 °C (2000 psi)
	100 °C/ 2000 psi (13.8 MPa)	200 °C/ 2000 psi (13.8 MPa)	
	method 1 mean (std dev) n = 3	method 2 mean (std dev) n = 3	
naphthalene	1590 (20)	3220 (160)	103%
biphenyl	202 (7)	1560 (30)	674%
acenaphthene	292 (11)	347 (9)	19%
acenaphthylene	167 (8)	722 (27)	332%
fluorene	245 (10)	406 (22)	66%
dibenzothiophene	267 (10)	606 (10)	127%
phenanthrene	5130 (270)	5040 (80)	−2%
anthracene	460 (7)	1240 (80)	169%
1-methylphenanthrene	512 (14)	2470 (210)	382%
2-methylphenanthrene	1020 (40)	1110 (80)	9%
3-methylphenanthrene	659 (25)	686 (24)	4%
9-methylphenanthrene	530 (18)	572 (5)	8%
1,7-dimethylphenanthrene	232 (10)	257 (12)	11%
fluoranthene	8400 (510)	8030 (70)	−4%
pyrene	5990 (350)	5860 (100)	−2%
3-methylfluoranthene	315 (24)	305 (25)	−3%
1-methylfluoranthene	244 (12)	268 (10)	10%
1-methylpyrene	536 (22)	569 (27)	6%
4-methylpyrene	301 (11)	454 (30)	51%
retene	737 (28)	923 (13)	25%
4H-cyclopenta[def]phenanthrene	308 (12)	362 (22)	18%
benzo[ghi]fluoranthene	1260 (70)	1130 (60)	−10%
benzo[c]phenanthrene	743 (28)	584 (27)	−21%
benz[a]anthracene	2610 (110)	2460 (60)	−6%
chrysene	6000 (210)	5410 (100)	−10%
triphenylene	1900 (70)	1490 (50)	−22%
benzo[b+j]fluoranthene	11320 (360)	9940 (170)	−12%
benzo[k]fluoranthene	2830 (80)	2530 (70)	−10%
benzo[a]fluoranthene	442 (21)	545 (20)	23%
benzo[e]pyrene	4720 (120)	4270 (100)	−9%
benzo[a]pyrene	2620 (50)	2500 (100)	−4%
perylene	720 (13)	660 (28)	−8%
benzo[ghi]perylene	5020 (180)	4730 (80)	−6%
indeno[1,2,3-cd]pyrene	4080 (140)	3910 (70)	−4%
dibenz[a,j]anthracene	386 (24)	374 (5)	−3%
dibenz[a,c+a,h]anthracene	817 (15)	819 (16)	0%
benzo[b]chrysene	369 (25)	486 (19)	32%
picene	608 (14)	612 (10)	1%
corenene	2390 (100)	2310 (90)	−3%
dibenzo[a,e]pyrene	672 (41)	689 (33)	3%
dibenzo[b,k]fluoranthene	909 (42)	1040 (4)	14%

significant differences were observed. At 200 °C naphthalene, biphenyl, fluorene, dibenzothiophene, and anthracene show substantially higher mass fractions (>30%) than when extracted at 100 °C in all the SRMs studied. For SRM 2975, large increases (>100%) are also observed for some other PAHs including benz[a]anthracene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, benzo[ghi]perylene, and benzo[b]chrysene when extracted at the higher temperatures (see Table 5).

However, the significant increases observed for SRM 2975 were not found for SRM 1650b, which supports previous work suggesting that organic compounds may be easier to extract from SRM 1650b compared to SRM 2975.<sup>12,33</sup>

When comparing the results at the three different temperatures (100 °C, 150 °C, and 200 °C for SRM 1649b only, see Table 2), a distinct trend of increasing mass fractions is observed for selected PAHs with each temperature (e.g., biphenyl, acenaphthene, fluorene, dibenzothiophene, anthracene, and coronene). However, for a number of the PAHs that exhibit substantial increases between 100 and 200 °C, the mass fraction increase comes only after 150 °C (e.g., naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, benz[a]anthracene, benzo[a]fluoranthene, benzo[b]chrysene, and benzo[a]pyrene) indicating that the threshold temperature for removal differs among the PAHs. For the nitrated-PAHs, the compound with the most substantial difference when extracted at the higher temperature is 9-nitroanthracene in SRMs 1649b, 1650b, and 2975 (>20%) with the difference for SRM 1649b at 550%. Several other nitrated-PAH showed differences of approximately 20% (5-nitroacenaphthene, 2-nitrofluoranthene, and 6-nitrochrysene).

The significant differences in extraction efficiency at the different temperatures may be due to several factors including the particulate matrix, how the compound is incorporated in the matrix, and the compound structure.<sup>34</sup> Braun et al.<sup>12</sup> used near-edge X-ray absorption fine structure (NEXAFS) spectroscopy to study SRM 1648, SRM 1650, and SRM 2975. The results from NEXAFS spectroscopy suggest that SRM 1650 is the more graphitic material with fewer but larger crystallites and hence less surface than SRM 2975 and that diesel particulate matter is not a major constituent of SRM 1648. Nguyen and Ball<sup>33</sup> noted that SRM 1650b and SRM 2975 have similar surface oxygen to carbon ratios but different percentages of extractable organic matter: SRM 1650b has 20.2% ± 0.4% (mass fraction)<sup>4</sup> and SRM 2975 has 2.7% ± 0.2% (mass fraction).<sup>5</sup> They obtained aqueous sorption isotherms for <sup>14</sup>C-labeled phenanthrene and 1,2,4-trichlorobenzene on the two diesel materials and concluded that for SRM 2975 adsorption was dominant while for SRM 1650b adsorption was dominant at low levels with absorption contributing at higher levels. The work of Nguyen and Ball<sup>33</sup> showed that surface chemistry and the organic phase content are important parameters for diesel particulate matter, and these parameters differ for the two diesel particulate SRMs. For these air and diesel particulate samples, there may also be a difference in the way that some of the PAHs are incorporated in the matrix thus influencing the ease of extraction under milder conditions. Jonker and Koelmans<sup>10</sup> concluded from their extraction study that a portion of the PAHs were sorbed to the planar surfaces with another fraction entrapped in the soot core thus making this fraction more difficult to extract. In this study, the largest increases in extraction efficiency at the higher temperature were found for PAHs with a substantial linear structure, such as naphthalene, anthracene (similar to the SFE study<sup>23</sup>), dibenzothiophene, and 9-nitroanthracene. The size (molecular mass) of the PAH does not appear to be the dominant factor, and planarity of the PAH may have an influence (e.g., biphenyl).

**Comparison of Results with SRM Certified, Reference, and Literature Values.** The results of this study were compared with the certified and reference values on the current Certificate of Analysis (COA) for SRM 1649b (Table 2), SRM 1650b (Table 4), and SRM 2975 (Table 5). For the current COA for SRM 1649b, the certified values for PAHs were determined

Table 4. Mass Fractions (ng/g) of Selected PAHs in SRM 1650b Diesel Particulate Matter as a Function of PLE Temperature and Pressure

PLE conditions	this study		this study		this study		% difference between ng/g at 200 and 100 °C (2000 psi) determined	ref 27 <sup>a</sup>		ref 29		certificate of analysis <sup>4</sup>	
	100 °C/2000 psi (13.8 MPa)	method 9 mean (std dev) n = 3	100 °C/3000 psi (20.7 MPa)	method 10 mean (std dev) n = 3	200 °C/2000 psi (13.8 MPa)	method 11 mean (std dev) n = 3		200 °C/3000 psi (20.7 MPa)	method 12 mean (std dev) n = 3	195 °C/2200 psi (15.2 MPa)	200 °C/3000 psi (20.7 MPa)	Certified; Reference	ref (100 °C/ 13.8 MPa)
naphthalene	4990 (410)		4720 (130)		7450 (280)		49%	7060 (400)				5070 ± 430	
1-methylnaphthalene	1600 (110)		1660 (100)		1910 (190)		20%	2063 (14)				1510 ± 120	
2-methylnaphthalene	3590 (130)		3460 (330)		4060 (110)		13%	4076 (91)				3050 ± 560	
biphenyl	987 (54)		997 (47)		3640 (150)		270%	3277 (88)					
acenaphthene	257 (19)		248 (21)		252 (22)		−1.8%	192 (19)				223 ± 24	3570 ± 370
acenaphthylene	379 (22)		369 (24)		1360 (110)		260%	1353 (54)				364 ± 29	1380 ± 120
fluorene	769 (34)		756 (51)		1323 (87)		72%	1265 (57)				765 ± 39	1260 ± 90
dibenzothiophene	9640 (510)		10200 (400)		21200 (1500)		120%	21600 (1100)				9180 ± 430	20500 ± 2200
phenanthrene	70500 (400)		72400 (300)		70500 (1300)		−0.1%	71090 (45)				69500 ± 1900	
anthracene	1560 (110)		1470 (130)		7360 (160)		370%	7470 (130)				7670 ± 470	
1-methylphenanthrene	30000 (570)		27600 (540)		31100 (450)		3.8%	32300 (1800)				28300 ± 1500	
2-methylphenanthrene	69500 (2500)		71900 (1600)		74300 (1300)		7.0%	71200 (5600)				70700 ± 2700	
3-methylphenanthrene	54000 (1000)		59100 (570)		61100 (900)		13%	58800 (4400)				55100 ± 1900	
9-methylphenanthrene	38700 (1300)		35300 (1000)		38500 (900)		−0.7%	36800 (3000)				35100 ± 1900	
1,7-dimethylphenanthrene	18000 (990)		16800 (580)		16500 (470)		−8.4%	16500 (1300)				17500 ± 1000	
fluoranthene	48980 (1000)		48400 (600)		50100 (1000)		2.4%	50200 (500)				47300 ± 800	
pyrene	44600 (1100)		44800 (1100)		45600 (500)		2.3%	45900 (660)				43400 ± 1600	
3-methylfluoranthene	6450 (260)		6300 (300)		6250 (140)		−3.1%	6570 (500)				6580 ± 210	
1-methylfluoranthene	3200 (130)		3230 (130)		3420 (60)		1.3%	3040 (120)				3090 ± 70	
1-methylpyrene	2046 (98)		1910 (110)		2230 (160)		9.1%	2050 (40)				2060 ± 270	
benzo[ghi]fluoranthene	11900 (570)		11700 (300)		11300 (260)		−5.1%	11800 (600)				10800 ± 1000	
benzo[c]phenanthrene	2960 (170)		2980 (220)		2840 (230)		−4.2%	2950 (260)				2510 ± 290	
benzo[a]anthracene	6680 (220)		6130 (160)		7620 (220)		14%	7870 (270)		7450 (400)		6180 ± 300	
chrysene	13130 (500)		13450 (450)		13590 (170)		3.5%	13760 (370)		16300 (80)		13300 ± 1100	
triphenylene	10200 (400)		9270 (360)		9820 (60)		−3.3%	10330 (340)				9170 ± 940	
3-methylchrysene	2330 (130)		2210 (110)		2120 (200)		−9.0%	2300 (200)				2100 ± 130	
6-methylchrysene	1540 (95)		1450 (110)		1610 (140)		4.6%	1530 (150)				1580 ± 30	
benzo[b+g]fluoranthene	9960 (180)		9670 (210)		9970 (320)		0.1%	10220 (210)		b			
benzo[k]fluoranthene	2100 (190)		2060 (130)		2190 (170)		4.4%	2220 (70)			b	2370 ± 210	
benzo[a]fluoranthene	371 (26)		413 (12)		427 (24)		15%	410 (21)				370 ± 29	
benzo[e]pyrene	6390 (260)		6280 (230)		6720 (90)		5.1%	6570 (510)				6300 ± 500	
benzo[a]pyrene	1160 (60)		1230 (90)		1790 (110)		55%	1680 (150)		8750 (970)	7760 (138)	1170 ± 90	
perylene	159 (11)		168 (16)		178 (13)		12%	169 (10)		2190 (29)	1950 (50)	165 ± 32	
benzo[ghi]perylene	6090 (190)		6110 (220)		7070 (360)		16%	7010 (120)		140 (40)	175 (4)	5910 ± 180	
indeno[1,2,3-cd]pyrene	4670 (170)		4460 (300)		4650 (260)		−0.5%	4590 (70)		8560 (1080)	7180 (66)	4440 ± 280	
dibenz[a,h]anthracene	347 (29)		398 (35)		439 (24)		27%	429 (31)		6830 (940)	6330 (248)	387 ± 51	

Table 4. continued

PLE conditions	this study		this study		this study		% difference between ng/g determined at 200 and 100 °C (2000 psi)	ref 27 <sup>a</sup>		ref 29		certificate of analysis <sup>d</sup>	
	100 °C/2000 psi (13.8 MPa)	method 9 mean (std dev) n = 3	100 °C/3000 psi (20.7 MPa)	method 10 mean (std dev) n = 3	200 °C/2000 psi (13.8 MPa)	method 11 mean (std dev) n = 3		195 °C/2200 psi (15.2 MPa)		200 °C/3000 psi (20.7 MPa)		ref (100 °C/13.8 MPa)	ref (200 °C/13.8 MPa)
dibenz[ <i>a,c</i> + <i>a,h</i> ]anthracene	761 (26)		792 (38)		813 (34)		6.8%						
benzo[ <i>b</i> ]chrysene	324 (15)		314 (21)		336 (30)		3.7%					290 ± 20	
picene	508 (45)		505 (29)		546 (40)		7.6%			750 (20)		499 ± 61	
corenene	9720 (260)		9240 (270)		9260 (230)		−4.7%			6470 (171)		9600 ± 1000	
dibenzo[ <i>a,e</i> ]pyrene	1170 (100)		1110 (30)		1160 (80)		−0.3%			487 (75)		1140 ± 120	
dibenzo[ <i>b,k</i> ]fluoranthene	1690 (50)		1630 (100)		1700 (80)		0.5%					1660 ± 150	

<sup>a</sup>The sample used in ref 27 is SRM 1650. SRM 1650b is from the same bulk material as SRM 1650 but stored in the refrigerator as a bulk material until bottled. <sup>b</sup>Reference 27 reported a value for benzo[*b*+*j*+*k*] of 14 000 ng/g with a standard deviation of 1 000 ng/g, and ref 29 reported a value for benzo[*b*]fluoranthene of 8950 ng/g with a standard deviation of 221 ng/g. <sup>c</sup>The certified values for benzo[*b*]fluoranthene and benzo[*j*]fluoranthene are (6770 ± 840) ng/g and (3240 ± 420) ng/g, respectively. <sup>d</sup>Reference 27 reported a value for dibenz[*a,h*]anthracene of 370 ng/g with a standard deviation of 40 ng/g, and ref 29 reported a value for dibenz[*a,h*]anthracene of 624 ng/g with a standard deviation of 14 ng/g. <sup>e</sup>The certified values for dibenz[*a,c*]anthracene and dibenz[*a,h*]anthracene are (438 ± 43) ng/g and (365 ± 71) ng/g, respectively.

based on six sets of results using Soxhlet extraction and PLE at 100 °C and 13.8 MPa all using dichloromethane as the extraction solvent.<sup>35</sup> The results of this study for 100 °C and 13.8 MPa using toluene are generally in good agreement with the certified values and reference values in the COA indicating that Soxhlet extraction and PLE at 100 °C and 13.8 MPa provide equivalent results. The reference values for PAHs that show significant differences in extraction recovery between 100 and 200 °C also generally agree with the results of this study using the same PLE conditions. However for a majority of PAHs with certified values, the values determined at 200 °C are higher (generally about 10%) than the certified values (including the uncertainties), e.g., phenanthrene, fluoranthene, pyrene, benzo[*ghi*]fluoranthene, benz[*a*]anthracene, benzo[*a*]pyrene, benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene, dibenzo[*a,e*]pyrene, and dibenzo[*b,k*]fluoranthene. For SRM 1648a, which was developed for the determination of trace element content, there are currently no values for PAHs on the COA. However, results for a very limited number of PAHs based on Soxhlet extraction were reported previously.<sup>36</sup>

For SRM 1650b, the current COA certified values are based on PLE at both 100 and 200 °C (both at 13.8 MPa) using toluene. Thus the results of this study (Table 4) would be expected to be similar and within the uncertainties of the certified values. The only exceptions observed are higher values for naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, benz[*a*]anthracene, benzo[*a*]pyrene, and benzo[*ghi*]perylene at 200 °C. For SRM 2975, the COA certified and reference values are based on Soxhlet extraction and PLE at 100 °C with dichloromethane or a toluene–methanol mixture. The certified and reference values on the COA for SRM 2975 are in good agreement with the current study with PLE at 100 °C. However, nearly all of the results of the current study at 200 °C are higher than the certified and reference values in the COA for SRM 2975.

For the nitrated-PAHs in SRM 1649b, reference values are provided on the COA based on Soxhlet extraction with dichloromethane. The results of this study for nitrated-PAHs are in good agreement with the reference values with the exception of 9-nitroanthracene which, as noted above, has a significantly higher value using PLE at 200 °C. For the two diesel particulate SRMs, the results of this study are generally in good agreement with the certified and reference values on the COAs again with 9-nitroanthracene higher in this study using PLE at 200 °C. Because of these higher values obtained using PLE at 200 °C, the certified and reference values for the PAHs and for selected nitrated-PAHs in all of these SRMs will be reevaluated.

Concerning the comparison of this study with literature values reporting higher extraction yields,<sup>27,29,30</sup> the results are not consistent or definitive. Bergvall and Westerholm<sup>29</sup> reported higher values for PAHs in SRM 1649a (see Table 2), and Turrio-Baldassarri et al.<sup>27</sup> reported higher values for PAHs and nitrated-PAHs in SRM 1650b (same material as SRM 1650) (see Table 4) compared to the certified and reference values. Bergvall and Westerholm<sup>29</sup> analyzed SRM 1649a for determination of PAHs of molecular mass >252 Da. SRM 1649b is from the same collection of bulk particulate matter as SRM 1649a, but it was sieved to a smaller particle size (123 μm for SRM 1649a vs 63 μm for SRM 1649b). However, the mass fraction values for PAHs in the two materials typically differ by less than 5%, so a comparison with the current study using SRM 1649b is appropriate. The results from Bergvall and Westerholm for mass fractions of PAHs of molecular mass 252 Da through 302 Da in SRM 1649a are consistently 50% to 100% greater than the current study for SRM

**Table 5. Mass Fractions (ng/g) of Selected PAHs in SRM 2975 Diesel Particulate Matter (Forklift) as a Function of PLE Temperature and Pressure**

PLE conditions	this study	this study	this study	this study	% difference between ng/g determined	ref 29	ref 30	certificate of analysis <sup>5</sup>
	100 °C/ 2000 psi (13.8 MPa) method 13	100 °C/ 3000 psi (20.7 MPa) method 14	200 °C/ 2000 psi (13.8 MPa) method 15	200 °C/ 3000 psi (20.7 MPa) method 16		200 °C/ 3000 psi (20.7 MPa)	200 °C/ 3000 psi (20.7 MPa)	Certified; Reference; information
	mean (std dev) <i>n</i> = 3	mean (std dev) <i>n</i> = 3	mean (std dev) <i>n</i> = 3	mean (std dev) <i>n</i> = 3		at 200 and 100 °C (2000 psi)		
naphthalene	2580 (210)	2050 (200)	4040 (180)	3980 (120)	57%			
1-methylnaphthalene	1060 (100)	1000 (100)	1140 (110)	1090 (100)	8.5%	8.5%		
2-methylnaphthalene	2100 (160)	2000 (60)	2380 (180)	2100 (200)	13%			
biphenyl	322 (12)	325 (22)	3010 (280)	2930 (90)	830%			
acenaphthene	527 (34)	5445 (41)	578 (40)	564 (89)	9.7%			
fluorene	349 (23)	564 (35)	2980 (190)	2790 (170)	760%			
dibenzothiophene	880 (100)	980 (81)	2240 (160)	2100 (170)	150%			
phenanthrene	18300 (500)	18100 (400)	20500 (600)	20800 (400)	12%			17000 ± 2800
anthracene	37.7 (1.6)	42.3 (2.1)	50.2 (3.4)	48.6 (1.4)	33%			38 ± 8
1-methylphenanthrene	974 (56)	965 (66)	961 (94)	967 (64)	−1.3%			
2-methylphenanthrene	2550 (120)	2370 (100)	2620 (200)	2600 (190)	2.7%			2000 ± 200
3-methylphenanthrene	1200 (100)	1030 (80)	1410 (80)	1320 (130)	18%			1000 ± 200
9-methylphenanthrene	480 (50)	460 (40)	610 (40)	570 (30)	27%			440 ± 90
fluoranthene	28200 (600)	27600 (600)	30700 (400)	31200 (500)	8.5%			26600 ± 5100
pyrene	1010 (60)	1100 (50)	1640 (150)	1440 (50)	62%			900 ± 240
benzo[ghi]fluoranthene	10400 (300)	10300 (400)	10800 (90)	10900 (300)	4.0%			10200 ± 500
benzo[c]phenanthrene	1440 (90)	1460 (100)	1620 (120)	1660 (120)	13%			1000 ± 400
benz[a]anthracene	387 (15)	362 (16)	984 (58)	956 (44)	150%			317 ± 66
chrysene	4800 (50)	4390 (70)	5760 (260)	5730 (50)	20%			4560 ± 160
triphenylene	4970 (60)	5220 (60)	5580 (90)	5820 (200)	12%			5220 ± 200
benzo[b+j]fluoranthene	18900 (200)	20600 (300)	19600 (1500)	20500 (700)	3.7%	<i>a</i>	<i>b</i>	<i>c</i>
benzo[k]fluoranthene	728 (26)	800 (54)	1720 (170)	1750 (70)	140%	1650 (193)	1610 (235)	678 ± 76
benzo[a]fluoranthene	68.1 (2.5)	68.9 (2.4)	69.6 (1.1)	64.7 (6.3)	2.3%			60 ± 20
benzo[e]pyrene	1210 (60)	1240 (110)	2190 (100)	2370 (120)	81%	2470 (205)	2260 (243)	1110 ± 100
benzo[a]pyrene	52.3 (1.6)	58.4 (4.6)	753 (52)	773 (40)	1300%	858 (73)	870 (97)	52.2 ± 5.3
perylene	61.6 (2.1)	61.5 (1.5)	78.9 (6.7)	84.5 (6.5)	28%	60 (7)	74 (9)	54 ± 9
benzo[ghi]perylene	504 (26)	514 (46)	1590 (80)	1570 (140)	220%	1740 (155)	1310 (285)	498 ± 44
indeno[1,2,3-cd]pyrene	1450 (110)	1560 (60)	2150 (180)	2120 (110)	49%	2920 (259)	1970 (213) <sup>d</sup>	1400 ± 200
dibenz[a,j]anthracene	365 (21)	381 (24)	433 (5)	430 (17)	19%			370 ± 70
dibenz[a,c+a,h]anthracene	541 (26)	525 (22)	595 (26)	535 (29)	9.9%	<i>e</i>	<i>d,f</i>	520 ± 80
benzo[b]chrysene	102 (9)	109 (9)	208 (11)	213 (16)	100%			80 ± 30
picene	924 (29)	935 (21)	911 (8)	926 (19)	−1.4%	1050 (126)	976 (92)	1000 ± 200
corenene	1300 (120)	1570 (160)	2130 (50)	2050 (160)	64%	6360 (721)	5070 (414)	1100 ± 200
dibenzo[a,e]pyrene	611 (29)	602 (54)	612 (38)	616 (32)	0.2%	192 (15)	226 (34)	570
dibenzo[b,k]fluoranthene	2370 (170)	2560 (150)	2610 (50)	2510 (30)	10%			2700

<sup>a</sup>Reference 29 reported a value for benzo[b]fluoranthene of 20 600 ng/g with a standard deviation of 1 550 ng/g. <sup>b</sup>Reference 30 reported a value for benzo[b]fluoranthene of 16 800 ng/g with a standard deviation of 1 770 ng/g using toluene/methanol (9/1 volume fraction). <sup>c</sup>The reference value for benzo[b]fluoranthene is (11 500 ± 3 600) ng/g, and the certified value for benzo[j]fluoranthene is (820 ± 110) ng/g. <sup>d</sup>Reference 30 reported a coelution between indeno[1,2,3-cd]pyrene and dibenz[a,h]anthracene. <sup>e</sup>Reference 29 reported a value for dibenz[a,h]anthracene of 393 ng/g with a standard deviation of 43 ng/g. <sup>f</sup>Reference 30 reported a value for dibenz[a,h]anthracene of 402 ng/g with a standard deviation of 43 ng/g using toluene–methanol (9:1 volume fraction).

1649b (coronene at 300% greater), with the exception of dibenzo[a,e]pyrene, which was similar to this study. Both Bergvall and Westerholm<sup>29</sup> and Turrio-Baldassarri et al.<sup>27</sup> results

for PAHs in SRM 1650b are consistent with the results of the current study at 200 °C, within the measurement uncertainties, with the exception of benzo[e]pyrene, benzo[k]fluoranthene,



picene, indeno[1,2,3-*cd*]pyrene, and benzo[*ghi*]perylene, which they report as about 20–30% higher. However, for SRM 1650b, Bergvall and Westerholm<sup>29</sup> reported values for dibenzo[*a,e*]pyrene and coronene that were 40–50% lower than the current study and the reference values. Turrio-Baldassarri et al.<sup>27</sup> reported nitrated-PAHs values for SRM 1650b that were consistent with this current study, with the exception of 2-nitrofluorene (a factor of 10 higher) and 3-nitrofluoranthene (factor of 3 higher). The high result for 3-nitrofluoranthene may be due to coelution with 2-nitrofluoranthene, which was separated in the current study. For SRM 2975 (Table 5), Masala et al.<sup>30</sup> found optimal conditions for PLE to be a toluene–methanol mixture (9:1, volume fraction) at 200 °C and 20.7 MPa with five 30 min static cycles. Using these conditions, they observed higher values compared to the certified values for a number of the molecular mass 252, 276, 278, 300, and 302 Da compounds. When using 100% toluene as the extraction solvent, Masala et al.<sup>30</sup> found lower mass fractions than those found by Bergvall and Westerholm<sup>29</sup> and, after some additional studies, suggested that the difference was caused by degradation during storage of the deuterated benzo[*a*]pyrene internal standard solution and by leaching of PAHs from the black Viton o-rings of the PLE cells during the study reported in ref 29. Our current study does substantiate some, but not all, of the observations of Bergvall and Westerholm,<sup>29</sup> Masala et al.,<sup>30</sup> or Turrio-Baldassarri et al.<sup>27</sup> that significantly higher extraction recoveries are obtained using PLE at 200 °C and 20.7 MPa compared to PLE at 100 °C.

## CONCLUSIONS

Increasing the temperature used for PLE is the dominant parameter in increasing the extraction efficiency for PAHs (and to some extent the nitrated-PAHs) from the air and diesel particulate matter SRMs. The maximum temperature and pressure of current commercially available PLE instrumentation are 200 °C and 20.7 MPa, respectively. At higher extraction temperatures than 200 °C, it may be possible to obtain even higher recoveries of PAHs and nitrated-PAHs from these air and diesel particulate matter SRMs.

For the assignment of a certified mass fraction value for an SRM requiring extraction to remove the compounds of interest, a discussion of the appropriate approach is warranted. When the first particulate matter SRM (SRM 1649) was issued in 1981 with certified values for selected PAHs,<sup>37</sup> the question of whether all the PAHs were extracted from the particulate matter was heavily debated. Previous NIST experience for particulate matter SRMs was based on measurements of elemental composition, and therefore the concept of assigning a value for the total content of an element after dissolution of the particulate matrix was a reasonable approach. However, for the determination of PAHs or other organic contaminants in air particulate matter, it is not a viable approach to dissolve the particle matrix and leave the PAHs intact as in the approach used for elemental measurements. Removal of the PAHs from the particulate matter using solvent extraction was required, and it was decided that the best approach was to extensively investigate different extraction methods (Soxhlet and ultrasonic extraction were the primary methods at the time) using different solvents to convince us that we were removing all, or at least as much as possible, considering extraction techniques available at the time. The extraction methods used to provide the certified values are described in detail on the COA, with the intent that if advances in extraction techniques in the future provided higher recoveries of PAHs, the certified values would be updated to reflect these improvements.

This was the case when SRM 1650b was reissued and only results obtained using PLE were used to determine the assigned values (i.e., no Soxhlet extraction was used). On the basis of previous studies<sup>17</sup> and this study with the air particulate SRMs, Soxhlet extraction (the classic benchmark for extraction studies) is equivalent to PLE at 100 °C and 13.8 MPa for most PAHs and nitrated-PAHs. Regarding extraction of PAHs from air and diesel particulate matter, are the PAHs adsorbed on the particle surfaces or are some PAHs incorporated into the particles during formation and would therefore not be accessible to the extraction solvent? Is the measurement of PAHs inside a particle relevant? All of these questions should be considered when using these SRMs for method validation and comparison.

The NIST perspective for value assignment of particulate matter for organic constituents has remained the same as in the early 1980s when SRM 1649 was first issued, i.e., use current state-of-the-art extraction techniques and report how it was done. On the basis of the results of this investigation, the certified and reference values assigned for PAHs and nitrated-PAHs in these four SRMs will be updated, and where significantly different results are obtained with different extraction methods, these differences will be noted on the COA.

## ASSOCIATED CONTENT

### Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [michele.schantz@nist.gov](mailto:michele.schantz@nist.gov). Phone: (301)975-3106. Fax: (301)977-0685.

### Present Address

<sup>†</sup>Department of Chemistry & Biochemistry, Adrian College, 110 S. Madison St., Adrian, MI 49221.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

## REFERENCES

- (1) Arey, J. *Environ. Health Perspect.* **2004**, *112*, 812–813.
- (2) Ulrich, K.; Wolffe, S.; Mayer, A.; Heeg, K.; Braunbeck, T.; Erdinger, L.; Bartz, H. *Environ. Sci. Pollut. Res.* **2010**, *17*, 1257–1267.
- (3) Ball, J. C.; Straccia, A. M.; Young, W. C.; Aust, A. E. *J. Air Waste Manage. Assoc.* **2000**, *50*, 1897–1903.
- (4) NIST. Certificate of Analysis, SRM 1650b Diesel Particulate Matter; 2006, [https://www-s.nist.gov/srmors/view\\_cert.cfm?srn=1650B](https://www-s.nist.gov/srmors/view_cert.cfm?srn=1650B).
- (5) Certificate of Analysis, SRM 2975 Diesel Particulate Matter (Industrial Forklift), NIST, 2009, [https://www-s.nist.gov/srmors/view\\_cert.cfm?srn=2975](https://www-s.nist.gov/srmors/view_cert.cfm?srn=2975).
- (6) Poster, D. L.; de Alda, M. J. L.; Schantz, M. M.; Sander, L. C.; Wise, S. A.; Vangel, M. G. *Polycyclic Aromat. Compd.* **2003**, *23*, 141–191.
- (7) Poster, D. L.; Benner, B. A.; Schantz, M. M.; Sander, L. C.; Wise, S. A.; Vangel, M. G. *Polycyclic Aromat. Compd.* **2003**, *23*, 113–139.
- (8) Bamford, H. A.; Bezabeh, D. Z.; Schantz, M. M.; Wise, S. A.; Baker, J. E. *Chemosphere* **2003**, *50*, 575–587.

- (9) Bezabeh, D. Z.; Bamford, H. A.; Schantz, M. M.; Wise, S. A. *Anal. Bioanal. Chem.* **2003**, 375, 381–388.
- (10) Jonker, M. T. O.; Koelmans, A. A. *Environ. Sci. Technol.* **2002**, 36, 4107–4113.
- (11) Endo, S.; Grathwohl, P.; Haderlein, S. B.; Schmidt, T. C. *Environ. Sci. Technol.* **2009**, 43, 3187–3193.
- (12) Braun, A.; Mun, B. S.; Huggins, F. E.; Huffman, G. P. *Environ. Sci. Technol.* **2007**, 41, 173–178.
- (13) NIST. Certificate of Analysis, SRM 1648a Urban Particulate Matter; 2008, [https://www-s.nist.gov/srmors/view\\_cert.cfm?srm=1648A](https://www-s.nist.gov/srmors/view_cert.cfm?srm=1648A)
- (14) NIST. Certificate of Analysis, SRM 1649b Urban Dust (Organics); 2009, [https://www-s.nist.gov/srmors/view\\_cert.cfm?srm=1649B](https://www-s.nist.gov/srmors/view_cert.cfm?srm=1649B)
- (15) Wise, S. A.; Sander, L. C.; Schantz, M. M.; Hays, M. J.; Benner, B. A. *Polycyclic Aromat. Compd.* **1999**, 13, 419–456.
- (16) Schantz, M. M. *Anal. Bioanal. Chem.* **2006**, 386, 1043–1047.
- (17) Schantz, M. M.; Nichols, J. J.; Wise, S. A. *Anal. Chem.* **1997**, 69, 4210–4219.
- (18) Sin, D. W.-M.; Fung, W.-H.; Lam, C.-H. *Analyst* **2002**, 127, 614–622.
- (19) Christensen, A.; Ostman, C.; Westerholm, R. *Anal. Bioanal. Chem.* **2005**, 381, 1206–1216.
- (20) Bergvall, C.; Westerholm, R. *Anal. Bioanal. Chem.* **2006**, 384, 438–447.
- (21) Letellier, M.; Budzinski, H.; Garrigues, P.; Wise, S. *Spectroscopy (Amsterdam, Neth.)* **1997**, 13, 71–80.
- (22) Shu, Y. Y.; Tey, S. Y.; Wu, D. K. S. *Anal. Chim. Acta* **2003**, 495, 99–108.
- (23) Benner, B. A., Jr. *Anal. Chem.* **1998**, 70, 4594–4601.
- (24) Hawthorne, S. B.; Trembley, S.; Moniot, C. L.; Grabanski, C. B.; Miller, D. J. J. *Chromatogr., A* **2000**, 886, 237–244.
- (25) Bates, M.; Bruno, P.; Caputi, M.; Caselli, M.; de Gennaro, G.; Tutino, M. *Atmos. Environ.* **2008**, 42, 6144–6151.
- (26) Yamaguchi, C.; Lee, W.-Y. *J. Chromatogr., A* **2010**, 1217, 6816–6823.
- (27) Turrio-Baldassarri, L.; Battistelli, C. L.; Iamiceli, A. L. *Anal. Bioanal. Chem.* **2003**, 375, 589–595.
- (28) Borsella, E.; Di Filippo, P.; Riccardi, C.; Spicaglia, S.; Cecinato, A. *Ann. Chim.* **2004**, 94, 691–698.
- (29) Bergvall, C.; Westerholm, R. *Anal. Bioanal. Chem.* **2008**, 391, 2235–2248.
- (30) Masala, S.; Ahmed, T.; Bergvall, C.; Westerholm, R. *Anal. Bioanal. Chem.* **2011**, 401, 3305–3315.
- (31) He, J.; Balasubramanian, R. *Anal. Lett.* **2009**, 42, 1603–1619.
- (32) Frenich, A. G.; Ocana, R. M.; Vidal, J. L. M. *J. AOAC Int.* **2010**, 93, 284–294.
- (33) Nguyen, T. H.; Ball, W. P. *Environ. Sci. Technol.* **2006**, 40, 2958–2964.
- (34) Sander, L. C.; Wise, S. A. Polycyclic Aromatic Hydrocarbon Structure Index; NIST Special Publication 922, 1997.
- (35) Wise, S. A.; Poster, D. L.; Kucklick, J. R.; Keller, J. M.; VanderPol, S. S.; Sander, L. C.; Schantz, M. M. *Anal. Bioanal. Chem.* **2006**, 386, 1153–1190.
- (36) Wise, S. A.; Benner, B. A.; Chesler, S. N.; Hilpert, L. R.; Vogt, C. R.; May, W. E. *Anal. Chem.* **1986**, 58, 3067–3077.
- (37) May, W. E.; Wise, S. A. *Anal. Chem.* **1984**, 56, 225–232.