

# PRESSURIZED LIQUID EXTRACTION OF DIESEL AND AIR PARTICULATE STANDARD REFERENCE MATERIALS: EFFECT OF EXTRACTION TEMPERATURE AND PRESSURE

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## SUPPORTING INFORMATION

### EXPERIMENTAL

Calibration solutions were prepared from SRM 2260a Aromatic Hydrocarbons in Toluene, SRM 1491a Methyl-Substituted Polycyclic Aromatic Hydrocarbons in Toluene, SRM 2264 Nitro PAHs in Dichloromethane I, and SRM 2265 Nitro PAHs in Dichloromethane II. Internal standard solutions were prepared from SRM 2269 Perdeuterated PAH-I Solution in Hexane/Toluene, SRM 2270 Perdeuterated PAH-II Solution in Hexane/Toluene, and perdeuterated 1-nitronaphthalene, 2-nitrofluorene, 9-nitroanthracene, 3-nitrofluoranthene, 1-nitropyrene, 6-nitrochrysene, and dibenzo[*a,i*]pyrene. The perdeuterated compounds were obtained from Cambridge Isotope Laboratories (Andover, MA). All solvents were HPLC-grade.

Six samples of SRM 1648a (approx. 200 mg), 12 samples of SRM 1649b (approx. 100 mg, exact mass known), 12 samples of SRM 1650b (approx. 20 mg, exact mass known), and 12 samples of

SRM 2975 (approx. 30 mg, exact mass known) were placed in individual PLE cells that were approximately half filled with hydromatrix. The samples were mixed with the hydromatrix. Additional hydromatrix was added to fill the excess cell volume. These mixtures were spiked with the internal standard solution (containing the perdeuterated compounds listed above along with SRM 2269 and SRM 2270) and extracted using the conditions summarized in Table 1 of the main paper.

Following extraction, the extracts were concentrated to approximately 0.5 mL using an automated evaporation system and eluted through an aminopropyl solid phase extraction (SPE) column (Sep Pak Classic, Waters Associates, Milford, MA) using 20 mL of 20% (volume fraction) of dichloromethane in hexane. The collected fractions were concentrated to 0.5 mL prior to gas chromatography with mass spectrometric detection (GC/MS) analysis. Three calibration solutions containing known masses of SRM 2260a,

SRM 1491a, SRM 2264, and SRM 2265 mixed with known masses of 2,2,4-trimethylpentane were processed under each set of PFE conditions along with one blank sample (only internal standards added to the hydromatrix in the extraction cell).

For separation and quantification of the PAHs, samples were analyzed using GC/electron ionization (EI)-MS with a 0.25 mm x 60 m capillary column with a proprietary non-polar stationary phase, 0.25  $\mu$ m film thickness. The nitrated PAHs of interest were quantified using GC/negative chemical ionization (NCI)-MS with a 0.25mm x 30 m 50% (mole fraction) methylpolysiloxane stationary phase, 0.25  $\mu$ m film thickness. All injections were on-column (1  $\mu$ L) with helium as a carrier gas.

## RESULTS AND DISCUSSION

Included in the supporting information are three figures illustrating the differences noted when changing pressurized liquid extraction parameters for selected polycyclic aromatic hydrocarbons (PAHs) in SRM 1649b (S-Figure 1), SRM 1650b (S-Figure 2), and SRM 2975 (S-Figure 3), two tables (Tables S-1 and S-2) illustrating the effect of increasing the number of extraction cycles from 3 to 5 and changing the solvent from toluene to toluene:methanol (9:1, v:v) for SRM 1650b and SRM 2975, respectively, and three tables (Supplemental Tables S-3, S-4, and S-5) summarizing the effects of temperature and pressure on the mass fractions of selected nitrated-PAHs in SRM 1649b, SRM 1650b, and SRM 2975, respectively.

## SUPPLEMENTAL REFERENCES

1. Certificate of Analysis, SRM 1649b Urban Dust (Organics); NIST (2009). [https://www-s.nist.gov/srmors/view\\_cert.cfm?srm=1649B](https://www-s.nist.gov/srmors/view_cert.cfm?srm=1649B)

2. Certificate of Analysis, SRM 1650b Diesel Particulate Matter; NIST (2006). [https://www-s.nist.gov/srmors/view\\_cert.cfm?srm=1650B](https://www-s.nist.gov/srmors/view_cert.cfm?srm=1650B)
3. Certificate of Analysis, SRM 2975 Diesel Particulate Matter (Industrial Forklift); NIST (2009). [https://www-s.nist.gov/srmors/view\\_cert.cfm?srm=2975](https://www-s.nist.gov/srmors/view_cert.cfm?srm=2975)
4. Masala, S., Ahmed, T., Bergvall, C., Westerholm, R. *Anal. Bioanal. Chem.* **2011**, 401, 3305-3315.
5. Turrio-Baldassarri, L.; Battistelli, C.L.; Iamiceli, A.L. *Anal. Bioanal. Chem.* **2003**, 375, 589-595.

Table S-1. Mass Fractions (ng/g as received) of Selected PAHs in SRM 1650b Diesel Particulate Matter

PLE conditions	this study 200 °C / 20.7 Mpa toluene; 3 static @ 30 min each mean (stdev) n=3	this study 200 °C /20.7 Mpa toluene:methanol (9:1); 5 static @ 30 min each mean (stdev) n=3
naphthalene	7060 (400)	7190 (190)
biphenyl	3277 (88)	3250 (80)
acenaphthene	192 (19)	189 (14)
fluorene	1265 (57)	1260 (90)
dibenzothiophene	21600 (1100)	20740 (90)
phenanthrene	71090 (45)	71680 (1260)
anthracene	7470 (130)	7450 (310)
fluoranthene	50200 (500)	50780 (940)
pyrene	45900 (660)	45120 (2560)
benzo[ghi]fluoranthene	11800 (600)	11280 (1010)
benzo[c]phenanthrene	2950 (260)	2890 (200)
benz[a]anthracene	7870 (270)	7960 (110)
chrysene	13760 (370)	13130 (680)
triphenylene	10330 (340)	10780 (660)
benzo[b+j]fluoranthene	10220 (210)	10970 (670)
benzo[k]fluoranthene	2220 (70)	2230 (46)
benzo[a]fluoranthene	410 (21)	408 (4)
benzo[e]pyrene	6570 (510)	6500 (80)
benzo[a]pyrene	1680 (150)	1680 (60)
perylene	169 (10)	158 (12)
benzo[ghi]perylene	7010 (120)	7040 (220)
indeno[1,2,3-cd]pyrene	4590 (70)	4400 (230)
dibenz[a,j]anthracene	429 (31)	423 (17)
dibenz[a,c+a,h]anthracene	810 (69)	818 (16)
benzo[b]chrysene	323 (14)	319 (7)
picene	520 (40)	519 (24)
corenene	9760 (320)	9810 (250)
dibenzo[a,e]pyrene	1180 (80)	1130 (60)

Table S-2. Mass Fractions (ng/g as received) of Selected PAHs in SRM 2975 Diesel Particulate Matter (Forklift)

	this study	this study	Reference [4]		
PLE conditions	200 °C / 3000 psi (20.7 MPa)	200 °C / 3000 psi (20.7 MPa)	200 °C / 3000 psi (20.7 MPa)		
	toluene; 3 static @ 30 min each	toluene:methanol (9:1); 5 static @ 30 min each	toluene:methanol (9:1); 5 static @ 30 min each		
	mean (stdev) n=3	mean (stdev) n=3			
naphthalene	3980 (120)	4040 (150)			
biphenyl	2930 (90)	2990 (110)			
acenaphthene	564 (89)	560 (6)			
fluorene	2790 (170)	2700 (150)			
dibenzothiophene	2100 (170)	2180 (100)			
phenanthrene	20800 (400)	20510 (1450)			
anthracene	48.6 (1.4)	47.7 (1.4)			
fluoranthene	31200 (500)	31000 (320)			
pyrene	1440 (50)	1460 (40)			
benzo[ghi]fluoranthene	10900 (300)	10670 (900)			
benzo[c]phenanthrene	1660 (120)	1620 (110)			
benz[a]anthracene	956 (44)	988 (56)			
chrysene	5730 (50)	5760 (280)			
triphenylene	5820 (200)	5820 (120)			
benzo[b+j]fluoranthene	20500 (700)	20550 (1230)	<sup>a</sup>		
benzo[k]fluoranthene	1750 (70)	1790 (80)	1610 (235)		
benzo[a]fluoranthene	64.7 (6.3)	66.1 (2.6)			
benzo[e]pyrene	2370 (120)	2380 (40)	2260 (243)		
benzo[a]pyrene	773 (40)	770 (20)	870 (97)		
perylene	84.5 (6.5)	83.7 (5.2)	74 (9)		
benzo[ghi]perylene	1570 (140)	1560 (70)	1310 (285)		
indeno[1,2,3-cd]pyrene	2120 (110)	2060 (120)	1970 (213) <sup>b</sup>		
dibenz[a,j]anthracene	430 (17)	438 (33)			
dibenz[a,c+a,h]anthracene	535 (29)	545 (25)	<sup>b,c</sup>		
benzo[b]chrysene	213 (16)	220 (13)			
picene	926 (19)	929 (15)	976 (92)		
corenene	2050 (160)	2120 (120)	5070 (414)		
dibenzo[a,e]pyrene	616 (32)	606 (33)	226 (34)		
<sup>a</sup> Reference 4 reported a value for benzo[b]fluoranthene of 16800 ng/g with a standard deviation of 1770 ng/g					
<sup>b</sup> Reference 4 reported a coelution between indeno[1,2,3-cd]pyrene and dibenz[a,h]anthracene.					
<sup>c</sup> Reference 4 reported a value for dibenz[a,h]anthracene of 402 ng/g with a standard deviation of 43 ng/g					

Table S-3. Mass Fractions (ng/g) of Selected Nitrated-PAHs in SRM 1649b Urban Dust as a Function of PLE Temperature and Pressure

	This study	This study	This study	This study		Certificate of Analysis[1]
PLE conditions	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)	% difference between ng/g determined	
	Method 5	Method 6	Method 7	Method 8	at 200 °C and 100 °C (2000 psi)	
	mean (stdev) n=3	mean (stdev) n=3	mean (stdev) n=3	mean (stdev) n=3		Reference
1-nitronaphthalene	7.36 (0.44)	7.11 (0.15)	7.79 (0.15)	7.90 (0.51)	5.9%	7.2 ± 0.1
2-nitronaphthalene	11.9 (1.1)	11.9 (0.2)	12.3 (1.1)	12.2 (0.6)	3.7%	11.4 ± 0.3
3-nitrobiphenyl	3.78 (0.16)	3.66 (0.12)	3.92 (0.22)	3.69 (0.21)	3.7%	3.5 ± 0.1
5-nitroacenaphthene	3.01 (0.11)	3.09 (0.12)	3.67 (0.20)	3.37 (0.29)	22%	3.1 ± 0.1
9-nitroanthracene	39.0 (1.6)	64.7 (2.1)	255 (38)	238 (11)	550%	34.6 ± 0.7
9-nitrophenanthrene	1.81 (0.03)	1.65 (0.05)	1.68 (0.06)	1.78 (0.08)	-7.2%	1.8 ± 0.1
3-nitrophenanthrene	20.1 (1.5)	22.8 (1.1)	20.1 (0.4)	22.4 (1.0)	-0.2%	22.1 ± 0.3
3-nitrofluoranthene	5.07 (0.25)	4.31 (0.25)	4.12 (0.15)	4.98 (0.16)	-19%	4.6 ± 0.1
2-nitrofluoranthene	266 (21)	277 (6)	307 (13)	292 (9)	15%	311 ± 5
1-nitropyrene	76.6 (1.2)	72.7 (2.5)	73.2 (2.3)	74.1 (2.5)	-4.4%	71.8 ± 1.3
2-nitropyrene	10.6 (0.4)	10.5 (0.6)	11.1 (0.5)	10.6 (0.5)	4.7%	10.8 ± 0.3
7-nitrobenz[a]anthracene	23.9 (0.4)	24.6 (0.6)	24.0 (1.8)	23.0 (1.5)	0.4%	24.2 ± 0.7
6-nitrochrysene	3.65 (0.25)	3.44 (0.17)	3.34 (0.12)	3.45 (0.26)	-8.4%	3.8 ± 0.1

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

	This study	This study	This study	This study		Reference [5] <sup>a</sup>	Certificate of Analysis[2]
PLE conditions	100 °C / 2000 psi (13.8 MPa)	100 °C / 3000 psi (20.7 MPa)	200 °C / 2000 psi (13.8 MPa)	200 °C / 3000 psi (20.7 MPa)	% difference between ng/g determined	195 °C / 2200 psi (15.2 MPa)	
	Method 9	Method 10	Method 11	Method 12	at 200 °C and 100 °C (2000 psi)		
	mean (stdev) n=3	mean (stdev) n=3	mean (stdev) n=3	mean (stdev) n=3			Certified; Reference
1-nitronaphthalene	82.7 (2.1)	87.6 (1.2)	85.1 (1.4)	85.7 (1.4)	2.9%	80 (10)	85.7 ± 1.3
2-nitronaphthalene	260 (13)	230 (10)	238 (7)	230 (6)	-8.4%	240 (10)	236 ± 3
2-nitrobiphenyl	16.2 (0.8)	16.6 (0.9)	16.6 (0.4)	16.2 (0.8)	-8.4%		15.2 ± 1.6
3-nitrobiphenyl	56.3 (1.8)	59.1 (1.6)	53.3 (2.2)	58.9 (1.8)	2.2%		58.1 ± 0.8
5-nitroacenaphthene	36.2 (2.1)	36.9 (1.2)	37.5 (1.2)	36.9 (1.6)	3.7%		36.9 ± 1.3
2-nitrofluorene	44.2 (1.6)	49.0 (2.6)	50.8 (3.8)	45.5 (1.5)	15%	580 (40)	45.5 ± 1.4
9-nitroanthracene	5810 (210)	5880 (100)	6950 (180)	6870 (340)	20%		5890 ± 310
9-nitrophenanthrene	590 (45)	564 (15)	521 (35)	550 (54)	-12%		538 ± 44
3-nitrophenanthrene	4240 (220)	4190 (170)	4200 (110)	4360 (220)	-0.8%		4320 ± 110
3-nitrofluoranthene	65.5 (2.6)	64.8 (2.2)	68.1 (4.0)	67.4 (2.7)	3.9%	180 (20)	65.1 ± 3.4
2-nitrofluoranthene	203 (10)	246 (12)	235 (9)	203 (17)	16%		208 ± 9
1-nitropyrene	19100 (400)	18600 (200)	18400 (600)	18200 (700)	-3.8%	20200 (400)	18200 ± 200
7-nitrobenz[a]anthracene	971 (64)	958 (67)	920 (74)	955 (55)	-5.2%		967 ± 42
6-nitrochrysene	48.2 (1.6)	47.8 (2.9)	47.2 (3.6)	45.6 (1.4)	-2.0%		45.5 ± 1.9

<sup>a</sup> The sample used in Reference [5] 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.

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

	This study	This study	This study	This study		Certificate of Analysis[3]
PLE conditions	100 °C / 2000 psi (13.8 MPa)	100 °C / 3000 psi (20.7 MPa)	200 °C / 2000 psi (13.8 MPa)	200 °C / 3000 psi (20.7 MPa)	% difference between ng/g determined	
	Method 13	Method 14	Method 15	Method 16	at 200 °C and 100 °C (2000 psi)	
	mean (stdev) n=3	mean (stdev) n=3	mean (stdev) n=3	mean (stdev) n=3		Reference
1-nitronaphthalene	41.3 (1.1)	47.2 (2.2)	42.2 (1.2)	45.5 (0.8)	2.1%	41 ± 5
2-nitronaphthalene	119 (10)	122 (9)	119 (11)	114 (2)	0.5%	112 ± 17
9-nitroanthracene	3220 (120)	3270 (150)	4090 (340)	3920 (140)	27%	2970 ± 450
9-nitrophenanthrene	456 (21)	482 (41)	481 (28)	476 (14)	5.5%	444 ± 47
3-nitrophenanthrene	180 (14)	186 (12)	199 (16)	198 (12)	10%	185 ± 17
3-nitrofluoranthene	4160 (120)	3820 (110)	3700 (120)	3820 (200)	-11%	3740 ± 590
2-nitrofluoranthene	237 (22)	255 (12)	266 (14)	216 (11)	12%	205 ± 53
1-nitropyrene	36800 (400)	37700 (1100)	32000 (1000)	35200 (400)	-13%	34800 ± 4700
7-nitrobenz[a]anthracene	3560 (170)	3480 (170)	3730 (220)	3850 (100)	4.9%	3460 ± 780
6-nitrochrysene	2510 (110)	2150 (110)	3110 (60)	2730 (90)	24%	2220 ± 450

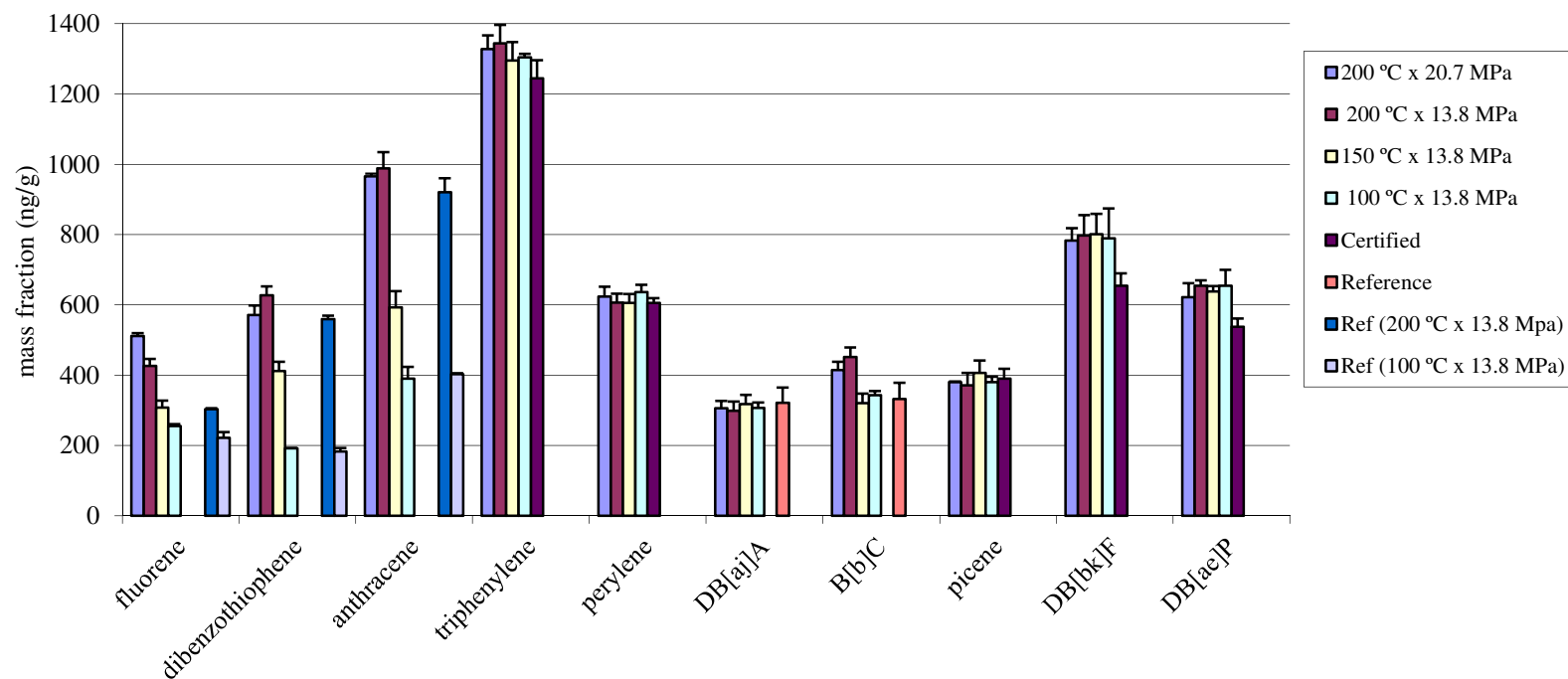


Figure S-1. Effect of PLE temperature and pressure for selected PAHs in SRM 1649b. The error bars represent standard deviations for the data from this study and expanded uncertainties for the certified and reference values calculated as detailed in the Certificate of Analysis for SRM 1649b [1]

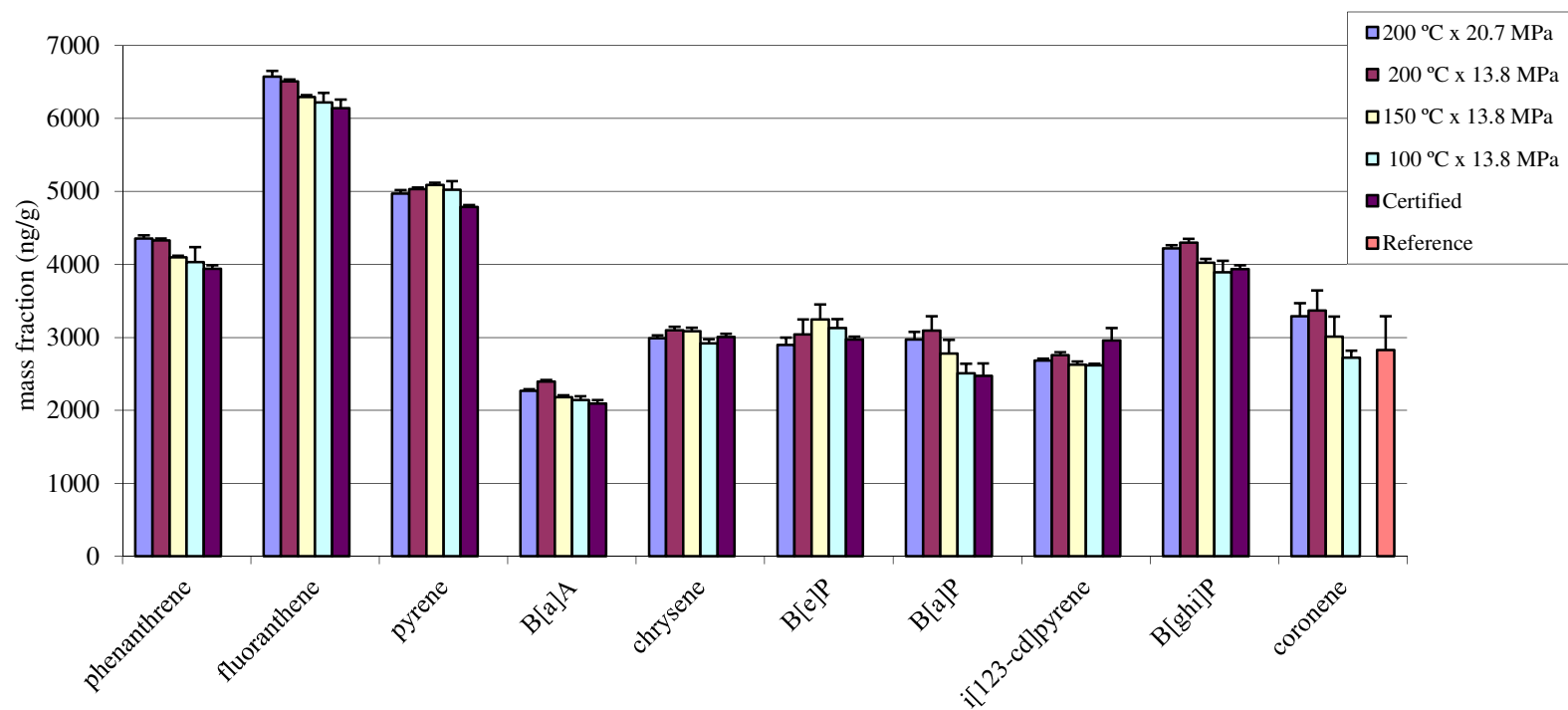


Figure S-1 (cont). Effect of PLE temperature and pressure for selected PAHs in SRM 1649b. The error bars represent standard deviations for the data from this study and expanded uncertainties for the certified and reference values calculated as detailed in the Certificate of Analysis for SRM 1649b [1]

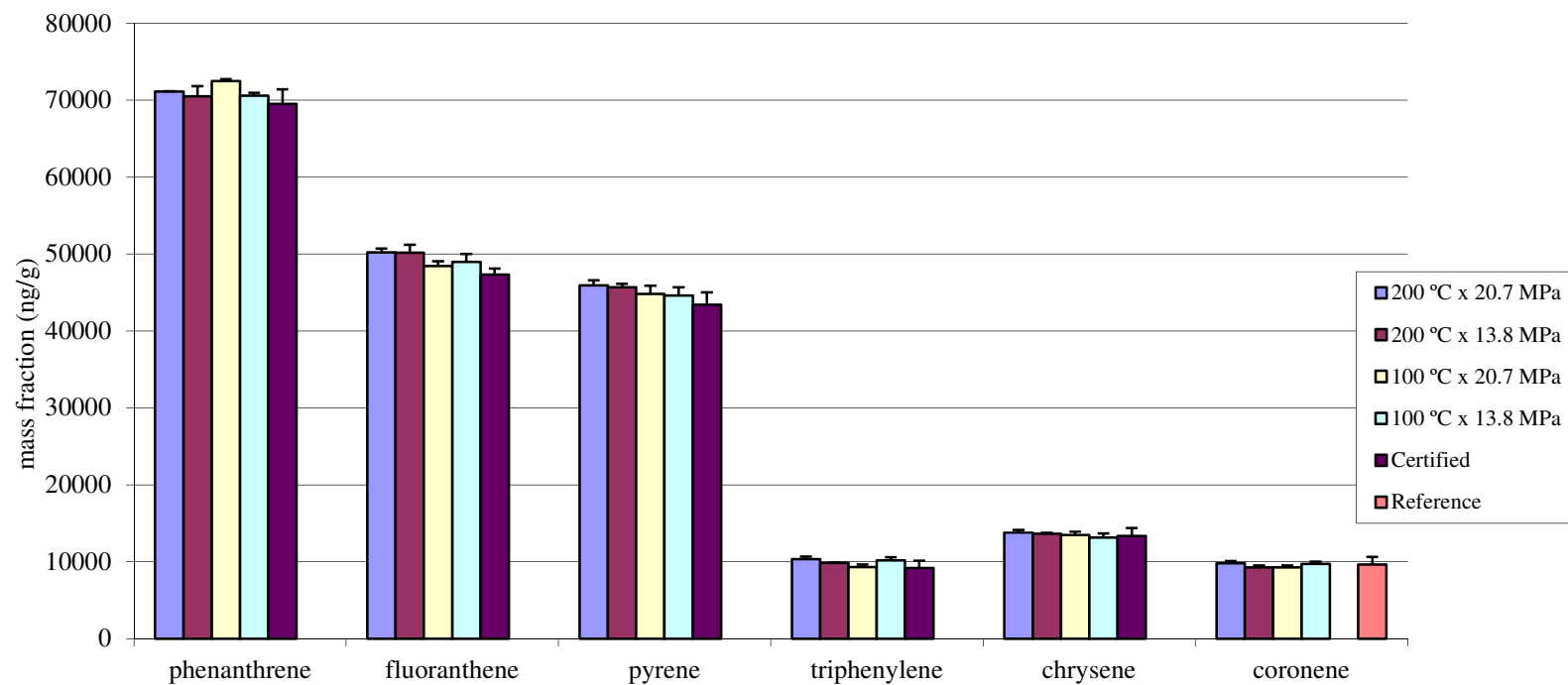


Figure S-2. Effect of PLE temperature and pressure for selected PAHs in SRM 1650b. The error bars represent standard deviations for the data from this study and expanded uncertainties for the certified and reference values calculated as detailed in the Certificate of Analysis for SRM 1650b [2]

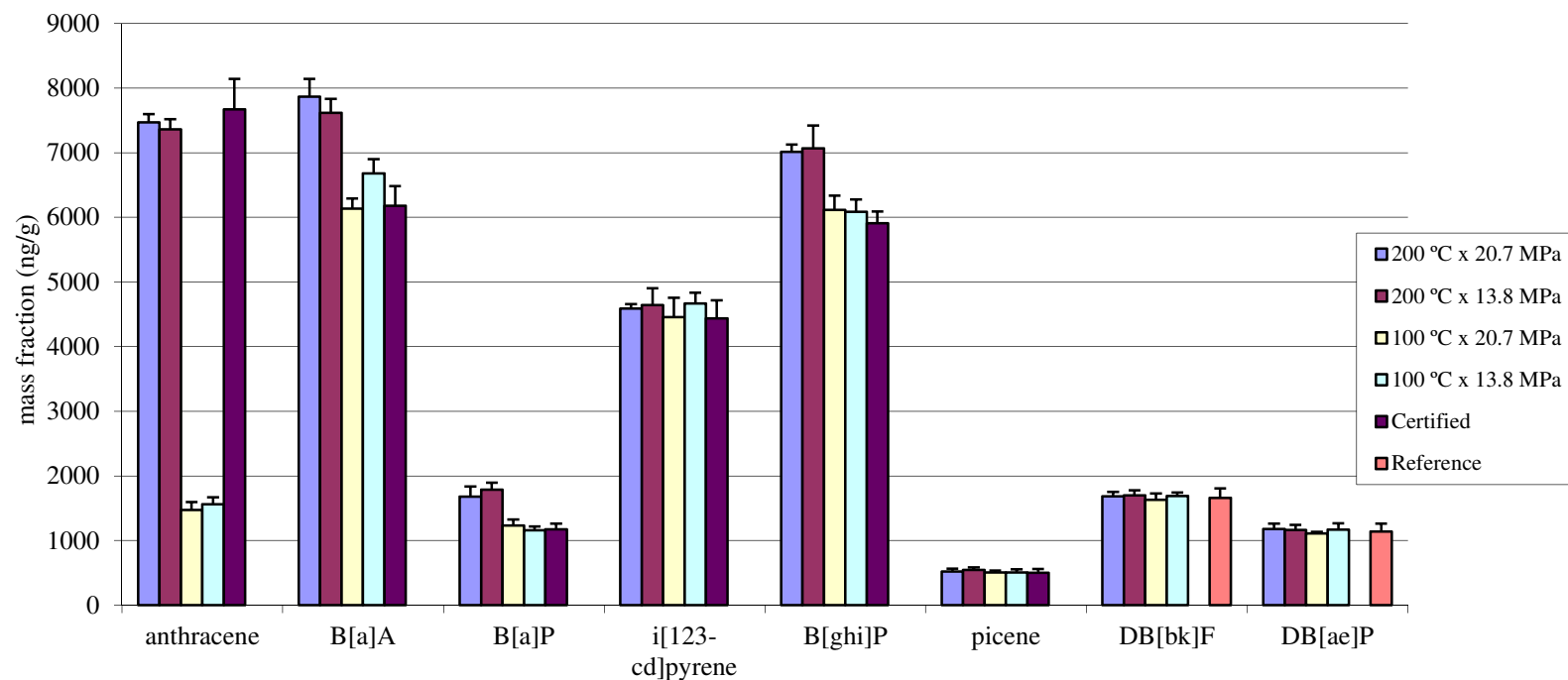


Figure S-2 (cont). Effect of PLE temperature and pressure for selected PAHs in SRM 1650b. The error bars represent standard deviations for the data from this study and expanded uncertainties for the certified and reference values calculated as detailed in the Certificate of Analysis for SRM 1650b [2]

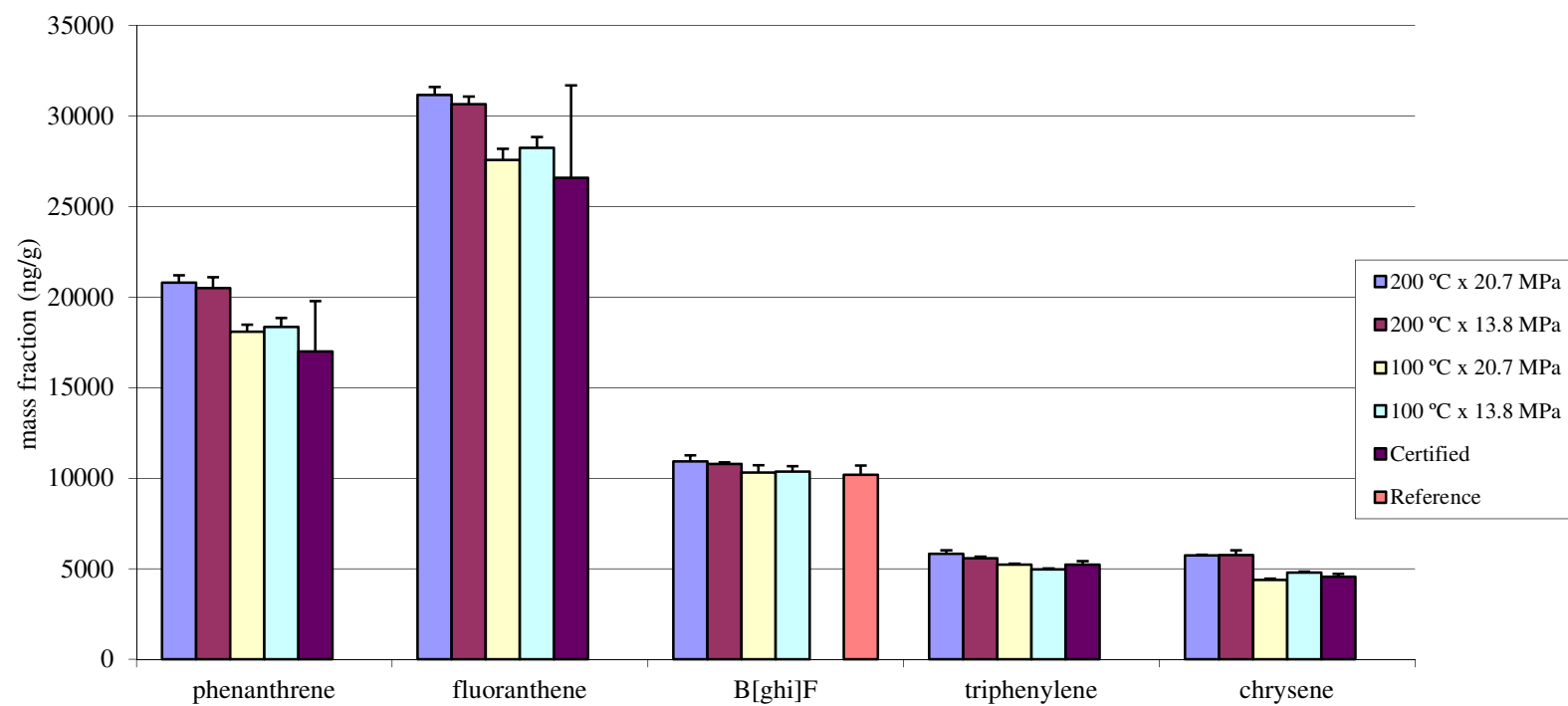


Figure S- 3. Effect of PLE temperature and pressure for selected PAHs in SRM 2975. The error bars represent standard deviations for the data from this study and expanded uncertainties for the certified and reference values calculated as detailed in the Certificate of Analysis for SRM 2975 [3]

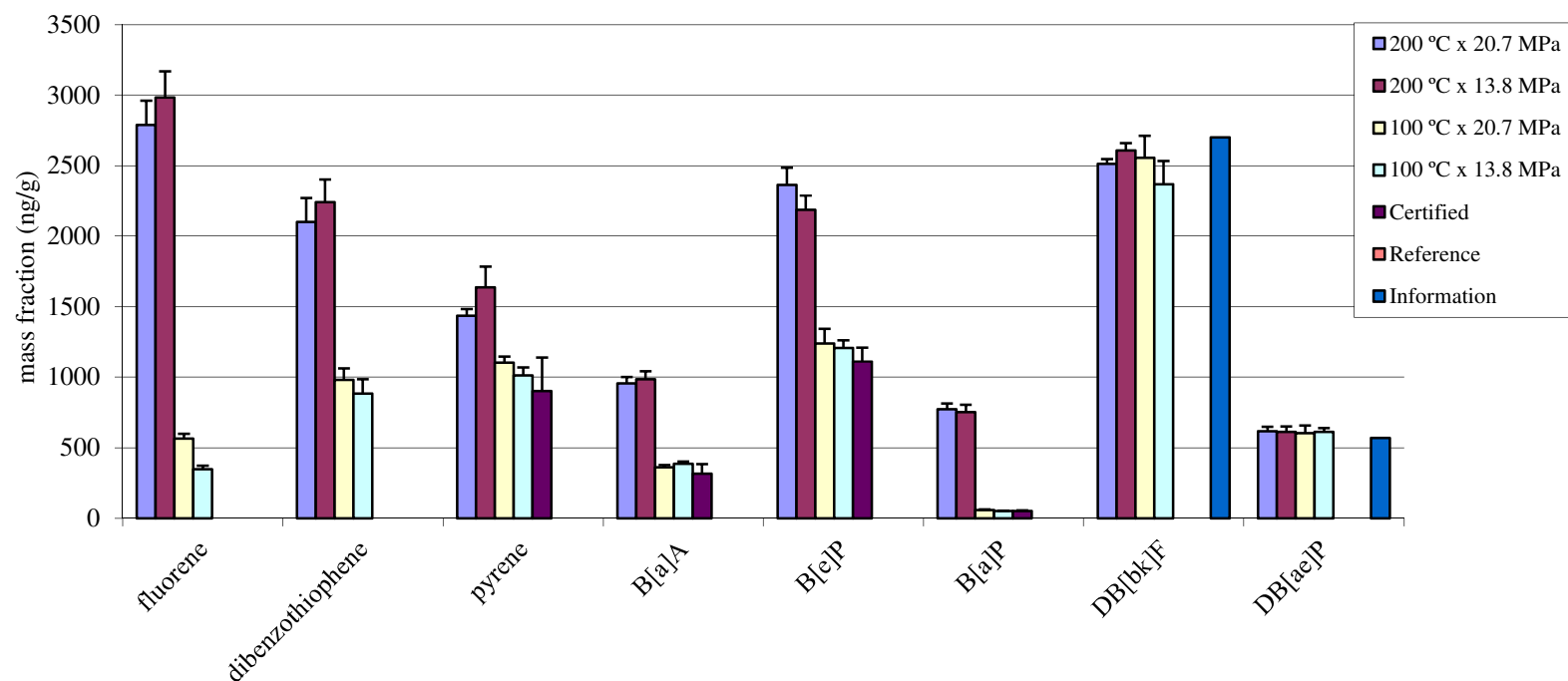


Figure S-3 (cont). Effect of PLE temperature and pressure for selected PAHs in SRM 2975. The error bars represent standard deviations for the data from this study and expanded uncertainties for the certified and reference values calculated as detailed in the Certificate of Analysis for SRM 2975 [3]