Determination of Thiaarenes and Polycyclic Aromatic Hydrocarbons in Workplace Air of an Aluminum Reduction Plant

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Quantitation of a variety of tetra-, penta-, and hexacyclic aromatic sulfur heterocycles (thiaarenes) in workplace air of an an aluminum reduction plant has been made by help of gas chromatography with atomic emission detection (GC-AED). Personal exposure to those thiaarenes and to polycyclic aromatic hydrocarbons depending on work categories has been evaluated. Summarized concentrations of the thiaarenes investigated have been found to be 0.4–19.0 μg/m^3. When using sulfur selective AED, samples could be analyzed without a prior separation of the thiaarenes from the PAH. The present data indicate a contribution of thiaarenes to the overall toxicity of coal tar pitch volatiles in this work environment.

Introduction

Sulfur containing polycyclic aromatic hydrocarbons (thiaarenes or PASH) are a known class of environmental contaminants. Thiaarenes, being present in matter of fossil origin as coal or mineral oil or derived products, are liberated into ambient air by combustion processes. Due to their chemical stability they are further distributed to other environmental compartments. Thiaarenes have been found to be generally more acute toxic than their analogous polycyclic aromatic hydrocarbons (PAH) (*1*). Some thiaarene compounds are potent mutagens and carcinogens (*2*–*6*). In different studies indications were found that thiaarenes increase the carcinogenic potential of environmental matter (*7, 8*). Fractions of PAH consisting of four to seven condensed rings that contained thiaarenes have shown a significantly increased cancerogenic activity compared to other sulfur free PAH fractions (*9*). For determination of thiaarenes in the environment, analyses have been made on matter from aquatic environment (*10*–*14*), on plants (*15*), on exhausts from combustion processes (*16*–*19*), and on ambient air (*20, 21*).

References that focus on the occurrence of thiaarenes in occupational environment have rarely been published (*22*). This may be due to lower concentrations involved in comparison to those of abundant PAH. According to the toxicological data available thiaarenes may contribute to health risks in several workplace environments that are known for high exposures to PAH (*23*–*29*) as e.g. tar, pitch, or asphalt production and handling, coke production, or aluminum reduction. However, an extensive quantification of thiaarenes has not yet been reported for any of the named work environments. Mutagenicity tests of indoor air samples from an aluminum reduction plant showed that a considerable part of the mutagenic activity originated from compounds not yet identified, beside contributions from PAH and nitrogen containing PAH (*27, 29*). Consequently, additional analytical data are needed to support assessments of human health risks at workplaces exposed to coal tar pitch volatiles. These data should include the class of thiaarenes.

The aim of this study was therefore to specify concentrations of individual thiaarenes in workplace air for the first time. The study is based on analytical methods described by the authors and on the recent finding of a large variety of thiaarenes present in the indoor air of an aluminum reduction plant (*30, 35*). Analyses were made in order to achieve thiaarene and PAH profiles according to different work categories. Particular attention was given to quantify tetra-, penta-, and hexacyclic thiaarenes due to findings about the toxicological impact of these species (*6*–*9*). The method used may be applicable as well for the analysis of these thiaarenes in ambient air or in other work environments.

Experimental Section

Chemicals. All PASH standards used were synthezised (*31*) or achieved from other laboratories. PAH standards were achieved from Larodan (Malmö, Sweden). All solvents (from Merck, Darmstadt, Germany or from Rathburn, Walkerburn, Scotland) were of analytical grade and were freshly distilled.

Sampling. Air sampling was performed with personal samplers, which has previously been described (*32*). The sampler holder is made of anodized aluminum. A 25 mm binder free A/E borosilicate glass fiber filter (Gelman Sciences, Ann Arbor, MI), and two 15 × 15 mm cylindrical polyurethane foam (PUF) plugs (Specialplast, Gillinge, Sweden) were used to trap the particulate and the semivolatile associated fractions, respectively. Air was pumped through the sampler using a battery-operated personal sampler pump (224-PCXR7, SKC, Eighty Four, PA). The flow rate was set to 1.5 L/min, and samples were collected during a working day (480 min), yielding a total air volume of 0.72 m^3. The second PUF plug was used to control the breakthrough of the sampling system. In each case of the sampling, breakthrough into the second plug was found to be less than 4% for phenanthrene, less than 2% for pyrene, and <1% for benzo[*a*]pyrene. Personal sampling was performed at different locations in two electrolysis halls of an aluminum reduction plant. Seventeen sampling intervals were performed during a period of about two months. Sample holders were placed in the respiratory zone. When protective masks were used, the sample holder was placed outside of the masks. Sixteen air samples were selected randomly for the analysis of thiaarenes from a pool of 94 samples, and all samples were taken for the analysis of PAH with regard to different work categories. The samples have been analyzed with respect to concentrations of individual PAH and thiaarene components and with respect to summarized concentrations (further named as total concentrations).

Extraction and Cleanup. Glass fiber filters and polyurethane foams were Soxhlet-extracted for 15 h in 50 mL of dichloromethane; the time of one extraction cycle was 1.5–2.0 min. For analysis of PAH, 2,2′-binaphthyl was added as internal standard prior to the extraction. For analysis of thiaarenes, an internal standard (benzo[1,2]phenaleno[4,3-*bc*]thiophene) was added after extraction. Two aliquots of

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10.1021/es981151t CCC: $18.00

TABLE 1. Total Concentrations of Thiaarenes and PAH (in μg/m^3) for Different Work Categories and Partition of Thiaarenes and PAH between the Semivolatile Phase and the Particulate Phase.

sample work category		thiaarenes			PAH		
		Σ (tot)	Σ (part)	Σ (gas)	Σ (tot)	Σ (part)	Σ (gas)
1	bolt screwing	6.2	5.1	1.1	94	30	64
2	oven operation/ burner sweeping	2.5	2.0	0.5	51	19	32
3	tapping	0.4	0.4		16	5	11
4	tapping	3.9	3.5	0.4	46	30	16
5	supervising	2.1	1.9	0.2	21	11	10
6	briquetting	4.7	4.1	0.6	53	29	24
7	bolt screwing	10.6	10.0	0.6	106	67	39
8	coordinating	4.0	3.5	0.5	53	36	17
9	metal transport	3.2	2.7	0.5	34	20	14
10	as sample 2	5.4	4.5	0.9	88	26	62
11	driving of anode material	4.8	4.4	0.4	57	39	18
12	mass filling/anode press driving	19.0	17.3	1.7	298	270	28
13	lubricating	8.3	7.0	1.3	118	69	49
14	as sample 2	9.0	8.3	0.7	182	51	131
15	blasting	3.4	3.0	0.4	53	22	31
16	oxide car driving	14.4	12.8	1.6	195	98	97

[a] Σ(tot): total concentration of the whole sample. Σ(part): total concentration of the particulate associated fraction. Σ(gas): total concentration of the semivolatile associated fraction.

TABLE 2. Distribution of Thiaarene Compounds between the Semivolatile and the Particulate Associated Fraction of Sample 1 (Concentrations in ng/m^3)

RI	compound[c]	particulate	semivolatile
348.2	phenanthro[4,5-*bcd*]thiophene	122	427
353.0	phenanthro[4,5-*bcd*]thiophene, meth	*b*	11
362.2	phenanthro[4,5-*bcd*]thiophene, meth	*b*	18
366.2	phenanthro[4,5-*bcd*]thiophene, meth	*b*	13
369.0	phenanthro[4,5-*bcd*]thiophene, meth	*b*	6
369.9	phenanthro[4,5-*bcd*]thiophene, meth	*b*	5
388.7	benzo[*b*]naphtho[2,1-*d*]thiophene	2361	317
392.2	benzo[*b*]naphtho[1,2-*d*]thiophene	305	58
395.2	benzo[*b*]naphtho[2,3-*d*]thiophene	529	48
402.6	$C_{16}H_{10}$S-thiaarene, meth	132	7
404.5	$C_{16}H_{10}$S-thiaarene, meth	92	10
405.0	$C_{16}H_{10}$S-thiaarene, meth	150	*b*
406.3	$C_{16}H_{10}$S-thiaarene, meth	17	*b*
407.4	$C_{16}H_{10}$S-thiaarene, meth	*b*	*b*
408.2	$C_{16}H_{10}$S-thiaarene, meth	34	*b*
408.5	$C_{16}H_{10}$S-thiaarene, meth	33	*b*
410.3	$C_{16}H_{10}$S-thiaarene, meth	41	*b*
410.9	$C_{16}H_{10}$S-thiaarene, meth	18	*b*
431.5	$C_{18}H_{10}$S-thiaarene	21	*b*
436.0	benzo[*b*]phenanthro[4,5-*bcd*]-thiophene	122	*b*
438.9	$C_{18}H_{10}$S-thiaarene	52	*b*
440.2	$C_{18}H_{10}$S-thiaarene	163	*b*
441.3	pyreno[1,2-*b*]thiophene	15	*b*
442.2	chryseno[4,5-*bcd*]thiophene	207	*b*
442.7	$C_{18}H_{10}$S-thiaarene	50	*b*
444.8	$C_{18}H_{10}$S-thiaarene	28	*b*
446.6	pyreno[2,1-*b*]thiophene	*b*	*b*
447.4	$C_{18}H_{10}$S-thiaarene	23	*b*
474.8	$C_{20}H_{12}$S-thiaarene	163	*b*
480.1	$C_{20}H_{12}$S-thiaarene	61	*b*
480.6	benzo[*b*]phenanthro[3,4-*d*]-thiophene	60	*b*
482.3	benzo[*b*]phenanthro[2,1-*d*]-thiophene	51	*b*
483.5	dinaphtho[2,1-*b*:2′3′-*d*]-thiophene	173	*b*
485.4	$C_{20}H_{12}$S-thiaarene	51	*b*
488.2	$C_{20}H_{12}$S-thiaarene	30	*b*
489.0	triphenyleno[2,1-*b*]thiophene	41	*b*
498.8	$C_{20}H_{12}$S-thiaarene	82	*b*
500.4	$C_{20}H_{12}$S-thiaarene	30	*b*
502.9	$C_{20}H_{12}$S-thiaarene	*b*	*b*
507.5	$C_{20}H_{12}$S-thiaarene	19	*b*

[a] RI: retention index according to ref 30. [b] <4 ng/m^3. [c] Methylated: meth.

5% of the extracts were preseparated in parallel on two open 60 mm × 6 mm i.d. glass columns packed with silica gel (0.063−0.2 mm, Merck, Darmstadt, Germany), which had been deactivated with 10% (w/w) of water. Eight milliliters of cyclohexane was used on each glass column to elute a fraction containing aliphatic compounds, mono- and dicyclic aromatic compounds, PAHs, and thiaarenes. The eluates were combined and narrowed nearly to dryness using a gentle stream of nitrogen and were taken up into about 0.5 mL *n*-pentane. After evaporation to a volume of about 100 μL, each sample was injected into the backflush-HPLC system described below. The time of flow reversal (3.0 min) was selected by evaluation of the elution time of anthracene and setting the time according to the start of the elution of the anthracene peak. The sampling interval for the backflush peak (between 5.0 and 9.0 min) was ascertained by using a set of standard compounds containing four to six condensed rings. For PAH analysis, the solutes were then transferred on-line to a connected GC setup equipped with a flame ionization detector (*33*). For GC-AED analysis, the backflush fraction was taken up, narrowed, and analyzed subsequently. Cleanup recoveries were investigated to be in the range of 97−100% in previous investigations (*30*).

Instrumentation. *HPLC.* The setup consisted of a Varian 9001 HPLC pump (Varian, Walnut Creek, CA), a Marathon autoinjector (Spark Holland, Emmen, Netherlands) which had a Rheodyne 7010 injector (Rheodyne, Cotati, CA) with a 100 μL injection loop, and a Hitachi L4000 UV detector (Merck-Hitachi, Germany) at 254 nm wavelength. The HPLC column used (10 cm × 4.6 mm) was packed with nitrophenylpropyl silica (Macherey-Nagel, Düren, Germany) of 5 μm particle size. As mobile phase *n*-pentane was taken, with a flow rate of 1 mL/min. The column was connected to the injector and the detector via a four-port switching valve to enable backflush of the mobile phase.

GC-AED. The setup used for PASH analysis has been described elsewhere in detail (*30, 34*). Analysis was performed using an HP Model 5890 Series II gas chromatograph (Hewlett-Packard, Avondale, PA) coupled to an HP 5921A atomic emission detector (AED). The gas chromatograph was equipped with an HP 7673 A automatic sample injector and an HP on-column injection inlet. This was fitted with a deactivated retention gap (0.4 m × 0.53 mm i.d., Hewlett-Packard) connected in series to a HP-5 fused silica column (50 m × 0.32 mm i.d., 0.5 μm film, Hewlett-Packard). The GC column was connected to the AED cavity by help of a piece of DB-5 fused silica column column (1 m × 0.25 mm i.d., 0.1 μm film, J&W Scientific, Folsom, CA). Helium of 99.9999% purity was used as a carrier gas at a linear velocity of 0.3 m/s. The detector was operated at the emission wavelengths of 193 nm (carbon) and 181 nm (sulfur) for selective detection. Makeup gas flow through the cavity was set to 30 mL/min for optimal sulfur response. Samples of 1 μL were injected on-column.

TABLE 3. Concentrations of Thiaarenes in Indoor Air Samples (in ng/m^3) of an Aluminum Melting Facility

		samples															
RI	compound[b]	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
348.2	phenanthro[4,5-*bcd*]thiophene	549	395		125	36	97	400	208	91	750	409	1333	892	376	364	1238
353.0	phenanthro[4,5-*bcd*]thiophene, meth	11						11			12		76	24			
362.2	phenanthro[4,5-*bcd*]thiophene, meth	18			14			17			20	9	89	31			138
366.2	phenanthro[4,5-*bcd*]thiophene, meth	13			17			13			10		89	43			115
369.0	phenanthro[4,5-*bcd*]thiophene, meth	6											52	24			84
369.9	phenanthro[4,5-*bcd*]thiophene, meth	5											42	14	10		82
379.7	phenanthro[4,5-*bcd*]thiophene, meth												26	13	40		
388.7	benzo[*b*]naphtho[2,1-*d*]thiophene	2678	883	346	1808	985	1971	4352	1825	1681	2432	1867	7053	2656	4315	1372	6928
392.2	benzo[*b*]naphtho[1,2-*d*]thiophene	363	132	47	275	160	287	621	358	201	339	261	1132	420	615	207	1008
395.2	benzo[*b*]naphtho[2,3-*d*]thiophene	577	208	80	365	268	402	1135	361	267	506	473	1912	824	1028	288	1629
402.6	$C_{16}H_{10}S$-thiaarene, meth	140	52		89	34	66	213	78	65	125	97	331	180	235	81	367
404.5	$C_{16}H_{10}S$-thiaarene, meth	102	85	101	72	36	72	188	58	57	104	78	169	121	189	40	275
405.0	$C_{16}H_{10}S$-thiaarene, meth	150	68		105	97	209	364	112	123	146	116	346	219	252	89	424
406.3	$C_{16}H_{10}S$-thiaarene, meth	17			16		28	60	24	24	35	29	93	59	52	15	103
407.4	$C_{16}H_{10}S$-thiaarene, meth												62	42	38		69
408.2	$C_{16}H_{10}S$-thiaarene, meth	34	13		36	13	49	105	34	32	42	39	174	83	83	30	149
408.5	$C_{16}H_{10}S$-thiaarene, meth	33	14		24	10	26	54	34	21		33	138	78	74	21	137
410.3	$C_{16}H_{10}S$-thiaarene, meth	41	20		32	9	39	61	29	13	31	39	178	71	66	22	115
410.9	$C_{16}H_{10}S$-thiaarene, meth	18	9		15		19	39	15	7	14	19	81	48	41		80
431.5	$C_{18}H_{10}S$-thiaarene	21	10		12		21	53	15	10	10	28	106	63	33	10	41
436.0	benzo[2,3]phenanthro[4,5-*bcd*]thio	122	46		75	34	119	289	78	49	63	145	586	350	131	66	160
438.9	$C_{18}H_{10}S$-thiaarene	52	13		20	12	33	106	24	8	11	29	174	67	35	26	46
440.2	$C_{18}H_{10}S$-thiaarene	163	77		104	45	132	264	83	86	115	126	505	173	198	111	195
441.3	pyreno[1,2-*b*]thiophene	15	12									15	59	23	31		
442.2	chryseno[4,5-*bcd*]thiophene	207	89		121	55	192	397	112	94	125	174	811	278	235	125	229
442.7	$C_{18}H_{10}S$-thiaarene	50	15		29		59	132	29			39	272	108			
444.8	$C_{18}H_{10}S$-thiaarene	28	12		17	11	30	54	24	19	21	36	115	51	31	15	33
446.6	pyreno[2,1-*b*]thiophene												55				
447.4	$C_{18}H_{10}S$-thiaarene	23	11		17	10	29	107	20	14	16	29	149	67	65	13	40
474.8	$C_{20}H_{12}S$-thiaarene	163	71	27	110	51	153	266	93	71	104	126	522	204	180	103	160
480.1	$C_{20}H_{12}S$-thiaarene	61	25		43	23	59	133	39	33	42	48	208	94	62	37	57
480.6	benzo[*b*]phenanthro[3,4-*d*]thiophene	60	28		35	17	50	107	29	32	42	39	161	94	52	31	57
482.3	benzo[*b*]phenanthro[2,1-*d*]thiophene	51	20		35	17	71	160	39	30	42	58	252	137	45	37	57
483.5	dinaphtho[2,1-*b*:2′3′-*d*]thiophene	173	70		121	61	181	320	98	73	115	145	607	239	176	89	149
485.4	$C_{20}H_{12}S$-thiaarene	51	21		29	17	49	87	29	20	21	39	136	71	42	22	44
488.2	$C_{20}H_{12}S$-thiaarene	30	11		17		23	37	10			26	64	35	21	14	22
489.0	triphenyleno[2,1-*b*]thiophene	41	20		32	17	46	107	29	20	21	39	144	63	45	27	33
498.8	$C_{20}H_{12}S$-thiaarene	82	32		46	24	102	160	44	33	52	68	352	102	66	44	57
500.4	$C_{20}H_{12}S$-thiaarene	30	11		17		39	80	20	10	9	29	149	55	21		22
502.9	$C_{20}H_{12}S$-thiaarene							26					68	24			
507.5	$C_{20}H_{12}S$-thiaarene	19	9		14		47	53	15			29	161	63	18	13	20

[a] RI: retention index according to ref 30. [b] Methylated: meth.

TABLE 4. Concentrations of PAH in Indoor Air Samples (in μg/m^3) of an Aluminum Melting Facility

	samples															
compound	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
phenanthrene	33.1	16.8	5.7	8.4	4.7	13.7	21.9	9.4	7.6	27.7	11.6	33.6	30.6	74.4	18.5	72.4
anthracene	5.0	2.5	0.5	1.3	0.5	2.3	3.9	1.5	1.0	4.8	2.4	5.8	6.6	3.6	2.5	14.3
3-methylphenanthrene	2.1	1.1	0.3	0.6	0.5	0.9	1.3	0.6	0.7	2.1	0.7	2.1	1.1	4.4	1.0	3.7
2-methylphenanthrene	2.6	1.3	0.4	0.7	0.2	1.0	1.8	0.9	0.6	2.7	0.8	2.6	1.4	5.7	1.2	4.7
1+4-methylphenanthrene	2.5	1.2	0.3	0.7	0.2	1.0	2.2	0.8	0.5	2.5	0.8	3.7	3.0	4.2	1.0	5.4
1-methylphenanthrene	0.9	0.5	0.1	0.3	2.6	0.3	0.7	0.3	0.2	0.9	0.3	1.2	0.6	1.8	0.4	2.5
fluoranthene	12.8	6.3	2.1	5.3	2.2	4.9	11.7	8.3	3.8	14.1	5.8	33.4	12.2	37.9	5.7	21.1
pyrene	9.6	4.7	1.4	4.2	0.4	3.8	9.9	7.1	2.8	11.5	4.8	34.8	8.5	9.6	4.0	20.8
2-methylpyrene	0.1	0.1		0.2	0.0	0.1	0.3	0.2	0.1	0.2	0.2	1.3	0.3	0.3	0.1	1.0
benz[*a*]fluorene	0.5	0.3	0.1	0.7	0.2	0.5	1.7	0.9	0.3	0.5	0.7	5.7	1.6	0.9	0.3	3.3
4-methylpyrene	0.2	0.1	0.0	0.3	0.1	0.2	0.5	0.3	0.1	0.3	0.3	2.5	0.4	0.5	0.1	1.9
1-methylpyrene	0.1	0.1	0.0	0.2	0.1	0.1	0.4	0.3	0.1	0.2	0.2	1.9	0.3	0.4	0.1	1.6
benz[*a*]anthracene	2.7	1.8	0.5	3.1	1.2	3.0	7.6	3.6	1.8	3.1	3.9	22.6	7.0	5.7	2.0	10.5
chrysene/triphenylene	4.7	3.2	1.0	4.4	2.3	4.1	7.9	4.4	3.3	5.3	4.8	26.0	6.5	9.8	3.6	12.5
benzo[*a*+*b*]fluoranthene	5.1	3.3	1.1	4.7	2.1	4.6	8.6	4.1	3.6	3.9	5.2	31.9	9.3	8.2	3.9	7.1
benzo[*j*+*k*]fluoranthene	1.6	1.1	0.4	1.5	0.6	1.6	2.9	1.4	1.1	1.3	1.9	10.9	3.4	2.3	1.2	2.3
benz[*e*]pyrene	3.1	2.0	0.6	2.8	1.2	2.9	5.4	2.5	2.2	2.3	3.3	18.3	5.3	4.6	2.5	3.5
benz[*a*]pyrene	2.6	1.6	0.4	2.4	0.9	3.2	6.9	2.8	1.7	1.7	3.9	23.5	7.5	3.0	1.8	3.5
perylene	0.7	0.4	0.1	0.6	0.2	0.8	1.8	0.7	0.4	0.4	1.0	6.1	2.2	0.8	0.4	0.7
indeno[1,2,3-*cd*]pyrene	1.6	1.1	0.2	1.5	0.5	1.8	4.0	1.6	1.0	1.0	2.3	14.6	5.4	1.9	1.1	1.1
picene	0.3	0.2	0.1	0.3	0.1	0.3	0.6	0.3	0.2	0.2	0.4	2.1	0.6	0.4	0.3	0.3
benzo[*ghi*]perylene	1.8	1.1	0.3	1.6	0.7	1.9	3.7	1.6	1.2	1.0	2.2	13.6	4.5	1.9	1.2	1.1

LC-GC. An on-line LC-GC setup which has been described elsewhere in detail was used for PAH analysis (*35*). LC fractions were transferred on-line to a GC (Varian 3700, with flame ionization detection) equipped with an uncoated deactivated retention gap (3 m, 0.53 mm i.d.) connected in series to a precolumn (DB-5, 2 m, 0.32 mm I. D., 0.25 μm film, J&W Scientific, Folsom, USA). The outlet of the precolumn was connected both to a solvent vapor exit (uncoated fused silica, 0.2 m, 0.53 mm i.d.) and to an analytical column (DB-5, 28 m, 0.32 i.d., 0.25 mm film, J&W Scientific). Hydrogen was used as carrier gas at a linear velocity of 0.5 m/s. Chromatograms were registered, stored, and processed by ELDS Win chromatography data system system (Chromatography Data Systems, Svartsjö, Sweden).

Results and Discussion

Analysis of Thiaarenes. Using atomic emission detection (AED), quantitation of numerous thiaarenes of different molecular weight by one surrogate thiaarene reference compound can be performed with errors of 4−11%, due to a highly linear and compound independent response of the sulfur specific trace (*34*). With the reservation of the limited accuracy described, this enables the quantitation of a lot of tentatively identified thiaarenes for which reference standards are not available. Furthermore, concentrations of thiaarenes can be correlated with those of PAH that have been estimated by other means. In this study, up to 41 tetra-, penta-, and hexacyclic thiaarenes were quantified for the 16 indoor air samples selected. All thiaarenes investigated have recently been identified by gas chromatography−mass spectrometry, by using reference compounds and retention indices from literature (*30, 38*). The detection limit of the method applied was determined to be 4 ng/m^3. Prior to the measurements, the relative precision of 5-fold measurements of one sample was determined. It was found to be below 3% relative standard deviation for main components and below 25% for components present at the detection limit, both in thiaarene and PAH analyses. All samples were then measured once. Data on the selectivity and the linear range of detection have been published in former studies (*30, 34*). Total concentrations of the thiaarenes depending on the work category and the partition of the thiaarenes between the semivolatile associated phase and the particulate associated phase are given in Table 1.

The median total concentration of the 16 samples was 6.4 μg/m^3, with variations between 0.4 and 19.0 μg/m^3. This corresponds to 6.9% of the median total concentration of all polycyclic aromatic compounds estimated in this study. Thiaarenes associated to particulates amounted to 80−100% of the whole sample, with an average of 88%. This relatively high value indicates that an effective reduction of exposure to the thiaarenes investigated may be possible by using dust-protective respirator masks (*39*). A correlation of the exposures on thiaarenes and the work categories chosen showed no specificity because concentrations varied largely within the same work category as is described in the PAH analysis part. Furthermore, in the case of thiaarene analysis the number of investigations was too limited to correlate different levels of exposure to individual work categories. The distribution of thiaarenes between the semivolatile associated and the particulate associated fraction for one sample is given in Table 2. Distributions between both fractions varied otherwise only to a small extent for the other samples.

Concentrations of individual thiaarene compounds determined for different work categories are listed in Table 3.

Main groups of components were phenanthro[4,5-*bcd*]thiophene and benzonaphthothiophenes with their methylated species as well as thiaarenes with molecular weights of 258 and 284 Dalton. The pattern of thiaarenes found resembles those of other sulfur selective chromatograms from the analysis of coal related material reported earlier by Burchill (*36*), Grimmer (*17*), or other authors (*18, 19*). The three benzonaphthothiophene isomers account for 49−72% of the total concentration, with an average of 61%; the main benzo[*b*]naphtho[2,1-*d*]thiophene accounts for 36−52%, with an average of 44%. Twelve components, each contributing to the total sulfur response with ≥2%, amount to 81−91% to the total concentration. Methylated thiaarenes, derivatives of phenanthro[4,5-*bcd*]thiophene and the benzonaphthothiophene isomers, amount to 1−3% and 8−12%, respectively. Dimethylated species could not be detected in the samples. Similar thiaarene patterns were found in all cases. Due to the relatively small variations in relative concentration, benzo[*b*]naphtho[2,1-*d*]thiophene may serve as a marker for a screening of total thiaarene concentrations of a variety of samples such as used in this study.

Investigations on thiaarene concentrations should take compounds into consideration that are already known for

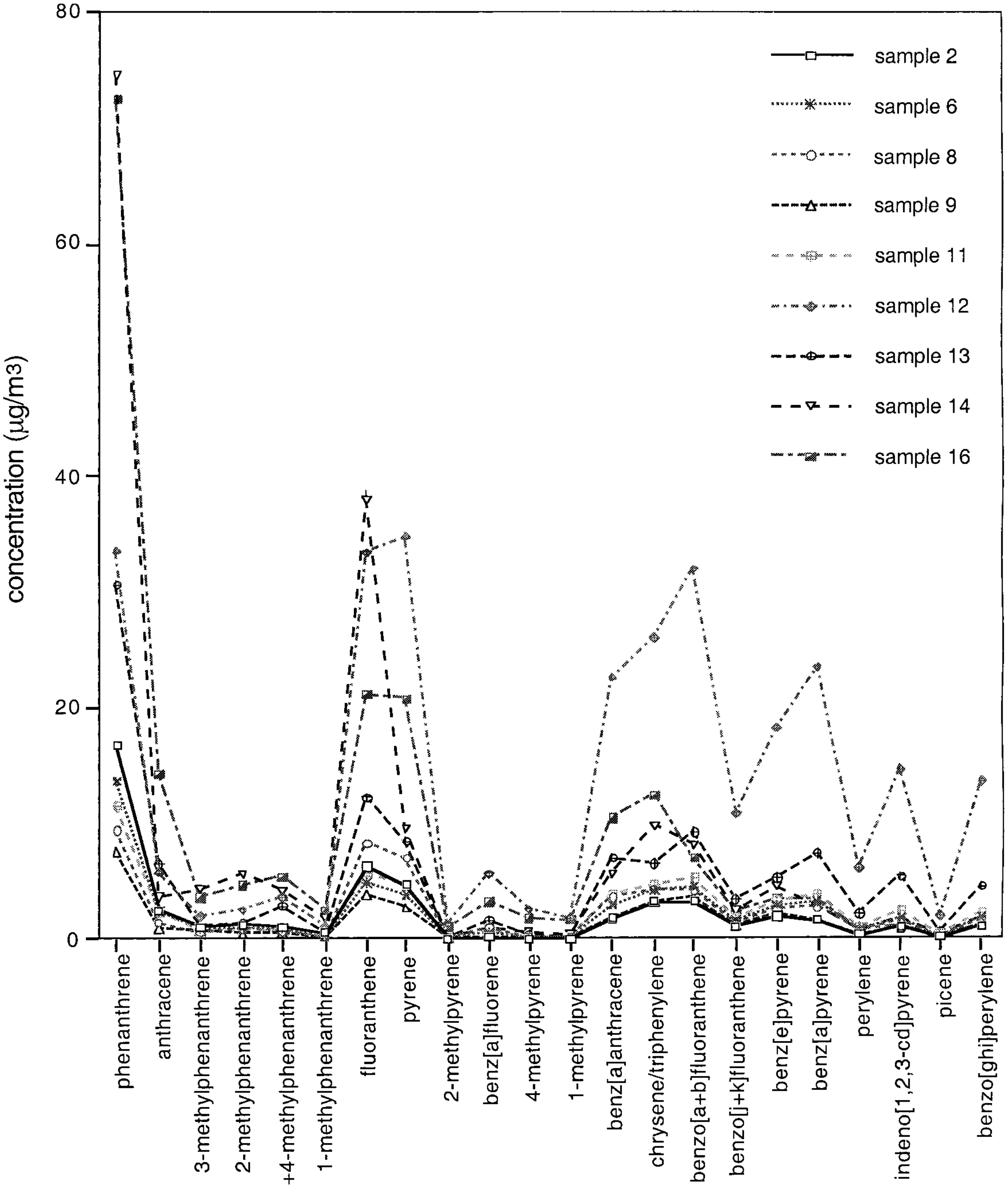

FIGURE 1. PAH profiles of indoor air samples from an aluminum reduction plant. Sample numbers refer to work categories listed in Table 1.

their mutagenic or cancerogenic activity. Components being relevant in our study were benzo[*b*]phenanthro[4,5-*bcd*]thiophene being present as a major component and known to exhibit a mutagenic activity higher than benzo[*a*]pyrene (*4*). The main component benzo[*b*]naphtho[2,1-*d*]thiophene whose sulfone metabolite is considered to be a potent mutagen (*37*) was found at high amounts in all samples, partly exceeding the environmental occupational exposure limit of 5 μg/m^3, set for benzo[*a*]pyrene in Sweden and Germany. Another mutagen, chryseno[4,5-*bcd*]thiophene (*5*) was found in almost all samples. The methylated benzonaphthothiophene isomers that are known to be mutagens (*6*) could not be determined due to the lack of reference standards in this study. Phenanthro[3,4-*b*]thiophene (*6*) was proved not to be present in the samples. Thiaarenes with carcinogenic activity being present were benzo[*b*]phenanthro[3,4-*d*]thiophene (*40*) and again benzo[*b*]naphtho[2,1-*d*]thiophene (*40*). Concentrations of the strongly cancerogenic dimethylated phenanthrothiophenes (*41*) were below the limit of detection. Dinaphtho[1,2-*b*:1′,2′-*d*]thiophene (*41*) could not be determined due to the missing reference standard. More reference standards would have been useful to achieve a comprehensive view on other thiaarenes that are known to be toxic from literature (*6*).

PAH Analysis. Twenty-two main PAH components amounting to about 70% of the total PAH content were also quantified by use of flame ionization detection. For this, the same samples that had been selected for thiaarene analysis have been taken to estimate PAH profiles and to correlate concentrations of PAH and thiaarenes. Detection limit for the quantification of PAH was determined to be 10−20 ng/m^3. All PAH investigated were identified earlier by gas chromatography−mass spectrometry. Coelution effects from minor components could be excluded since mass spectra of

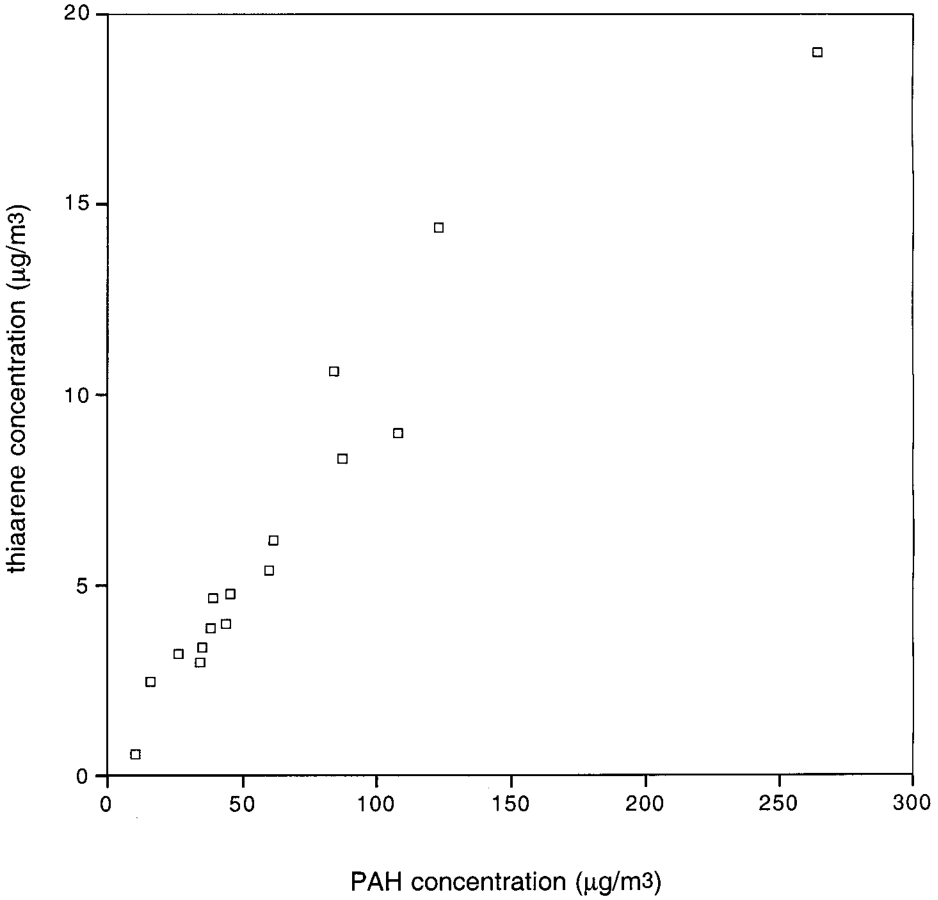

FIGURE 2. Correlation of PAH and thiaarene concentrations (µg/m^3) of indoor air samples from an aluminum reduction plant

the concerned PAH showed no interferences and since the samples were not complex with respect to possibly interfering alkylated PAH. The median total concentration of the 16 samples was 92 µg/m^3, with variations between 16 and 298 µg/m^3. The median concentration of benzo[*a*]pyrene was 4.2 µg/m^3, with 23.5 µg/m^3 at maximum. The total concentrations as well as partition of the PAH between the semivolatile associated and the particulate associated fraction are given in Table 1. PAH associated to particulates amounted generally to 29−68% of the total PAH content, with an average of 49%. This is less than found for the thiaarene fraction and may be explained by the exclusion of the three-ring thiaarenes in the cleanup procedure for thiaarene analysis when applying the same backflush conditions as for PAH analysis. Leaving the contribution of the three-ring PAH outside as has been done for the thiaarenes, the relative amounts of the particle-associated PAH were comparable to those values achieved for thiaarenes, varying between 56 and 99% with an average of 79%. Profiles of PAH determined for different work categories are shown in Table 4.

The profiles were found to be qualitatively comparable to each other suggesting the use of a marker substance for comprehensive monitoring as e.g. pyrene. The profiles were as well comparable with those that have been estimated earlier by Björseth (*25*) and Alfheim (*26*). Nine of 16 PAH profiles are visualized in Figure 1.

All 94 samples have been analyzed in order to evaluate exposures to PAH for different work categories. Thirty-one of them were obtained from individuals occupied with one work category, the other samples originated from multiple work categories. Based on samples that had been taken at the same time interval and in the same hall of the plant, single and multiple work categories showed a similar level of exposure, mostly deviating by less than a factor of 2 to the median of all categories. On the contrary, at each of the 17 sampling intervals concentrations in hall A of the plant were higher than in hall B, by a factor of 1.4 to 5.0, with an average factor of 2.6. Furthermore, day-by-day variations of concentrations were found for the same work category and the same hall during the sampling period: values averaged for all work categories varied in hall A between 34 and 87 ng/m^3 and in hall B between 12 and 82 ng/m^3.

By using a uniform cleanup procedure and two detection techniques both exhibiting a compound independent response, a direct correlation of PAH and thiaarene concentrations is possible. A correlation may be useful to confirm that relative contributions of thiaarenes to the overall exposure to polycyclic aromatic compounds are constant for different PAH concentrations.

Figure 2 which shows the correlation of PAH and thiaarene concentrations has been derived from values in Table 1. The coefficient of correlation was found to be 0.93 indicating a strong covariation of the PAH and thiaarene concentrations.

In conclusion, the present data suggest some major thiaarenes or their metabolites of known toxicity to be considered besides the commonly investigated PAH, when the overall toxicity of coal tar pitch volatiles is estimated. Estimation of those thiaarenes is facilitated by use of the atomic emission technique. Since toxicity of individual thiaarene compounds is known to vary greatly, it is necessary to identify more thiaarenes by the use of reference compounds.

Acknowledgments

We wish to thank Milton Lee and Curt White for providing several thiaarene standards. Ulrica Carstensen, University Hospital of Umeå, and Tohr Nilsson, Hospital of Sundsvall, are kindly acknowledged for taking the samples. Anita

Engqvist is kindly acknowledged for supporting the cleanup procedure. The study was supported by the Swedish National Institute for Working Life.

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Received for review November 9, 1998. Revised manuscript received January 28, 1999. Accepted February 4, 1999.

ES981151T