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# Determination of polycyclic aromatic sulfur heterocyclic compounds in airborne particulate by gas chromatography with atomic emission and mass spectrometric detection

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## Abstract

An analytical method is presented for the determination of tetra-, penta- and hexacyclic aromatic sulfur heterocyclic compounds (thiaarenes) in workplace air. Using a clean-up procedure for the isolation of polycyclic aromatic hydrocarbons and high-resolution gas chromatography with atomic emission detection, selective detection of thiaarenes was possible in the presence of abundant homocyclic aromatic hydrocarbons. Applying the method to an indoor air sample from an aluminium melting facility, more than 130 sulfur-containing components were detectable of which 53 components were identified as thiaarenes. Quantification of all identified thiaarenes by using one internal standard was possible due to the compound independent sulfur response of an atomic emission detector. The summarized concentration of all sulfur-containing polycyclic aromatic compounds isolated was found to be  $12 \mu\text{g}/\text{m}^3$ . © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Air analysis; Environmental analysis; Thiaarenes; Polynuclear aromatic hydrocarbons; Sulfur compounds

## 1. Introduction

Sulfur-containing polycyclic aromatic hydrocarbons (thiaarenes or PASHs) have been of concern for decades because they constitute a major class of ubiquitous 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 were found to be generally more acute toxic than their analogous homocyclic aromatic hydrocarbons (PAHs) [1].

Some thiaarene isomers are potent mutagens and carcinogens [2–5]. In different studies indications were found that thiaarenes may increase the carcinogenic potential of environmental matter [6,7]. So, fractions of PAHs consisting of four to seven condensed rings that contained thiaarenes have shown a significantly increased carcinogenic activity compared to other sulfur-free PAH fractions [8]. Chemical analysis of thiaarenes has been investigated extensively in order to characterize matter of fossil origin [9–27] or to develop methods of analysis [28–38]. Other objects have been used to investigate the degradation behaviour of thiaarenes [39–42] or their occurrence in different compartments in the environment [43–54]. Regarding the latter, investigations have been made on matter from aquatic

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environment [44–48], on effluents and exhausts from combustion processes [50–53] and to a lesser extent on ambient air [54,55]. References which focus on the occurrence of thiaarenes in occupational environment have rarely been published [56]. This may be due to lower concentrations involved in comparison to those of parent PAHs. However, thiaarenes can be expected to be present in several workplace environments that are known for high exposures to PAHs [57–62]. Therefore, an object of this study was to investigate the maximum thiaarene concentrations that may be found in one kind of workplace environment, the indoor air of an aluminium melting facility.

Being chemically very similar to their homocyclic analogues, thiaarenes have to be determined as selectively as possible. Clean-up procedures for the separation of thiaarenes from PAHs, based on oxidation–reduction processes [23,25] have been found to alter the composition of the samples due to the lack of selective oxidation–reduction [23,34]. On the other hand, chromatographic methods such as ligand exchange chromatography were not found to be suitable for a nondiscriminating class separation [21,34,35,63]. One approach that could avoid insufficient selectivity with respect to PAHs may be the application of high-resolution gas chromatography with a sulfur-specific, highly selective detector [24,34]. Several selective detection techniques are known to be suitable for the determination of thiaarenes [12,15,20–22,28,29,38]. Among them, techniques based on sulfur chemiluminescence detection (SCD) [29,38], atomic emission detection (AED) [14,15,29,53] or mass spectrometry (MS) [14,16,19,23–25,28,51] seem to be favourable tools showing a selective, sensitive and linear response. AED was used for quantification in the present study, since the linear dynamic range of AED has been found to be less compound dependent than the one of SCD [29] and MS [64,65]. Both the lack of synthesized thiaarene standards and the huge number of thiaarene isomers that may occur in environmental samples necessitate a detection technique that exhibits a response being as compound independent as possible, for quantification purposes. Recently, it has been shown for an atomic emission detector, that quantification of numerous thiaarene isomers of different molecular mass by one surrogate thiaarene reference compound can be performed with errors of

a few percent, due to a highly linear and compound independent response of the sulfur specific trace [66]. With the reservation of the limited accuracy described, this finding may enable the successful quantification of a lot of tentatively identified thiaarene isomers by AED for which reference standards are not available. Additionally, a more reliable estimation of the total amount of thiaarenes in a sample may be possible. In consequence, this would enable one to correlate total amounts of thiaarenes with those of parent PAH that have been estimated by other means. As an additional detection technique, complementary to AED, MS with electron impact (EI) and with negative ion chemical ionization (NICI) was applied for tentative identification.

The aim of this study has been to present an analytical method for the determination of thiaarenes occurring in workplace air by means of GC–AED and GC–MS. Various thiaarene isomers that originate from coal tar pitch have been quantified for the first time. The investigation focuses on the isolation, identification and quantification of tetra-, penta- and hexacyclic thiaarenes, based upon findings about the toxicological impact of these fractions of thiaarenes [6–8]. As an application, two indoor air samples from an aluminium melting facility have been analyzed. The results of the analysis are compared with data from literature.

## 2. Experimental

### 2.1. Instruments and techniques

#### 2.1.1. Gas chromatography–atomic emission detection

Analysis was performed using an HP Model 5890 Series II gas chromatograph (Hewlett-Packard, Avondale, PA, USA) coupled to an HP 5921A atomic emission detector. 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 (1 m×0.25 mm

I.D., 0.1  $\mu\text{m}$  film, J & W Scientific, Folsom, CA, USA). Helium of 99.9999% purity was used as a carrier gas at a linear velocity 0.30 m/s. The GC–AED system was controlled by an HP 9000 Chem-Station. The detector was operated at the emission wavelengths of 193 nm (carbon) and 181 nm (sulfur) for selective detection, with reagent gases recommended by the manufacturer. All detector parts were heated to 320°C. The reagent gases hydrogen and oxygen were kept at a pressure of 70 p.s.i. and 30 p.s.i., respectively (1 p.s.i.=6894.76 Pa). Nitrogen was used as spectrometer purge gas at a flow of 2 l/min. Make-up gas flow through the cavity was set to 30 ml/min for optimal sulfur response. The solvent venting time was 4.2 min. One  $\mu\text{l}$  of sample was injected on-column. The GC oven temperature was set to 35°C for 2 min, increased to 160°C at a rate of 25°C/min and followed by a program ramp of 3°C/min to 300°C final temperature, which was kept for 50 min.

### 2.1.2. Mass spectrometry

An Incos 50 quadrupole mass spectrometer (Finnigan MAT, San Jose, CA, USA) connected to a Varian 3400 gas chromatograph (Varian, Palo Alto, CA, USA) equipped with a HP-5 column (50 m  $\times$  0.32 mm I.D., 0.17  $\mu\text{m}$  film, Hewlett-Packard) was used in EI and NICI modes for complementary solute identification. Chemical ionization (CI) was achieved by using methane of >99.995% purity. The electron energy was set to 70 eV (EI) or 110 eV (NICI). Analyses were performed in both full-scan and selected ion monitoring (SIM) mode. The scan range was  $m/z$  45–330 with a scan cycle time of 0.6 s. For SIM analyses the mass of the  $\text{CHS}^+$  ion ( $m/z$  45) was investigated for selective detection of sulfur containing compounds. Otherwise, masses of the single or double charged molecular ions ( $\pm 1$  u) of the thiaarenes and some of their mono-methylated forms were investigated (molecular masses 198, 212, 234, 248, 258, 272 and 284).

### 2.1.3. Liquid chromatography

For sample clean-up a Varian 9001 high-performance liquid chromatography (HPLC) pump (Varian, Walnut Creek, CA, USA) was used together with a Marathon autoinjector (Spark Holland, Emmen, Netherlands) which contained a Rheodyne 7010

injector (Rheodyne, Cotati, CA, USA) with a 100  $\mu\text{l}$  injection loop. The HPLC column used (75 mm  $\times$  4.6 mm) was packed with nitrophenylpropyl silica (Macherey–Nagel, Düren, Germany) of 5  $\mu\text{m}$  particle size. As mobile phase *n*-pentane was taken, with a flow-rate of 1.0 ml/min. The column was connected to the pump and the detector via a four-port switching valve to enable backflush of the column [67]. Detection was done by a Hitachi L4000 UV detector (Merck–Hitachi, Germany) at 254 nm wavelength. Chromatograms were registered, stored and processed by an Elds 900 chromatography data system (Chromatography Data Systems, Svartsjö, Sweden).

## 2.2. Chemicals

All thiaarene standards used were synthesized [68] or obtained from other laboratories. All solvents (from Merck or Rathburn) were of analytical grade and were freshly distilled.

## 2.3. Sampling

Air sampling was performed with a personal sampler, which has previously been described [69]. The sampler holder is made of anodized aluminium. A 25-mm binder free A/E borosilicate glass fiber filter (Gelman Sciences, Ann Arbor, MI, USA), and two 15  $\times$  15 mm cylindrical polyurethane foam (PUF) plugs (Specialplast, Gillinge, Sweden) were used to trap the particulate and the semi-volatile associated fractions, respectively. Air was pumped through the sampler using a battery-operated personal sampler pump (224-PCXR7, SKC, Eighty Four, PA, USA). 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<sup>3</sup>. Personal sampling was performed in the electrolysis hall of an aluminium reduction plant.

## 2.4. Clean-up

The glass fibre 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 min. After extraction, aliquots (200  $\mu\text{l}$ ) were taken and an internal standard (benzo[1,2]phenaleno[4,3-

*bc*]thiophene) was added. Each aliquot was divided into two portions and pre-separated 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 ml of cyclohexane was used as solvent on each glass column. The fractions eluted contained 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 0.5 ml *n*-pentane. After evaporation to a volume of about 100  $\mu$ l, each sample was injected into the HPLC system described above. The time of flow reversal at 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 standard of thiaarene compounds containing four to six condensed rings. The backflushed fraction was collected and subsequently analyzed by GC–AED.

## 2.5. Evaluation

### 2.5.1. Clean-up recoveries

Six thiaarene standard compounds of different molecular masses were used for recovery tests of the clean-up. The clean-up steps, pre-fractionation on deactivated silica gel and pre-separation by nitrophenylpropyl silica gel, were treated together. Recoveries were obtained by using a recovery standard consisting of three thiaarenes each closely eluting to the six thiaarenes that were to be examined. In order to test the recoveries, solutions containing the six thiaarene standards were prepared by submitting them to chromatography on deactivated silica gel and then injecting them into the HPLC system, once with and once without a column, collecting the effluent and then adding the recovery standard. This was done in order to correct for the actual volume of the sample. Each recovery test and each mixing of reference solutions, standard plus recovery standard, was made nine-fold. Concentrations of the individual compounds in the different solutions were 50–100 ng/ $\mu$ l, and 100  $\mu$ l per solution was used in the tests. Yields were determined by use of the AED sulfur trace.

### 2.5.2. Quantification

Quantitative data from indoor air samples were obtained using the AED sulfur trace. For quantification of both the minor and the major components, an appropriate amount of internal standard was chosen. The concentrations of the identified thiaarenes were estimated by relating their response to the response of the internal standard (I.S.). The concentrations of all detected but unidentified sulfur containing polycyclic aromatic compounds were estimated by the same way. One particular indoor air sample that has been known to contain high concentrations of homocyclic PAHs was chosen from a series of different indoor air samples for quantification of thiaarenes.

## 3. Results and discussion

### 3.1. Clean-up

HPLC using nitrophenylpropyl silica gel has been applied successfully for the selective enrichment of PAHs consisting of three and more condensed rings, from complex urban air samples [70]. The above described isolation procedure may be applicable also for the selective enrichment of corresponding thiaarenes. To ensure non-discriminating isolation of thiaarenes by this polar bonded phase, recovery tests were performed in this study. This may allow a comparison with other polar bonded phases tested earlier with regard to recoveries of thiaarenes [71]. As can be seen from Table 1, liquid chromatography using nitrophenylpropyl silica gel yields quantitative recoveries for the thiaarenes that contain four and more condensed rings. However, the methylated dibenzothiophene was largely excluded from the fraction, eluting earlier than thiaarenes consisting of more than three rings.

Fig. 1 illustrates the chromatographic pre-fractionation of different kinds of thiaarenes used in the recovery tests. The peaks under hump B were the reference compounds to recover quantitatively, peak A contained the methylated dibenzothiophene.

### 3.2. Identification

In an indoor air sample of an aluminium melting

Table 1  
Recoveries (%) of the clean-up of selected thiaarene reference compounds

Name	$M_r$	Height/area	R.S.D. (%)
3-Methyldibenzothiophene	198	4/5	3.0/3.0
Benzo[ <i>b</i> ]naphto[2,3- <i>d</i> ]thiophene	234	101/99	2.4/1.6
Benzo[2,3]phenanthro[4,5- <i>bcd</i> ]thiophene	258	97/99	3.1/0.6
Benzo[1,2]phenaleno[4,3- <i>bc</i> ]thiophene	258	97/97	1.9/1.0
Benzo[ <i>b</i> ]phenanthro[3,4- <i>d</i> ]thiophene	284	97/99	1.9/0.7
Triphenyleno[2,3- <i>b</i> ]thiophene	284	99/97	3.6/1.8

$M_r$ =Molecular mass; Height/area=intergration mode applied; R.S.D.=relative standard deviation for nine measurements.

facility, over 130 sulfur-containing polycyclic aromatic components were detected. As the complex chromatogram of Fig. 2 shows, mainly five groups of components could be classified: phenanthro[4,5-*bcd*]thiophene and benzonapthothiophenes with their methylated species as well as thiaarenes with molecular masses of 258, 284 and components exceeding 284.

With the clean-up procedure applied, no interferences from PAHs were observed on the sulfur-selective line of the AED system. This was examined by monitoring the AED carbon-selective line. A selective determination of thiaarenes was thus possible and a laborious procedure for the separation of thiaarenes from abundant PAHs was not required. On

the other hand, the selectivity of the high-resolution GC column was inadequate to resolve all thiaarene isomers. For 16% of the components, marked coelution hampered integration and proper identification. Otherwise, about 80% of the components were resolved at resolution factors of 0.8 and about 50% were resolved at resolution factors of 1 or higher. 39% of all components have been identified by comparison with reference standards, by means of GC-MS or by comparison of their retention data with data from literature. The chromatogram in Fig. 2 exhibits a pattern which is comparable to those patterns found in other sulfur-specific chromatograms from the analysis of coal related material reported earlier by Burchill et al. [24], Grimmer et al. [51] or other authors [52,53]. In this study, numerous minor components, as e.g., components with molecular masses exceeding 284, were detected additionally due to the high sensitivity of the AED system. An enhanced resolution was achieved as well, being essential for quantification of individual components. Table 2 gives information about thiaarenes identified and quantified, retention times, retention indices, molecular masses, concentrations and how the components were identified.

GC-MS was used in the SIM mode throughout to provide sufficient sensitivity. Using EI for ionization, intensities of the ion currents corresponded sufficiently well with the intensities of the AED sulfur-selective responses for most components to correlate both techniques directly for identification purposes (see Figs. 3 and 4). Yet, intensities achieved by EI-MS were sufficient only for the identification of some major components.

Application of NICI with methane as ionizing agent made identification of minor components possible. As can be seen from Figs. 3 and 4,

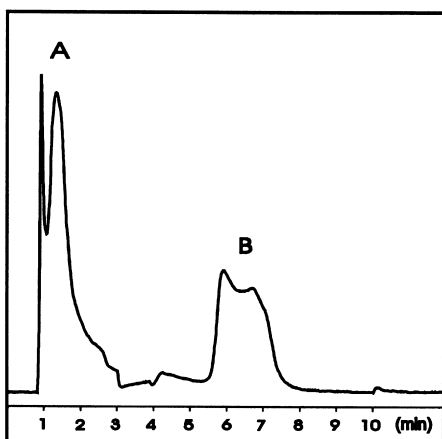


Fig. 1. Liquid chromatographic separation of thiaarene standard compounds on nitrophenylpropyl silica gel; peak A contains the test compound 3-methyldibenzothiophene, hump B contains the test compounds benzo[*b*]naphto[2,3-*d*]thiophene, benzo[2,3]phenanthro[4, 5-*bcd*]thiophene, benzo[1, 2]phenaleno[4, 3-*bc*]thiophene, benzo[*b*]phenanthro[3,4-*d*]thiophene and triphenyleno[2,3-*b*]thiophene.

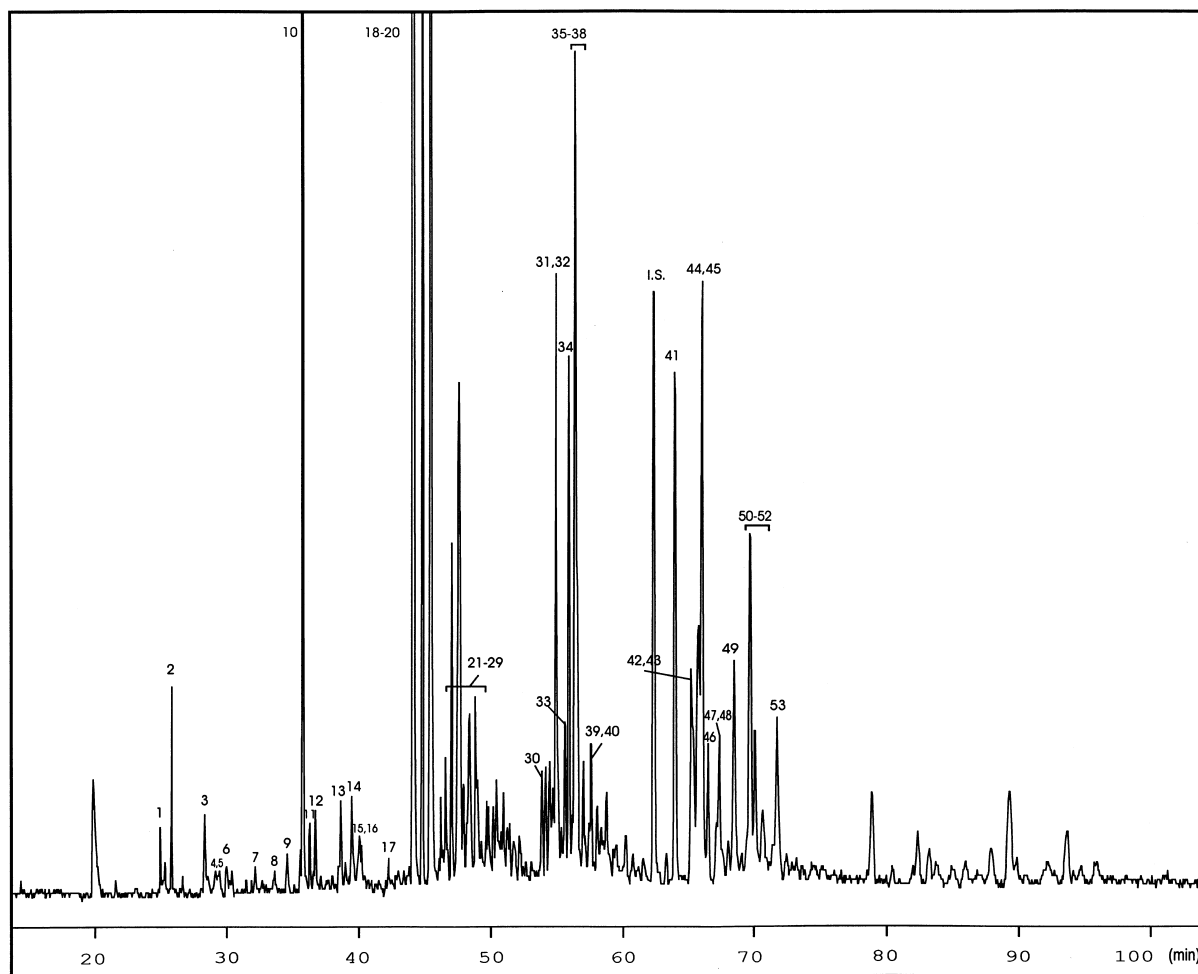


Fig. 2. Sulfur-selective GC–AED chromatogram of sulfur-containing polycyclic aromatic compounds in indoor air of an aluminium reduction plant. For peak identification see Table 2.

ionization yields in the NICI mode differ from those in the EI mode and from signals on the AED sulfur-selective trace. Therefore, a comparison of EI and NICI data was necessary prior to a correlation of NICI data with the sulfur-selective chromatogram of the AED system.

### 3.3. Quantification

Based on a sampling volume of  $0.7 \text{ m}^3$ , the minimum detectable level of the method was  $4 \text{ ng/m}^3$  of a component when using AED (signal-to-noise ratio of 3). Although exhibiting a significantly

higher sensitivity of detection than AED, NICI-MS could not be applied for quantification because its response was found to be largely compound dependent. Applying a second sample for quantification, the thiaarenes identified have been quantified by help of the I.S. benzo[1,2]phenaleno[4,3-*bc*]thiophene. In an earlier investigation concerning the quantification of thiaarenes by application of the AED technique, a reliable quantification of numerous thiaarenes with different molecular masses was possible when this I.S. was used [66]. Unidentified minor components were assumed to be sulfur-containing polycyclic aromatic compounds, based on the selectivity of the

Table 2

List of thiaarenes identified and quantified in indoor air of an aluminium melting facility

No.	$t_R$ (min)	RI	$M_r$	Compound	ID	Conc.
1	25.00	295.7	184	Dibenzothiophene	Lit	24
2	25.89	300.0	184	Naphto[2,1- <i>b</i> ]thiophene	Lit	30
3	28.33	311.8	198	4-Methyldibenzothiophene <sup>a</sup>	Lit	<4
4	29.18	316.0	198	2- and 3-Methyldibenzothiophene	Lit	<4
5	29.47	317.4	198	4-Methylnaphto[2,1- <i>b</i> ]thiophene	Lit	<4
6	30.01	320.0	198	1-Methyldibenzothiophene <sup>b</sup>	Lit	<4
7	32.18	330.6	212	Dibenzothiophene, dimethylated	Lit	<4
8	33.68	337.9	212	Dibenzothiophene, dimethylated	Lit	<4
9	34.64	342.6	212	Dibenzothiophene, dimethylated	Lit	<4
10	35.81	348.2	208	Phenanthro[4,5- <i>bcd</i> ]thiophene	MS	355
11	36.35	350.9	222	Phenanthro[4,5- <i>bcd</i> ]thiophene, methylated	Lit	22
12	36.78	353.0	222	Phenanthro[4,5- <i>bcd</i> ]thiophene, methylated	Lit	24
13	38.67	362.2	222	Phenanthro[4,5- <i>bcd</i> ]thiophene, methylated	Lit	31
14	39.49	366.2	222	Phenanthro[4,5- <i>bcd</i> ]thiophene, methylated	Lit	43
15	40.08	369.0	222	Phenanthro[4,5- <i>bcd</i> ]thiophene, methylated	Lit	24
16	40.25	369.9	222	Phenanthro[4,5- <i>bcd</i> ]thiophene, methylated	Lit	14
17	42.28	379.7	222	Phenanthro[4,5- <i>bcd</i> ]thiophene, dimethylated	Lit	13
18	44.13	388.7	234	Benzo[ <i>b</i> ]naphto[2,1- <i>d</i> ]thiophene	Std	2749
19	44.84	392.2	234	Benzo[ <i>b</i> ]naphto[1,2- <i>d</i> ]thiophene	Std	456
20	45.46	395.2	234	Benzo[ <i>b</i> ]naphto[2,3- <i>d</i> ]thiophene	Std	1092
21	47.05	402.6	248	C <sub>16</sub> H <sub>10</sub> S-thiaarene, methylated	MS	216
22	47.50	404.5	248	C <sub>16</sub> H <sub>10</sub> S-thiaarene, methylated	MS	436
23	47.61	405.0	248	C <sub>16</sub> H <sub>10</sub> S-thiaarene, methylated	MS	77
24	47.93	406.3	248	C <sub>16</sub> H <sub>10</sub> S-thiaarene, methylated	MS	71
25	48.20	407.4	248	C <sub>16</sub> H <sub>10</sub> S-thiaarene, methylated	MS	76
26	48.37	408.2	248	C <sub>16</sub> H <sub>10</sub> S-thiaarene, methylated	MS	79
27	48.45	408.5	248	C <sub>16</sub> H <sub>10</sub> S-thiaarene, methylated	MS	76
28	48.87	410.3	248	C <sub>16</sub> H <sub>10</sub> S-thiaarene, methylated	MS	176
29	49.02	410.9	248	C <sub>16</sub> H <sub>10</sub> S-thiaarene, methylated	MS	150
30	53.87	431.5	258	C <sub>18</sub> H <sub>10</sub> S-thiaarene	MS	66
31	54.91	436.0	258	Benzo[2,3]phenanthro[4,5- <i>bcd</i> ]thiophene	Std	338
32	55.10	436.8	258	C <sub>18</sub> H <sub>10</sub> S-thiaarene	MS	51
33	55.61	438.9	258	C <sub>18</sub> H <sub>10</sub> S-thiaarene	MS	77
34	55.90	440.2	258	C <sub>18</sub> H <sub>10</sub> S-thiaarene	MS	208
35	56.16	441.3	258	Pyreno[1,2- <i>b</i> ]thiophene	Std	31
36	56.38	442.2	258	Chryseno[4,5- <i>bcd</i> ]thiophene	Std	274
37	56.50	442.7	258	C <sub>18</sub> H <sub>10</sub> S-thiaarene	MS	189
38	56.98	444.8	258	C <sub>18</sub> H <sub>10</sub> S-thiaarene	MS	51
39	57.41	446.6	258	Pyreno[2,1- <i>b</i> ]thiophene	Std	14
40	57.60	447.4	258	C <sub>18</sub> H <sub>10</sub> S-thiaarene	MS	62
41	64.06	474.8	284	C <sub>20</sub> H <sub>12</sub> S-thiaarene	MS	327
42	65.29	480.1	284	C <sub>20</sub> H <sub>12</sub> S-thiaarene	MS	113
43	65.42	480.6	284	Benzo[ <i>b</i> ]phenanthro[3,4- <i>d</i> ]thiophene	Std	187
44	65.82	482.3	284	Benzo[ <i>b</i> ]phenanthro[2,1- <i>d</i> ]thiophene	Std	223
45	66.09	483.5	284	Dinaphto[2,1- <i>b</i> :2'3'- <i>d</i> ]thiophene	Std	686
46	66.56	485.4	284	C <sub>20</sub> H <sub>12</sub> S-thiaarene	MS	133
47	67.20	488.2	284	C <sub>20</sub> H <sub>12</sub> S-thiaarene	MS	52
48	67.40	489.0	284	Triphenyleno[2,1- <i>b</i> ]thiophene	Std	164
49	68.51	493.7	284	C <sub>20</sub> H <sub>12</sub> S-thiaarene	MS	163
50	69.71	498.8	284	C <sub>20</sub> H <sub>12</sub> S-thiaarene	MS	206
51	70.09	500.4	284	C <sub>20</sub> H <sub>12</sub> S-thiaarene	MS	83
52	70.66	502.9	284	C <sub>20</sub> H <sub>12</sub> S-thiaarene	MS	59
53	71.74	507.5	284	C <sub>20</sub> H <sub>12</sub> S-thiaarene	MS	137

No.=Number of compound;  $t_R$ =retention time (min); RI=retention index according to Refs. [30,66];  $M_r$ =molecular mass; ID=identification done by: Lit=literature data, Std=reference standard, MS=mass spectrometry; Conc.=concentration (ng/m<sup>3</sup>); <sup>a</sup> coeluting with 2-methylnaphto[2,1-*b*]thiophene; <sup>b</sup> coeluting with 8-methylnaphto[2,1-*b*]thiophene.

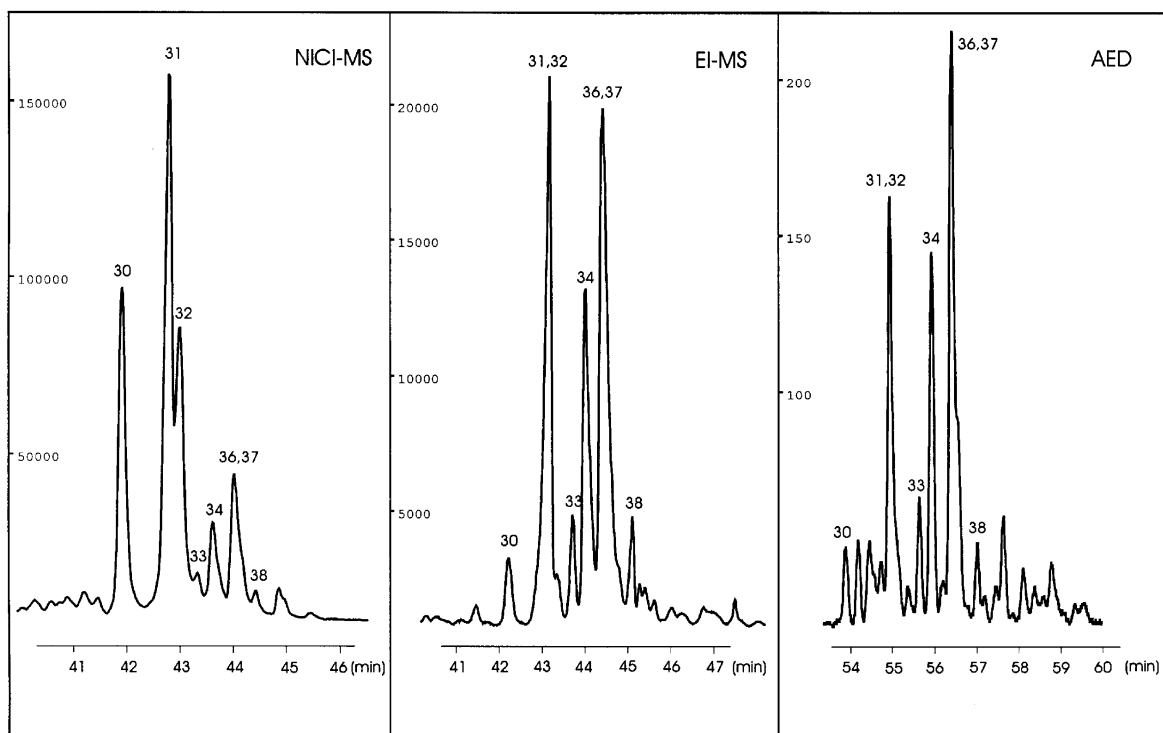


Fig. 3. GC–NICI-MS and GC–EI-MS ion currents (SIM mode) for components with the molecular mass of 258 and corresponding sulfur-selective GC–AED chromatogram. For peak identification see Table 2.

separation scheme applied. For the estimation of the sum of all sulfur containing heterocycles (total concentration), the unidentified components were quantified by the same way as the identified species. This procedure is based on the assumption that AED exhibits a molar and compound independent response not only for the thiaarenes investigated earlier, but for thiaarenes in general. The thiaarenes that have been identified amount to 88% of the sum of all sulfur containing heterocycles, yielding the specified concentration. These are listed in Table 2. The total concentration, based on 80 components present in the second sample, was  $11.5 \mu\text{g}/\text{m}^3$ . The three main benzonaphthothiophene isomers account for over 37% of the total concentration; 11 components, each contributing to the total sulfur response with more than 2%, amount to 62% to the total concentration. Groups of components derived from compounds with the molecular masses 234, 258, 284 and more than 284 amount to 52, 16, 22 and 5%, respectively to the total concentration.

Methylated thiaarenes, derivatives of phenanthro[4,5-*bcd*] thiophene and the benzonaphthothiophene isomers amount to 1 and 12%, respectively. Dimethylated species could not be detected in the samples. In an earlier study that used a comparable clean-up scheme, the two particular indoor air samples of this study have been investigated with respect to the quantification of homocyclic PAHs. The first sample, being used for identification in this study, showed three-times higher concentrations of homocyclic PAHs than did the second sample. In agreement to this, in the first sample significantly more thiaarenes could be detected. This indicates that even higher concentrations of thiaarenes may be present than quantified from the second sample. Further work will be made in order to correlate thiaarene concentrations with concentrations of PAHs that are present in the same sample. The results of this study demonstrate that the method presented is suitable for the determination of personal exposure to thiaarenes at levels in the work environment as low



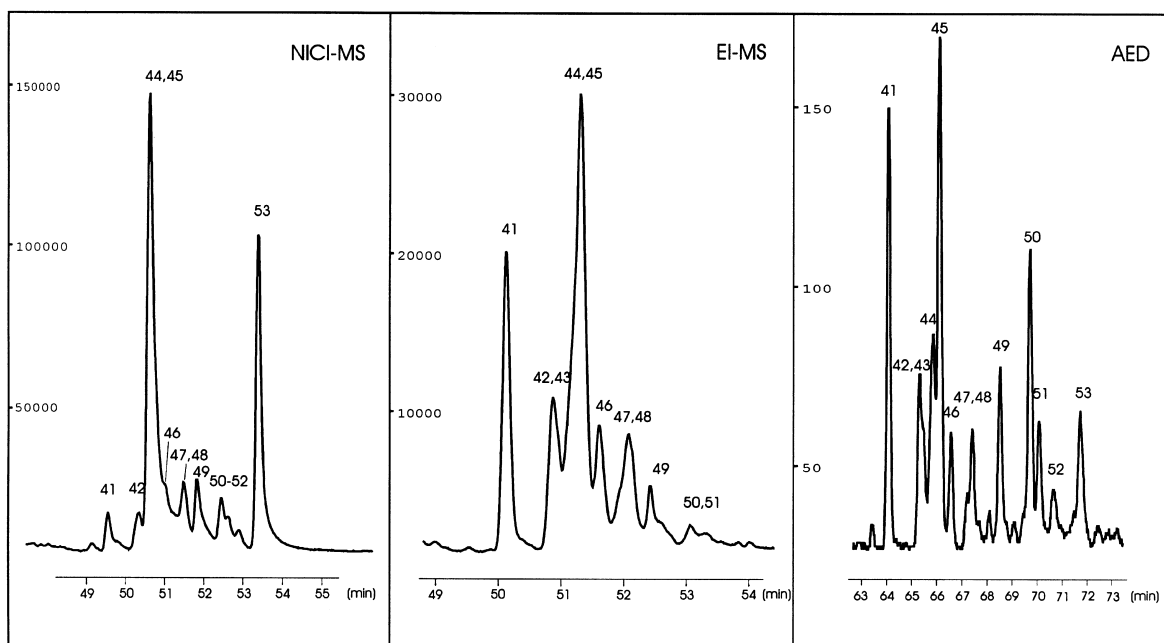


Fig. 4. GC–NICI-MS and GC–EI-MS ion currents (SIM mode) for components with the molecular mass of 284 and corresponding sulfur-selective GC–AED chromatogram. For peak identification see Table 2.

as a few  $\text{ng}/\text{m}^3$ , based on a sampling volume of less than  $1 \text{ m}^3$ .

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