

Identification and Determination of Highly Carcinogenic Dibenzopyrene Isomers in Air Particulate Samples from a Street Canyon, a Rooftop, and a Subway Station in Stockholm

CHRISTOFFER BERGVALL AND
ROGER WESTERHOLM*

Department of Analytical Chemistry, Arrhenius Laboratory,
Stockholm University, SE-10691 Stockholm, Sweden

This study presents determined levels of the highly carcinogenic dibenzopyrene isomers dibenzo(*a,l*)pyrene, dibenzo(*a,e*)pyrene, dibenzo(*a,i*)pyrene, and dibenzo(*a,h*)pyrene as well as three other polycyclic aromatic hydrocarbons (PAHs)—benzo(*a*)pyrene, perylene and coronene—in ambient particulate material samples from a street canyon, a rooftop, and an underground subway station in Stockholm, Sweden. To our knowledge, these are the first reported determinations of dibenzopyrene isomers in air particles from either Stockholm or a subway station. Taking into account both concentration and toxic equivalence factors (TEFs), the PAH with the highest carcinogenic potency in the analyzed samples was dibenzo(*a,l*)pyrene, and the sum carcinogenic potency of the determined dibenzopyrenes was about 1–4 times higher than that of benzo(*a*)pyrene in the analyzed samples. These findings indicate that it is important to analyze the dibenzopyrene isomers as well as benzo(*a*)pyrene; the common approach of using benzo(*a*)pyrene as an indicator substance could lead to underestimates of the potential carcinogenic potency of PAHs in ambient air. The results also indicate that the relative carcinogenic potency of the determined dibenzopyrenes and benzo(*a*)pyrene in air particles from Stockholm is similar to that of air particles sampled in Washington in 1976–1977, despite general improvements in air quality in the intervening period. However, more data are needed to characterize temporal variations in dibenzopyrene levels in locations such as subway stations, suburbs, road tunnels, and metropolitan areas. There is also a need to identify and characterize both stationary and mobile PAH sources with respect to emission of dibenzopyrene isomers.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds that are formed during the incomplete combustion of organic matter in air. Some PAHs are known to be carcinogenic to animals and are thus potentially carcinogenic to humans. The most well-known PAH is benzo(*a*)pyrene (B(*a*)P), which is classified by the International Agency for Research on Cancer (IARC) in group 1, i.e., as

* Corresponding author phone: +46-8-162440; fax: +46-8-156391; e-mail: roger.westerholm@anchem.su.se.

TABLE 1. Sample Descriptions

sample site, year	start day/month, time	stop day/month	sampling time hh:min	abbrev
rooftop, 2005	4/10, 12:32	5/10	23:51	A1
rooftop, 2005	5/10, 12:29	6/10	24:27	A2
rooftop, 2005	6/10, 13:06	7/10	24:23	A3
rooftop, 2005	7/10, 13:37	8/10	25:36	A4
rooftop, 2005	8/10, 15:32	10/10	42:41	A5
rooftop, 2005	10/10, 10:21	11/10	26:03	A6
rooftop, 2005	11/10, 12:31	18/10	168:02	A7
rooftop, 2005 ^a	18/10, 12:39	25/10	167:52	A8
rooftop, 2006	27/4, 15:21	3/5	168:08	A9
street canyon, 2003 ^a	7/7, 08:00	11/7	96:05	H1
street canyon, 2003 ^a	14/7, 08:25	18/7	97:05	H2
street canyon, 2003 ^a	21/7, 09:10	25/7	96:19	H3
subway station, 2003 ^a	10/6, 12:00	12/6	52:45	M1
subway station, 2003 ^a	12/6, 17:05	13/6	22:05	M2
subway station, 2003 ^a	23/6, 09:50	24/6	25:10	M3

^a Samples extracted with toluene. See the *Analysis, Identification, and Quantification* section for details.

carcinogenic to human beings (1). A way to compare PAHs with respect to cancer potency is to use Toxic Equivalence Factors (TEFs). The TEF of B(*a*)P is set to one by definition, while compounds with TEFs larger than one are more carcinogenic than B(*a*)P and vice versa. Some dibenzopyrenes have TEF values ranging from 1 to 100 (2), making them important from a health perspective. Furthermore, the dibenzopyrene isomers dibenzo(*a,l*)pyrene, dibenzo(*a,e*)pyrene, dibenzo(*a,i*)pyrene, and dibenzo(*a,h*)pyrene are considered to be potential human carcinogens by the U.S. Department of Health and Human Services (3). IARC classifies dibenzo(*a,l*)pyrene as probably carcinogenic to human beings (group 2A) and dibenzo(*a,i*)pyrene and dibenzo(*a,h*)pyrene as possibly carcinogenic to human beings (group 2B) (1). Furthermore, according to Platt et al. (4), dibenzo(*a,l*)pyrene is probably the most potent chemical carcinogen ever tested. Dibenzopyrene isomers have been identified and determined in diverse sample matrixes such as tar cork (5), coal tar (6, 7), cigarette smoke condensates (5), soils (8–10), sediments (6–9, 11), diesel particles (12–14), gasoline vehicle emissions (5), water samples (15), waste incinerator emissions (16), and working environments (13). Dibenzopyrene isomers have also been identified and determined in Standard Reference Material Urban Dust (SRM 1649; 1649a) (6, 7, 17, 18) and ambient air (19–21).

Historically B(*a*)P has been used as an indicator of carcinogenic PAHs in ambient air (2), as it is the most studied PAH in animal experiments (22). The World Health Organization (WHO) has published a unit risk estimate, based on studies of lung cancer risks in coke-oven workers, of 8.7 × 10⁻⁵ per ng/m³ of B(*a*)P (22).

However, the WHO guidelines state that “evaluation of, for example, B(*a*)P alone will probably underestimate the carcinogenic potential of airborne PAH mixtures, since co-occurring substances are also carcinogenic”. They also point out that this unit risk estimate is only valid as long as the relative PAH concentrations in the ambient air do not differ substantially from those in the coke-oven emissions. Boström

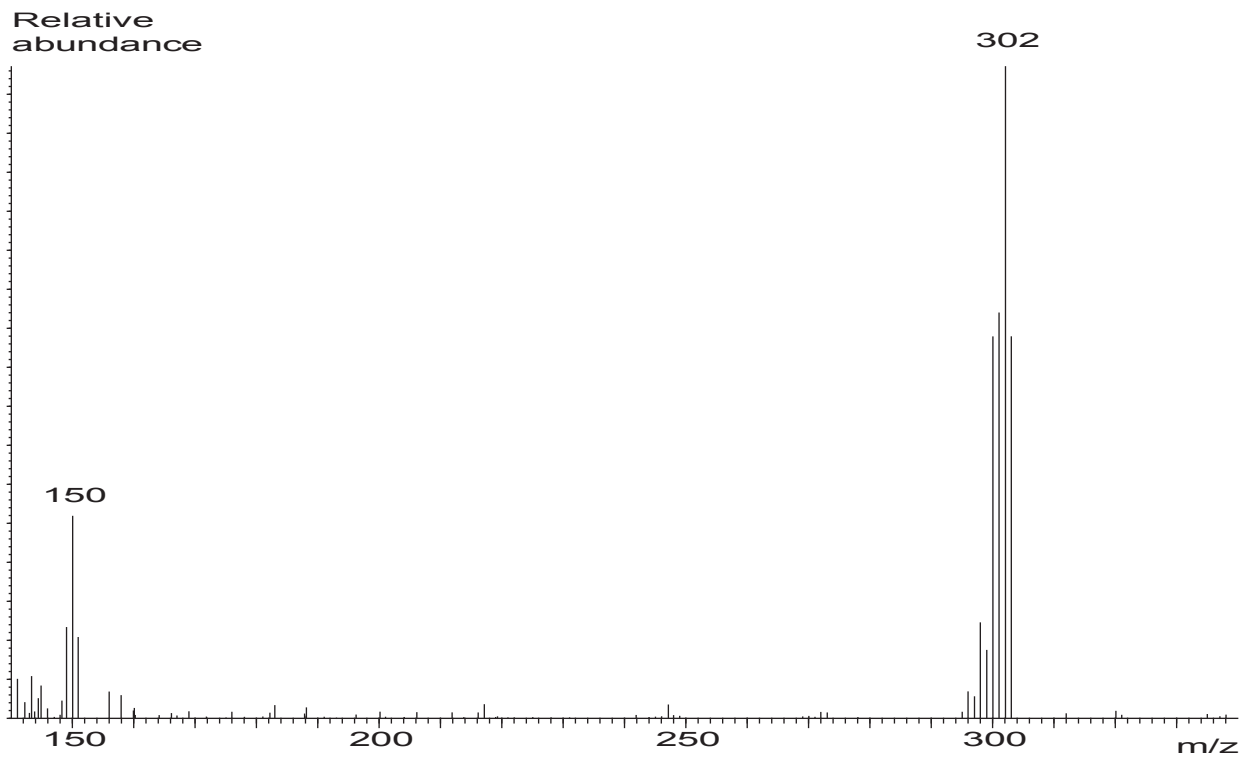


Figure 1 Full scan mass spectrum of peak 1 obtained from sample M3.

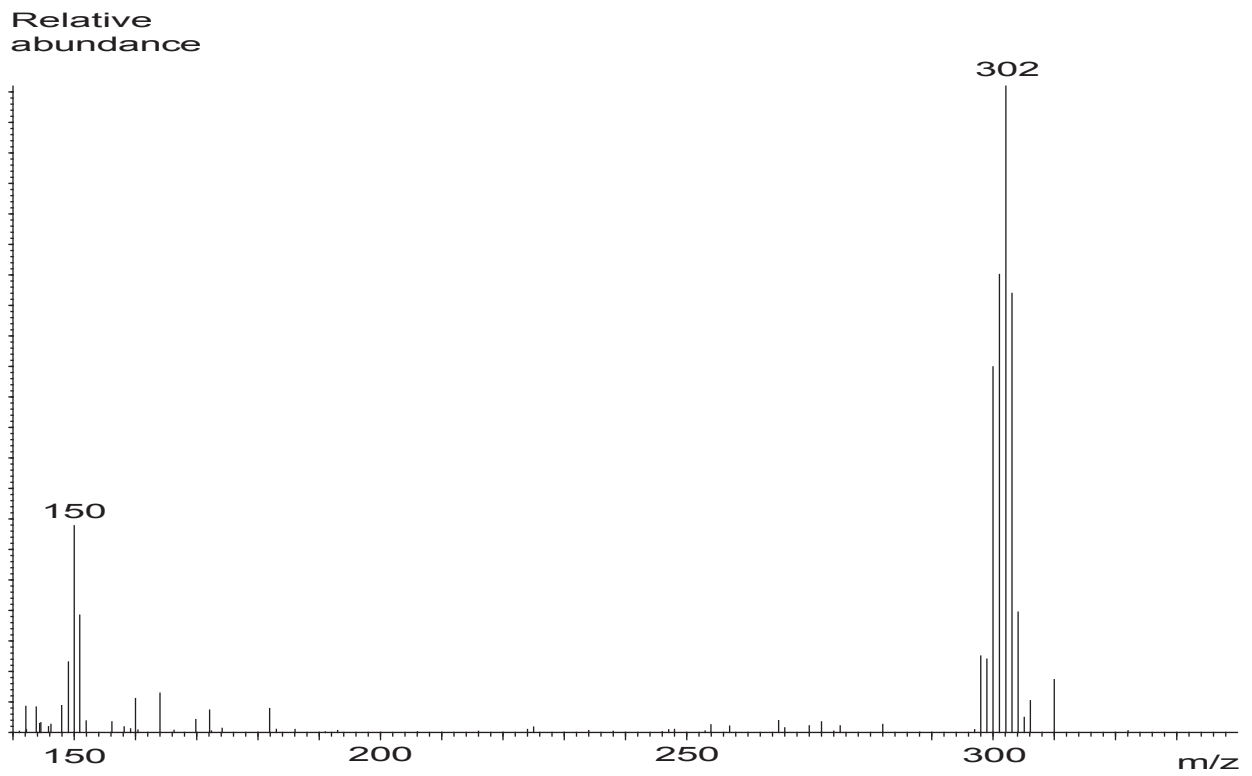


Figure 2 Full scan mass spectrum of peak 1 obtained from SRM 1649a.

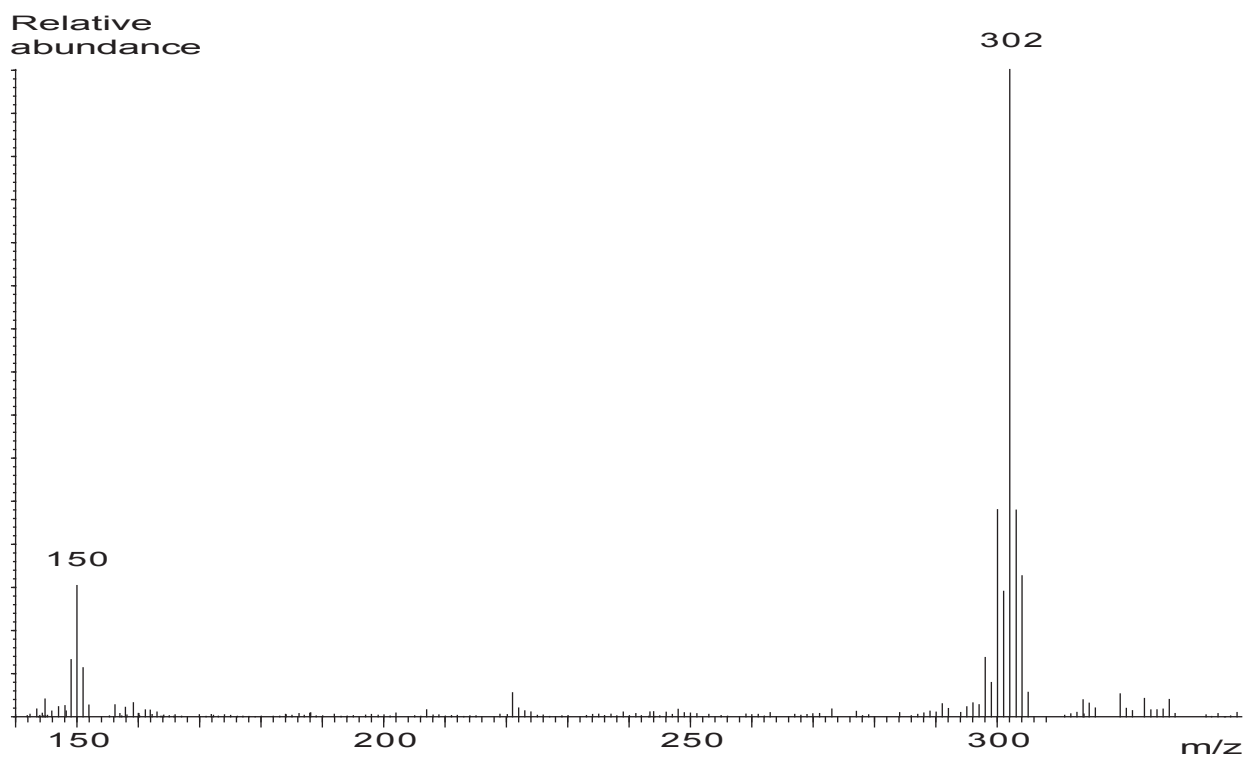


Figure 3 Full scan mass spectrum of peak 4 obtained from sample M3.

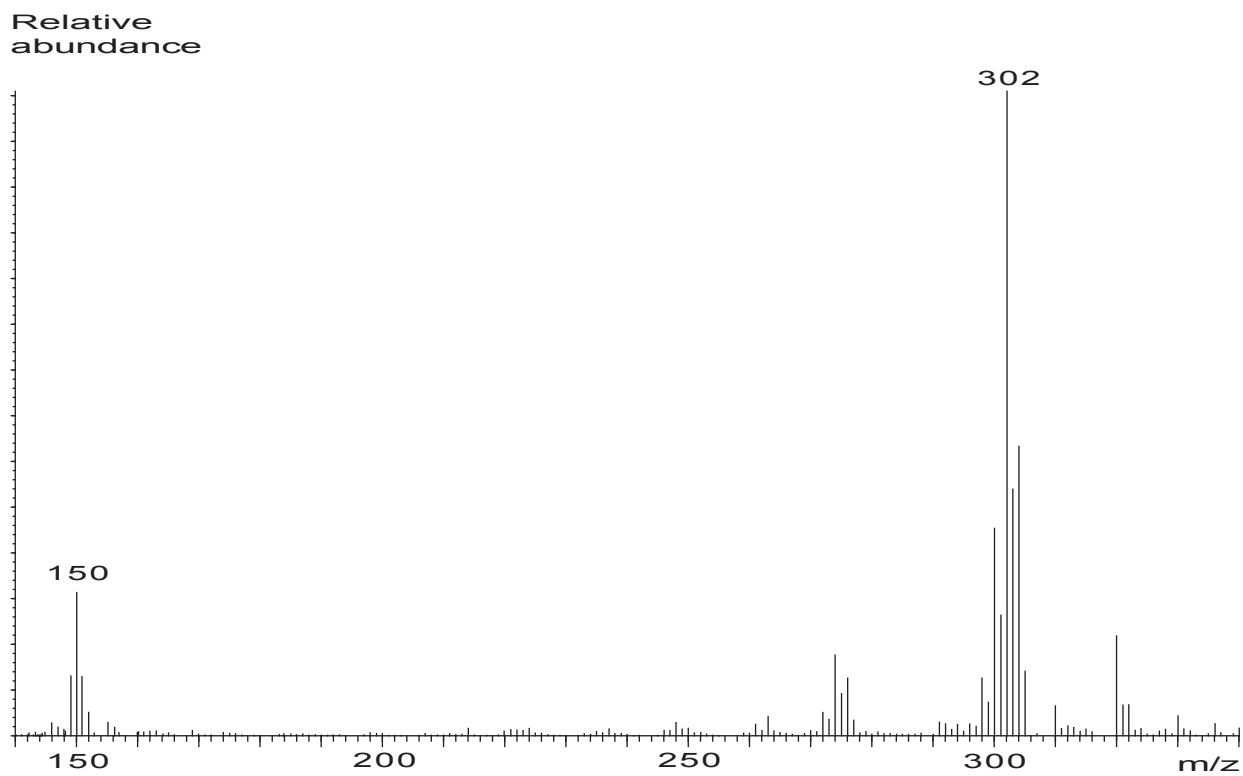


Figure 4 Full scan mass spectrum of peak 4 obtained from SRM 1649a.

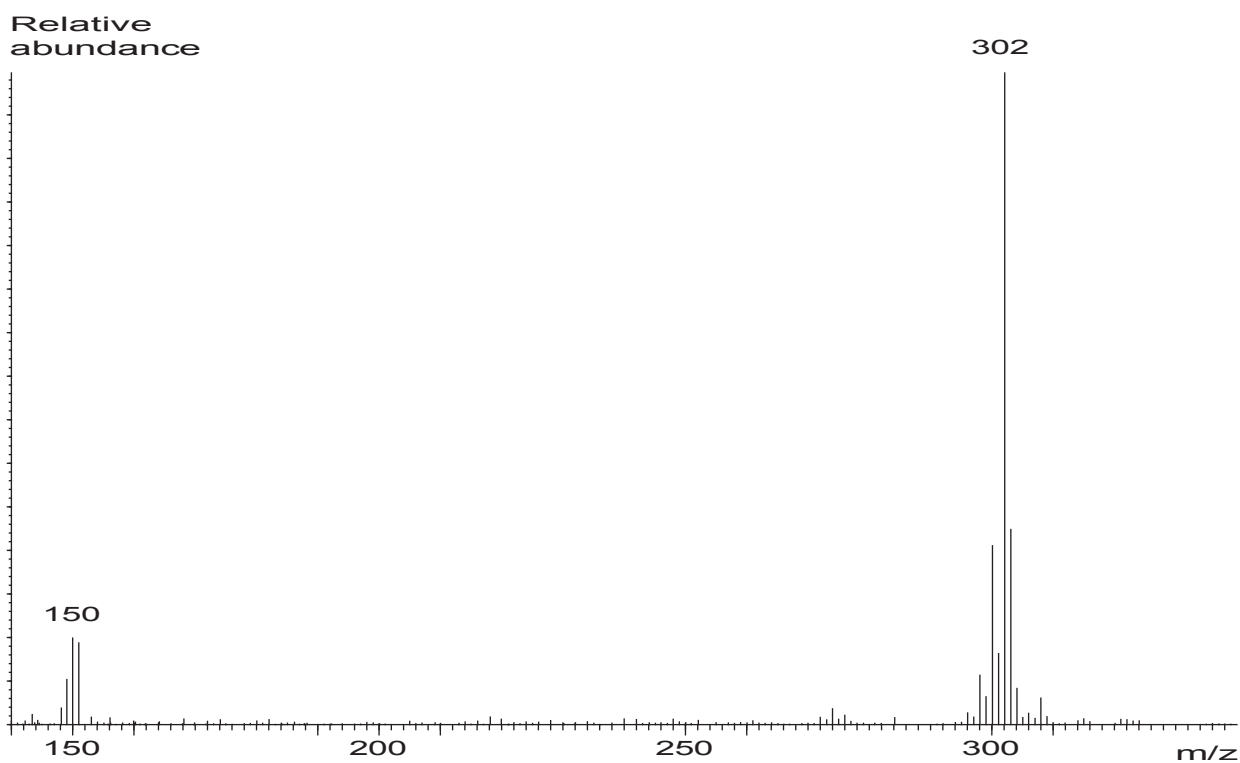


Figure 5 Full scan mass spectrum of peak 14 obtained from sample M3.

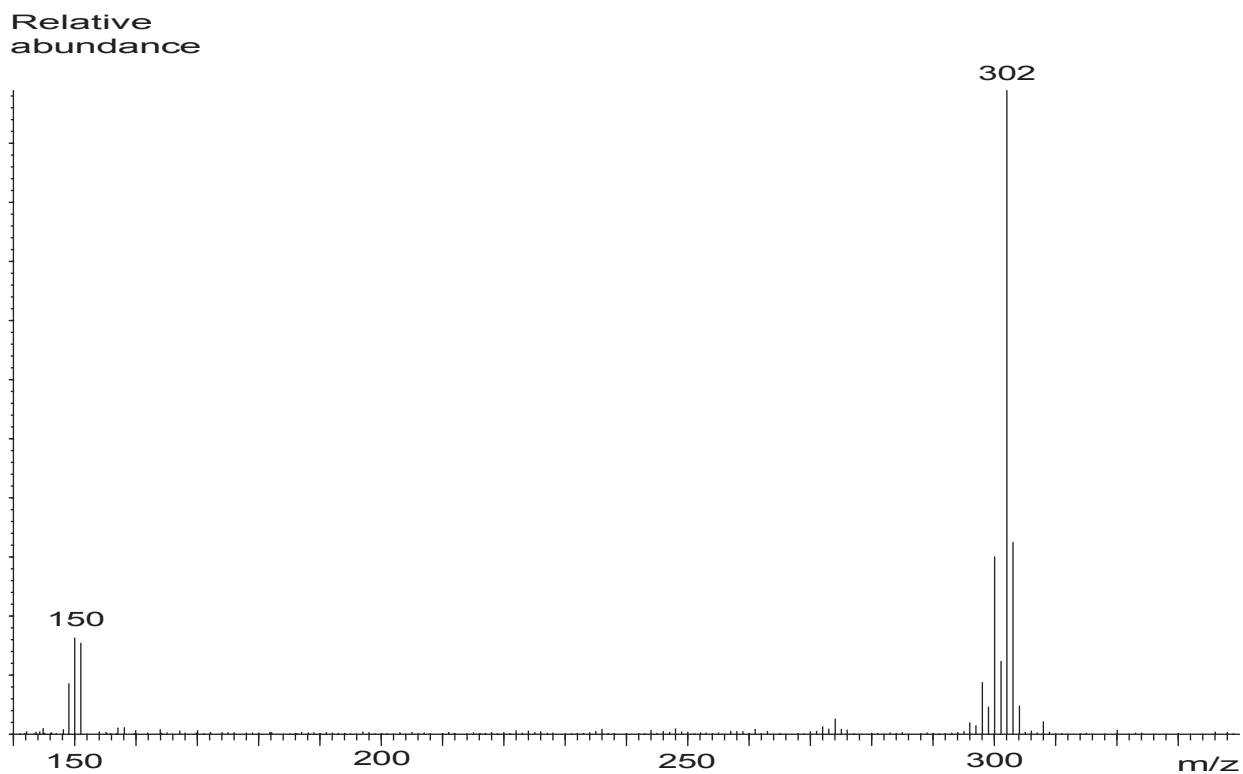


Figure 6 Full scan mass spectrum of peak 14 obtained from SRM 1649a.

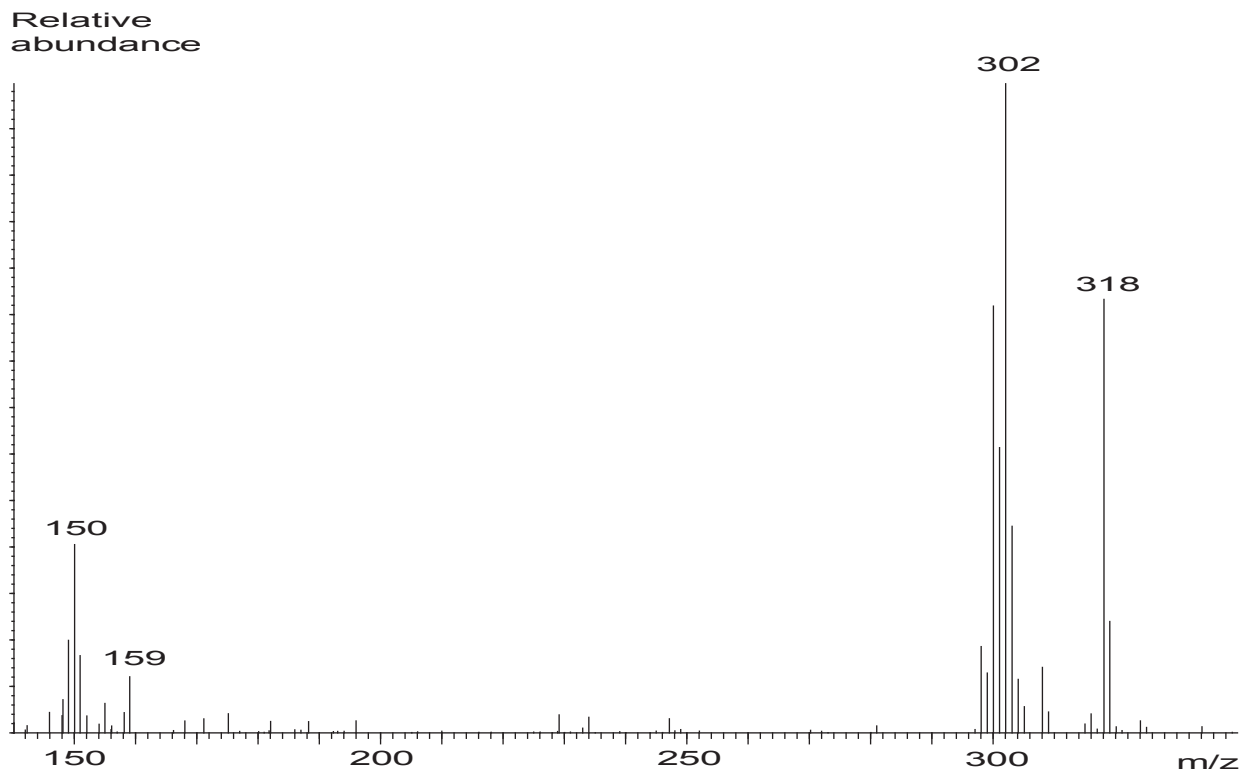


Figure 7 Full scan mass spectrum of peak 2 obtained from sample M3.

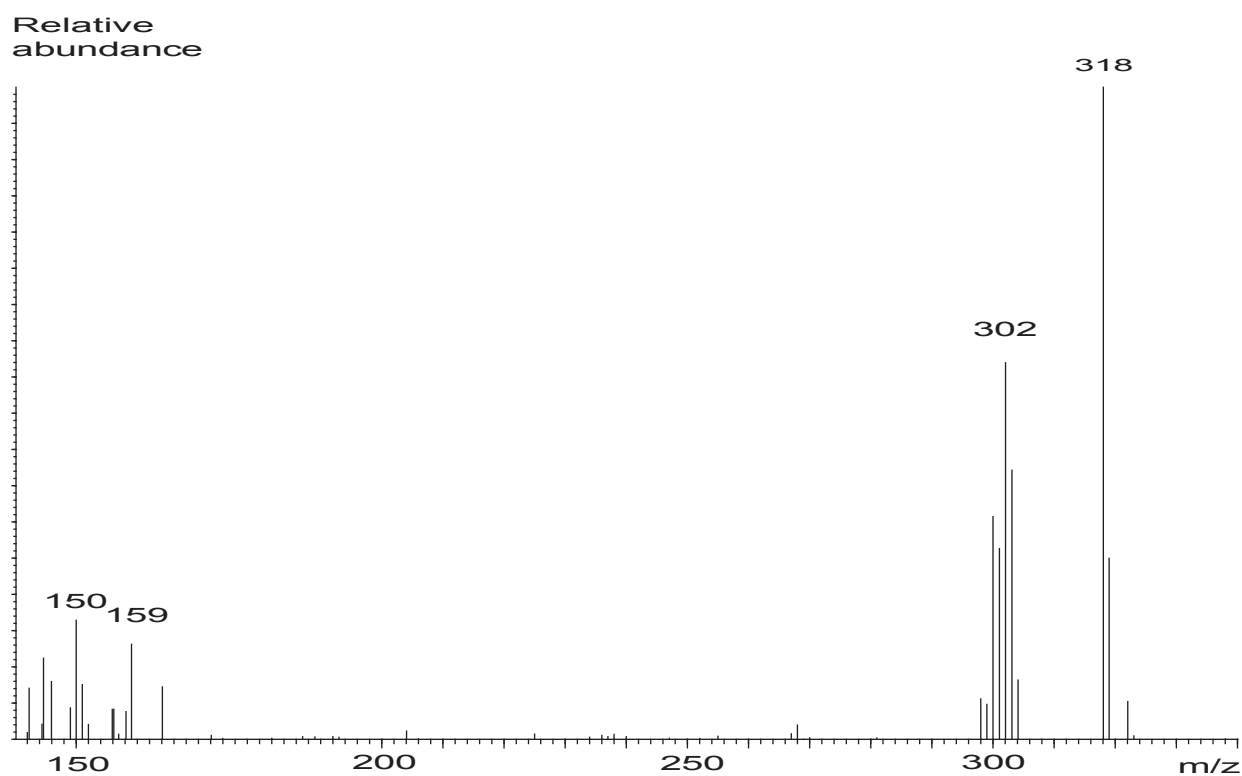


Figure 8 Full scan mass spectrum of peak 2 obtained from SRM 1649a.

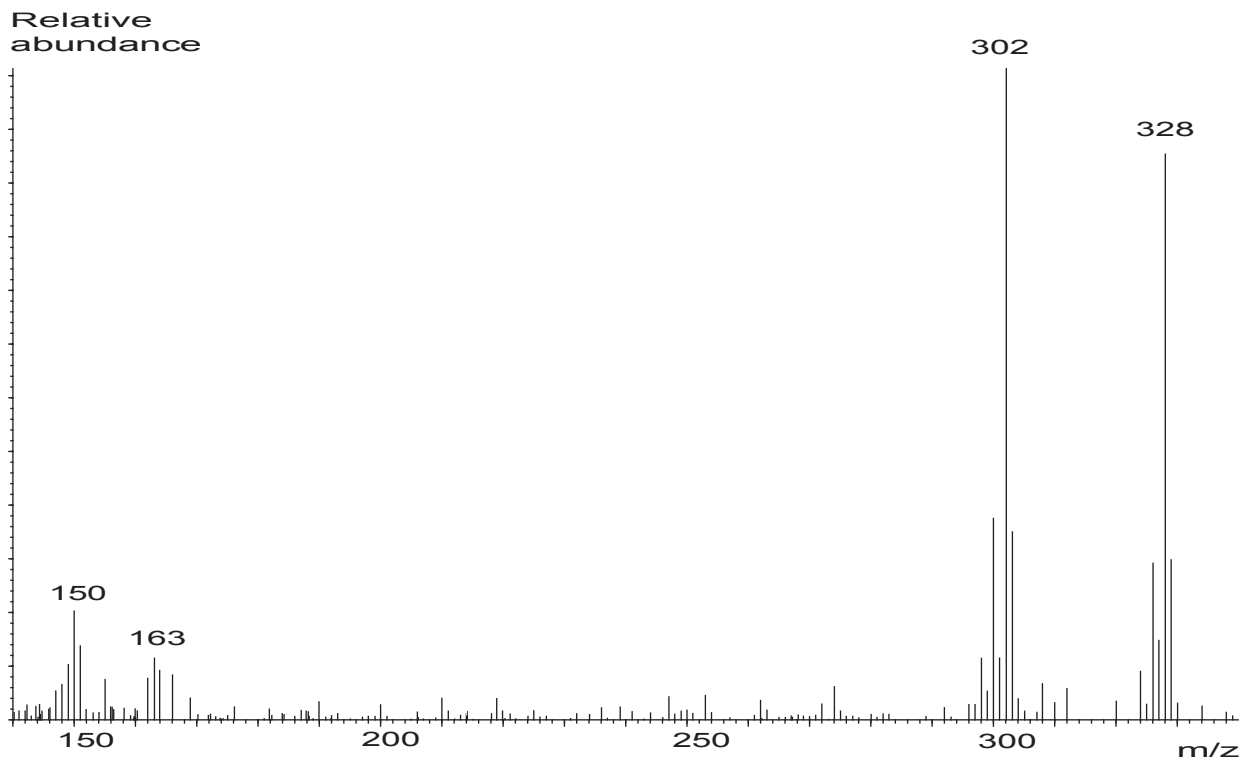


Figure 9 Full scan mass spectrum of peak 17 obtained from sample M3.

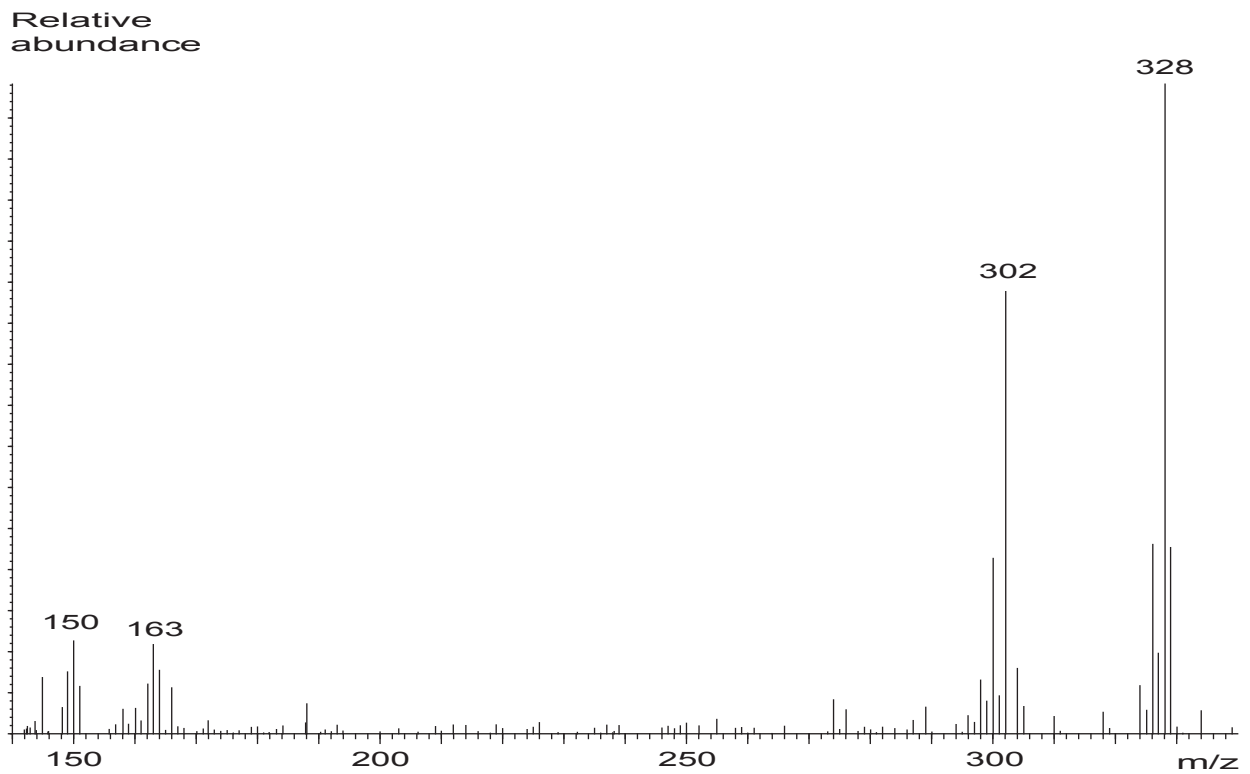


Figure 10 Full scan mass spectrum of peak 17 obtained from SRM 1649a.

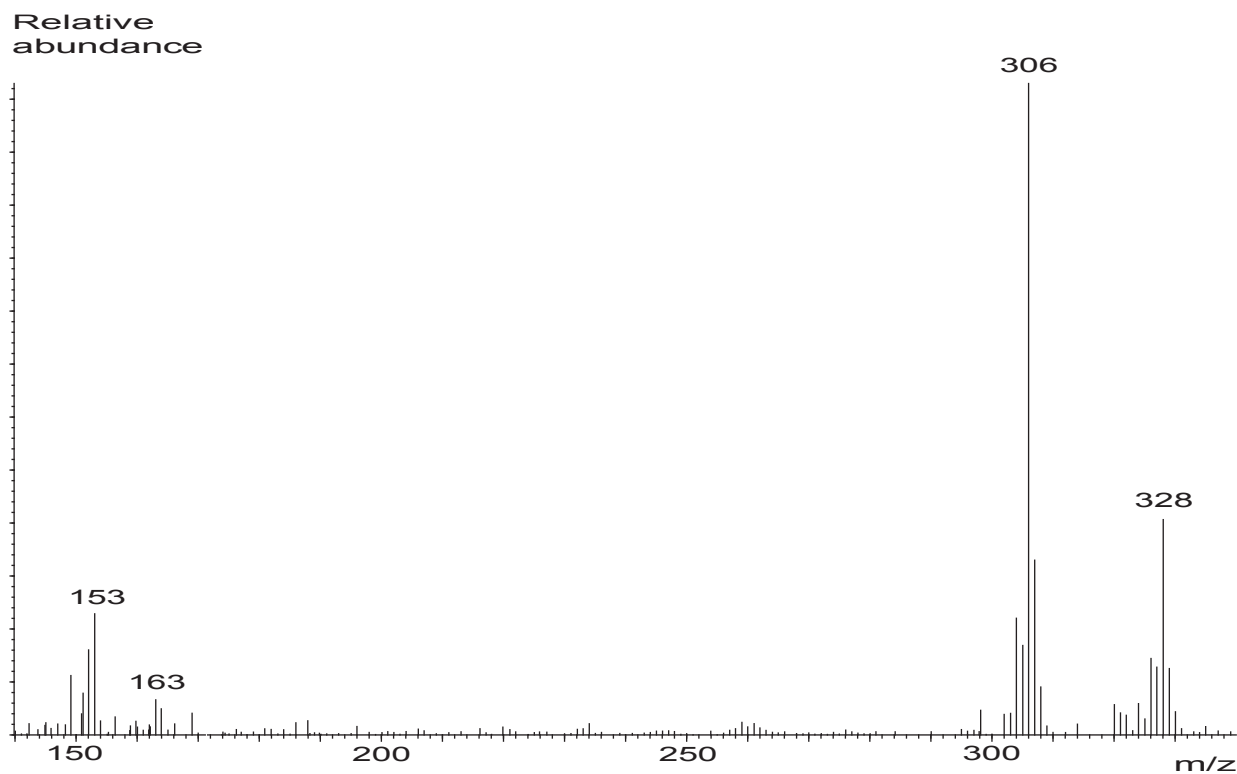


Figure 11 Full scan mass spectrum of peak 21 obtained from sample M3.

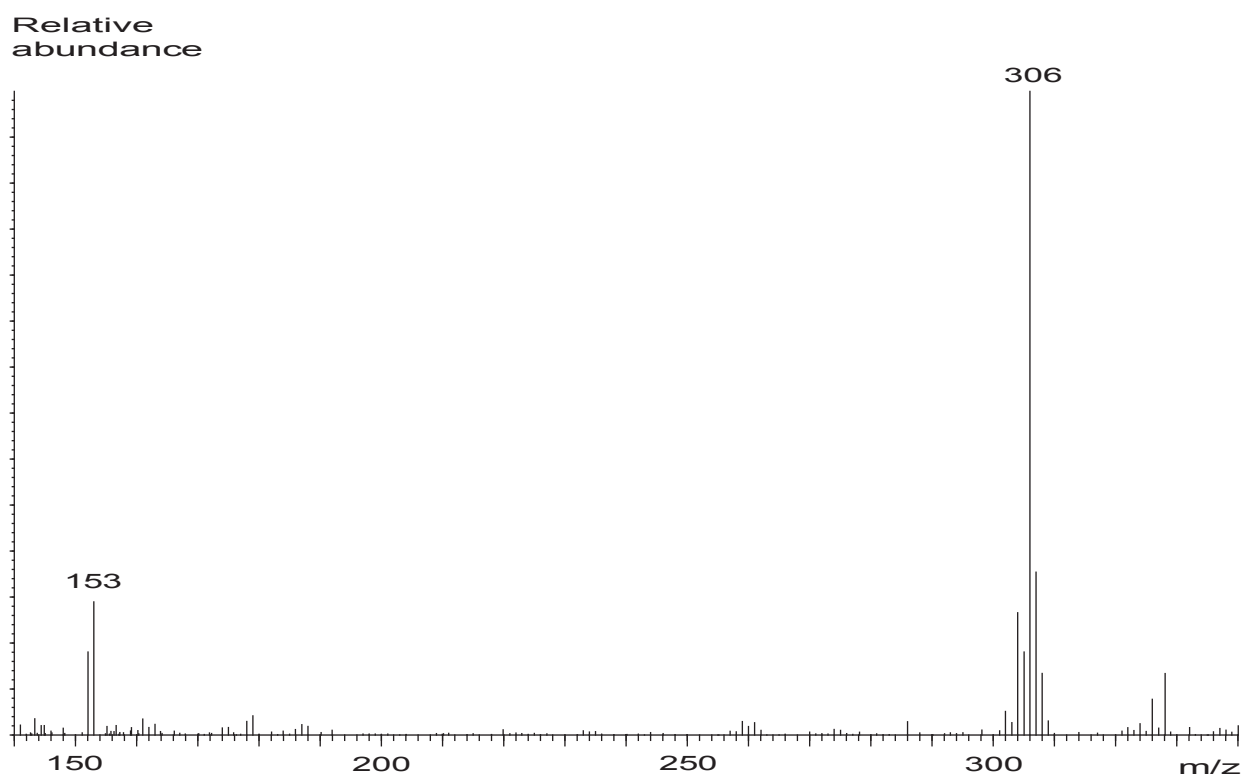


Figure 12 Full scan mass spectrum of peak 21 obtained from SRM 1649a.

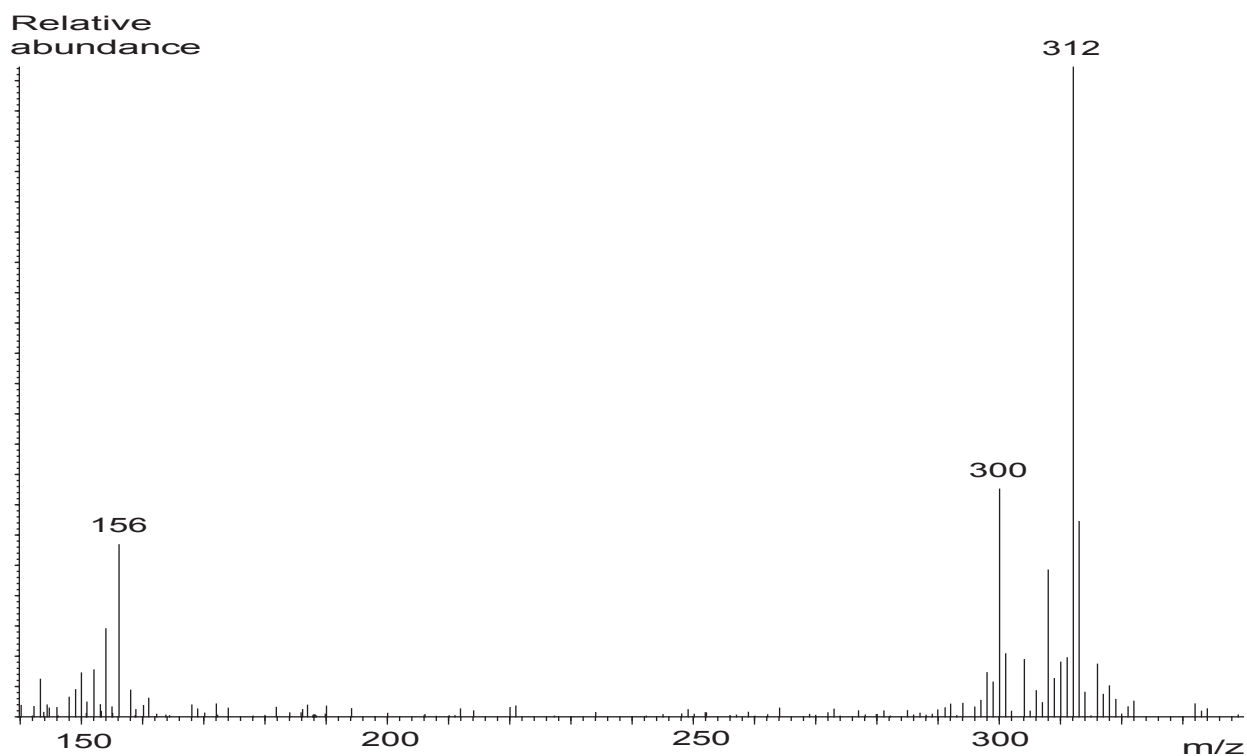


Figure 13 Full scan mass spectrum of peak 24 obtained from sample M3.

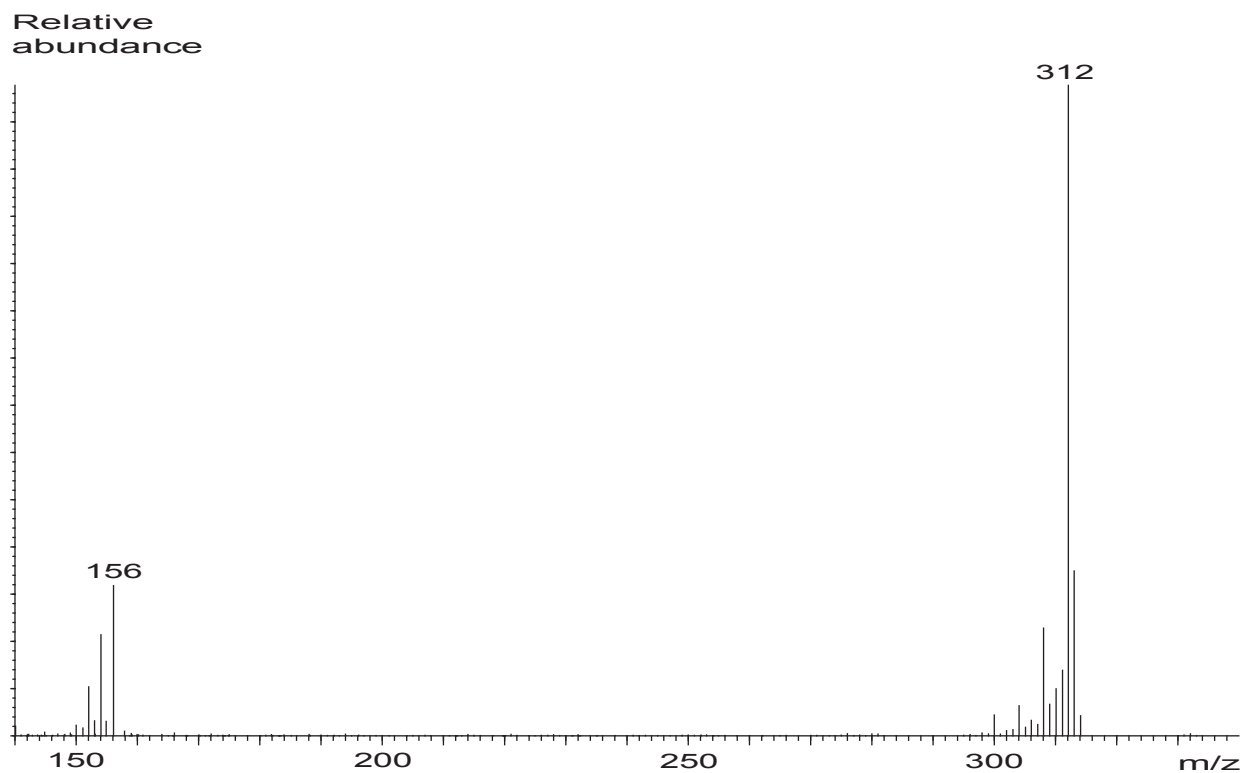


Figure 14 Full scan mass spectrum of peak 24 obtained from SRM 1649a.

TABLE 2. Validation of Acetone versus Toluene as Solvent for Extraction of the SRM 1649a Urban Dust Sample^a

PAH	toluene, n = 4	acetone, n = 4	(18)	(7)	(26)
B(a)P	2428 ± 373	2296 ± 432	2553 ± 224	nd	2509 ± 87 (C)
perylene	651 ± 101	597 ± 113	660 ± 63	nd	646 ± 75 (C)
dibenzo(a,l)pyrene	30 ± 3.7	28 ± 3.8	25 ± 4	47.2 ± 4.8	nd
dibenzo(a,e)pyrene	537 ± 84	535 ± 72	nd	566 ± 25	630 ± 80 (R)
coronene	4538 ± 99	4431 ± 320	4142 ± 162	4400 ± 460	nd
dibenzo(a,i)pyrene	162 ± 29	138 ± 25	161 ± 13	154 ± 11	130 ± 10 (R)
dibenzo(a,h)pyrene	66 ± 13	48 ± 11	53 ± 10	39.2 ± 6.4	53 ± 2 (R)

^a Mean values (pg/mg) ± standard deviation; nd, not determined; n, number of chemical analysis made; C, certified NIST value; R, reference NIST value.

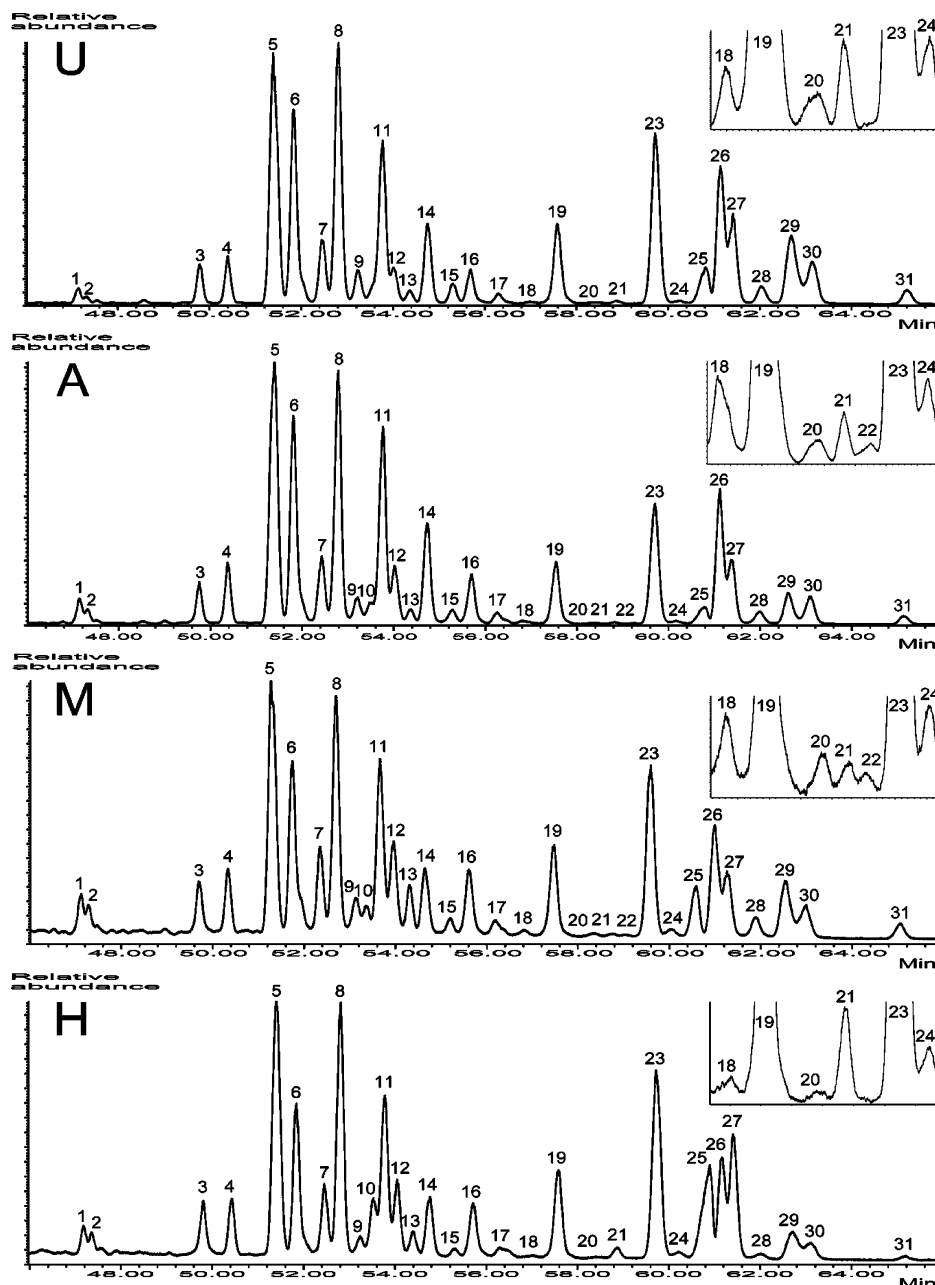


FIGURE 1. GC/MS chromatograms obtained in selected ion monitoring mode (extracted ion m/z 302) of Standard Reference Material 1649a (U) and Stockholm ambient air particulate matter originating from the following: A, Arrhenius laboratory rooftop; M, Mariatorget subway station; and H, street canyon of Hornsgatan. For peak numbering refer to Table 3.

et al. (2) accept the WHO unit risk estimate for humans and that the epidemiological data on lung cancer in coke-oven workers provide the best basis for qualitative risk estimates. They also note that B(a)P has been found to be a major

carcinogenic contributor in studies in which both the relative carcinogenicity and measured concentrations of PAHs in ambient air have been considered, supporting its use as an indicator of carcinogenic PAHs. However, Collins et al. (23)

TABLE 3. Peak Numbering for Identified and Tentatively Identified Compounds

peak no.	peak identity
1	unknown MW 302
2	unknown MW 302+MW 318
3	dibenzo(<i>b,e</i>)fluoranthene ^a
4	unknown MW 302
5	naphtho(1,2- <i>b</i>)fluoranthene ^a
6	naphtho(1,2- <i>k</i>)fluoranthene ^a
7	naphtho(2,3- <i>b</i>)fluoranthene ^a
8	dibenzo(<i>b,k</i>)fluoranthene ^a
9	dibenzo(<i>a,k</i>)fluoranthene ^a
10	unknown
11	dibenzo(<i>j,l</i>)fluoranthene ^a
12	naphtho(1,2- <i>e</i>)pyrene ^a
13	dibenzo(<i>a,l</i>)pyrene ^b
14	unknown MW 302
15	naphtho(2,3- <i>k</i>)fluoranthene ^a
16	naphtho(1,2- <i>a</i>)pyrene ^a
17	unknown MW 302+MW 328
18	unknown
19	naphtho(2,3- <i>e</i>)pyrene ^a
20	unknown
21	unknown MW 306
22	unknown
23	dibenzo(<i>a,e</i>)pyrene ^b
24	coronene-D ₁₂ MW 312
25	coronene
26	naphtho(2,1- <i>a</i>)pyrene ^a
27	dibenzo(<i>e,l</i>)pyrene ^a
28	naphtho(2,3- <i>a</i>)pyrene ^a
29	benzo(<i>b</i>)perylene ^a
30	dibenzo(<i>a,l</i>)pyrene ^b
31	dibenzo(<i>a,h</i>)pyrene ^b

^a Tentatively identified by comparison to chromatogram from ref 7.
^b Identified using reference standards. ^c MW, molecular weight.

showed that dibenzo(*a,l*)pyrene made a five times greater contribution than B(*a*)P to the carcinogenicity of samples of ambient air they tested (based on values obtained by multiplying the TEFs and concentrations of the respective compounds). Due to this finding and the fact that the dibenzopyrene isomers analyzed in the study presented here—dibenzo(*a,l*)pyrene, dibenzo(*a,e*)pyrene, dibenzo(*a,i*)pyrene, and dibenzo(*a,h*)pyrene—have been assigned similar or higher TEF values than B(*a*)P, Boström et al. (2) proposed that dibenzopyrenes should be regularly analyzed and dibenzo(*a,l*)pyrene should be considered as an additional indicator of carcinogenic PAHs.

In the present study a recently developed analytical method for identifying and determining B(*a*)P, perylene, coronene, and the dibenzopyrene isomers dibenzo(*a,l*)pyrene, dibenzo(*a,e*)pyrene, dibenzo(*a,i*)pyrene, and dibenzo(*a,h*)pyrene (18) has been applied to assess, for the first time, the levels of these dibenzopyrene isomers in ambient air particulate materials sampled in Stockholm.

Experimental Section

Air Samples. Ambient air particulate material samples were collected at three different locations in Stockholm: the roof (approximately 22 m above ground) of the Arrhenius laboratory building on Stockholm University's main campus; in the canyon of the busy street Hornsgatan (3 m above the street and ca. 3 m from the facade of the nearest building) in the downtown area of Stockholm Södermalm; and in the air of the Mariatorget subway station (3 m above the platform at the center of the northbound platform), which is also located in Södermalm. The Hornsgatan and Mariatorget sampling sites are described in more detail by Gidhagen et al. (24) and Johansson and Johansson (25), respectively. The rooftop air particle material samples were collected on Teflon-

TABLE 4. Determined Air Concentrations in µg/m³ of B(*a*)P, Perylene, Coronene, Dibenzo(*a,l*)pyrene, Dibenzo(*a,e*)pyrene, Dibenzo(*a,i*)pyrene, and Dibenzo(*a,h*)pyrene^a

sample	A1	A2	A3	A4	A5	A6	A7	A8	A9	H1	H2	H3	M1	M2	M3
<i>n</i>	2	2	2	2	2	2	4	4	4	4	4	4	4	4	4
B(<i>a</i>)P	585 ± 50	58 ± 2.48	90 ± 5.8	93 ± 4.9	194 ± 0.58	217 ± 6.8	101 ± 3.6	144 ± 9.6	113 ± 1.9	177 ± 4.7	169 ± 2.1	89 ± 1.3	169 ± 8.6	90 ± 7.9	1089 ± 62
perylene	100 ± 6.0	10 ± 0.45	17 ± 1.3	15 ± 0.78	28 ± 0.14	36 ± 1.1	16 ± 0.7	23 ± 1.4	17 ± 0.48	32 ± 7.8	31 ± 0.44	17 ± 0.20	34 ± 1.8	19 ± 1.8	238 ± 14
coronene	206 ± 10	40 ± 2.8	64 ± 6.6	81 ± 6.1	144 ± 1.3	135 ± 3.8	103 ± 3.1	116 ± 7.6	113 ± 6.1	230 ± 101	249 ± 7.9	164 ± 4.1	85 ± 4.4	42 ± 4.3	156 ± 12
dibenzo(<i>a,l</i>)pyrene	13 ± 0.67	1.6 ± 0.073	2.9 ± 0.010	2.2 ± 0.27	2.6 ± 0.0069	5.8 ± 0.23	1.6 ± 0.10	1.1 ± 0.098	1.4 ± 0.044	2.4 ± 0.94	2.1 ± 0.16	1.5 ± 0.11	3.2 ± 0.65	2.1 ± 0.26	7.3 ± 0.72
dibenzo(<i>a,e</i>)pyrene	57 ± 3.0	12 ± 0.26	18 ± 0.70	20 ± 1.5	30 ± 1.3	39 ± 1.6	17 ± 0.9	17 ± 1.0	23 ± 0.58	21 ± 2.7	18 ± 1.3	12 ± 0.53	17 ± 3.3	9.3 ± 0.76	45 ± 4.7
dibenzo(<i>a,i</i>)pyrene	16 ± 0.56	2.2 ± 0.19	2.8 ± 0.093	4.5 ± 0.52	8.1 ± 0.15	8.7 ± 0.51	4.4 ± 0.18	4.6 ± 0.23	4.8 ± 0.17	2.8 ± 1.3	2.5 ± 0.042	1.8 ± 0.075	4.0 ± 0.68	2.6 ± 0.62	13 ± 1.6
dibenzo(<i>a,h</i>)pyrene	4.5 ± 0.30	0.66 ± 0.14	0.75 ± 0.045	1.4 ± 0.17	2.4 ± 0.044	2.8 ± 0.15	1.1 ± 0.05	1.9 ± 0.12	0.95 ± 0.079	0.81 ± 0.39	0.59 ± 0.036	0.39 ± 0.15	2.4 ± 0.41	1.5 ± 0.69	5.8 ± 0.69

^a Mean values ± standard deviation; *n*, number of chemical analysis made. For sample abbreviations see Table 1.

TABLE 5. Toxic Equivalence Factors, TEF

compound	TEF	reference
B(a)P	1	by definition, 2
dibenzo(a,l)pyrene	100	30
dibenzo(a,e)pyrene	1	23, 31
dibenzo(a,i)pyrene	10	23, 31
dibenzo(a,h)pyrene	10	23, 31

coated glass fiber filters (Ø149 mm, Pallflex T60A20, Pallflex Inc., Putnam, CT) using a constant flow (about 8.4 m³/h) pump device built in-house. In the street canyon/subway station PM₁₀ particle samples were collected on glass fiber filters (Whatman EPM 2000, 20.3 × 25.4 cm, England) using a Sierra-Andersen/GMV model 1200 PM₁₀ high-volume sampler at a flow of about 70 and 89 m³/h for the street canyon and for the subway station, respectively. After sampling the filters were folded, wrapped in aluminum foil, and stored in a freezer at -20 °C until chemical analysis. Additional sample data are shown in Table 1. Furthermore, for comparison National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1649a Urban Dust (26) (Washington air particles sampled in 1976–1977) was also analyzed.

Analysis, Identification, and Quantification. Each filter (at room temperature) was weighed, directly cut into at least two parts, which were directly individually weighed and analyzed to allow corresponding sample volumes, and measures of the uncertainty (standard deviation of clean up and analysis) of determined analyte concentrations, to be calculated. Briefly, the extraction and analytical procedures used (described in detail in ref 18) were as follows. The filter parts were placed in disposable test tubes, deuterated internal surrogate standards (B(a)P-D₁₂ and dibenzo(a,i)pyrene-D₁₄) and 5 mL of extraction solvent were added, the samples were ultrasonically extracted for 10 min, and the extracts were filtered through nylon syringe filters prior to precleaning using silica solid-phase extraction (SPE) cartridges. The aliphatic/PAH-enriched fractions were analyzed using online hyphenated high performance liquid chromatography (HPLC)-gas chromatography (GC)-mass spectrometry (MS) in selected ion monitoring (SIM) and full-scan modes. In the latter the scan interval was set to 50–450 m/z, but the instrumental parameters were otherwise identical to those used in SIM mode. Blank filter samples were cleaned up and analyzed at the same time as the air particulate samples in order to check for contamination and memory effects from the analytical method.

The analytical method used in the present study initially involved extraction of the particle samples with acetone as solvent. However, during the analysis of the subway samples it was noticed that using toluene as extraction solvent improved the extraction yields of the dibenzopyrenes. Hence, the SRM 1649a Urban Dust sample was re-extracted and analyzed using toluene as the extraction solvent. The results obtained, which are compared to those obtained using acetone as the extraction solvent in Table 2, agree well with previously reported concentrations (7, 18) and NIST-certified and reference concentrations (26) for SRM 1649a Urban Dust.

Results and Discussion

Figure 1 shows GC/MS chromatograms (SIM, extracted ion *m/z* 302) of air particle samples, extracted using toluene, obtained from (A) the rooftop, (H) the street canyon, (M) the subway station, and (U) SRM 1649a Urban Dust. The chromatograms are very similar regarding relative peak intensities indicating that the PAH profile, MW 302, in Washington 30 years ago is similar to the present situation in Stockholm. B(a)P, perylene, coronene, and the dibenzopyrene isomers determined in this study were identified

on the basis of their retention times and standard addition using reference standards. Other PAHs with a molecular weight of 302 were also tentatively identified (Table 3), based on comparison with a published chromatogram of SRM 1649a Urban Dust (7), which has similar relative peak intensities to the chromatograms of the air particulate material analyzed here. Furthermore, the *m/z* 302 ion dominated in background-corrected full-scan spectra for peaks 3–9, 11, 13–16, 19, 23, and 26–31 in the SRM 1649a sample and the subway station sample; peaks 5–8, 11, 14, 16, 19, 23, 26, 27, 29, and 30 in the rooftop sample; and peaks 3–8, 11, 13, 14, 19, 23, 26, 27, 29, and 30 in the street canyon sample.

Other, unknown peaks were also found in the particle samples analyzed, Figure 1. These peaks were further investigated using full-scan mass spectra obtained from a cleaned-up 71-mg SRM 1649a sample and from the sample with the highest peak intensities, M3. There were no major differences in the spectra obtained from these samples. Spectra are presented in the Supporting Information. Peaks 1, 2, 4, 14, 17, and 21 appear in chromatograms from all samples, Figure 1. Obtained spectra of peaks 1, 4, and 14 are very similar and show typical PAH fragmentation patterns (27); the molecular ion (M⁺), *m/z* 302, being the most abundant, followed by the molecular ion with losses of one or more hydrogen atoms and the doubly charged molecular ion, [M - 2H]²⁺ *m/z* 150. Peak 2 seems to represent two, coeluting compounds: one yielding a fragmentation pattern similar to those of peaks 1, 4, and 14, with *m/z* 302 and 150 ions, indicative of a PAH with a molecular weight of 302, and the other yielding *m/z* 318 and 159 ions, indicative of a PAH with a molecular weight of 318 (and hence M⁺ *m/z* 318 and M²⁺ *m/z* 159); however, no fragments due to losses of hydrogen atoms from the molecular ion can be seen. Spectrum of peak 17 is indicative of a PAH with molecular weight 302 (M⁺ *m/z* 302 and [M - 2H]²⁺ *m/z* 150) coeluting with a PAH with molecular weight 328 (M⁺ *m/z* 328 and [M - 2H]²⁺ *m/z* 163). The spectrum of peak 21 shows that the detected signal at *m/z* 302 in SIM mode probably originates from a fragment of a compound with M⁺ *m/z* 306. The spectrum is characteristic of PAH fragmentation with the abundant M⁺ ion *m/z* 306 and the M²⁺ ion *m/z* 153. In the spectrum from sample M3, ions characteristic of a PAH with molecular weight 328 also appear, i.e., M⁺ *m/z* 328 and [M - 2H]²⁺ *m/z* 163. The ion *m/z* 328 is also visible in the SRM 1649a spectrum, although its relative intensity is much lower. Peak 24 is the result of fragments from the volumetric internal standard coronene-D₁₂, molecular weight 312. The spectrum obtained from M3 also seems to contain a PAH with molecular weight 300. Peak 24 was not seen in our previous study of SRM 1649a (18), because only a tenth as much coronene-D₁₂ was present in samples analyzed in the cited study, where coronene-D₁₂ was used as an internal surrogate standard. For the other unknown peaks, i.e., peaks 10, 18, 20, and 22, no sufficiently clear mass spectra were obtained to merit publication.

Table 4 shows the determined air concentrations of B(a)P, perylene, coronene, dibenzo(a,l)pyrene, dibenzo(a,e)pyrene, dibenzo(a,i)pyrene, and dibenzo(a,h)pyrene. Comparing the determined concentrations of the 24 h samples, i.e., A1–A4 and A6 and the weekend sample A5 a relative large variation can be seen. The determined concentrations in samples A7 (autumn), A8 (autumn), and A9 (spring), which were sampled over approximately 1 week, are quite similar, indicating that there were no major differences between spring and autumn in this respect. The determined concentrations of the street canyon samples, H1 and H2, are similar and somewhat higher than the determined concentrations of the H3 sample. The determined concentrations of the subway station samples are quite different indicating relatively large day-to-day variations, but the sample M1 was sampled over ap-

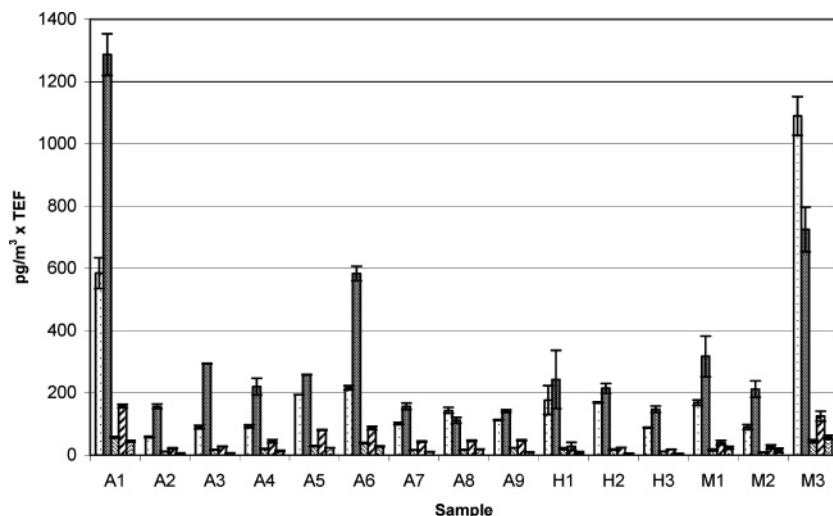


FIGURE 2. Determined carcinogenic potencies, expressed in $\text{pg/m}^3 \times \text{TEF}$, of the dibenzopyrenes and B(a)P in the Stockholm air particle samples. Bars from left to right: B(a)P, dibenzo(a,l)pyrene, dibenzo(a,e)pyrene, dibenzo(a,i)pyrene, and dibenzo(a,h)pyrene. For sample abbreviations see Table 1.

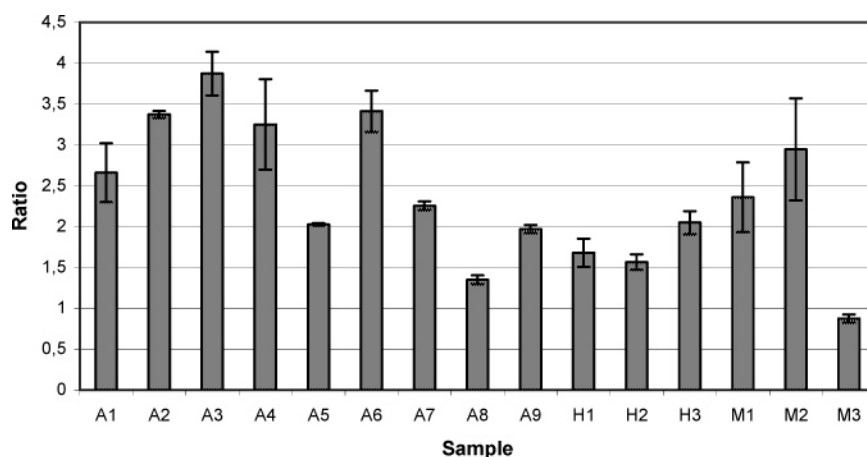


FIGURE 3. Carcinogenic contributions for the sum of the dibenzopyrenes, relative to the carcinogenic contribution for B(a)P in the Stockholm air samples: $[\sum (\text{pg/m}^3 \text{ dibenzopyrene} \times \text{TEF})] / (\text{pg/m}^3 \text{ B(a)P} \times \text{TEF})$. For sample abbreviations see Table 1.

proximately 53 h. The subway sample M3 had the largest B(a)P, perylene, and dibenzo(a,h)pyrene concentrations determined in this study, which is difficult to explain without further investigation of additional samples. Previous reports on determined concentrations of these dibenzopyrene isomers in ambient air samples are scarce. However, Allen and co workers (20) analyzed air particle matter collected in June 1994 from a rooftop in Boston, U.S.A., and found dibenzo(a,e)pyrene concentrations of $0.133 \pm 0.021 \text{ ng/m}^3$. In another study Krieger and Wright (21) analyzed air particle matter collected in July and August in Riverside, CA, taken during 12-h periods to investigate day and night variations. The determined daytime/nighttime concentrations of dibenzo(a,l)pyrene, dibenzo(a,e)pyrene, dibenzo(a,i)pyrene, and dibenzo(a,h)pyrene, in pg/m^3 , were 18/18, 1.7/3.6, $<0.5/ <0.5$, and $<0.5/ <0.5$, respectively. The relatively high concentration of dibenzo(a,l)pyrene compared to the other dibenzopyrene isomers is contradictory to the results obtained in this study, where the concentration of dibenzo(a,l)pyrene was found to be lower than the concentrations of dibenzo(a,e)pyrene and dibenzo(a,i)pyrene in the analyzed samples. The mean of the B(a)P concentrations, Table 4, determined at Hornsgatan in this study, 0.145 ng/m^3 , correlates well with the previous reported B(a)P concentration of 0.13 ng/m^3 (average from 2 weeks per month sampled from June to December 2004) in samples taken at the same sampling site (28). Quite high B(a)P, perylene, and coronene levels have

previously been reported at Hornsgatan by Colmsjö and co-workers (29), i.e., 2.1, 0.4, and 4.8 ng/m^3 , respectively. Colmsjö et al. (29) also reported B(a)P, perylene, and coronene concentrations from the subway station Mariatorget of 1.0, 0.1, and 1.3 ng/m^3 , respectively. However, their results emanate from the year 1986 and are not representative for the present situation.

Since each PAH has a different carcinogenic activity, concentration is not a good measure for health risk assessments. A better way to estimate the carcinogenic potency of the compounds present is to multiply their respective concentrations and TEF values. The TEF values used in this study are displayed in Table 5. Carcinogenic potencies were calculated for the determined dibenzopyrene isomers and B(a)P in the analyzed samples, and the results show that dibenzo(a,l)pyrene, although not the most abundant compound, was the major carcinogenic contributor of the determined PAH in all samples except M3, where B(a)P had the highest carcinogenic potency, Figure 2. Figure 3 shows the carcinogenic potency of the sum of determined dibenzopyrenes compared to B(a)P in each sample collected. The mean ratios of carcinogenic potency between the dibenzopyrenes and B(a)P for the six samples A1–A6, the three samples A7–A9, the three samples H1–H3, and the three samples M1–M3 were 3.1 ± 0.7 , 1.9 ± 0.5 , 1.8 ± 0.3 , and 2.1 ± 1.1 , respectively. These >1 ratios indicate that the dibenzopyrenes had greater carcinogenic potency than B(a)P

in the Stockholm ambient air samples analyzed. Corresponding ratios for the SRM 1694a Urban Dust sample based on data from Table 2 (concentrations in pg/mg) are 2.3 ± 0.1 (acetone extraction) and 2.4 ± 0.05 (toluene extraction). These data indicates that the relative air particle concentrations (and therefore also carcinogenic potencies) between the dibenzopyrenes and B(a)P are similar in Stockholm as in Washington 30 years ago, i.e., 1976–1977. This is also supported by the similar *m/z* 302 chromatographic profiles shown in Figure 1. This finding is somewhat unexpected, since Stockholm urban air quality has generally improved in the intervening time. Collins et al. (23) have calculated carcinogenic potencies by applying TEFs to the data set of Krieger and Wright (21), and their results indicate that the carcinogenic contribution of dibenzo(*a,l*)pyrene was also greater than that of B(a)P in the Californian samples they analyzed. In their study the carcinogenic potency of dibenzo(*a,l*)pyrene was five times higher than that of B(a)P. These findings, together with the results of the present study, imply that it is important to measure these dibenzopyrene isomers, in particular dibenzo(*a,l*)pyrene, as well as B(a)P in order to determine the carcinogenic potency of PAHs in ambient air. Furthermore, this indicates that using only B(a)P as an indicator will probably lead to underestimates of the carcinogenic potency of PAH mixtures in ambient air. These results support the conclusions of Boström and co-workers (2), who suggest that dibenzopyrenes should be analyzed and that dibenzo(*a,l*)pyrene might be, along with B(a)P, a suitable indicator for carcinogenic PAHs. However, there are many PAHs in ambient air for which no TEF values and/or analytical methods are available. The carcinogenic contributions of these PAHs are therefore unknown. Also, one should have in mind that a great discrepancy exists between TEF values determined in different studies. For example the TEF value of dibenzo(*a,l*)pyrene varies between 1 and 100 in different studies (2). It is also not clear if the assumption of additivity of carcinogenic potency of PAHs in an air mixture is valid (2). Furthermore, the conclusions drawn in this study are based only on a few analyzed samples. Therefore there is a need to verify them and to investigate the seasonal variations of these dibenzopyrene isomers and B(a)P in different locations in Stockholm as well as other large cities such as suburbs, road tunnels, and metropolitan areas. Furthermore, there is a need to identify and characterize in more detail both stationary and mobile PAH sources that contribute to air pollution of dibenzopyrenes.

Acknowledgments

Christer Johansson, ITM Stockholm University, is acknowledged for valuable comments and for providing the filter samples taken in downtown Stockholm, i.e., Hornsgatan and Mariatorget subway station. The authors gratefully acknowledge Lena Elfver for skillful laboratory assistance. This study was financed by Stockholm University and the Swedish Emission Research Programme (Emissionsforskningsprogrammet, EMFO).

Supporting Information Available

Full-scan mass spectra of peaks 1, 2, 4, 14, 17, 21, and 24 from subway sample M3 and SRM 1649a Urban Dust. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Straif, K.; Baan, R.; Grosse, Y.; Secretan, B.; El Ghissassi, F.; Coglianò, V. Carcinogenicity of polycyclic aromatic hydrocarbons. *Lancet. Oncol.* **2005**, *6*, 931–932.
- (2) Boström, C.-E.; Gerde, P.; Hanberg, A.; Jernström, B.; Johansson, C.; Kyrklund, T.; Rannug, A.; Törnqvist, M.; Victorin, K.; Westerholm, R. Cancer risk assessment, indicators, and guide-

lines for polycyclic aromatic hydrocarbons in the ambient air. *Environ. Health Perspect.* **2002**, *110* (3), 451–488.

- (3) U.S. Department of Health and Human Services. *Polycyclic Aromatic Hydrocarbons: 15 Listings*; Eleventh Report on Carcinogens; 2005. Available at <http://ntp.niehs.nih.gov/ntp/roc/eleventh/profiles/s150pah.pdf> (accessed December 2006).
- (4) Platt, K.; Dienes, H.; Tommasone, M.; Luch, A. Tumor formation in the neonatal mouse bioassay indicates that the potent carcinogen dibenzo[def,p]chrysene (dibenzo[*a,l*]pyrene) is activated in vivo via its trans-11,12-dihydrodiol. *Chem.-Biol. Interact.* **2004**, *148*, 27–36.
- (5) Seidel, A.; Frank, H.; Behnke, A.; Schneider, D.; Jacob, J. Determination of dibenzo[*a,l*]pyrene and other fjord-region PAH isomers with mw 302 in environmental samples. *Polycyclic Aromat. Compd.* **2004**, *24*, 759–771.
- (6) Wise, S.; Deissler, A.; Sander, L. Liquid chromatographic determination of polycyclic aromatic hydrocarbon isomers of molecular weight 278 and 302 in environmental standard reference materials. *Polycyclic Aromat. Compd.* **1993**, *3*, 169–184.
- (7) Schubert, P.; Schantz, M.; Sander, L.; Wise, S. Determination of polycyclic aromatic hydrocarbons with molecular weight 300 and 302 in environmental-matrix standard reference materials by gas chromatography/mass spectrometry. *Anal. Chem.* **2003**, *75*, 234–246.
- (8) Kozin, I.; Gooijer, C.; Velthorst, N. Direct determination of dibenzo[*a,l*]pyrene in crude extracts of environmental samples by laser-excited Shpol'skii spectroscopy. *Anal. Chem.* **1995**, *67*, 1623–1626.
- (9) Kozin, I.; Gooijer, C.; Velthorst, N.; Harmsen, J.; Wieggers, R. Direct determination of isomeric polycyclic aromatic hydrocarbons in environmental samples by conventional and laser excited Shpol'skii spectroscopy. *Int. J. Environ. Anal. Chem.* **1995**, *61*, 285–297.
- (10) Pace, C.; Betowski, L. Measurement of high-molecular-weight polycyclic aromatic hydrocarbons in soils by particle beam high performance liquid chromatography-mass spectrometry. *J. Am. Soc. Mass Spectrom.* **1995**, *6*, 597–607.
- (11) Kozin, I.; Gooijer, C.; Velthorst, N.; Hellou, J.; Zitko, V. Isomer specific detection of PAHs and PAH metabolites in environmental matrices by Shpol'skii luminescence spectroscopy. *Chemosphere* **1996**, *33*, 1435–1447.
- (12) Sauvain, J.; Vu Duc, T.; Huynh, C. Development of an analytical method for the simultaneous determination of 15 carcinogenic polycyclic aromatic hydrocarbons and polycyclic aromatic nitrogen heterocyclic compounds. Application to diesel particulates. *Fresenius J. Anal. Chem.* **2001**, *371*, 966–974.
- (13) Sauvain, J.; Vu Duc, T.; Guillemin, M. Exposure to carcinogenic polycyclic aromatic compounds and health risk assessment for diesel-exhaust exposed workers. *Int. Arch. Occup. Environ. Health* **2003**, *76*, 443–455.
- (14) Sauvain, J.; Vu Duc, T. Approaches to identifying and quantifying polycyclic aromatic hydrocarbons of molecular weight 302 in diesel particulates. *J. Sep. Sci.* **2004**, *27*, 78–88.
- (15) Yu, S.; Campiglia, A. Direct determination of dibenzo[*a,l*]pyrene and its four dibenzopyrene isomers in water samples by solid-liquid extraction and laser-excited time-resolved Shpol'skii spectrometry. *Anal. Chem.* **2005**, *77*, 1440–1447.
- (16) Mininni, G.; Sbrilli, A.; Guerriero, E.; Rotatori, M. Polycyclic aromatic hydrocarbons formation in sludge incineration by fluidised bed and rotary kiln furnace. *Water, Air, Soil Pollut.* **2004**, *154*, 3–18.
- (17) Durant, J.; Lafleur, A.; Plummer, E.; Taghizadeh, K.; Busby, W.; Thilly, W. Human lymphoblast mutagens in urban airborne particles. *Environ. Sci. Technol.* **1998**, *32*, 1894–1906.
- (18) Bergvall, C.; Westerholm, R. Determination of dibenzopyrenes in standard reference materials (SRM) 1649a, 1650, and 2975 using ultrasonically assisted extraction and LC-GC-MS. *Anal. Bioanal. Chem.* **2006**, *384*, 438–447.
- (19) Allen, J.; Dookeran, N.; Smith, K.; Sarofim, A.; Taghizadeh, K.; Lafleur, A. Measurement of polycyclic aromatic hydrocarbons associated with size-segregated atmospheric aerosols in Massachusetts. *Environ. Sci. Technol.* **1996**, *30*, 1023–1030.
- (20) Allen, J.; Durant, J.; Dookeran, N.; Taghizadeh, K.; Plummer, E.; Lafleur, A.; Sarofim, A.; Smith, K. Measurement of C₂₄H₁₄ polycyclic aromatic hydrocarbons associated with a size-segregated urban aerosol. *Environ. Sci. Technol.* **1998**, *32*, 1928–1932.
- (21) Krieger, R.; Wright, J. In *Ambient monitoring of selected PAH in California*; Paper 97-WP100A.06; Air and Waste Management Association 90th Annual Meeting and Exhibition: Toronto, Ontario, June 8–13, 1997.

- (22) World Health Organization. *Air Quality Guidelines for Europe*, 2nd ed.; WHO regional publications: Copenhagen, 2000; European series No. 91.
- (23) Collins, J.; Brown, J.; Alexeeff, G.; Salmon, A. Potency equivalency factors for some polycyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbon derivatives. *Regul. Toxicol. Pharmacol.* **1998**, *28*, 45–54.
- (24) Gidhagen, L.; Johansson, C.; Langner, J.; Olivares, G. Simulation of NO_x and ultrafine particles in a street canyon in Stockholm, Sweden. *Atmos. Environ.* **2004**, *38*, 2029–2044.
- (25) Johansson, C.; Johansson, P.-Å. Particulate matter in the underground of Stockholm. *Atmos. Environ.* **2003**, *37*, 3–9.
- (26) SRM 1649a Urban Dust. *Certificate of Analysis*; National Institute of Standards and Technology: Gaithersburg, U.S.A., 2001. Available at https://srmors.nist.gov/certificates/view_cert2pdf.cfm?certificate=1649A (accessed Dec 2006).
- (27) Lee, M.; Novotny, M.; Bartle, K. In *Analytical Chemistry of Polycyclic Aromatic Compounds*; Academic Press Inc.: New York, 1981.
- (28) Burman, L. In *The Air in Stockholm 2004 (in Swedish)*; Yearly report from the Environmental and Health Protection Administration; Stockholm, Sweden. Available May 2005 at http://www.miljo.stockholm.se/arkiv/artiklar/050614_luft.asp (accessed Dec 2006).
- (29) Colmsjö, A.; Zebur, Y.; Östman, C.; Wadding, Å.; Söderström, H. Polynuclear aromatic compounds in the ambient air of Stockholm. *Chemosphere* **1986**, *15* (2), 169–182.
- (30) Muller, P. In *Scientific Criteria Document for Multimedia Standards Development Polycyclic Aromatic Hydrocarbons (PAH); Part 1: Hazard Identification and Dose-Response Assessment*; CN: Standard Development Branch, Ontario Ministry of Environment and Energy: Ontario, 1997.
- (31) California Environmental Protection Agency. In *Benzo(a)pyrene as a Toxic Air Contaminant; Part B Health Assessment*; Air Resources Board: Berkeley, CA, 1994. Available at <http://www.arb.ca.gov/toxics/id/summary/bap.pdf> (accessed Dec 2006).

Received for review September 19, 2006. Revised manuscript received November 3, 2006. Accepted November 7, 2006.

ES062232P