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DETERMINATION OF SUBSTITUTED POLYCYCLIC AROMATIC HYDROCARBONS IN URBAN AIR PARTICULATE MATTER

METHOD DEVELOPMENT AND QUANTITATIVE RESULTS

by

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SUMMARY

A method has been developed for the determination of substituted polycyclic aromatic hydrocarbons (PAH) in air particulate matter. To avoid loss of reactive compounds during long-term soxhlet extraction of the exposed filters a method based on liquid CO_2-extraction at low temperatures has been developed. The samples were prefractionated into different groups of substituted PAH using high performance liquid chromatography on an activated silica column. Using this technique trace compounds with high mutagenic and/or carcinogenic properties can be quantified with a minimum of interferences caused by major inactive substance groups. Some selected nitro- and keto-PAH as well as aza-arenes and parent PAH were quantified in summer and winter samples collected at St. Olavs gate in Oslo. Concentration levels comparable with those for parent-PAH were found for keto-PAH. Since most of the direct mutagenic activity can be found in the most polar fractions, additional investigations were carried out to identify as many compounds as possible present in these fractions. Preseparation on neutral and acidic-buffered silica followed by methylation using diazomethan was employed for this purpose. Preliminary experiments showed further that the mutagenic activity is mainly caused by compounds with molecular weights below 500.

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DETERMINATION OF SUBSTITUTED POLYCYCLIC AROMATIC HYDROCARBONS IN URBAN AIR PARTICULATE MATTER

METHOD DEVELOPMENT AND QUANTITATIVE RESULTS

1 INTRODUCTION

In recent years a large number of studies have been carried out to investigate the health effects of ambient air pollution caused by traffic, residential heating and industrial sources etc. Of special interest is the correlation between the biological activity (such as mutagenicity and carcinogenicity) of sample extracts and the presence of special compound classes. The polycyclic aromatic hydrocarbons (PAH) are the only group whose concentration level is fairly well-known in both urban air and in emissions from different sources. Investigations to correlate the mutagenic activity of air samples with the concentration of carcinogenic PAH indicate that only a minor part of the total mutagenicity can be explained by the PAH level (1-4). These findings were confirmed by studying the mutagenic potential of diesel engine exhaust (5). The results showed further that other heterocyclic and/or substituted PAH (such as nitro-PAH and keto-PAH) were responsible for the major part of both direct and indirect (after S9-enzyme activation) mutagenic activity. As a consequence of these findings a search for these compounds classes in air particulate matter from urban areas was started (6,7). Since these compounds are more reactive, less stable and may occur in lower concentrations than their parent PAH, the use of analytical methods employed for unsubstituted PAH may cause some complication:

- loss of reactive compounds during long-term soxhlet extraction procedures.

- due to the complex sample composition the identification and quantification of trace compounds with high mutagenic activity can be interfered by major inactive substance groups.

- the commonly used prefractionation into fractions of different polarity on deactivated silica does not separate optimally substituted PAH compound classes of different biological activities. Loss of highly polar, acidic or basic compounds is a further problem.

- decomposition during gas chromatographic analysis is another problem which has been reported (8).

The present report summarizes the development of a quantification method for substituted PAH and its application to urban air samples. The method allows the determination of nitro-PAH, carbazoles, keto-PAH, aza-arenes and some other groups in air particulate matter and is based on the following elements:

- liquid CO_2-extraction.

- use of high performance liquid chromatography (HPLC) employing an in-situ activated silica column for fractionation.

- high resolution gas chromatography (HRGC) on cross-linked fused silica capillaries directly coupled to the ion source of the mass spectrometer.

- use of negative ion chemical ionization for quantification.

2 METHOD DEVELOPMENT

Table 2.1 summarizes the step-by-step procedure of the analysis technique developed for substituted PAH. A more detailed description is given in (9). The method allows the group separation of all important substituted PAH groups with a minimum of overlap (see Figure 2.1). Table 2.2 shows the recovery of the procedure for some substituted PAH, which was within 76-115% including the very reactive 9-nitroanthracene (easily oxidized to 9-anthracenone). An exception are basic amino-PAH and naphthols. Soxhlet extraction with methylene chloride gave average recoveries of 35-80%. The most significant decrease in comparison to CO_2-extraction was found for keto-PAH (∼20%) and for 9-nitroanthracene (∼45%). The results of the quantitative analysis of parent PAH collected on glass fiber filters using CO_2-extraction are similar to those obtained for cyclohexane soxhlet extraction (10). Table 2.3 summarizes the results for 3 samples.

Table 2.1: Determination of substituted PAH in air.
Step-by-step procedure.

(1) Precleaning of collection materials by soxhlet extraction or heat treatment (only filters) (see (10)).

(2) Exposure of filter and 2 plugs, 400-1000 m^3, 20 m^3/h, 1-2 days.

(3) Liquid CO_2 extraction at 40-50 bar, 175 g dry ice,25ml extractor, 3-6 hours.

(4) Fractionation of the residue (in 1 ml CH_2Cl_2) by HPLC on an in-situ activated silica column (see (9)).

(5) Collection of 5 fractions (I: parent PAH, II: NO_2-PAH, III: Carbazoles, IV: Keto-PAH, hydroxy-PAH, V: Aza-arenes) using a set of indicator compounds.

(6) HRGC on a 25 m SE 54 or OV 1 (cross-linked) fused silica capillary

(7) Mass spectrometry using negative ion chemical ionization (CH_4 at 0.6 mbar, 200^{0} C ion source temperature), or electron impact ionization (only aza-arenes) or electron capture detection.

(8) Identification: Scan range 35-450 amu, detection limit 50 pg.
Quantitative analysis: Selected ion detection, detection limit: < 1 pg.

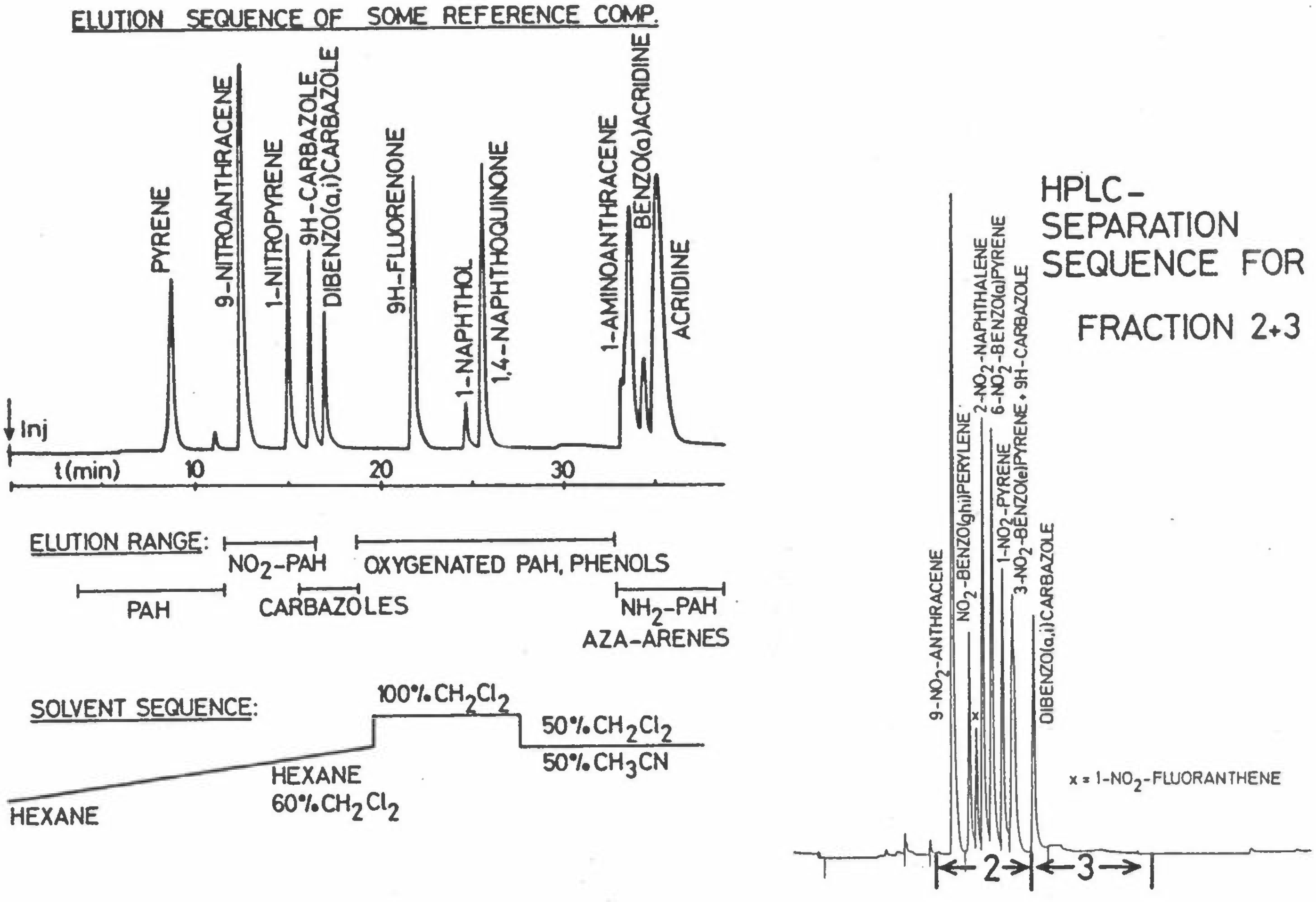

Figure 2.1: Fractionation of substituted PAH on in-situ activated silica. The solvent program, the elution sequence of some reference compounds and the fractions collected are marked. The solvent flow was 2.8 ml/min. The elution sequence of some NO_2-PAH and carbazoles shows a minimal overlap between the two compound groups.

Table 2.2: Recovery of some substituted and heteorocyclic PAH after liquid CO_2 extraction and HPLC fractionation[1].

Compound	n	$\bar{x}$(%)	s_r(%)
2-Nitronaphthalene	4	86	6
2-Nitroanthracene	3	76	5
1-Nitropyrene	4	102	13
9H-Carbazole	4	100	8
Dibenzo(a,i)carbazole	3	116	8
9-Fluorenone	4	91	4
1,4-Naphthoquinone	4	83	9
9,10-Phenanthroquinone	4	80	10
Quinoline	3	92	7
Benzo(f)quinoline	3	101	4
Indeno(1,2,3-ij)isoquinoline	3	106	3
Benz(a)acridine	3	112	19
1-Naphthol	4	34	18
1-Aminoanthracene	4	0	-

[1] n, number of parallel determinations: $\bar{x}$, mean recovery; s_r, relative standard deviation. Concentration range: 10 ng/µl.

Biological tests have shown that a considerable part of the mutagenic activity is found in the polar HPLC fractions (IV+V). Since irreversible adsorption or decomposition of reactive polar compounds from air extracts at a silica column surface is possible, different treatments of the silica surface with inorganic salts were tested. Covering of the surface with a thin acidic or basic salt layer opens the possibility to facilitate the elution or to retain reactive polar compounds. In a first step an acidic buffered silica-column was prepared. Acidic organic compounds were easily eluted with a minimum of interaction with the column surface while basic compounds were completely retained. The preparation procedure of the column and the HPLC fractionation applied to an urban air sample is summarized in Table 2.4. To make an analysis of the collected fractions by HRGC possible, acidic compounds were methylated using diazomethane. A similar fractionation using a basic buffered silica column is in progress.

Table 2.3: Comparison of CO_2- and cyclohexane soxhlet-extraction for some selected parent PAH. Average of three exposed glass fiber filters (urban area).

Component	Amount found by CO_2-extraction[1)] $\bar{x}$ (%)	Range %
Fluoranthene	105	99-117
Pyrene	95	92-101
Benzo(a)anthracene	101	84-112
Chrysene/Triphenylene	93	73-107
Benzo(e)pyrene	82	65-101
Benzo(a)pyrene	109	80-125
Benzo(ghi)perylene	88	68-130

1) Cyclohexane-extraction = 100%; 6 months storage at -20 °C between both analysis.

Table 2.4: Sample fractionation on acidic buffered silica, step-by-step procedure (see also (11)).

(1) Ultrasonic treatment (2 min.) of a slurry of silica (Partisil 10, Chrompack, Middelburg, The Netherlands) and 0.1 M $NaHSO_4$ solution adjusted to pH 1 using H_2SO_4.

(2) Removal of the solution excess by filtering. Drying of the silica at 80 °C under vacuum for 20 h.

(3) Slurry-packing of a 250 x 4.6 mm i.d. column using hexane.

(4) Collection of 5 sample fractions using the same procedure as shown in Table 1 and Figure 1. The column was not activated as this may destroy the acidic coating.

(5) Methylation of acidic compounds using diazomethane in ether (formed by decompositon of N-ethyl-N-nitroso-N-guanidine with sodium hydroxide solution, see (12)).

3 DETERMINATION OF SUBSTITUTED PAH IN AIR SAMPLES FROM OSLO

3.1 Idenfication of compounds found in the most polar fractions IV and V.

Earlier investigations have shown that a considerable part of mutagenic activity is located in the more polar fractions of diesel exhaust (5) and urban air samples (2, 13). However, only little is known about the composition of these fractions mainly due to analytical problems. Most of the compounds present in these fraction are too polar for GC analysis and need derivatisation. Loss by irreversible adsorption and compound decomposition are further problems. As can be seen from Figure 2.1 different substituted PAH groups such as keto-PAH, hydroxy-PAH and aza-arenes are eluted in these fractions. To identify other compounds than PAH in these fractions, one winter sample extract was divided into two parts which were fractionated and analyzed as shown in Figure 3.1.1. In addition the concentrations of keto-PAH and aza-arenes were determined as outlined under 3.4. The compounds identified by GC/MS are listed in Table 3.1.1-3.1.3. The results can be summarized as follows:

- Salicylic acid was used as a test compound to evaluate the adsorption characteristics of non- and acidic-buffered silica. Recovery from the latter was complete. On normal silica the compound was completely retained.

- Fractionated on non-treated silica, fraction IV contained mainly keto-PAH, organic phosphates (plasticizers used in roof-paper production etc.), dehydroabietic acid (from wood combustion) and some bases such as benzo(c)cinnoline. Methylation made the detection of traces of aliphatic acids possible (Figure 3.1.2 and Table 3.1.1). Fraction V (Figure 3.1.3 and Table 3.1.2) contained the majority of organic acids, some dehydroabietic acid and coffeine (local source).

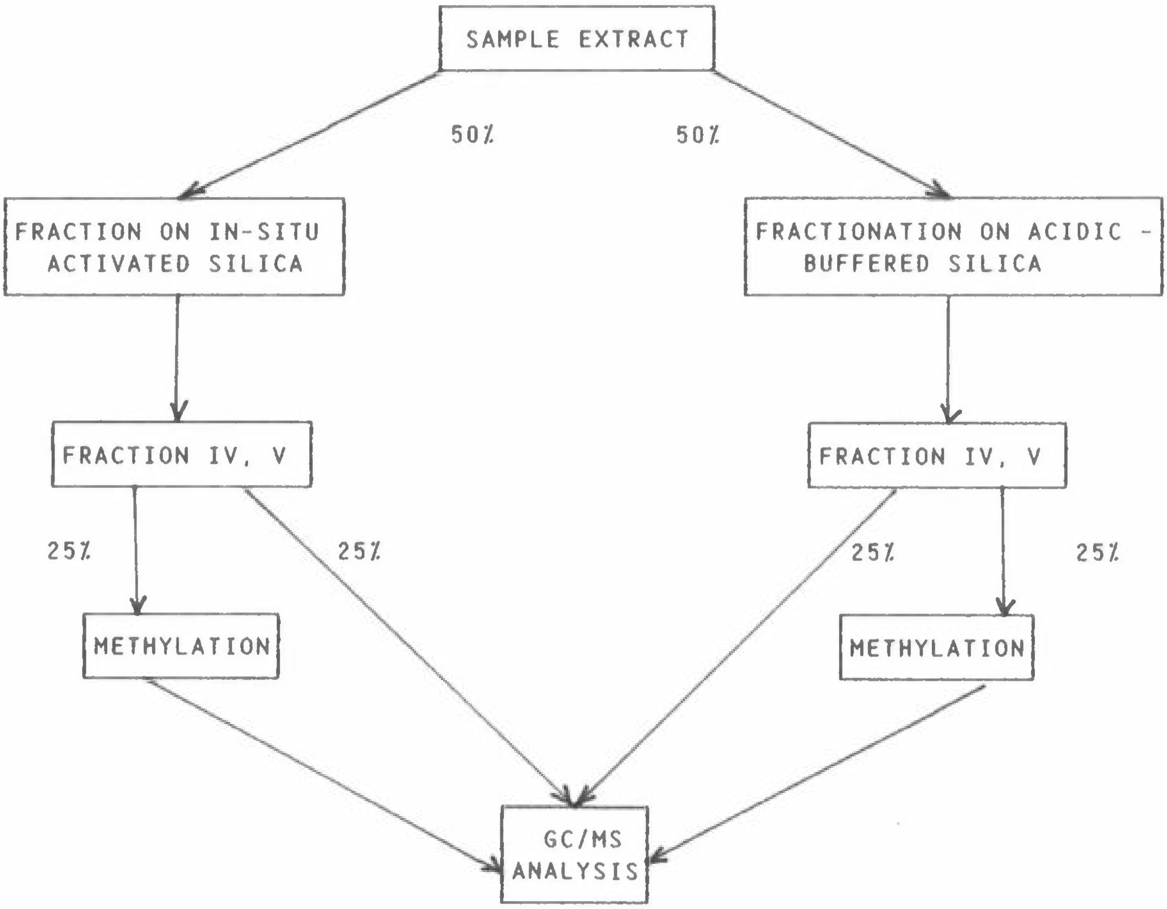

Figure 3.1.1 Sample fractionation and identification of compounds in fraction IV and V (see Table 2.1) from winter sample 1 (see Table 5).

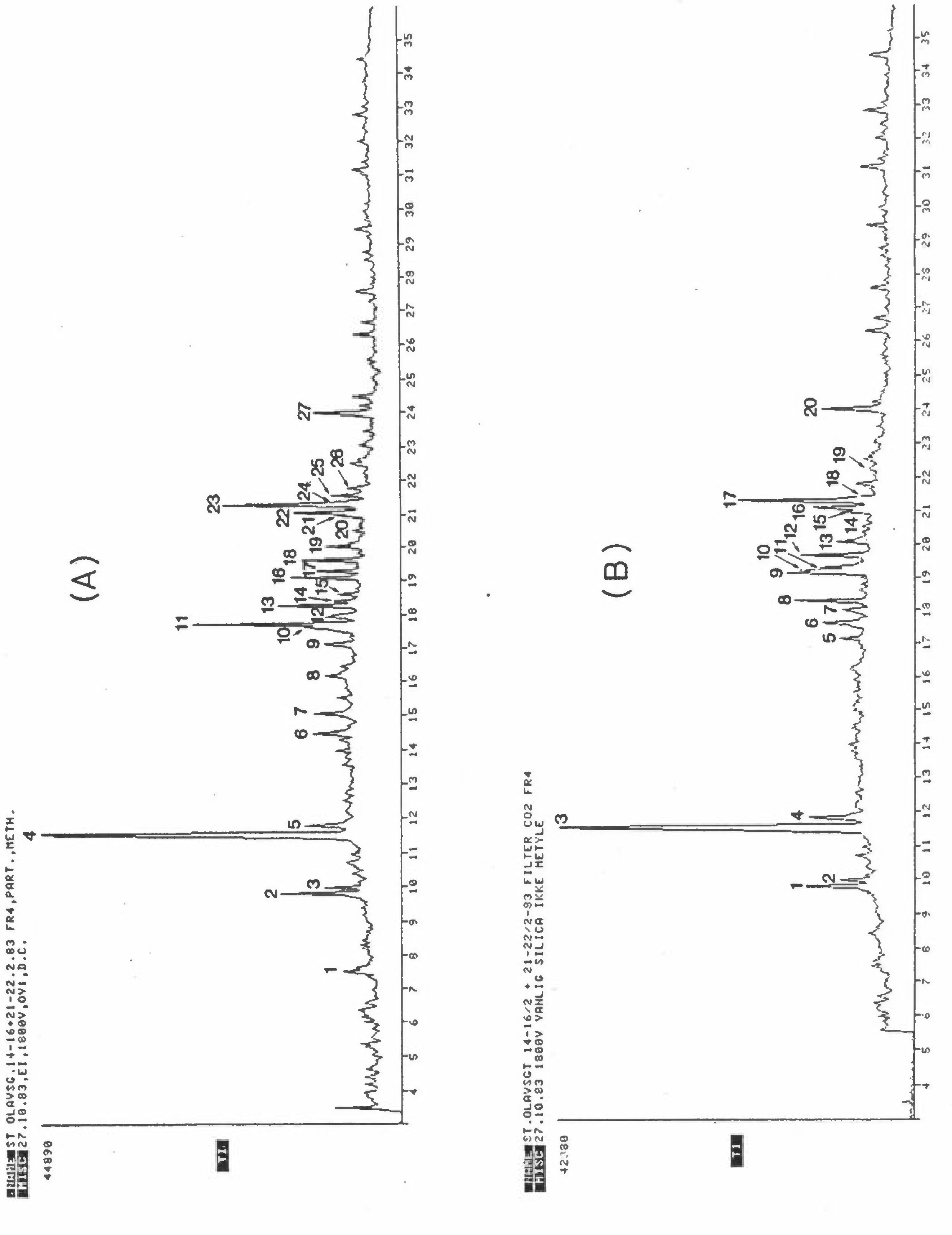

Figure 3.1.2: Reconstructed total ion chromatogram of fraction IV separated on non-treated but activated silica.
(A) after methylation, (B) not methylated.

Table 3.1.1: Identified compounds in fraction IV separated on non-treated but activated silica.

FRACTION 4 DERIVATIZED, UNTREATED SILICA			
Peak no.	Ret.time (min.)	Mol. weight	Structure
2	9.80	180	Benzo(c)cinnoline
3	9.98	?	Phthalate
4	11.52	?	Phthalate
5	11.78	198	1H,3H-naphtho(1,8-cd)pyran-1,3-dione
6	14.47	296	Octadecenoic acid methylester
7	15.05	298	Octadecanoic acid methylester
11	17.73	314	Dehydroabietic acid methylester
12	18.00	230	Benz(de)antracenone or isomer
13	18.27	326	Triphenylphosphate
14	18.40	326	Eicosanoic acid methylester
16	19.10	230	Benzo(de)anthracenone or isomer
17	19.32	314	Hexadecanoic acid dihexylester
18	19.63	340	Methyltriphenylphosphate
19	20.07	340	Methyltriphenylphosphate
21	20.93	354	Dimethyltriphenylphosphate
23	21.28	?	Phthalate
24	21.38	354	Dimethyltriphenylphosphate
25	21.58	354	Docosanoic acid methylester
26	21.78	354	Dimethyltriphenylphosphate
27	24.02	254	Benzo(cd)pyrenone or isomer

Table 3.1.1: Cont.

FRACTION 4, NOT DERIVATIZED, UNTREATED SILICA			
Peak no.	Ret.time (min.)	Mol. weight	Structure
1	9.83	180	Benzo(c)cinnoline
2	9.98	?	Phthalate
3	11.47	?	Phthalate
4	11.83	198	1H,3H-naphtho(1,8-cd)pyran-1,3-dione
7	18.00	230	Benzo(de)anthracenone or isomer
8	18.27	326	Triphenylphosphate
9	19.12	230	Benzo(de)anthracenone or isomer
10	19.20	300	Dehydroabietic acid
11	19.30	314	Hexadecanoic acid dihexylester
12	19.65	340	Methyltriphenylphosphate
13	20.08	340	Methyltriphenylphosphate
15	20.98	354	Dimethyltriphenylphosphate
17	21.30	?	Phthalate
18	21.40	354	Dimethyltriphenylphosphate
19	22.23	368	Trimethyltriphenylphosphate
20	24.02	254	Benzo(c)pyrenone or isomer

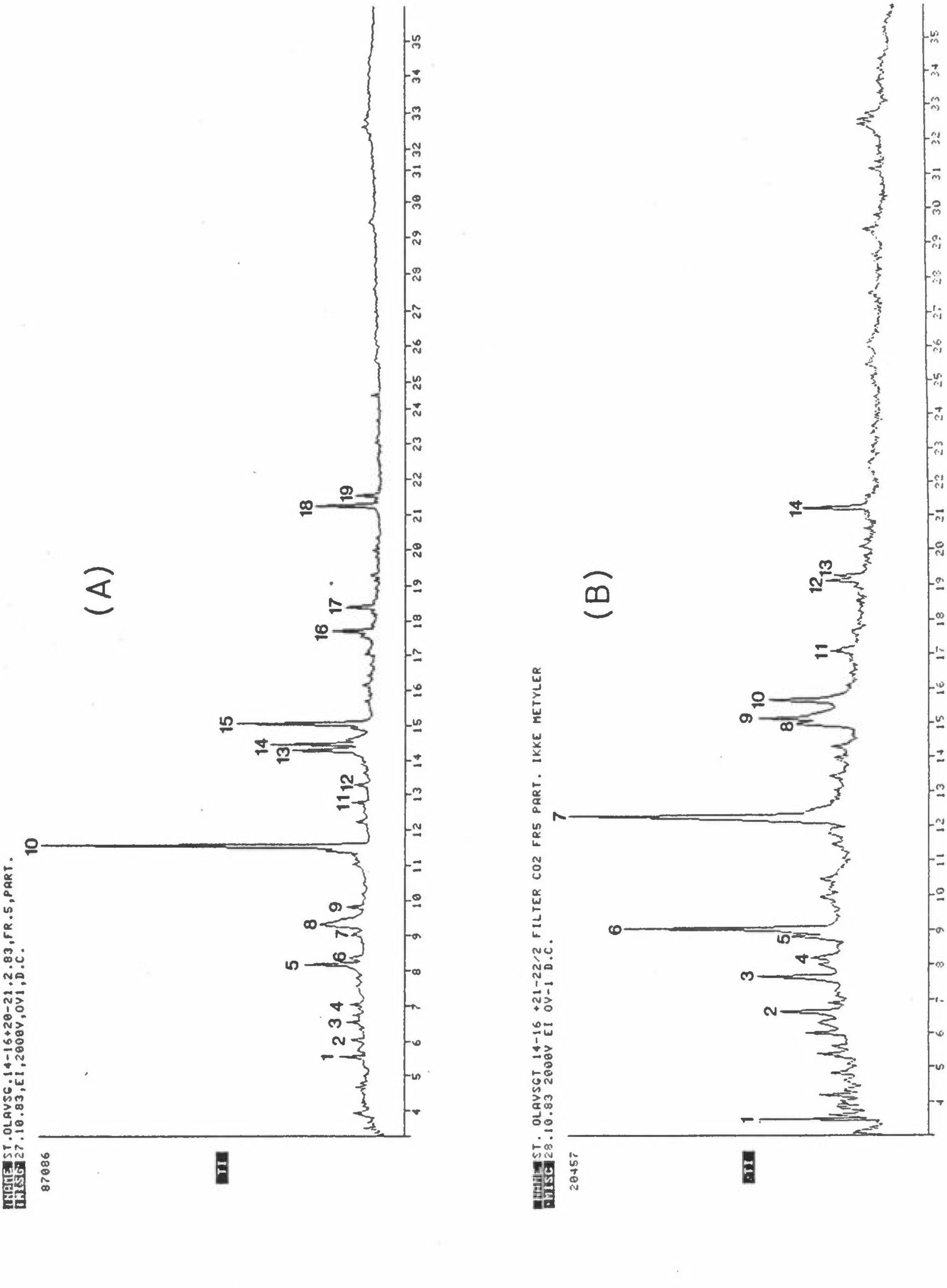

Figure 3.1.3: Reconstructed total ion chromatogram of fraction V separated on non-treated but activated silica. (A) after methylation, (B) before methylation.

Table 3.1.2: Identified compounds in fraction V separated on non-treated but activated silica.

FRACTION 5, DERIVATIZED, UNTREATED SILICA			
Peak no.	Ret.time (min.)	Mol. weight	Structure
1	5.57	214	Dodecanoic acid methylester
2	6.05	196	Benzaldehyde, 3,4,5-trimethoxy-
3	6.55	186	2-Naphthalenecarboxylic acid methylester
5	8.18	242	Tetradecanoic acid methylester
7	9.03	194	1H-Purine-2,6-dione,3,7-dihydro-1,3,7-trimethyl - or isomer (coffeine)
8	9.33	194	1H-Purine-2,6-dione, 3,7-dihydro-1,3,7-trimethyl - or isomer (coffeine)
9	9.83	256	Pentadecanoic acid methylester
10	11.57	270	Hexadecanoic acid methylester
11	12.80	284	Hexadecanoic acid, methyl-, methylester
12	13.30	284	Hexadecanoic acid, methyl-, methylester
13	14.30	294	Octadec-9-ynoic acid methylester
14	14.48	296	Octadecenoic acid methylester
15	15.07	298	Octadecanoic acid methylester
16	17.72	314	Dehydroabietic acid methylester
17	18.43	326	Eicosanoic acid methylester
18	21.28	?	Phthalate
19	21.58	354	Docosanoic acid methylester

Table 3.1.2: Cont.

FRACTION 5, NOT DERIVATIZED, UNTREATED SILICA			
Peak no.	Ret.time (min.)	Mol. weight	Structure
2	6.62	182	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-
3	7.67	196	Ethanone 1-(4-hydroxy-3,5-dimethoxyphenyl)
5	8.83	228	Tetradecanoic acid
6	9.00	194	1H-Purine-2,6-dione, 3,7-dihydro- 1,3,7-trimethyl - or isomer (coffeine)
7	12.20	256	Hexadecanoic acid
8	14.97	280	9,12-Octadecadienoic acid
10	15.67	284	Octadecanoic acid
12	19.13	300	Dehydroabietic acid
14	21.27	?	Phthalate

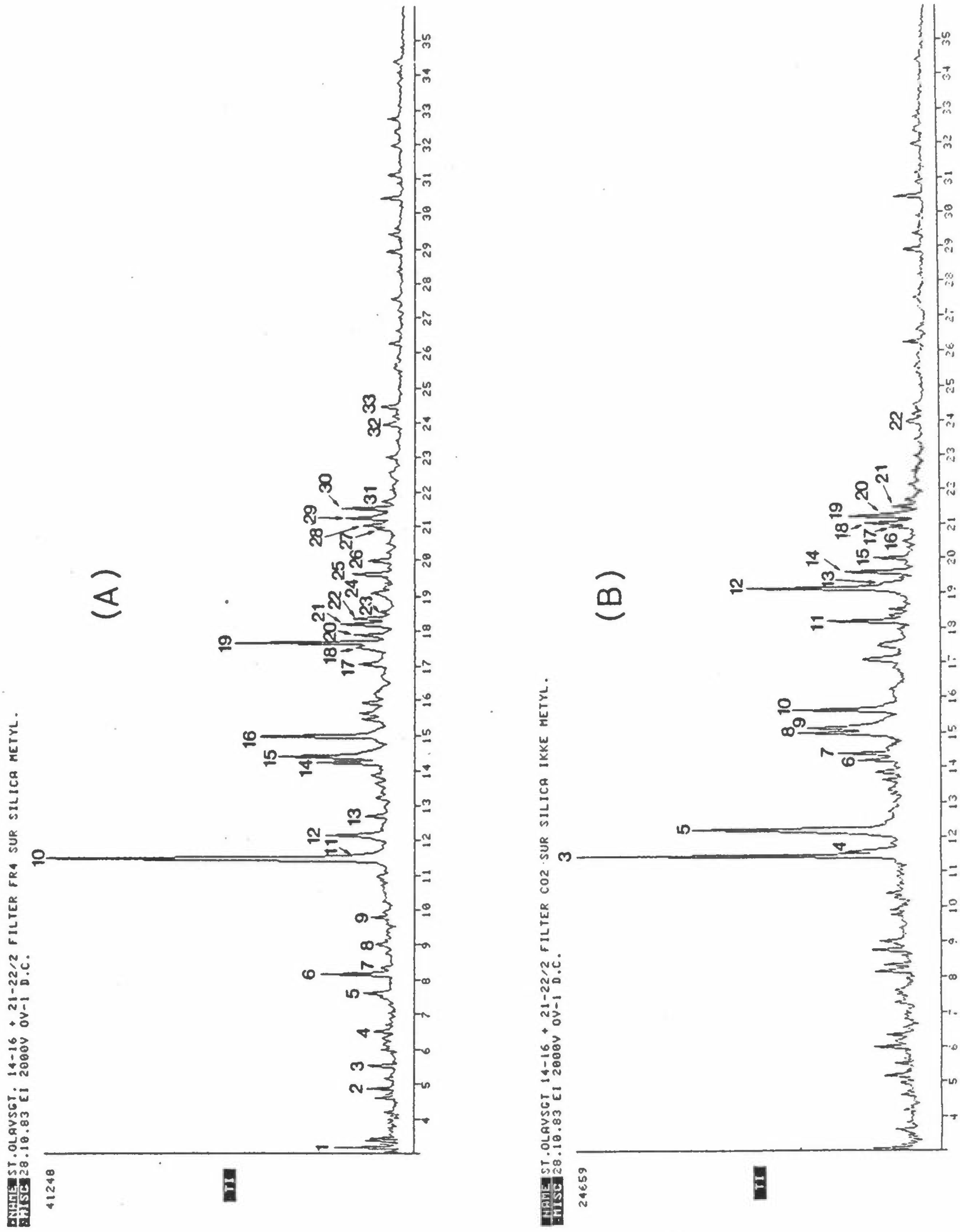

Figure 3.1.4: Reconstructed total ion chromatogram of fraction IV separated on acidic buffered silica.
(A) after methylation, (B) before methylation.

Table 3.1.3: Identified compounds in fraction IV separated on acidic buffered silica.

FRACTION 4, DERIVATIZED, BUFFERED SILICA pH 1			
Peak no.	Ret.time (min.)	Mol. weight	Structure
1	3.20	152	Benzoic acid, 2-hydroxy-methylester
3	5.55	214	Dodecanoic acid methylester
4	6.52	186	2-Naphthalenecarboxylic acid methylester
5	7.63	196	Ethanone, 1-(4 hydroxy-3,5-dimethoxy-phenyl)-
9	9.78	256	Pentadecanoic acid methylester
10	11.47	?	Phthalate
11	11.62	198	1H, 3H-naphtho(1,8-cd)pyran-1,3-dione
12	12.15	256	Hexadecanoic acid
13	12.72	284	Hexadecanoic acid, methyl-,methylester
14	14.23	294	Octadec-9-ynoic acid methylester
15	14.42	296	Octadecenoic acid methylester
16	14.97	298	Octadecanoic acid, methylester
18	17.55	312	1-Phenanthrenecarboxylic acid, 1,2,3,4,4a, 10a-hexahydro-1, 4a-dimethyl-7-(1-methylethyl)-, methylester
19	17.68	314	Dehydroabietic acid methylester
21	18.22	326	Triphenylphosphate
22	18.35	326	Eicosanoic acid methylester
	19.07	230	Benzo(de)anthracenone or isomer
24	19.10	300	Dihydroabietic acid
25	19.60	340	Methyltriphenylphosphate
26	19.98	340	Methyltriphenylphosphate
27	20.93	354	Dimethyltriphenylphosphate
29	21.25	?	Phthalate
30	21.52	354	Docosanoic acid methylester
31	21.73	354	Dimethyltriphenylphosphate
32	23.95	254	Benzo(cd)pyrenone or isomer

Table 3.1.3: Cont.

FRACTION 4, NOT DERIVATIZED, BUFFERED SILICA pH 1			
Peak no.	Ret.time (min.)	Mol. weight	Structure
3	11.47	?	Phthalate
4	11.60	198	1H,3H-naphtho(1.8-cd)pyran-1,3-dione
5	12.22	256	Hexadecanoic acid
6	14.22	294	Octadec-9-ynoic acid methylester
7	14.40	296	Octadecenoic acid methylester
8	14.97	298	Octadecanoic acid methylester
9	15.12	264	Octadecadienal
10	15.65	284	Octadecanoic acid
11	18.20	326	Triphenylphosphate
12	19.03	230	Benzo(de)anthracenone or isomer
13	19.15	300	Dehydroabietic acid
14	19.58	340	Methyltriphenylphosphate
15	20.00	340	Methyltriphenylphosphate
17	20.97	354	Dimethyltriphenylphosphate
19	21.23	?	Phthalate
20	21.35	354	Dimethyltriphenylphosphate
21	21.52	354	Dimethyltriphenylphosphate
22	23.97	254	Benzo(cd)pyrenone or isomer

- Fractionation on acidic-buffered silica led to the following changes (Figure 3.1.4 and Table 3.1.3):

  1. Basic compounds such as coffeine, benzo(c)cinnoline were irreversibly adsorbed.

  2. Higher amounts of aliphatic acid were found. In addition some PAH carboxylic acids were eluted.

  3. All organic acids were found in fraction IV instead of V, which indicates a strongly reduced interaction between the column material and the compounds. No compound amounts of importance could be found in fraction V.

  4. The elution of keto-PAH in fraction IV remained unchanged but some of them were covered by organic acids.

- Methylation of the extracts increased the number of organic acids detected due to less adsorption in the gas chromatographic separation step.

- When HPLC-fraction IV and V from the acid-buffered and the normal silica were concentrated prior to GC/MS-analysis, a brown precipitate was formed. This was most evident in fraction IV from the acid buffered silica. The fact that the precipitate was redissolved by methylation, indicates that the precipitation is formed by phenolic or acidic compounds. The compounds or group of compounds are not seen when analysed by GC/MS neither before or after methylation probably because of too low volatility.

On the basis of these findings one can conclude that acidic-treated silica gives a higher recovery of polar acidic compounds. In addition interferences from basic compounds can be eliminated. Comparing the results with the separation on non-treated silica, additional information about acid - or basic properties of the found compounds is obtained. Figure 3.1.2 shows the differences in the gas chromatograms obtained for fraction IV. Work is in progress to repeat the fractionation with basic buffered silica to get more information about basic compounds. This is of special interest since many carcinogenic compounds are bases.

3.2 Influence of polymeric compounds present in the sample extract on the analysis procedure and biological short-term tests.

Filter extracts always contain a certain amount of high molecular weight compounds (molecular weight >500). These substances may cause the following problems:

- Most of these compounds are more soluble in polar solvents and are therefore mainly found in fraction III-V, which are eluted with more polar solvents. In these fractions normally a precipitate is formed after reducing the solvent volume. The separation due to polarity is overlapped by a separation due to solubility which influences the composition of the different fractions. Direct inlet probe mass spectrometry gave no additional information about the composition of the preciptate. Studies using fast atom bombardment will be carried out in near future.

- Polymeric products can be deposited and pyrolyzed in the hot injector during GC-analysis causing a lot of interfering signals.

Therefore a method was developed to remove compounds with molecular weights >500 from the samples. Microgel high performance liquid chromatography was used. Details of the method are described elsewhere (9). Furthermore it was of interest to know if the removed high molecular fraction had any biological activity. Therefore a winter sample (no. 8, see Table 3.4.1) was divided into 4 parts. One part was tested directly with the Ames test. The second part was divided into two fractions, one containing polymeric compounds (molecular weight ⩾500) and one with low-molecular compounds (m.w. ⩽500). The tests were carried out at Statens institutt for folkehelse and are summarized in Table 3.2.1, appendix 1. The following conclusions could be drawn:

- All mutagenic activity found in the unfractionated sample was concentrated in the fraction with molecular weight <500. No mutagenic activity was measured in the high molecular weight fracton. No cytotoxicity was introduced by the fractionation procedure.

Table 3.2.1: Mutagenic response of a winter sample extract (no. 8, see Table 3.4.1) in the Salmonella assay (Ames test). For further information, see Appendix 1.

	Revertants per m^3 air TA100 - S9	Revertants per m^3 air TA98 + S9
Unfractionated sample	14.3	16.5
HPLC-fraction 1 - 6	toxic	toxic
Gelpermeation fraction 1 molecular weight >500	-	-
Gelpermeation fraction 2	13.3	14.8

Though more tests have to be carried out to confirm the results, microgel permeation chromatography seems to be a helpful technique to remove undesired polymeric precipitates from the sample without affecting its mutagenic properties.

Furthermore the applicability of the HPLC fractionation procedure in connection with biological tests was investigated. The third part of the winter sample was fractionated into 5 fractions and an additional fraction was eluted with methanol (fraction 6). As can be seen from Appendix 1 all fractions had an exceptional high degree of cytotoxicity and no quantitative information about mutagenicity could be obtained by the Ames test. Comparable blank samples of the fractionation procedure did not show any cytotoxicity. Since no reasonable explanation for the cytotoxicity of the sample could be found, an additional sample was fractionated. To enable a comparison with another fractionation procedure developed at the Central Institute for Industrial Research (14) a wood combusiton emission samples containing a large amount of substituted PAH was chosen. Though the two fractionation procedures differed somewhat concerning the collection of the more polar fractions the results of the Ames tests were comparable and no strong cytotoxicity could be found. The results are summarized in Appendix 1.

3.3 Sample extract stability

Preliminary studies with standard solutions containing different substituted PAH showed that some compounds were rather unstable in solution. Since the stability of a sample during storage is of great importance, storage tests with different solvents were carried out at -18^0C and at room temperature. Mixtures of substituted PAH are less stable at room temperature than their parent-PAH. Hydroxy-, amino- and some nitro-PAH are completely decomposed after 2 weeks when methylene chloride is used as solvent. Storage in cyclohexane at -18^0C diminished the compound decomposition considerably. The main reason is transformation of the solvent to the solid state at this temperature. When dimethyl sulfoxide was used as solvent comparable stabilities as for cyclohexane were obtained. Table 3.3.1 summarizes the results. In addition it was found that pure solutions of some amino-PAH (e.g. 1-amino-anthracene) were extremely unstable and a brown precipitate was formed after some days.

Table 3.3.1: Stability test of standard solutions containing substituted PAH. Recovery rates are given in % relative to pyrene[a].

Compound	Solvent CH_2Cl_2		Solvent cyclohexane	
	$96h/-18^0$C	$312h/20^0$C	$96h/-18^0$C	$312h/20^0$C
1.4-Naphthoquinone	87	76	101	88
1-Naphthol	97	0	91	43
9H-Fluorenone	101	93	101	108
Acridine	100	79	97	48
9H-Carbazole	91	85	102	96
9-Nitroanthracene	106	24	76	13
1-Aminoanthracene	6	0	79	0
Benz(a)acridine	103	79	81	60

[a] Precision of the gas chromatographic determination is ca ± 3%. Average of two parallels.

3.4 Quantitative determination of some selected substituted PAH in urban air samples from Oslo

To get a better knowledge about the concentration level of substituted PAH in urban air, a quantitative analysis of some winter and summer samples were carried out. Particulate matter of about 450-1000m^3 of air was collected on glass fiber filters as described in (10). Vapor phase sampling was carried out using polyurethane foam plugs (10). The samples were extracted and fractionated using the procedure described before. Quantification was carried out using the following methods:

Parent - PAH

Hewlett Packard 5880A, flame ionization detector.
Injector temperature : 300^{0}C.
Detector temperature : 300^{0}C.
Carrier gas : He, 6 ml/min (1.4 bar).
Capillary : SE52, 25 m x 0.3 mm i.d.
0.1 µm film thickness.
Injection volume : 0.5 µl, splitless injection.
Temperature program : 40 - 100^{0}C, 30^{0}C/min,
100 - 300^{0}C, 8^{0}C/min.

Quantification method: Internal standard
Internal reference compounds: 3,6-dimethylphenanthene
2,2'-binaphthyl

All quantified compounds were commercially available (for sources of reference compounds see (9)).

NO_2-PAH and keto-PAH

Hewlett Packard 5985B, GC/MS system
Injector temperature : 270^{0}C.
Interface temperature: 280^{0}C.
Carrier gas : He, 3 ml/ml.
Capillary : OV1, 25 m x 0.32 mm i.d.

fused silica, 0.17 µm film thickness, direct coupled.

Injection volume : 1 µl, splitless injection.

Temperature program : 40 - 130^0C, 30^0C/min,
130 - 280^0C, 5^0C/min.

Ionization mode : Negative ion chemical ionization
0.4 torr CH_4, 200^0C source temperature
95 eV electron energy.

Selected ion monitoring with dwell time 50 ms, total cycle time 250 ms.

Aza-arenes

Same conditions as for NO_2-PAH except ionization mode: Electron impact ionization, 70 eV, standard conditions.

Quantification of NO_2-PAH, keto-PAH and aza-arenes

Quantification method: External standard.
No reference compounds were found being suitable as internal standard with comparable chemical and physical behaviour and not being present in the sample. All quantified compounds were available as reference compounds from different sources (9).

Ions used in the selected ion monitoring mode for quantification:

Nitronaphthalenes :	173	Quinolines :	143
Nitrobiphenyls :	199	Methylquinoline :	157
Nitrofluorenes :	211	5,6-Benzoquinoline :	179
Dinitronaphthalenes:	218	Indeno(1,2,3-i,j)iso-quinoline:	203
9-Nitroanthracene :	223	Acenaphtho(1,2-b)pyridine :	203
1-Nitropyrene :	247	Benzo(l,m,n)phenanthridine :	203
6-Nitrobenzo(a)pyrene:	297	Dibenzofluorenone :	280
Naphthoquinone :			
Fluorenone :	180		
Anthraquinone :	208		
Benzo(de)anthracenone:	230		

The results of the quantitative analysis are listed in the Tables 3.4.2 - 3.4.5. Table 3.4.1 gives additional information about sampling conditions. The following conclusions seem to be viable:

- as expected the highest concentrations for all compound classes were found in the winter samples.

- only traces of NO_2-PAH were found in the September samples. Comparable results were reported for 1-nitropyrene in summer samples from Ås, Grenland (13). In February values up to 200 pg/m^3 for single compounds could be found, which are considerably higher values than those reported by Nielsen (15) from particulate matter sampled in Denmark.

NO_2-PAH are direct mutagens of high activity. Therefore it is difficult to compare the biological activity caused by NO_2-PAH with that from parent-PAH (indirect mutagens) present at much higher concentration levels. Schützle et al. (5) found that more than 40-60% of the total mutagenic activity of diesel emission samples was concentrated in the fraction containing NO_2-PAH. This fraction was only 4-6% of the total weight of the sample.

Table 3.4.1: Samples collected for identification and quantification of substituted PAH in urban air particulate matter.

Sample No.	Sampling date	Sample volume [m^3]	Average flow velocity [l/min]
1	14-16/2-83	694	319
2	18-19/2-83	496	324
3	30/8-1/9-83	1056	367
4	5-7/9-83	921	319
5	13-15/9-83	960	342
6	20-22/9-83	972	356
7	26-28/9-83	960	340
8	17-26/1-83	3056	344

Table 3.4.2: Aerosol concentrations of some parent PAH at St. Olavs gate in February and September 1983

Compound name	[ng/m^3]						
	14-16/2+21-22/2	18/19-2	30/8-1/9	5-7/9	13-15/9	20-22/9	26-28/9
Phenanthrene	2.6	1.7			0.1	0.1	0.2
Anthracene	0.6	0.2					
2-methylphenanthrene	1.7	1.6			0.1	0.1	0.1
2-methylanthracene	0.6	0.5					
1-methylphenanthrene	1.4	1.3			0.1	0.1	0.1
Fluoranthene	8.8	8.9	0.2	0.3	0.5	0.4	0.6
Pyrene	11.9	12.3	0.2	0.4	0.6	0.5	0.9
Benzo(a)fluorene	6.5	5.4		0.3	0.4	0.2	0.5
Retene	2.4	1.2			0.1		
Benzo(b)fluorene	3.7	2.7		0.2	0.2	0.1	0.2
Benzo(g,h,i)fluoranthene	7.7	5.8	0.1	0.3	0.6	0.3	0.5
Cyklopenta(cd)pyrene	23.1	13.2	0.2	0.3	0.4	0.7	0.4
Benz(a)anthracene	4.4	4.4	~0.1	0.2	0.5	0.2	0.4
Chrysene/Triphenylene	6.4	5.1	0.2	0.3	0.7	0.3	0.5
Benzo(b/j/k)fluoranthenes	8.0	7.5	0.4	1.0	2.4	0.9	1.7
Benzo(e)pyrene	4.0	3.4	0.4	0.6	1.5	0.8	1.0
Benzo(a)pyrene	4.3	4.0	0.1	0.4	1.1	0.4	0.7
Perylene	0.7	0.8		0.1	0.3	0.2	0.2
Inden-(1,2,3-c,d)pyrene	2.9	2.5	0.2	0.4	1.1	0.3	0.9
Dibenzo(ac/ah)anthracenes	0.2	0.2			0.1		
Benzo(g h i)perylene	5.5	4.5	0.4	1.2	2.7	0.9	2.0
Anthanthrene	1.5	1.0			0.2		
Coronene	2.8	3.6		0.6	1.2	0.3	1.1
1,2,4,5-dibenzopyrene							
Sum ng/m^3	112.0	91.8	2.5	6.6	14.9	6.8	12.0

Table 3.4.3: Aerosol concentrations of some major NO_2-PAH at St. Olavs gate in February and September 1983.

	$[ng/m^3]$							
Compound name	14-16/2+21-22/2	18/19-2	30/8-1/9	5-7/9	5-7/9 PUR-plug	13-15/9	20-22/9	26-28/9
Sum nitronaphthalenes	0.016	0.025	0.001	0.001	0.006	0.001	0.001	0.001
Sum nitrobiphenyls	0.009	0.011	n.d.	n.d.	0.003	n.d.	n.d.	n.d.
Sum nitrofluorenes	0.04	0.04	n.d.	n.d.	0.003	n.d.	n.d.	n.d.
Sum dinitronaphthalenes	0.15	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
9-nitroanthracene	0.17	0.10	0.002	0.003	0.003	0.001	0.004	0.014
1-nitropyrene	0.22	0.10	0.01	0.04	n.d.	0.06	0.022	0.072
6-nitrobenzo(a)pyrene	0.062	n.d.	0.006	0.006	n.d.	n.d.	n.d.	0.014
Sum $[ng/m^3]$	0.67	0.28	0.02	0.05	0.02	0.06	0.03	0.10

n.d.: not detected or close to detection limit.

Table 3.4.4: Aerosol concentrations of some aza-arenes at St. Olavs gate in February and September 1983.

	[ng/m^3]							
Compound name	14-16/2+21-22/2	18/19-2	30/8-1/9	5-7/9	5-7/9 PUR-plug	13-15/9	20-22/9	26-28/9
Quinoline	0.075	0.049	n.d.	n.d.	0.011	0.008	0.003	0.016
Isoquinoline	0.53	0.89	0.007	0.008	0.16	0.037	0.082	0.39
Methylisoquinolines	0.84	2.48	0.04	0.111	0.35	0.14	0.49	0.98
5,6-Benzoquinoline	0.17	0.19	0.002	0.002	0.009	0.013	0.008	0.022
Indeno(1,2,3-i,j)iso quinoline	0.15	0.18	n.d.	0.002	n.d.	0.008	0.005	0.016
Acenaphtho(1,2-b)pyridine	0.15	0.14	n.d.	0.002	n.d.	0.007	0.004	0.013
Benzo(l,m,n)phenanthridine	0.08	0.13	n.d.	0.005	n.d.	0.014	0.005	0.028
Sum [ng/m^3]	1.99	4.06	0.013	0.13	0.53	0.23	0.60	1.47

Table 3.4.5: Aerosol concentrations of some major keto-PAH at St. Olavs gate in February and September 1983.

Compound name	$[ng/m^3]$						
	14-16/2+21-22/2	18/19-2	30/8-1/9	5-7/9	13-15/9	20-22/9	26-28/9
Naphthoquinone	0.07	0.08	0.001	0.002	0.001	0.002	0.005
Fluorenone	0.21	0.67	0.005	0.009	0.002	0.02	0.006
Anthraquinone + isomers	11.8	15.0	0.1	0.23	0.05	0.37	0.55
Benzo(de)anthracenone + isomers	6.3	6.1	0.06	0.38	0.02	0.35	0.72
Benzo(cd)pyrenone	8.4	5.4	0.12	1.07	0.7	0.73	1.33
Dibenzofluorenone + isomers	0.2	0.3	0.004	0.02	<0.001	0.02	0.05
Sum $[ng/m^3]$	26.7	27.6	0.29	1.71	0.77	1.49	2.66

Artifact formation of NO_2-PAH during sampling is a problem which has been discussed extensively in the literature. Recent results have been published which indicate that about 10-15% of the NO_2-PAH found in diesel emissions are formed during sampling (16). However, the emission sampling conditions favor the formation of NO_2-PAH (high temperature, high NO_x concentration and particle content).

- the concentration level of keto-PAH was about the same as for parent-PAH in September. In February the level decreased to about 25% of the parent-PAH. This means that keto-PAH are the only group of substituted PAH which is present in concentrations comparable to parent-PAH. High temperatures in September and more day light favors the formation of keto-PAH which explains the increased level compared to the parent compounds. The concentration levels found found in February are about a factor of 5 higher than those reported in a German study of airborne particulate matter (6). A better extraction efficiency of the present method is a possible explanation. Little is known about the mutagenicity of keto-PAH. A few benzopyrene ketones have been reported to be direct-acting mutagens (17) as well as oxidation products of pyrene and some hydroxy-PAH (18). Fluorenone has been found to be a stimulator of microsomal expoxide hydrase (19). As can be seen from Appendix 1 the major part of the mutagenic activity without S9-activation is found in the keto-PAH fraction.

- The concentration level of the measured aza-arenes is rather low compared with the values for parent-PAH and keto-PAH. The main sources for aza-arenes are coal (20) crude petroleum (21) and products from coal-liquification. Once again higher values were found in the winter samples. Similar concentration levels were found in samples taken in

Oslo in March 1981 and in air particulate matter from New York (22). However, the differences are less significant than for other groups of PAH. Since little is known about other sources of aza-arenes it is difficult to explain the increased values at the end of September. Both quinoline, the methylquinolines and all 3-5 ring aza-arenes have a moderate to medium carcinogenic activity.

- All substituted PAH are more polar and have a decreased vapor pressure compared with the parent- and methylated PAH. Their occurance in the vapor phase should therefore be less dominant as observed for parent-PAH (23). To get an idea about the distribution between particulate matter and the vapor phase the polyurethane foam plugs of one sample were extracted by CO_2. Since the volume of the CO_2-extractor was not big enough the extraction was carried out by cutting the plugs into 4 pieces. However, this made the extraction procedure extremely time-consuming. Some preliminary results showed that the CO_2-extraction efficiency is only about 50% for polyurethane foam (recovery rates between 30 and 50%). Therefore, only one sample was treated in that way. Investigations to use Freon F12 low-temperature extraction for polyurethane foam is in progress. Surprisingly both keto-PAH and aza-arenes occure in larger concentrations in the vapor phase than adsorbed to particulate matter. Similar results were reported for aza-arenes (24). Work is in progress to overcome the problems mentioned above to make a proper quantification of the vapor-phase possible.

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APPENDIX 1

Comparison of the mutagenic response in the Salmonella assay of a fractionated wood combustion sample using the procedures developed by SI and NILU.

Bacteria	TA 98 Revertants per g dry wood			
	SI		NILU	
	-S9	+S9	-S9	+S9
Fraction I			0	0
Fraction II	<90	920	120	1010
Fraction III	140	<90	170	50
Fraction IV	90	<90	120	170
Fraction V	610	660	1460*	420
Fraction VI	toxic	<90	370	0
Sum:	840	1670	2240	1650
Not fractionated sample:	1570	2610		
Blank I-V			0	0
Blank VI			0	0

*Estimate due to toxic effects of the fraction. The results are based on the lowest test dosis and are probably too low.

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2001 LILLESTRØM

Deres ref.
Vår ref. 365/TA
Dato 6.12.83

LUFTEKSTRAKSJONSPROSEDYRE M CO_2 (HPLC fraksjon 1-6) OG GPC-FRAKSJONERING (2 fraksjoner)

Alle prøver ble innledningsvis testet i QRA for å få et inntrykk av deres cytotoksisitet. Prøvevolum var 90 ul, som tilsvarer:

- ufraksjonert prøve 27,5 m^3 luft
- HPLC fraksjon 1: 13,8 " "
- HPLC fraksjon 2-6: 27,5 " "
- GPC fraksjon 1: 24,8 " "
- " " 2: 27,5 " "

Den ufraksjonerte prøven var svakt mutagen (1,30 mutanter/10^6 overlevende mot kontroll 0,44 mut/10^6 overlev.), og svakt cytotoksisk (17% toksisitet). HPLC fraksjonene viste alle meget høy cytotoksisitet (ned i 1-2% overlevende), og det er på et slikt grunnlag ikke mulig å si noe om deres mutagene potensiale. GPC fraksjon 1 og 2 viste svak mutagen aktivitet (h.h.v. 0,6 og 0,8 mut./10^6 overlevende), men ingen tegn til cytotoksisitet.

På bakgrunn av resultatene i QRA gikk man over til V. Ames, og reduserte prøvevolumene pga den sterke cytotoksisiteten. Alle fraksjoner ble testet med TA 98 + S9, prøvevolum 20, 40 og 60 ul. Resultatene viste samme tendens som i QRA. Den ufraksjonerte luftprøven ga doseavhengig, mutagen respons (134-349 mutanter pr. skål, gj.snitt 16,5 mut/m^3 luft), og viste ingen tegn til cytotoksisitet. HPLC fraksjon 1-6 viste sterk, doseavhengig toksisitet bedømt ved mikroskopering av bakgrunnen, og ingen mutagenitet. GPC fraksjon 2 ga omtrent samme respons som den ufraksjonerte prøve (gj.snitt 14,8 mut/m^3 luft), og ingen av de to GPC fraksjonene viste tegn til toksisitet.

For å fange opp eventuelle direktevirkende mutagener ble alle fraksjoner avslutningsvis testet med TA 100 - S9, og samme prøvevolumer (20,40 og 60 ul). Som ventet ble cytotoksisiteten noe

(2)

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større uten aktiveringsenzym tilstede, men ellers ble resultatene som tidligere. Den ufraksjonerte prøven ga i gj.snitt 14,3 mutanter/m^3 luft, GPC fraksjon 2 i gj.snitt 13,3 mut/m^3 luft.

På grunn av den sterke cytotoksisiteten ble også blindprøver kjørt på h.h.v. aktivert og ikke aktivert kolonne, testet. Disse prøvene ga negativt utslag både når det gjelder mutagenitet og toksisitet.

Fordi luftprøven i utgangspunktet ga såpass lav mutagen respons var det ikke mulig å redusere prøvevolumet ytterligere, og det er derfor ikke mulig å si noe om mutageniteten i de forskjellige HPLC fraksjonene.

På bakgrunn av de resultatene som foreligger her, virker ikke CO_2-ekstraksjonsprosedyren hensiktsmessig for opparbeidelse av luftprøver for biologisk testing.

GPC fraksjoneringen falt heller ikke så gunstig ut, da all mutagen aktivitet forble samlet i en fraksjon. Denne prosedyren bevirket imidlertid ikke at luftprøven ble toksisk.

Med hilsen

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TITTEL Determination of substituted polycyclic aromatic hydrocarbons in urban air particulate matter.		PROSJEKTLEDER M. Oehme NILU PROSJEKT NR. N-8307
FORFATTER(E) H. Stray, A. Mikalsen, M. Oehme		TILGJENGELIGHET** A OPPDRAGSGIVERS REF.

OPPDRAGSGIVER
Utvalg for miljøgifter, SI, Postboks 350, OSLO 3

3 STIKKORD (á maks. 20 anslag)

Particulate matter	Substituted PAH	Quantitative determination

REFERAT (maks. 300 anslag, 5-10 linjer)

En kvantitativ metode for bestemmelse av substituerte polysykliske aromater i partikkelfasen er beskrevet. Flytende CO_2-ekstraksjon, forseparasjon på aktivert silica og gasskromatografisk separsjon kombinert med negativ ion massespektrometri anvendes. Kvantative resultater fra vinter- og sommerprøver samlet i St. Olavsgate, Oslo diskuteres.

TITLE

ABSTRACT (max. 300 characters, 5-10 lines.

A method for quantitative determination of substituted polycyclic aromatics in air particulate matter is described based on liquid CO_2-extraction, prefractionation on activated silica and gas chromatographic separation combined with negative ion mass spectrometry. Results from winter and summer samples collected at St. Olavsgate, Oslo, are reported.

**Kategorier:

Åpen - kan bestilles fra NILU	A
Må bestilles gjennom oppdragsgiver	B
Kan ikke utleveres	C