



ELSEVIER

Journal of Chromatography A, 846 (1999) 295–306

JOURNAL OF  
CHROMATOGRAPHY A

## Gas chromatographic determination of synthetic musk compounds in Norwegian air samples

Roland Kallenborn<sup>a,b,\*</sup>, Robert Gatermann<sup>a,b</sup>, Sissel Planting<sup>a,b</sup>, Gerhard G. Rimkus<sup>c</sup>,  
Margrete Lund<sup>a,b</sup>, Martin Schlabach<sup>a,b</sup>, Ivan C. Burkow<sup>a,b</sup>

<sup>a</sup>Norwegian Institute for Air Research (NILU), Polar Environmental Centre, N-2007 Kjeller, Norway

<sup>b</sup>Norwegian Institute for Air Research (NILU), Polar Environmental Centre, N-9296 Tromsø, Norway

<sup>c</sup>Official Food and Veterinary Institute Schleswig-Holstein, P.O. Box 2743, D-24517 Neumünster, Germany

### Abstract

A new method is described for the simultaneous analysis of nitro and polycyclic musks in air samples. Additional considerations are given to the aspects of sample preparation and blank problems. For the first time concentration levels of synthetic musks in selected Norwegian air samples were determined. In a preliminary investigation using ambient air samples prepared for the determination of persistent organic pollutants, musk xylene concentrations were between 8 and 19  $\text{pg}/\text{m}^3$ . A new sample preparation for the simultaneous analysis of polycyclic and nitro musks is presented. Both GC-electron impact (EI) MS and GC-negative ion chemical ionisation (NICI) MS were compared as detection methods. GC-EI-MS is to be preferred for the determination of synthetic musks since GC-NICI-MS is not sensitive enough for the determination of polycyclic musks. Blank problems occurred which have to be carefully considered during the whole work-up procedure. One indoor air sample was taken in the laboratory where the clean-up of the samples took place to evaluate laboratory air contamination. A concentration for 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclo[g]-2-benzopyrane of 2470  $\text{pg}/\text{m}^3$  was found using gas chromatographic separation coupled with mass spectrometric detection in the electron impact mode (GC-low-resolution EI-MS). A set of four ambient air samples taken nearby the institute facilities was analysed for both nitro and polycyclic musks. For polycyclic musks, concentrations up to 130  $\text{pg}/\text{m}^3$  (GC-EI-MS) were determined and for musk xylene a concentration maximum in ambient air samples 54  $\text{pg}/\text{m}^3$  (low resolution EI-MS) was found. Critical considerations about laboratory contamination, clean-up and analysis of ambient air samples are given. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Air analysis; Environmental analysis; Musk compounds

### 1. Introduction

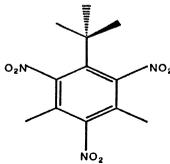
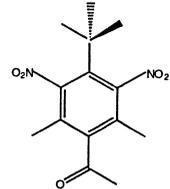
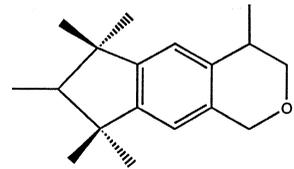
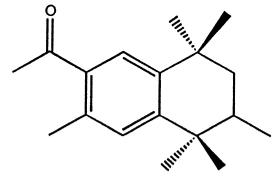
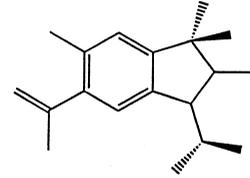
Synthetic musk compounds are a relatively heterogenic group of chemicals, with large differences in their chemical structure (Table 1). Being strong fragrances with the typical musk odour, these compounds are used extensively during the past century in perfume and toiletry industry as surrogates

for natural musks. The group of synthetic musks can be divided in two main subgroups: nitro musks (e.g., musk xylene and musk ketone) and polycyclic musks (e.g., Tonalide and Galaxolide). Nowadays, polycyclic musk compounds are mainly used in the European fragrance industry, whereas nitro musks are used in the US [1]. Chinese and Indian manufacturers are worldwide leaders in production and export of nitro musk fragrances [2].

In the early 1980s the occurrence of nitro musks in

\*Corresponding author.

Table 1  
Structures, CAS number and IUPAC nomenclature of the selected synthetic musk compounds

Structure	IUPAC nomenclature	Brand name	CAS No.	Abbreviation
	1- <i>tert.</i> -Butyl-3,5-dimethyl-2,4,6-trinitrobenzene	Musk xylene	81-15-2	MX
	4-Acetyl-1- <i>tert.</i> -butyl-3,5-dimethyl-2,6-dinitrobenzene	Musk ketone	81-14-1	MK
	1,3,4,6,7,8,-Hexahydro-4,6,6,7,8,8,- hexamethylcyclo[g]-2-benzopyrane	Galaxolide, Abbalide, Pearlide	1222-05-5	HHCB
	1-(5,6,7,8-Tetrahydro-3,5,5,6,8,8,- hexamethyl-2-naphthalenyl)-ethanone	Tonalide, Fixolide	1506-02-1	AHTN
	1-[2,3-Dihydro-1,1,2,6-tetramethyl-3- (1-methylethyl)-1H-inden-5-yl]-ethanone	Traseolide	68140-48-7	ATII

biological samples and river water was proven for the first time by a Japanese research group [3]. Considerable concentrations were found in freshwater fish from sampling sites at the river Tama nearby Tokyo. Almost ten years after this first evidence of the occurrence of nitro musks in environmental samples, new evidence was published for considerable levels of this group of compounds in the European environment [2]. First calculations on their physical properties (e.g., lipophilic properties and stability) indicated a surprisingly high accumula-

tion potential in biological systems [2,4,5]. Today, synthetic musk compounds are identified and quantified in a large number of environmental samples using various analytical methods [1–9].

Due to the physical properties of the two groups of synthetic musks, four main detection methods coupled with gas chromatography are used for the determination. For nitro musk compounds, capillary gas chromatography with electron capture (GC–ECD) and nitrogen–phosphorus detection (NPD) are suitable tools for trace analysis [1,7,8,11]. In addi-

tion, capillary gas chromatography coupled with low-resolution mass spectrometry in the negative ion chemical ionisation mode (GC–NICI-MS) is a very sensitive way to determine nitro musk chemicals [2,6,8,10]. For polycyclic musks, mainly gas chromatography with low-resolution mass spectrometry in the electron impact mode (GC–EI-MS) is used for the determination [7,9]. In a few cases, also high-resolution mass spectrometry has been applied for the quantification of polycyclic musk compounds [7].

In the present investigation special focus is laid upon analytical methods related to the simultaneous determination of nitro and polycyclic musks in ambient air samples using different ionisation modes for the GC–low-resolution MS analysis.

## 2. Experimental

### 2.1. Sample collection

Ten ambient air samples collected at Lista (South Norway) in 1997 already analysed for persistent organic pollutants (POPs) in the “Comprehensive Atmospheric Monitoring Program (CAMP)” were used for preliminary musk analyses. Air samples (24–36 h) were taken with a sample volume of about 500–600 m<sup>3</sup> air. Furthermore, four air samples (24–38 h, 500–1200 m<sup>3</sup> volume) and a two-day low-volume indoor air sample (108 m<sup>3</sup> volume) for the simultaneous analysis of synthetic musks were taken at Kjeller, near Oslo (Norway). The sample list is given in Table 2. The high-volume sampling system as described earlier [12] was used. Particles were collected on a glass fibre filter of 142 mm diameter (GFF, Gelman type AE, No. 61635, >99% cut-off for 0.2 μm). Compounds in the gas phase were adsorbed on two polyurethane foam plugs in series (PUF, 100 mm diameter, 50 mm thickness and density of 25 kg/m<sup>3</sup>). The ambient air samples were kept frozen at –30°C until further preparation for analysis. A low-volume sample device was employed for an indoor air sample in the laboratory [17].

### 2.2. Chemicals and reagents

For quantification of all compounds crystalline reference material was used and obtained from

Promochem (Wesel, Germany). <sup>13</sup>C-isotope labelled α-benzene hexachloride (HCH), as internal standard was purchased from Cambridge Isotope Labs. (Woburn, MA, USA). For the simultaneous determination of synthetic musks a deuterated ([<sup>2</sup>H<sub>9</sub>]-musk xylene, provided by G.G. Rimkus and M. Wolf, was used. Solvents of pesticide grade were employed (E. Merck, Darmstadt, Germany).

### 2.3. Sample preparation methods

Method 1: The PUF/GFF samples taken at Lista were cleaned and prepared for the analysis of POPs as published earlier [12].

Method 2: A modified sample preparation for the analysis of synthetic musks in the five air samples, taken at Kjeller was developed. Different solvent systems were tested for silica fractionation. The reliability of the new method was estimated with additional analyses of one unexposed PUF/GFF (blank) and one indoor air sample (estimation of laboratory contamination).

### 2.4. Sample extraction and clean-up for the simultaneous determination of synthetic musks

Internal standard [<sup>2</sup>H<sub>9</sub>]musk xylene was added to the PUF-plugs prior to sample extraction. The glass fibre filter and PUF-plugs were Soxhlet-extracted with 300 ml *n*-hexane–diethyl ether (9:1) for 8 h. After volume concentration to 0.5 ml with a Zymark Turbovap 500 system (Hopkinton, MA, USA), a chromatographic clean-up was carried out on 8 g precleaned silica (E. Merck, particle size 63–200 μm, activated at 600°C for 8 h) in a column of 200×15 mm covered with 1 g precleaned Na<sub>2</sub>SO<sub>4</sub> (8 h at 600°C). The first fractionation was performed as follows: fraction 1: 48 ml *n*-hexane, fraction 2: 50 ml *n*-hexane–ethyl acetate (9:1, v/v), fraction 3: 50 ml *n*-hexane–ethyl acetate (4:1, v/v), fraction 4: 50 ml *n*-hexane–ethyl acetate (1:1, v/v) according a fractionation method introduced by Weichbrodt et al. [13]. Fraction 2 contains all musk compounds of interest. Fractions 3 and 4 contained different persistent organic pollutants. Due to insufficient clean-up of fraction 2 one additional test was undertaken to improve the silica fractionation. For this test a new column system was employed. A glass column (25×1 cm I.D.) was filled with 4 g precleaned activated

Table 2  
Sample list and concentration values for the Norwegian air samples<sup>a</sup>

Sample No.	Musk method (pg/m <sup>3</sup> )												POP method (pg/m <sup>3</sup> )									
	A		B		C		D		E		F		1	2	3	4	5	6	7	8	9	10
Sample type	Ambient air		Ambient air		Ambient air		Ambient air		Indoor air		Blank											
Sample volume (m <sup>3</sup> )	1110		907		1020		1190.5		108		–		570	570	571	571	566	570	578	575	571	571
Sampling period	18–20 Nov.		7–9 Dec.		9–11 Dec.		15–17 Dec.		17–20 Dec.		20 Dec.		Week 19	Week 20	Week 21	Week 22	Week 23	Week 24	Week 25	Week 26	Week 27	Week 32
	1998		1998		1998		1989		1998		1998		(1997)	(1997)	(1997)	(1997)	(1997)	(1997)	(1997)	(1997)	(1997)	(1997)
Ionisation mode	NICI		EI		NICI		EI		NICI		EI											
	MX	17	46 (i)	35	64	17	20 (i)	23	54	530	500	4	6 (i)	8	15	15	15	15	13	10	19	19
MK	6	7 (i)	24	45 (i)	5	4	6	4 (i)	120	110	1	2 (i)										
AHTN	Int	44	30.7 (i)	76	76 (i)	41	110 (i)	46	1110	600	<dl	4										
HHCB	Int	130	676 (c), (i)	223	116 (c)	110	105 (c), (i)	116	4790 (c)	2470	<dl	15										
ATTI	–	10 (i)		15 (i)	–	19 (i)	–	6 (i)	–	430	–	1 (i)										
Remarks	3 separate analyses																					
Blanks													1	2	3	4	Average	SD				
																	(n=4)					
MX													2	2	3	2	2	0.4				

<sup>a</sup> Samples, prepared according to the Musk method, were taken at Kjeller. Ambient air samples, prepared according to the POP method, were taken at Lista (South Norway).

(i)=Isotope ratio deviates more than 20%.

(c)=Co-elution HHCB/ATTI.

Int=Interference.

<dl=Below detection limit.

silica. The following modification was carried out: fraction 1: 30 ml *n*-hexane, fraction 2: 30 ml with *n*-hexane–ethyl acetate (99:1, v/v), fraction 3: 30 ml *n*-hexane–ethyl acetate (9:1, v/v), fraction 4: fractionation 1: 30 ml *n*-hexane–ethylacetate (1:1, v/v), fractionation 2: 30 ml ethylacetate. The percentage distribution of the silica fractionation tests is given in Table 3. For further clean-up this modified fractionation method was used for the preparation of the air samples as described in Table 2.

After a volume concentration by a gentle stream of nitrogen (5.0 quality) to ca. 0.2 ml, tetrachloronaphthalene (TCN) was added as recovery standard to fraction 3 (*n*-hexane–ethyl acetate, 9:1).

### 2.5. Gas chromatographic separation and quantification

The ambient air samples taken at Lista and prepared according to method 1 (POP) were analysed for musk xylene using GC–NICI-MS only. Air samples collected in particular for the determination of synthetic musks at Kjeller were analysed with both GC–NICI-MS and GC–EI-MS for comparison.

For the GC–NICI-MS analyses, a Hewlett-Packard (HP) 5890 Series II gas chromatograph was equipped with a 25 m HP Ultra 2 column (0.2 mm I.D., film thickness 0.11 µm). Aliquots (1 µl) of the

sample extracts were injected in splitless mode. A splitless time of 2 min and an injector temperature of 260°C were applied. Helium (5.0 quality) was used as a carrier gas with a constant flow pressure of 113 kPa (70°C). The following temperature program was applied: 90°C (2 min isotherm) then rising by 20°C/min to 150°C, 1.5°C/min to 180°C and 30°C/min to 280°C (2 min isotherm). The transfer line temperature was set to 280°C.

The GC–NICI-MS analyses were carried out on a gas chromatograph coupled to a Hewlett-Packard 5989 quadrupole low-resolution mass spectrometer. The mass spectrometer was used in the NICI mode. Methane was used as reactant gas at an ion source pressure of 0.5 kPa and an ion source temperature of 200°C. Selected ion monitoring (SIM) was employed for quantification. For each compound the target ions and the reference ions (usually  $M^-$  and  $[M+1]^-$ ) were recorded in the SIM mode with a dwell time of 50 ms for each ion and up to 10 ions per group.

For the GC–EI-MS analyses, a CE instrument 8560 Mega II gas chromatograph (Milan, Italy) was equipped with a 30 m J&W (Folsom, CA, USA) DB5MS capillary column (0.25 mm I.D., film thickness 0.25 µm) and a guard column (2.5 m×0.53 mm I.D., deactivated, J&W). The columns were connected with a quick-seal connector (J&W). A 2-µl aliquot of the sample extract was injected in on-

Table 3  
Percentage distribution of the silica fractionation tests<sup>a</sup>

Compounds	Fractionation 1			
	Fraction 1 100% <i>n</i> -Hexane	Fraction 2 <i>n</i> -Hexane–ethyl acetate (9:1)	Fraction 3 <i>n</i> -Hexane–ethyl acetate (4:1)	Fraction 4 <i>n</i> -Hexane–ethyl acetate (1:1)
<i>n</i> =1				
ATII/HHCB	0	100	0	0
AHTN	0	100	0	0
MX	0	99	1	1
D9 MX	0	99	0	0
MK	0	88	12	0
	Fractionation 2			
<i>n</i> =3	100% <i>n</i> -Hexane	100% Ethyl acetate	<i>n</i> -Hexane–ethyl acetate (99:1)	<i>n</i> -Hexane–ethyl acetate (9:1)
ATII/HHCB	0	0	100±2	0
AHTN	0	0	100±2	0
MX	0	0	100±2	0
D9 MX	0	0	100±2	0
MK	0	0	100±3	0

<sup>a</sup> The determination of the distribution was performed by GC–NICI-MS on a 25 m HP-Ultra 2 capillary column (co-elution between HHCB and ATII). For abbreviations see Table 1.

column mode. Helium (5.0 quality) was used as carrier gas with a flow velocity of 35–40 cm/s (180°C). The following temperature program was applied: 70°C (2 min isotherm) then rising by 6°C/min to 260°C (5 min isotherm). The transfer line temperature was set to 280°C.

The GC–EI–MS analyses were carried out on a gas chromatograph coupled to a Finnigan MD 800 quadrupole low-resolution mass spectrometer (San Jose, CA, USA). The mass spectrometer was used in the EI mode with the ion source temperature set to 160°C. SIM was used for quantification. For each compound the target ions and the reference ions (usually  $M^+$  and  $[M-15]^+$ ) were recorded in the SIM mode with a dwell time of 100 ms for each ion and up to 17 ions in one group. The  $m/z$  values used for quantification and determination of the isotope ratio are summarised in Table 5.

### 3. Results and discussion

#### 3.1. Quality control and method evaluation

##### 3.1.1. Quality control

For the determination of synthetic musks in environmental samples a detailed quality control and assurance program is essential to minimise the potential contamination risk. In a study published by Helbling et al. in 1996 [6] a detailed description about the role of contamination for the trace analysis of musk xylene in environmental samples is presented. The authors pointed out, that extensive use of soap and cremes for cleaning purposes in the laboratory lead to a permanent musk contamination. Therefore, special precautions have to be taken in order to detect and avoid elevated blank values. This is especially needed for the analysis of lipid rich tissue samples due to the highly lipophilic character of the analytes [2,6].

In our study the following precautions were employed: (1) laboratory blanks were taken and treated with the same preparation and clean-up procedures as the real samples. (2) A two-day indoor low-volume air sample was taken to estimate the overall laboratory contamination level. (3) Concentration values are only considered as reliable when

the value was more than three-times the detection limit.

Although the preparation method used for synthetic musk analysis in the four ambient air samples from Kjeller is not accredited, the same quality assurance measures were employed as demanded for standard analysis according to the European Union (EU) standard 45 000 to ensure the highest possible reliability of the data achieved.

##### 3.1.2. Method evaluation

For high-volume air samples a sample set consisting of one glass fibre filter (GFF) and two polyurethane foam plugs was employed. The two plugs and the filter were extracted and analysed separately in order to estimate the distribution of the synthetic musks and to assess possible breakthrough (sample C). The results of the GC–EI–MS analyses are listed in Table 4. For all polycyclic musks the highest concentrations were found in plug 1, whereas for musk xylene a relatively equal distribution between GFF and plug 1 were determined. For musk ketone the main fraction was found in plug 1, however, elevated values were found in plug 2. Thus, breakthrough is possible but not likely in the concentration range found (isotope ratio deviates: possible interference in the chromatogram). The levels measured were all above the detection limits. However, the influence of the laboratory air as an important contamination source during clean-up and sample preparation should not be neglected (see Section 3.1.5). The high values of the indoor air sample demonstrate this contamination risk (Table 2: sample D). Nevertheless, no clear indications for breakthrough could be found. Thus, the sampling device can be considered as a reliable method for the

Table 4  
Distribution of synthetic musks on the sampling set (GFF, PUF 1, PUF 2) of sample C determined by GC–EI–MS<sup>a</sup>

Compound	GFF	PUF plug 1	PUF plug 2
MX	24	33	7
MK	6 i	21 i	20 i
AHTN	15	54	8
HHCB	25 i	172	26
ATTI	4 i	9 i	2 i

<sup>a</sup> Concentrations are given in pg/m<sup>3</sup> air.

i=Isotope ratio deviates more than 20%, interference possible.

collection of air samples for the analysis of synthetic musks.

### 3.1.3. Gas chromatographic evaluation

Chromatographic co-elution occurred for GC–NICI-MS measurements. A sufficient separation between HHCB and ATII was not achieved on the 25 m HP Ultra 2 capillary column used for the gas chromatographic separation. However, with a J&W DB5MS column used for the GC–EI-MS measurements all polycyclic musks were baseline separated (Fig. 1). The two stationary phases used for HP Ultra 2 and J&W DB5MS column are different according to the producers. The stationary phase of the Ultra 2 contains 5% phenylsilylated and 95% methylsilylated

polysiloxan, whereas the stationary phase of the DB5MS is containing 5% phenylsilylated and 95% methylsilylated polysiloxan. Thus, these small differences might cause the considerable improvement of the HHCB/ATII separation. According to the here presented results the 30 m DB5MS capillary column is more suitable for the synthetic musk separation than the HP Ultra 2. These findings are in agreement with data found in the literature for the excellent separation properties of the DB5MS column [14,15]. These good separation properties in conjunction with a doubled film thickness lead to better chromatographic results for the GC–EI-MS analyses (Fig. 1). However, the insufficient clean-up of the samples restrict the chromatographic performance. These

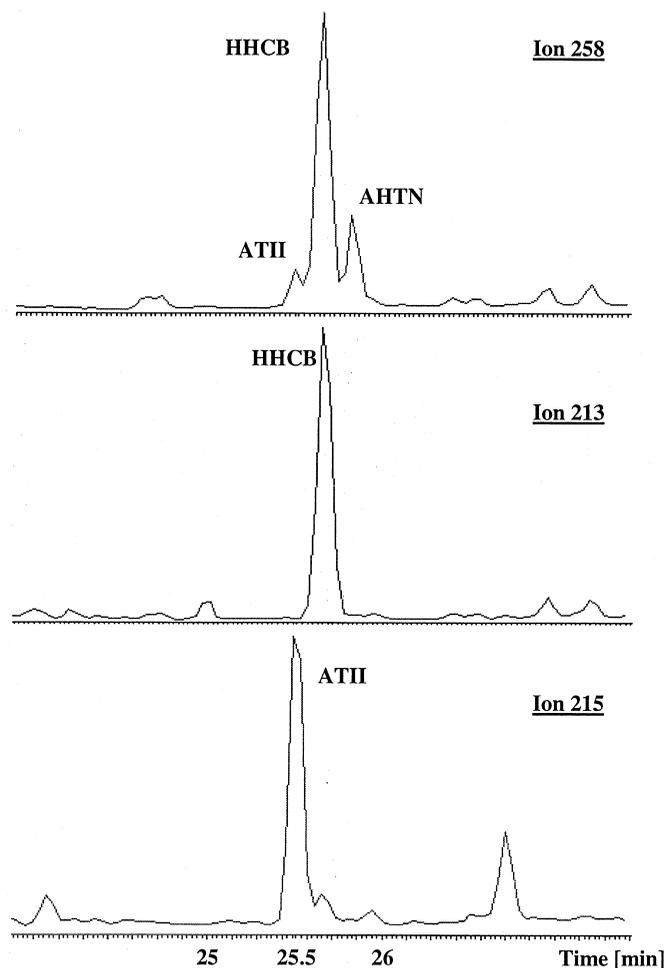


Fig. 1. Separation of HHCB and ATII on the 30 m DB5MS capillary column (GC–EI-MS) in sample F (indoor sample).

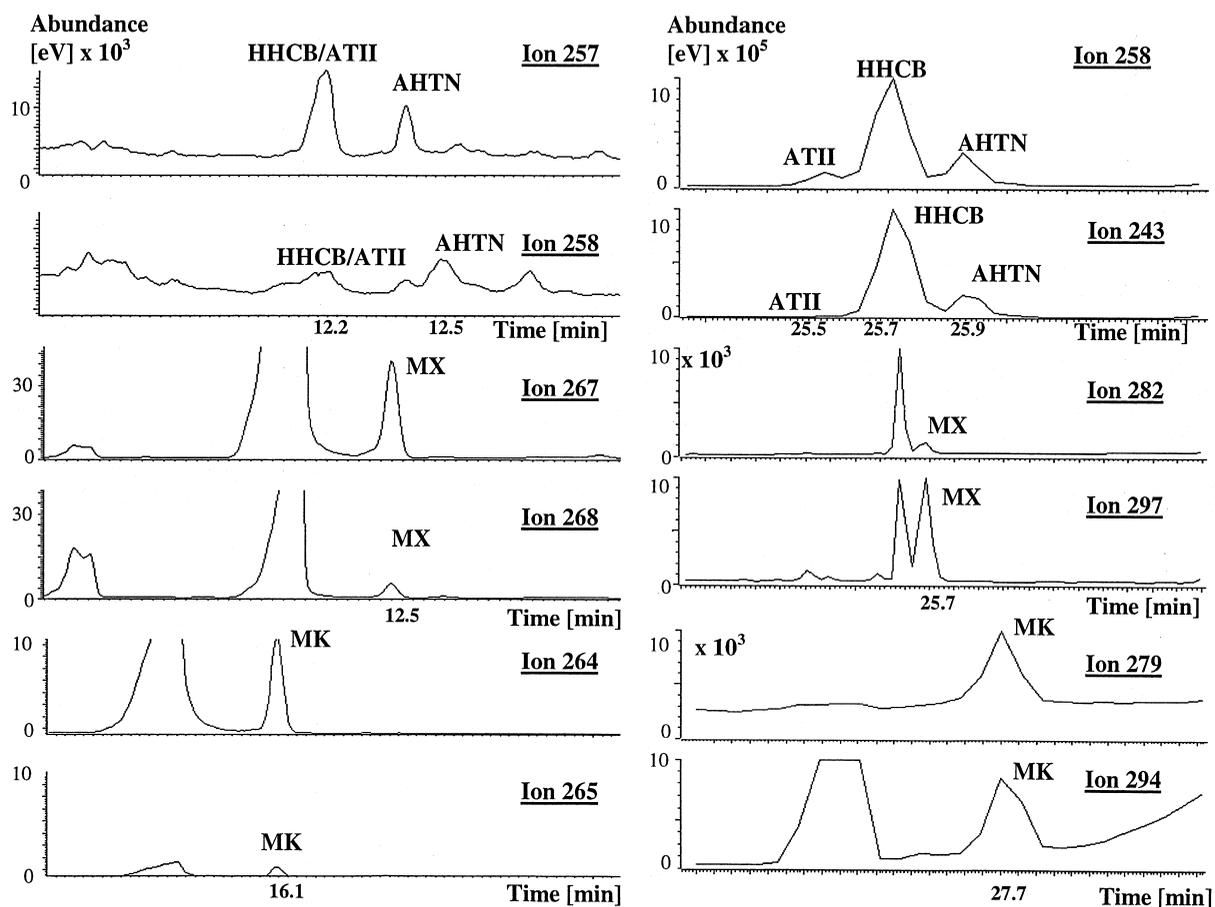


Fig. 2. Selected ion monitoring (SIM) fragmentations of a selected air sample (D) analysed by (left) GC–low-resolution NICI-MS (25 m Ultra 2) and (right) GC–low-resolution EI-MS (30 m DB5MS).

restrictions will, therefore, be subject for further efforts towards substantial improvements of the quality of the clean-up procedure for the musk analysis in ambient air samples.

The amount of ATII in all air samples was

determined by GC–EI-MS. In all samples measured, the ATII concentration varied between 2 and 11% of the HHCB concentration. For  $m/z$  values used in the GC determination of polycyclic and nitro musk compounds using NICI-MS and EI-MS, see Table 5.

Table 5

Retention times and  $m/z$  values used for the determination of polycyclic and nitro musk compounds with GC–NICI-MS and GC–EI-MS

Compounds	Low-resolution NICI-MS		Low-resolution EI-MS	
	Target ion ( $m/z$ )	Reference ion ( $m/z$ )	Target ion ( $m/z$ )	Reference ion ( $m/z$ )
MX	267	268	282	297
MK	264	265	279	294
ATII	257	258	215	258
HHCB	257	258	243	213
AHTN	257	258	243	258

Table 6  
Recovery test with a standard mixture of known concentrations using GC–NICI-MS

Parallels ( $n=3$ ) Compound	Average concentration ( $\text{pg}/\mu\text{l}$ )	RSD (%)	Expected concentration ( $\text{pg}/\mu\text{l}$ )	Relative deviation (%)
D9-MX	102	9	100	2
ATII/HHCB	7645	7	12 333	–31
AHTN	4010	7	4620	16
MX	5200	1	4170	9
MK	6359	4	5370	26

### 3.1.4. Recovery evaluations

A standard mixture containing all synthetic musk compounds of interest was used to determine general recovery rates for the analytical method. This standard mixture with defined concentrations for all compounds was treated with the clean-up procedure chosen for musk analysis. Recovery rates were calculated after GC–NICI-MS analysis. The percentage deviation from the expected 100% concentration values is listed in Table 6. Except for ATII/HHCB (31%) all concentrations determined deviated below  $\pm 30\%$  from the expected values. Therefore, for the clean-up procedure an average recovery about 80% can be assumed for synthetic musks, which is in agreement with official quality assurance criteria for POP analysis in the Arctic Monitoring and Assessment Programme (AMAP) quality control guideline [16]. Nevertheless, especially for polycyclic musks, high detection limits and deviations from the isotope ratios larger than 20% occur and demonstrate the limits of the GC–NICI-MS method. The detection limits for synthetic musks analysed with GC–NICI-MS were calculated based on the lowest possible area values for calculation in the chromatograms. The detection limits for GC–EI-MS were estimated based on the blank concentrations determined. These estimated detection limits were listed in Table 7.

### 3.1.5. Laboratory contamination

Since the laboratory facilities used for clean-up and analysis had to be considered as one of the main contamination sources for synthetic musks [6] an indoor air sample was taken in the laboratory according to the sampling method described elsewhere [17]. The sample is listed as sample D in Table 2. A concentration value for HHCB/ATII (low-resolution NICI-MS) as the main constituent of  $4790 \text{ pg}/\text{m}^3$  (low-resolution EI-MS result for HHCB only:  $2470 \text{ pg}/\text{m}^3$ ) were found. These high concentration values for all musks analysed demonstrate clearly the need for special care concerning quality control measures during sample preparation and clean-up for synthetic musk analysis. The elevated concentrations for sample B (determination of possible breakthrough in the sample device) give additional indication for the influence of laboratory contamination. The sum of all concentration values from the three separate analyses exceeds the levels determined in the other ambient air samples considerably. The triple analysis and consequently the threefold exposure to the laboratory contamination clearly cause these elevated values. The general conclusion should, therefore, be that even accredited procedures used for routine trace analysis of persistent organic pollutants are not sufficient to exclude

Table 7  
Detection limits determined for GC–NICI-MS and GC–EI-MS measurements

Compound	Sample type ( $\text{pg}/\text{m}^3$ )					
	Ambient air		Indoor air		Blank	
	NICI	EI	NICI	EI	NICI	EI
Polycyclic musks	20–50	5–10	20–30	5–10	5–10	4–5
Nitro musks	0.2–0.5	6–12	0.2–0.5	6–12	0.1	10

sample and laboratory contamination of synthetic musk. Thus, special care for the sample preparation (i.e., isolated storage of samples and solvents, separate laboratory facilities and equipment for clean-up and sample preparation, special restrictions for use of solvents) has to be introduced when working with trace analysis of synthetic musks.

### 3.1.6. Comparison of two ionisation modes for the mass spectrometric detection of synthetic musks

In Fig. 2 fragmentograms for HHCB and MX are given for a typical ambient air sample for both GC–NICI-MS and GC–EI-MS analysis. Due to the relative mild clean-up procedure for the air samples (e.g., use of sulphuric acid as agent for the destruction of interfering matrix compounds is avoided), the cleanliness of the samples is not sufficient and needs further improvement (as mentioned above). These limitations affect especially the GC–NICI-MS analysis where deviations from the expected isotope ratios (ratio target ion/reference ion) often occur for polycyclic musk. Due to interferences in the GC–NICI-MS analysis, the high detection limits for polycyclic musks lead to additional uncertainties concerning the determination of concentrations for air samples. Strong deviations (more than 20%) from the expected isotope ratios are indications for possible interferences and are therefore listed as additional information in all tables dealing with air concentrations. However these differences might be mainly caused by the use of two unlike capillary columns but not the two ionisation modes. Due to these chromatographic differences, stronger interferences occurred in the GC–NICI-MS measurements and lead to elevation of the detection limits for nitro musks for GC–NICI-MS. At the other hand, the detection limits for polycyclic musks are low for GC–EI-MS compared to GC–NICI-MS (blank and concentration values listed in Table 2). However, the variations found in air concentrations of synthetic musks for the two ionisation modes compared are within a range which can still be explained by instrument design differences. Thus, both ionisation modes used are well fit for the concentration ranges of synthetic musks in ambient air samples.

### 3.2. (A) Preliminary analysis of nitro musks in Norwegian ambient air samples

For a first test of synthetic musks in ambient air, ten samples already prepared according to method 1 and quantified for POPs, taken during the 1997 monitoring campaign for the CAMP project were analysed. For the analysis of the already prepared samples the internal standard [ $^{13}\text{C}$ ]- $\alpha$ -HCH was used for concentration determination. The origin of the samples, sampling dates and volumes are listed in Table 2. Due to the use of concentrated sulfuric acid during clean-up of the air samples only musk xylene could be analysed with a reliable recovery rate (>80%). Recovery tests revealed a loss of about 80% of musk ketone due to degradation during the sulfuric acid treatment of the air samples. These findings support the results already published by Rimkus et al. [4] and demonstrate the need of special caution during the work-up procedures. However, the musk xylene passed the standard treatment with recovery rates of 80–100%.

The results of these first analyses are summarised in Table 2 as well. The concentration levels for musk xylene in the Lista ambient air samples, demonstrate the need for further investigations on the fate of synthetic musks in the environment. Except for one, all concentration values (range 8–19  $\text{pg}/\text{m}^3$ ) exceed the  $3\times$ blank level and are therefore to be considered as reliable. The levels in ambient air for musk xylene are comparable with the levels of polychlorinated biphenyls (PCBs) analysed in the same samples covering a concentration range from 1 to 27  $\text{pg}/\text{m}^3$ . Since the levels found for musk xylene in Norwegian ambient air samples are comparable with those for PCBs a similar input as documented for PCBs might be possible. This data set represents the first attempt to quantify musk xylene in ambient air samples.

### 3.3. (B) Simultaneous analysis of nitro and polycyclic musk compounds in air samples

As polycyclic musks become more important as fragrance and often exceed the levels of nitro musks considerably [5], there is a need for an efficient trace analytical method for both nitro and polycyclic

musks. Selected ion fragmentograms covering target and reference ions of the musk compounds analysed are presented in Table 5. In this study four ambient air samples presenting a volume in the range of 900–1200 m<sup>3</sup> were taken at Kjeller. Sampling dates and volumes as well as concentration data are listed in Table 2. Concentrations were calculated based on both GC–EI-MS and GC–NICI-MS data. Blank values using an unexposed PUF/GFF set for analysis were determined as well.

In all air samples analysed, HHCB was by far the dominating synthetic musk compound followed by AHTN. The concentrations of nitro musks and ATII were relatively low (3–12% of the total synthetic musk load). This finding reflects probably the fact, that polycyclic compounds is nowadays the synthetic musk group mainly used, whereas the use of nitro musks in toiletry products is decreasing in Europe. However, a partial degradation by photolysis of nitro musks in the atmosphere cannot be excluded.

Concentration differences for musk xylene determined by GC–NICI-MS between the air samples from Lista and Kjeller can be seen (Table 2). The ambient air samples taken at Kjeller are in average higher contaminated than the Lista samples. In contrast to Lista, the sampling area in Kjeller is strongly influenced by a densely populated urban area, namely the Norwegian capital Oslo (the distance to the centre of Oslo is 25 km). In Lista an average concentration of 14 pg/m<sup>3</sup> ( $n=10$ ) was observed, whereas the Kjeller air average concentration was determined with 19 pg/m<sup>3</sup> ( $n=3$ ). However, no striking evidence was found for human impact. Please note, since sample C has to be considered as contaminated (see method evaluation), this MX value was not included in the average calculation.

Due to quality criteria mentioned in Section 3.1.2, the GC–EI-MS data should be used for further discussions about the general patterns of synthetic musks in ambient air (Table 2). The theoretically calculated “detection limit” for the GC–EI-MS data (method evaluation) is a useful measure for quality control of the presented data. A 3–5-fold of the concentrations for polycyclic musks (AHTN and HHCB/ATII) compared to nitro musks (MX and MK) was found in Kjeller ambient air. This finding

is in accordance with patterns found in other environmental samples [5,7,8].

It could be shown that a simultaneous determination of polycyclic and nitro musks is possible and should be preferred because a fast analysis, covering a comprehensive number of musk compounds can be carried out by using one analytical method only for both types of synthetic musks. According to our experiences, both GC–NICI-MS and GC–EI-MS are sensitive enough for ambient air concentrations. However, a careful evaluation of the capillary column used for the separation of polycyclic musk should be carried out prior to analysis in order to avoid co-elution. Further optimisation of the method to solve interferences and improve the clean-up of the air is in progress. The synthetic musk concentrations found in the laboratory air sample demonstrate clearly the dominating role of indoor contamination during the sample preparation for musk analysis.

## Acknowledgements

The presented research program was partially financed by “NILUS Strategic Institute Program for the Investigation of Persistent Organic Pollutants in Arctic Air” funded by the Norwegian Environmental Ministry and the research project 125745/720 “Synthetic Musks in the Norwegian Environment” funded by the Norwegian Research Council (NFR). We thank the Norwegian Pollution Control Authority (SFT) for the financial support of the CAMP monitoring programme. The authors wish to express their gratitude to Stein Manø, Gro Hammerseth and Gerd Staff Knutsen for the preparation and the help during analyses of the samples.

## References

- [1] R. Gatermann, J. Hellou, H. Hühnerfuss, G.G. Rimkus, V. Zitko, *Chemosphere* (1999) in press.
- [2] G.G. Rimkus, M. Wolf, *Chemosphere* 30 (1995) 641–651.
- [3] T. Yamagishi, T. Myazaki, S. Horii, S. Kaneko, *Arch. Environ. Contam. Toxicol.* 12 (1983) 83–89.
- [4] G.G. Rimkus, W. Butte, H.J. Geyer, *Chemosphere* 35 (1997) 1497–1507.

- [5] G.G. Rimkus, H. Brunn, *Ernährungs-Umschau* 43 (1996) 442–449.
- [6] K.S. Helbling, P. Schmid, C. Schlatter, *Chemosphere* 29 (1994) 477–484.
- [7] K. Bester, H. Hühnerfuss, W. Lange, G.G. Rimkus, N. Theobald, *Water Res.* 32 (1998) 1857–1863.
- [8] R. Gatermann, H. Hühnerfuss, G. Rimkus, M. Wolf, S. Franke, *Marine Pollut. Bull.* 30 (1995) 221–227.
- [9] G.G. Rimkus, M. Wolf, *Chemosphere* 33 (1996) 2033–2043.
- [10] C. Fernandez, M. Carballo, J.V. Tarazona, *Chemosphere* 32 (1996) 1805–1811.
- [11] R. Gatermann, H. Hühnerfuss, G. Rimkus, A. Attar, A. Kettrup, *Chemosphere* 36 (1998) 2535–2547.
- [12] M. Oehme, J.E. Haugen, M. Schlabach, *Sci. Total Environ.* 160/161 (1995) 139–152.
- [13] M. Weichbrodt, W. Vetter, E. Scholz, B. Luckas, *Organohalogen Comp.* 35 (1998) 195–198.
- [14] D. Fraisse, O. Paise, L. Nguyen Hong, M.F. Gonnord, *Fresenius J. Anal. Chem.* 348 (1994) 154–158.
- [15] E. Abad, J. Caixach, J. Rivera, *J. Chromatogr. A* 786 (1997) 125–134.
- [16] AMAP, Method Performance Criteria and Quality Control Measures for the Determination of Persistent Organic Compounds (POPs) in Ambient Air, Precipitation and Water, Working Group “Quality Control Programme”, Workshop on Techniques of POP Measurements in Northern Environments, Waterloo, Ontario, Canada, 16–18 June 1994. Available from Arctic Monitoring and Assessment Programme (AMAP) Secretariat, P.O. Box 8100, Dep., N-0032 Oslo, Norway.
- [17] O.A. Braathen, M. Schlabach, POPs in indoor air, accepted at the Indoor Air Conference 1999, Edinburgh, Scotland, 8–13 August 1999.