On-Site Solid-Phase Extraction and Laboratory Analysis of Ultra-Trace Synthetic Musks in Municipal Sewage Effluent Using Gas Chromatography-Mass Spectrometry in the Full Scan Mode

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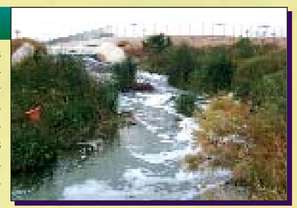
1 Abstract

Fragrance materials, such as synthetic musks in aqueous samples, are normally analyzed by GC/MS in the selected ion monitoring (SIM) mode to provide maximum sensitivity after liquid-liquid extraction of 1-L samples. A 1-L sample, however, usually provides too little analyte for full-scan data acquisition. An on-site extraction method for extracting synthetic musks from 60 L of wastewater effluent has been developed. Such a large sample volume permits high quality, full-scan mass spectra to be obtained for various synthetic musk compounds. Quantification of these compounds was conveniently achieved from the full-scan data directly, without preparing SIM descriptors for each compound to acquire SIM data. This method reduces labor and solvent used.



2 Introduction

Ultra-trace levels of numerous compounds found in effluents from tertiary sewage treatment plants and in surface waters require large concentration factors before high-quality, full-scan mass spectra can be obtained for comparison to mass spectral libraries. Good retention of both non-polar and polar compounds on a solid-phase adsorbent is required to ensure retention of most organic compounds. The Environmental Chemistry Branch of the USEPA has developed a convenient sampling method performed in the field to avoid transport of large water volumes and possible contamination from laboratory air. Organic compounds in large volumes of sewage treatment plant effluent were collected on solid-phase extraction cartridges. Eight of 15 target analytes (synthetic musks and musk metabolites) were identified and quantified by GC/MS from full scan data.

3 Sampling

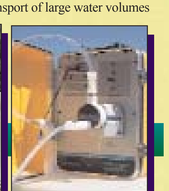
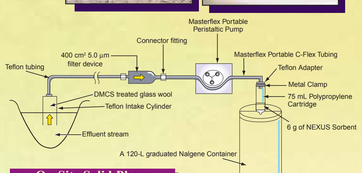


Figure 1



On-Site Solid Phase Extraction Assembly

The sampling train in Figure 1 was assembled at each site. A coarse filter composed of a wad of glass wool deactivated with dimethyldichlorosilane (DMDCS) removed large particles and algae, and a 400 cm^2, 5.0 µm pore-size filter removed most remaining particulate matter. The twice filtered water is drawn by and passed through a peristaltic or diaphragm pump and finally through a cartridge containing the sorbent, 6 g of a 1:1 (poly-methyl methacrylate):(polystyrene cross-linked with 50% divinylbenzene) sorbent (NEXUS, Harbor City, CA). The sorbent retained most organic compounds. After over 6 hours of pumping, the volume of water in the graduated 120-L container was recorded. The amount varied from 45 L when the effluent was turbid to 85 L when the effluent sampled was visibly clear. Previous laboratory experiments determined that breakthrough did not occur for any target analyte after 100 L of spiked deionized water was passed through a cartridge. The cartridge was wrapped in Aluminum foil, transported to the laboratory on ice and the analytes were immediately desorbed from the solid-phase cartridge.

4 Extraction

The extraction scheme is diagramed in Figure 2. Concentration of the final extract to 400 µL provided concentration factors of 1.1 x 10^5 to 2.1 x 10^5.

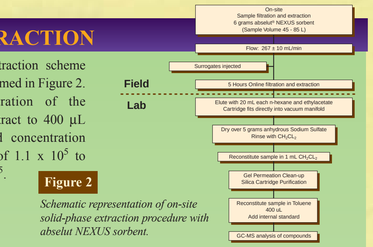


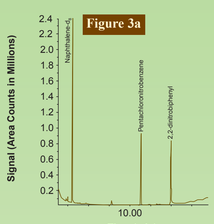
Figure 2

Schematic representation of on-site solid-phase extraction procedure with absolut NEXUS sorbent.

5 Total Ion Chromatograms

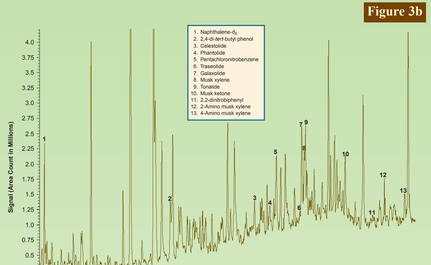
Figure 3a shows the field blank devoid of analytes, and Figure 3b illustrates that dozens of compounds were present in the sewage treatment plant effluent. Tentative identifications were made for many of these compounds through comparison of their mass spectra with those in the NIST library residing on the data system. However, the focus of our work was the synthetic musks used as additive in laundry detergents, soaps, cologne, shampoo, and other scented consumer products. The synthetic musks and surrogate standards are labeled in Figure 3b.

Figure 3a



Total ion chromatogram of field blank.

Figure 3b



Total ion chromatogram of synthetic musks in 45 L STP effluent sample.

6 Synthetic Musks

The 15 synthetic musks and musk metabolites in Tables 1-3 were purchased or synthesized to determine their retention times, recoveries, and minimum detection limits, and to obtain mass spectra for compounds not present in the NIST library. The nine compounds with structures drawn in blue were found in sewage treatment effluent. The two in red (see Tables 1 and 2) were banned for use in the United States.

Table 1. Trade and CAS names, structures, log K_{ow}, molecular weight, formulae and Registry Numbers, for seven polycyclic musks.

Trade and CAS Name (Acronym)	Chemical Structure	Log K_{ow}	Wt.	Molecular Formula	CAS Number
Galaxolide, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-[g]-2-benzopyran (HHCB)		5.9[a]	258.40	$C_{18}H_{26}O$	1222-0565
Tonalide, 1-(5,6,7,8-tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthalenyl)-ethanone (AHTN)		5.7[a]	258.40	$C_{18}H_{26}O$	1506-02-1
Traseolide, 1-(2,3-dihydro-1,1,2,6-tetramethyl-3-(1-methylethyl)-1H-inden-5-yl)-ethanone (ATII)		6.3[b]	258.40	$C_{18}H_{26}O$	68140-48-7
Celestolide, 1-(6-(1,1-dimethylethyl)-2,3-dihydro-1,1-dimethyl-1H-inden-4-yl)-ethanone (ADBI)		5.4[b]	244.38	$C_{17}H_{24}O$	13171-00-1
Cashmeran, 1,2,3,5,6,7-hexahydro-1,1,2,3,3-pentamethyl-4H-inden-4-one (DPMI)		5.0[b]	206.32	$C_{14}H_{22}O$	33704-61-9
Phantolide, 1-(2,3-dihydro-1,1,2,3,3-hexamethyl-1H-inden-5-yl)-ethanone (AHMI)		5.9[b]	244.38	$C_{18}H_{26}O$	15323-35-0
Versalide, 7-Acetyl-4-ethyl-1,1,4,6-tetramethyltetralin (AETT)		5.7[b]	258.40	$C_{18}H_{26}O$	88-29-9

[a] Ref. [5].
[b] Estimated values derived by Hansch and Leo fragmentation method in Ref. [2].

7 List of Ions

The retention times, quantitation ions, and confirmation ions for each compound are listed in Table 4. Table 4 shows the characteristic ions used for identification and measurement of musk compounds from STP effluent samples. The total ion chromatographic peaks for Galaxolide had the same retention time as standard used and confirmed the analyte's identity.

Table 2. Trade and CAS names, structures, log K_{ow}, molecular weight, formulae and Registry Numbers, for five nitro musks.

Trade and CAS Name (Acronym)	Chemical Structure	Log K_{ow}	Wt.	Molecular Formula	CAS Number
Musk ketone, 1-tert-butyl-3,5-dimethyl-2,6-dinitro-4-acetyl-benzene (MK)		4.3[a]	294.31	$C_{14}H_{18}N_2O_5$	81-14-1
Musk moskene, 4,6-dinitro-1,3,3,5-pentamethylindane (MM)		5.0[b]	278.31	$C_{14}H_{18}N_2O_4$	116-66-5
Musk ambrette, 2,6-dinitro-3-methoxy-4-tert.-butyl toluene (MA)		5.7[b]	268.27	$C_{12}H_{16}N_2O_5$	83-66-9
Musk xylene, 1-tert-butyl-3,5-dimethyl-2,4,6-tri-nitrobenzene (MX)		4.8[a]	297.27	$C_{12}H_{15}N_3O_6$	81-15-2
Musk tibetene, 1-tert-butyl-2,6-dinitro-2,4,5-tri-methylbenzene (MT)		5.9[b]	266.29	$C_{13}H_{18}N_2O_4$	145-39-1

[a] Ref. [5].
[b] Estimated values derived by Hansch and Leo fragmentation method in Ref. [2].

8 Recoveries and Minimum Detection Limits

As listed in Table 3, the NEXUS sorbent provided excellent recoveries for the target compounds. The average recoveries for triplicate experiments with 20, 40, and 60 µL of a solution containing 20 µg/mL of each musk compound and metabolite were between 80% and 97% for spiked sewage treatment plant effluent. The minimum detection limits listed were between 0.02 and 0.30 ng/L (pptr) for all 15 target analytes, based on a 3:1 signal-to-noise criterion for the ion chromatogram of each quantitation ion.

Table 3. Trade and CAS names, structures, log K_{ow}, molecular weight, formulae and Registry Numbers, for three nitro musk metabolites.

Trade and CAS Name (Acronym)	Chemical Structure	Log K_{ow}	Wt.	Molecular Formula	CAS Number
Amino musk ketone: 2-amino-1-tert.-butyl-3,5-dimethyl-6-nitro-4-acetyl-benzene (2-AMK)		5.1[a]	264.32	$C_{14}H_{20}N_2O_3$	---
4-Amino musk xylene: 4-amino-1-tert.-butyl-3,5-dimethyl-2,6-dinitrobenzene (4-AMX)		4.8[b]	267.28	$C_{12}H_{17}N_3O_4$	107342-55-2
2-Amino musk xylene: 2-amino-1-tert.-butyl-3,5-dimethyl-4,6-dinitrobenzene (2-AMX)		4.8[b]	267.28	$C_{12}H_{17}N_3O_4$	107342-67-6

[a] Estimated values derived by Hansch and Leo fragmentation method in Ref. [5].

9 Musk compounds found in sewage treatment plant effluents

Table 4 provides the concentrations of synthetic musks and musk metabolites found at three sites sampled on two dates.

Eight of the 15 target analytes were found in one or more of the sample extracts. Use of versalide and musk ambrette was banned in 1980 and 1995, respectively, based on nerve damage in rats. The absence of these compounds in water samples suggests that the ban has been honored by producers of products that contain synthetic musks.

Table 4. Characteristic ions used for identification and measurement of musk compounds.

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
[$^2H_8$]Naphthalene (I.S.)	4.33	136	137, 137, 108
Cashmeran	10.01	191	192, 135, 206
Celestolide	10.46	229	244, 187, 230
Phantolide	10.97	229	244, 187, 230
Pentachloronitrobenzene (surr.)	11.06	237	295, 214, 265
Musk xylene	11.45	243	248, 258, 259
Musk ambrette	11.69	253	268, 254, 251
Traseolide	11.84	215	216, 173
Galaxolide	11.89	243	258, 213, 244
Tonalide	12.00	243	258, 244, 201
Musk xylene	11.99	282	297, 283
Musk moskene	12.23	263	278, 264, 221
Musk tibetene	12.76	251	266, 252, 115
Musk ketone	13.71	279	294, 128, 280
2,2'-dinitrobiphenyl (surr.)	13.95	198	168, 139, 115
Amino musk ketone	14.36	264	249, 215, 191
2-Amino musk xylene	14.51	267	252, 218, 160
4-Amino musk xylene	14.92	252	267, 218, 235

I.S., internal standard; Surr., surrogate.

Table 5. Percent spike recovery data from 60-1 sample[a] (n = 3).

Analytes	Nanopure Water (% RSD)	STP Effluent (% RSD)	MDL (ng/L)
Musk xylene	102 (4)	97 (6)	0.02
Musk ketone	98 (3)	95 (5)	0.20
Musk ambrette	101 (5)	96 (7)	0.30
Musk moskene	96 (4)	92 (4)	0.03
Musk tibetene	98 (2)	95 (7)	0.02
Versalide (AETT)	99 (5)	96 (6)	0.02
Galaxolide (HHCB)	99 (3)	97 (5)	0.02
Phantolide (AHDI)	97 (3)	91 (5)	0.02
Cashmeran (DPMI)	99 (4)	94 (6)	0.02
Celestolide (ADBI)	98 (3)	96 (8)	0.02
Traseolide (ATII)	95 (5)	90 (8)	0.02
Tonalide (AHTN)	107 (3)	94 (6)	0.02
4-Amino musk xylene	87 (5)	80 (10)	0.30
2-Amino musk xylene	89 (7)	82 (11)	0.25
Amino musk ketone	96 (6)	92 (8)	0.25

[a] Recovery data from extraction through GPC steps.

Table 6. Concentrations (ng/L) of synthetic musk compounds and nitro musk metabolites in STP effluent stream.

Analytes	85 L[a]	65 L[a]	85 L[b]	45 L[b]	60 L[c] (% RSD)
Galaxolide	158	111	152	35.0	40.8 (1.8)
Traseolide	83.8	34.5	126	6.6	<MDL
Tonalide	67.3	47.1	92.2	26.6	36.8 (2.5)
Musk ketone	27.5	21.5	23.4	21.3	<MDL
Phantolide	2.1	0.3	3.0	0.5	2.4 (4.3)
Celestolide	2.1	0.3	5.0	0.5	2.4 (7.2)
4-Amino musk xylene	1.4	11.6	<MDL	31.5	<MDL
Musk xylene	1.3	<MDL	<MDL	0.5	<MDL
2-Amino musk xylene	<MDL	<MDL	0.9	<MDL	<MDL
Musk moskene	<MDL	<MDL	<MDL	<MDL	<MDL
Musk tibetene	<MDL	<MDL	<MDL	<MDL	<MDL
Cashmeran	<MDL	<MDL	<MDL	<MDL	<MDL
Amino musk ketone	<MDL	<MDL	<MDL	<MDL	<MDL
Musk ambrette	<MDL	<MDL	<MDL	<MDL	<MDL
Versalide	<MDL	<MDL	<MDL	<MDL	<MDL

[a] Effluent sample downstream from a tertiary sewage treatment plant's discharge pipe (n = 1).
[b] Effluent sample taken 14 days later from same location (n = 1).
[c] Effluent sample near a different tertiary sewage treatment plant's discharge pipe (n = 3).

10 Conclusion

The sampling train, solid phase absorbent, and extraction method used provided concentration factors exceeding 1 x 10^5, which provided detection limits of less than 1 ng/L (pptr) for 15 target analytes. Recoveries of at least 80% were obtained for 15 compounds having a range of polarities. The total ion chromatograms indicated that dozens of other compounds were also extracted. This methodology should be equally useful for other sets of target analytes present in sewage treatment plant effluents.

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