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Journal of Chromatography B, 858 (2007) 177–183
JOURNAL OF CHROMATOGRAPHY B
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SPE/SPME–GC/MS approach for measuring musk compounds in serum and breast milk

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Received 8 March 2007; accepted 19 August 2007
Available online 26 August 2007

Abstract

Musks can be used to provide distinctive odor or scent in many personal care products. Musk compounds have received growing attention in recent years by environmental scientists and regulatory agencies because of their increasing production volume and widespread environmental presence. A combined separation approach using solid phase extraction (SPE) and solid phase micro extraction (SPME) coupled to detection by gas chromatography mass spectrometry was developed for measuring four polycyclic musk compounds (Galactoside®, Tonalide®, Muskene®, Celestolide®) in serum and milk. The SPE and SPME separation steps were fully automated and required minimal sample handling. The method, which requires only 1 mL serum or breast milk to achieve limits of detection of 0.03–0.3 ng/mL, is applicable in biomonitoring studies for human internal dose measurement of polycyclic musk compounds.
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Keywords: Musks; SPE; SPME; Gas chromatography; Mass spectrometry

1. Introduction

Musks are high production volume chemicals used to provide distinctive odor or scent in many personal care products especially deodorants, antiperspirants, perfumes, creams and body lotions [1]. After production and use, musks may enter the waste water treatment plants or sewage system and distribute in the aquatic environment [2]. Musks are lipophilic compounds that can accumulate in fatty tissues similar to more lipophilic chemicals including polychlorinated pesticides [3,4]. However, the fact that musks do not seem to accumulate in fat tissue in age dependent manner suggests a metabolic pathway of elimination [3,4]. Humans are expected to be exposed to musks mainly by dermal contact and by inhalation [5,6]. Although the health implications of exposure to musks, such as possible relations to dermal allergies and respiratory problems, are not fully understood, musk compounds have received growing attention in recent years by environmental scientists and regulatory agencies [7].

Analytical methods published between 1995 and 2005 for the measurement of musk compounds in air, water, sediments, aquatic biota and sewage sludge were summarized in a recent review [8]. In general, the analytical approach for the extraction of musks from fish [9], and biological matrices such as blood [10,11], adipose tissue [12] and milk [4] takes advantage of the lipophilic and dipolar nature of musk compounds. First, a lipid fraction is separated by liquid–liquid extraction [3,4,10,11,13]. Then, this lipid fraction is cleaned further by gel-permeation and/or normal phase chromatography using non-polar/polar organic eluents [3,4,13–16]. Last, the resulting extract is generally analyzed by gas chromatography/mass spectrometry (GC/MS). These methods have good sensitivity with limits of detection (LOD) in the low pg/g range. However, these methods were labor intensive and required relatively large volumes of both sample (2–10 mL) and organic solvents (10–100 times the sample volume). Some of these characteristics are not ideal for biomonitoring studies which typically require the analysis of at least several hundreds of samples.

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1570-0232/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.jchromb.2007.08.027

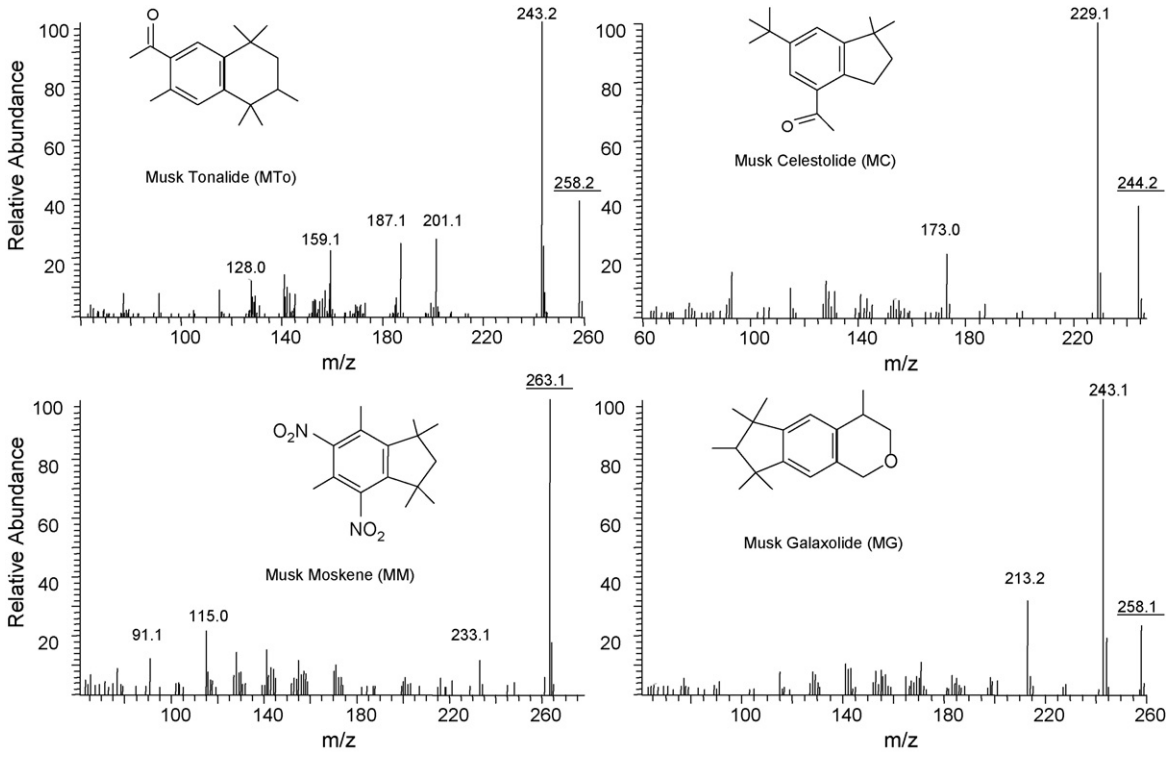

Fig. 1. Chemical structure of and mass spectra of musk analytes with molecular ion underscored.

We report on the development of a method for measuring four polycyclic musk compounds (Galactoside®, Tonalide®, Muskene®, Celestolide®) in human serum and breast milk (Fig. 1). The novel aspect of this method is the combined use of two automated extraction techniques, solid phase extraction (SPE) and solid phase micro extraction (SPME). By using this combined approach, we were able to simplify sample preparation, reduce sample size to 1 mL of serum or breast milk, and maximize selectivity and throughput (∼30 unknowns per day) compared to previous methods, while still maintaining adequate sensitivity (LODs ranged from 0.03 to 0.3 ng/mL). The applicability of the method is demonstrated with analysis of human serum and milk samples.

2. Experimental

2.1. Reagents and materials

Standard solutions (50 μg/mL) of Galaxolide® (MG, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[*g*]-2-benzopyrane [1222-05-5]), Tonalide® (MTo, 7-acetyl-1,1,3,4,4,6-hexamethyltetralin [1506-02-1]), Celestolide® (MC, 4-acetyl-1,1-dimethyl-6-tert-butylindane [13171-00-1] and Moskene® (MM, 1,1,3,3,5-pentamethyl-4,6-dinotroindane [116-66-5]) were purchased from LGC Promochem (Wesel, Gemany). Isotopically labeled D_{15}-Musk Xylene® (D_{15}-MX, D_{15}-1-(1,1-dimethylethyl)-3,5-dimethyl-2,4,6-trinitrobenzene) was obtained from EQ Laboratories, Atlanta, GA, USA. Water was type A HPLC grade obtained in-house using a water purification system (Aqua Solutions, Inc., Jasper, GA, USA). HPLC grade methanol was purchased from Caledon, Ontario, Canada); formic acid (98%) from EM Science Gibbstown, NJ, USA. All chemicals and solvents were used without further purification.

Seven spiking solutions containing all four analytes were prepared by serial dilutions in methanol to final concentrations such that a 50-μL spike in 1 mL of serum or milk would cover a concentration range from 0.005 to 5 ng/mL. The D_{15}-MX internal standard solution was prepared such that a 50-μL spike would give 1 pg/mL concentration in 1 mL of serum or milk.

The quality control (QC) materials were prepared from calf serum (Gibco, Grand Island, NY, USA) or pooled breast milk purchased from Mother's Milk Bank (San Jose, CA, USA). Three different serum and breast milk pools were prepared. One pool was used as a blank QC, and the other two were enriched with analytes to obtain low concentration (low QC) and high concentration (high QC) pools. These serum and breast milk pools were dispensed in small aliquots (ca. 3 mL) into vials prerinsed with hexane, and stored at −20 °C until used.

2.2. Preparation of serum and milk samples

All samples, including spiked serum or milk, QCs, blanks and unknowns, were prepared and processed using the same SPE/SPME procedure (Fig. 2). To an 8-mL glass test tube containing 3 mL 0.1 M formic acid, 1 mL methanol, and 50 μL internal standard solution, 1 mL of serum or breast milk was added. Calibration standards were prepared in a similar way but adding 50 μL calibration standard solution instead of serum or milk. The contents of all tubes were vortex-mixed, and the tubes

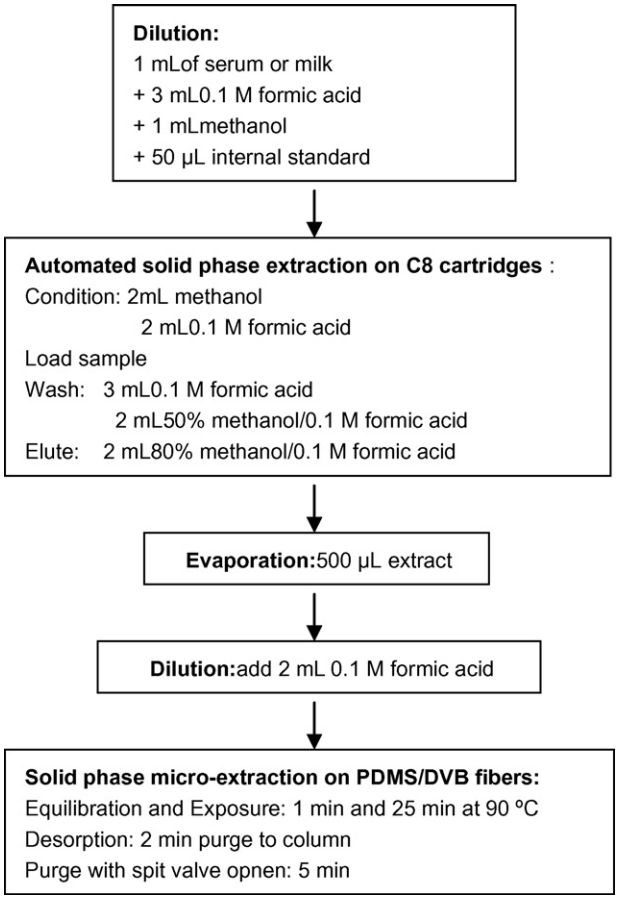

Fig. 2. Sample processing procedure.

were placed on a Zymark RapidTrace Station (Zymark Corporation, Hopkinton, MA, USA) for the automated solid phase extraction (SPE).

2.3. Automated solid phase extraction

Before each extraction run, the extractor lines were purged with methanol and water. Next, one 100 mg 1 mL Bond Elute C8 cartridge (Varian, Lake Forest, CA, USA) per sample was conditioned with HPLC-grade methanol (2 mL) and 0.1 M formic acid (2 mL). Afterward, the sample was loaded onto the cartridge at 1 mL/min. Then, the cartridge was washed with 3 mL 0.1 M formic acid and with 2 mL 50% methanol/0.1 M formic acid. The musk compounds were eluted from the SPE column with 3 mL 85% methanol/0.1 M formic acid and the eluate was collected in a 4 mL tube. The volume of the SPE eluate was reduced to ∼500 μL under a stream of nitrogen (NM120L gas generator, Peak Scientific Ltd., Bedford, MA, USA) in a Turbovap evaporator (Zymark Corporation) at 45 °C for a period of time ranging from 45 to 60 min.

2.4. Automated solid phase microextraction

The concentrated SPE extract was diluted with 2 mL 0.1 M formic acid, vortex mixed, transferred into a 10 mL head space vial, and sealed with a magnetic cap with a PTFE-faced septum. The rest of the SPME procedure was performed automatically using a CTC Combi PAL^{TM} LEAP GC autosampler (LEAP Technologies, Inc., Carrboro, NC, USA) equipped with a heated agitator. A bonded PDMS/DVB 65 μm film thickness fiber (Supelco, Bellefonte, PA, USA) was used. For each sample, the automated sequence started by transferring the headspace vial to the agitator, set to 90 °C, and the vial was equilibrated at this temperature for 1 min. The equilibration was followed by exposing the fiber to the head space of the vial for 25 min while agitating at 100 rotation/min. After the exposition period, the fiber was immediately inserted into the 280 °C GC injector (vide infra) for 2 min purge time (purge flow: 1 mL/min) and for an extra 5-min desorption period with the split valve open to avoid carry over. To prevent clogging of the inlet liner, a Merlin microseal (Agilent Technologies, Wilmington, DE, USA) was used instead of a rubber inlet septum.

2.5. Gas chromatography

The GC analysis was carried out on an HP 6890 gas chromatograph (Agilent Technologies) equipped with a Supelco Rtx-5Sil MS, 0.25 mm × 30 m × 0.25 μm capillary column with helium as carrier gas (10 psi constant pressure). The GC oven temperature program was as follows: 60 °C hold for 2 min, increase to 280 °C at 13 °C/min and hold for 1.5 min; total run time was 25 min.

2.6. Mass spectrometry

The HP 5973 mass spectrometer (Agilent Technologies) was operated with an electron ionization (EI) probe; the transfer line temperature was 280 °C, the source temperature was 230 °C, the quad temperature was 150 °C and electron multiplier was set to −70 eV. Mass spectra were acquired in full scan mode (Fig. 1). The most intense ions were chosen as quantitation ions in the selected ion monitoring (SIM) mode. The SIM acquisition was divided into three time-segments with 100 ms dwell time for each ion. The amu values of the quantitation ions/confirmation ions were as follows: segment 1, 229/244 (MC); segment 2, 243 (MG and MTo), 294 (D_{15}-MX); and segment 3, 263/278 (MM).

2.7. Data processing

The data acquisition was performed using the Chemstation software (Agilent Technologies). The data files were exported from Chemstation format into .AIA format, then, using the Xcalibur software (ThermoFinningan, San Jose, CA, USA), converted into .RAW format by the Xconvert program (part of the Xcalibur package). Data were processed using Xcalibur. The ratio of each analyte peak area to the internal standard (D_{15}-MX) peak area was used for quantification. Seven standard analyte concentrations encompassing the entire linear range of the method were used to construct a calibration curve of area ratio versus standard concentration. The calibration curves were weighted by the reciprocal of the standard amount ($1/x$).

2.8. Quality control

Each sample batch contained a maximum of 30 unknowns along with 2 low QC and 2 high QC samples, 2 reagent blanks and 7 calibration standards (without serum or milk). Since calibration standards and all other samples were processed through the same entire SPE/SPME process, any potential solvent contribution was automatically corrected by the calibration curve intercept.

3. Results and discussion

We developed the present method for the purposes of biomonitoring of selected synthetic musk compounds. Biomonitoring provides human internal dose information [17–19]; this information in the context of demographic, race, gender as well as environmental and toxicokinetic data can be used for both human exposure and risk assessment purposes. The statistical relevance of biomonitoring data is largely determined by the number of samples analyzed and the number of samples with accurately detectable concentrations. These considerations translate into two main practical laboratory requirements: high sample throughput and trace level sensitivity, even when using small amounts of sample.

To meet the above requirements, we took advantage of both the lipophilic and semi-volatile nature of musk compounds during the SPE/SPME steps. Specifically, since both the SPE and the SPME steps were automated, manual sample handling was minimal thus facilitating a high throughput. The SPE/SPME approach was also convenient because it eliminated the need for aqueous to non-aqueous solvent exchange before GC/MS analysis. Only removal of the methanol content in the SPE eluent was required, minimizing potential analyte losses due to evaporation that could adversely impact the sensitivity of the method. In addition, potential contamination from solvents and equipment during the SPE step that could also affect sensitivity was minimized by using a relatively small amount (3 mL) of 85% methanol for elution.

3.1. Comments on the procedure

Dilution with a mixture of water, formic acid and alcohols is a common practice for denaturation of the matrix proteins while keeping the sample sufficiently homogenous and the lipophilic analytes dissolved [20,21]. We also found that addition of 0.1 M formic acid and 20% methanol was necessary for optimal sample conditioning and adsorption of the analytes on the SPE cartridge.

During SPE, we used the lipophilic properties of the musks to separate them from the serum or milk proteins, similar to reversed phase methods developed for other persistent organic pollutants [14,21]. Specifically, we tested Bond Elute C8 and C18 silica (Varian, Walnut Creek, CA, USA) and Oasis HLB (Waters, Milford, MA, USA) SPE columns. Oasis HLB and C18 sorbents provided good recovery only if the analytes eluted with 5 mL 100% methanol. By contrast, using 100 mg Bond Elute C8 cartridges, the analytes could elute with 3 mL 85% methanol. Minimizing the amount and the methanol content of the SPE eluent was important to reduce the elution of lipids which otherwise suppressed the partitioning of the musk compounds into the head space and reduced analyte recovery by the SPME extraction (vide supra). Therefore, we chose the Bon Elute C8 as the SPE sorbent. With our experimental conditions, the recoveries of the analytes ranged from 78 to 90% (serum) and 62 to 69% (breast milk) (Table 1).

During the SPME step, we used the semi-volatile nature of the analytes to separate them from less volatile residual serum and milk components, similar to published methods for measurement of musks in waste water [22,23]. We found that the SPME recovery was affected more by the methanol and lipid content of the SPE extract and less by the volume of liquid in the head space vial. Therefore, after partial evaporation, the SPE concentrate was diluted with 2 mL of 0.1 M formic acid/water. Formic acid did not affect the SPME recovery (not shown) but reduced the degree of precipitation of the endogenous proteins during fiber exposure. The PDMS/DVB SPME fiber was chosen based on the published data that included a thorough discussion of the kinetics of the uptake by the SPME fiber [22]. The effects of experimental conditions (e.g., formic acid/methanol

Table 1
Mean and standard deviation of solid phase extraction recoveries, accuracy of standard concentration recoveries, and blank concentrations

Analyte	Matrix	LOD (ng/mL)	SPE recovery[a]	Spiked concentration recovery[b] at 0.5 and 5 ng/mL		Endogenous conc.[c] (ng/mL)
MC	Serum	0.03	90 ± 9	82 ± 34	78 ± 20	<0.03
	Milk	0.03	62 ± 5	106 ± 26	78 ± 10	<0.03
MG	Serum	0.3	86 ± 18	73 ± 22	79 ± 18	0.28 ± 0.07
	Milk	0.3	72 ± 6	117 ± 21	60 ± 18	0.64 ± 0.15
MTo	Serum	0.3	78 ± 10	97 ± 31	101 ± 24	0.15 ± 0.03
	Milk	0.3	68 ± 12	103 ± 9	64 ± 10	0.19 ± 0.07
MM	Serum	0.03	90 ± 4	133 ± 11	128 ± 6	0.12 ± 0.04
	Milk	0.03	69 ± 8	83 ± 44	104 ± 7	0.36 ± 0.09

[a] Calculated by RF_b/RF_a, where the two response factors, RF_b and RF_a, were determined by triplicate measurement of samples spiked with internal standard before SPE, and with 5 ng/mL standards before and after SPE separation, respectively.

[b] Calculated from triplicate measurements in serum or milk spiked with the calibration standard; results were reduced by endogenous calf serum and breast milk levels.

[c] Endogenous levels calculated from triplicate measurement of calf serum and breast milk without spiking with standards.

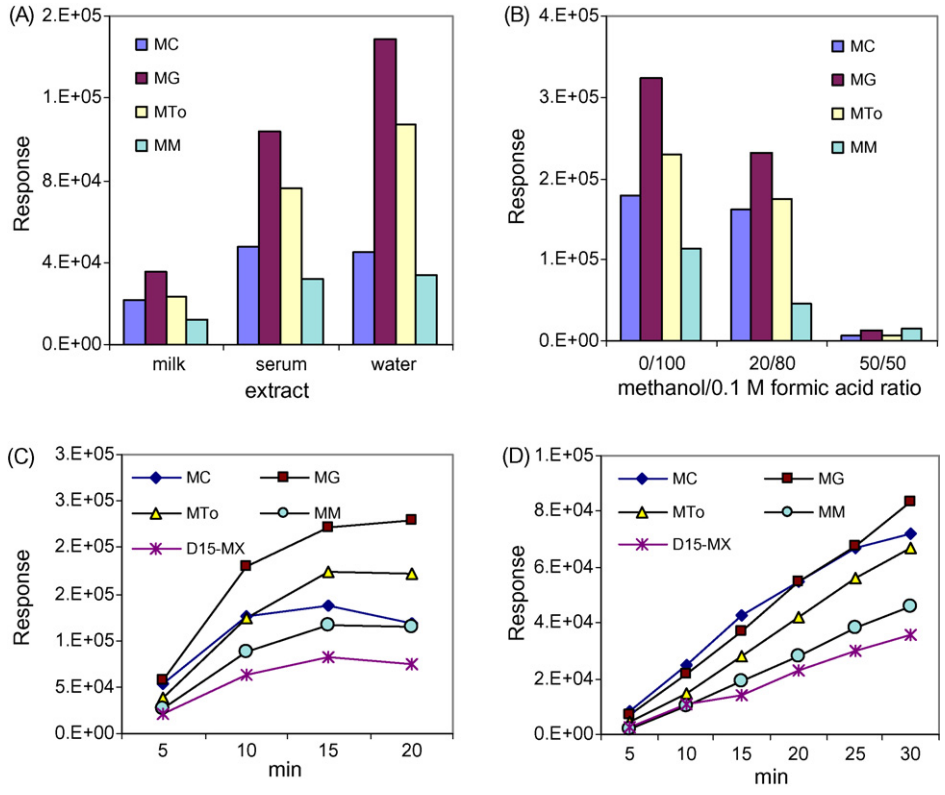

Fig. 3. The effect of experimental conditions on the SPME recovery: (A) matrix type, (B) methanol/0.1 M formic acid ratio, (C) exposure time (serum extract), and (D) exposure time (milk extract).

ratio, matrix, and head space exposure time) on the SPME recovery of the musks are shown in Fig. 3. The uptake of the musks by the SPME fiber reached equilibrium in 20 min (Fig. 3) in the serum extracts, while linear uptake was observed over 30 min in the milk extracts. The uptake of the most volatile of the analytes, MC, reached equilibrium first both in serum (15 min) and in milk (30 min). This observed difference in uptake was most likely caused by the residual lipid content in serum versus milk. Since the extent of the matrix effect was similar for the analytes and the D_{15}-MX internal standard, it could be corrected by

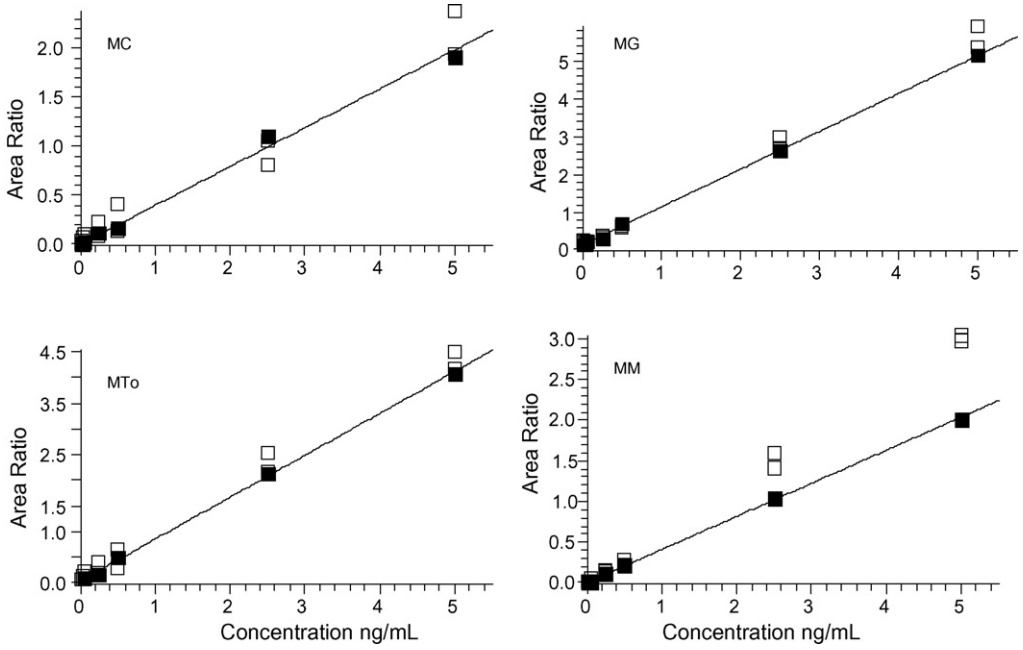

Fig. 4. Calibration curves for spiked water after SPE/SPME separation (full squares) with superimposed data points for extract of spiked serum and milk samples (empty squares).

using area ratio versus concentration calibration curves (Fig. 4). To increase sample throughput we choose 20 min exposure time in all matrices. We were able to use one fiber for the analysis of up to 300 samples without significant loss in sensitivity and reproducibility.

3.2. Evaluation of method performance

Since the available calf serum and breast milk contained musk compounds at concentrations up to 0.6 ng/mL (Table 1), calibration in the 0.005–0.5 ng/mL range could not be achieved from spiked serum or milk. Therefore, calibration standards were prepared in 0.1 M formic acid. The SPE–SPME–GC/MS method LOD was calculated as $3S_0$, where S_0, determined from the replicate analysis of low-level standards, is the standard deviation as the concentration approaches to 0 [24]. The $3S_0$ were 0.01–0.1 ng/mL. However, since contribution from the reagents, estimated from average intercept/slope values, was also in the 0.01–0.1 ng/mL range, we used the more conservative three times the reagent blank contribution as our method LOD (Table 1).

The presence of residual matrix components in the serum extract did not substantially decrease SPME recovery (Fig. 3). In contrast, residual matrix components in the milk extract, most likely lipids, did decrease the SPME recovery to 20–30% (Fig. 3). However, as it is shown by the area ratio versus concentration curves in Fig. 4, the D_{15}-MX internal standard sufficiently corrected for the recovery difference between matrices, and the area ratios remained in a 20–30% tolerance range for all analytes. To determine method accuracy, calf serum or breast milk was spiked at 0.1–5 ng/mL standard concentrations and analyzed repeatedly. The concentration of the spiked milk and serum was calculated using calibration standards prepared without serum or milk and without the SPE step, only by SPME–GC/MS in 2 mL 0.1 M formic acid (Fig. 4). The measured concentrations in serum and milk were reduced by the endogenous amounts to obtain the measured spiked concentration. The accuracy of the spiked concentration recovery was expressed as a percentage of the expected value at 0.5 and 5 ng/mL concentration (Table 1). At 0.5 ng/mL, the expected concentration of most unknown samples (Fig. 5), accuracies ranged between 73 and 133%.

The precision of the method was determined by calculating the average coefficient of variation (CV) of 20 repeated measurements of the low QC and high QC materials during a 4-week period. The average CVs were in the 10–24% range, acceptable for a non-isotope-dilution GC/MS method (Table 2).

3.3. Measurement of musk compounds in human serum and milk

To demonstrate the performance of the method, we analyzed serum samples collected from 7 anonymous adults in Atlanta, GA during March 2004 and 26 milk samples also from anonymous lactating women. The number of serum samples with above LOD levels (mean [min–max concentration])

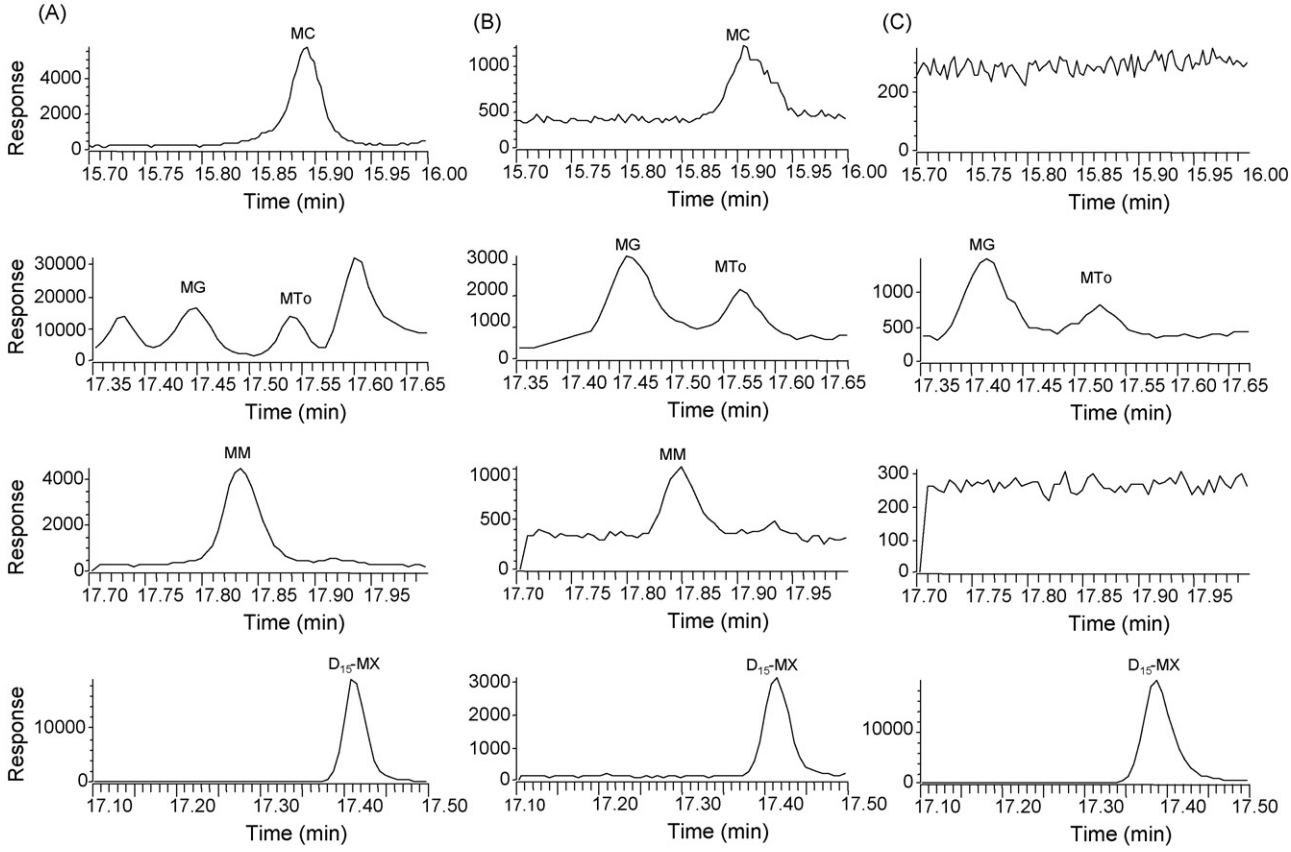

Fig. 5. Typical GC/MS chromatograms of synthetic musks extracted from spiked 0.5 ng/mL calf serum (A) and breast milk (B), and from a reagent blank (C).

Table 2
Mean concentration (ng/mL) and precision (expressed as the average coefficient of variation [CV%]) calculated for 20 repeated analysis of spiked quality control calf serum and breast milk (QC)

Analyte	Matrix	QC high		QC low	
		Mean	CV%	Mean	CV%
MC	Serum	3.7	10	0.41	24
	Milk	3.6	14	0.62	20
MG	Serum	1.8	13	0.42	22
	Milk	2.5	21	0.63	23
MTo	Serum	2.5	19	0.38	17
	Milk	1.7	18	0.47	19
MM	Serum	3.4	13	0.38	24
	Milk	2.8	13	0.55	22

were 4 for MC (0.16 ng/mL [0.04–0.47 ng/mL]), 2 for MG (1.04 ng/mL [0.38–1.70 ng/mL], and 4 for MM (0.12 ng/mL [0.05–0.28 ng/mL]. The number of milk samples with above LOD levels were 7 for MC (0.21 ng/mL [0.06–0.90 ng/mL]), 7 for MG (0.8 ng/mL [0.35–2.29 ng/mL], 5 for MTo (0.56 ng/mL [0.46–0.72 ng/mL] and 1 for MM (0.12 ng/mL). Assuming an approximate 1.74% lipid content in milk as suggested before [25], these breast milk concentrations of MG (20.1–131.6 ng/g lipid) and MTo (26.4–41.4 ng/g lipid) are within the range of concentrations reported by Reiner et al. for Massachusetts women (<5–415 ng/g and <5–144 ng/g, respectively) [25].

4. Summary and conclusions

The interesting aspect of this work is the combined use of SPE and SPME for the preconcentration of musk compounds from biological matrices. We believe that by taking advantage of both the lipophilic and semivolatile nature of musk compounds, we developed a selective and sensitive method that meets the demands of large scale biomonitoring studies: high sample throughput (∼30 unknowns/day), adequate sensitivity (LODs range from 0.03 to 0.3 ng/mL), minimal sample handling as a result of the automation of the SPE and SPME steps, and using only 1 mL sample. Furthermore, the method was successfully validated using serum and milk collected from persons with no documented exposure to Galactoside®, Tonalide®, Muskene®, and Celestolide® which suggests that this method could be used for assessment of the general population exposure to polycyclic musk compounds.

References

[1] J.L. Reiner, K. Kannan, Chemosphere 62 (2006) 867.
[2] G.G. Rimkus, Toxicol. Lett. 111 (1999) 37.
[3] K. Kannan, J.L. Reiner, S.H. Yun, E.E. Perrotta, L. Tao, B. Johnson-Restrepo, B.D. Rodan, Chemosphere 61 (2005) 693.
[4] G.G. Rimkus, M. Wolf, Chemosphere 33 (1996) 2033.
[5] P.A. Cadby, W.R. Troy, M.G.H. Vey, Regul. Toxicol. Pharmacol. 36 (2002) 246.
[6] W.W. Nazaroff, C.J. Weschler, Atmos. Environ. 38 (2004) 2841.
[7] B. Bridges, Flavour Fragrance J. 17 (2002) 361.
[8] A.M. Peck, Anal. Bioanal. Chem. 386 (2006) 907.
[9] L.I. Osemwengie, S. Steinberg, J. Chromatogr. A 993 (2003) 1.
[10] J. Angerer, H.U. Kafferlein, J. Chromatogr. B 693 (1997) 71.
[11] K.S. Helbling, P. Schmid, C. Schlatter, Chemosphere 29 (1994) 477.
[12] Y. Wan, Q.W. Wei, J.Y. Hu, X.H. Jin, Z.B. Zhang, H.J. Zhen, J.Y. Liu, Environ. Sci. Technol. 41 (2007) 424.
[13] L. Duedahl-Olesen, T. Cederberg, K.H. Pedersen, A. Hojgard, Chemosphere 61 (2005) 422.
[14] M. Bauer, F. Hilpert, N. Arnold, J. Pfisterer, W. Jonat, H. Kruse, J. Anal. Toxicol. 29 (2005) 110.
[15] G.G. Rimkus, M. Rummler, I. Nausch, J. Chromatogr. A 737 (1996) 9.
[16] H.P. Hutter, P. Wallner, H. Moshammer, W. Hartl, R. Sattelberger, G. Lorbeer, M. Kundi, Chemosphere 59 (2005) 487.
[17] J. Angerer, M.G. Bird, T.A. Burke, N.G. Doerrer, L. Needham, S.H. Robison, L. Sheldon, H. Zenick, Toxicol. Sci. 93 (2006) 3.
[18] L.L. Needham, D.G. Patterson, D.B. Barr, J. Grainger, A.M. Calafat, Anal. Bioanal. Chem. 381 (2005) 397.
[19] J.L. Pirkle, L.L. Needham, K. Sexton, J. Expos. Anal. Environ. Epidemiol. 5 (1995) 405.
[20] K. Janak, E. Jensen, G. Becher, J. Chromatogr. B 734 (1999) 219.
[21] K. Conka, B. Drobna, A. Kocan, J. Petrik, J. Chromatogr. A 1084 (2005) 33.
[22] C. Garcia-Jares, M. Llompart, M. Polo, C. Salgado, S. Macias, R. Cela, J. Chromatogr. A 963 (2002) 277.
[23] T. Heberer, S. Gramer, H.J. Stan, Acta Hydrochim. et Hydrobiol. 27 (1999) 150.
[24] J.K. Taylor, Quality Assurance of Chemical Measurements, Lewis Publishers, Chelsea, MI, 1987.
[25] J.L. Reiner, C.M. Wong, K.F. Arcaro, K. Kannan, Environ. Sci. Technol. 41 (2007) 3815.