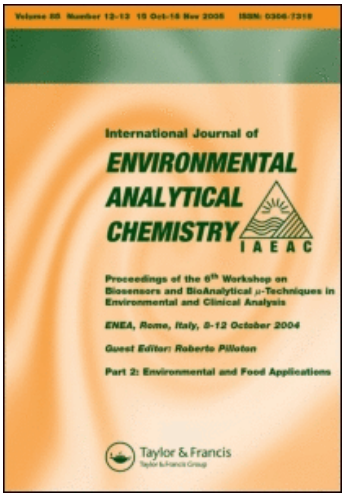

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Characterization of volatile effluents of livestock buildings by solid-phase microextraction

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CHARACTERIZATION OF VOLATILE EFFLUENTS OF LIVESTOCK BUILDINGS BY SOLID-PHASE MICROEXTRACTION

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This article presents two examples of the application of SPME to the characterisation of gaseous effluents from animal sheds. In the first example the volatile fraction of swine manure was analysed by solid-phase microextraction combined with gas-phase chromatography–mass spectrometry (SPME-GC-MS). To find the best extraction conditions for volatile components, six types of SPME fibre were tested. Carboxen-PDMS fibre performed best, enabling us to extract and identify 101 compounds of varying polarity and molecular weight. The second example shows that it is possible to concentrate the volatile components in various animal shed atmospheres by simple exposure of a fibre inside the building. Direct injection into a mass spectrometer ionisation source (SPME-MS) of the volatile components thus trapped provided signatures characteristic of the four different animal shed atmospheres studied. The practical simplicity of the SPME-MS method makes it a good candidate for rapid identification and monitoring of animal shed atmospheres.

Keywords: SPME; Odour analysis; Spectral signature; Swine manure

INTRODUCTION

The adverse environmental effects of the expansion of high-productivity animal farming are now widely recognised. These effects concern the soil and groundwater but also the air [1]. Foul-smelling gaseous emissions are a particular nuisance to nearby residential areas, and can even be a health hazard for exposed persons [2]. The characterisation of these volatile effluents is thus important both to determine their composition and to develop rapid monitoring methods. For this purpose analytical methods that combine rapidity and simplicity have had to be developed or adapted. Solid-phase microextraction (SPME) is a recent trapping method for volatile organic compounds (VOCs) already applied to environmental monitoring [3]. Coupled to gas-phase chromatography and mass spectrometry (SPME-GC-MS), this method provides detailed information on the volatile fractions of matrices or atmospheres [4–6]. Directly coupled to the mass spectrometer, without prior chromatographic separation, SPME-MS provides

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mass spectra or signatures characteristic of the global composition of gas mixtures. SPME-MS has already been successfully used in agrifood applications, e.g., for rapid classification/recognition operations [7–9] and prediction of the aromatic characteristics of foodstuffs [10].

This article presents two examples of the application of SPME to the characterisation of gaseous effluents from animal sheds. First, the performance of six types of SPME fibre for the analysis of liquid pig manure by SPME-GC-MS is compared. The second example shows that it is possible to concentrate the volatile components of various animal shed atmospheres by simple exposure of a fibre inside the building, and offers a new method for the rapid characterisation of these atmospheres by SPME-MS.

EXPERIMENTAL

Nature and Origin of Samples

Pig Manure

The pig manure came from Large White piglets weaned three weeks previously and raised on concrete full-slatted floors (Romillé Experimental Station, Ille-et-Vilaine, France). Three litres of fresh manure were collected in 1-L glass containers, cooled to $+4^{\circ}C$ and immediately brought to the laboratory. To compare the extraction performance of six types of SPME fibre with no change in the manure composition, several aliquots of manure were placed in 20-mL glass flasks of the type used classically to generate a VOC headspace (flask ref. 5182-0837, butyl/teflon septum cap ref. 9301-0976, crimp ring ref. 9301-0721, Agilent Technologies, Les Ulis, France) and frozen at $-20^{\circ}C$. The flasks were thawed for 90 min at ambient temperature before fibre extraction of the VOCs.

Animal Shed Atmospheres

The atmospheres were those of four animal housing facilities: a piggery (48 pigs in a fattening shed on concrete full-slatted floors), a cattle shed (12 steers on straw), a sheep shed (32 lambs on straw) and an animal house (250 mice raised in a ventilated facility).

Analysis of the Volatile Fraction of Pig Manure

Extraction of Volatile Components

The six SPME fibres tested were those most readily commercially available at the time of the study; Carboxen-polydimethylsiloxane (C-PDMS, thickness 75 μm, Supelco, Saint-Quentin-Fallavier, France), polydimethylsiloxane (PDMS, thickness 100 μm, Supelco), polydimethylsiloxane-divinylbenzene (PDMS-DVB, thickness 65 μm, Supelco), polyacrylate (PA, thickness 85 μm, Supelco), Carbowax-divinylbenzene (CW-DVB, thickness 65 μm, Supelco) and divinylbenzene-Carboxen/polydimethylsiloxane (DVB-C-PDMS, thicknesses 50/30 μm, Supelco). After conditioning (30 min in the injector at the optimal temperature required according to the phase), each

SPME fibre was introduced into the flask containing the liquid manure and exposed in the headspace for 15 min at 21°C.

Desorption–Injection of the Volatile Components

The desorption of the compounds adsorbed on the SPME fibre took place in the splitless injector of the chromatograph. The optimal injection temperature set according to the nature of each fibre type was 280°C for C-PDMS and PA, 260°C for PDMS, DVB-C/PDMS and PDMS-DVB, and 250°C for CW-DVB. To eliminate interference from compounds inherent to the fibre or flasks (septum cap, walls), a blank from a 15-min fibre extraction in an empty closed flask was run before each analysis.

Separation and Identification of Volatile Components

The analysis line was composed of a gas-phase chromatograph (model 6890 A, Agilent Technologies, Palo Alto, CA) coupled to a quadrupole mass spectrometer (model 5973, Agilent Technologies, with ionisation by electron impact at 70 eV). The chromatograph was equipped with a 60-m long capillary column (SPB5, 60 m × 0.32 mm × 1 µm, Supelco). The entry flow rate into the mass spectrometer was 1 mL min^{-1} (99.9995% pure helium, Messer, France). The mass range used was 33 to 250 atomic mass units (amu) and the analysis duration was 70 min. Molecules were identified by comparison of experimental spectra with those of data banks Wiley 275 K [11] and MassLib 406 K [12], and by comparison of experimental retention indices with those in the data bank of Kondjoyan and Berdagué [13]. For each molecule, the area of the chromatographic peak was obtained by integration of the corresponding ion current. The resulting areas were expressed in arbitrary units of area (aua).

Rapid Analysis of the Volatile Fractions of the Animal Shed Atmospheres

Extraction of Volatile Compounds

For these experiments, the C-PDMS fibre, which performed best during separative analysis, was used. Three C-PDMS fibres were simultaneously exposed for 120 min inside each of the four animal facilities. The fibres were placed in the buildings 1 m from the ground, away from areas of turbulence such as doorways and ventilation openings. After exposure, the fibres were isolated from the atmosphere by inserting the metal needle of the SPME syringe system into an inert septum cap (ref. 5181-3383, Agilent Technologies). The fibres were then brought to the laboratory. Altogether 12 samples (3 fibres × 4 animal sheds) were taken.

Desorption and Injection of Volatile Components

Like the volatile components of the manure, the compounds adsorbed on the C-PDMS fibres were desorbed in the splitless injector of the chromatograph at the temperature prescribed by the supplier. However, the volatile compounds were not separated by gas-phase chromatography, but directly transferred into the mass detector through a short transfer line (HP-retention gap ref. 19091-60620, Agilent. length 3 m, diameter 0.10 mm). In these conditions, one analysis took 5 min. The signal (total ion current)

obtained took the form of an asymmetric peak and had a total duration of 5 min, for a half-height width ranging between 0.25 and 0.5 min. The average mass spectrum, resulting from the simultaneous ionisation and fragmentation of all the injected molecules, formed the crude instrumental signature of the atmospheres analysed. The mass range used was $33 < m/z < 150$ amu.

Analysis of Spectral Signatures

The initial spectra thus obtained contained 118 mass fragments. The mass fragments smaller than 45 amu were ignored because of their multiple and ill-defined origin (ambient air, carrier gas). Also, only the mass fragments above the detection threshold (10^5 abundance units as determined by Begnaud and Berdagué [14]) were considered as informative and so only these were subsequently used. The final refined spectra containing only 96 mass fragments were then processed. Before statistical analysis these spectra were normalised (each fragment was expressed as a percentage of the total abundance of the mass fragments). This operation emphasises the shape of the spectrum rather than the intensity of the signal. This mode of expression eliminates the variations in response level linked to fluctuations of the mass detector sensitivity, or to varying adsorption levels of the volatile components on the SPME fibre [7]. The influence of the "type of atmosphere" factor on the intensity of each mass fragment was estimated using the Fisher F value calculated after analysis of variance using the model

$$I_{Fj,n} = \beta_0 + TE_j + \varepsilon_n$$

where $I_{Fj,n}$ = intensity of the mass fragment considered; β_0 = mean effect; TE_j = effect of the "type of atmosphere" with $j = 4$; ε_n = residual variance with $n = 3$. Selection of the four most discriminant mass fragments from the shed atmospheres made after exhaustively testing all the combinations of four possible fragments among all the available fragments (criterion for the selection of the most discriminant combination: Wilks' lambda). A hierarchical cluster classification (based on calculation of Euclidean distances and on aggregation of individuals by Ward's method [15] was then established from the four mass fragments selected. All the calculations were carried out with Statistica software.

RESULTS AND DISCUSSION

Comparison of the Performance of Different SPME Fibres for the Analysis of the Volatile Fraction of Pig Manure

The individual performance of each fibre was evaluated on the basis of the range and quantity of substances extracted. Table I gives the results of the SPME-GC-MS analysis of pig manure headspace extracted with the six fibres tested. The C-PDMS fibre gave signals that were markedly richer and more intense than the other fibres. The total abundance (intensity) of the ion current measured for all the chromatographic peaks obtained with the C-PDMS fibre was 4.7×10^9 against 3.6×10^8 aua for the PDMS and 1.1×10^9 aua for the DVB-C-PDMS fibre (Table I). These results confirm the

TABLE I SPME-GC-MS analyses of the volatile fraction of the slurry sample. Qualitative and semi-quantitative comparison between the six different SPME phases

Compound[a]	*RI*	*RT*	*Rel*	*Total ionic current/10*^{4} (aua)					
				Carboxen-PDMS	*PDMS-DVB*	*DVB-Carboxen-PDMS*	*Carbowax-DVB*	*Polyacrylate*	*PDMS*
Alkanes									
Cyclohexane	657	11.61	b	427	–	–	–	–	–
Methylcyclohexane	719	14.96	c	161	–	–	–	–	–
Alkenes									
Octene	800	19.47	a	3016	–	–	–	–	–
p-Cymene	1031	33.44	a	602	–	–	–	–	–
Limonene [19]	1036	33.71	a	3392	1668	2113	1974	264	653
Alcohols									
2-Propanol	nd	5.78	a	718	–	–	–	–	–
2-Butanol	602	8.66	a	1223	–	–	–	–	–
2-Methyl-1-propanol [3]	623	9.77	a	633	–	–	–	–	–
1-Butanol [4]	654	11.45	a	5053	50	44	63	–	–
3-Pentanol	690	13.36	a	679	–	–	–	–	–
2-Methyl-2-pentanol	724	15.22	b	97	–	–	–	–	–
3-Methyl-1-butanol	726	15.38	a	781	–	–	–	–	–
2-Methyl-1-butanol	731	15.61	b	753	–	–	–	–	–
1-Pentanol	761	17.32	a	1784	–	–	35	–	–
3-Hexanol	793	19.09	a	105	–	–	–	–	–
1-Hexanol	866	23.63	b	141	–	–	–	–	–
2-Heptanol [14]	897	25.57	a	50	–	–	–	–	–
Phenol [17]	977	30.33	a	26 686	2932	3735	4761	3590	292
3-Octanol	994	31.35	a	470	80	68	103	23	17
2-Ethyl-1-hexanol	1028	33.25	a	211	25	25	34	–	8
3,5,5-Trimethyl-1-hexanol	1049	34.43	c	160	–	–	10	–	–
p-Cresol [20]	1073	35.77	a	83 340	163	20 935	20 438	15 294	3318
Diethylstyrol [21]	1096	37.07	c	1093	–	–	–	–	–
4-Ethylphenol [24]	1165	40.70	a	7808	1886	2129	2187	1779	782
4-Ethenylphenol [25]	1216	43.29	b	92	–	–	–	–	–
2-Phenoxy-ethanol	1226	43.80	b	44	–	–	–	–	–
Dibutyl-*p*-cresol [29]	1526	57.36	c	218	–	40	52	–	60
Bisphenol	nd	64.72	b	1144	474	–	218	1462	–

(*continued*)

TABLE I Continued

Compound[a]	*RI*	*RT*	*Rel*	*Total ionic current/10*^{4} (aua)					
				Carboxen-PDMS	*PDMS-DVB*	*DVB-Carboxen-PDMS*	*Carbowax-DVB*	*Polyacrylate*	*PDMS*
Aldehydes									
3-Methylbutanal	648	11.09	a	155	–	–	–	–	–
Benzaldehyde	964	29.59	a	378	–	–	–	567	32
Nonanal	1104	37.51	a	14	–	–	14	–	14
Dodecanal	1411	52.47	a	–	200	–	–	–	–
Ketones									
Acetone	nd	5.72	a	1013	–	–	–	–	–
2-Butanone [2]	nd	8.51	a	2980	–	–	8	–	–
2-Pentanone	678	12.69	a	256	–	–	–	–	–
3-Pentanone [6]	688	13.23	a	1117	–	–	9	–	–
3-Hexanone	782	18.46	a	284	–	–	–	–	–
2-Hexanone	786	18.72	a	112	–	–	–	–	–
Cyclopentanone	788	18.82	b	70	–	–	–	–	–
2-Methylcyclopentanone	840	22.04	b	257	–	–	–	–	–
3-Methylcyclopentanone	846	22.41	b	101	–	–	–	–	–
3-Heptanone	884	24.79	a	43	–	–	–	–	–
2-Heptanone	888	25.01	a	225	–	–	23	–	–
3-Octanone	986	30.85	a	2536	332	364	546	43	75
2-Octanone	990	31.09	a	243	30	38	53	–	8
2-Nonanone	1091	36.81	a	240	45	55	80	–	25
2-Undecanone	1294	47.12	a	109	29	38	42	21	29
2,6-bis-*tert*-Butylbenzoquinone	1485	55.65	c	159	–	–	–	–	–
Acids									
Carbon dioxide	nd	3.97	a	10 735	22 235	39 068	3049	10 822	15 212
Acetic acid [5]	nd	8.20	a	2277	–	–	244	–	–
Propanoic acid	681	12.83	a	1613	–	–	135	–	–
2-Methyl-propanoic acid	744	16.38	a	1432	–	–	111	–	–
Butanoic acid [9]	779	18.30	a	4424	98	–	259	70	39
Isovaleric acid [11]	833	21.57	a	7115	–	–	95	–	–
2-Methylbutanoic acid [12]	843	22.20	a	1051	–	–	48	–	–
Pentanoic acid [13]	872	24.04	a	1285	–	–	37	–	–
4-Methylpentanoic acid	935	27.86	b	51	–	–	–	–	–

Hexanoic acid	966	29.69	a	105	–	–	–	–	–
Benzoic acid [23]	1156	40.21	a	756	67	16	–	–	–
Esters									
Methyl butanoate	715	14.72	b	63	–	–	–	–	–
Butyl acetate	812	20.25	a	56	–	–	–	–	–
Amines and nitrogen heterocycles									
1-Methyl-1*H*-pyrrole	735	15.88	a	66	–	–	–	–	–
Pyridine	738	16.05	a	193	–	–	–	–	–
1*H*-Pyrrole	749	16.64	a	136	–	–	–	–	–
n-Acetylpyrrole	957	29.17	b	20	–	–	2	–	–
4-Isothiocyanato-1-butene	984	30.74	b	50	–	–	8	–	–
Benzonitrile	988	31.06	a	99	35	–	–	–	41
1*H*-Indole [27]	1305	47.64	a	8590	4591	6170	4644	3977	2263
Benzamide	1339	49.19	b	66	–	–	–	–	29
Skatole [28]	1402	52.07	a	8527	8135	8499	7693	6727	5319
Sulfides and thiols									
Sulfur dioxide	nd	4.37	a	3029	53	124	–	173	32
Methanethiol	nd	4.87	a	5878	649	1137	145	797	91
Dimethylsulfide [1]	nd	6.36	a	86 125	1942	2954	1249	363	462
Carbon disulfide	nd	6.86	a	8642	–	648	24	–	–
Propenethiol	612	9.16	a	30	–	–	–	–	–
2-Thiabutane	614	9.29	a	340	–	–	–	–	–
Dithiomethane	661	11.81	b	146	82	105	49	29	18
Thiophene	665	11.93	a	96	–	–	–	37	–
2-Thiapentane	707	14.27	b	48	–	–	–	–	–
Dimethyldisulfide [7]	742	16.23	a	99 564	6080	6752	4784	1636	1252
2-Methyl-thiophene	771	17.88	a	203	–	–	8	–	–
3-Methyl-thiophene	780	18.36	a	89	–	–	–	–	–
1,3-Dithiethane	806	19.89	c	81	–	4	–	–	–
Methylsulfoxide [10]	827	21.21	b	3399	–	68	–	–	–
2,3-Dithiapentane	838	21.87	b	27	–	–	–	–	–
2,4-Dithiapentane	892	25.26	a	791	56	47	47	–	–
Dimethylsulfone	909	26.34	a	32	–	–	–	–	–
1-(Methylthio)-pentane [15]	918	26.83	c	399	–	57	57	–	–
S-Methylpentanethioate [16]	942	28.26	c	171	–	–	16	–	–
Dimethyltrisulfide [18]	978	30.42	a	57 503	7675	9036	11797	1444	1577
Tetrahydrothiophen-3-one	1005	31.97	b	158	13	13	–	–	–

(*continued*)

TABLE I Continued

Compound[a]	*RI*	*RT*	*Rel*	*Total ionic current/10⁴ (aua)*					
				Carboxen-PDMS	*PDMS-DVB*	*DVB-Carboxen-PDMS*	*Carbowax-DVB*	*Polyacrylate*	*PDMS*
1,2,4-Trithiolane	1107	37.67	b	81	–	–	–	–	–
2,4,5-Trithiahexane [22]	1139	39.33	c	168	34	43	47	–	9
2-(Methylthio)-phenol	1175	41.20	b	46	–	–	–	–	–
Hexathiepane	1220	43.48	b	54	–	–	–	–	–
1,4-Dimethyltetrasulfide [26]	1237	44.31	b	6806	692	1428	2925	–	2220
Aromatics									
Toluene [8]	766	17.58	a	10 977	621	1428	453	81	69
p-Xylene	864	23.53	b	48	–	–	–	–	–
Styrene	893	25.38	a	71	–	–	–	–	–
Furans									
2-Methylfurane	606	8.87	a	181	–	–	–	–	–
3-Methylfurane	614	9.27	b	650	–	–	–	–	–
2,5-Dimethylfurane	700	13.90	a	63	–	–	–	–	–
γ-Butyrolactone	911	26.43	a	–	4754	–	–	–	1699
Total ionic current of the peaks				4.9×10^9	6.6×10^8	1.1×10^9	6.9×10^8	4.9×10^8	3.6×10^8

RI = retention index on SPB-5 (nd = not determined), RT = retention time (min), Rel = reliability of the identification or structural proposal (a = mass spectrum and Kovats index in agreement with the corresponding literature data, b = mass spectrum consistent with spectra found in the literature, c = tentative of identification by mass spectrum). The numbers between square brackets located after the name of the compounds correspond to the labelled peaks on Fig. 1. [a]Only compounds with abundance $> 10^4$ aua are considered.

TABLE II Number of compounds extracted and identified according to the type of fibre

Compounds[a]	*Carboxen-PDMS*	*PDMS-DVB*	*DVB-Carboxen-PDMS*	*Carbowax-DVB*	*Polyacrylate*	*PDMS*	*Total count*[b]
Alkanes	2	–	–	–	–	–	2
Alkenes	3	1	1	1	1	1	3
Alcohols	23	7	7	10	5	6	23
Aldehydes	3	1	–	1	1	2	4
Ketones	16	4	4	7	2	4	16
Acids	11	3	2	8	2	2	11
Esters	2	–	–	–	–	–	2
Amines and nitrogen heterocycles	9	3	2	4	2	4	9
Sulfides and thiols	26	10	14	12	7	8	26
Aromatics	3	1	1	1	1	1	3
Furans	3	1	0	0	0	1	4
Number of extracted molecules	101	31	31	44	21	29	103

[a]Only compounds with abundance $>10^4$ aua are considered; [b]total count = total number of compounds collected on all fibres.

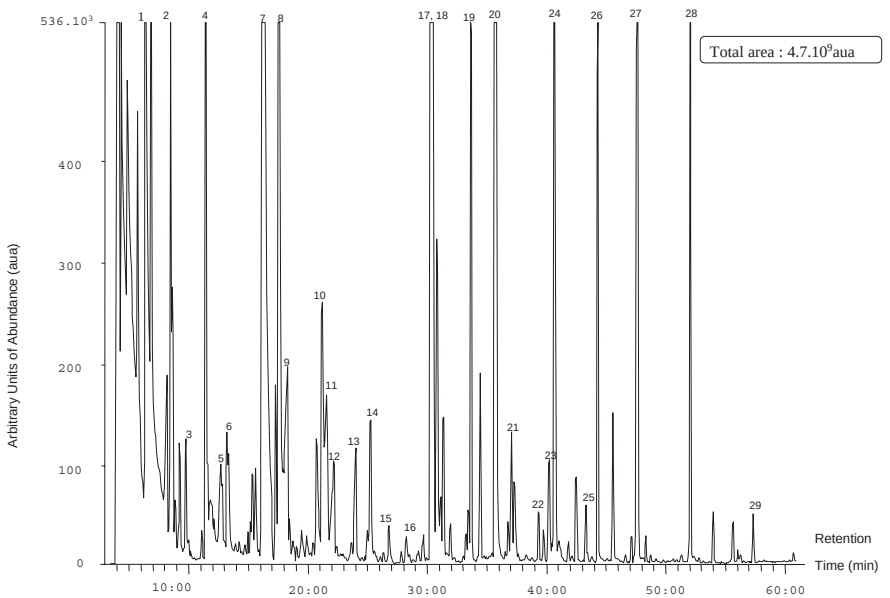

FIGURE 1 Chromatogram of volatile compounds of pig slurry obtained by SPME-GC-MS, using a C-PDMS fibre. See Table I for identities of the labelled peaks.

observations of Popp and Paschke [16] and Shirey [17], who found the C-PDMS fibre performed best for the analysis of volatile fractions extracted from air or water. This fibre extracted 101 substances of widely ranging polarity and molecular weight belonging to 11 chemical families (Table II). An example of a chromatogram obtained with this fibre is presented in Fig. 1. The main chemical families implicated in odourous emissions from pig farms [18,19] were extracted: volatile aliphatic branched-chain fatty acids, nitrogen heterocycles (pyrrole, indole and scatole derivatives), thiols and mercaptans. These compounds mostly stem from the catabolism of amino acids, either directly or after a series of secondary reactions [18,20]. The C-PDMS phase

showed a particular affinity for volatile fatty acids (11 acids, from C2 to C6) and sulfur compounds (26 identified), consistent with the findings of Abalos *et al.* [6] for volatile fatty acids and Pérès *et al.* [7] for sulfur compounds. The affinity properties of the C-PDMS phase are especially useful if the composition of the headspace has to be correlated with odour nuisance levels, because several sulfur compounds and volatile fatty acids identified here are implicated in smells from pig farms [21]. Among the 103 compounds extracted by the six fibres, only dodecanal and γ-butyrolactone were absent from the compounds extracted by the C-PDMS fibre. These two compounds (neither are responsible for odour nuisance) were extracted by the PDMS-DVB and PDMS fibres, known for their affinity for high molecular weight volatile compounds [22]. The different SPME fibres tested included both homogeneous polymer phases (PA and PDMS) and biphasic systems composed of porous particles embedded in a polymer phase (C-PDMS, PDMS-DVB, CW-DVB and DVB-C/PDMS). For the biphasic systems the trapping of the VOCs involved processes of absorption (mainly limited by the affinity of the compounds for the absorbing phase and their concentration in it) and of adsorption (limited by surface area and pore size). The better performance of the C-PDMS fibre is attributable to the preferential involvement of adsorption processes in the pores of Carboxen, which because of their small diameter (10 Å on average) are better suited to the trapping of small chemical entities [22–24].

Discrimination Between Animal Shed Atmospheres

In view of its better performance, the C-PDMS fibre was selected to concentrate the atmospheric volatile components by simple exposure inside the livestock buildings. To compare the trapping abilities of the C-PDMS fibre in an animal shed atmosphere with those described above for manure headspace analysis, we carried out a separative analysis by GC-MS after exposing the fibre for 120 min in a piggery. In these conditions the desorption of the trapped compounds gave a total ion current of 2.6×10^9 aua with the possibility of identifying 98 compounds (data not presented). These values are close to those obtained after exposure of the fibre to manure headspace in a closed flask (total ion current 4.7×10^9 aua and 101 compounds identified), confirming that VOC trapping by simple atmospheric contact can be efficient. The direct analysis of shed atmospheres by SPME-MS (with no chromatographic step) also gave relatively intense signals (pig shed 11×10^8 aua, cattle shed 5.8×10^8 aua, sheep shed 3.3×10^8 aua, animal house 2.5×10^8 aua), particularly for the pig shed. The mean normalised spectra or signatures of the four shed atmospheres are presented in Figs. 2A, 2B, 2C and 2D. These spectra are visually different, suggesting that the SPME-MS method is *a priori* adequately sensitive to characterise animal shed atmospheres. The fragments most significantly influenced by the type of atmosphere ($F_{\text{Fisher}} > 4$; $p < 0.05$) were those with $m/z = 47$, 49, 50, 59, 60, 74, 87, 91, 92, 93, 100, 107, 108 and 121 (Fig. 2E). Separative analysis by SPME-GC-MS indicated that these fragments originated mainly from sulfur compounds ($m/z = 47$ and 49) or phenols such as *p*-cresol and 4-ethylphenol ($m/z = 87$, 107 and 108) from the catabolism of amino acids, or from carboxylic acids characteristic of fermentation or amino acid de-amination reactions carried out by intestinal anaerobic bacteria (fragment 60), or from terpenes (fragments $m/z = 93$ and 121) present in the pelleted mouse feed and in litter. These VOCs are classically found in animal shed atmospheres [25] and, except for the terpenes, are recognised as contributing to odour nuisance. The selection of the most discriminant

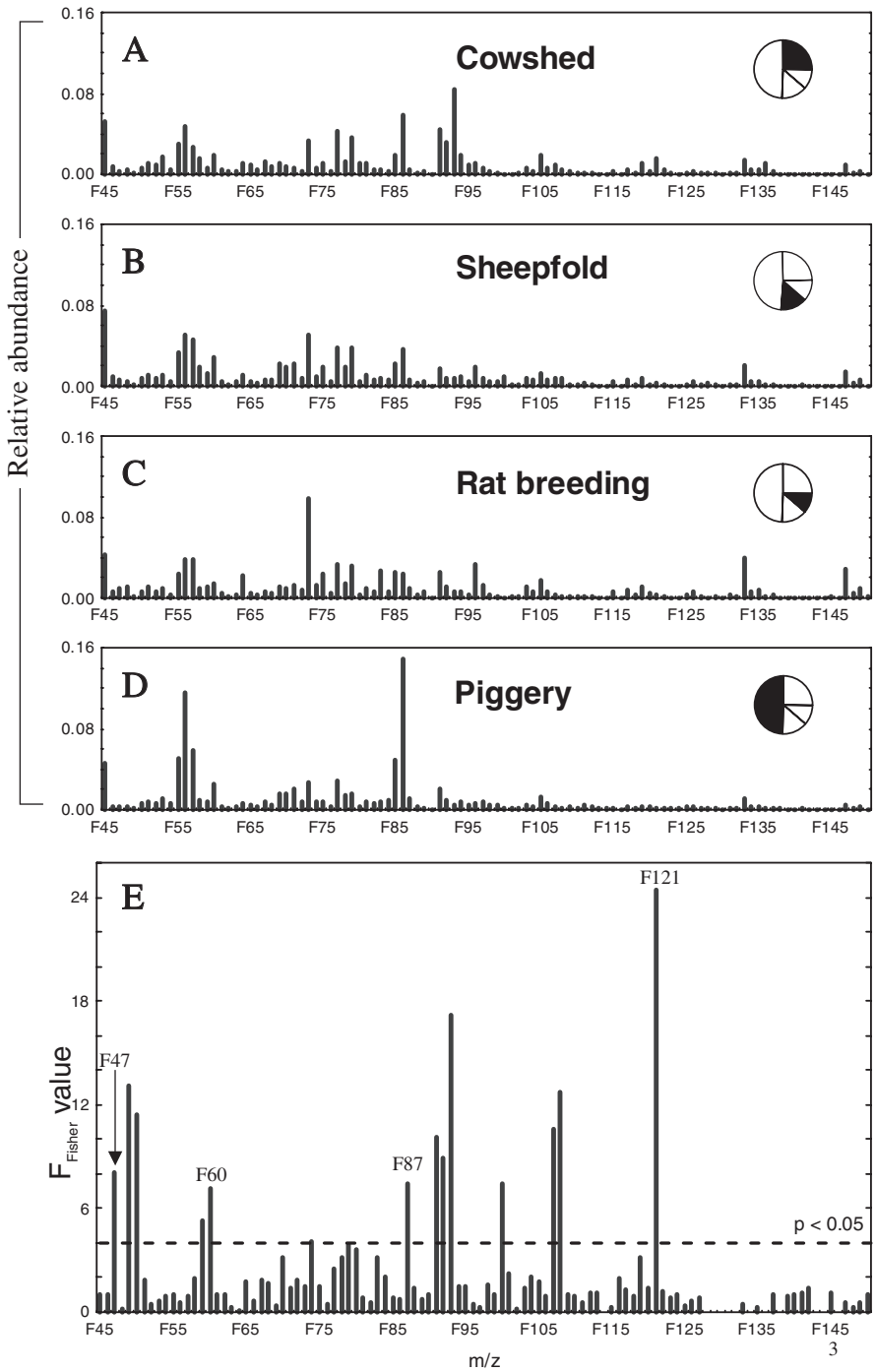

FIGURE 2 A–D: Normalised mass spectra originating from the four different types of atmosphere. The highlighted sectors represent the relative abundance of each atmosphere. E: Effect (F_{Fisher} value) of the ''type of atmosphere'' on the mass fragments intensity. The four mass fragments used for the computation were 47, 60, 87 and 121.

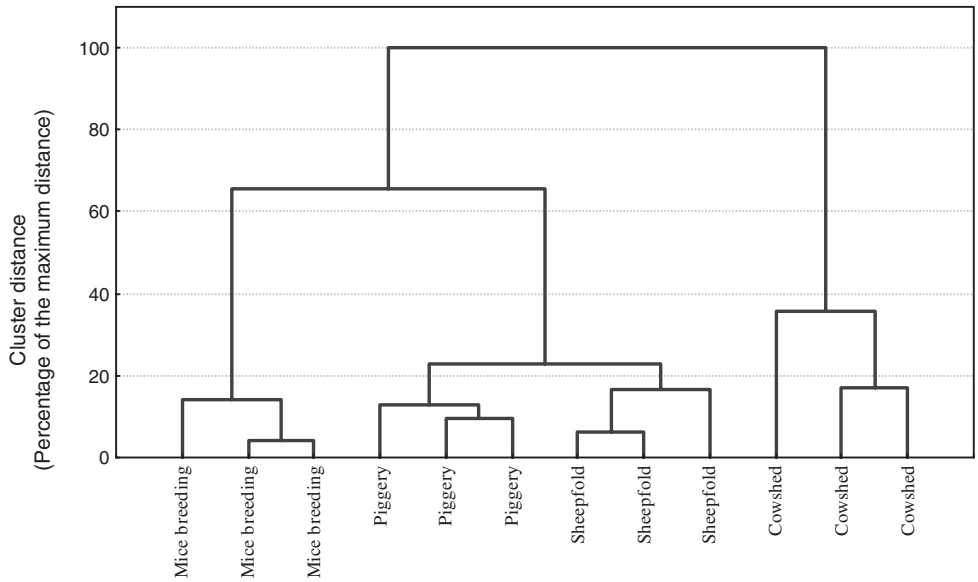

FIGURE 3 Hierarchical clustering of the four types of breeding atmospheres (computations performed from four mass fragments: $m/z = 47$, 60, 87, 121).

mass fragments of the animal shed atmospheres resulted in the retention of only four fragments: $m/z = 47$, 60, 87 and 121. The most probable chemical origin of these fragments has already been described (sulfur compounds: $m/z = 47$, volatile fatty acids: $m/z = 60$, phenolic compounds $m/z = 87$ and terpenes $m/z = 121$). The ascending rank order (Fig. 3) allowed a clear distinction between the four animal shed atmospheres from a fraction of the total information contained in the spectral signatures; i.e., four mass fragments out of the 96 present in the normalised spectra.

CONCLUSION

SPME is a simple and effective analytical tool for the sampling of volatile components both in headspace and in the atmospheres of animal sheds.

The separative SPME-GC-MS approach provides very rich information on the composition of biological effluents. The best extraction performance was obtained with the C-PDMS fibre, which displayed a strong affinity for sulfur compounds and volatile fatty acids, and also allowed analysis of nitrogen compounds such as indole and scatole. All these compounds are implicated in odour nuisance associated with animal farming, which also argues in favour of SPME/C-PDMS extraction.

The non-separative SPME-MS approach readily provides signatures characteristic of the atmospheres of animal sheds. These signatures enabled us to distinguish clearly between the four animal facilities we tested, using only a small part of the total spectral information obtained. The practical simplicity of the SPME-MS method makes it a good candidate for rapid identification and monitoring of animal shed atmospheres.

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