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Influence of extraction parameters and medium on efficiency of solid-phase microextraction sampling in analysis of aliphatic aldehydes

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Abstract

The main sorption conditions were optimized in the solid-phase microextraction (SPME) analysis of aldehydes that have different degrees of saturation. Aliphatic aldehydes were analyzed quantitatively in oil matrix and in aqueous solution by GC–MS using SPME sampling. The effectiveness of the immersion and the headspace techniques was compared in water. Samples were analyzed by gas chromatography with mass spectral detection using a medium polar CP WAX 52 CB column. The optimal exposure time was 30 min at 40°C using a 100 μm poly(dimethylsiloxane) coating. A ratio of liquid to headspace volume of 1:1 resulted in the best extraction in headspace analysis. Principal component analysis (PCA) was carried out to find similarities among various aldehydes and among conditions of optimization. The PCA identifies three clusters corresponding to analysis conditions (immersion in water, headspace above water and headspace above oil). The aldehydes behave similarly with the exception of dienals.

Keywords: Solid phase microextraction; Extraction methods; Principal component analysis; Headspace analysis; Aldehydes

1. Introduction

Since solid-phase microextraction (SPME) is based on the partitions of the analyte in the solution, in the headspace of the sample and in the coating of the fiber, the efficiency of the extraction depends on all the parameters of the equilibrium processes. SPME has been developed in 1989–1992 for the fast and easy analysis of volatile and semivolatile compounds being present in water [1–3]. In the process of this method a direct extraction and sorption of the analyte from a solution or from the headspace over the solution take place followed by a desorption step into the injector of the gas chromatograph. The principle of SPME is an equilibrium partitioning process of the solute between the coating of a silica fiber and the solution or the headspace. Analytes are not completely extracted from the matrix. Recovery depends on the partitioning of the analytes among the two or three phases present in the sampling vial.

Quantification is based on the determination of the sorbed amount of solute in the coating of the fiber [2,4]. SPME can be optimized by properly selecting the type of the fiber coating, the sampling time, the temperature of the extraction, and the ratio of liquid to headspace volume in case of headspace sampling [5].

A rapid and simple method was introduced for quantification of volatile aliphatic aldehydes in sunflower oil in our earlier works [6,7]. Headspace SPME sampling technique combined with ion trap GC–MS analysis was found to be satisfactory for detection and quantitation of volatile components with carbon chain up to C_{11} in vegetable oils. Use of

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library search can confirm the identity of certain compounds. Carryover from the SPME fiber has been eliminated by heating the fiber in the injection port of the gas chromatograph between two runs. Distribution constants of aliphatic aldehydes with different degrees of saturation were determined at fixed sampling parameters. Moreover, depletion of the analyte was examined by repeated extraction from the same vial as well.

The well known methods for the determination of volatile content of vegetable oils are the injection of an aliquot of the headspace over the oil [8], by purging all volatiles from the oil itself [9], or the purge and trap technique [10] when the volatiles are purged from the oil under mild conditions before injecting into the gas chromatograph. Applying the two former methods the oil being exposed to heat can be oxidized during the analysis, while the purge and trap technique is rather expensive, complex and needs long analysis time. Because of the quickness, the simplicity and the low cost SPME can be an advantageous sampling technique in the analysis of volatile compounds.

Principal component analysis (PCA) [11–13] is an important tool to analyze large data tables to extract additional information not otherwise assessable. The optimization conditions, the response factors characteristic to the apparatus and the equilibrium process of partition can be arranged easily in a matrix form. The various aldehydes are ordered in rows, whereas the columns correspond to the response factors at different sampling time, different temperature, ratio of headspace and bulk material volume, and type of analysis (e.g. immersion, etc.).

The first aim of present work was to study the influence of the size of fiber coating, of the sampling time, of the temperature and of the ratio of liquid to headspace volume on the efficiency of extraction of aliphatic aldehydes from sunflower oil and from water. As a second aim we seek regularities by subjecting the quantitative results to PCA. The measured aldehyde levels were expressed in ion counts which depend on the response factor of the detector and on the partition coefficients of the solutes (both types of characteristics have been determined previously [7]). This way, any influence of the recoveries could also be determined by PCA. To exclude any misinterpretation coming from the different response factors and various partition constants every parameter was optimized for each individual component. No tendency or comparison was studied in the series of the aldehydes.

2. Experimental

2.1. Materials

2-Heptenal, 2-octenal, 2-nonenal, 2-decenal, 2-undecenal, *trans,trans*-2,4-heptadienal, *trans,trans*-2,4-octadienal, *trans,trans*-2,4-nonadienal, *trans,trans*-2,4-decadienal and the specially refined sunflower oil [6] were obtained from Unilever, Vlaardingen, Netherlands. Heptanal, octanal and nonanal were Sigma products.

2.2. Conditions

Samples for SPME optimization were prepared by spiking 20 ng/μl of a mixture of all aldehydes into the sunflower oil and into distilled water. Individual solutions of 20 ng/μl heptanal and 2-undecenal in sunflower oil were prepared as well.

For SPME sampling 7 μm and 100 μm poly(dimethylsiloxane) fibers (Supelco) and 6 ml volume screw-cap vials with silicone septum covered by TFE liner were used. For headspace gas sampling by SPME the septum of the vial was pierced in the center to facilitate the insertion of the SPME needle. The vial was immersed into an ultrathermostate heated to the sorption temperature. Then the SPME needle was pushed into the septum surface and the fiber was depressed by the plunger. The end of the fiber was about 1 cm above the surface of the liquid phase. For immersion SPME experiments the vials were completely filled by aqueous solutions of aldehydes. After the sorption time the fiber was retracted into the needle and the holder was withdrawn followed by the insertion of the needle into the injector of the gas chromatograph. The fiber was extended by the plunger and the analysis program started. After 1 min desorption time at 220°C the fiber was retracted, then the needle was removed from the injection port.

For reducing the tailing effect [5,14] a narrow (0.75 mm I.D.) inlet liner was applied. The tailing of

peaks could be completely eliminated in case of fairly high boiling compounds. A remarkable reduction was achieved at low boiling analytes. After every run the SPME fiber was conditioned for 30 min at 220°C in the injector of the gas chromatograph followed by a blank analysis to exclude the memory effect of the fiber.

The analysis was performed by a Finnigan MAT GCQ GC–MS apparatus having a quadrupole ion-trap mass analyzer. The separation has been carried out on a 30 m long CP WAX 52CB (ChromPack) column with 0.25 mm I.D. and 0.25 μm film thickness. Column temperature setting was programmed from 40°C with 4°C/min increase rate up to 160°C (hold for 5 min), followed by a 20°C/min increase rate to 210°C (hold for 10 min). The carrier gas was helium with 35 cm/s constant linear velocity. Splitless injection was used.

Mass spectral detection was taken in electronimpact (EI^+) mode at 70 eV ionization energy both by *full scan* (in 10–650 amu mass range) and in *selected ion monitoring* (SIM) modes with 0.5 s/scan velocity and an acquisition treshold=0. The temperatures of the ion source and of the transfer line were 160°C and 220°C, respectively. Compounds were identified after detecting spectra by *full scan* mode. Peak areas were determined from single ion chromatograms of the most intensive ions of certain components (i.e. $m/z^+=81$ in case of dienals and 41 for the other aldehydes). Retention times of certain analytes were obtained from the proper full scan measurements. The detection limit was reduced by using SIM method [15] and a fairly articulated chromatogram could be obtained as it is demonstrated in Fig. 1.

2.3. Principles of PCA

In the course of defining principal components the original variables are transformed into new ones. The principal components are, in fact, linear combinations of the original variables. Their values are the component *scores*. The linear coefficients are called the component score coefficients. The linear coefficients of the inverse relation are the *loadings*, i.e. the correlation coefficients between the original variables and the principal components. The algorithms for PCA can be found in ref. [11]. The principal components are orthogonal (independent). Further on, they are ordered in such a way that the variance of the first principal component is the greatest, the variance of the second is smaller, and so on, whereas that of the last one is the smallest. The solution is achieved by an eigenvalue calculation.

The columns of data matrices are intercorrelated, i.e. the data are redundant. The method of PCA [11–13] makes use of the intercorrelations by starting from the correlation matrix of the variables, and it eliminates the redundancy from the data.

A basic assumption in the use of PCA is that the score and loading vectors corresponding to the largest eigenvalues contain the most useful information relating to a specific problem and that the remaining ones comprise mainly the noise, i.e. for a practical problem it is sufficient to retain only a few components accounting for a large percentage of the total variance [11].

3. Results and discussion

The sorbed masses of the aldehydes were compared after headspace SPME sampling in the case of sunflower oil and water matrices, and from aqueous solution by immersion SPME. The reproducibility of headspace sampling was found to be RSD=19%, calculated from 12 runs [7]. RSD means the relative standard deviation of the values of detected analyte level. The average error in SPME method [18] can be characterized by RSD=2.5–37%.

There were indications [16] that in case of multicomponent systems a competition can be observed for the active places of the coating of the SPME fiber. By increasing extraction time the higher-boiling compounds might displace the previously sorbed lower-boiling ones. The sorbed quantities of the low-boiling heptanal ($t_{ret}=10.75$ min) and the high-boiling 2-undecenal ($t_{ret}=29.33$ min) were determined from individual solutions and from aldehyde mixtures using sunflower oil matrix to make clear the existence of the mentioned displacing effect.

3.1. Effect of the size of the fiber

The molecular weight and the polarity of the analyte determine the type of the fiber coating used

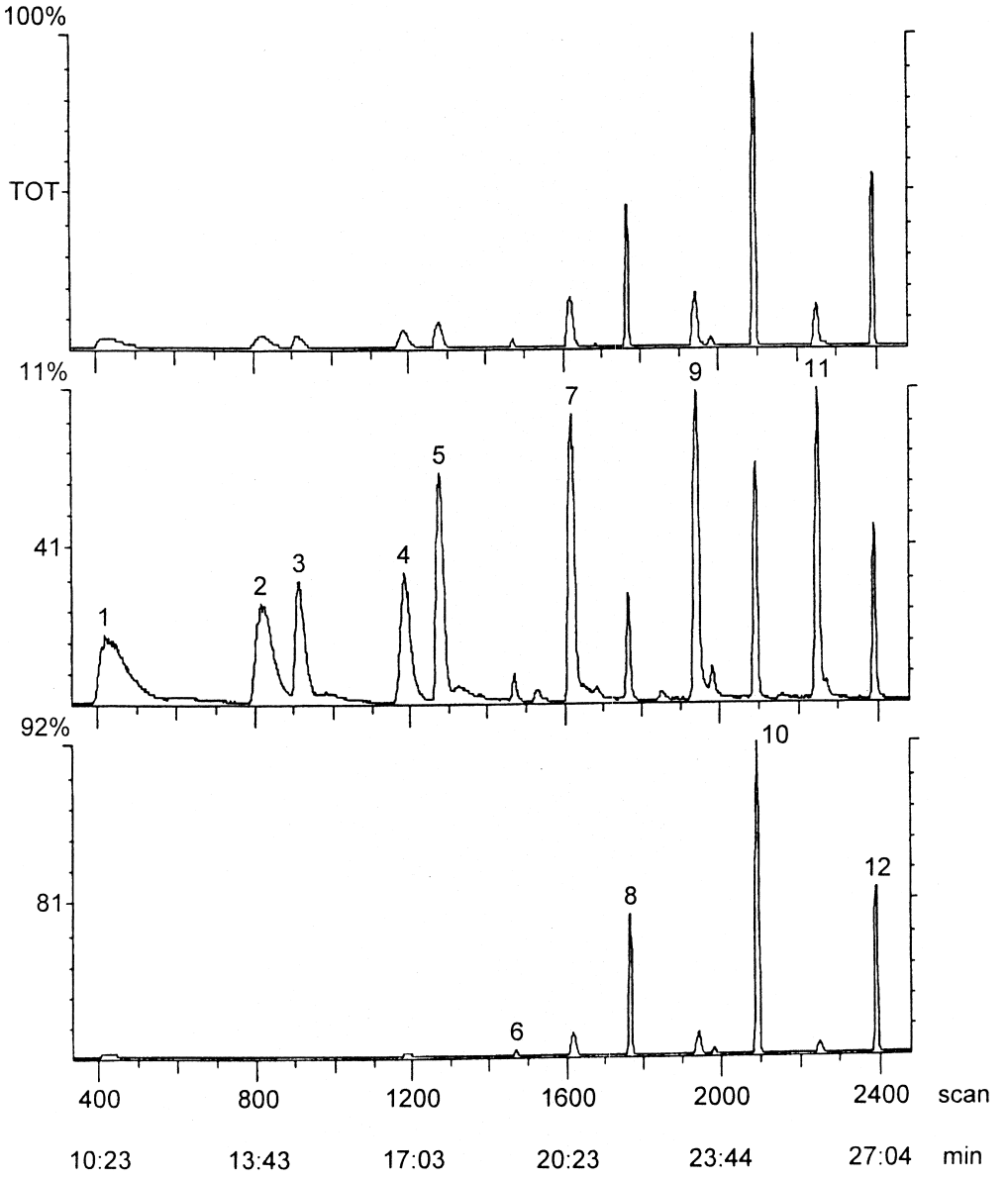

Fig. 1. Total ion chromatogram of aliphatic aldehydes by headspace SPME sampling from water matrix in selected ion monitoring mode. 1: heptanal, 2: octanal, 3: heptenal, 4: nonanal, 5: octenal, 6: heptadienal, 7: nonenal, 8: octadienal, 9: decenal, 10: nonadienal, 11: undecenal, 12: decadienal.

[5]. Poly(dimethylsiloxane) coating is recommended for analysis of medium polar compounds, while polyacrylate coated fiber is suggested to extract very polar analytes from polar matrix. Low molecular weight or volatile compounds usually require a 100 μm fiber coating. Larger molecular weight (or semivolatile) compounds can be more effectively extracted with a 7 μm coating. In our case both the molecular weights and the volatilities of the analytes are rather different, therefore the size of the fiber coating should be optimized. SPME sampling was performed using 7 μm and 100 μm poly(di-

Table 1
Sorbed masses of aldehydes (given in ion counts, 10^2) by headspace SPME sampling from sunflower oil with 7 and 100 μm poly(dimethylsiloxane) fibers at different solution to headspace ratios (s/h). Sampling time: 30 min, temperature: 40°C

	s/h=1.0		s/h=0.5		s/h=0.2	
	7 μm	100 μm	7 μm	100 μm	7 μm	100 μm
Heptanal	104	264	57	241	39	206
Octanal	69	106	45	107	30	105
Heptenal	48	304	45	275	41	271
Nonanal	116	175	97	150	82	116
Octenal	27	189	23	173	19	167
Heptadienal	139	1217	70	1124	66	1095
Nonenal	50	181	30	148	17	134
Octadienal	83	1246	58	1048	49	1041
Decenal	18	123	16	105	13	86
Nonadienal	81	1224	54	944	44	899
Undecenal	30	111	17	108	13	73
Decadienal	66	614	49	566	31	360

methylsiloxane) fibers. In Tables 1, 2 the sorbed amounts of the analytes (expressed in ion counts) were compared at different solution to headspace ratios and at different sampling times. The levels of the sorbed aldehydes were found to be higher in all cases when using the 100 μm poly(dimethylsiloxane) fiber.

It can be established that both the 7 μm and 100 μm poly(dimethylsiloxane) fibers can be recommended for analysis of the aldehydes studied but in former cases the sample capacity is reduced. Other conclusions were drawn from the determination of hydrocarbons in water [17]: the use of weaker (7 μm) coating was more efficient. No significant difference was found in recoveries by using various size fiber coatings in the extraction of organochlorine pesticides from water [18]. When the matrix is a non-polar lipid type material, distribution constants of the analytes are lower than in the case of an aqueous medium [19], and according to our experiences, thicker fiber coating seems to be necessary.

3.2. Effect of the ratio of liquid to headspace volume

The quantity of the sorbed mass of the analyte in

Table 2
Sorbed masses of aldehydes (given in ion counts, 10^2) by headspace SPME sampling from sunflower oil with 7 and 100 μm poly(dimethylsiloxane) fibers at different sampling times. Solution to headspace ratio: 1.0, extraction temperature: 40°C

	10 min		20 min		30 min		40 min	
	7 μm	100 μm	7 μm	100 μm	7 μm	100 μm	7 μm	100 μm
Heptanal	19	254	47	391	104	364	22	263
Octanal	18	114	31	180	69	106	49	109
Heptenal	15	334	27	398	48	304	23	308
Nonanal	26	158	42	218	116	175	36	195
Octenal	13	221	20	257	27	189	17	186
Heptadienal	41	155	57	1680	139	1217	58	963
Nonenal	9	195	13	245	50	181	6	168
Octadienal	28	1497	38	1665	83	1446	32	1020
Decenal	66	107	15	119	18	123	8	184
Nonadienal	27	1138	32	1157	81	1224	34	1291
Undecenal	20	98	27	106	30	111	28	217
Decadienal	19	432	27	599	66	614	20	899

the SPME fiber coating depends both on the volumes of the solution and of the headspace over the liquid [4]:

$$n = C_0V_1V_2K/(KV_1 + K_2V_3 + V_2) \quad (1)$$

where n means the sorbed mass, C_0 is the initial concentration of the analyte in the solution, V_1, V_2 and V_3 are the volumes of the coating, of the solution and of the headspace, respectively. K is composed from partition coefficients of the analyte between coating/headspace (K_1) and headspace/solution (K_2). That means $K=K_1K_2$.

As it can be seen in Table 1 the increase of the ratio of liquid to headspace volume slightly improves the efficiency of extraction with any size fiber coating. According to Eq. (1) an increase of the headspace volume (V_3) accompanied by a decrease of the solution volume (V_2) in a given system results in lower sorbed mass (n) on the fiber. The headspace volume was not reduced further because in case of $V_3 \ll V_2$, sampling from the headspace does not affect the amount sorbed by the coating [4]. The entire volume of sampling vials has not been increased because the efficiency of the extraction is not presumed to be enhanced if the relative volumes of liquid and headspace remain the same [5].

3.3. Effect of the sampling time

The influence of sampling time on the aldehyde level extracted by the fiber coating can be followed in Tables 2, 3. Equilibration time being linearly related to the partitioning coefficients [20] can be an important parameter for optimization of the SPME procedure. Components of a multicomponent mixture reach the equilibrium at different times [21] and the analytes having various sizes and boiling points may displace each other [16].

Regarding these systems 30 min sorption time was found to be optimal in all cases. In that time the major part of aldehydes have achieved their equilibria, and considerable desorption of the most volatile components has not been commenced yet. It can be seen in Table 2 that the desorption of certain analytes was much more expressive if 7 μm film coating was used.

The desorption of the low-boiling heptanal started as soon as 20 min, but the high-boiling 2-undecenal has not reached the equilibrium even at 40 min. The sorbed masses of both of these aldehydes were also determined when the SPME determination has been carried out from sunflower oil sample containing exclusively heptanal or 2-undecenal. The extracted quantity of heptanal was an order of magnitude higher in absence of competition for the active places of the SPME fiber, while there was no significant difference found in case of 2-undecenal.

3.4. Effect of the extraction temperature

Compared to other techniques of determination of

Table 3
Sorbed masses of aldehydes (given in ion counts 10^2) by headspace (HS) and immersion SPME sampling from water with 100 μm poly(dimethylsiloxane) fibers at different sampling times. Solution to headspace ratio: 1.0, the aqueous volume at immersion: 6 ml, extraction temperature: 40°C

	10 min		20 min		30 min		40 min	
	HS	Immersion	HS	Immersion	HS	Immersion	HS	Immersion
Heptanal	2955	2187	4531	4813	3237	5674	2106	4295
Octanal	7117	3678	8183	4200	7537	4680	6997	3671
Heptenal	3795	1903	3913	1221	4019	942	3926	815
Nonanal	7125	2217	7146	2631	8616	2134	9676	1191
Octenal	3968	2567	3957	2731	3887	2826	3253	2579
Heptadienal	6628	139	7143	147	8281	151	11 750	89
Nonenal	4624	2358	4803	2667	5778	2879	6945	2101
Octadienal	63 117	8517	63 668	9295	68 043	9406	59 068	8370
Decenal	5170	2162	6009	2529	6829	2890	7944	3045
Nonadienal	68 430	8741	74 480	9531	78 785	11 195	83 754	11 711
Undecenal	5280	1371	5639	1579	7463	1989	8323	2183
Decadienal	30 320	562	34 368	756	66 507	924	70 368	1533

Table 4
Sorbed masses of aldehydes (given in ion counts 10^2) by headspace SPME sampling from sunflower oil with 100 μm poly(dimethylsiloxane) fibers at different temperatures and sampling times. Solution to headspace ratio: 1.0

	40°C		50°C		60°C		70°C	
	10 min	30 min	10 min	30 min	10 min	30 min	10 min	30 min
Heptanal	254	364	315	278	368	181	403	96
Octanal	114	106	192	255	97	94	294	90
Heptenal	334	304	395	296	436	263	481	237
Nonanal	158	175	193	171	224	166	256	162
Octenal	221	189	289	184	389	179	418	175
Heptadienal	1549	1217	1662	1180	2081	115	2110	1101
Nonenal	195	181	236	175	271	169	309	165
Octadienal	1497	1446	1543	1410	1614	1372	1652	1343
Decenal	107	123	139	117	165	112	190	107
Nonadienal	1138	1224	1189	1188	1247	1154	1269	1124
Undecenal	98	111	101	106	113	103	119	99
Decadienal	432	614	486	590	512	555	539	524

volatile compounds SPME is considered to be a rapid method. However, at low sorption temperature the extraction can be the most time consuming part of the analysis. Distribution coefficients, especially Henry's constants are temperature dependent [22–24].

It is a common experience (including our results) in the study of the extraction conditions of different systems both by using immersion and headspace methods that the sorbed mass on the SPME fiber decreases by increasing the sampling temperature [21,25–27]. Reduced amounts of sorbed analytes have been measured in headspace SPME analysis of hydrocarbons, alcohols, ketones and esters [21] at higher than 15°C extraction temperature. The same tendency was observed during determination of BTEX fraction from water by immersion SPME [27] at 30 min sampling time. When the extraction time was 5 min the quantity of the sorbed mass increased at temperatures up to 45°C and decreased at higher temperatures.

The dependence of the sorbed mass of aldehydes in the fiber coating was determined in 40–70°C range of extraction temperature at 10 min and 30 min sampling times in case of headspace SPME analysis from sunflower oil, and at 30 min extraction by headspace immersion methods from aqueous solution (Tables 4, 5).

Table 5
Sorbed masses of aldehydes (given in ion counts, 10^2) by headspace (HS) and immersion SPME sampling from water with 100 μm poly(dimethylsiloxane) fibers at different temperatures. Solution to headspace ratio: 1.0, the aqueous volume at the immersion: 6 ml, extraction time is 30 min

	40°C		50°C		60°C		70°C	
	HS	Immersion	HS	Immersion	HS	Immersion	HS	Immersion
Heptanal	3237	5674	2786	5264	2478	4966	2170	4753
Octanal	7537	4680	7125	4313	6654	4059	6233	3897
Heptenal	4019	942	3521	911	3148	895	2899	876
Nonanal	8616	2134	8257	2090	7896	1854	7541	1460
Octenal	3887	2826	3562	2666	3255	2412	2877	2199
Heptadienal	8281	151	8110	136	7956	115	7902	100
Nonenal	5778	2879	5343	2587	4742	2357	3971	2012
Octadienal	68 043	9406	65 087	9113	60 032	8915	55 421	8610
Decenal	6829	2890	6525	2599	5754	2265	4963	2000
Nonadienal	78 785	11 195	74 625	10 583	71 327	10 013	67 892	9416
Undecenal	7463	1989	6825	1823	6516	1691	6378	1433
Decadienal	66 507	924	62 355	879	58 974	836	55 690	743

At lower extraction times the level of sorbed aldehydes was found to be higher at elevated temperatures. Opposite tendencies were observed at longer exposure times.

The extraction can be more efficient by applying longer sorption times at lower temperatures [25]. On the other hand, long sampling times are disadvantageous [16] in extraction of rather volatile compounds and make the entire analysis time too long. According to our results, and taking into consideration that by 10 min of extraction most of the analytes have not achieved the equilibrium yet, headspace SPME analysis can be found to be fairly efficient at 30 min sampling time at 40°C.

3.5. Effect of the media

The influence of the matrix can be followed by comparing similar data of Tables 1, 3. These tables contain the sorbed masses measured in ion counts. Since the response of the mass detector depends exclusively on the type of the analyte, the extractions have been carried out from different matrices containing *similar* concentration of aldehydes, so the actual ion counts measured for each compound may give information about the efficiency of the analysis.

It can be established that about an order of magnitude higher amount of analytes could be obtained from water than from sunflower oil. When halogenated volatiles were determined from food–water matrix [16] lower partitions of the analytes have been found with increasing food lipid content. The partitioning of the analytes between liquid and headspace can be described by Henry's law. Henry's constants strongly depend on the matrix material. When headspace SPME is applied to lipids the concentrations of volatile compounds in the headspace are typically lower than if they are present in water. Therefore the sorbed mass in the fiber coating must be reduced as well.

Regarding aldehydes which contain less than two double bonds no considerable difference was observed between immersion and headspace methods in case of SPME analysis of the same compounds from aqueous solution. Literature data [4] suggest that the concentration of analytes in the fiber coating does not change when the fiber is immersed either in liquid or in the headspace after the equilibrium is attained. The sorbed quantities on the fiber were found to be not the same but very close values in the two different sampling systems indicating that all components of the aldehyde mixture have not achieved the equilibrium completely. On the other hand, the displacing effect discussed earlier might be different in the two systems. Although dienals have also reached approximately the equilibrium after 30 min exposure time, their subtraction was found to be less efficient by immersion than by headspace. The extraction might be hindered by the interaction between the water and dienal molecules.

The sorbed mass is decreased by increasing the values of the partition coefficient (K_2) between the headspace and the solution (Eq. (1)). In the present case, when the ratio of the headspace to the solution was not higher than 5, and the largest value of $K_2 = 0.373$ for heptenal [7] the mentioned effect plays subordinate role.

By taking mass spectra in *full scan* mode 0.1–1 ng/μl of studied compounds could be detected in sunflower oil matrix [6]. Lower values belong to unsaturated, while higher ones to saturated aldehydes. Using SIM mode during the analysis the detection limit of the same aldehydes has been reduced to 50–500 pg/μl. In aqueous solution, due to the more efficient extraction, detection limits were found to be lower (5–50 pg/μl). The detection limit of dienals by immersion method is higher.

3.6. Principal component analysis

The results summarized in Tables 1–5 were subjected to PCA. The input matrix consisted of 26 columns differing in sampling time, in temperature, in the type of analysis (immersion in water, headspace above water, headspace above oil), and in ratio of headspace to liquid volume. The rows correspond to the eleven aldehydes, whereas the matrix elements were the response factors at the given analysis conditions and are expressed in total ion counts. The effect of the size of the fiber was not analyzed because of the triviality of the achievable outcome. The influence of the different response factors of aldehydes was included into PCA by giving the amounts of the analyzed compounds directly in ion counts.

First the correlation matrices were computed. Four

principal components explain more than 95% of the total variance. That is the input matrix can be represented by four new variables. All of the analysis conditions are similar to each other. The first principal component correlates better than 0.7 with the majority of the analysis conditions but not in experiment 10 (Table 6).

The second principal component differentiates between samples in oil and in water. Negative values are samples corresponding to oil analyses. Three well-defined clusters can be seen in addition to one outlier in Fig. 2.

The reason for the outlier is not well understood, it may derive from an experimental error or number 10 constitutes an extreme, the longest extraction time applied. Both clusters ''B'' and ''C'' belong to aqueous solutions, ''B'', however, corresponds to headspace experiments whereas ''C'' to immersion probes. Cluster ''A'' contains all the headspace-oil samples. The subgroups in each cluster cannot be rendered to analysis conditions unambiguously.

Similarly to analysis conditions the analytes embody similarities from the point of view of response factors under the conditions studied. Fig. 3 shows one main cluster and 4 outliers.

The outliers coincide with dienals, the sorption and response characteristics of which are very different from those of the normal chain aldehydes and aldehydes containing one double bond only.

4. Conclusions

The levels of sorbed aldehydes were found to be

Table 6
Unrotated factor loadings (correlation coefficients between the old variables (columns) and new variables (abstract factors)[a]

Number of variables (columns)	Factor 1	Factor 2	Factor 3	Factor 4
1	**0.85804**	−0.446178	−0.113867	−0.089334
2	**0.84747**	−0.464241	−0.124200	−0.089813
3	**0.78344**	−0.554795	−0.139586	−0.121546
4	**0.78260**	−0.554652	−0.147092	−0.117949
5	**0.85090**	−0.461800	−0.091752	−0.078304
6	**0.92681**	−0.300148	−0.020957	−0.037535
7	**0.92790**	−0.303969	−0.013238	−0.028008
8	**0.93133**	−0.292543	0.000696	−0.030082
9	**0.92583**	−0.301439	0.009378	−0.034761
10	0.33354	−0.159977	−0.371061	**0.838536**
11	**0.88074**	−0.419945	0.020105	−0.007503
12	**0.87752**	−0.415145	−0.098731	−0.056225
13	**0.91554**	0.285232	0.165460	0.045602
14	**0.75422**	0.527468	−0.222629	−0.151363
15	**0.91031**	0.294285	0.187216	0.056311
16	**0.71575**	0.565738	−0.222738	−0.267930
17	**0.83825**	0.231279	0.414054	0.171280
18	**0.84163**	0.213027	0.426888	0.148599
19	**0.84030**	0.212005	0.429883	0.152019
20	**0.83927**	0.208907	0.432484	0.155429
21	**0.70690**	0.582276	−0.198819	−0.277875
22	**0.76041**	0.490521	−0.214821	−0.299447
23	**0.62058**	0.408917	−0.556547	0.321150
24	**0.61738**	0.395769	−0.561495	0.332343
25	**0.81387**	0.210192	0.458107	0.192662
26	**0.75076**	0.566114	−0.108513	−0.195662
Explained variance	170.14593	40.198385	20.045925	10.416039
Proportion of total variance, %l	65.9	16.1	7.87	5.45

[a] Values larger than 0.7 are indicated in bold.

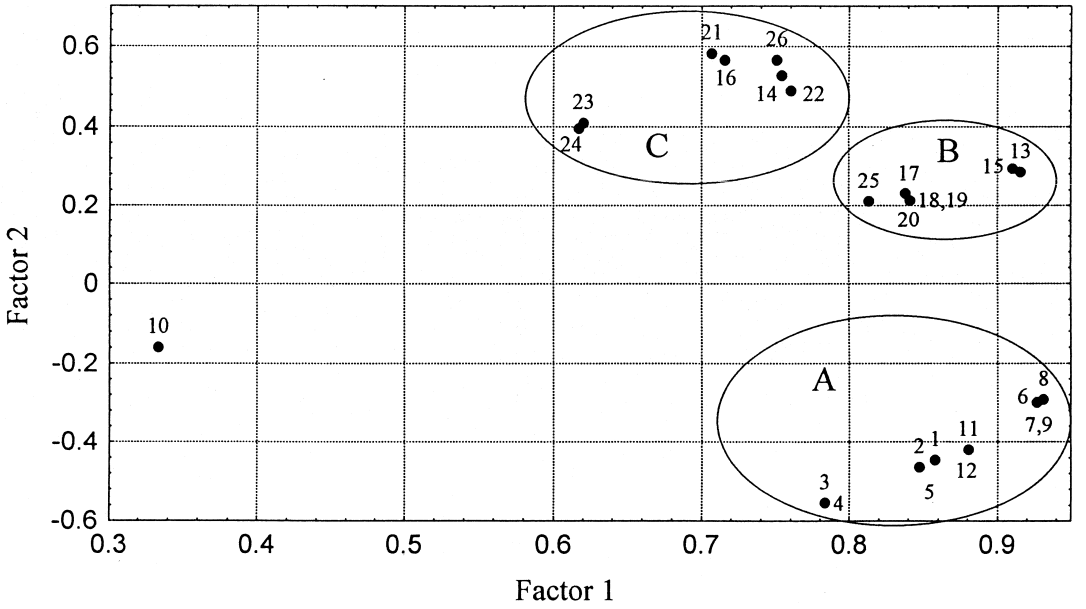

Fig. 2. Principal Component Analysis of data obtained in the analysis of aliphatic aldehydes by all studied circumstances I. Loadings. 1: headspace from oil 40°C 10 min, 2: headspace from oil 50°C 10 min, 3: headspace from oil 60°C 10 min, 4: headspace from oil 70°C 10 min, 5: headspace from oil 40°C 20 min, 6: headspace from oil 40°C 30 min, 7: headspace from oil 50°C 30 min, 8: headspace from oil 60°C 30 min, 9: headspace from oil 70°C 30 min, 10: headspace from oil 40°C 40 min, 11: headspace from oil 40°C 30 min s/h=0.5, 12: headspace from oil 40°C 30 min s/h=0.2, 13: headspace from water 40°C 10 min, 14: immersion from water 40°C 10 min, 15: headspace from water 40°C 20 min s, 16: immersion from water 40°C 20 min, 17: headspace from water 40°C 30 min, 18: headspace from water 50°C 30 min, 19: headspace from water 60°C 30 min, 20: headspace from water 70°C 30 min, 21: immersion from water 40°C 30 min, 22: immersion from water 50°C 30 min, 23: immersion from water 60°C 30 min, 24: immersion from water 70°C 30 min, 25: headspace from water40°C 40 min, 26: immersion from water 40°C 40 min.

higher when using 100 μm rather than 7 μm thick poly(dimethylsiloxane) coating on the fiber. Increasing the ratio of liquid to headspace volume more efficient extraction has been achieved by using any size fiber coating. Exposure time of 30 min at 40°C was found to be optimal. Under these conditions most of the aldehydes have already achieved equilibrium with the exception of a considerable desorption of the lower-boiling components. The desorption of higher-boiling analytes from 7 μm coating was much more significant than from thicker film. Much higher quantity of heptanal was extracted from oil containing exclusively this compound than from the aldehyde mixture. Similar effect was not observed in case of 2-undecenal.

The extraction of unsaturated and one double bond-containing aldehydes was much more efficient from water both by immersion of the fiber into the aqueous solution and into the headspace than by headspace SPME from sunflower oil. The headspace method was found to be more sensitive in water for dienals as well.

Aliphatic aldehydes with carbon chains up to C_{11} could be easily analyzed by SPME sampling technique combined with the ion trap GC-MS method. Using *selected ion monitoring* method 50–500 pg/μl detection limit has been attained in sunflower oil and 5–50 pg/μl in water.

Principal component analysis is able to classify analysis conditions for quantification and, similarly, to differentiate between aldehydes from the point of view of sorption and response characteristics.

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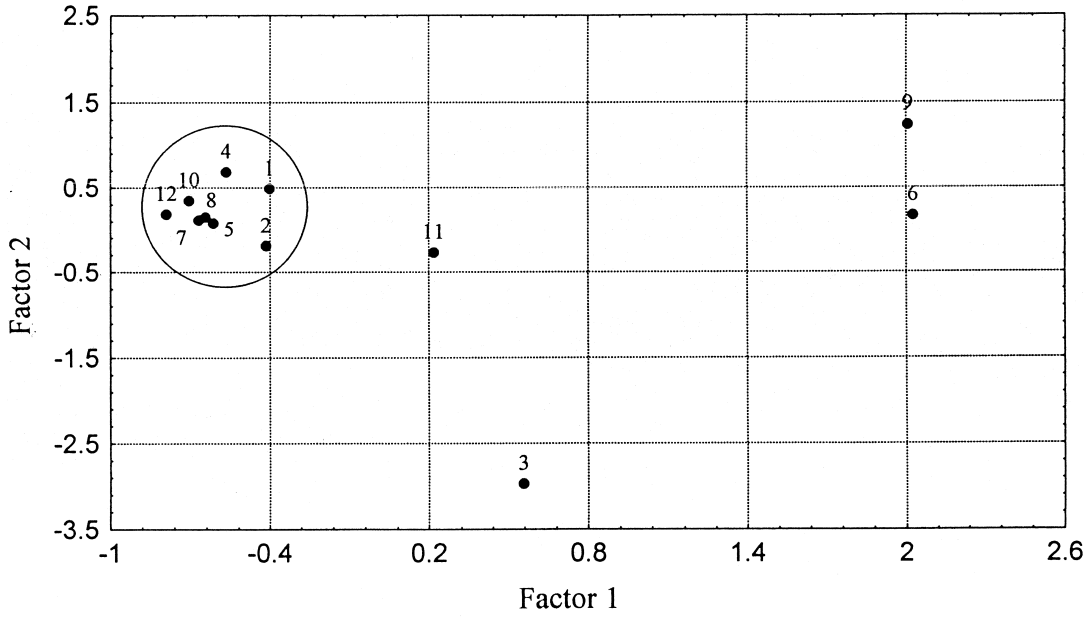

Fig. 3. Principal Component Analysis of data obtained in the analysis of aliphatic aldehydes by all studied circumstances II. Scores. 1: heptanal, 2: octanal, 3: heptenal, 4: nonanal, 5: octenal, 6: heptadienal, 7: nonenal, 8: octadienal, 9: decenal, 10: nonadienal, 11: undecenal, 12: decadienal.

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References

[1] R.P. Belardi, J. Pawliszyn, Water Pollut. Res. J. Canada 24 (1989) 179–191.
[2] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145–2148.
[3] D. Louch, S. Motlagh, J. Pawliszyn, Anal. Chem. 64 (1992) 1187–1199.
[4] Z. Zhang, J. Pawliszyn, Anal. Chem. 65 (1993) 1843–1852.
[5] Z.E. Penton, Adv. Chromatogr. 37 (1997) 205–235.
[6] Á. Keszler, K. Héberger, M. Gude, J. High Resolut. Chromatogr. 21 (1998) 368–370.
[7] Á. Keszler, K. Héberger, M. Gude, Chromatographia 47 (1998) 127–132.
[8] J.J. Langenfeld, S.B. Hawthorn, D.J. Miller, J. Chromatogr. A 740 (1996) 139–145.
[9] J.A. Fioriti, J. Am. Oil Chem. Soc. 54 (1977) 450–455.
[10] J.A. Singleton, H.A. Pattel, J. Am. Oil Chem. Soc. 57 (1980) 405–409.
[11] S. Wold, K. Esbensen, P. Geladi, Chemometrics, Intell. Lab. Systems 2 (1987) 37–52.
[12] K. Héberger, A. Lopata, J. Chem. Soc., Perkin Trans 2 (1995) 91–96.
[13] K. Héberger, Á. Keszler, M. Gude, Lipids 34 (1999) 83–92.
[14] D.M. Wyatt, J. Chromatogr. Sci. 25 (1987) 257–261.
[15] Á. Keszler, B. Kazinczy, L. Kótai, Fresenius J. Anal. Chem. 363 (1999) in press.
[16] K.G. Furton, J.R. Almirall, J. High Resolut. Chromatogr. 18 (1995) 625–629.
[17] J.J. Langenfeld, S.B. Hawthorn, D.J. Miller, Anal. Chem. 68 (1996) 144–155.
[18] R. Young, V. Lopez-Avila, W.F. Beckert, J. High Resolut. Chromatogr. 19 (1996) 247–256.
[19] B.D. Page, G. Lacroix, J. Chromatogr. 648 (1993) 199–211.
[20] J. Dewulf, H. Van Langenhove, M. Everaert, J. Chromatogr. A 761 (1979) 205–217.
[21] R.J. Bartelt, Anal. Chem. 69 (1998) 364–372.
[22] G.A. Robbins, S. Wang, D.J. Stuart, Anal. Chem. 65 (1993) 3113–3118.
[23] J.C. Hutter, G.F. Vandergrift, N. Luis, D.H. Redfield, AIChE J. 40 (1994) 166–177.
[24] T.K. Poddar, K.K. Sirkar, J. Chem. Eng. Data 41 (1996) 1329–1332.
[25] B. Schäfer, P. Henning, W. Engewald, J. High Resolut. Chromatogr. 18 (1995) 587–592.
[26] D. Gorlo, L. Wolska, J. Namiesnik, International Symposium on Advances in Chromatography and Electrophoresis Szeged, Hungary, 1998, Abstract 26.
[27] C.L. Arthur, L.M. Killam, K.D. Buchholz, J. Pawliszyn, J.R. Berg, Anal. Chem. 64 (1992) 1960–1966.