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Volatile Fraction of Milk: Comparison between Purge and Trap and Solid Phase Microextraction Techniques

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The aim of this research was to validate the results obtained previously by purge and trap (PT) and to investigate the ability of solid phase microextraction (SPME), a more rapid and less expensive technique, to discriminate drinking milk subjected to different heat treatments (i.e., pasteurization, ultrahigh temperature, "in-bottle" sterilization) and produced at different factories. The data obtained by both methods were processed by multivariate statistical analysis. PT and SPME showed comparable repeatability, although with different performances for the yield of extraction, and allowed the three milk categories to be distinguished. Within the chemical class of methyl ketones, 2-heptanone was found to be the most discriminating compound, and the possibility of using the concentration of this volatile as a marker for heat treatment was investigated.

KEYWORDS: SPME; purge and trap; flavor; drinking milk; heat treatment

INTRODUCTION

To improve the knowledge of compounds responsible for milk flavor, the volatile fraction has been widely studied by several authors by applying different extraction techniques (*1*−*5*). Volatile compounds were found to be modified both by the technological heat treatment adopted for the production of drinking milk and during its shelf life (*6*−*20*).

Vacuum distillation followed by solvent extraction, purge and trap (PT), and, more recently, solid phase microextraction (SPME) are the most widely applied techniques to isolate milk flavor. The evolution of these techniques is intended to reduce the time of analysis, the sample manipulation, and, consequently, the formation of artifacts. Both PT and SPME analyze the headspace composition, although the former allows only a dynamic extraction to be carried out.

Several examples of applications of PT to milk samples are available in the literature (*5*, *20*−*24*). The possibility of using SPME in the evaluation of milk volatiles has been investigated particularly by Marsili (*25*−*27*), who also made a comparison between this technique and PT analysis. SPME showed a higher precision in detecting off-flavors due to lipid oxidation than the PT technique and, at the same time, was less expensive and less influenced by the presence of artifacts. Van Aardt (*28*) verified the effectiveness of recovery of acetaldehyde in milk, flavored milk, and spring water.

As far as a comparison between SPME and PT is concerned, Elmore et al. (*29*) studied the flavor composition of cola; both techniques showed comparable reproducibility, but PT appeared to be a more sensitive technique, especially when trace analysis was performed.

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In our previous research (*20*), the PT technique, applied to evaluate the volatile fraction of drinking milk, was shown to be able to discriminate drinking milks subjected to different heat treatments. The aim of this research was to validate the results obtained by PT and to investigate the ability of SPME, which is a more rapid and less expensive technique, to perform the same type of discrimination. Moreover, it was investigated whether the concentration of a volatile substance may be used as a marker for the severity of heat treatment.

MATERIALS AND METHODS

Sampling. Thirty-eight samples of whole drinking milk produced at different factories were collected on the market. They belonged to four different categories on the basis of the severity of heat treatment: "high-quality pasteurized" (8 samples), "fresh pasteurized" (9 samples), ultra-high temperature (UHT; 16 samples), and "in-bottle-sterilized" milk (5 samples).

Different categories of drinking milk are defined by the Italian legislation as follows.

"High-quality pasteurized" milk is subjected to only one pasteurization treatment (at least 71.7 °C for 15 s) and has both a soluble whey protein concentration >15.5% (expressed on the total protein content) and a positive reaction to peroxidase enzyme. This type of milk should be stored at a temperature of 1−6 °C for no longer than 4 days.

"Fresh pasteurized" milk is subjected to only one pasteurization treatment and has both a soluble whey protein concentration >14% (expressed on the total protein content) and a positive reaction to peroxidase enzyme. This type of milk should be stored at a temperature of 1−6 °C for no longer than 4 days.

"UHT" milk is subjected to ultrahigh-temperature treatment (at least 135 °C for 1 s) followed by aseptic packaging. Shelf life should not exceed 90 days at room temperature.

"In-bottle-sterilized" milk is subjected to high-temperature treatment (e.g., 120 °C for 30 min) after packaging. Shelf life should not exceed 180 days at room temperature.

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Table 1. Volatile Compounds Obtained by Purge and Trap Technique (Micrograms per Kilogram)

	pasteurized milk[a]			UHT milk[a]			in-bottle-sterilized milk[a]		
compound	mean	SD	P1	mean	SD	U1	mean	SD	S1
acetone	166.9	80.3	158.9	35.9	13.9	30.2	224.6	35.9	227.8
2-butanone	81.9	38.1	29.2	8.2	2.7	5.8	84.4	19.5	64.4
3-methylbutanal	0.0	0.0	0.0	0.5	0.4	0.2	0.9	0.5	1.4
2-pentanone	3.1	1.7	0.5	3.9	1.5	4.8	48.1	4.3	35.4
pentanal	1.8	0.3	1.4	2.3	1.9	1.0	4.8	3.3	1.7
dimethyl disulfide	0.0	0.0	0.0	1.5	1.2	0.3	1.5	1.1	0.4
toluene	2.9	1.1	4.1	3.4	2.5	2.4	8.6	4.3	7.9
hexanal	3.8	0.8	3.2	2.6	0.6	2.7	3.6	0.7	3.5
2-heptanone	2.6	1.1	2.7	9.1	1.2	10.5	64.5	9.1	52.0
heptanal	2.4	1.6	1.7	2.1	1.0	1.9	2.5	1.1	2.4
limonene	4.1	3.7	1.6	6.6	4.6	14.0	3.3	3.7	4.7

[a] Mean and SD are derived from Contarini et al. (*20*).

Table 2. Volatile Compounds Obtained by Solid Phase Microextraction Technique (Micrograms per Kilogram)

		pasteurized milk (16)[a]			UHT milk (15)			in-bottle-sterilized milk (4)	
no.	compound		mean	SD		mean	SD	mean	SD
1	dimethyl sulfide	[3][b]	1.2	0.7		0.0	0.0	3.3	3.0
2	acetone		33.8	10.0		20.2	15.6	55.0	17.3
3	tetrahydrofuran	[9]	3.9	1.5	[5]	1.6	2.4	2.2	1.6
4	2-butanone		13.9	13.5		5.7	7.0	13.8	3.3
5	2-pentanone		0.0	0.0		9.4	6.7	44.5	10.4
6	toluene		0.0	0.0		0.0	0.0	3.7	2.0
7	2-hexanone		0.0	0.0		0.0	0.0	6.4	4.4
8	2-heptanone	[2]	10.4	8.3		67.5	50.7	253.0	57.6
9	2-nonanone	[2]	2.5	0.4		16.7	12.9	62.6	16.6
10	benzaldehyde		0.0	0.0	[2]	0.2	0.6	4.9	1.4
11	2-undecanone		0.0	0.0		4.0	3.0	16.3	3.5

[a] Numbers in parentheses indicate the number of samples for each group [b] Numbers in brackets indicate number of samples in which the compound was detected.

Thirty-five milk samples were analyzed by SPME, and three samples were analyzed by the PT technique (one fresh pasteurized, one UHT, and one in-bottle-sterilized milk). Pasteurized milk samples were analyzed 2 days before their expiration date and UHT and in-bottle-sterilized samples 70 and 150 days before their expiration dates, respectively. Before analyses, pasteurized milk was stored at 4 °C, and UHT and in-bottle-sterilized milks were stored at room temperature.

Purge and Trap. Volatile compounds were extracted and analyzed by GC-FID, following the procedure reported by Contarini et al. (*20*).

Solid Phase Microextraction. A divinylbenzene/Carboxen/polydimethylsiloxane, 50/30 μm, 2 cm length fiber was used. Fifteen grams of milk sample was weighed in a 20 mL crimp-top vial (23 × 75 mm, Chrompack, Middelburg, The Netherlands), supplemented with 1 mL of aqueous solution of the internal standard methyl butanoate (0.5 mg/L, Aldrich Chemical Co., Milwaukee, WI). A microstirring bar was placed into the vial, which was sealed with an aluminum cap provided with a needle-pierceable septum. The sample was allowed to equilibrate to 45 °C in a thermostatic bath for 5 min; extraction was carried out for 30 min under stirring. Samples were analyzed in duplicate. The fiber was conditioned at 270 °C for 30 min in a GC split/splitless injector before analysis.

Gas chromatographic analysis of volatile compounds adsorbed on the SPME fiber was carried out with an HP INNOWAX capillary column (cross-linked polyethylene glycol, Agilent, Avondale, PA), 60 m length, 0.32 mm internal diameter, 0.5 μm film thickness. A Hewlett-Packard 5890 series II gas chromatograph equipped with a Hewlett-Packard 5989A mass spectrometer was used. To achieve sharper peaks, the split/splitless injector was provided with a 0.75 mm i.d. inlet liner (Supelco, Bellefonte, PA). During the injection phase, splitless mode was adopted and the injector temperature was held at 270 °C for 3 min. The following gas chromatographic conditions were used: thermal desorption of volatile compounds was carried out by keeping the SPME fiber in the split/splitless injector at 270 °C for 3 min; oven temperature was held at 40 °C for 8 min, programmed to 220 °C at a rate of 4 °C/min, and held at 220 °C for 20 min. Helium was used as carrier gas at a flow rate of 1.0 mL/min. MS temperatures adopted were as follows: interface, 220 °C; source, 200 °C; quadrupole, 100 °C; acquisition was performed in electron impact (EI) mode (70 eV) by 1.6 scans/s, and the mass range used was m/z 35−270.

Peak identification was performed by comparison with mass spectra of the Wiley library (*30*). The identification of the compounds was confirmed by the comparison of both the retention times and mass spectra of authentic standards analyzed under the same conditions. Authentic standards of acetone, 2-butanone, 3-methylbutanal, 2-pentanone, pentanal, dimethyl disulfide, toluene, hexanal, 2-heptanone, heptanal, limonene, tetrahydrofuran, dimethyl sulfide, benzaldehyde, 2-nonanone, and 2-undecanone were obtained from Aldrich (Milwaukee, WI).

Quantitative results, expressed as micrograms per kilogram, were obtained by comparison with the area of internal standard.

Statistical Analysis. Data for volatile compounds were subjected to multivariate statistical analysis by using the PARVUS package (*31*). The 43 milk samples (objects) and 11 volatile compounds (variables) obtained from the PT analysis in the previous work (*20*) were considered as an evaluation set, and the 3 samples analyzed in this research were introduced as a test set (**Table 1**). Statistical processing of the data obtained from SPME analysis was performed on 35 milk samples (objects) and 9 volatile compounds (variables), as reported in **Table 2**.

These data sets were subjected to the following statistical analyses.

Data Standardization by Autoscaling (32). Autoscaling was applied to all data in order to consider all variables independently of their different numerical values. Hence, all variables had the same weight because they had a mean = 0 and unitary variance.

Principal Component Analysis (PCA) (32). PCA is an exploratory data analysis, which, through the calculation of linear combinations of original variables, allows the number of dimensions to be considerably reduced while maintaining most of the information (expressed as percent variance) of the data set.

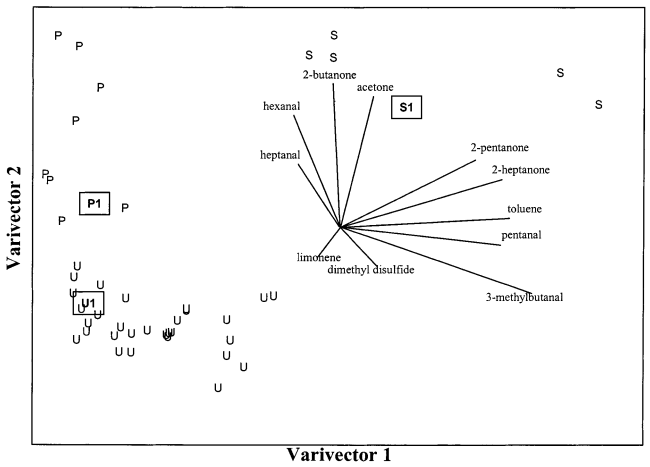

Figure 1. PCA biplot of 11 volatile compounds (variables) and 46 milk samples (objects) obtained by PT: (P, U, S) pasteurized, UHT, and in-bottle-sterilized milk from Contarini et al. (*20*), respectively; (P1, U1, S1) pasteurized, UHT, and in-bottle-sterilized milk analyzed to validate the model.

RESULT AND DISCUSSION

Demonstration of the Effectiveness of the Purge and Trap Technique. Three milk samples (P1, U1, and S1) were analyzed by the PT technique, under the same experimental conditions as those reported in our previous work (*20*). **Table 1** shows the data for mean and standard deviation (SD) obtained from our previous research and results from new milk samples. It is worth noting that these results were in good agreement with the range observed previously for the three different heat treatments.

To validate the multivariate statistical model (**Figure 1**), the old data were used as an evaluation set, whereas the results for the same 11 compounds obtained from the new milk samples were introduced as a test set (i.e., their values did not contribute to the calculation of the model). The three new samples (in squares) were placed together with those reflecting the same heat treatment category. This result appeared to be very satisfactory. Also, it showed that the procedure was well standardized, that is, applicable by different operators at different times, and the statistical model was also reliable for milk samples produced from different factories.

Performances of Solid Phase Microextraction. To verify whether the SPME technique may be applied to the analysis of milk volatile compounds, some preliminary experiments were carried out to test suitable parameters for extraction. A sample amount of 15 g and an extraction time of 30 min were chosen. One milliliter of methyl butanoate (0.5 μg) in distilled water was added as an internal standard (the same amount as for PT analysis).

Figure 2 shows an example of GC-MS profiles of pasteurized, UHT, and in-bottle-sterilized milk samples. Important differences were found between the samples. Eleven volatile compounds were identified (see **Table 2** for a list of compounds numbered), and most of them belonged to the chemical class of ketones. Within these compounds, those having a higher molecular weight (i.e., from 2-pentanone to 2-undecanone) showed an increase directly correlated to the severity of heat treatment. This behavior has also been observed by other authors (*10*−*11*, *13*, *33*) even applying different techniques.

The quantitative results obtained by SPME were submitted to PCA analysis. It should be noted that these values were calculated without any correction factor for the internal standard; as a consequence, they did not represent an absolute concentration, but they may be reasonably suitable for an internal comparison.

Figure 3 shows the biplot of the first and second eigenvectors (81% of the total variance explained) of the 35 samples (objects) and 9 compounds (variables). Due to their absence in pasteurized and UHT milks, toluene and 2-hexanone were excluded from the data set. Along the axis of the first eigenvector, a separation between UHT (U) and in-bottle-sterilized milks (S) can be observed. This separation in mainly due to the contribution of the variables having a high loading on this eigenvector (2-pentanone, 2-heptanone, 2-nonanone, and 2-undecanone). The separation between UHT and pasteurized milks (P and HP) resulted from the contribution of both the first and second eigenvectors. This suggested that the variables having a significant loading on the second eigenvector (acetone and 2-butanone) also played an important role in discriminating the above-mentioned heat treatments. No differences were detected between "high-quality" (HP) and "fresh" (P) pasteurized milks, that is, within the pasteurized category.

The groups of both UHT and in-bottle-sterilized milk samples appeared to be more scattered than those obtained by the PT technique (**Figure 1**). The main reason for this difference may be the origin of the milk samples. In this experimental work, different factories (i.e., different technological processes and, in particular, different qualities and sources of raw material) were used, whereas only one producer was used in the previous work.

Table 2 shows the quantitative data obtained by SPME analysis. Individual mean and standard deviation were calculated by taking into account only the samples in which the compound was detected. The values obtained, particularly for pasteurized milk, seemed to indicate a smaller sensitivity of SPME with respect to PT (**Table 1**). A more detailed investigation of individual compounds allowed some interesting observations to be drawn. **Figure 4** shows the mean values for ketones of in-bottle-sterilized milk, obtained by both SPME and PT.

It is worth noting that the yield of extraction by the two techniques was dependent upon the molecular weight of compounds. The PT technique was shown to be able to better extract the compounds having a smaller weight (acetone and 2-butanone). Conversely, the SPME technique, tested with a three-phase fiber (divinylbenzene/Carboxen/polydimethylsiloxane) using a polar capillary column, provided better recovery of those compounds having a higher carbon number (2-heptanone, 2-nonanone, and 2-undecanone). Both techniques seemed to have comparable recovery of 2-pentanone. The same behavior was also observed for mean values for pasteurized and UHT milk.

Performances of SPME were also evaluated by calculating repeatability on six replicates of the same milk sample (**Table 3**). SPME technique showed coefficients of variation of 5−31%; this result was comparable with that obtained by the PT technique (*20*). Similar conclusions on the precision of both methods were reported by Marsili (*26*) and Elmore et al. (*29*) in research on volatile compounds of milk and a cola-flavored beverage, respectively.

Suitability of 2-Heptanone as a Heat Treatment Marker. Among the different volatile compounds detected by both techniques, methyl ketones seemed to have the highest correlation to the severity of heat treatment on drinking milk. A preliminary evaluation of the concentration of these compounds, detected by both PT and SPME, in the different milk categories allowed 2-heptanone to be selected as a possible discriminating

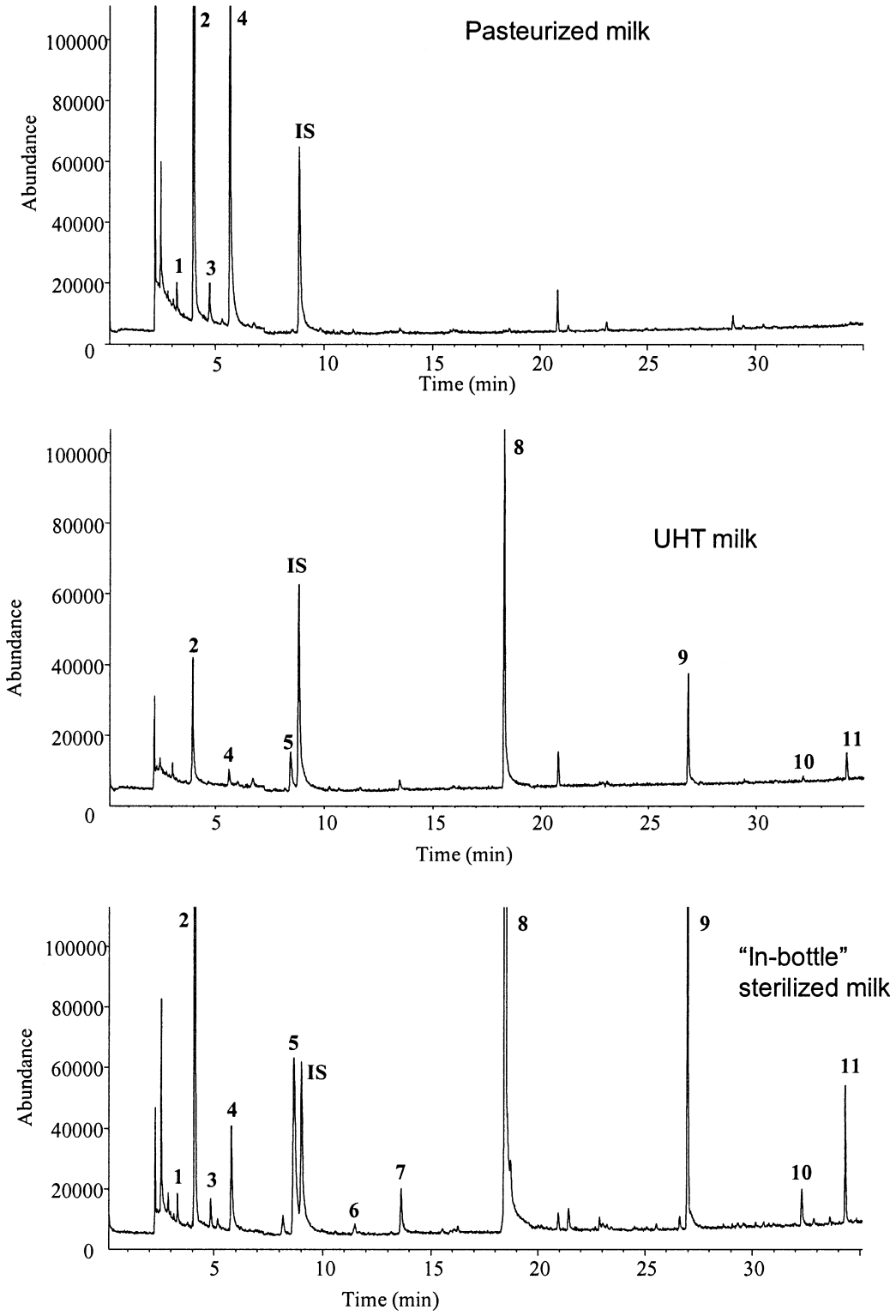

Figure 2. GC-MS profiles for the three milk categories obtained by SPME technique (numbering is the same as in **Table 2**).

parameter. This compound derives from the decarboxylation of a β-ketoacid with eight carbon atoms, naturally biosynthesized in the mammary gland (*10*).

Table 4 shows the ranges of 2-heptanone concentration determined by both PT and SPME. The values reported for the PT technique were taken from our previous work (*20*) and updated with the three milk samples analyzed in this research. The concentration of this compound varied within three well-separated ranges according to the different heat treatments applied.

As reported above, the two techniques resulted in different yields of extraction and, consequently, provided different ranges for each milk category. Nevertheless, a discrimination between milk categories was obtained. Even when the uncertainty of the measurement (CV% calculated for the repeatability of 2-heptanone) was applied to the limits observed for each category, a

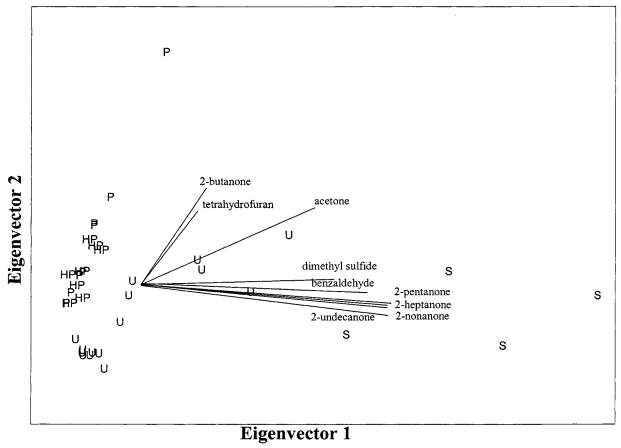

Figure 3. PCA biplot for 9 volatile compounds (variables) and 35 milk samples (objects) obtained by SPME: (P, U, S) pasteurized, UHT, and in-bottle-sterilized milk, respectively.

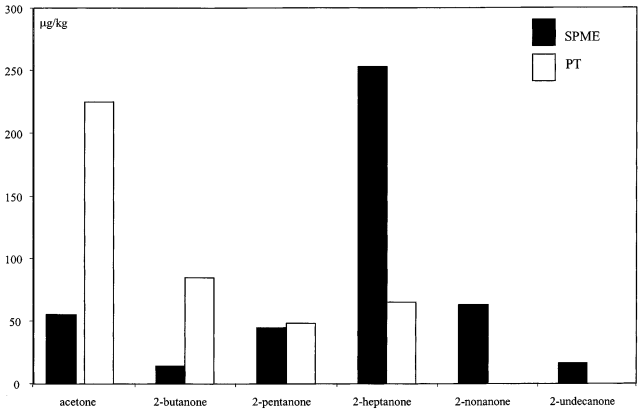

Figure 4. Mean values for the concentration of ketones in in-bottle-sterilized milk analyzed by both PT and SPME.

Table 3. Results from Six Replicates of Solid Phase Microextraction Analysis on a Sample of In-Bottle-Sterilized Milk

compound	mean (μg/kg)	SD	CV%
dimethyl sulfide	7.7	2.4	31.3
acetone	43.8	6.9	15.7
tetrahydrofuran	3.4	0.5	14.9
2-butanone	13.8	1.4	9.9
2-pentanone	39.7	2.4	6.1
toluene	6.1	0.5	8.4
2-hexanone	7.9	0.4	5.4
2-heptanone	272.4	25.0	9.2
2-nonanone	67.8	11.4	16.7
benzaldehyde	3.9	1.1	28.9
2-undecanone	17.4	3.4	19.3

satisfactory classification of milk subjected to different heat treatments was achieved. As a consequence, the concentration of 2-heptanone, which is currently only calculated by comparison with the area of the internal standard, seemed to be a suitable marker for heat treatment. To this end, new investigations on the SPME evaluation of the real concentration of this compound in milk, together with the other methyl ketones, and the use of the FID instead of the MS detector are being carried out.

Development and standardization of an analytical procedure based on the extraction of the volatile fraction by SPME, GC-FID analysis, and quantification of only one compound may result in a simple method for routine applications in the dairy field. This type of evaluation may be used as a first screening to control milk heat treatment, thus reducing the number of specific determinations (e.g., lactulose and furosine), which are quite expensive and time-consuming and often require specific instrumentation.

Table 4. Ranges of 2-Heptanone Concentration (Micrograms per Kilogram) for the Three Milk Categories

	pasteurized milk			UHT milk			in-bottle-sterilized milk		
method	no. of samples	min	max	no. of samples	min	max	no. of samples	min	max
PT	9	1.4	5.0	31	6.4	11.7	6	52.0	80.7
SPME	16	0.0	16.3	15	28.7	169.0	4	203.5	325.8

	min − CV%[a]	max + CV%	min − CV%	max + CV%	min − CV%	max + CV%
PT	1.3	5.5	5.8	12.9	46.8	88.7
SPME	0.0	17.8	26.1	184.2	185.2	358.4

[a] CV% = 10.0 for PT (see ref *20*); CV% = 9.2 for SPME (see **Table 3**).

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