ELSEVIER

Food Chemistry 71 (2000) 407–415

Food Chemistry

www.elsevier.com/locate/foodchem

Relationships between the volatile compounds evaluated by solid phase microextraction and the thermal treatment of tomato juice: optimization of the blanching parameters

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Received 4 January 2000; received in revised form 27 April 2000; accepted 31 May 2000

Abstract

Tomato juice contains volatile compounds that are originally detected in fruit, such as terpenes, and others that are originated during processing by lipoxygenase activity, carotenoid co-oxidation and Maillard reaction that can be activated during the thermal treatments. This paper reports the analysis of the volatile compounds of tomato juice sampled by solid phase microextraction (SPME) and the optimization of the blanching parameters in tomato juice, using the volatile compounds as markers. One hundred and ninety volatile compounds, including ketones, aldehydes, alcohols, esters, ethers, hydrocarbons, sulfur, nitrogen and oxygen compounds, phenols, oxygen-containing heterocyclic compounds, free acids and lactones, were identified or tentatively identified by the GC–MS technique. The thermal treatment mainly modifies saturated and unsaturated C_6 alcohols and aldehydes, esters, ketones and carotenoid derivatives. The optimal conditions for the blanching, selected by response surface modelling (RSM), were 67°C for 24 min and 86°C for 3.5 min for the *cold break* and the *hot break* treatments, respectively.

Keywords: Volatile compounds; Thermal treatment; Solid phase microextraction (SPME); Tomato juice

1. Introduction

The volatile compounds present in fresh and processed tomato are included in various chemical classes such as ketones, aldehydes, alcohols, esters, ethers, hydrocarbons, sulfur, nitrogen and oxygen compounds, phenols, oxygen-containing heterocyclic compounds, free acids and lactones (Baldwin, Nisperos-Carriedo, Baker & Scott, 1991; Buttery, Teranishi & Ling, 1987; Buttery, Teranishi, Ling & Turnbaugh, 1990; Buttery, Teranishi, Flath & Ling, 1990; Linforth. Savary, Pattenden & Taylor, 1994; Petrò-Turza, 1986–1987; Porretta & Ghizzoni, 1994).

Different methods, such as distillation, solvent extraction, head-space analysis and the solid phase microextraction (SPME) have been proposed to analyse volatile compounds in foods (Bertuccioli, 1980; Montedoro, 1985; Montedoro, Bertuccioli & Anichini, 1978; Zhang & Pawliszyn, 1993). The SPME is a relatively new method that can be used to evaluate the volatile compounds present in the vapour and/or in the liquid phase of solid and liquid foods (Servili, Selvaggini, Begliomini & Montedoro, 1998; Zhang & Pawliszyn, 1993).

During processing the endogenous enzymes catalyze the formation of important compounds of tomato flavour. In fact saturated and unsaturated C_6 and C_9 alcohols and aldehydes, that are impact compounds of fresh tomato, are originated by lipoxygenase activity, while terpene and carotenoid derivatives can be released from odourless glycosidic compounds by glycosidase activities (Begliomini, Montedoro, Servili, Pertuccioli & Federici, 1995; Buttery, Takeoka, Teranishi & Ling, 1990; Charron, Cantliffe & Heath, 1995; Marlatt, Ho & Chien, 1992). The tomato processing includes thermal treatments applied to inactivate enzymes (blanching) or to stabilize the product (sterilization) that cause changes in sensory and nutritional characteristics of tomato derivatives due to co-oxidation reactions of carotenoids and Maillard

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0308-8146/00/$ - see front matter
PII: S0308-8146(00)00187-4

reaction (Jiang & Ooraikul, 1989; McDonald, McCollum & Baldwin, 1996; Rouseff & Leahy, 1995; Schreier, Drawert & Bhiwapurkar, 1979).

The aim of this work is the optimization of the blanching thermal treatment parameters of tomato juice, using as markers the volatile compounds evaluated by SPME.

2. Materials and methods

2.1. Materials

Tomato samples (cultivar FM 6203) were grown in experimental fields of Perugia Agricultural University (Perugia, Italy) during 1996 and 1997. One hundred grams of tomato fruit were homogenized for 60 s at 25°C using an Ultra-Turrax T 25 omogenizer (IKA Labortechnik, Staufen, Germany), the homogenized juice was stirred for 15 min at 25°C to activate endogenous enzymes, then 100 ml of a saturated solution of $CaCl_2$ (1:1 v/v) were added and the mixture was used to evaluate volatile compounds as reported below.

Authentic reference chemical compounds were obtained from Fluka (Milan, Italy) and Aldrich (Milan, Italy).

2.2. Instrumental analysis

2.2.1. Solid phase microextraction

Five grams of tomato juice were put in a 20 ml vial and thermostated for 15 min at 29°C; a SPME fibre (65 μm Carbowax/divinylbenzene) (Supelco, Inc., Bellefonte, PA, USA) was exposed to the sample head-space for sampling the volatile compounds for 27 min at the above mentioned temperature (Servili et al., 1998).

The volatile compounds were desorbed by inserting the fibre into the GC injector set at 250°C in splitless mode using a splitless inlet liner of 0.75 mm ID for 10 min.

The peak areas of the chemical substances analyzed in triplicate on the same sample showed a coefficient of variation of 15% or lower.

All the SPME operations were automated using a Varian 8200 CX AutoSampler (Varian, Walnut Creek, CA, USA).

2.2.2. GC–MS analysis

A GC Varian 3600 equipped with a split/splitless injector coupled with a mass spectrometer Varian Saturn 3 (Varian, Walnut Creek, CA, USA) was used. A fused-silica capillary column DB-Wax, 50 m, 0.32 mm ID, 1 μm film thickness (J & W Scientific, Folsom, CA, USA) was employed. The column was operated with helium at a pressure of 15 psi with a flow rate of 2.2 ml/min and a linear velocity of 30.7 cm/s at 35°C.

The GC oven heating was started at 35°C, this temperature was maintained for 8 min, then increased to 45°C at a rate of 1.5°C/min, increased to 150°C at a rate of 3°C/min, increased to 180°C at a rate of 4°C/min, increased to 210°C at a rate of 3.6°C/min where it was held for 14.51 min; the total time of analysis was 80 min. The injector was always maintained at 250°C. The temperature of the transfer line was fixed to 220°C.

The mass spectrometer was operated in the electron ionization (EI) mode at an ionization voltage of 70 eV in the mass range of 10–350 a.m.u. at a scan rate of 1 s/scan and a manifold temperature of 180°C. The GC–MS was operated through the Saturn GC–MS Version 5.2 software (Varian, Walnut Creek, CA, USA). The volatile compounds were verified by comparison of the mass spectral data and the retention times with those of authentic reference compounds. When standards were not available the identification of the volatile compounds was carried out comparing mass spectral data with those of the NIST-92 library and they are indicated in the list as tentative of identification.

The integration of all the chromatographic peaks was performed choosing the three masses, among those specific for each compound, with the highest intensities as to selectively discriminate them from the nearest neighbours. The results of the peak areas were expressed as area counts.

2.3. Optimization of the blanching parameters of tomato juice

The thermal treatment was performed using the microwave oven Bauknecht MCG 1731 (Germany). According to the preliminary results obtained in a previous paper (Servili et al., 1998), the optimization of time and temperature of the blanching was performed at two different conditions corresponding to the industrial processes *cold break* and *hot break*.

The data were collected according to a "central composite design " (CCD) with the central point replicated

Table 1
Blanching parameters of the central composite design (CCD) of two sets of conditions

	Cold break		Hot break	
Experiment No.	Time (min)	Temperature (°C)	Time (min)	Temperature (°C)
1	10	67	1	87
2	15	62	2	82
3	15	72	2	92
4	25	60	4	80
5	25	75	4	95
6	35	62	6	82
7	35	72	6	92
8	40	67	7	87
9	25	67	4	87
10	25	67	4	87
11	25	67	4	87

Table 2
Head-space volatile compounds found in tomato juice

		References[b]			References
Alcohols					
2	Methanol	1	53	(*E,E*)-2,4-hexadienal	
4	Ethanol	2	55	(*E*)-2-heptenal	3,4,7
13	2-Methyl-l-propanol	1	69	Nonanal	6
21	l-Penten-3-ol	4	75	2,4-Hexadienal (i)[a]	
27	2-Methoxy-ethanol		78	(E)-2-Octenal	
31	2-Methyl-l-butanol	1,3,4,5,6	86	(*E,E*)-2,4-heptadienal[a]	
38	l-Pentanol	4,5,6	92	2,4-Heptadienal (i)[a]	5
42	2-Ethoxy-ethanol		98	Benzaldehyde	1
54	(*Z*)-2-Penten-l-ol	1	110	(*E,Z*)-2,6-nonadienal[a]	1
59	l-Hexanol	4,6	119	2,6,6-Trimethyl-l-cyclohexen-l-carboxaldehyde (G)	
61	(*E*)-3-Hexen-l-ol	2,3,4,5	121	4-Methylbenzaldehyde	1
67	(Z)-3-hexen-l-ol	1	123	(E)-2-decenal	1
74	2,2-Dimethyl-l-hexanol[a]	2,3,5,6	127	Phenylacetaldehyde	4,6,7
81	l-Octen-3-ol	1,5	131	Geranial[a]	1
83	l-Heptanol	1	132	2-Hydroxybenzaldehyde	1
84	6-Methyl-5-hepten-2-ol	1	134	2,4-Nonadienal[a]	
85	4-Isopropyl-l-methyl-2-cyclohexen-l-ol[a]	3,4,5,6	136	4-Ethyl-benzaldehyde[a]	6
90	6-Methyl-l-heptanol[a]		138	Neral[a]	1
91	2-Decen-l-ol[a]		141	2,5- or 2,4-Dimethyl-benzaldehyde[a]	6
93	2-Methyl-cyclohexanol		142	2-Undecenal[a]	1
99	Linalool	4,6	144	2,4-Decadienal[a]	2
100	(Z)-l-Methyl-4-isopropyl-2-cyclohexen-l-ol[a]	5,6	149	2,4-Decadienal (i)[a]	2
101	l-Octanol	1	179	3-Phenyl-2-propenal[a]	
104	4-Methylen-6-hepten-2-ol or 4-octyn-2-ol[a]				
106	2-Propyl-l-heptanol[a]		*Ethers*		
113	Terpinen-4-ol	4,6	11	Hexyl-octyl-ether[a]	
115	2-Octen-l-ol[a]	1	111	Diethylene glycolmono-methyl-ether	
116	2-Octen-l-ol (i) [a]	1	118	Diethylene glycol ethyl-ether or diethyl-ether[a]	
122	1,2-Ethanediol		139	2-Hydroxyethylether[a]	
125	l-Nonanol		171	Triethylene glycol	
126	4-Methyl-5-decanol[a]				
128	2-Butyl-l-octanol		*Sulfur compounds*		
150	1-Decanol or 3,7-dimethyl-l-octanol[a]		10	Dimethyl disulfide	4,5
155	Nerol	5,6	22	3- or 2-Ethyl-thiophene[a]	
160	Geraniol	5,6	68	Dimethyltrisulfide[a]	
162	Benzyl alcohol	5,6	70	2-Thiophene-methanamine[a]	5
163	Phenyl-ethyl alcohol[a]	3,4,6	73	2-Isobutyl-thiazole	7
164	Nerolidol	1	89	2-Methyl-2-thiazoline	4,6
177	l-Tridecanol[a]	1			
182	2-Ethyl-l-dodecanol[a]		*Free acids*		
185	Eugenol or isoeugenol[a]	2,4,5	87	Acetic acid	1
188	3,7,11-Trimethyl-l-dodecanol[a]		102	Propionic acid	2,6
190	Famesol	1	130	3-Methylbutyric acid	
			157	Hexanoic acid	4
Aldehydes			170	2-Hexenoic acid[a]	1
3	3-Methylbutanal[a]	4,5	178	Octanoic acid	1
7	Pentanal	1	184	Nananoic acid	1
9	Hexanal	3,4,5,7			
12	4-Pentenal[a]		*Phenols*		
25	Heptanal		37	3,5-Dimethyl-phenol	1
28	(*Z*)-3-Hexenal[a]	2,4,7,8	63	2,3,5-Trimethyl-phenol	1
32	(*E*)-2-Hexenal	2,4,5,7	71	2,3,5,6-Tetramethyl-phenol[a]	
47	Octanal	1	159	2-Methoxy-phenol	
174	Phenol	1	35	Gamma-terpinen	
175	4-Ethyl-2-methoxy-phenol[a]		36	1,2,4- or 1,2,3-trimethylbenzene[a]	1
186	2- or 3- or 4-ethyl-phenol[a]		41	*p*-Cymene	5,6
			44	*m*-Cymene	
Lactones			45	1,2,3- or 1,2,4-Trimethylbenzene[a]	1
124	Butyrolactone[a]	1	50	1,4- or 1,3-Diethylbenzene[a]	1

(continued on next page)

Table 2 (*continued*)

		References[b]			References
			51	Butylbenzene	1
Ketones			57	l-Methyl-4-propylbenzene[a]	
				2-Ethyl-1,3-dimethylbenzene	
6	3-Pentanone		60	or 1,2,3,4-tetramethylbenzene[a]	
8	l-Penten-3-one	2,3,4	62	2-Ethyl-1,3-dimethylbenzene (i)[a]	
15	3-Penten-2-one	1	66	1,2,3- or 1,2,4-Trimethylbenzene[a]	3,4,5
				2,6-dimethyl-2,6-octadiene	
24	5-Methyl-2-hexanone		72	or 3,3,6-Trimethyl-l,4-heptadiene[a]	
26	cyclopentanone		77	3-Ethyl-2-methyl-1,3-hexadiene[a]	
39	5-Methyl-3-heptanone	1	79	1,2,4,5-Tetramethylbenzene	5
46	2-Octanone	1	80	2-Butenylbenzene[a]	
48	4-Octen-3-one[a]		82	Cyclopentene or 1,4-pentadiene[a]	
49	3-Hydroxy-2-butanone	1	95	2,5,5-Trimethyl-1,3,6-heptatriene[a]	
56	6-Methyl-5-hepten-2-one	3,4,5,7	97	l-Isopropyl-2,3- or 4,5-dimethyl-cyclopentene[a]	
112	(*E*)-6-methyl-3,5-heptadiene-2-one[a]	1	107	Divinylbenzene[a]	
137	Megastigmatrienone[a]		109	1,2-Dihydronaphthalene	
152	2-Hydroxy-acetophenone	1	129	l-(Cyclohexylmethyl)-4-(l-methylethyl)-cyclohexane[a]	
				2,4,6	
			133	1,2-Dimethyl-3-(l-isopropenyl)-cyclopentane	
153	Geranylactone			or l-methyl-4-methylencycloheptane[a]	
156	Nerylactone		135	1-Heptadecyne or l-octadecyne[a]	
158	*acda*-Ionone	1	140	(2-ethyl-l-methyl-butylidene)-cyclohexane[a]	
165	*β*-Ionone	3,4,5,6	143	Naphthalene	1
168	4-(Dimethylamine)-3-methyl-2-butanone[a]		183	Styrene	1
172	2-Cyclohexen-l-one	4			
173	2-Methyl-cyclohexanone		*Nitrogen- and oxygen-containing compounds*		
176	Pseudo-ionone	4,5	58	1-Nitro-pentane	
181	Pseudo-ionone(i)[a]	5	65	2-Ethenyloxy-ethanol[a]	
187	4-Hydroxy-2- or 3-methyl-acetophenone[a]	6	146	3-Ethoxy-propanal or propylene oxyde[a]	
			151	Etheniloxy-isooctane[a]	
Esters					
40	Methyl-3-hexenoate[a]		*Oxygen-containing heterocyclic compounds*		
43	Hexylacetate	1	1	2-Methylfuran	2
52	3- or 4-Hexenyl acetate[a]	1	5	2-Ethylfuran	1
94	1,2-Ethanediyl di-formate[a]		17	3,4-Dihydro-2H-pyran	
108	Isobomyl acetate[a]	1	19	Butyl-oxirane	
120	1,2-Ethanediyl mono-formate[a]		33	2-Pentylfuran[a]	4,5
147	Methyl salicylate	4	64	1,4-Dioxane or 1,3,6-trioxane[a]	1
148	Propylene carbonate		76	3-(4-Methyl-3-pentenyl)-furan[a]	
154	2-Hydroxy-ethyl-benzoate[a]		88	Furfural	8
180	Triethyl-1,1,2-ethane-tricarboxylate		96	5,6- or 3,4-Dihydro-2H-pyran-2-carboxaldehyde[a]	
			103	5-Ethoxy-dihydro-2(3H)-furanone[a]	
Hydrocarbons			105	5-Methylfurfural	5,8
14	Ethylbenzene	6	114	5-Ethyl-2(5H)-furanone[a]	
16	*p*-Xylene	1	117	2-Methyl-1,3-dioxolane	
18	*o*-Xylene	1	145	3,4-Dihydro-2H-pyran-2-carboxaldehyde[a]	
20	2,5-Dimethyl-1,6-Octadiene[a]		161	2-Methylbenzofuran	
23	*m*-Xylene	1	166	2,2′-bi-1,3-dioxolane[a]	
29	Alpha-phellandrene	1	167	2-Methanol-1,3-dioxoland[a]	
30	Propylbenzene		169	2-(Hydroxymethyl)tetrahydropyran	
34	3-Decyne or 3-dodecyne[a]		189	2-Methoxy-1,3-dioxolane	

[a] Tentative of identification

[b] (1) Petro-Turza (1986–1987); (2) Baldwin et al., (1991); (3) Buttery et al., (1987); (4) Buttery, et al. (1990); (5) Buttery et al. (1990); (6) Marlatt et al, (1992); (7) Linforth et al., (1994); (8) Buttery et al., (1995).

three times (Box, Hunter & Hunter, 1978). For the *cold break,* times ranged between 10 and 40 min and temperatures between 60 and 75°C, while for the *hot break,* times ranged between 1 and 7 min and temperatures between 80 and 95°C (Table 1). The samples were analyzed by SPME, according to the procedure above reported.

2.4. Statistical analysis

2.4.1. Principal components analysis (PCA)

A PCA model was built to analyse the influence of different thermal treatments on the volatile compounds of the processed tomato. The chemometric package

"SIMCA- P v. 7.01", Umetri AB, Umeå, Sweden was used.

The analytical data were put in a matrix with the rows corresponding to the samples (n objects) and the columns corresponding to the analytical parameters (k variables). The raw data were normalized, with the subtraction of the mean, and autoscaled, dividing these results by the standard deviation.

The number of significant components has been found applying the cross validation. The results of PCA modelling are presented in the graphical form (Bisani, Clementi & Wold, 1982a,b; Wold et al., 1984).

2.4.2. Optimization by response surface modelling (RSM)

RSM was performed with the chemometric package "MODDE- v. 4.0", Umetri AB, Umeå, Sweden.

Two preliminary PCA models were made, one for each set of processing conditions, for selecting few variables (volatile compounds), among those with the highest absolute values of loadings, that are relevant in defining the fresh or the cooked tomato flavour of tomato juice.

To optimize the blanching parameters the original data, expressed as peak area (Y), were transformed in a desirability function (d_i) using a linear transformation, according to Derringer and Suich (1980) with a little modification, so to obtain a range of desirability between 0.1 and 1:

$$di = \frac{0.9^* Y + 0.1^* Y_{max} - Y_{min}}{Y_{max} - Y_{min}}$$

(for the fresh tomato flavour compounds)

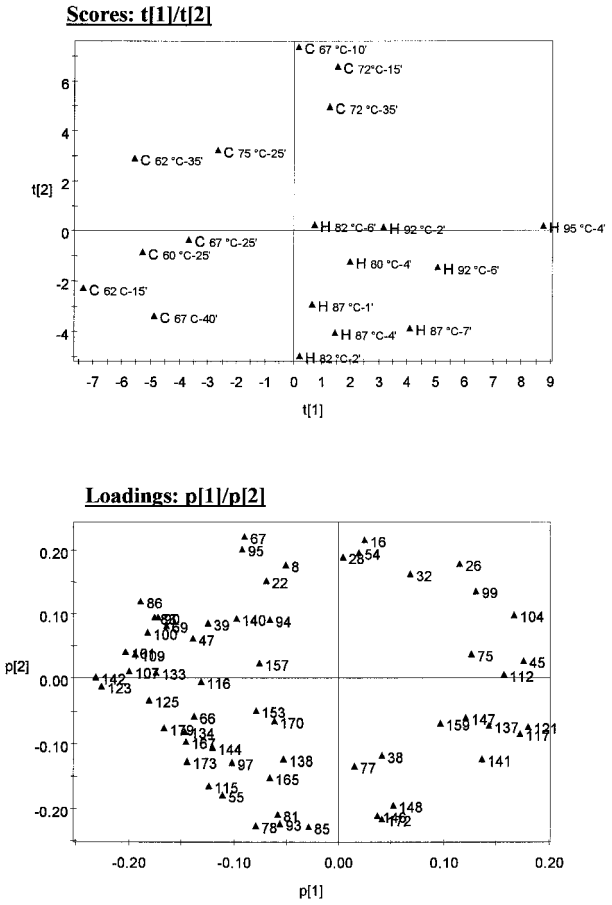

Fig. 2. Score-plot and loading-plot of the first two principal components of PCA of tomato juice sampled with SPME at different times and temperatures of thermal treatment corresponding to *cold break* (C) and *hot break* (H) conditions, respectively. (see Table 2 for variables).

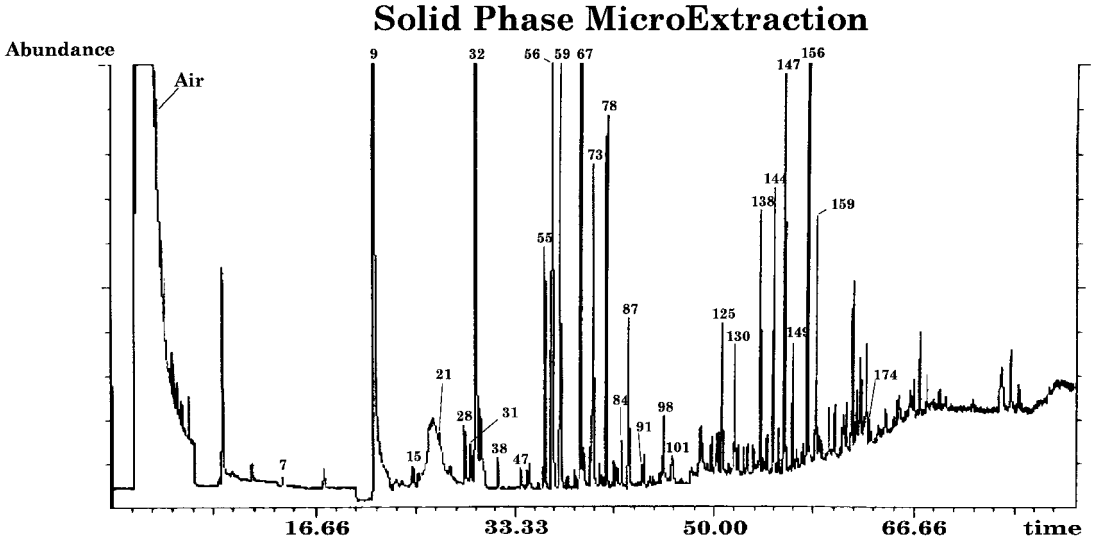

Fig. 1. Capillary GC–MS analysis of volatile compounds of tomato juice evaluated using SPME (see Table 2 for peak references).

$$di = \frac{-0.9^* Y + Y_{max} - 0.1^* Y_{min}}{Y_{max} - Y_{min}}$$

(for the cooked flavour compounds)

Y_{min} and Y_{max} corresponded to the minimum and the maximum value of peak area, respectively.

The overall desirability (D) was calculated as the geometric mean of the individual d_i values:

$$D = \sqrt[n]{d_1^* d_2^* \ldots^* d_n}$$

The partial least squares analysis (PLS) was employed for developing the model (Clementi, Cruciani, Giulietti, Bertuccioli & Rossi, 1990).

3. Results and discussion

One hundred and ninety volatile compounds were sampled: 102 of them were identified in tomato juice, the remaining were tentatively identified as reported in the ''materials and methods'' section (Table 2). These compounds include different chemical classes such as ketones, aldehydes, alcohols, esters, ethers, hydrocarbons, sulfur, nitrogen and oxygen compounds, phenols, oxygen-containing heterocyclic compounds, free acids and lactones. A typical GC–MS chromatogram of the volatile compounds in tomato juice sampled using SPME is reported in Fig. 1.

Thermal treatments strongly modify sensory and nutritional quality of tomato derivatives. In this ambit critical points in tomato processing are the blanching and the sterilization that, due to the Maillard reaction activation and polyunsaturated fatty acids oxidation, promote the genesis of volatile compounds related to the cooked flavour. The impact compounds of the fresh tomato flavour, on the contrary, originated by lipoxygenase activity and carotens cooxidation, decreased during thermal treatments (Buttery, Teranishi, Ling et al., 1990; Rouseff & Leahy, 1995; Schreier et al., 1979; Servili et al., 1998). The consumer's tendency, moreover, is more and more addressed towards a product that would preserve the characteristic of the fresh tomato fruit (Langlois, Etiévant, Pierron & Jarrot, 1996; Porretta & Ghizzoni, 1994). The blanching parameters, such as time and temperature of treatment, are usually selected according to the inactivation of endogenous

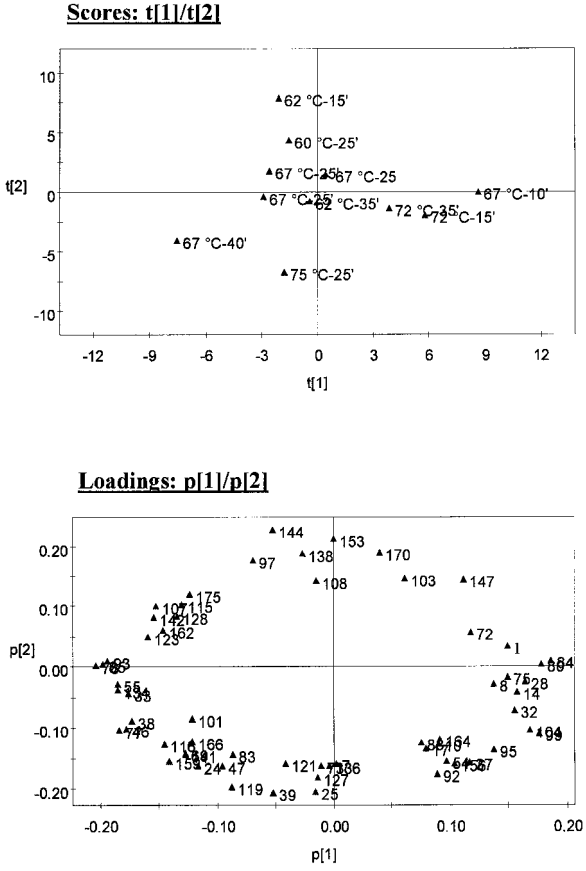

Fig. 3. Score-plot and loading-plot of the first two principal components of PCA of tomato juice sampled with SPME referred to the *cold break* treatment (see Table 2 for variables).

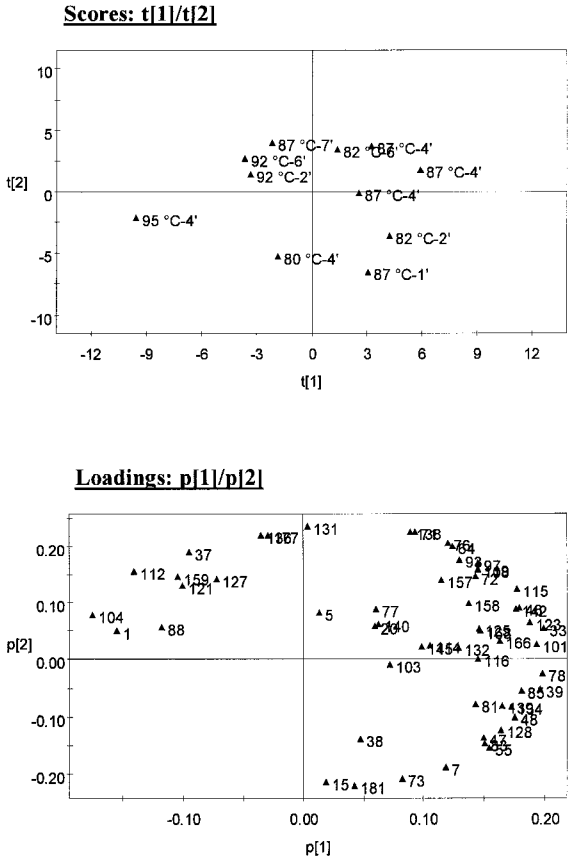

Fig. 4. Score-plot and loading-plot of the first two principal components of PCA of tomato juice sampled with SPME referred to the *hot break* treatment (see Table 2 for variables).

enzymes (Begliomini et al., 1995). In a previous paper, moreover, preliminary results concerning the influence of the blanching treatment in the volatile composition of tomato juice were reported (Servili et al., 1998). Consequently the volatile compounds may be fruitfully used as a marker to optimize the analytical parameters of the thermal treatment, promoting the genesis of the compounds correlated with the fresh tomato flavour and, at the same time, minimizing the formation of the cooked flavour. The optimization of the blanching parameters of tomato juice was studied at two sets of conditions: *cold break* and *hot break*.

Principal component analysis was preliminarily applied to investigate the effect of the thermal treatment on the volatile composition of tomato juice. The model explains 69% of the total variance with three components and the relative score-plot shows two clusters of objects, mainly distributed along the first component, containing the samples treated under *cold break* and *hot break* conditions, respectively (Fig. 2). The loading-plot put in evidence that the variables, responsible for this sample discrimination, with the highest absolute value of loadings are 1-octanol, nonanal, *(E)*-2-decenal, 2,4-hexadienal, linalool, 3-hexen-1-ol and 1-penten-3-one. This confirms previous results about the effect of the blanching treatment on the volatile compounds with a sensory impact on tomato juice flavour (Servili et al., 1998) and shows that the two treatment conditions, *cold*

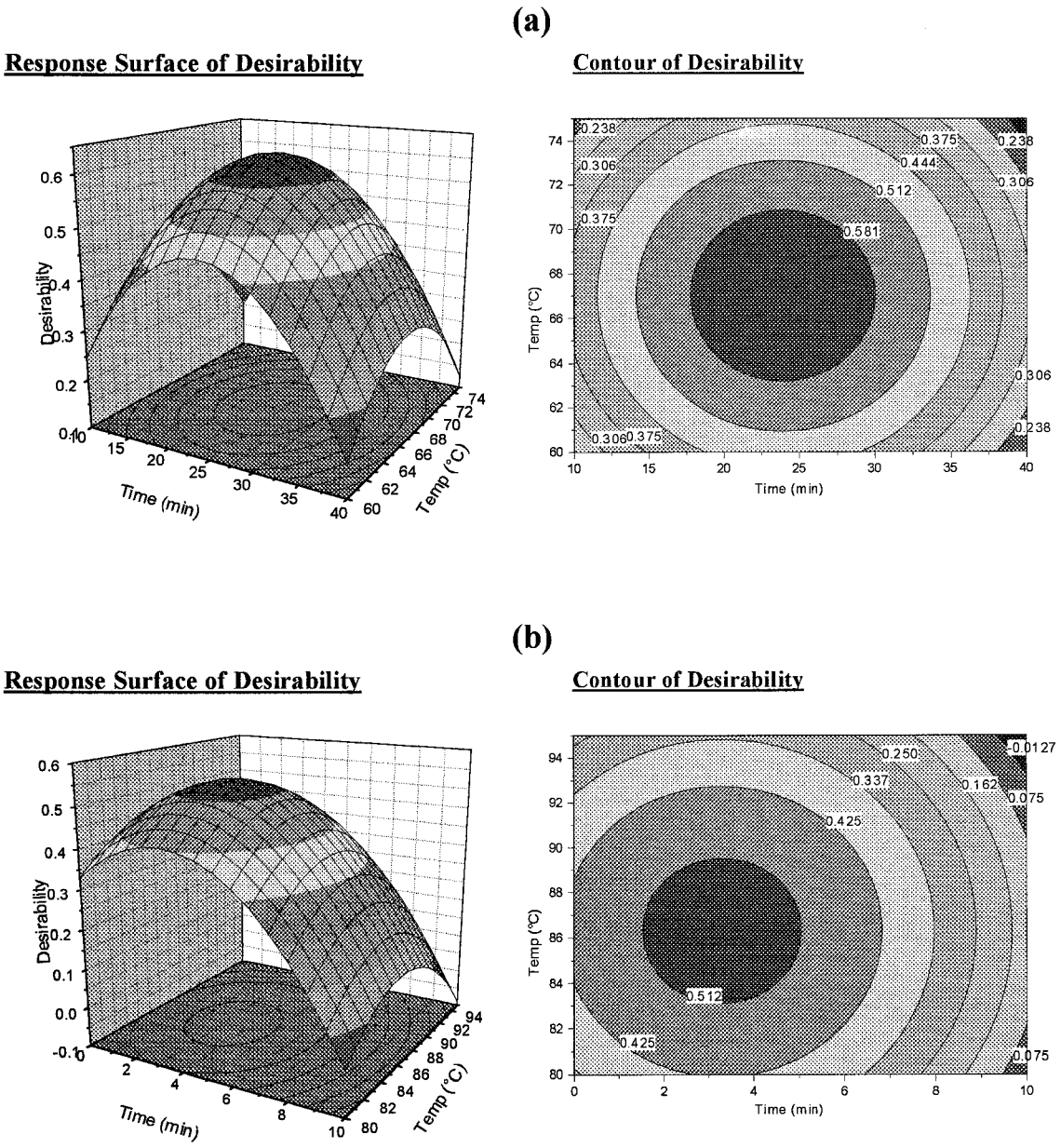

Fig. 5. Response surfaces modelling (RSM) and contour plots obtained using the PLS built to optimize the treatments conditions of time and temperature of the blanching, using the volatile compounds as markers: (a) *cold break* condition; (b) *hot break* condition.

break and *hot break*, can be used separately in the optimization of the operative procedures.

As reported in the "materials and methods" section, before attempting the optimization study, two PCA models were built, one for each treatment, for selecting the few variables (chemical compounds) with the highest absolute loading values and, therefore, more affected by the heating process.

The *cold break* and *hot break* models explain, with three components, the 72% and the 79% of the total variance, respectively. The score-plot of the first model put in evidence that along the first principal component the distribution of the objects is mainly due to the time of the thermal treatment, while in the second one the effect of the temperature is shown (Fig. 3). The score-plot of the *hot break* condition shows, on the contrary, that the main effect (first component) of the treatment is due to the temperature and the time effect can be seen along the second component (Fig. 4).

The loading-plots reported in Figs. 3 and 4 show that thermal treatment affects, in a different way, the genesis of the aroma compounds during heating in the *cold break* and *hot break* operative conditions. In fact, different chemical compounds have remarkable relevance as the loadings with higher absolute values in the two models point out. As a consequence of these results, the volatile compounds chosen were different for the two models.

The few variables used in the optimization study were selected, among the volatile compounds with the highest loadings, according to their potential contribution to the fresh or the cooked flavour of tomato juice. The influence of volatile compounds on the sensory note of tomato juice was established according to the literature (Baldwin et al., 1998; Buttery, Teranishi, Ling et al., 1990; Petrò-Turza, 1986–1987; Porretta & Ghizzoni, 1994). In this ambit, six compounds selected as fresh tomato flavour markers, pentanal, 2,4-hexadienal, *(E)*-2-octenal, neral, 2,4-decadienal and β-ionone) and 2-methylfuran and 2,4-nonadienal, chosen as cooked flavour markers, were used for the optimization study of the *cold break* treatment (Buttery, Takeoka & Ling, 1995; Petrò-Turza; Servili et al., 1998). The RSM model, that explains the 82% of the total variance, gives as result 67°C for a time of 24 min as optimal conditions for the *cold break* treatment (Fig. 5a).

The *hot break* operative condition, on the contrary, was optimized using five variables (pentanal, 3-penten-2-one, *(E)*-2-octenal, geranial and β-ionone as fresh flavour markers) while 2-pentylfuran, 3-(4-methyl-3-pentenyl)-furan and furfural were selected as cooked flavour compounds. The results of the RSM model, explaining the 82% of the total variance, show that the optimal conditions for the *hot break* treatment are 86°C for 3.5 min (Fig. 5b).

The models applied to the blanching parameters show the best time and temperature combinations of thermal treatment conditions that preserve volatile compounds correlated to the fresh sensory notes in tomato juice.

A similar experimental research can be applied to the sterilization process to minimize the loss of volatile and non-volatile compounds that are responsible for the sensory and nutritional characteristics of fresh fruit in the processed tomato (Leoni & Bellucci, 1980; Petrò-Turza, 1986–1987; Porretta, 1991; Rouseff & Leahy, 1995).

The optimization study could be extended to the nutritional characteristics of tomato juice and tomato derivatives taking into account other substances strongly affected by thermal treatment, such as lycopene and β-carotene, that may be used as nutritional markers of quality.

4. Conclusions

One hundred and ninety volatile compounds were sampled by SPME, 102 of them were identified while the remaining were tentatively identified in tomato juice using the GC–MS technique. These compounds belong to the following chemical classes: ketones, aldehydes, alcohols, esters, ethers, hydrocarbons, sulfur, nitrogen and oxygen compounds, phenols, oxygen-containing heterocyclic compounds, free acids and lactones.

The thermal treatment mainly modifies saturated and unsaturated C_6 alcohols and aldehydes, esters, ketones and carotenoid derivatives. The response surface Modelling (RSM) performed using the volatile compounds of tomato juice to optimize the blanching operative conditions, discriminates 67°C for 24 min and 86°C for 3.5 min for the *cold break* and the *hot break* treatments, respectively.

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