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Study on volatile components in salami by reverse carrier gas headspace gas chromatography-mass spectrometry¹

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Abstract

Salami are a typical seasoned sausage of Italy; a number of types are produced, according to local traditional recipes. As industrial production has taken place, a number of problems rise in obtaining products similar to the traditional ones. The use of selected microbial starters is permitted by Italian law for some years and at present, micro biological research is engaged in selecting starters similar to the ones isolated from traditional products, with the aim of obtaining organoleptic characteristics close to the ones of traditional recipes. A study was carried out concerning the characterisation of volatile components of salami by headspace capillary gas chromatography–mass spectrometry. As during the sampling step, analytes could reach the analytical column, the carrier gas rate was back flushed in the latter, while a pre column was used as cold trap. Then GC–MS analysis follows. By these techniques, we were able to highlight typical profiles of different salami, as well as monitoring the ripening of a traditional and a starter added salami. Main peaks are of fermentative origin, while also peaks from spices were detected. Ethyl propionate was used as internal standard to be able to normalise the peaks amounts. © 1999 Elsevier Science BV. All rights reserved.

Keywords: Food analysis; Headspace analysis; Sample handling; Volatile organic compounds

1. Introduction

Salami are traditional Italian meat seasoned preserves obtained by different types of pork meat, chopped in several measures, depending on type of salami, added with swine fat, spices, sugar and microbial starter.

Seasoning time depends on type of products, as well as on its dimension; during seasoning, a number of chemical transformations take place, thanks to microbial activity, mainly, even if chemical reactions happens.

The first change is sugar fermentation, carried out by microbial starter, that leads to the pH dropping to acid ambient, so stabilising product against undesirable microbial spoilage.

Further chemical modifications take place, producing a number of compounds, many of which directly involved in product flavour and taste, that's to say, in its typical characteristics.

In 1992 and following years, the (now) European Union (EU) adopted some Reglements dealing with typical products: EEC Reglement 2081 [1] is the first

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EU law concerning Protection of Denomination of Origin (DOP) and of Geographical Origin (IGP).

Among other foods, a number of meat based foods are DOP or IGP and, among these, two Italian typical salami appear: Varzi and Brianza.

The typicality deals with area of production, methods of productions and other parameters; its control is based, among other parameters, on the organoleptic characteristics that, as said before, depends on ripening; to obtain a quite objective evaluation of aroma, instrumental methods are necessary, this paper represents a first approach to the study of volatile components of salami; the problem is so much a part of the wide problem dealing with food aroma analysis.

Chemical analysis of food aroma, in as much as it is usually present in limited amounts, must be carried out by means of techniques involving concentration of volatile fraction, followed by extraction and cleanup.

The applied techniques must be wary of widespread characteristics of stability, polarity, volatility and solubility, as well as chemical reactivity that often characterise sample components. The presence of interfering compounds, often in great amounts, is a further problem and requires the use of suitable procedures for their removal. A peculiar case is the one that involves the presence of large amounts of fat, that limit the possibility of using solvents, as well as of high temperatures in any step.

Techniques applied to volatile fraction study belong to two main groups: (1) techniques based upon extraction of volatiles, and (2) techniques that realise a concentration of the headspace itself.

Among the former, distillation or steam distillation has been widely applied, even if the possibility of artifacts formation is high, because of temperature (e.g. lipid oxidation) as well as the lack of more volatile components can take place when reduced pressure is applied. Solvent extraction, too has been applied; in this case, too, some problems can occur, because of the interfering substances whose presence can become important after solvent concentration.

Solid-phase extraction (SPE) leads to a reduction in solvents volumes used, so realising a reduction in interfering substances from solvents; SPE, anyway, often has not satisfactory characteristics of linearity between amount of sample introduced and amount of retained analytes, so that a new assessment is necessary for each type of food. In SPE, solvents are used anyway and most of them are able to dissolve fatty substances, even of high molecular mass, that could lead to problems in the gas chromatographic analysis that follows.

The other approach to analysis of volatile components is based upon headspace analysis; in this case, too, a number of techniques are available. The main advantage of headspace analysis if compared to the above discussed techniques is that the analysis is carried out on an untreated sample.

Headspace techniques are the most suitable ones for the study of very volatile components, while they are not so much suitable for higher-boiling ones, as they are not present inside the headspace in a representative amount. Among low-boiling compounds, therefore, the sampling technique used plays an important role as a balancing factor between different boiling point compounds. The composition of headspace being determined by Raoult's law, the use of a sampling pressure as low as possible is mandatory.

2. Experimental

2.1. Sampling

Two main groups of samples were considered. On one hand we studied some trade salami, different for origin and technology, those sampled were: Milano, Felino, Filzetta, Cacciatorino. Campagnolo, Soppressa, Piccante (with chilli Capsicum), on the other hand, we studied samples with the same composition and seasoning conditions, half of which were obtained by traditional technology and half by means of selected microbial starter inoculation.

2.2. Headspace sampling

The head space sampling technique used is the one assessed by Barcarolo et al [2,3]; salami (about 10 g, exactly weighed) were weighted into a 100 ml vial to which was added internal standard (ethyl propionate, $35.6 \mu g$, Sigma) then the vials were sealed with aluminium–rubber septum (Supelco, Bellefonte, PA, USA). Vials, septa and every other device were

stored in a oven at 120°C until analysis time, to be sure that no strange substances could reach the sample.

Vials with salami were conditioned at 70°C for 15 min before analysis, then stripping was carried out for 90 s, into an heated block (70°C). Stripping was realised with helium, at a rate of 8 ml/min.

Volatile components are driven into a capillary tube that is inside a cryogenic trap (liquid nitrogen), that can be cooled to between -1 and -150° C that is connected in a on column mode to a capillary gas chromatograph Carlo Erba GC 8000. The connection to the analytical column, therefore, is not direct, as an Y press fit is inserted and connected to a vapour exit valve. During the sampling step, helium is back flushed through the analytical column and exits through this vapour exit device. This is realised with the aim of avoiding any contamination of the analytical column with incondensible gases or other substances, whose presence could lead to false positive results or to the presence of interfering substances.

2.3. GC-MS analysis

At the end of sampling (purging) time, desorption (really deicing) of volatile components takes place, by heating of the trap to 240°C and transfer of analytes to the analytical column. The electronic 8-port valve switches, so that helium flow comes back to the original flow direction. The analytical column used is a capillary fused-silica column 50 $m \times 0.32$ mm I.D., coated with PS 264 (Mega, Milan, Italy), 3 µm film thickness.

The capillary GC system is coupled directly to a MD 800 mass spectrometer (Carlo Erba, Milan, Italy). GC conditions were the following: oven initial temperature 40°C, hold for 6 min, then programmed to 180°C at a rate of 5°C/min, then 5 min at 180°C, then at 7°C/min to 200°C, held 2 min, and finally at 7°C/min to 240°C. A final 5 min at 240°C follows.

Transfer line temperature was kept at 250°C.

A mass spectrometer scanned from m/z 29 to m/z 300 at 0.5 s cycle time. The ion source was set at 150°C and spectra was obtained by electron impact (70 eV).

Identification of compounds was carried out by comparison of retention times and mass spectra of some standards (when available), study of the MS spectra and comparison with members of the NBS library.

3. Results and discussion

Two examples of total ion current (TIC) of salami samples of different types are reproduced in Fig. 1(A and B): even if resolution is not optimum for low boiling peaks, the ones eluted starting from 12 min present good focusing, with no tailing phenomena; it is important to point out that with the adopted technique, no absorption medium is used, so that when by temperature effects the stripped substances are driven into the analytical column, some band broadening effects may occur, mainly for low boiling compounds. Obviously, the amount of substance has a great importance within these phenomena, as is stressed by the well focused peak of acetaldehyde that is near to the not well focused one of ethanol.

As regards the applicative aspects of the present work it is possible to see that even within the analyzed samples where main peaks are the same, important differences occur in their magnitude depending on the sample. Peak identification is reported in the Table 1, where identified compounds are listed: they are 50; we can observe the presence of different groups of compounds, that could be put in a relationship with different origins:

(a) Fermentative origin: surely acetaldehyde, ethanol, acetone, propanol, 2-butanol and some others could originate from fermentative phenomena, as they are well known results of metabolic activity of microorganisms; amino acids catabolism originate from 2- and 3-methylbutanol, 2- and 3methylbutanol by leucine and isoleucine decarboxylation and oxidative deamination, while dimethylsulfide originates from cysteine [4].

(b) Oxidative origin: hexanal, 2-hexenal, heptanal, octanal and nonanal could be of oxidative origin, as these aldehydes are well known as lipid autoxidation products; furthermore, also methylketones such as 2-butanone and 2 heptanone as well as alcohols and cyclofuranic compounds [5-10].

(c) Seasoning origin: these compounds could originate thanks to seasoning time, as they require longer periods to be formed: main compounds of this



Fig. 1. TIC of volatile components in different types of salami: "Campagnolo" (A) and "Felino" (B). Peak numbers refer to the ones reported in Table 1 and Table 2: 3=ethanol, 4=acetone, 5=carbon disulfide, 9=butanal, 10=2-butanol, 11=ethyl acetate, 22 ethyl propionate (I.S.), 27=1-pentanol, 29=hexanal, 36=heptanal.

Table 1 Aroma compound content (mg/10 g) of different salami (internal standard: ethyl propionate at 0.04 ml=35.6 mg)

No.	$t_{\rm R}$ (min)	Identification	Content (mg/10 g)						
			SA	SB	SC	SD	SE	SF	SG
1	4.34	Acetaldehyde	18.00	24.28	33.14	46.85	31.57	32.41	72.95
2	4.90	Methylmercaptan	1.81	0.85	4.26	1.04	_	0.52	1.06
3	5.91	Ethanol	45.62	56.02	47.54	115.76	128.37	65.24	106.36
4	7.00	Acetone	62.02	91.57	75.57	98.85	103.82	56.96	117.08
5	8.99	Carbon disulphide	27.21	45.94	41.11	150.79	92.05	97.76	131.21
6	9.81	Propanol	4.19	5.54	1.67	25.31	45.02	10.64	23.18
7	10.11	2-Methylpentane	1.32	2.70	0.98	9.58	5.65	4.03	11.26
8	10.86	3-Methylpentane	0.48	1.00	0.29	3.48	2.10	2.08	3.73
9	11.45	Butanal	6.42	5.49	3.84	8.12	3.23	6.09	21.79
10	11.85	2-Butanol	_	0.32	0.43	1.39	101.56	0.56	_
11	12.71	ethyl acetate	1.81	2.54	1.27	3.85	5.85	1.69	6.08
12	13.23	Isobutanol	0.45	0.54	0.12	0.71	0.90	0.23	3.30
15	15.08	Butyl formate	2.92	1.51	0.51	1.96	2.73	0.71	1.31
16	15.18	4-Methyl-2-pentanone	0.89	0.83	1.14	3.36	0.92	1.71	5.74
17	15.32	Cyclohexane	0.28	0.50	0.33	1.52	0.94	1.01	1.50
18	16.10	1-Penten-3-ol	1.44	2.23	1.00	3.07	1.90	4.47	8.53
19	16.38	2.2.4-Trimethylpentane	0.24	0.29	0.18	0.55	0.39	0.46	1.32
20	16.67	2.3-Pentanedione	0.84	1.04	0.52	1.59	1.34	1.05	3.69
21	17.17	2.4-Hexadienal	0.53	0.46	0.52	1.59	0.81	0.59	1.84
22	17.68	Ethyl propionate (I.S.)	_	_	_	_	_	_	_
23	18.73	3-Methyl-1-butanol	0.39	0.26	0.14	0.71	0.53	0.25	4.31
24	18.95	2-Methyl-1-butanol	0.11	0.06	0.04	0.27	0.15	0.09	0.99
25	19.66	Pyridine	0.09	0.08	0.06	_	_	_	_
26	19.90	5-Methyl-l-heptene	0.47	0.21	0.30	0.25	0.20	0.27	2 95
20	20.34	l-Pentanol	2.48	3.13	2.53	4.79	1.96	6.14	8.45
28	20.81	Toluene	0.47	0.38	0.46	1.62	0.78	0.55	1 40
29	22.08	Hexanal	71.16	78.65	117.02	208 25	107.10	142.00	250.40
30	22.00	Ethyl isovalerate	0.02	0.02	0.03	0.05	-	-	0.13
31	24.43	2-Hevenal	0.02	0.02	0.05	0.03	0.03	0.12	0.15
32	25.15	n-Heyanol	0.15	0.09	0.11	0.15	0.03	0.12	0.73
32	25.13	Ethylbenzene	0.06	0.10	006	023	0.45	0.19	0.75
34	25.45	m_Xylene	0.00	0.03	0.06	0.25	0.00	0.09	0.27
35	25.70	2-Entanone	0.07	0.04	0.00	0.23	0.02	0.00	0.19
36	26.20	2-Eptanone Hentanal	1.17	0.04	1 49	1 46	0.02	1 10	5.67
37	28.75	a-Tuione	1.17	0.00	1.49	0.04	0.74	1.10	0.42
38	28.27	or Dinene	0.04	0.00	0.03	0.30	0.08	0.00	1.25
30	20.02	2 Hentenal	0.04	0.20	0.03	0.30	0.08	0.09	0.83
37 40	20.00	1 Hepten 3 ol	0.25	0.15	0.23	0.55	0.10	0.25	0.03
40	29.99	Sabinana	0.20	0.23	0.03	0.55	0.30	0.49	2 20
41	20.60	Ethyl bayanooto	0.01	0.47	0.03	0.30	0.14	0.09	0.11
42	20.92	Q Dinono	0.01	0.02	0.08	0.03	-	0.01	1.04
45	30.83	p-Fillelle	0.15	0.50	0.02	0.31	0.00	0.15	1.94
44	31.03		0.28	0.18	0.37	0.33	0.15	0.22	0.82
45	31.27	1,2,3-1rimethylbenzene	0.01	-	0.01	0.02	0.02	0.02	-
40	31.99	Carene	0.09	0.05	0.05	0.12	0.08	0.07	0.06
4/	32.42	<i>p</i> -Cymene	0.01	-	-	0.06	-	0.01	0.04
48	32.64	Limonene	0.07	0.16	0.04	0.24	0.10	0.15	1.27
49	33.34	2-Octenal	0.09	0.06	0.10	0.25	0.05	0.20	0.23
50	35.00	Nonanal	0.12	0.07	0.16	0.34	0.11	0.14	0.38

Samples: SA=Milano; SB=Felino; SC=Filzetta; SD=Cacciatorino; SE=Campagnolo; SF=Soppressa; SG=Piccante (with capsicum).

Table 2 Aroma compound content (mg/10 g) of (internal standard: ethyl propionate at 0.04 ml=35.6 mg)

No.	$t_{\rm R}$ (min)	Identification	Content (mg/10 g)					
			St 0	St 10	St 20	St 30	St 40	
1	4.34	Acetaldehyde	38.28	41.05	32.59	43.15	47.00	
2	4.90	Methylmercaptan	0.20	0.21	0.29	0.35	0.22	
3	5.91	Ethanol	53.29	76.19	76.08	84.56	96.84	
4	7.00	Acetone	78.35	115.02	127.43	156.41	164.50	
5	8.99	Carbon disulfide	8.86	5.82	0.88	1.91	1.78	
6	9.81	Propanol	36.92	39.52	29.81	40.40	26.51	
7	10.11	2-Methylpentane	2.44	2.16	2.13	3.20	2.68	
8	10.86	3-Methylpentane	0.74	1.18	1.01	1.88	1.66	
9	11.45	Butanal	30.40	23.98	16.74	26.91	26.84	
10	11.85	2-Butanol	0.59	10.30	11.51	34.39	5.25	
11	12.71	Ethyl acetate	2.44	9.43	5.65	6.43	10.34	
12	13.23	Isobutanol	4.43	1.00	1.20	1.82	1.07	
13	13.43	2-Methyl-1-pentene	2.65	3.12	3.71	4.80	4.36	
14	14.67	3-Methylbutanal	9.95	5.95	5.66	12.03	5.00	
15	15.08	Butyl formate	19.68	10.42	9.74	19.67	9.44	
16	15.18	4-Methyl-2-pentanone	3.41	2.88	3.21	2.75	2.51	
17	15.32	Cyclohexane	5.09	4.56	5.12	4.59	5.32	
18	16.10	1-Penten-3-ol	12.62	10.63	10.63	14.41	8.76	
19	16.38	2,2,4-Trimethylpentane	4.74	3.72	4.68	3.52	4.17	
20	16.67	2,3-Pentanedione	0.55	0.16	0.09	0.30	0.05	
21	17.17	2,4-Hexadienal	1.78	1.67	1.01	1.70	1.46	
22	17.68	Ethyl propionate	(I.S.)	_	_	-	_	
23	18.73	3-Methyl-1-butanol	7.54	1.47	1.30	1.08	1.74	
24	18.95	2-Methyl-1-butanol	1.40	0.38	0.40	0.37	0.39	
25	19.66	Pyridine	0.45	0.39	0.88	1.55	0.31	
26	19.90	5-Methyl-1-heptene	1.62	1.54	1.60	1.68	1.48	
27	20.34	1-Pentanol	63.95	45.98	25.13	26.60	37.47	
28	20.81	Toluene	2.70	2.24	2.05	3.01	2.16	
29	22.08	Hexanale	268.83	227.37	145.40	233.61	205.67	
30	24.43	Ethyl isovalerate	0.14	0.21	0.21	0.20	0.22	
31	24.68	2-Hexenal	0.91	0.60	0.32	0.78	0.33	
32	25.15	<i>n</i> -Hexanol	14.56	6.16	1.57	1.39	2.06	
33	25.43	Ethylbenzene	0.47	0.29	0.28	0.26	0.24	
34	25.76	<i>m</i> -Xylene	0.46	0.34	0.32	0.37	0.27	
35	26.20	2-Heptanone	1.58	1.04	0.71	1.18	0.87	
36	26.73	Heptanal	12.72	6.43	3.42	7.03	3.99	
37	28.27	α-Tujone	0.19	0.10	0.16	0.42	0.04	
38	28.82	α-Pinene	0.91	0.77	0.81	2.41	0.46	
39	29.22	2-Heptenal	1.07	0.75	0.35	0.78	0.31	
40	29.99	1-Hepten-3-ol	1.18	0.90	0.53	1.24	0.34	
41	30.41	Sabinene	1.32	0.82	1.04	3.17	0.30	
42	30.60	Ethyl hexanoate	0.31	0.77	0.71	0.70	0.70	
43	30.83	β-Pinene	0.95	0.71	0.79	2.16	0.36	
44	31.03	Octanal	3.05	1.48	0.72	1.46	0.73	
45	31.27	1,2,3-Trimethylbenzene	0.08	0.03	0.05	0.05	0.02	
46	31.99	Carene	0.26	0.16	0.17	0.67	0.10	
47	32.42	<i>p</i> -Cymene	0.06	0.05	0.04	0.12	0.03	
48	32.64	Limonene	0.51	0.41	0.31	1.10	0.20	
49	33.34	2-Octenal	0.53	0.42	0.14	0.38	0.11	
50	35.00	Nonanal	0.54	0.38	0.13	0.36	0.11	

Samples: St=Starter added salami at different times, as days: 0, 10, 20, 30 and 40.

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Table 3 Aroma compound content (mg/10 g) of (internal standard: ethyl propionate at 0.04 ml=35.6 mg)

No.	$t_{\rm R}$ (min)	Identification	Content (mg/10 g)					
			Ct 0	Ct 10	Ct 20	Ct 30	Ct 40	
1	4.34	Acetaldehyde	21.18	32.28	27.16	36.26	31.60	
2	4.90	Methylmercaptan	0.19	0.11	0.10	0.13	0.04	
3	5.91	Ethanol	30.18	72.58	48.44	61.95	72.44	
4	7.00	Acetone	62.58	88.20	82.06	88.74	101.63	
5	8.99	Carbondisulfide	3.14	14.74	0.86	0.95	0.48	
6	9.81	Propanol	16.91	24.89	22.36	24.74	28.02	
7	10.11	2-Methylpentane	1.25	2.05	3.15	1.86	1.04	
8	10.86	3-Methylpentane	0.37	1.57	0.56	0.65	0.54	
9	11.45	Butanal	18.78	12.00	17.40	18.45	21.77	
10	11.85	2-Butanol	0.26	8.72	14.64	24.19	4.89	
11	12.71	Ethyl acetate	2.12	9.03	3.53	3.65	5.69	
12	13.23	Isobutanol	2.67	0.51	1.13	0.85	1.27	
13	13.43	2-Methyl-1-pentene	1.53	2.94	2.64	2.85	2.10	
14	14.67	3-methylbutanal	5.71	3.75	7.73	7.56	5.36	
15	15.08	Butyl formate	11.67	4.53	15.74	7.98	10.71	
16	15.18	4-Methyl-2-pentanone	2.54	1.66	2.77	3.55	2.38	
17	15.32	Cyclohexane	2.05	5.41	3.51	3.09	3.32	
18	16.10	1-Penten-3-ol	6.77	6.70	8.86	9.15	9.87	
19	16.38	2,2,4-Trimethylpentane	2.45	2.34	3.70	3.56	3.02	
20	16.67	2,3-Pentanedione	0.18	0.22	0.28	0.19	0.24	
21	17.17	2,4-Hexadienal	1.29	1.02	1.27	0.98	1.35	
22	17.68	Ethyl propionate	(I.S.)	-	_	_	_	
23	18.73	3-Methyl-1-butanol	4.48	0.76	1.08	0.70	1.44	
24	18.95	2-Methyl-1-butanol	0.90	0.22	0.39	0.21	0.42	
25	19.66	Pyridine	0.31	0.18	1.25	0.43	0.86	
26	19.90	5-Methyl-1-eptene	1.11	0.70	1.36	1.50	2.13	
27	20.34	1-Pentanol	37.00	14.11	25.20	21.32	37.42	
28	20.81	Toluene	2.16	1.38	2.44	1.94	2.38	
29	22.08	Hexanal	144.28	153.21	125.43	152.93	169.37	
30	24.43	Ethyl isovalerate	0.06	0.10	0.12	0.08	0.20	
31	24.68	2-Hexenal	0.78	0.15	0.62	0.48	0.69	
32	25.15	<i>n</i> -Hexanol	9.52	1.22	1.52	0.76	5.60	
33	25.43	Ethylbenzene	0.29	0.13	0.21	0.17	0.31	
34	25.76	<i>m</i> -Xylene	0.33	0.13	0.35	0.28	0.33	
35	26.20	2-Heptanone	1.24	0.27	0.87	0.80	1.25	
36	26.73	Heptanal	10.21	2.04	5.65	4.60	8.22	
37	28.27	α-Tuione	0.12	0.11	0.25	0.15	0.19	
38	28.82	α-Pinene	0.74	0.56	1.29	1.01	1.17	
39	29.22	2-Heptenal	1.00	0.23	0.67	0.62	0.80	
40	29.99	1-Hepten-3-ol	1.07	0.06	0.88	0.67	1.10	
41	30.41	Sabinene	1.04	0.47	1.66	1.11	1.40	
42	30.60	Ethyl hexanoate	0.40	0.20	0.75	0.56	1.01	
43	30.83	B-Pinene	0.72	0.72	1.16	1.01	1.01	
44	31.03	Octanal	2.83	0.48	1.08	0.92	1.98	
45	31.27	1.2.3-Trimethylbenzene	0.07	0.03	0.04	0.04	0.02	
46	31.99	Carene	0.23	0.19	0.29	0.25	0.02	
47	32.42	<i>p</i> -Cymene	0.05	0.03	0.07	0.06	0.08	
48	32.42	Limonene	0.39	0.05	0.54	0.48	0.55	
49	33 34	2-Octenal	0.61	0.20	0.28	0.70	0.35	
50	35.00	Nonanal	0.64	0.04	0.20	0.27	0.30	
50	55.00	Tomanar	0.04	0.04	0.27	0.23	05	

Samples: Ct=test at different times, as days: 0, 10, 20, 30 and 40.

type are esters: butyl formate, propyl acetate, ethyl isovaleriate.

(d) Spices origin: surely terpenes, also considering their weak presence: α -tujone, α - and β -pinene, sabinene, carene, *p*-cymene, limonene [9]. Some of these compounds are present in high amounts in an SG sample, that is salami with Capsicum.

(e) Environmental origin (?) this is just a tentative origin: in this group we suggest to list 1,2,3-trimethylbenzene, 2,2,4-trimethylpentane, ethylbenzene.

Quantitative evaluation was carried out by internal standard method; as standard substances were not available for each identified compound, we put the response factor as one for any substance.

Even if a higher number of samples should be necessary to lead to significant evaluation, nevertheless, we can consider that the approach to volatile components could be an interesting analytical tool for salami characterisation: from a quantitative point of view, in fact, we can observe that some compounds are highly represented in some type of salami and negligible in the other type. Methyl mercaptane, e.g., is four-fold present in "Filzetta" rather than in other type, in "Campagnolo" it is absent; the latter is more rich in some aldheydes as well as 2-methyl-1-pentene and 3-methyl-butanol. "Cacciatorino", together with "Piccante" has a higher value of hexanal, while eptanal is five-fold higher in "piccante" than in all the other samples.

Data concerning comparison of samples with and without microbial starter (data reported in Table 2 and Table 3) show a substantial identity in present compounds, even if some light quantitative differences can be noted.

Starter added samples (St 0-5t40) and control samples (CtO-Ct 40), in fact show as main components to be the same as already observed for trade samples discussed above; some unusual distribution is observed for some analytes as, e.g. hexanal, that has a flex at 20 days, while some other compounds, as butyl formiate and 2-butanol show an increasing trend from 0 to 30 days, then drop at 40 days.

The interesting result is, in this case, that the possibility exists of monitoring the ripening process by means of volatile components that are surely involved in defining organopeptic characteristics of products; on the other hand at the seasoning end, the starter added samples and the control seem quite similar as volatile components, even if this result appears to be obtained with different rates.

4. Conclusion

The results of the present paper are, in our opinion, interesting both from an analytical point of view, as they admit the separation and identification of a number of analytes in a rather simple way, without solvents at all, both by an applicative point of view, as the presence and amount of many analytes can be related to specific stage of salami ripening, as well as to peculiar fermentative activity, linked to specific bacterial strains. The use of these kind of data to characterise peculiar products is predictable, as well as the use of these findings as a help in selecting a microbial starter which is able to reproduce and standardize some kind of taste.

References

- Reg. (EEC) 2081/92, 14 July 1992, EEC Official Journal L208, 24 July 1992.
- [2] R. Barcarolo, P. Casson, C. Tutta, J. High Resolut. Chromatogr. 15 (1992) 307.
- [3] R. Barcarolo, P. Casson, J. High Resolut. Chromatogr. 20 (1997) 24.
- [4] G. Johansson, J.L. Berdagueè, M. Larsson, N. Tran, E. Borch, Meat Sci. 38 (1994) 203.
- [5] J.L. Berdagueè, C. Garcia, V.P.C. 11 (1990) 319.
- [6] A. Yasuhara, T. Shibamoto, Food Chem. 37 (1990) 13.
- [7] T.C.Y. Hsieh, S.S. Williams, W. Vejaphan, S.P. Meyers, J. Am. Oil Chem. Soc. 66 (1989) 114.
- [8] W. Grosch, Lebensm. Technol. 21 (1988) 261.
- [9] R.G. Berger, C. Macku, B. German, T. Shibamoto, J. Food Sci. 55 (1990) 1239.
- [10] O. Kandler, Forum Mikrobiol. 5 (1982) 16.