GLOBAL ANALYTICAL SOLUTIONS

GERSTEL

AppNote 9/2000

Flavor Profiling of Different Olive Oils with Rancidity-Monitoring by Thermal Extraction GC/MS

Andreas Hoffmann, Arnd Heiden
Gerstel GmbH & Co. KG, Eberhard-Gerstel-Platz 1,
D-45473 Mülheim an der Ruhr, Germany

Key Words
Olive Oil, Flavor, Off-Flavor, Rancidity, Thermal Desorption

Abstract
Flavor is an important quality criterion for virgin olive oils. The identification of the compounds causing the flavor or off-flavor therefore is the key for quality control. Their analysis in olive oils usually requires more or less cumbersome sample preparation like liquid/liquid extraction, solid phase extraction or distillation techniques, often with the drawback of organic solvent use. Headspace and purge & trap methods do not use organic solvents, but their analyte range is restricted to the volatiles and therefore characterizes more the compounds contributing to aroma/smell of a sample, not the flavor/taste.

Direct thermal extraction of olive oil in an inert atmosphere under controlled temperature conditions can be used to easily analyze the volatile and semi-volatile compounds contributing to flavor. 10 µl of olive oil are injected into an empty glas tube and inserted into a thermal desorption unit (TDS). The TDS was ramped to 80°C with high desorption

flow, allowing the analytes to be transferred into a PTV-liner and trapped at sub-ambient temperatures (-150°C), while retaining the oil-matrix in the TDS tube. After completion of sample transfer, the PTV was ramped to 280°C, releasing the extracted compounds into a GC-MS system for subsequent analysis at very high sensitivity.

Introduction

Virgin olive oil has a delicate and unique flavor. Many volatile compounds responsible for this flavor derive from the degradation of triacylglycerols, polyunsaturated fatty acids (18:2, 18:3) or phospholipids. This complex process of chains of enzymatic reactions has been described in literature as "lipoxygenase pathway" [1]. Other compounds derive from autoxidation of fatty acids.

Morales et al. identified more than 50 compounds with dynamic headspace-GC/MS techniques and tried to determine their contribution to the flavor by means of GC-Olfactrometry [2,3].

Reiners and Grosch [4] correlated analytical results with olfactory flavor perception by determining odor thresholds of potent odorants and calculating so called odor activity values through dividing the found concentrations in their samples with the corresponding threshold values.

But there are not only compounds that contribute to the delicate flavor of virgin olive oils. A large number of volatiles can be formed during autoxidation of unsaturated acyl lipids and many of them can cause off-flavors. Pentane, pentanal, hexanal and 2,4-decadienal have been proposed as indicators since their formation runs parallel to the formation of the compounds which cause the off-flavors. Ullrich and Grosch [5] described an experimental setup to determine the most intense flavor compounds formed during autoxidation of linoleic acid (18:2). A list with aroma description is given in table I:

Table I. Volatile flavor compounds formed during autoxidation of linoleic acid and methyl-linoleate [5].

Compound	Aroma Description
Pentanal	Pungent
Hexanal	Green
1-Octen-3-one	Mushroom-metallic
2(E)-Heptenal	Fatty-soapy-fruity
1-Octen-3-ol	Mushroom
3-Octen-2-one	Spicy-fatty-nutty
2(Z)-Octenal	Fatty-fruity-slight green
2(E)-Octenal	Fatty-nutty
3(Z)-Nonenal	Green-cucumber
3(E)-Nonenal	Fatty
2(E)-Nonenal	Cucumber-tallowy
2,4-Nonadienal	Green
2(E),4(E)-Nonadienal	Fatty-soapy
2,4-Decadienal	Tallowy-fruity
2(E),4(E)-Decadienal	Deep fried

Experimental procedures, especially for sample preparation techniques like liquid/liquid extraction or distillation, so far were cumbersome and time extensive.

For quality control purposes it is therefore desirable to be able to accurately profile the compounds contributing to flavor and aroma (which can span a wide range of volatility) with an easy-to-use anlytical setup, but without sacrificing data quality.

Direct thermal extraction permits the analysis of all the described volatiles and semi-volatiles without any sample preparation. This technique is highly reproducible and sensitive, and requires no solvents.

Experimental

Instrumentation. All analyses were performed on a GC (6890, Agilent Technologies) with mass selective detection (5973, Agilent Technologies). The GC was equipped with a Thermal Desorption unit with autosampling capacity (TDS 2 & TDS A, Gerstel) and a PTV (CIS 4, Gerstel).

Sample Preparation. The olive oil was used as it is, for the rancidity test 2 ml of olive oil were given in a 10 ml headspace vial, crimped and exposed to sunlight for several days.

Operation. A glasswool plug is inserted into an empty thermal desorption tube and 10 µl olive oil is injected into that plug. The tube is than placed into the TDS A autosampler rack, where it stays sealed until analysis.

Analysis Conditions. Analytes were desorbed at 80°C for 20 minutes with a 50 mL/min gas flow and cold trapped in the CIS 4 inlet using a silanized glass wool packed liner at -150°C.

Samples were transferred to the column in the split mode (1:10) and analyzed by GC-MSD on a 50m x 0.2mm x 0.5µm HP-1 column (Agilent) except where noted in the figures.

Results and Discussion

Three different italian virgin olive oils, originating from Tuscany (T), Bardolino (B) and Liguria (L), were purchased from retail trade. Table II gives an overview of the compounds identified in at least one of the oils.

Table II. Compounds identified in three different italian virgin olive oils.

No.	RT	Compound	Odor Description	T	B	L
1	5.32	Ethanol	Alcoholic [4]	+	+	+
2	5.57	Acetone		+	+	+
3	5.80	Pentane		+	+	+
4	6.32	Butanal		-	+	-
5	6.47	2-Methyl Propenal	Malty [4]	+	+	-
6	6.84	Acetic Acid	Vinegar-like [4]	-	+	+
7	7.22	Ethyl Acetate		+	+	+
8	7.22	Hexane		+	-	+
9	7.37	2,3-Dimethylbutene		+	+	+
10	7.51	Isobutanol		+	+	+
11	7.77	2-Butenal		+	-	+
12	7.98	3-Methyl Butanal	Malty [4]	+	+	+
13	8.23	2-Methyl Butanal	Malty [4]	+	+	+
14	8.72	1-Pentene-3-ol		+	+	+
15	8.91	Pentanal	Pungent [5]	+	+	+
16	8.96	3-Pentanone		+	+	+
17	9.57	Heptane		+	+	+
18	10.07	3-Methyl-1-butanol		+	+	+
19	10.19	2-Methyl-1-butanol		+	+	+
20	10.39	trans-2-Pentenal		+	+	+
21	11.07	cis-2-Pentenol		+	+	+
22	11.88	Hexanal	Green, leaf-like [4]	+	+	+
23	12.05	Ethyl Butyrate	Cheesy, fruity [4]	+	-	+
24	12.23	Octene		+	+	+
25	12.60	Octane		+	+	+
26	12.70	2-Octene		+	-	+
27	13.18	Hexyl Methyl Ether		+	-	+
28	13.25	Methyl 3-Hexenyl Ether		+	-	-
29	13.50	2-Hexenal	Green, apple-like [4]	+	+	+
30	13.84	cis-3-Hexenol		+	+	+
31	14.16	trans-2-Hexenol		+	+	+
32	14.26	Hexanol		+	+	+

Table II (cont.). Compounds identified in three different italian virgin olive oils.

No.	RT	Compound	Odor Description	T	B	L
33	17.03	trans-2-Heptenal	Fatty, soapy, fruity [5]	+	+	+
34	17.15	Benzaldehyde		+	-	+
35	17.43	4,8-Dimethyl-1,7-nonadiene		+	+	+
36	17.97	2,3-Octanedione		+	+	+
37	18.10	6-Methyl-5-heptene-1-one		-	-	+
38	18.32	2,4-Heptadienal		+	+	+
39	18.39	Benzyl Methyl Ether		+	-	+
40	18.73	Octanal	Citrus-like [4]	+	+	+
41	18.79	2,4-Heptadienal		-	+	+
42	18.85	cis-3-Hexenyl Acetate	Banana-like [4]	+	-	+
43	19.55	Benzyl Alcohol		+	+	+
44	20.27	Limonene		-	+	-
45	20.61	trans-β-Ocimene		-	+	+
46	21.49	Guaiacol	Phenolic, burnt [4]	-	+	-
47	21.73	Citral		+	-	+
48	21.77	Methyl Benzoate		+	+	+
49	22.07	Nonanal	Citrus-like [4]	+	+	+
50	22.23	Phenyl Ethyl Alcohol		+	+	+
51	22.79	4,8-Dimethyl-1,3,7-nonatriene		+	-	+
52	23.74	Ethyl Phenol		+	+	+
53	24.15	Ethyl Benzoate		+	+	+
54	24.24	Nonanol		+	+	+
55	25.00	Methyl Salicylate		+	+	+
56	25.17	p-Vinyl Phenol		+	+	+
57	25.26	Decanal		+	+	+
58	26.86	2-Decenal		+	+	+
59	27.76	2,4-Decadienal (isomer 1)	Deep-fried [4]	+	+	+
60	28.38	2,4-Decadienal (isomer 2)	Deep-fried [4]	+	+	+
61	28.55	Methyl Anisate		+	+	+
62	30.73	p-Hydroxyphenyl Ethyl Alcohol		-	+	+
63	31.01	Cyclosativen (?)		+	+	+
64	31.11	α-Copaene or α-Cubebene		+	+	+
65	32.22	Methoxynaphthalene		+	+	+
66	33.80	α-Farnesene		+	+	+
67	34.03	α-Muurolene or α-Cadinene		+	+	+
68	34.48	Cadinene		+	+	+

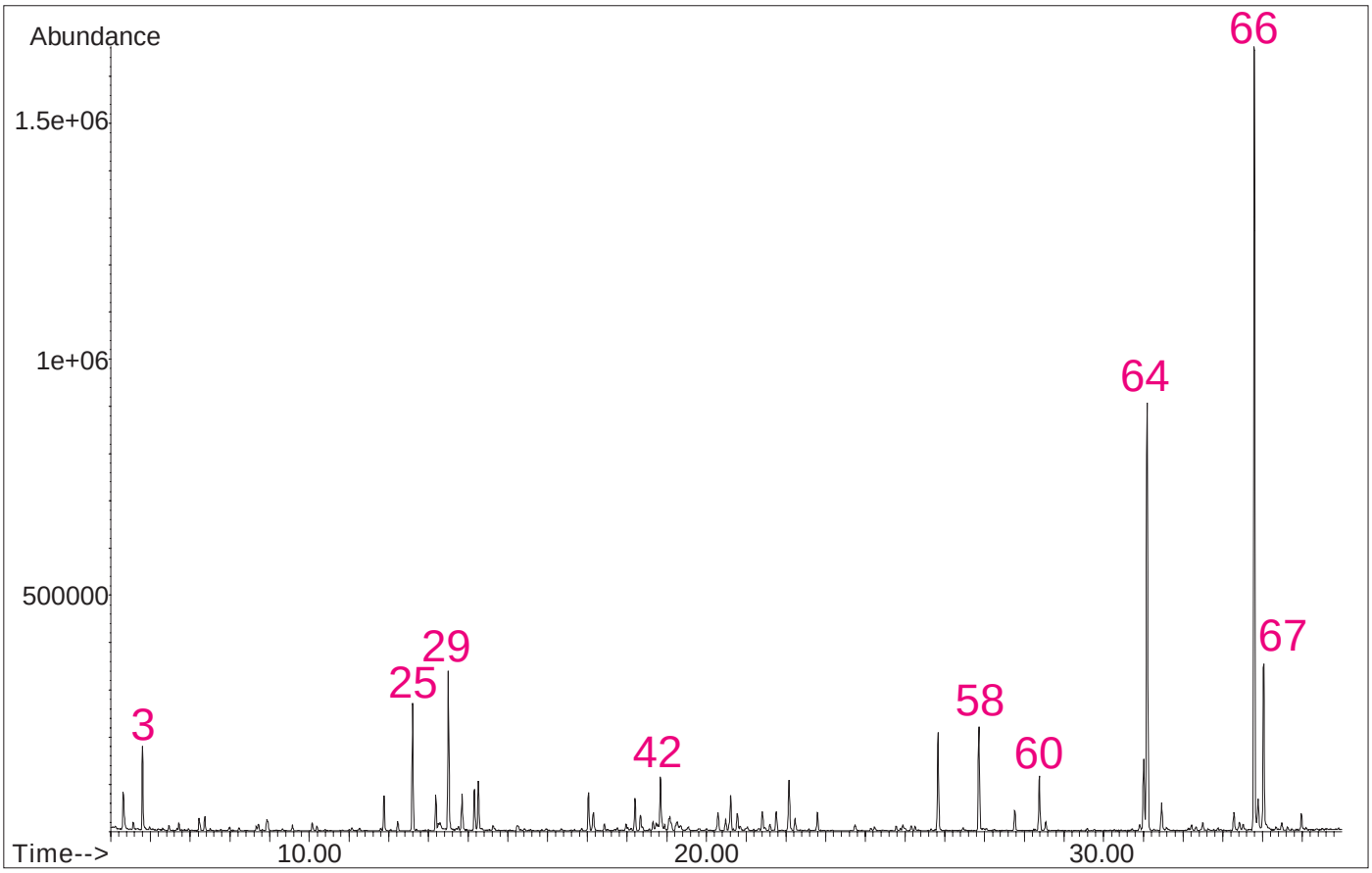

Figure 1. Thermal extraction of virgin olive oil from Tuscany, full scale, compound identification see table II.

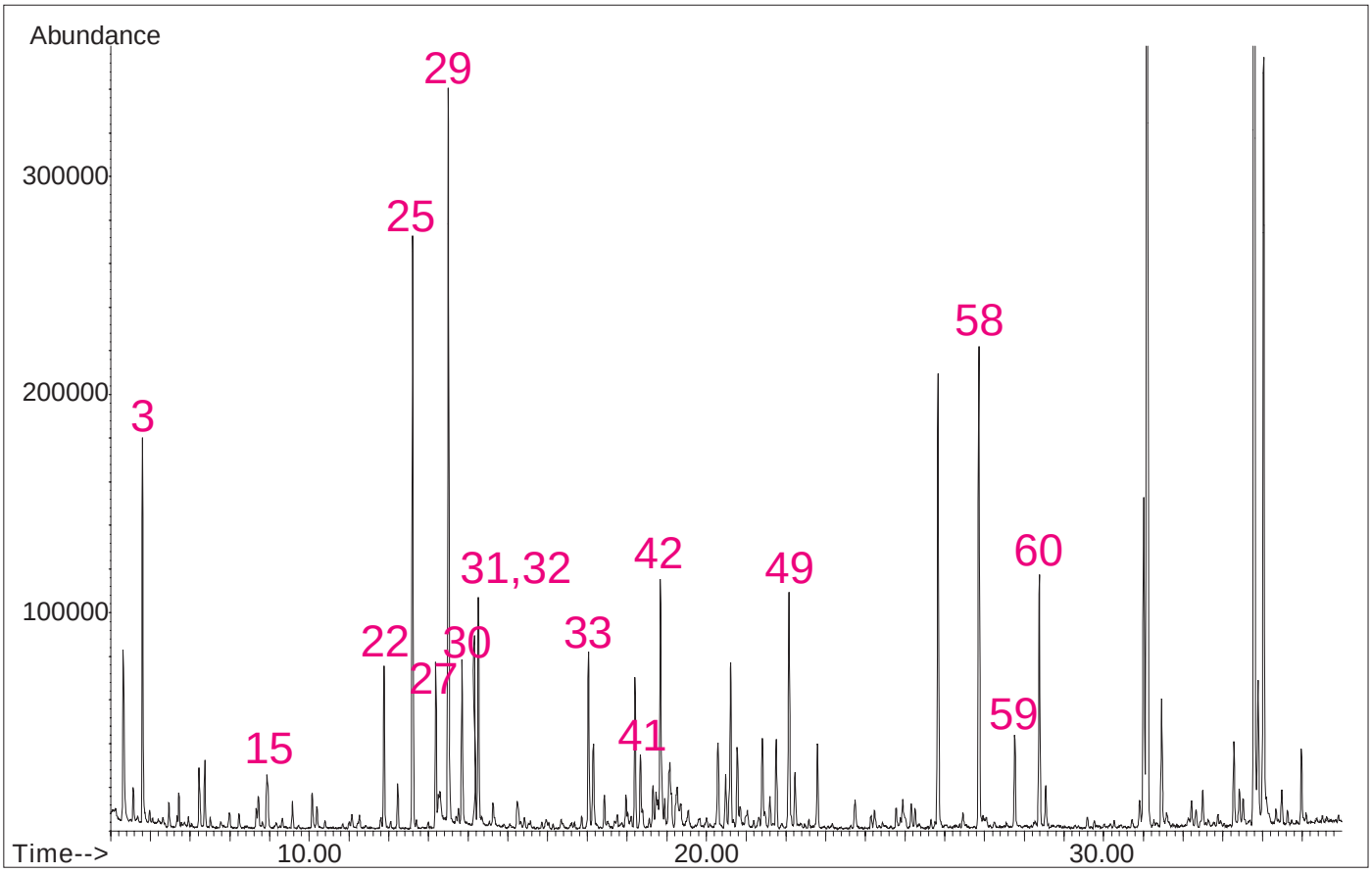

Figure 2. Thermal extraction of virgin olive oil from Tuscany, scaled, compound identification see table II.

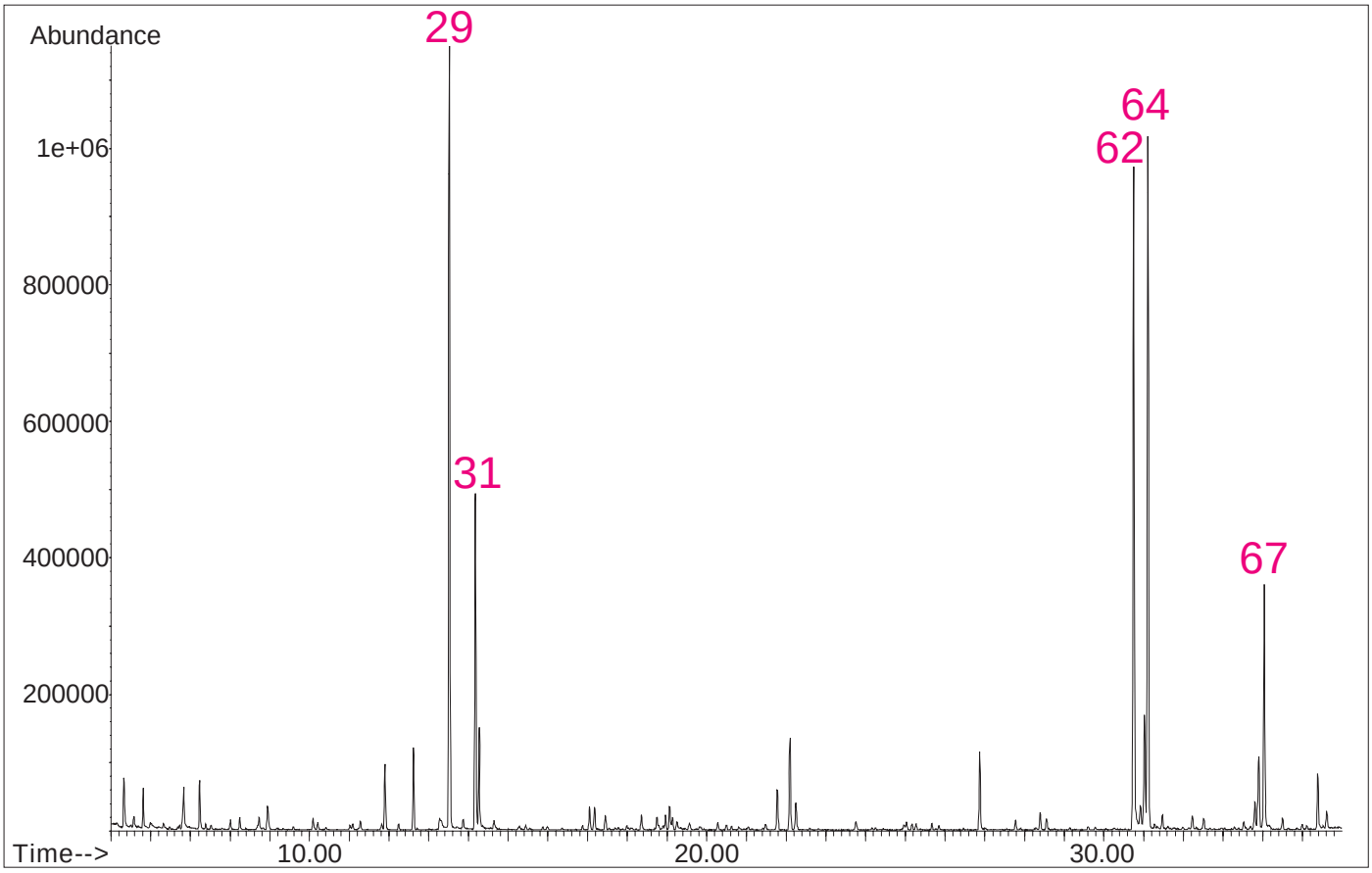

Figure 3. Thermal extraction of virgin olive oil from Bardolino, full scale, compound identification see table II.

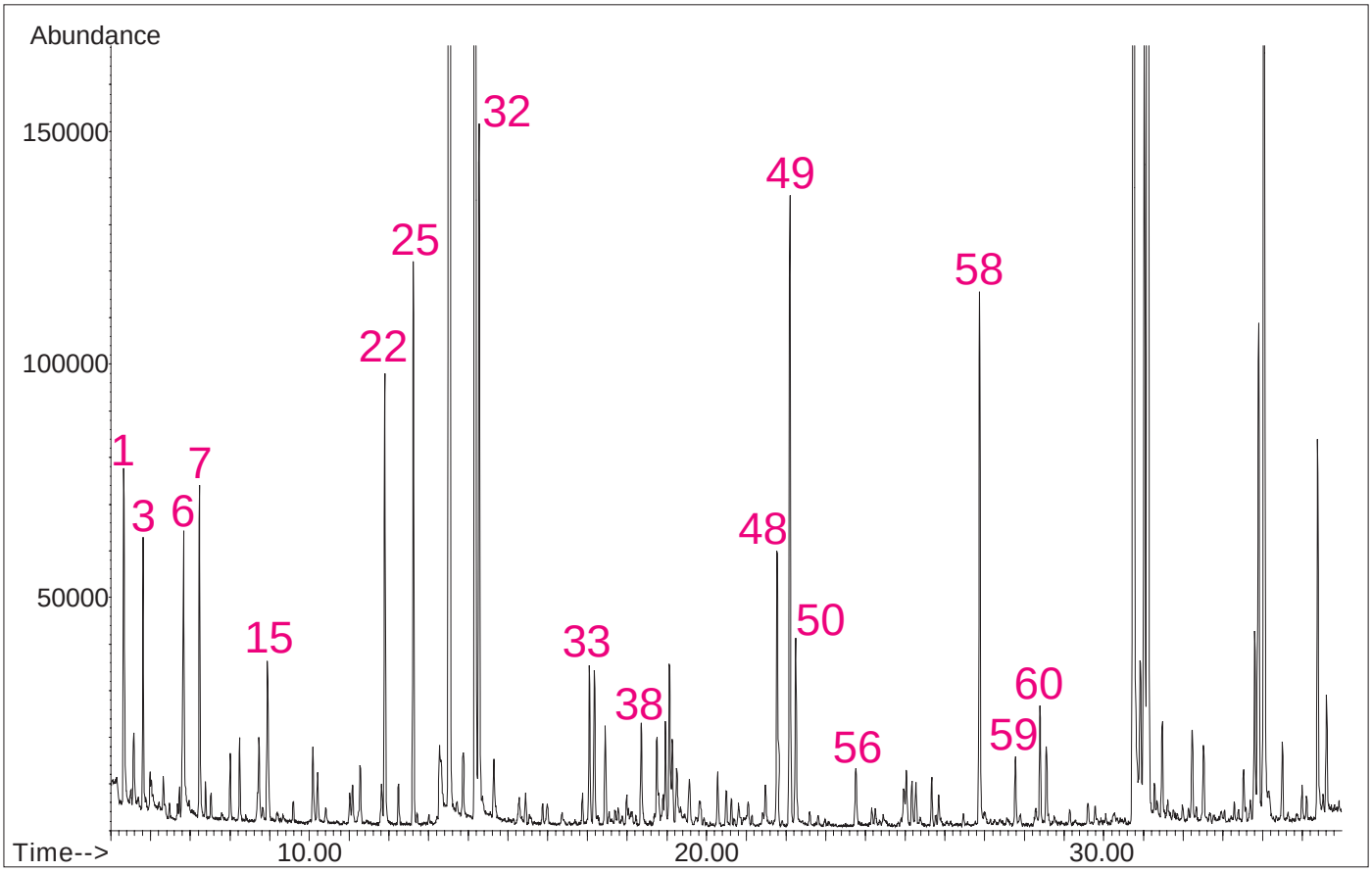

Figure 4. Thermal extraction of virgin olive oil from Bardolino, scaled, compound identification see table II.

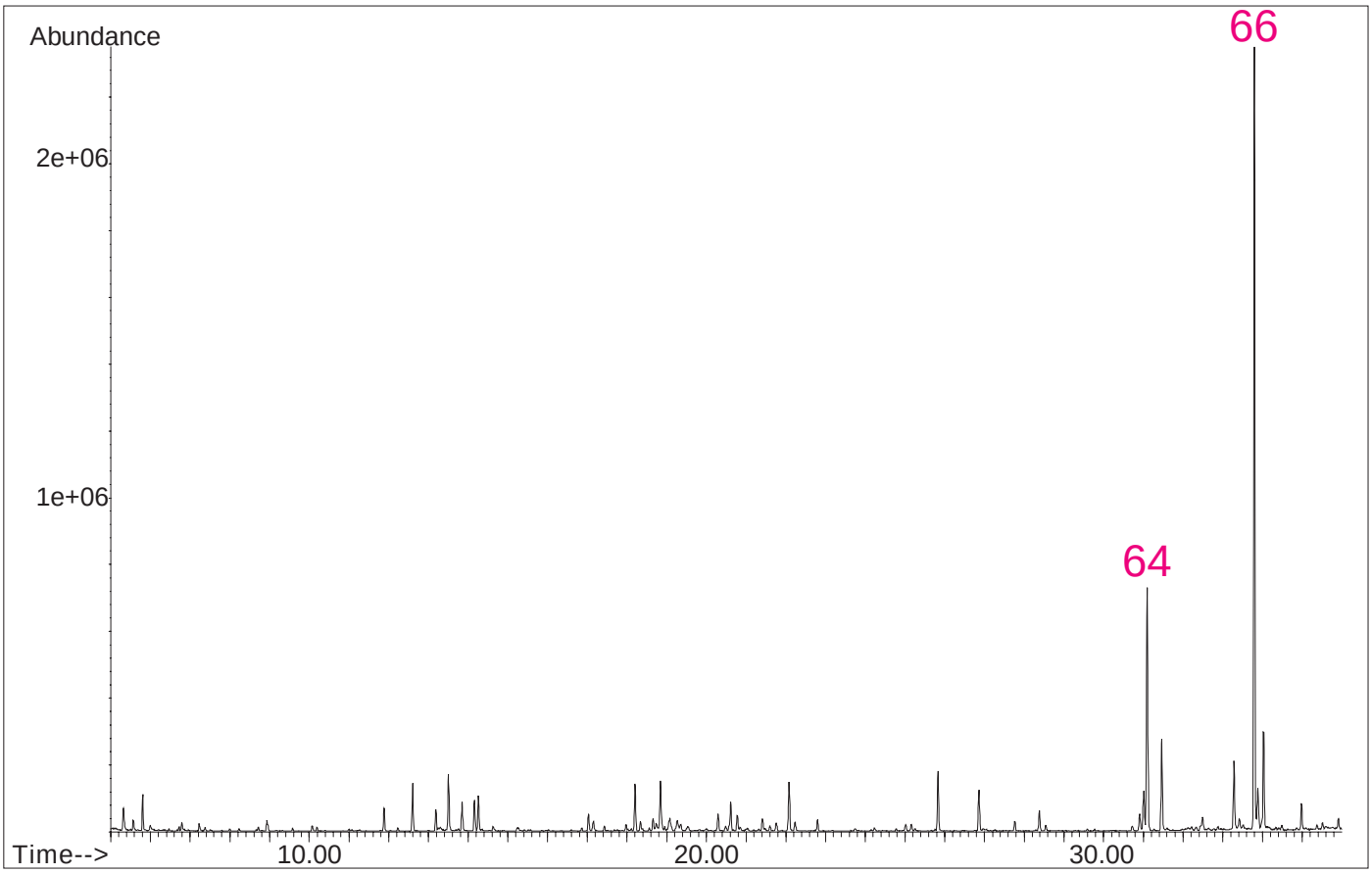

Figure 5. Thermal extraction of virgin olive oil from Liguria, full scale, compound identification see table II.

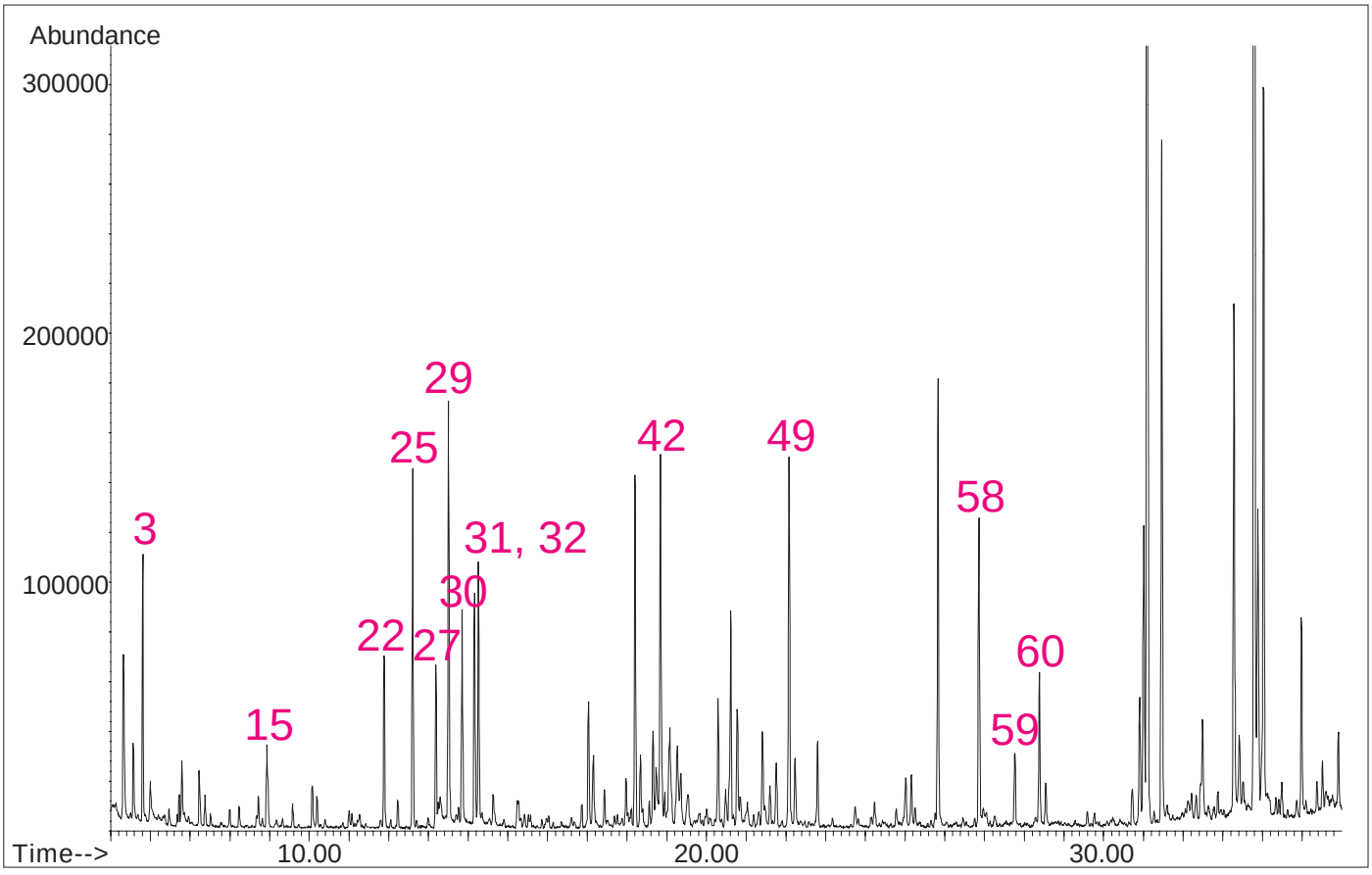

Figure 6. Thermal extraction of virgin olive oil from Liguria, scaled, compound identification see table II.

For the rancidity experiment two traces of an olive oil were compared, one before and one after exposure to sunlight. The treated oil showed a dramatic increase in volatile compounds. Table III lists the compounds identified, comparing relative peak areas of the compounds found in the fresh oil (oil A) and the treated oil (oil B). Compounds formed during autoxidation of linoleic acid (18:2) are highlighted in green, those who are believed to be the most intense flavor compounds formed [5] are highlighted in red.

Table III. Compounds identified in fresh (A) and treated (B) olive oil.

No.	RT	Compound	Oil A	Oil B
1	2.92	Acetaldehyde	85.292	745.156
2	3.20	Pentane	2.446.078	7.034.401
3	3.61	2-Butenal	94.737	2.020.621
4	4.12	Acetic Acid	1.154.322	4.170.467
5	5.03	3-Methyl Butanal	722.831	2.260.350
6	5.28	2-Methyl-2-pentene Oxide	n.d.	3.293.934
7	6.74	trans-2-Pentenal	n.d.	2.714.533
8	7.08	Hexanal	3.475.414	18.769.582
9	8.46	trans-2-Hexenal	7.509.593	3.708.439
10	8.66	2-Butanone	n.d.	2.320.097
11	8.82	trans-2-Hexenol	3.582.123	4.134.290
12	8.88	Hexanol	2.169.047	2.889.388
13	11.44	trans-2-Heptenal	488.812	10.329.825
14	12.11	1-Octene-3-ol	n.d.	5.651.395
15	12.36	6-Methyl-5-heptene-2-one	196.774	1.441.509
16	12.51	1-Pentylfuran	316.751	1.444.403
17	12.85	Octanal	452.828	3.492.780
18	14.51	trans-2-Octenal	343.116	3.438.024
19	15.89	Nonanal	1.829.626	14.397.837
20	17.53	trans-2-Nonenal	n.d.	903.777
21	18.54	2,5-Dimethyl-2,4-hexadiene	n.d.	3.346.280
22	20.40	trans-2-Decenal	1.597.890	7.018.566
23	21.30	2,4-Decadienal (isomer 1)	738.122	654.430
24	21.92	2,4-Decadienal (isomer 2)	1.389.870	879.798
25	23.15	Undecanal	192.863	1.384.870

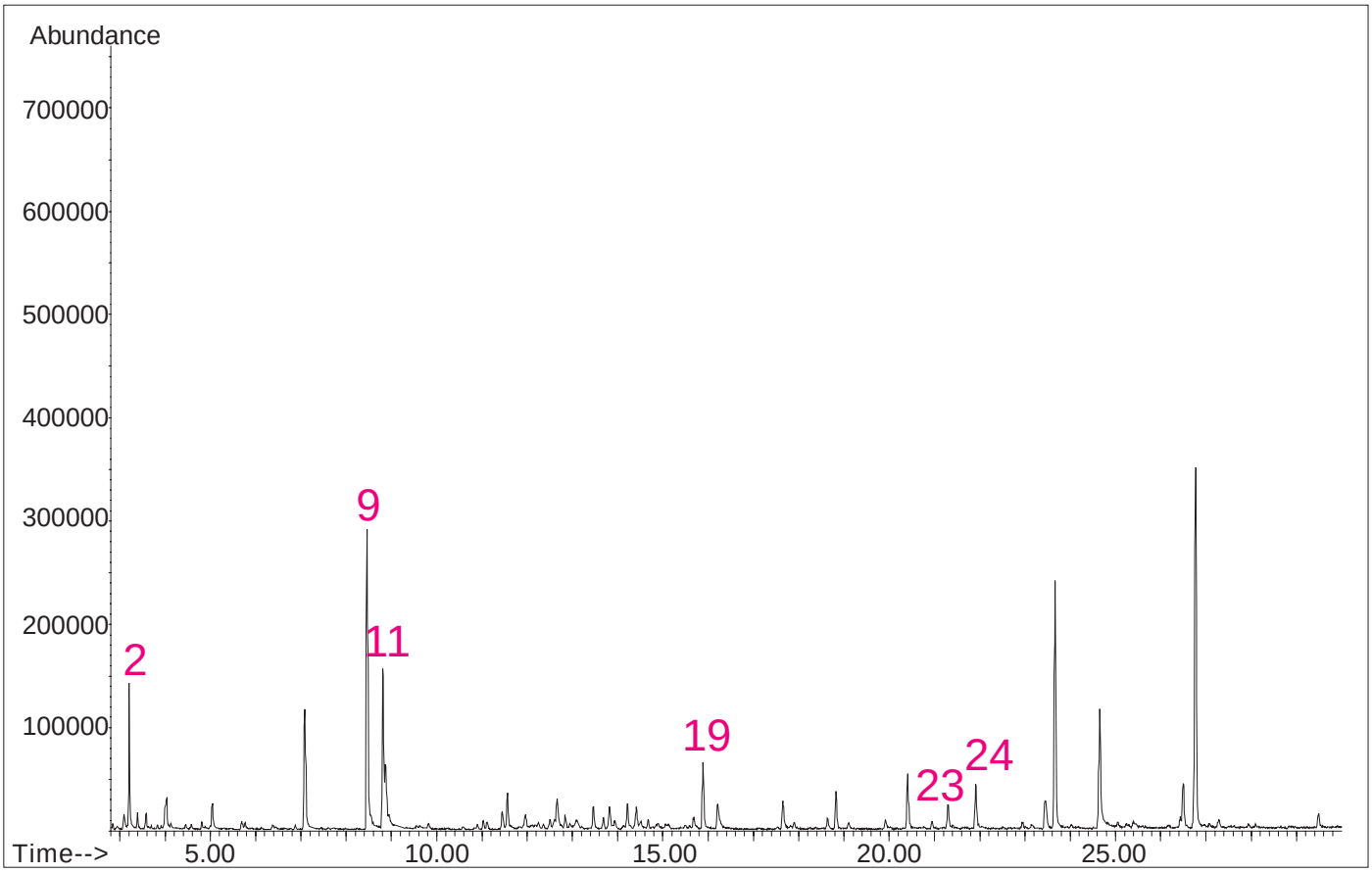

Figure 7. Thermal extraction of virgin olive oil, fresh, 30 m HP5-MS (0.25 mm x 0.25 µm), compound identification see table III.

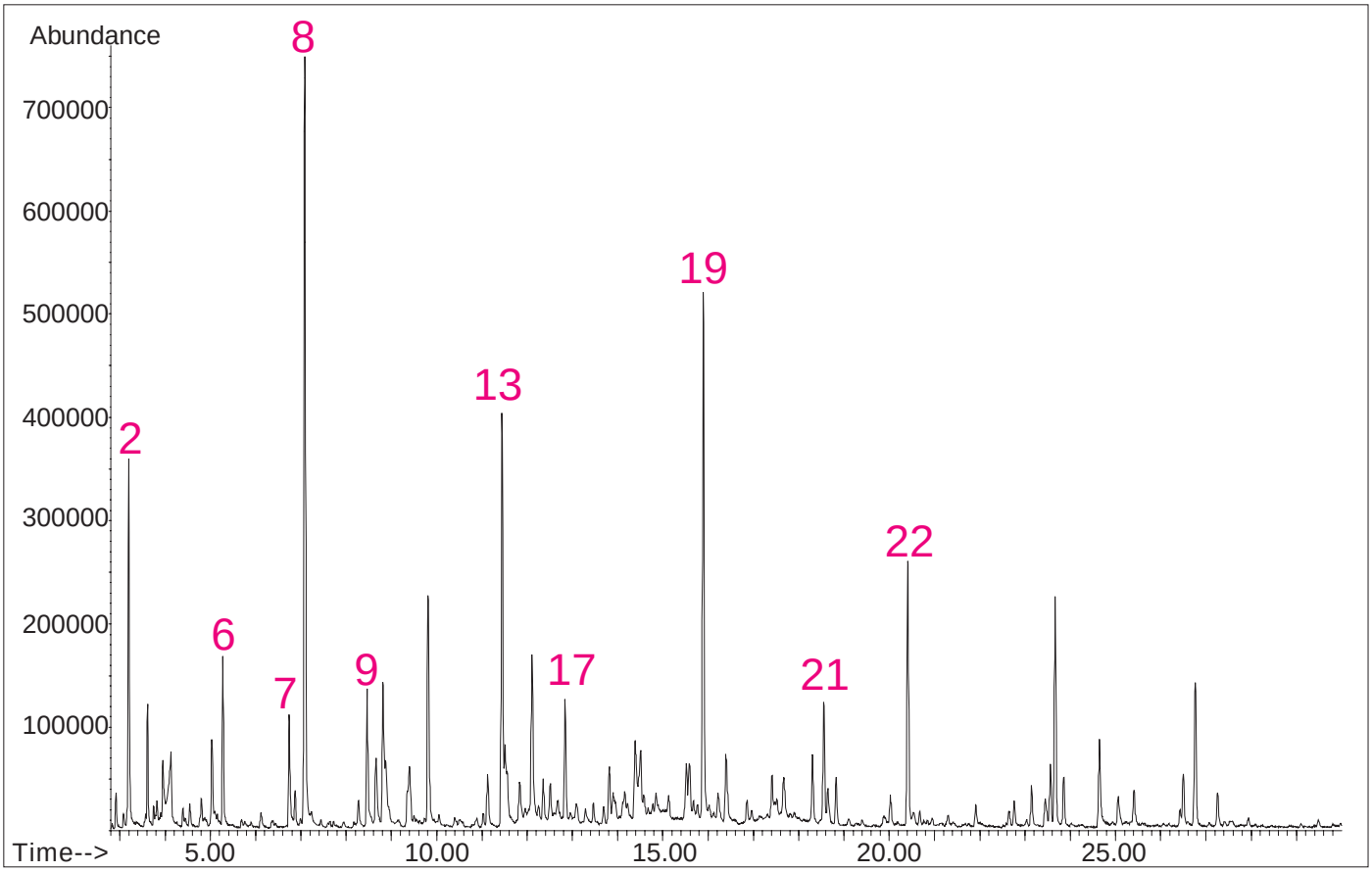

Figure 8. Thermal extraction of virgin olive oil, exposed to sunlight, 30 m HP5-MS (0.25 mm x 0.25 µm), compound identification see table III.

Conclusions

Direct thermal extraction has turned out to be an extremely powerful sample introduction-tool for the analysis of flavors and off-flavors in virgin olive oils. No sample preparation other than placing some olive oil in a thermal desorption tube is necessary, solvent extraction or distillation techniques can be totally avoided.
The entire method can be fully automated and provides high sensitivity and accuracy.

References

[1] B.A. Vick and D.C. Zimmermann, The metabolism structure and function of plant lipids, edited by P.K. Stumpf, J.B. Mudd and W.D. Nes, Plenum Press, New York and London 1987, The lipoxygenase pathway.

[2] M.T. Morales, R. Aparicio and J.J. Rios, J. Chrom. A. 1994, 668, 455-462.

[3] M.T. Morales, M.V. Alonso, J.J. Rios and R. Aparicio, J. Agric. Food Chem. 1995, 43, 2925-2931.

[4] J. Reiners and W. Grosch, J. Agric. Food Chem. 1998, 46, 2754-2763.

[5] F. Ullrich and W. Grosch, Z. Lebensm. Unters. Forsch. 1987, 184, 277-282.

GERSTEL GmbH & Co. KG
Eberhard-Gerstel-Platz 1
45473 Mülheim an der Ruhr
Germany
+49 (0) 208 - 7 65 03-0
+49 (0) 208 - 7 65 03 33
gerstel@gerstel.com
www.gerstel.com

GERSTEL Worldwide

GERSTEL, Inc.
701 Digital Drive, Suite J
Linthicum, MD 21090
USA
+1 (410) 247 5885
+1 (410) 247 5887
sales@gerstelus.com
www.gerstelus.com

GERSTEL AG
Wassergrabe 27
CH-6210 Sursee
Switzerland
+41 (41) 9 21 97 23
+41 (41) 9 21 97 25
swiss@ch.gerstel.com
www.gerstel.ch

GERSTEL K.K.
1-3-1 Nakane, Meguro-ku
Tokyo 152-0031
SMBC Toritsudai Ekimae Bldg 4F
Japan
+81 3 5731 5321
+81 3 5731 5322
info@gerstel.co.jp
www.gerstel.co.jp

GERSTEL LLP
10 Science Park Road
#02-18 The Alpha
Singapore 117684
+65 6779 0933
+65 6779 0938
SEA@gerstel.com
www.gerstel.com

GERSTEL (Shanghai) Co. Ltd
Room 206, 2F, Bldg.56
No.1000, Jinhai Road,
Pudong District
Shanghai 201206
+86 21 50 93 30 57
china@gerstel.com
www.gerstel.cn

GERSTEL Brasil
Av. Pascoal da Rocha Falcão, 367
04785-000 São Paulo - SP Brasil
+55 (11)5665-8931
+55 (11)5666-9084
gerstel-brasil@gerstel.com
www.gerstel.com.br

Awarded for the active pursuit of environmental sustainability