

Carbonyl Odorants Contributing to the In-Oven Roast Beef Top Note[†]

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Among the few papers related to the gas chromatography (GC)–olfactometric determination of important odorants in cooked beef aroma, only one uses roasting conditions, but none of them investigates the appealing aroma during the cooking of the piece of meat. The present paper investigates this top note as perceived from the oven, by analyzing the oven headspace using GC–“SNIF”, a GC–olfactometric technique. From the different functional classes of odorants participating in overall in-oven aroma, this first paper focuses only on the role of aldehydes and ketones, as they represent the majority of aroma compounds formed during cooking. To ascertain the identification of these odorants, a microderivatization technique was used, based on (2,3,4,5,6-pentafluorophenyl)hydrazine. The resulting hydrazones exhibit very specific mass spectrometric fragments, leading to a sensitive and specific detection. A total of 23 carbonyl compounds were shown to contribute to the roast beef top note.

KEYWORDS: Roast beef; aroma; aldehydes; ketones; derivatization; GC-MS; GC–olfactometry

INTRODUCTION

Beef is one of the main sources of meat consumed by humans. This explains why about 100 papers have been dedicated to the analysis of its aroma, according to the TNO compilation (1). These studies are based on a variety of different cooking modes. From these investigations, hundreds of volatile constituents have been identified, but such an abundance of data is misleading, because only a few of these compounds play a significant role in the overall aroma quality. Nevertheless, the TNO compilation still gives a list of more than 340 aroma compounds for roast and grilled beef volatiles. In recent papers, the determination of the most important aroma contributors has been performed by gas chromatography–olfactometry (GC–O) in stewed and boiled beef (2–7) and in roasted and fried beef (8–10) as well as in the warmed-over flavor of reheated beef (11) (Table 1).

The present work intends to investigate the top note of the roast beef, as perceived when the piece of meat is roasting in a traditional oven. This note is very typical of such a cooking process, and it imparts the major appealing character of roast beef, first in the kitchen, but also when the meat is served. As the choice of culinary additives is highly dependent on local/national preferences, and because they would modify the headspace composition, the meat was cooked without any ingredients such as salt, oil, or herbs, so as to determine only

odorants originating from the beef meat itself. Only the work by Cerny et al. is close to these conditions, but with some significant differences (9):

- Small beef cubes were fried in a pan (initial temperature: 250 °C), instead of the whole piece of beef being roasted in an oven (200 °C).
- Peanut oil was added, whereas cooking without any additive was targeted here. Some impact odorants were suspected to originate from the heated oil.
- The chilled meat was solvent extracted, which could lead to a loss of top note constituents upon solvent removal. In addition, extracting the aroma from the whole meat was a different objective from that of the present work, the aim of which was to elucidate the in-oven top note.

Therefore, the analysis of the top note released in the air during roasting was undertaken using in-oven conditions. As aldehydes and ketones represent the major functional classes contributing to the overall fried beef aroma (8), this first paper focuses only on the role of carbonyl compounds in the aroma top note of roast beef, using a specific microderivatization technique. The identification of other odorants, such as sulfur compounds, that were perceived in the course of the same GC–O experiment, will be reported in a separate paper, as they occur in much lower amount than carbonyl derivatives and require a different approach.

Almost all previous GC–O analyses have been based on dilution (or concentration) techniques, with two exceptions: One involved a mixed technique combining perceived intensities and stimuli duration (3), and the other used odor detection frequencies (10). Because the latter method, often referred to as GC–

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[†] Dedicated to Dr. F. Naef on the occasion of his 65th birthday.

Table 1. Aldehydes and Ketones Contributing to the Beef Aroma after Different Cooking Procedures According to the Literature Based on GC-O Analyses (References in the Text)^a

aldehydes	ketones
acetaldehyde	
hexanal	2-butanone
2-methylbutanal	2-heptanone
3-methylbutanal	2-octanone
heptanal	3-octanone
octanal	2-nonanone
nonanal	2-decanone
decanal	2-undecanone
undecanal	2-dodecanone
12-methyltridecanal	2-tridecanone
(<i>E</i>)-2-hexenal	1-octen-3-one^b
(<i>E</i>)-2-heptenal (?)	(<i>Z</i>)-1,5-octadien-3-one
(<i>E</i>)-2-octenal	4-methyl-3-penten-2-one
(<i>Z</i>)-2-octenal	2,3-butanedione
(<i>E</i>)-2-nonenal^b	2,3-pentanedione
(<i>Z</i>)-2-nonenal	β -ionone
(<i>E</i>)-2-decenal	
(<i>E</i>)-2-undecenal	
(<i>E</i>)-2-dodecenal	
(<i>E,E</i>)-2,4-nonadienal	
(<i>E,Z</i>)-2,6-nonadienal	
(<i>E,E</i>)-2,4-decadienal^b	
(<i>E,Z</i>)-2,4-decadienal	
phenylacetaldehyde	
<i>trans</i> -4,5-epoxy-(<i>E</i>)-2-decenal	

^a Compounds specifically found in roast beef are in bold. Non-carbonyl odorants are not compiled in this list. ^b Possibly due to the heating of hydrogenated peanut oil, according to Cerny et al. (9).

“SNIF”, has been investigated for its reproducibility and quantitative performances (12, 13), it was chosen for the present study.

MATERIALS AND METHODS

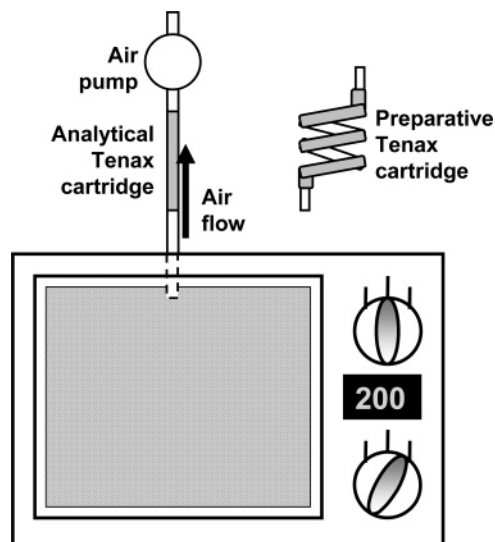
Materials. The meat (sirloin beef, from a Swiss breeding origin) was purchased from Aligro supermarket (Geneva, Switzerland). (2,3,4,5,6-Pentafluorophenyl)hydrazine was supplied by Acros Organics (Geel, Belgium). Aldehydes and ketones were purchased from Aldrich, Fluka (Buchs, Switzerland) or Acros, except undecanal, 12-methyltridecanal, (*E,E*)-2,4-nonadienal, 1-nonen-3-one, β -ionone (Firmenich), (*E*)-2-undecanal (TCI, Tokyo, Japan), (*E*)-2-tridecanal, (*E*)-2-tetradecanal, (*E,E*)-2,4-octadienal (Bedoukian, Danbury, CT), (*E,E*)-2,4-undecadienal (Avocado, Heysham, U.K.), and 1-octen-3-one (Interchim, Montluçon, France). *trans*-4,5-Epoxy-(*E*)-2-decenal was prepared according to the method of Schieberle and Grosch (14).

Cooking. In a typical experiment, the piece of beef (~500 g) was put into a domestic electric oven that was previously heated at 200 °C. No ingredient was added to the meat (no salt, no oil). The roasting was pursued until the temperature in the middle of the meat reached a temperature of 65–70 °C.

Headspace (HS) Trapping for GC-O. A tube was introduced into the upper wall of the oven and connected in series to a standard analytical Tenax cartridge and an air pump (KNF, Balterswil, Switzerland). After 15–20 min, when the inner meat temperature had reached 45 °C, the air pump was started to continuously extract the headspace containing the aroma from the oven at a 70 mL/min air flow (Figure 1).

For GC-O analyses, standard Tenax cartridges were used (6.35 × 8.9 mm tubes containing 100 mg of Tenax). Each cartridge was connected in series between the oven exit and the pump for 2 min, under a flow of 70 mL/min (Figure 1). Three cartridges were used successively.

Large-Scale Headspace Trapping. For the large-scale trapping of volatiles, 3 g of Tenax was packed in a coil cartridge (Figure 1), which was connected between the oven and the air pump for the whole roasting

**Figure 1.** Scheme of headspace collection during beef roasting.

duration (i.e., from an inner temperature of 45 °C up to 65–70 °C within 15–17 min), under a flow of 100–120 mL/min.

After the roasting, the preparative cartridge containing volatiles and some humidity was removed from the oven outlet and installed in the oven of a gas chromatograph to desorb the trapped compounds using a flow of helium (~13 mL/min) in backflush mode. The trap outlet was connected to a Silcosteel capillary (20 cm × 0.53 mm, Restek, Anwil, Switzerland), itself connected to a cold trap (0 °C) outside the chromatograph. The oven was programmed from 40 °C (10 min) to 250 °C at 4 °C/min. A solid-phase microextraction fiber (SPME) fiber (PDMS/DVB, 65 μ m, Supelco, Buchs, Switzerland) was exposed for 30 min to the headspace of the resulting condensate (~300–350 μ L) in a closed vial (2 mL), under magnetic stirring. Immediately after the headspace (HS) sampling, the fiber was desorbed in the injector of the GC (250 °C, 5 min) and analyzed according to the conditions described hereafter.

GC-Mass Spectrometry–O (GC-MS-O). The Tenax trap was simultaneously analyzed by GC-MS and GC-O using the GC-MS–multisniffing hardware previously described (15). Volatiles were desorbed from Tenax (250 °C, 5 min) using an ATD400 thermal desorber (Perkin-Elmer, Norwalk, CT). They were refocused in an internal Tenax cold trap (–30 °C) and desorbed at 220 °C for 2 min. Helium was used as carrier gas at a pressure of 10.9 psi. The gas chromatograph was equipped with a Supelcowax 10 column (60 m length, 0.53 mm i.d., 1.0 μ m phase thickness). The column was kept for 2 min at 40 °C, increased at 4 °C/min to 240 °C, and maintained for 20 min. MS conditions were identical to those of Debonneville et al. (15).

Raw GC-O data were treated according to the GC-SNIF method, with the appropriate plug-in of the Galaxie software (Varian-JMBS, Fontaine, France) (15). Nine panelists per GC-O session were asked to use a free vocabulary to describe odors perceived at the sniff-port. Sensory descriptors from the olfactogram peaks were compared to our descriptor databanks built from authentic samples and to literature data (Table 3).

Derivatization of Carbonyl Compounds. The sample used was obtained as described under Large-Scale Headspace Trapping. Prior to being exposed to the beef condensate, the SPME fiber was exposed for 30 min to the headspace of 10 mL of an aqueous solution of (2,3,4,5,6-pentafluorophenyl)hydrazine (0.795 g/L).

The preparation of (2,3,4,5,6-pentafluorophenyl)hydrazones from authentic carbonyl compounds was achieved according to the procedure described by Stashenko et al. (16) and using aqueous solutions containing 0.60 mg/L of carbonyls. As >96% of conversion into the hydrazone was observed when 11 aliphatic aldehydes were derivatized at the same time (C-4 to C-14, 0.6 mg/L of each), the reagent loaded on the fiber was in a sufficient excess for the analysis of the roast beef condensate. In this sample, the amount of carbonyl compounds was much lower according to GC peak areas.

Table 2. Carbonyl Compounds Identified in the Roast Beef Headspace

aldehydes/ketones	SPME ^a		SPME + PFPH ^b		ref	first olfactogram			second olfactogram			aroma contribution ? (this work)
	polar	polar	nonpolar	KI ^c	KI ^d	found ^e	NIF ^f (%)	KI ^d	found ^e	NIF ^f (%)		
ethanal	–	+	+	712	728	?	21.4		–			+ ^g
propanal	–	+	–?	826	828	?	74.3	827	+	21.3		+
2-methylpropanal	–	–	+	814		–			–			–
butanal	–	+	+	895	895	+	28.4					+
2-methylbutanal	–	–	+	926		–		925	? ^h	10.7		–
3-methylbutanal	–	–	+	932	933	+	41.3	936	+	36.6		+
pentanal	+	+	+	1004		–	70.6	1011	+	10.7		–
hexanal	+	+	+	1114	1108	+	41.6	1105	+	53.1		+
heptanal	+	+	+	1215	1211	+	53.1	1219	+	30.3		+
octanal	+	+	+	1317	1314	+	32.1	1312	+	32		+
nonanal	+	+	+	1420	1418	+	85	1417	+	53.1		+
decanal	+	+	+	1525	1521	+	63.7	1524	+	53.1		+
undecanal	+	+	+	1634	1634	+	53.3	1630	+	21		+
dodecanal	–	+	+	1738		–			–			–
tridecanal	–	+	–	1844		–			– ⁱ			–
12-methyltridecanal	–	–	–	1883	1889	?		1884	?	10.7		?
tetradecanal	–	+	–	1948		–		1947	+	10.7		+
(E)-2-propenal	–	+	+	852		–			–			–
(E)-2-butenal	–	+	+	1082		?		1083	?	10.7		–
(E)-2-pentenal	+	+	–	1173		–		1174	–	10.8		–
(E)-2-hexenal	+	+	–	1259	1264	+	31.9	1263	+ ^j	42.6		+
(E)-2-heptenal	+	+	+	1362	1366	+	15	1361	?	21.3		+
(E)-2-octenal	+	–	+	1467	1468	+	70.2	1463	+	45.8		+
(E)-2-nonenal	+	–	+	1573	1572	+	80.4	1572	+	63.8		+
(E)-2-decenal	+	–	+	1682	1673	+	47.7	1674	+	21.3		+
(E)-2-undecenal	+	–	+	1789		–		1790	+	21.2		–
(E)-2-dodecenal	+	–	–	1889	1889	?	21.2	1901	?	21.3		–
(E)-2-tridecenal	?	–	–	1982		–		1983	?	10.8		–
(E)-2-tetradecenal	–	–	–	2098		–			–			–
(E,E)-2,4-hexadienal	–	–	–	1441		–		1443	–	32		–?
(E,E)-2,4-heptadienal	+	–	–	1530	1526	?	36.6	1524	?	53.1		+
(E,E)-2,4-octadienal	+	–	–	1632	1634	?	53.3	1630	?	21		+? ^k
(E,E)-2,4-nonadienal	+	–	–	1741	1747	+	74.4	1744	+	39		+
(E,E)-2,4-decadienal	+	–	–	1850	1855	+	50.5		–			+
(E,E)-2,4-undecadienal	+	–	–	1958		–			–			–
2-propanone	–	+	+	827	828	?	74.3	827	?	21.3		?
2-butanone	–	–	–?	920		–			–			–
2-pentanone	–	–	+	1015		–		1018	?	10.7		–
2-hexanone	–	–	+	1150		–		1153	?	21.4		–
2-heptanone	+	–	?	1206	1205	+	31.8	1205	+	10.7		+
2-octanone	+	–	+	1313		+		1307	+	42.6		?
2-nonanone	+	–	+	1415		+		1405	+	31.8		–
2-decanone	+	–	+	1519		+		1515	+	10.6		–
2-undecanone	+	–	+	1626		–			–			–
2-dodecanone	+	–	+	1731		–			–			–
2-tridecanone	+	–	+	1836		–			–			–
3-octanone	+			1280	1277	?	21.3	1277	?	21.4		–
1-octen-3-one	?			1324	1328	+	74.3	1324	+	36.1		+
1-nonen-3-one				1427	1430	+	84.9	1428	+	53.2		+
(Z)-1,5-octadien-3-one	?			1402		–			–			–
2,3-butanedione	?			996	994	+	70.6	995	+	84.9		+
2,3-pentanedione	?			1093		–		1094	?	21.3		–
phenylacetaldehyde	–	–	+	1689	1692	+	74.3	1696	+	33.8		+
β-ionone	?			1986		–		1983	?	10.8		–

^a HS-SPME analysis of the roasting condensate. ^b HS-SPME analysis of the condensate after PFPH derivatization. ^c Retention indices of authentic compounds with the ATD400/GC/MS system (Supelcowax 10). ^d Retention indices of odorants in the beef olfactogram (Supelcowax 10). ^e Identified in the Saturn-MS trace. ^f NIF units are the detection frequencies of GC-O peaks (*f*). ^g Nonquantitatively trapped on Tenax. ^h Panelists did not generate any descriptor. ⁱ Descriptors indicate a butyric-like odor. ^j Coeluted with an unknown compound. ^k Coeluted with undecanal.

GC-MS Analysis of Large-Scale HS Trapping. SPME analyses were performed with a HP 6890 gas chromatograph (Agilent Technologies, Wilmington, DE). The column outlet was directly coupled to the EI source of a HP 5973 mass spectrometer (Agilent Technologies). The injector and MS source temperatures were 250 and 230 °C, respectively. Two different columns were used:

A Supelcowax 10 (Supelco), 30 m length, 0.25 mm i.d., 0.25 μm phase thickness, was kept at 60 °C for 5 min, increased at a 4 °C/min rate to 220 °C, and maintained at 220 °C for 18 min. Helium was used as carrier gas at a flow of 1.3 mL/min.

A SPB1 (Supelco), 30 m length, 0.25 mm i.d., 0.25 μm phase thickness, was kept at 60 °C for 2 min, increased at a 5 °C/min rate to

220 °C, and maintained at 220 °C for 23 min. Helium was used as carrier gas at a flow of 1.0 mL/min.

In both cases, the injector was maintained in splitless mode for 2 min for SPME desorption.

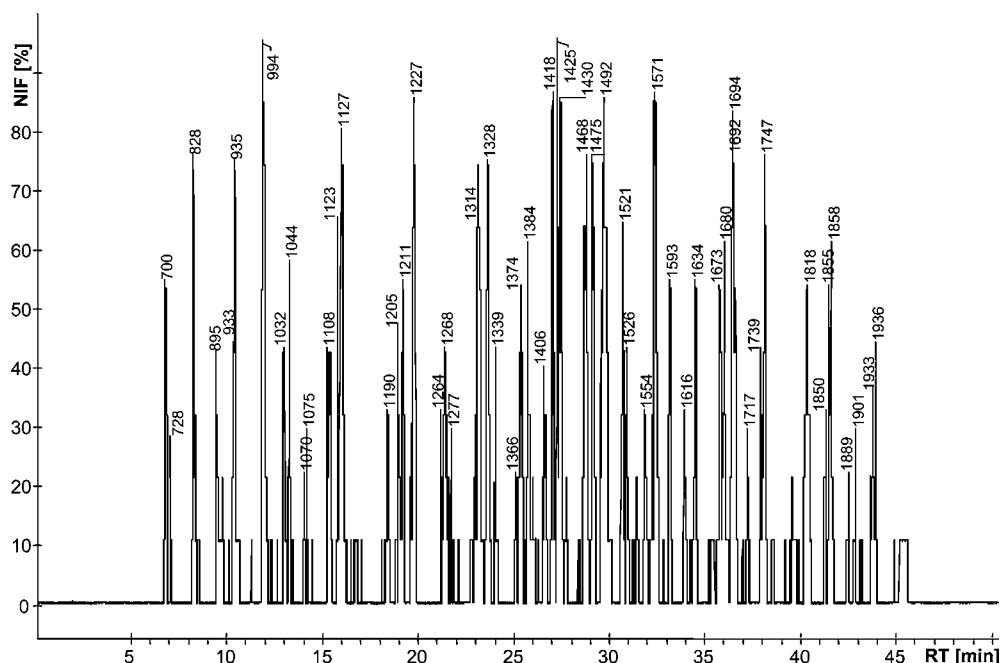
RESULTS AND DISCUSSION

Roast Beef Olfactogram. To best fit the usual roasting conditions of beef, the piece of meat was cooked in a domestic oven. Roasting conditions were determined by a professional cook to ensure a high palatability of the resulting roast beef. This was then tasted by a panel (six assessors experienced in

Table 3. Odor Descriptors (Free Vocabulary) of Carbonyl Odorants Detected in the Roast Beef Headspace (First Olfactogram, **Table 2**), and Comparison with Literature Data

aldehydes/ketones	KI	odor descriptors ^a	literature descriptors
ethanal	728	grilled (weak), acetaldehyde-like	diluted: reminiscent of coffee or wine; pungent, fruity; pungent, ether (26–28)
propanal	828	caramel, sweet (2), alcoholic, “cooked”, broth, spicy, earthy, mud	diluted: roasted coffee; solvent-like, solvent, pungent (26–28)
butanal	895	smoky, fish, amylic, aldehyde-enal or dienal	diluted: banana, green-fresh; pungent, green; pungent, green (26–28)
3-methyl butanal	933	bad, meaty, fish, rotten, aldehyde (2), valeric acid, fatty	unpleasant, sour, repulsive; diluted: banana, overripe; malty, malt (26–28)
hexanal	1108	green, fresh grass, aldehyde, hexanal	fatty-green, grassy, tallowy, leaf-like, grass, tallow, fat (26–28)
?	1123	sour, hot plastic, flowery, green, fatty, alcoholic, fruity	
heptanal	1211	aldehyde, green	oily-fatty, rancid, almost fruity if diluted; fatty, fat, citrus, rancid; green, fatty, oily (4, 26–28)
limonene + unknown	1227	irritant, green (2), heavy, tea, fatty, geranium (2), salty, dienal, pungent, spicy, rosy	
octanal	1314	green, lemon, citrus, aldehyde	diluted: sweet, orange-, honey-like, slightly fatty; fatty, fat, soap, lemon, green (26–28)
nonanal	1418	sea, aldehyde, citrus, green, citronella grass	fatty-floral, waxy; diluted: floral-waxy, rosy, sweet; tallowy, fruity; fat, citrus, green (26–28)
decanal	1521	fatty, rancid, meaty, burnt, tobacco, aldehyde, green overcooked	sweet-waxy, orange peel; diluted: citrus peel; orange skin, flowery; soap, orange peel, tallow (26–28)
undecanal	1634	mild, alcoholic, floral, green (2), lemon, aldehyde, sea	waxy-floral, refreshing, fruity; diluted: citrus (26); oil, pungent, sweet (28)
12-methyltridecanal ?	1889	no descriptor	tallowy, sweaty (27)
(E)-2-octenal	1468	aldehyde, green, floral, dienal (2), fatty (2), cardboard, aldehyde, amine	fatty, nutty (27). green, nut, fat (28)
?	1475	fatty, burnt meat, walnut, burnt, earthy, bad, hot oil	
(E)-2-nonenal	1572	paper, fatty (2), iris, nauseating, aldehyde, dienal, wood, nutty, nonylenic aldehyde	diluted: orris, waxy, slightly green. tallowy, cucumber; paper (26–28)
(E)-2-decenal	1680	green, fat	waxy-orange, sweet-aldehydic (26); tallow (28). pungent, green, sweet, fruity, fatty (8)
(E,E)-2,4-heptadienal	1526	aldehyde, green, broth, spicy	fatty; nut, fat (27, 28)
?	1616	hot oil, metallic, floral, aldehyde, orange	
(E,E)-2,4-octadienal	1634	mild, alcoholic, floral, green (2), lemon, aldehyde, sea	green-vegetable, grassy (26); green, seaweed, cucumber (28)
?	1673	green (2), aggressive, aldehyde (2), cardamon, decenal, strong, sea	
(E,E)-2,4-nonadienal	1747	dienal-enal, aldehyde, pan, swatted bug, insect, fatty, bad, rancid	green-vegetable; diluted: cucumber, violet leaf; fatty; fat, wax, green (26–28)
(E,E)-2,4-decadienal	1855	plastic, tailing odor	fatty-green, orange; deep-fried; fried, wax, fat (26–28)
2-heptanone	1205	citrus, grapefruit, limonene, floral, cheese	soapy, fruity (27); soap (28)
2-octanone	1314	(coeluted with octanal ?)	soap, gasoline (28)
1-octen-3-one	1328	old water, mushroom (3), cellar	mushroom, metallic (27); mushroom, metal (28)
1-nonen-3-one	1430	mushroom	pungent, mushroom (28)
2,3-butanedione	994	diacetyl, butter (7)	buttery (27); butter (28)

^a Numbers in parentheses indicate the number of panelists who gave the same descriptor.

**Figure 2.** Roast beef olfactogram (corresponding to the first experiment in **Table 2**).

cooking and/or flavors) and considered as being a typical roast beef flavor, with an appealing aroma and taste. The headspace

was extracted from the oven through a Tenax trap. Three traps were successively used during the roasting process to perform

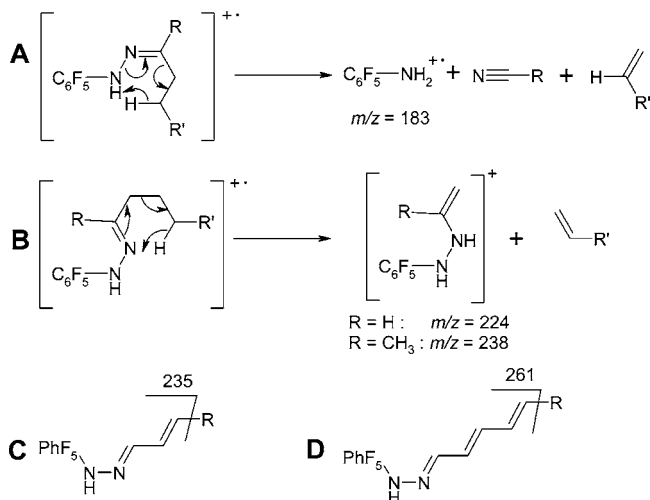


Figure 3. Characteristic MS fragments of hydrazones under electron impact: (A) all carbonyls; (B) aliphatic aldehydes and methyl ketones; (C) 2-enals; (D) 2,4-dienals.

a GC-O analysis by the whole panel (**Figure 2**) according to the GC-SNIF technique (12) and using the multisniffing port previously developed (15). Only aldehydes and ketones are listed in **Table 2**, according to the objective of the present work, whereas the investigation of N- and S-containing constituents will be reported in a subsequent paper.

A significant variability of the olfactogram was found between two repetitions of beef roasting from different pieces

of meat despite the same cooking conditions (**Table 2**). Aroma contributors remained the same, but intensity differences occurred in terms of panel detection frequency [NIF (12)]. The missing odorants in one aromagram mostly corresponded to a low detection frequency in the other aromagram. As these differences are larger than the normal variability of the GC-SNIF technique [± 1 panelist (12)], they are most likely due to the meat composition differences from one animal to another and to the repeatability of the cooking. Many parameters have been said to influence the final meat aroma of beef, such as differences in the animal feeding (3), in the animal breed and meat aging (17), and in the cooking temperature (18, 19).

Large-Scale HS Sampling. Due to the great number of aldehydes and ketones that have been reported to be important odorants of the cooked meat aroma, particularly for fried and roast beef (8, 9), carbonyl compounds were specifically investigated. Some of them were clearly identified by the MS detection that was simultaneously performed with the GC-O analysis. Many others were either below the detection threshold of the MS or hidden by more abundant volatiles. Therefore, a large-scale headspace trapping was performed during the whole roasting time (details under Materials and Methods). The aroma was recovered from the resulting aqueous solution using two methods: headspace sampling with a SPME fiber or headspace sampling with a SPME fiber previously saturated with a derivatization reagent

Derivatization. Recent derivatizations of aldehydes use *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine oximes (PFBO) (20, 21) or (2,3,4,5,6-pentafluorophenyl)hydrazine (PFPH) (22).

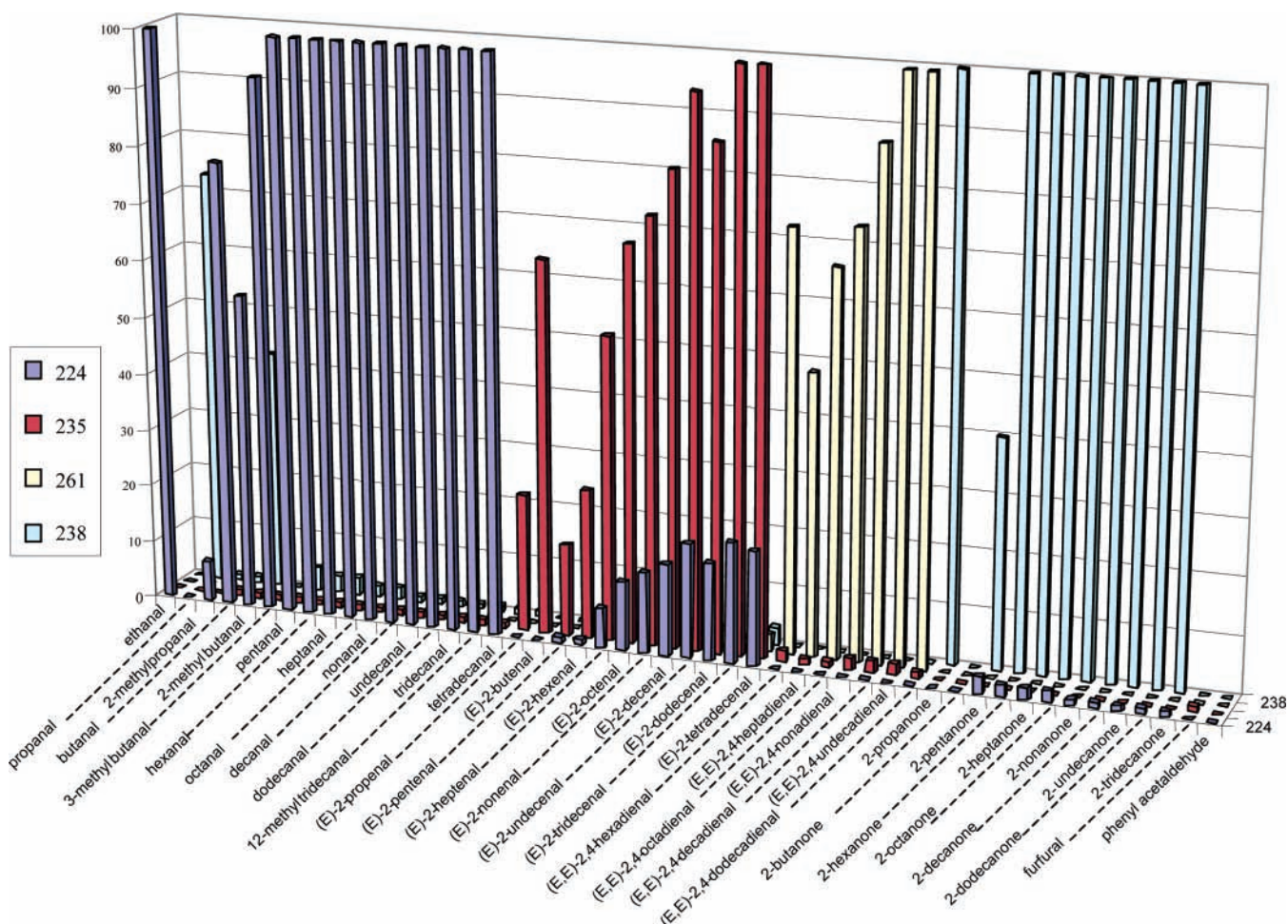


Figure 4. Specific fragments of aldehyde and methyl ketone hydrazones (*m/z* 224, 238, 235, and 261).

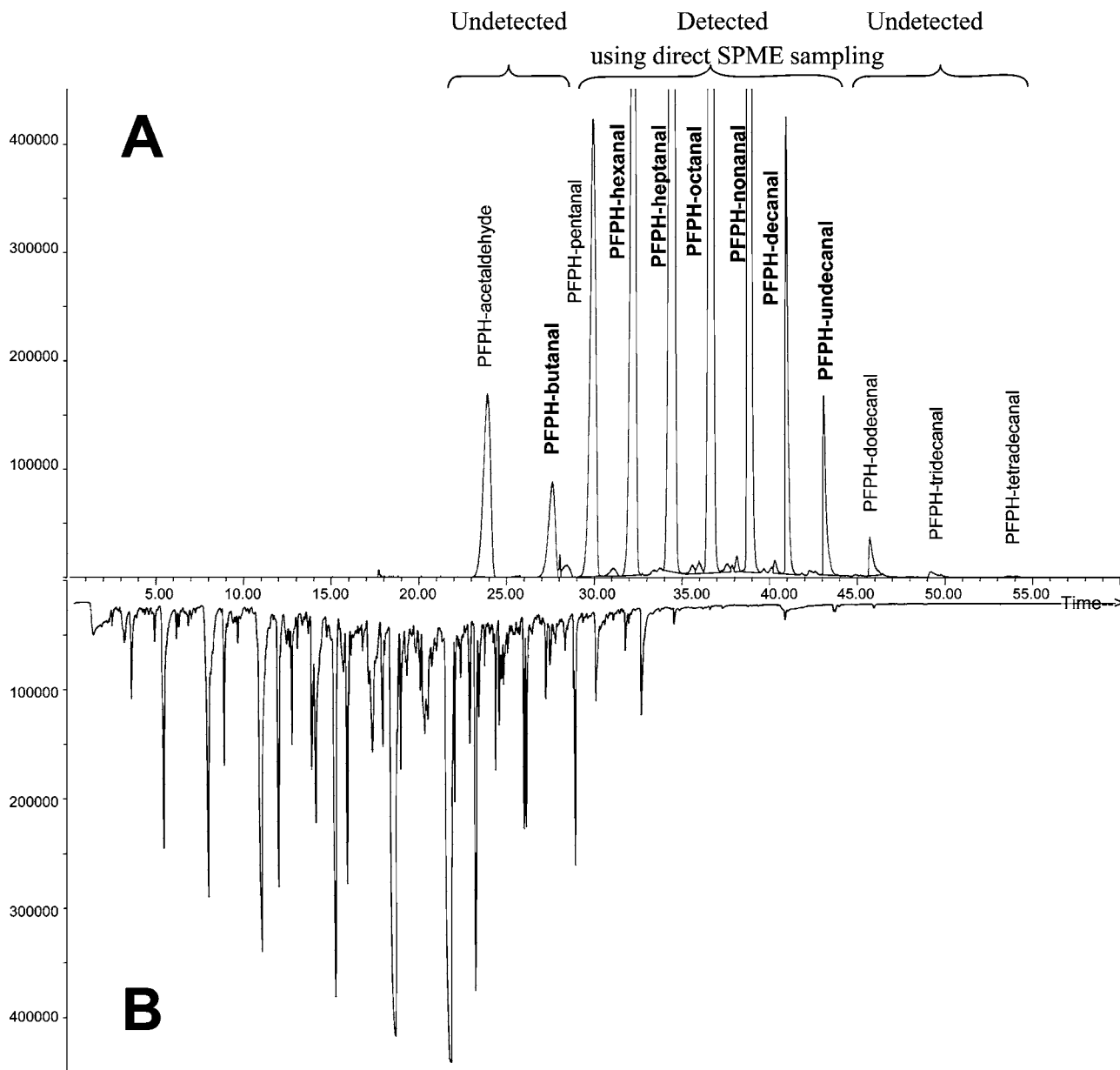


Figure 5. SPME-GC/MS screening of aliphatic aldehydes in roast beef headspace: **(A)** after PFPH derivatization (ion 224); **(B)** comparison with the scan acquisition of the underivatized SPME injection (polar column). Aldehydes found in the olfactogram are given in bold type.

Both procedures have been adapted for the microscale determination of aldehydes using on-fiber SPME derivatization (16, 23). However, molecular ions of PFBO derivatives are often missing, which limits the specificity of resulting spectra. Therefore, the PFPH/SPME technique was investigated in this study.

Mass spectra of all pentafluorophenylhydrazones yielded an abundant molecular ion and underwent characteristic fragmentations that make their detection and identification easy. All spectra exhibited a fragment at m/z 182 due to the cleavage of the N–N bond, plus a second abundant fragment at m/z 183 (Figure 3A), due to a possible elimination of a nitrile as hypothesized in the case of dimethylhydrazone fragmentation (24). However, such a mechanism would suggest a restricted abundance of this ion for short-chain aldehydes (fewer than four carbons), in contrast with the observed abundances (e.g., 55 and 100% for ethanal- and propanal-PFPH, respectively).

Spectra of aliphatic aldehyde and methyl ketone derivatives exhibited an intense ion (m/z 224 and 238, respectively) corresponding to the McLafferty rearrangement (Figure 3B).

This rearrangement is confirmed by the absence of these fragments in the spectra of propanal and 2-butanone derivatives, as their carbon chain is too short to allow the six-centers concerted mechanism.

As expected, these fragments (224, 238) were almost absent in spectra of hydrazones prepared from 2-enals and 2,4-dienals. These compounds were characterized by intense fragments at m/z 235 and 261, respectively (Figure 3C,D). The specificity of the hydrazone pattern is illustrated in Figure 4.

Identification of Aroma Contributors. As the amount of volatiles trapped in a standard analytical cartridge for a GC-O determination was often too low for a positive identification (two criteria required, e.g., retention index and mass spectrum), large-size cartridges were used. When the identity of a given odorant was suspected on the basis of its sensory descriptor and its retention index in the olfactogram, its identity was confirmed by retention and spectral data generated by the MS of the multisniffing system. However, the abundance of several carbonyl compounds remained insufficient, or their peaks were hidden by more abundant ones, to obtain a clear mass spectrum.

Therefore, the odorants trapped by the preparative cartridge were recovered and derivatized using pentafluorophenyl hydrazine, which gave very characteristic hydrazone spectra. The identity of underivatized carbonyl compounds was then supported by the retention index, the sensory descriptors of the GC-O analysis, and the MS spectrum when available, plus the MS spectrum and the retention index of corresponding PFPH derivatives, if possible on two phases.

The hydrazone trace of m/z 224 is shown in **Figure 5**. Aliphatic aldehydes were clearly and specifically visualized in contrast to the same SPME sample without derivatization (dotted line). For instance, butanal was undetectable in nonderivatized experiments performed in scan mode, whereas it was clearly perceived in the beef olfactogram. Its occurrence could be confirmed only owing to the retention index and the mass spectrum of its PFPH derivative.

Carbonyl compounds found in the roast beef top note with or without PFPH derivatization are summarized in **Table 2**. 12-Methyltridecanal, a very specific beef-aroma compound (7), was not detected in GC-MS analyses, even as a PFPH derivative. Its olfactive detection by panelists was unclear as they did not describe the odor they perceived at the expected retention index (1889), and the possible contribution of this peak to the overall aroma remains low (NIF < 33%, **Figure 2**). Its absence was expected for two reasons: (1) It is a high-boiling compound so that its absence in the headspace is not surprising. (2) In the literature, it has been identified when mild cooking conditions were used [e.g., stewed beef (7)] and not under higher cooking temperature [fried or roasted beef (8, 9)].

In **Figure 2** and **Table 2**, ethanal does not exhibit a high detection frequency. In fact, this compound has a low breakthrough volume in Tenax and could be partially lost, leading to an underevaluation of its contribution to the overall aroma. According to published data (25), all other carbonyl compounds detected in this study exhibited breakthrough volumes higher than the headspace volume passed through each analytical cartridges (140 mL), and so they were quantitatively trapped.

Five odorants with descriptors similar to carbonyl compounds remained unknown at indices 1123, 1227, 1475, 1616, and 1673. Their descriptors are listed in **Table 3**, together with those of all identified carbonyl compounds. For the latter, the free-vocabulary descriptors generated by the panel were compatible with those given in the literature.

Most of the 24 aldehydes and ketones positively identified in this study have been previously mentioned as being important odorants in cooked beef in general. Compared to the literature, the major difference lies in the role of methyl ketones, which do not significantly participate in the overall aroma under our roasting conditions. Conversely, in the present study, a much greater number of aldehydes than found using the conditions of Cerny et al. (9) seem to play a role in the aroma.

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