

第9章：香氣化合物

From "Food Chemistry (H.-D. Belitz, · W. Grosch, and · P. Schieberle ed., 4th edition, Chap. 5, pp. 340-402, Springer"

5.1.2 Impact Compounds of Natural Aromas

食品中揮發性物質的濃度很低，約10-15 mg/kg。且通常都含相當多種類的成分，特別是熱處理或再發酵製成的食物中的揮發化合物達800種以上，水果及蔬菜中存在的種類也種類多。

然而僅其中的少數對香氣的貢獻是重要的。被認為香氣物質的化合物，首先在食品中的濃度要大於其氣味閾值(odor threshold)，若低於者但其混合物的濃度高於閾值也可能會貢獻香氣。

香氣物質中，提供香氣特徵的物質特別受重視，稱為關鍵氣味物(key odorants) (特徵影響香氣化合物 character impact aroma compounds)。

Table 5.2. Odor threshold values in water of some aroma compounds (20 °C)

Compound	Threshold value (mg/l)
Ethanol	100
Maltol	9
Furfural	3.0
Hexanol	2.5
Benzaldehyde	0.35
Vanillin	0.02
Raspberry ketone	0.01
Limonene	0.01
Linaleol	0.006
Hexanal	0.0045
2-Phenylethanal	0.004
Methylpropanal	0.001
Ethylbutyrate	0.001
(+)-Nootkatone	0.001
(-)-Nootkatone	1.0
Fillbertone	0.00005
Methylthiol	0.00002
2-Isobutyl-3-methoxypyrazine	0.000002
1-p-Menthene-8-thiol	0.00000002

以nootkatone (葡萄柚皮精油的重要香氣化合物)為例，兩種光學異構物的香氣強度顯著不同，並有時造成香氣品質與特性的差異。

5.1.3 Threshold Value 閾值

- 剛足以辨識出一種化合物的氣味之最低濃度稱之為氣味閾值(odor threshold)(recognition threshold 識別閾值)。
- 檢測閾值(detection threshold) 的濃度更低，即可檢測出該化合物但其香氣性質仍未能清楚確定。
- 閾值的測定常採用嗅聞 (orthonasal value 前鼻腔道值) 和品評樣品(retronasal value 後鼻腔道值)。除少數的例子外，本章節中只列出前鼻腔道值。
- 閾值濃度可用於比較氣味物質的強度(intensity)或效力(potency)。

- 香氣化合物的閾值濃度取決於蒸氣壓(vapor pressure)，蒸氣壓同時受到溫度及介質的影響，和其它產生氣味物質間的交互作用也會導致氣味閾值的大幅提升。

Table 5.3. Influence of 4-hydroxy-2,5-dimethyl-3(2H)-furanone (HD3F) on the odor threshold of aroma substances in water

Compound	Threshold value (µg/l)		Ratio II to I
	I ^a	II ^b	
4-Vinylguaiacol	100	90	0.9
2,3-Butanedione	15	105	7
2,3-Pentanedione	30	150	5
2-Furfurylthiol	0.012	0.25	20
β-Damascenone	2 × 10 ⁻³	0.18	90

^a I, odor threshold of the compound in water.
^b II, odor threshold of the compound in an aqueous HD3F solution having a concentration (6.75 mg/l, aroma value A = 115) as high as in a coffee drink.

Table 5.4. Comparison of threshold values^a in water and beer

Compound	Threshold (mg/kg) in	
	Water	Beer
n-Butanol	0.5	200
3-Methylbutanol	0.25	70
Dimethylsulfide	0.00033	0.05
(E)-2-Nonenal	0.00008	0.00011

^a Odor and taste.

一種化合物的**香氣值** (“**aroma value**” A_x) 定義：

$$A_x = C_x / a_x$$

C_x : 食品中化合物X的濃度

a_x : 食品中化合物X的odor threshold

The **law of Stevens** for physiological stimuli:

$$E = k \cdot (S - S_0)^n$$

E: perception intensity

k: constant

S: concentration of stimulant

S_0 : threshold concentration of stimulant

指數 n (冪函數)表示氣味強度隨濃度而變化的幅度大小。

- 此外，也須考慮不易評估的加成作用 (additive effects)。這可以混合物試驗取得基本的了解，雖然香氣調性 (aroma note) 相同的化合物之混合物強度為加成的，但混合物的強度通常低於個別強度的加總。
香氣調性明顯不同的物質，僅氣味強度約略相等時，混合物的氣味輪廓就由參與成分的氣味輪廓共同構成，如一種組成分的強度占優勢，該成分就大部分或完全決定混合物的氣味輪廓。

5.1.5 Off-Flavors, Food Taints

- 不良風味 (off-flavor)** 源自非正常會存在食品中的外來香氣物質、主要氣味物質損失、或者各自香氣物質的濃度比率有所改變。

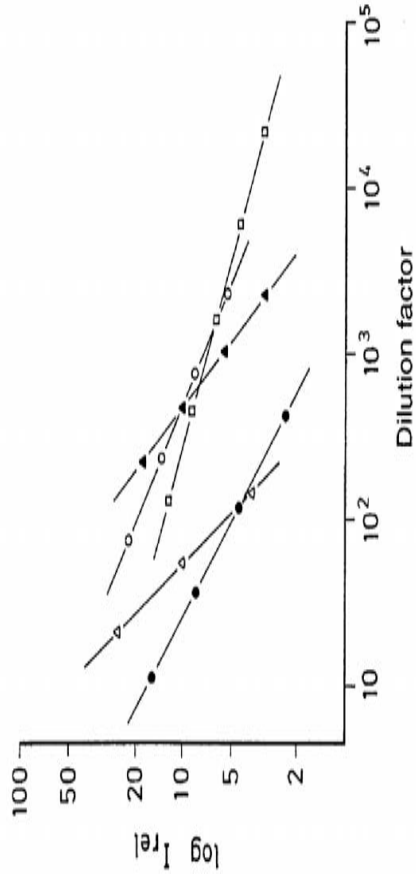


Fig. 5.1.1. Relative odor intensity I_{rel} (reference: n-butanol) as a function of the stimulant concentration (according to Dravnieks, 1977).

Air saturated with aroma substance was diluted. ● — ● — α -pinene, ○ — ○ — 3-methylbutyric acid methyl ester, Δ — Δ — hexanoic acid, \diamond — \diamond — 2,4-hexadienal, \square — \square — hexylamine

- 圖5.3 說明食品中香氣瑕疵(缺失)的起因。氣味污染物質經由空氣或水媒介，然後濃縮、再進入食物。

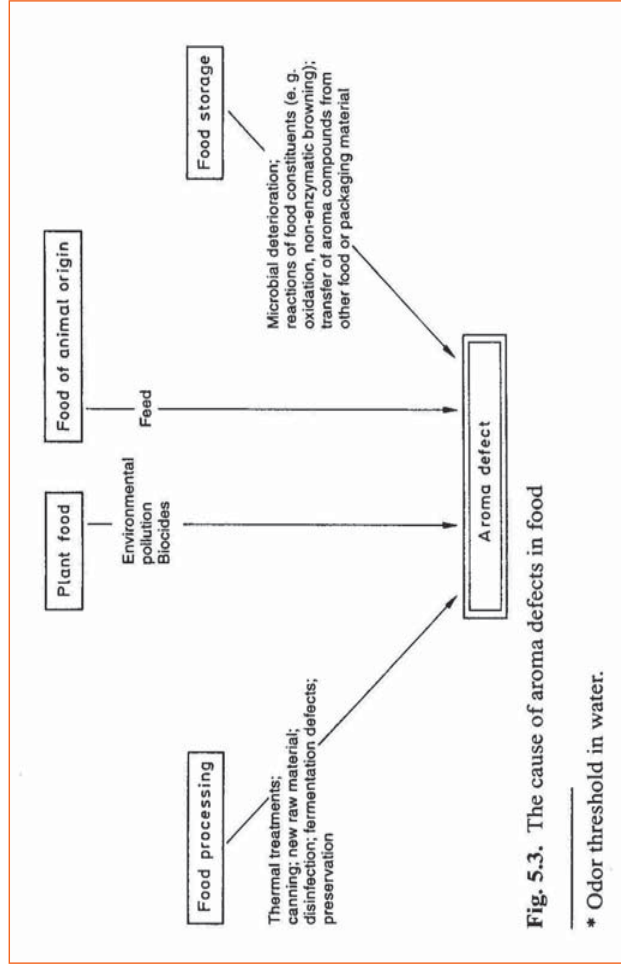
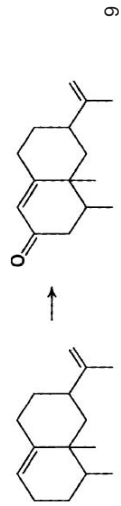


Fig. 5.3. The cause of aroma defects in food

* Odor threshold in water.

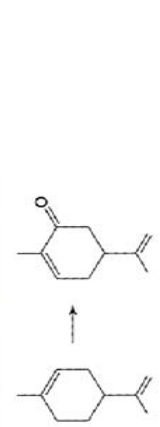
Food product	Off-flavor	Cause
Milk	Sunlight flavor	Photooxidation of methionine to methional (with riboflavin as a sensitizer)
Milk powder	Bean-like	The level of O ₃ in air too high: ozonolysis of 8,15- and 9,15-isolinoleic acid to 6-trans-nonenal
Milk powder	Gluey	Degradation of tryptophan to o-amino-acetophenone
Milk fat	Metallic	Autooxidation of pentaene- and hexaene fatty acids to octa-1,cis-5-dien-3-one
Milk products	Malty	Faulty fermentation by <i>Streptococcus lactis</i> , var. <i>multigenes</i> ; formation of phenylacetaldehyde and 2-phenylethanol from phenylalanine
Peas, deep froze	Hay-like	Saturated and unsaturated aldehydes, octa-3,5-dien-2-one, 3-alkyl-2-methoxypyrazines, hexanal
Orange juice	Grapefruit note	Metal-catalyzed oxidation or photooxidation of valencene to nootkatone



- 源自食品加工和貯藏中產生的一些不良風味的舉例(表 5.5)

來自微生物的代謝產物：

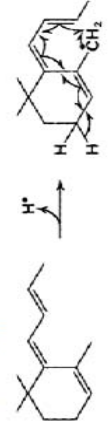
- Skatole (類似糞便味，10 µg/kg*)
- 2-Methylisoborneol (泥濘土味，0.03 µg/kg*)
- Geosmin (土味，(-/+)光學異構物：0.01/0.08 µg/kg*)
- 2,4,6-Trichloroanisole (類似發霉味：3.10-5 pg/kg 水)：五氯酚殺菌劑受黴菌的裂解與甲基化而生成



Passion fruit juice

Aroma flattening during pasteurization

Oxidation of (6-trans-2'-trans)-6-(but-2'-enyliden)-1,5,5-trimethylcyclohex-1-ene to 1,1,6-trimethyl-1,2-dihydronaphthalene:



H⁺

H⁺

Ox

Beer

Sunlight flavor

Beer

Phenolic note

Photolysis of humulone: reaction of one degradation product with hydrogen sulfide yielding 3-methyl-2-buten-1-thiol

Faulty fermentation: hydrocinnamic acid decarboxylation by *Hafnia protea*

5.2 Aroma Analysis

香氣物質是由高歧異的不同化合物群組成，有些是高反應性或者在食品中的含量非常低。定性及定量分析香氣化合物時常遇到的困難就是來自這般的樣貌，其它的問題如香氣化合物鑑定、化學構造解析與官能性質的特性等的釐清。

解析食品香氣的步驟是階段性的，逐步進行下列的分離、畫分、儀器及官能分析：

- Isolation of the volatile compounds
- Differentiation of the aroma substances from the remaining components of the volatile fraction by dilution analyses
- Concentration and identification
- Quantification and calculation of aroma values
- Simulation of the aroma on the basis of the analytical results
- Omission experiments

5.2.1 Aroma Isolation 香氣物質分離

- 原料用量
- 溫和的方法分離揮發物質(考慮一些人為物質易形成)

Table 5.6. Possible changes in aromas during the isolation of volatile compounds

Reaction
<i>Enzymatic</i>
1. Hydrolysis of esters (cf. 3.7.1)
2. Oxidative cleavage of unsaturated fatty acids (cf. 3.7.2.3)
3. Hydrogenation of aldehydes (cf. 5.3.2.1)
<i>Non-enzymatic</i>
4. Hydrolysis of glycosides (cf. 5.3.2.4 and 3.8.4.4)
5. Lactones from hydroxy acids
6. Cyclization of di-, tri-, and polyols (cf. 5.3.2.4)
7. Dehydration and rearrangement of tert-allyl alcohols
8. Reactions of thiols, amines, and aldehydes (cf. 5.3.1.4) in the aroma concentrate

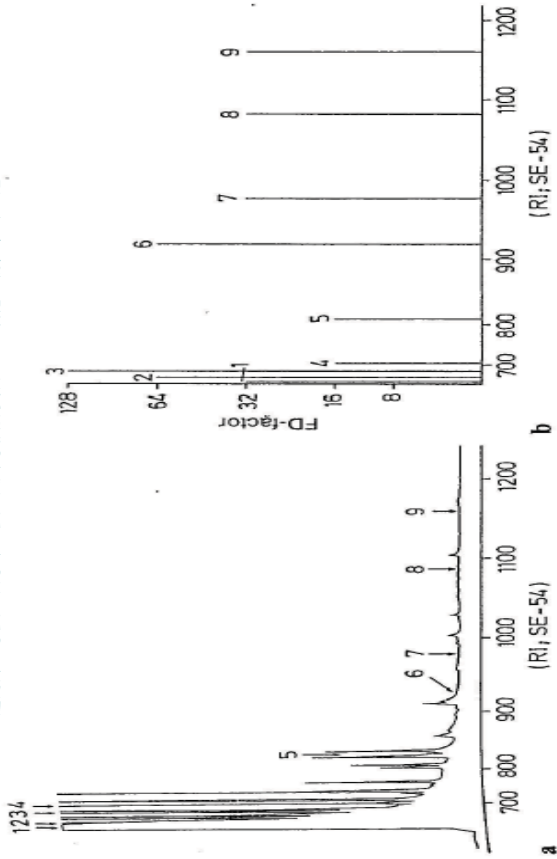


Fig. 5.4. Headspace analysis of aroma substances of white-bread crust. a Capillary gas chromatogram (the arrows mark the positions of the odorants), b FD chromatogram. Odorants: 1 methylpropanal, 2 diacetyl, 3 3-methylbutanal, 4 2,3-pentanedione, 5 butyric acid, 6 2-acetyl-1-pyrroline, 7 1-octen-3-one, 8 2-ethyl-3,5-dimethylpyrazine, 9 (E)-2-nonenal (according to Schieberle and Grosch, 1992)

- 食品中含enzymes會改變香氣（蔬果均質時，水解酶打斷酯類香氣物質，脂氧合酶連同氫過氧化物解離酶作用新生成的揮發化合物，使香氣更豐富）。
- 須考慮香氣物質 binding 食品固形物基質之能力。故，端視樣品特性的不同而選擇合適的香氣分離方法與條件。
- 揮發至蒸氣空間(vapor space)的香氣物質可採用很溫和的方式—上部空隙/頂空分析(headspace analysis)，但取得的量很少。食品中的重要香氣物質的濃度原本就低，可能因而GC分析時看不出偵測訊號。這些香氣物質僅能以GC-sniffing (GC-嗅聞)方式測定。偵測器不同靈敏度也有差異(Fig. 5.4)

◎水相食品的分散液可以真空蒸餾(vacuum distillation)分離揮發性香氣化合物，會夾帶一些水。高度揮發化合物經冷卻、濃縮於冷卻阱(cool trap) (圖5.5)。在整個蒸餾過程，如果食品或萃取物是多油的，香氣物質的產量會減低(表5.7)。

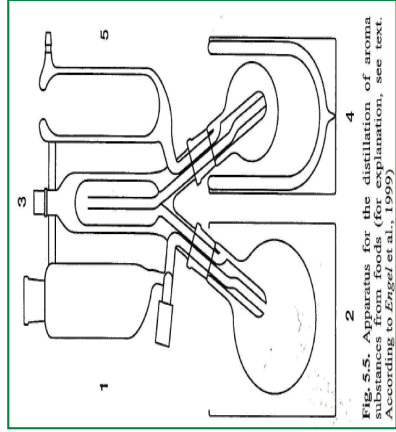


Fig. 5.5. Apparatus for the distillation of aroma substances from foods (for explanation, see text. According to Engel et al., 1999)

高真空度(≈6 mPa)→液狀食品或萃取物(1)滴入蒸餾瓶(水浴35-40°C；2)→揮發物和溶劑蒸氣進入蒸餾頭部(3)→distillate流入受器(4)→液態氮冷凝；Dewar flask (5)保護真空幫浦

Table 5.7. Yields of aroma substances on distillation under vacuum^a

Aroma substance (amount) ^a	Yield ^b (%)	
	Model I	Model II
3-Methylbutyric acid (1.9 µg)	91	31
Phenylacetaldehyde (4.2 µg)	84	21
3-Hydroxy-4,5-dimethyl-2(5H)-furanone (2.2 µg)	100	3.3
2-Phenylethanol (3.7 µg)	100	10.7
(E,E)-2,4-Decadienal (1.4 µg)	100	3.4
(E)-β-Damascenone (0.9 µg)	100	2.8
Vanillin (3.7 µg)	100	0.4

^a Amount in the model solution: I in diethylether (50 ml), II in a mixture of diethylether (50 ml) and triglycerides (50 ml)

^b Distillation in the apparatus shown in Fig. 5.5 at 35°C

◎固態食品的萃取，添加水可提高香氣物質的產量。
Likens-Nickerson裝置(Fig. 5.6)。常用低沸點溶劑使後續的濃縮較易進行，在常壓或有些真空下，對食品施加熱處理可能引起一些反應而改變香氣組成。

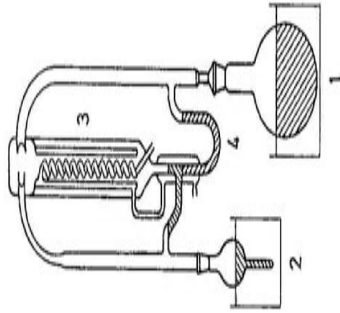


Fig. 5.6. Apparatus according to Likens and Nickerson used for simultaneous extraction and distillation of volatile compounds.
1 Flask with heating bath containing the aqueous sample, 2 flask with heating bath containing the solvent (e.g. pentane), 3 cooler, 4 condensate separator: extract is the upper and water the lower phase

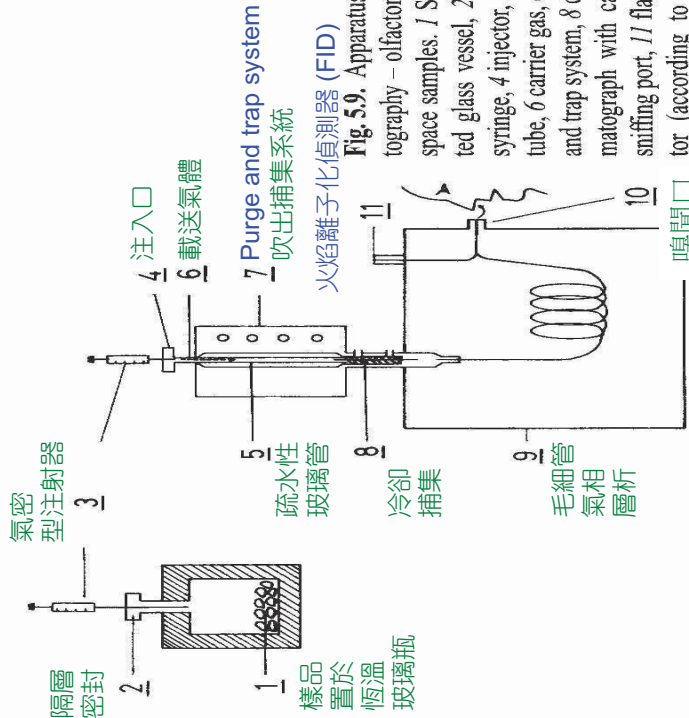


Fig. 5.9. Apparatus for the gas chromatography - olfactometry of static headspace samples. 1 Sample in thermostated glass vessel, 2 septum, 3 gas tight syringe, 4 injector, 5 hydrophobed glass tube, 6 carrier gas, e.g., helium, 7 purge and trap system, 8 cold trap, 9 gas chromatograph with capillary column, 10 sniffing port, 11 flame ionization detector (according to Guth and Grosch, 1993)

Table 5.8. Isolation of odorants from cherry juice – Comparison of distillation in vacuo (I) with simultaneous distillation and extraction (II)

Odorant	I	(µg/l)	II
Benzaldehyde	202		5260
Linalool	1.1		188

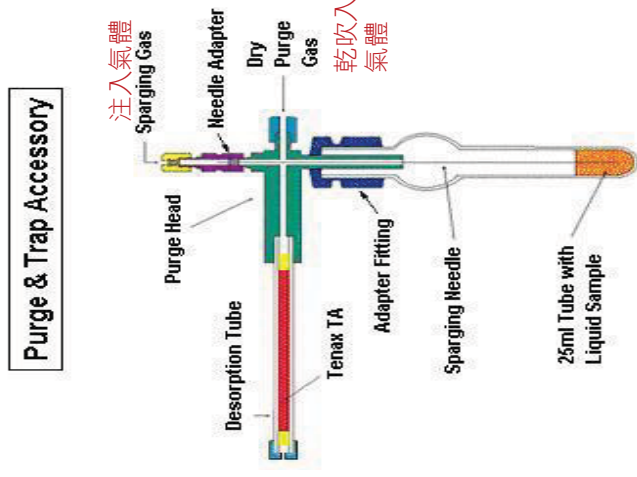
- Table 5.8 shows the extent to which some aroma substances are released from glycosides during simultaneous distillation/extraction.

5.2.1.2 Gas Extraction

◎固體或液體樣品中的揮發性化合物使用惰性氣體(氮、二氧化碳、氮氣等)吹掃(purge)出來，吸附在多孔性球型聚合物(Tenax GC, Porapak Q, Chromosorb 105)，然後再回收化合物。殘留的水分量少而可忽略(Table 5.9)，揮發物的脫附通常是以梯度升溫逐步達成。

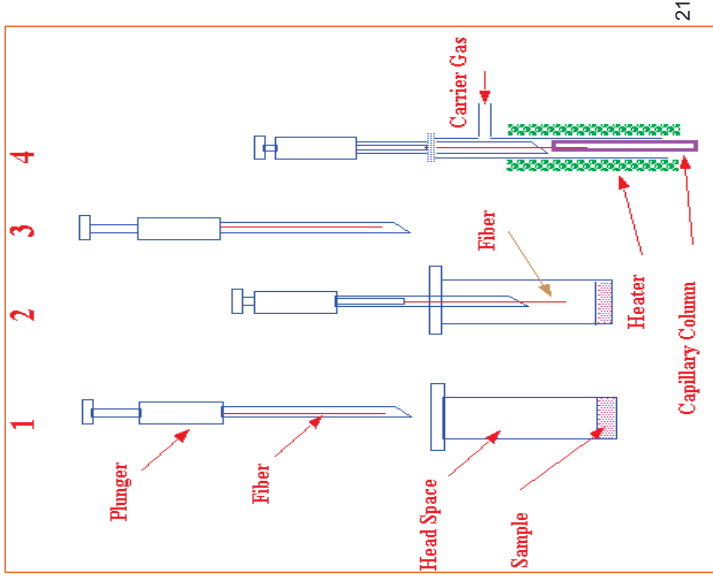
5.2.1.3 Headspace Analysis

- 步驟：食物密封於容器內 → 加熱至一定溫度並維持一定時間，使結合於食物與揮發而存在蒸氣相之間達到平衡 → 吸取一定體積的上部空隙注入GC分析。
水分含量及注射體積過多時會明顯降低GC的分離效率，**僅主要揮發物被偵測器測得**。
靜態(static)上部空隙分析提供一項重要的貢獻，即香氣物質出現在圖譜的位置可同時用olfactometry測定。
更多且雜的物質時，可利用動態(dynamic)上部空隙分析或固相微萃取 (solid phase microextraction, SPME)。



在SPME分析，對實驗條件的要求相當高，除了固體相，氣味物質樣品和體積濃度、樣品基質和脫附過程，以及吸附時間都會影響產率。

進行SPME定量分析時，採用標識內部標準品 (labelled internal standards) 即可排除這些的影響。(cf. 5.2.6.1)



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- 只做一次GC官能評定(文獻常出現)的意義不大，因移動相氣體中香氣物質的感知是取決於和aroma value全無關連的 limiting quantities，諸如分析食品數量、揮發物區分的濃縮程度、GC分離所注入樣品的量等。解決這樣的受限，乃將揮發物區分以溶劑逐步稀釋，然後進行GC/olfactometric 分析，直至嗅聞不出香氣物質，如此得知風味稀釋係數(flavor dilution factor, FD factor)。AEDA結果以 FD chromatogram表示，以FD係數對應滯留時間[改以滯留係數(retention index, RI)表示]繪圖。

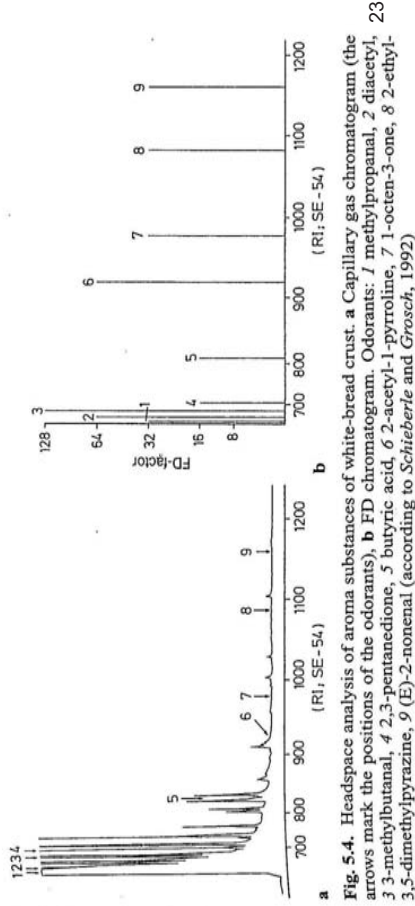


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5.2.2 Sensory Relevance

- 研究同時集中在那些顯著貢獻於香氣的化合物，在GC圖譜上位置的偵測藉助於稀釋分析(dilution analyses)。

5.2.2.1 Aroma Extract Dilution Analysis (AEDA)

- 香氣萃取物稀釋分析是將蒸餾取得的氣味濃縮物，以GC毛細管柱分離，測定香氣物質的滯留時間，移動相氣體離開分離毛細管柱後(GC/olfactometry)，分叉進入偵測器與進行sniffing detection (或不分叉，第二次再做嗅聞測定)。

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但是後述表5-15的品評試驗結果，指出 methional 並非主要的貢獻成分，雖然其AV值高(表5-14)。

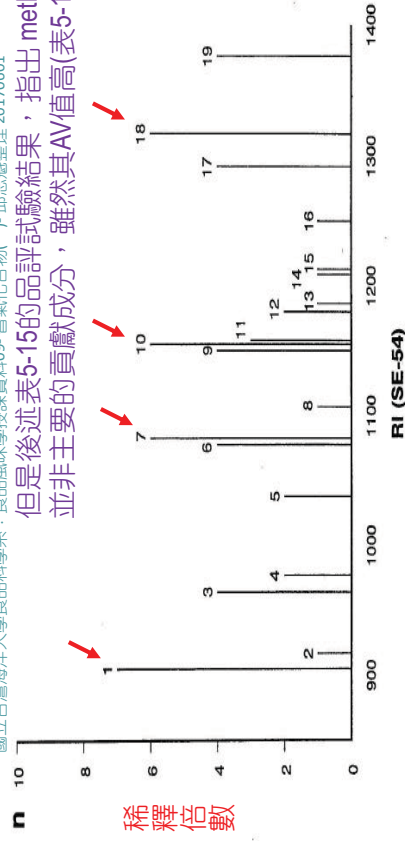


Fig. 5.8. FD chromatogram of the volatile fraction of French fries. Ordinate: n, number of 1 + 1 dilutions. Abscissa: retention index (RI) on the capillary SE-54. The following odorants were identified: 1 methional, 2 2-acetyl-1-pyrroline, 3 dimethyltrisulfide, 4 1-octen-3-one, 5 phenylacetaldehyde, 6 2-ethyl-3,6-dimethylpyrazine, 7 2-ethyl-3,5-dimethylpyrazine, 8 nonanal, 9 (Z)-2-nonenal, 10 2,3-diethyl-5-methylpyrazine, 11 (E)-2-nonenal, 12 2-ethyl-3-ethyl-5-methylpyrazine, 13 2-isobutyl-3-methoxypyrazine, 14 dimethyltetrasulfide, 15 (E,E)-2,4-nonalenal, 16 (Z)-2,4-decadienal, 17 (E,Z)-2,4-decadienal, 18 (E,E)-2,4-decadienal, 19 trans-4,5-epoxy-(E)-2-decenal (according to Wagner and Grosch, 1997)

炸薯條例(圖5.8)，鑑定稀釋因子介於21-27間的19種香氣物質(圖5.8註腳)。從稀釋因子值都同樣較高，推知methional (1)、2-ethyl-3,5-dimethylpyrazine (7)、2,3-diethyl-5-methylpyrazine (10) 與 (E,E)-2,4-decadienal (18) 貢獻炸薯條的香氣。

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5.2.2.2 Headspace GC Olfactometry

AEDA用樣品的回收問題，**高揮發性氣味物**被丟掉或在圖譜中被溶劑波峰掩蓋。解決：採取食品上部的氣體注入GC，被移動相氣體載送至**cold trap**處濃縮(Fig. 5.9)，當注入GC快速蒸發後，樣品被載送氣體帶入毛細管進行層析，試驗者在毛細管尾端嗅聞、測出何時出現氣味物，同時也用GC偵測直至無氣味物被測出。

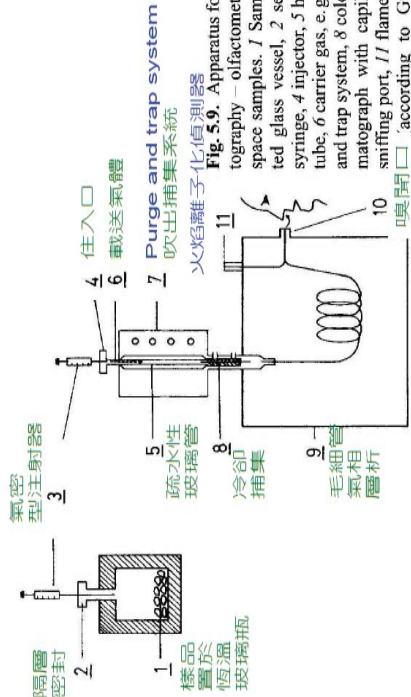


Fig. 5.9. Apparatus for the gas chromatography – olfactometry of static headspace samples. 1 Sample in thermostated glass vessel, 2 septum, 3 gastight syringe, 4 injector, 5 hydrophobed glass tube, 6 carrier gas, e.g., helium, 7 purge and trap system, 8 cold trap, 9 gas chromatograph with capillary column, 10 sniffing port, 11 flame ionization detector, according to Guth and Grosch, 1957

炸薯條 (圖 5.10) 為例：methanethiol (1)、methylpropanal (2) 及 dimethyltrisulfide (10) 等的氣味在第6次稀釋後仍可測得，只有 methanethiol (1) 至第7次稀釋仍測出，但第8次稀釋已聞不到，事實上，進一步實驗確認 methanethiol (1) 就是主要氣味物。

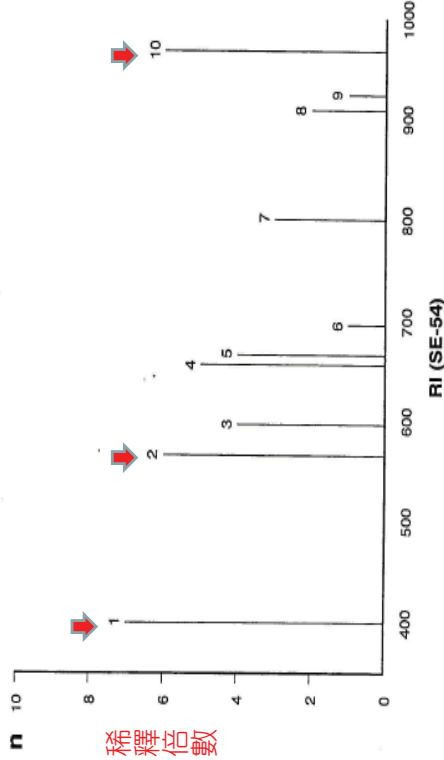


Fig. 5.10. FD chromatogram of static headspace samples of French fries. Ordinate: n, number of 1 + 1 dilutions. Abscissa: retention index (RI) on the capillary SE-54. The following odorants were identified: 1 methanethiol, 2 methylpropanal, 3 2,3-butanedione, 4 3-methylbutanal, 5 2-methylbutanal, 6 2,3-pentanedione, 7 hexanal, 8 methional, 9 2-acetyl-1-pyrroline, 10 dimethyltrisulfide (according to Wägner and Grosch, 1997)

Table 5.11. Column chromatographic preliminary separation of an aroma extract of roasted coffee

Fraction*	Aroma substance
A	2-Methyl-3-furanthiol, 2-furfurylthiol, bis(2-methyl-3-furyl)disulfide, 3-methyl-2-butenethiol
B	2,3-Butanedione, 3-methylbutanal, 2,3-pentanedione, trimethylthiazole, 3-mercaptop-3-methylbutylformiate, 3-isopropyl-2-methoxypyrazine, phenylacetaldehyde, 3-isobutyl-2-methoxypyrazine, 5-methyl-5(H)-cyclopentapyrazine, p-anisaldehyde, (E)-β-damascenone
C	Methional, 2-ethenyl-3,5-dimethylpyrazine, linalool, 2,3-diethyl-5-methylpyrazine, guaiacol, 2-ethenyl-3-ethyl-5-methylpyrazine, 4-ethylguaiacol, 4-vinylguaiacol
D	2-/3-Methylbutyric acid, trimethylpyrazine, 3-mercaptop-3-methyl-1-butanol, 5-ethyl-2,4-dimethylthiazole, 2-ethyl-3,5-dimethylpyrazine, 3,4-dimethyl-2-cyclopentenol-1-one, 4-hydroxy-2,5-dimethyl-3(2H)-furanone, 5-ethyl-4-hydroxy-2-methyl-5(2H)-furanone, 3-hydroxy-4,5-dimethyl-2(5H)-furanone, 5-ethyl-3-hydroxy-4-methyl-2(5H)-furanone, vanillin

* Chromatography at 10–12 °C on a silica gel column (24 × 1 cm, deactivated with 7% water); elution with mixtures of pentane-diethylether (50 ml, 95 + 5, v/v; fraction A; 30 ml, 75 × 25, v/v; Fraction B; 30 ml, 1 + 1, v/v; Fraction C) and with diethylether (100 ml, Fraction D).

5.2.4 Chemical Structure

- **質譜儀 (mass spectrometer, MS)** 是解析香氣物質的構造不可欠缺的工具，GC沖提(elute)的物質已足夠提供產生有用的 MS圖譜。如有對應的參考物質，香氣物質的鑑定依據mass spectrum、至少兩種極性不同毛細管柱的retention indices 及 odor thresholds等的一致性。
 - 如無參考物質，依下列步驟鑑定：
 - ◎ 1H-NMR (可能的話再包括 ¹³C-spectrum)
 - ◎ Mass spectrum

5.2.5 Enantioselective Analysis

- 光學異構物(enantiomers)：氣味性質 (odor quality) 及閾值會差異大。
- Fig. 5.12 中，3S,3aS,7aR-enantiomer (No. 6 in Table 5.12) 在 8 種異構物中的氣味閾值最低，在紅酒中被命為 **wine lactone**；有兩種(No. 3 and 8) 是無氣味的。

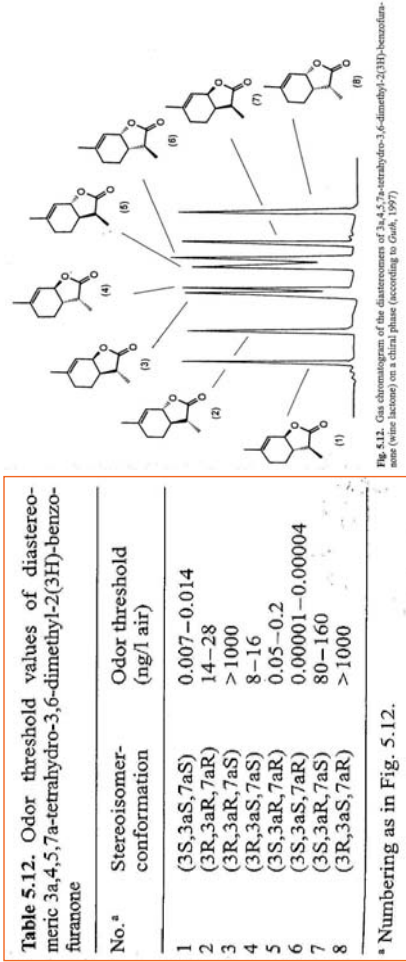


Fig. 5.12. Gas chromatogram of the diastereomers of 3a,4,5,7a-tetrahydro-3,6-dimethyl-2(3H)-benzofuranone (wine lactone) on a chiral phase (according to Guib, 1997)

- 各種光學異構物的存在比率：**enantiomeric excess (ee)**，測定 **ee 值** 的常用方法為 enantioselective gas chromatographic analysis of the aroma substance on a **chiral phase**, e.g., peralkylated cyclodextrins.

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5.2.6.2 Aroma Values (AV)

- 假定：高香氣值(AV)的氣味物強力貢獻於食品的香氣。
- 炸薯條氣味物質的香氣值，取決於它們在油中的氣味閾值 (Table 5.14)。Methanethiol、methional、methylpropanal 和 2-methylbutanal 表 現最大的香氣值，因而，列為炸薯條最重要的氣味物質。

Table 5.14. Volatile compounds with high aroma values in French fries^a

Compound	Concentration ^b (μg/kg)	Odor threshold ^c (μg/kg)	Aroma value ^d
Methanethiol	1240	0.06	2×10^4
Methional	783	0.2	3.9×10^3
Methylpropanal	5912	3.4	1.7×10^3
2-Methylbutanal	10599	10	1.1×10^3
trans-4,5-Epoxy-(E)-2-decenal	771	1.3	592
3-Methylbutanal	2716	5.4	503
(E,Z)-2,4-Decadienal	1533	4	383
4-Hydroxy-2,5-dimethyl-3(2H)-furanone	2778	25	111
2,3-Diethyl-5-methylpyrazine	41	0.5	83
(E,E)-2,4-Decadienal	6340	180	35
2,3-Butanedione	306	10	31
2-Ethyl-3,5-dimethylpyrazine	42	2.2	19
2-Ethenyl-3-ethyl-5-methylpyrazine	5.4	0.5	11
3-Isobutyl-2-methoxypyrazine	8.6	0.8	11
2-Ethyl-3,6-dimethylpyrazine	592	57	10

^a Potato sticks deep-fried in palm oil.
^b Results of IDA.
^c Odor threshold of the compound dissolved in sunflower oil.
^d Quotient of concentration and odor threshold.

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5.2.6 Quantitative Analysis, Aroma Values

5.2.6.1 Isotopic Dilution Analysis (IDA)*

- 採用傳統方法做香氣物質的定量分析常得到不正確的數值，原因：高蒸氣壓、萃取度差（特別從含水食品之極性香氣物質）、重要成分的不穩定性(如thiols)等。
- 如**內部標準品**的化學構造和分析對象很相似，定量分析結果是正確的（標準誤差低於10%）。**最為相似的：採用分析物的同位素異位體。**

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5.2.7 Aroma Model, Omission Experiments

- **最後，鑑定的氣味物質必須實際上產生所要的香氣。**
- 以一定的濃度溶於適合的介質，溶解混合用的溶劑稱之 **aroma model**，例如**乙醇水混合物**適合紅酒；在固體食品部分，作法就得妥協，模式的香氣輪廓就和實際食品比對。
- 在模式中省略一至數個香氣物質，品評試驗確認出 **主要貢獻成分**。

Table 5.15. Aroma model for French fries as affected by the absence of one or more odorants^a

Exp. No.	Odorant omitted in the model	Number ^b
1	Methanethiol	5
2	(E,Z)-2,4-Decadienal and (E,E)-2,4-decadienal	5
3	Methylpropanal, 2- and 3-methylbutanal	4
4	trans-4,5-Epoxy-(E)-2-decenal	4
5	2-Ethyl-3,5-dimethylpyrazine and 3-ethyl-2,5-dimethylpyrazine	4
6	1-Octen-3-one, (Z)-2- and (E)-2-nonenal	1
7	Methional	0

^a Models lacking in one or more components were each compared to the model containing the complete set of 19 odorants.

^b Number of the assessors detecting an odor difference in triangle tests, maximum 5.

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Table 5.15. Aroma model for French fries as affected by the absence of one or more odorants^a

Exp. No.	Odorant omitted in the model	Number ^b
1	Methanethiol	5
2	(E,Z)-2,4-Decadienal and (E,E)-2,4-Decadienal	5
3	Methylpropanal, 2- and 3-methylbutanal	4
4	trans-4,5-Epoxy-(E)-2-decenal	4
5	2-Ethyl-3,5-dimethylpyrazine and 3-ethyl-2,5-dimethylpyrazine	4
6	1-Octen-3-one, (Z)-2- and (E)-2-nonenal	1
7	Methional	0

^a Models lacking in one or more components were each compared to the model containing the complete set of 19 odorants.

^b Number of the assessors detecting an odor difference in triangle tests, maximum 5.

- If methanethiol and the two decadienal iso-mers are missing in Experiments 1 and 2, the aroma has no similarity to that of French fries. All five testers were in agreement. The Strecker aldehydes with the malt odor (Exp: 3), 4,5-epoxydecenal (Exp: 4) and both pyrazines (Exp: 5) are also important for the aroma because their absence was noticed by four of the five testers. 1-Octen-3-one, (Z)-2- and (E)-2-nonenal are of no importance for the aroma (Exp: 6). Surprisingly, this also applies to methional (Exp: 7) although it has the second highest aroma value (cf. Table 5.14) and smells of boiled potatoes. It is obvious that methional is masked by other odorants occurring in the aroma model. In French fries, the odor note "like boiled potatoes" is probably produced by methanethiol in combination with pyrazines.

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5.3.1 Nonenzymatic Reactions

- **食物加熱**：哪些氣味物生成？多少量？決定於化學反應的一般參數，包括：前驅物質的化學構造和濃度、溫度、時間和環境因子，諸如pH值、氧氣與水分含量。
- 這些揮發物所生成的量是否足以彰顯出香氣，取決於其香氣閾值(odor thresholds)以及與其它氣味物值間的交互作用。
- 非酵素性反應引起的室溫下的香氣變化，**僅長時間貯藏後始顯現**，**脂質過氧化**、**胺基酸的梅納反應**及**關連的Strecker降解**都扮演部分的影響。在烤及炸期間的高溫下，香氣變多樣複雜化，食物表面乾燥，碳水化合物、蛋白質、脂質及如酚酸類等其他組成分發生熱裂解而產生氣味物，以及其他化合物。

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5.3 Individual Aroma Compounds

- 根據稀釋和香氣模擬試驗的結果，顯示食品中已鑑定的8000種揮發性化合物，僅其中的**5%貢獻食品的香氣**。揮發性區分中的氣味物質數量低其主原因在於嗅覺得特別專一性 (參照 cf. 5.6)。
- 重要的氣味物質根據其形成為非酵素性或酵素性反應而分類之，並依化合物的種類分項，有些香氣化合物在非酵素性或酵素性反應都可形成 (參照5.3.1 與 5.3.2項)。

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- **僅一或二種組成分的裂解就形成大量的揮發性化合物是非酵素反應的特徵。**
- 譬如 cysteine 及 xylose 在 tributyrin 中200°C加熱，得到41種硫化化合物，含 20 種 thiazoles、11 種 thiophenes、2 種 dithiolanes及1種dimethyltrithiolane。但即使這樣激烈的條件，大部分所生成的濃度仍遠低於比較高氣味閾值(cf. 5.6項)。只有其中的一小部分是 **aroma active**。

5.3.2 Enzymatic Reactions

- 香氣化合物經由許多的反應而生成，這些反應只是動植物、微生物正常代謝的部分，以組織的破壞而開啟**酵素反應特別重要**，**經驗上如蔬果的完整性受損或切片等**。酵素也能**間接參與**香氣的形成，提供初期階段如自可用的蛋白質釋出胺基酸、自多醣類出醣類、或自酚類化合物釋出 ortho-quinones，這些成分再繼續進行非酵素反應轉變成香氣化合物。以這樣的方式，酵素增進麵包、肉類、啤酒、茶及可可亞的香氣。

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5.4 Interactions with Other Food Constituents

- 香氣和脂質、蛋白質及碳水化合物相互作用影響食物內揮發物的保留(retention)，及在氣相中的量。因而交互作用影響食品香氣的強度及性質，這樣的交互作用無法在真正的食品系統清楚解析，只能用模式系統模擬。
- 油脂量不同乳化物含的香氣成分—diacetyl, (Z)-3-hexenol, (E,Z)-2,6-nonadienol, allyl isothiocyanate and allyl thiocyanate。圖5.32(a)：20%油脂樣品具典型平衡的乳瑪琳氣味，油脂量若減少，香氣急遽改變；圖5.32(b)：5%樣品因香氣輪廓中奶油和脂肪氣味的強度減弱，變成具有非典型的乳脂狀及刺激氣味；圖5.32(c)：1%樣品以刺激、芥末般的香氣調性主。

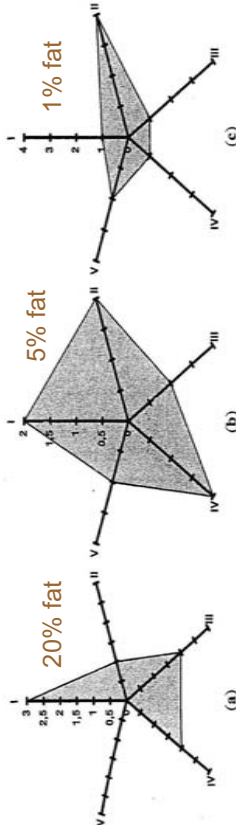


Fig. 5.32. Influence of the fat content on the aroma profile of emulsions; a) 20% fat, b) 5% fat, c) 1% fat. The intensities of the aroma qualities buttery (D), pungent, sharp (II), fatty (III), sweet (IV) and green (V) were evaluated as 1 (weak) to 4 (strong) (according to *Widder and Fischer, 1996*)

- 氣味強烈的(E,Z)-2,6-nonadienol在上部空隙中的濃度低於偵測閾值，但在headspace GC-olfactometry時可聞出此氣味物質；從表5.35結果，該醇類及(Z)-3-hexenol在20%樣品已不再貢獻香氣，在1%樣品，(E,Z)-2,6-nonadienol、allyl isothiocyanate及allyl thiocyanate佔優勢並產生green, mustard-like aroma。

Table 5.35. Mayonnaise model: gas chromatography/olfactometry of headspace samples

Aroma substance ^a	Odor quality	Odor intensity ^b		
		1% fat	5% fat	20% fat
Diacetyl	Buttery	3	4	>4
(Z)-3-Hexenol	Green	2	1	0
(E,Z)-2,6-Nonadienol	Green, fatty	4	<1	0
Allyl isothiocyanate	Pungent, mustard-like	4	3	<1
Allyl thiocyanate	Pungent, mustard-like	4	3	<1

^a Components of an aroma cocktail to which an oil emulsion was added.

^b Intensity on sniffing the carrier gas stream 1 (weak) – 4 (strong).

- 上部空隙分析結果：香氣的激烈變化歸因於隨油脂含量的減少而脂溶性成分(Z)-3-hexenol、allyl isothiocyanate及allyl thiocyanate於氣相中的濃度增加，水溶性diacetyl的留存則不受影響(Fig. 5.33)。

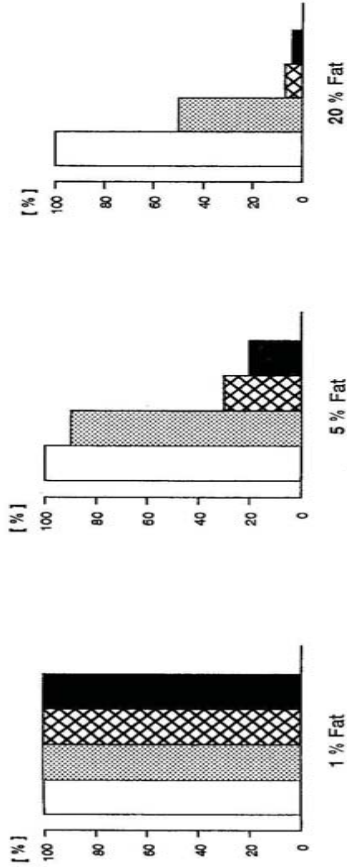


Fig. 5.33. Influence of the fat content of an emulsion on the concentration of aroma substances in the gas phase (according to *Widder and Fischer, 1996*)

5.4.1 Lipids

- 在 o/w 乳化系統中(cf. 8.15.1)，香氣化合物的分配係數(distribution coefficient) K 關連於aroma activity:

$$K = C_o / C_w$$

C_o ：油相中的香氣化合物濃度

C_w ：水相中的香氣化合物濃度

- 在同質構造系列，如正烷醇(n-alkane alcohols) (參照圖5.34)之K值隨鏈長而增加，油相中的溶解度依疏水性(來自鏈長的增加)而比率上升，蒸氣壓的產生剛好相反，即因香氣化合物疏水性的增加而下降，且隨油相體積的增加而蒸氣壓降低，同時氣味閾值則上升。

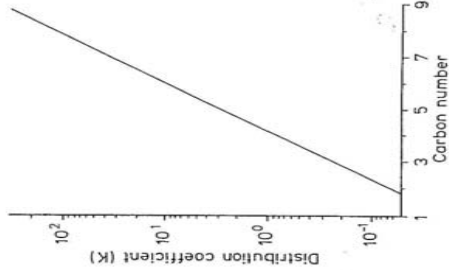


Fig. 5.34. Distribution of n-alkanols in the system oil/water (according to *McNulty and Karel, 1973*)

Fig. 5.35：2-heptanone的溶解度，在全脂奶 > 在脫脂奶，後者有如水相，當被油脂取代，氣相中的2-heptanone濃度最低。

- 1：2-heptanone本身
- 2：in water
- 3：in skim milk
- 4：in whole milk

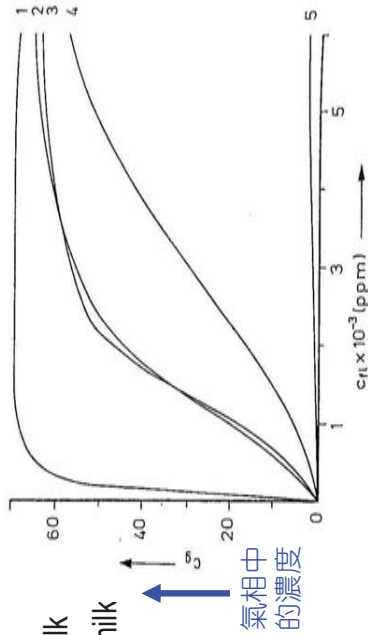


Fig. 5.35. Influence of the medium on 2-heptanone concentration in the gas phase (according to Nawar, 1966). 2-Heptanone alone (1), in water (2), in skim milk (3), in whole milk (4), in oil (5). c_g : concentration in liquid; c_g : concentration in gas phase (detection signal height from headspace analysis)

5.5 Natural and Synthetic Flavorings

- Aromatized food 賦香食品**：香氣濃縮物 (aroma concentrates)、香精(essences)、萃取物(extracts)和個自化合物 (individual compounds)。由一定比率而混合組成 "composed" → flavorist → an aroma mixture
- 憑經驗開發的**香氣配方** "aroma formulation" 首要取決於調香師的經驗與個人的感官評定，以及香氣的物理解化學分析結果提供佐助。規範食品賦香的立法措施因各國而異。

5.4.2 Proteins, Polysaccharides

- 蛋白質對揮發性化合物的吸附特性(Fig. 5.36)。乙醇的結合量最大，可能借助於氫鍵；非極性香氣化合物的結合在疏水性蛋白質表面區域。
- 透過公式計算K值或specific binding capacity。

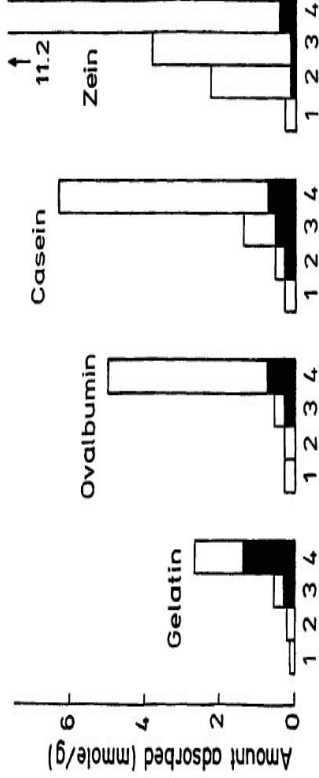


Fig. 5.36. Sorption of volatile compounds on proteins at 23 °C (according to Maier, 1974). Hexane (1), ethyl acetate (2), acetone (3), ethanol (4). □ plus ■: maximal sorption, ■: after desorption

- 目前，非酒精性飲料占賦香食品中第一位的比重(表5.38)。在各種的香氣型態中，以柑橘(citrus)、薄荷(mint)和紅色果實(red fruit) 香氣占多數(Table 5.39)。

Table 5.38. Binding of aroma compounds by proteins (0.4% solutions at pH 4.5)

Aroma compound	Total binding constant $K' \cdot 10^3 \text{ (l mol}^{-1}\text{)}$	
	Bovine serum albumin	Soya protein
	20 °C	60 °C
Butanal	9.765	11.362
Benzaldehyde	6.458	6.134
2-Butanone	4.619	5.529
1-Butanol	2.435	2.786
Phenol	3.279	3.364
Vanillin	2.070	2.490
2,5-Dimethylpyrazine	0.494	
Butyric acid	0.	
	20 °C	60 °C
	10.916	9.432
	5.807	6.840
	4.975	5.800
	2.100	2.950
	3.159	3.074
	2.040	2.335

Table 5.39. Use of aromas in the production of foods

Product group	Percentage (%) ^a
Non-alcoholic beverages	38
Confectionery	14
Savoury products ^b , snacks	14
Bread and cakes	7
Milk products	6
Desserts	5
Ice cream	4
Alcoholic beverages	4
Others	8

^a Approximate values.

^b Salty product line like vegetables, spices, meat.

5.5.1 Raw Materials for Essences 香精

- 在德國，用於食品賦香的香氣約60%來自植物，故標示為“**natural aroma substances**”。其餘的香氣化合物是合成的，然而其中的99%在化學上和天然者是相同的，而僅1%是自然界不存在的。

5.5.1.1 Essential Oils 精油

- 精(揮發性)油最好是以蒸氣蒸餾植物，如丁香花蕾、肉豆蔻、檸檬、香菜、小茴香和荳蔻果實等而取得。蒸氣蒸餾後，精油從水層分離出、澄清與貯存。加工處理過程中所選用的壓力和溫度在於使香氣物質受到熱分解、氧化或水解的可能損失達到最低的程度。

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- 採用**液態二氧化碳**也可得到好產率。此揮發性溶劑可透過蒸餾完全除去，而油萃取物部分(**resin, absolute**) 常含有超過10%的揮發性香氣化合物，以及脂質、蠟質、植物色素和使用溶劑可萃取出的其它物質。萃取後，可續用層析或逆流 (counter-current)分離法來分離所要的**香氣畫分**，**如果使用的溶劑以蒸餾無法去除，所得產物即稱為萃取物(extract)**。萃取物的氣味強度和純精油相比是明顯較弱的，當用作賦香日時相差102-103倍。

5.5.1.3 Distillates 蒸餾物

- 果汁中的香氣組成分在蒸餾濃縮過程比在水相中更易揮發，因此，香氣揮發物冷凝後收集之(cf. 18.2.11)，此蒸餾物(distillates) 經過進一步的精製步驟後，製出高濃縮的香氣畫分。

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- 許多精油如來自柑橘類者含有貢獻香氣少且會迅速自氧化和重合(“樹脂形成**resin formation**”)的 terpene hydrocarbons，這些不需要的精油組成分，譬如來自橘油 (orange oil)之 limonene 可用**畫分蒸餾 (fractional distillation)**移除。畫分蒸餾也可用於增濃或分離一種單獨的香氣化合物，通常，這化合物是精油的主要組成分。

5.5.1.2 Extracts, Absolues

- 當原料中的精油含量低、或香氣組成分受到蒸氣蒸餾的破壞、或香氣因其在水中的溶解性而損失時，原料中精油的回收就採用**萃取法**。例如某些的香草或香茅料與一些水果粉末，Hexane, triacetin, acetone, ethanol, water and/or edible oil or fat are used as solvents.

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5.5.1.4 Microbial Aromas

- Cheese aroma concentrates offered on the market have an aroma intensity at least 20-fold higher than that of normal cheese. They are produced by the combined action of lipases and *Penicillium roqueforti* using whey and fats/oils of plant origin as substrates. In addition to C₄-C₁₀ fatty acids, the aroma is determined by the presence of 2-heptanone and 2-nonanone.

5.5.1.5 Synthetic Natural Aroma Compounds

- 雖然很多食品的香氣化合物已鑑定，由於經濟因素也僅有限的數量是以商業規模合成。
- 全世界最重要的香氣化合物 **vanillin**：alkaline hydrolysis of lignin (sulfite waste of the wood pulp industry) → coniferyl alcohol →converts to vanillin by oxidative cleavage。A distinction can be made between natural and synthetic vanillin by using quantitative ¹³C analysis.

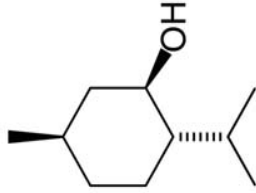
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- **Citral** 檸檬醛最重要來源為檸檬草(*Cymbopogon flexuosus*) 的蒸氣蒸餾油。
- **menthol 薄荷醇** 主要由石化業取得的鄰甲酚(m-cresol)所合成。
- **Thymol 麝香草(百里)酚** is obtained by alkylation and is then further hydrogenated into racemic menthol. A more expensive processing step then follows, in which the racemic form is separated and 1(-)-menthol is recovered. The d-optical isomer substantially decreases the quality of the aroma (cf. 5.3.2.4).

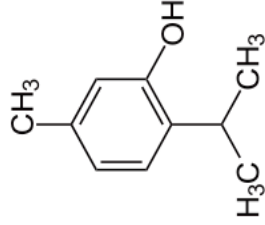
5.5.1.6 Synthetic Aroma Compounds

- 不存在食品材料的合成風味劑(**Table 5.41**)。Ethyl vanillin 乙基香草醛除外，在食品賦香上重要性小。

- **薄荷醇(menthol)**是在葉片裡製造的，也就是**薄荷油**的主要成分，是環類**單萜**的一種。是植物所產生的高揮發性精油，其成份多為半萜、單萜及倍半萜，尤其在氣候溫暖時產量更高。某些重要的植物色素是類萜或含類萜基的化合物。



- **百里酚(thymol)**為**單萜**，是對異丙基甲苯（或對撒花烴，cymene）的酚衍生物。分子式C₁₀H₁₄O，與**香芹酚**(carvacrol)是同分異構體，由於被發現於**百里香**(thyme)中而得名。**萃**取得到的百里酚是白色結晶固體，有令人愉快的芳香氣味。百里酚是很強的**防腐劑**，用於控制蜜蜂上的**瓦蟻**數量、書籍**裝訂**以及添加至**三氯氮****溴乙烷**中作為**麻醉劑**。百里酚也是香煙中**599種添加劑**之一(1994)，被用作**增味劑**。



- Citral, or 3,7-dimethyl-2,6-octadienal or lemonal, is either of, or a mixture of, a pair of **terpenoids** with the molecular formula C₁₀H₁₆O. The two compounds are **double bond isomers**. The **E-isomer** is known as **geranial** or **citral A**. The **Z-isomer** is known as **neral** or **citral B**.
- 各植物精油中的檸檬醛含量為：檸檬香桃木 (90-98%)，**Listsea citrata** (90%)，**山雞椒** *Listsea cubeba* (70-85%)，**檸檬草** (65-85%)，**檸檬茶樹精油** (70-80%)，**丁香羅勒** *Ocimum gratissimum* (66.5%)，**Lindera citriodora** (~65%)，**Calypranthes paniculata** (~62%)，**苦橙葉精油** (36%)，**檸檬馬鞭草** (30-35%)，**史泰格尤加利** (26%)，**香蜂草** (11%)，**青檸** (6-9%)，**檸檬** (2-5%)。

Table 5.41. Synthetic Flavoring Materials (not naturally occurring in food)

Name	Structure	Aroma description
Ethyl vanillin		Sweet like vanilla (2 to 4-times stronger than vanillin)
Ethyl maltol	cf. 5.3.1.2	Caramel-like
Musk ambrette		Musk-like
Allyl phenoxylacetate		Fruity, pineapple-like
α-Amyl cinnamic aldehyde		Floral, jasmine and lilies
Hydroxycitronellal		Sweet, flowery, liliaceous
6-Methyl coumarin		Dry, herbaceous
Propenylguaiacethol (vanatropes)		Phenolic, anise-like
Piperonyl isobutyrate		Sweet, fruity, like berry fruits

5.5.2 Essences

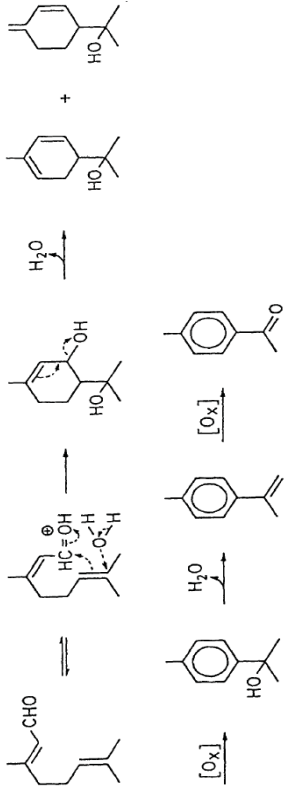
- The flavorist composes essences from raw materials. 為得到最佳香氣，調配比率要迎合食品加工的要求，譬如彌補加熱時的損失。調配香氣的配方是經驗的，長期累積各種問題的經驗。

5.5.3 Aromas from Precursors

- 食品的香氣是要加熱，the impact aroma compounds 產生自梅納反應，可增加反應中的前驅物質質量來增強；某些是直接添加的，有些則是要事先的釋出而增量，這藉由食品中添加蛋白質及多醣類水解酶來達成。

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- Citral在酸性介質（檸檬汁）中也不安定，平衡時，立體異構物 geranial 及 neral 以65/35比率組成。
- **Formula 5.54**反應：neral 環狀化成不安定的p-menth-1-en-3,8-diol，易脫水形成各種p-menthadien-8-ols，接著再形成p-cymene、p-cymen-8-ol及α,p-dimethylstyrene；p-Methylacetophenone由最後的化合物在A8-雙鍵處氧化性斷裂而生成，p-methylacetophenone連同p-cresol相當程度貢獻檸檬汁貯藏所生成的不良風味，Citral也是p-cresol的前驅物質。
- In citrus oils, limonene and γ-terpinene are also attacked in the presence of light and oxygen. Carvone and a series of limonene hydroperoxides are formed as the main aroma substances.



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5.5.4 Stability of Aromas

食品貯藏期間香氣物質會變化。例如醛類及硫醇類(thiols)分別對酸類及disulfides特別敏感而易氧化，且不飽和醛類會進行下列的反應而裂解：

- (E)-2-hexenal及citral 是提供leaf green及citrus notes的重要賦香劑，(Z)-3-Hexenal是鮮榨果汁香氣的重要貢獻成分之一，安定性低於(E)-2-hexenal (Table 5.42)，故鮮少用於賦香。
- (E)-2-hexenal在非極性溶劑如三酸甘油酯中的損失比在極性介質更加迅速，它在後者的安定性大於hexanal。

Table 5.42 Half-life periods in the degradation of C₆ and C₇ aldehydes in different solvents at 38 °C^a

Aldehyde	Water/ Ethanol (8 + 2, v/v)	Buffer ^b / Ethanol (8 + 2, v/v)	Triacetin
n-Hexanal	100	91	86
(E)-2-Hexenal	256	183	71
(Z)-3-Hexenal	42	36	26
n-Heptanal	79	76	73
(E)-2-Heptenal	175	137	57
(Z)-4-Heptenal	200	174	64

^a The half-life period is given in hours.
^b Na-citrate buffer of pH 3.5 (0.2 mol/l).

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5.5.5 Encapsulation of Aromas

- 香氣利用膠囊化來保護。
- 適合包接的材料為多醣類：gum arabic, maltodextrins, modified starches, and cyclodextrins。

(續)

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