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# Analysis of Aromatic Caramel

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*ABSTRACT*

*Aromatic caramel is composed of saccharides (sucrose, fructose and glucose) and a lot of degradation products which contribute to its aroma and flavour. Identification of these species currently needs preliminary extraction. A new device is presented in this paper to avoid this step using a continuous trapping on adsorbent when heating, followed by a thermal desorption and overall analysis. Fifty-seven compounds were detected by this technique and also by solvent extraction and vapour analysis during cooking. Some unexpected intermediate volatile molecules were noted which can play an important role in the formation of the flavouring compounds.*

## INTRODUCTION

Aromatic caramel is generally obtained by heating sucrose in the presence (or not) of an acidic or alkaline catalyst. Thermal treatments produce a large mixture of many species which make up flavour, fragrance and colour (Adrian, 1987).



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Thus, industrial caramel contains residual sucrose, mono- and oligosaccharides, mainly glucose and fructose, and several degradation compounds, principally 5-hydroxymethylfurfural (5HMF) (Heynes *et al.*, 1966; Greenshields, 1973; Goretti *et al.*, 1980; Theander, 1985; Handwerk & Coleman, 1988).

Exhaustive qualitative and quantitative analysis, generally by capillary gas chromatography (GC) alone or coupled with mass spectroscopy (MS) (Cottier *et al.*, 1989) requires preliminary solvent extraction (Shaw *et al.*, 1967; Walter & Fagerson, 1968; Carnevale, 1975; Keeney, 1975; Wilks *et al.*, 1977; Patey *et al.*, 1985).

As a consequence, compounds which are present only at trace level cannot be observed even though they are of interest both for knowledge of reaction mechanisms and characterisation of the final product. Only a few major molecules such as 2-furancarboxaldehyde and other by-products have been clearly identified.

Recently, a technique was developed and patented in our laboratory (Casier *et al.*, 1988) which allows efficient analysis of volatile compounds without the solvent extraction step. This new experimental device, described in the patent, presents the following main advantages: the injection time is very short (thermal rate of 12 000°C . m n$^{-1}$); the exact temperature into the trap is always known, which allows adaptation in every case. As a consequence, the very narrow injection band leads to a high chromatographic resolution. This process needs preliminary adsorption of volatile moieties and the device based on thermal gravimetric analysis (TGA) of sucrose during heating is described in this paper.

The results were compared with those obtained by the usual solvent extraction from an industrial sample prepared under the same conditions and with the analysis of vapours collected during the caramelization process.

## MATERIALS AND METHODS

Industrial caramel is prepared by heating, up to 195°C, a mixture of 10 kg of sucrose, 1·7 kg of water and 2·5 g of citric acid; 2·8 kg of water are added at the end of cooking.

### Solvent extraction

Various solvents have been checked to cover a wide range of polarity: pentane, methylene chloride, diethyl phthalate, diethyl ether, Forane® (registered mark from Atochem, France). The best results were observed with methylene chloride.

The counter-current extraction with 100 $cm^3$ of solvent was performed in a glass column filled with a caramel solution (30% dry matter). Then, solvent was evaporated down to 0·1 $cm^3$ and the mixture was analyzed.

Vapours originating from the industrial cooking vessel were collected and condensed on a cold surface, when browning appeared, and submitted to extraction as previously described.

## Analytical methods

High performance liquid chromatography (HPLC) of sugars was performed with a $\mu$-Bondapak-$NH_2$ PE radial column, fitted to a Waters 6000A instrument, and connected to a differential refractometer Waters R400. 5HMF analysis was achieved also by HPLC with a $\mu$-Bondapak C18 PE radial column.

Capillary gas chromatography (Hewlett-Packard 5890) was performed in a column (0·25 mm × 50 m) coated with Carbowax 20M (film thickness 0·20 $\mu$m). The identification was achieved by mass spectroscopy (Hewlett-Packard MSD 5970—240°C, 70 eV).

## Thermal gravimetric analysis

A mixture of sucrose, water and citric acid was introduced in the nacelle of a thermal balance (Fig. 1). Initial medium composition and surface:volume ratio allow comparisons between this device and the industrial process.

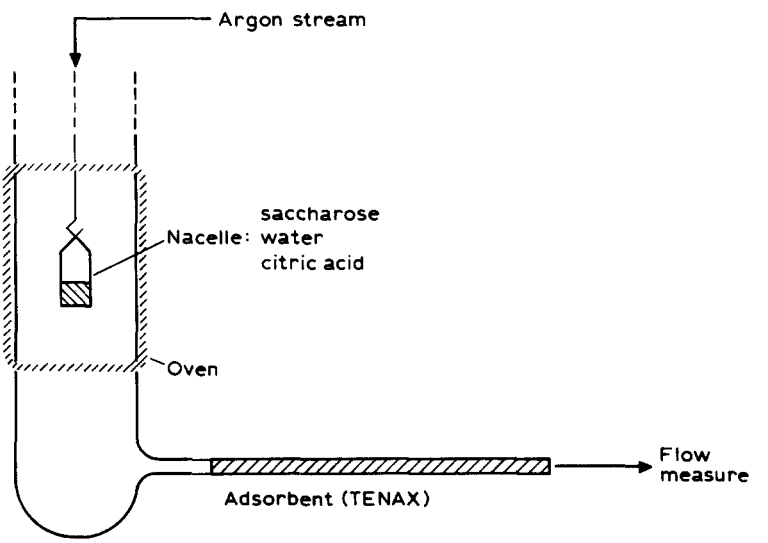


**Fig. 1.**

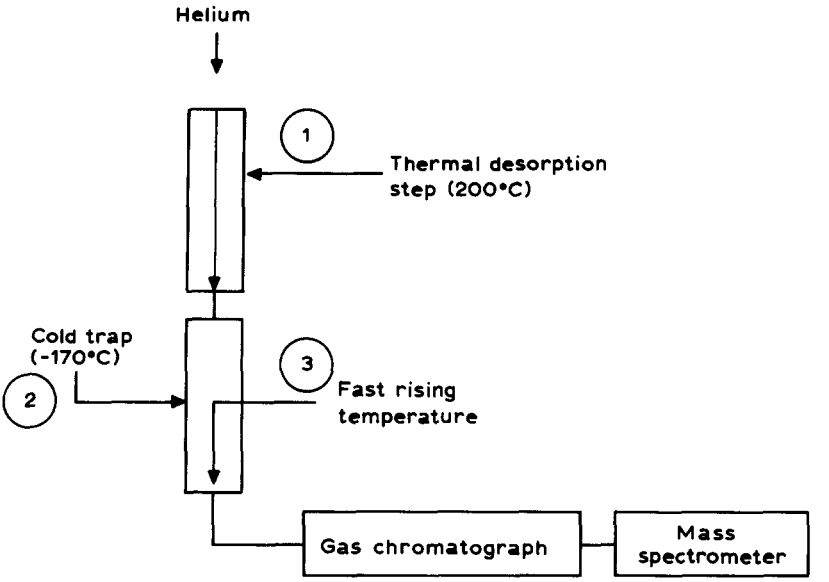


Fig. 2.

Temperature was then raised; volatile compounds were collected under an argon stream after caramelization initiation and absorbed on Tenax (2,6-diphenylparaphenylen oxide) as they were developing during heating, as described in Fig. 1. It must be emphasized that the Tenax tube was fitted only after water elimination (Fig. 3, point A) otherwise analytical problems occur.

The Tenax tube was then introduced into an oven (Fig. 2). After thermal desorption (1), compounds were driven by an inert gas (helium) to a cold

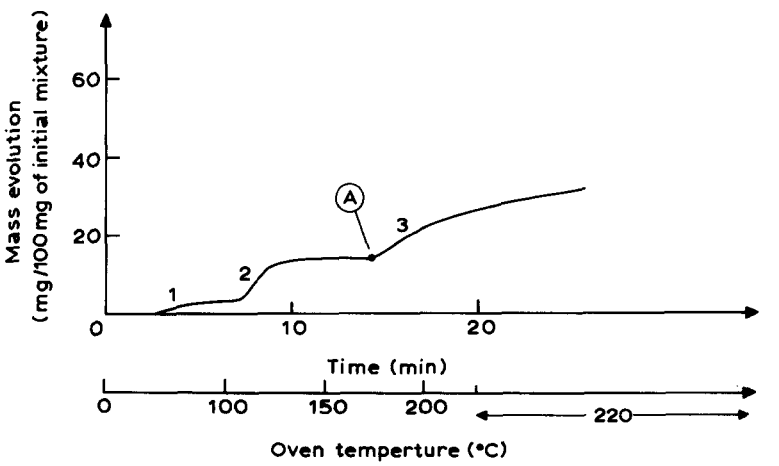


Fig. 3.

capillary tube (2) which stops their migration. When desorption was achieved, instantaneous injection of the compounds was accomplished in the chromatograph by very fast rising of temperature (3).

## RESULTS AND DISCUSSION

The various steps of caramelization are well identified by TGA. It can be seen in Fig. 3 that two preliminary mass departures occur which can be explained by free water (step 1) followed by bound water losses (step 2). At point A, hydrolysis of sucrose is largely achieved and we have shown that, depending on the exact experimental conditions, its remaining content does not exceed 30%. Moreover, one water molecule is necessary to hydrolyze one molecule of sucrose which does not change the weight balance. Calculation has established that mixture weight at point A exactly takes this fact into account.

A typical industrial aromatic caramel contains a ratio of fructose:glucose:sucrose of 3:4:3. Some presence of melibiose and xylose was shown by HPLC and also traces of coloured higher weight molecular species after dialysis.

Thirty-three compounds were identified by solvent extraction directly on industrial aromatic caramel solution (see in Fig. 4 an example of GC–MS), twelve other products by vapour analysis and twelve more by the adsorption device. The fifty-seven compounds are listed in Table 1. It is interesting to note that the three methods appear to be complementary.

We have developed an attempt to quantify the analysis on the species chosen for the following reasons:

(i) They belong to different chemical families characteristic of the product.
(ii) They are present at significant levels.
(iii) They are spread all over the chromatogram.
(iv) They are eluted before the drift of the base line.

The following compounds were actually selected:

—1-Hydroxy-2-propanone (peak 2 in Fig. 4).
—2-Furancarboxaldehyde (peak 4).
—Furfuryl alcohol (peak 7).
—2-Furancarboxylic acid, methyl ester (peak 11).

Quantitative work needed preliminary determinations of the extraction yields and chromatographic response coefficients on reference solutions.

**TABLE 1**
GC–MS Compound Identification
Industrial Aromatic Caramel Analysis after Solvent Extraction with:

(1) **Methylene chloride**
Formic acid
2-Propanone
1-Hydroxy-2-propanone
2-Methyl-1-propanol
Propanoïc acid, methyl ester
1-Butanol
3-Hydroxy-2-butanone
3-Methyl-3-butene-2-ol
1,2-Butanediol
3-Methyl-2-oxobutanoïc acid, methyl ester
Dihydro(3H)2-furanone = butyrolactone
5-Methyl(3H)2-furanone = $_{\alpha}$angelica lactone
5-Methyl(5H)2-furanone = $_{\beta}$angelica lactone
Dihydro-2-methyl(2H)3-furanone
2-Furancarboxaldehyde
5-Methyl-2-furancarboxaldehyde
5-Hydroxymethyl-2-furancarboxaldehyde
2-Hydroxymethylfuran = alcool furfurylique
2-Furancarboxylic acid, methyl ester
3-Furancarboxylic acid, methyl ester
2-Acetylfuran
2-Methylcyclopentanone
3-Methyl-1,2-cyclopentanedione
2,4-Dimethyl-2-hydroxymethyl-1,3-dioxolane
3,4-Dihydro(2H)pyrane
3-Hydroxy-2-methyl(4H)4-pyranone = maltol
5-Hydroxy-2-methyl(4H)4-pyranone = allo maltol
3,5-Dihydroxy-2-methyl(4H)4-pyranone
2-Methyl-3-methylendioxan
1-Methyl-3-(1-methylethyl)cyclohexen

(2) **Diethylphthalate**
2-Propanone
* 2-Propanol
* Hexanoïc acid
* Heptanoïc acid

Vapour Analysis after Solvent Extraction with Methylene Chloride

* Carbon dioxide
1-Hydroxy-2-propanone
* 2-Methyl-3-pentanone
* (3H)2-Furanone
Dihydro(3H)2-furanone

**TABLE 1**—*contd.*

| | |
|---|---|
| | 5-Methyl(3H)2-furanone |
| * | 3,4-Dimethyl(5H)2-furanone |
| | 2-Furancarboxaldehyde |
| | 5-Methyl-2-furancarboxaldehyde |
| | 5-Hydroxymethyl-2-furancarboxaldehyde |
| | 2-Hydroxymethylfuran = alcool furfurylique |
| * | 2-Furancarboxylic acid |
| | 2-Furancarboxylic acid, methyl ester |
| | 2-Acetylfuran |
| * | 2,5-Dimethyl-4-hydroxy(2H)3-furanone = furaneol |
| * | 2,3-Dihydro-4-(1-methylpropyl)furan |
| * | 2-Cyclopenten-1-one |
| * | 1,3-Cyclopentanedione |
| | 3-Methyl-1,2-cyclopentanedione |
| | 3-Hydroxy-2-methyl(4H)4-pyranone = maltol |
| | 5-Hydroxy-2-methyl(4H)4-pyranone = allo maltol |
| * | 5,6-Dihydro-3,5-dihydroxy-2-methyl(4H)4-pyranone |
| * | 5-Furfurylfurfural |
| * | 5-(5-Methylfurfuryl)furfural |
| | Vapour Analysis after Adsorption on Tenax |
| | Carbon dioxide |
| * | Formaldehyde |
| | Formic acid |
| * | Acetic acid |
| * | Hydroxyacetaldehyde |
| * | Ethanediol |
| | 2-Propanone |
| | 1-Hydroxy-2-propanone |
| * | 2-Propenoïc acid |
| * | 2-Butanone |
| * | Cyclobutanone |
| * | 2,3-Butanedione |
| * | 2,3-Pentanedione |
| * | Furan |
| * | 2-Methylfuran |
| * | 3-Methylfuran |
| | (3H)2-Furanone |
| | 5-Methyl(5H)2-furanone |
| | 2-Furancarboxaldehyde |
| | 5-Hydroxymethyl-2-furancarboxaldehyde |
| | 2-Hydroxymethylfuran |
| | 3-Furancarboxylic acid, methyl ester |
| | 2-Acetylfuran |
| | 5,6-Dihydro-3,5-dihydroxy-2-methyl(4H)4-pyranone |

New compounds identified by each specific method are indicated by an asterisk.

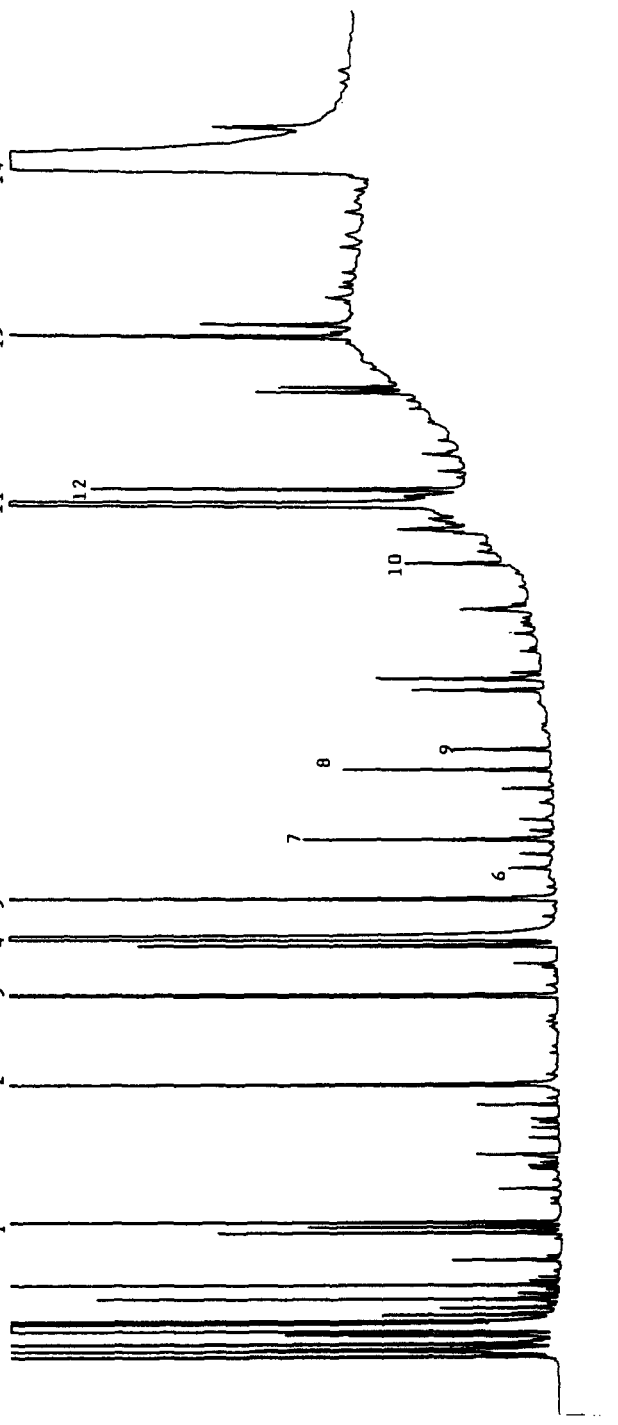


**Fig. 4.** 1; Butanol-1. 2; 2-Propanone 1-hydroxy. 3; α-Angelicalactone. 4; 2-Furancarboxaldehyde. 5; Furan 2-acetyl. 6; Butyrolactone. 7; Furfuryl alcohol. 8; (2H)pyran-3,4-dihydro. 9; Cyclopentanone-2-methyl. 10; (4H)pyran-4-one 5-hydroxy 2-methyl. 11; 2-Furancarboxylic acid, methyl ester. 12; 3-Furancarboxylic acid, methyl ester. 13; (4H)pyran-4-one 5,6-dihydro 3,5-dihydroxy 2-methyl. 14; 5-(Hydroxymethyl)-2-furancarboxaldehyde.

In the aromatic caramel analyzed in Fig. 4, we found: 330 ppm; 800 ppm; 13 ppm and 12 ppm, respectively, for these four compounds. We also determined, by HPLC analysis, 4000 ppm of 5HMF.

This schedule could be extended to other molecules but too high dilutions must be avoided for compounds at trace levels.

Solvent extraction is rather selective and volatile or polar molecules are not easily analyzed. Moreover, concentration operations often result in loss of some compounds.

Adsorption on Tenax is not selective as it is only concerned with products which have been carried out by the gas stream under the set conditions. This explains why the same products are not found by these different techniques.

Only seventeen of the products listed in Table 1 were also noted by Cottier *et al.* (1989). This apparent disagreement comes probably from other catalytic conditions.

Finally, it must be emphasized that some identified compounds have been correlated by sensorial analysis with caramel organoleptic characteristics. Among the species of Table 1, there are a number of volatile and very low molecular weight compounds, especially in vapours; these may not be present in the final product. This suggests a route towards understanding formation mechanisms of substances which occur during sucrose heating. Aromatic caramel quality is directly related to this fundamental aspect and a better knowledge of caramelization could also lead to process rationalization and optimization.

## ACKNOWLEDGMENTS

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