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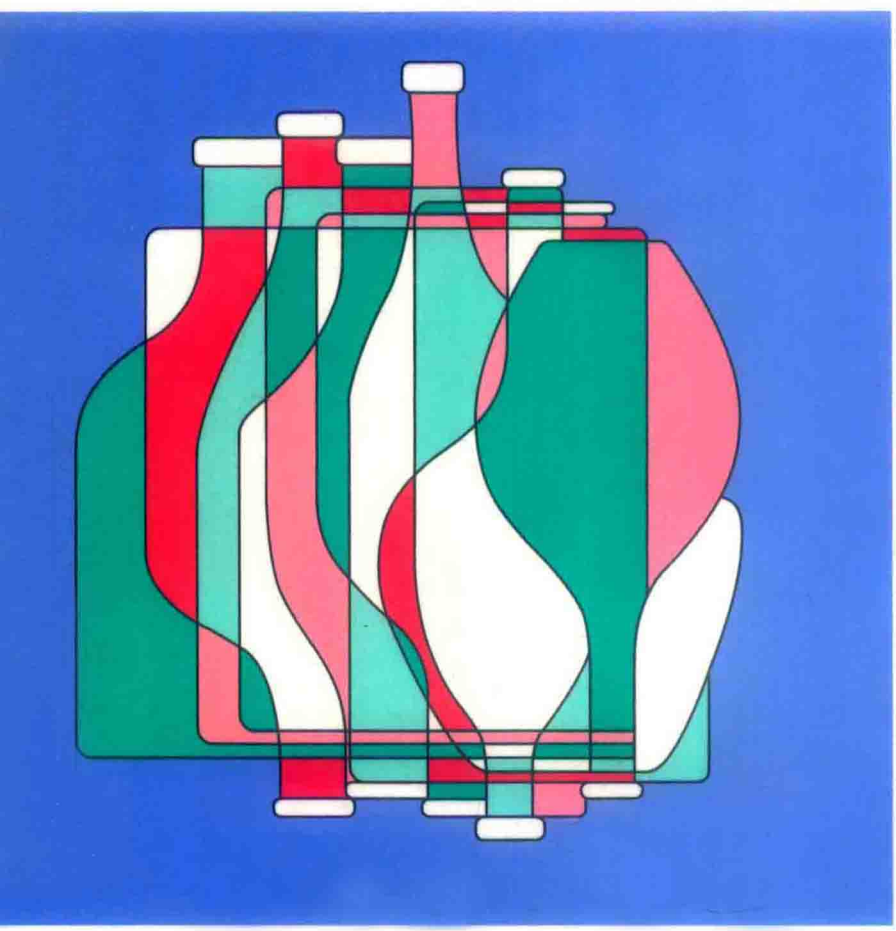
Distilled Beverage Flavour

Recent Developments

Edited by
J. R. Piggott and A. Paterson



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Piggott/Paterson

Distilled Beverage Flavour

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Preface

This book represents the proceedings of an international symposium held at Stirling University, Scotland, between 7th and 10th June 1988, by the Sensory Panel of the Food Group of the Society of Chemical Industry. The symposium was held to review advances in understanding of distilled beverage flavour made since the first symposium in 1983. At the first meeting, the current status of knowledge was reviewed for the main groups of products; at this meeting it was clear that progress has been made in the ability to control flavours of distilled beverages in some areas, but that many problems remain to be solved. Particular problems identified were the absence of any satisfactory means of linking sensory and physico-chemical data for complex flavours, though in some cases this can be done; incomplete understanding of the maturation process in traditional matured beverages; and the problem of authentication of beverages. Many opportunities were also identified.

The chapters here are arranged in four sections. The first section is devoted to methods of analysis, both sensory and instrumental, of distilled beverage flavours and sensory properties. The second section contains contributions discussing traditional products of the distilled beverage industry, while the third section covers the opportunities and problems of new products. Finally, some new methods and processes for production are described. The book is completed by a final chapter summarising progress since 1983.

We are pleased to acknowledge the assistance given by many people in arranging this symposium: the staff

of Stirling University for their help and hospitality; the staff of the Society of Chemical Industry for their patience; the hosts of the social events for making the symposium enjoyable as well as instructive; the contributors for producing typescripts promptly; and the publishers.

J.R. Piggott and A. Paterson

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Current issues in flavour research

Henk Maarse and Frans van den Berg
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Zeist, The Netherlands

1. INTRODUCTION

Application of chromatography, particularly in combination with mass spectrometry, has led to the identification of a large number of constituents in distilled beverages [1,2,3]. Despite these impressive results more attention should be given to sensory analysis to help the flavour analyst in selecting those compounds that are important for the flavour of a product.

In Section 2 we will discuss this topic by describing sensory techniques that are being used in combination with chromatographic analysis.

New developments in chromatographic techniques in combination with mass spectrometry and Fourrier Transform infra-red spectrometry have recently been extensively reviewed [4] and will not be discussed in this paper.

The maturation flavour is a very important part of the overall flavour of alcoholic beverages such as cognac and whisky. New developments in this field will be reviewed in Section 3.

For some people adulteration of alcoholic beverages is an attractive way of making money. Although many administrative measures have been taken, these do not fully prevent frauds. Thus, modern techniques are being proposed and tested in many countries. In Section 4 the possible uses of these techniques in the determination of the origin of wine distillates are shown.

2. COORDINATION OF SENSORY AND INSTRUMENTAL ANALYSES

2.1 Multidimensional gas chromatography

An elegant way to improve the separation power of a GC system is to use two columns in series, a pre-column and an analytical column. Interesting fractions from the first column can be introduced on-line into the second column to be further separated into individual components.

Good examples of multidimensional GC (MDGC) in flavour research are the studies of Nitz et al.[5,6] who used a GC with two ovens, which were independently temperature-programmable (Siemens Model Sichromat 2). A scheme of the total system is depicted in Figure 1-a. A detailed description of this system, based on the methods introduced by Deans [7] and further developed by Schomburg et al. [8,9], can be found in the original literature [5,6]. Below the procedure is described and the possibilities of the system are shown.

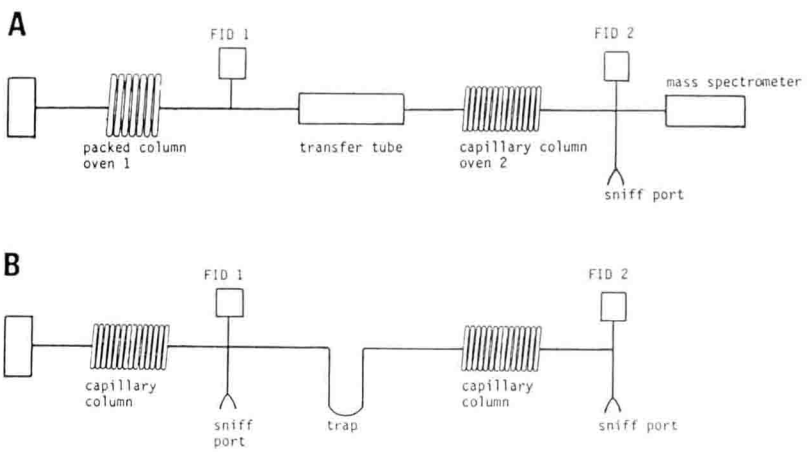

Figure 1 Two-column switching systems for multidimensional GC
a. Schematic drawing of the Siemens system (Model Sichromat 2) for total transfer from packed to capillary columns with intermediate trapping and a device for parallel MS/sniffing or MS/FID registration.
b. Schematic drawing of the Chrompack Music system for total transfer from pre-columns to analytical columns with intermediate trapping and a device for parallel sniffing/FID registration or trapping/FID registration.

Depending on the problem the pre-column may be a packed column, a medium-resolution wide-bore capillary column or a high-resolution capillary column of similar dimensions but with a polarity differing from the analytical column.

In the examples described in the literature the first column was a packed column and the second one a capillary column. Selected fractions from the first column were trapped on a cooled transfer tube. The trapped compounds were re-injected into the second column by heating the tube. Compounds separated on this column can be directly monitored with a FID detector or the effluent can be split for simultaneous MS registration. Furthermore, parallel sniffing and MS detection can be performed.

Nitz and Julich [5] used this system to trace and identify the volatile components characteristic of the flavour of cooked cauliflower. Preliminary analysis by GC-MS was not successful: the mass spectra of relevant compounds were of low purity and could not be interpreted. Therefore, 4 µl of the concentrate were injected on to the packed column of the MDGC system, the fractions between 19.4 and 20.6 min and between 23 and 26 min were trapped and re-injected on to the second column (Figure 2-a).

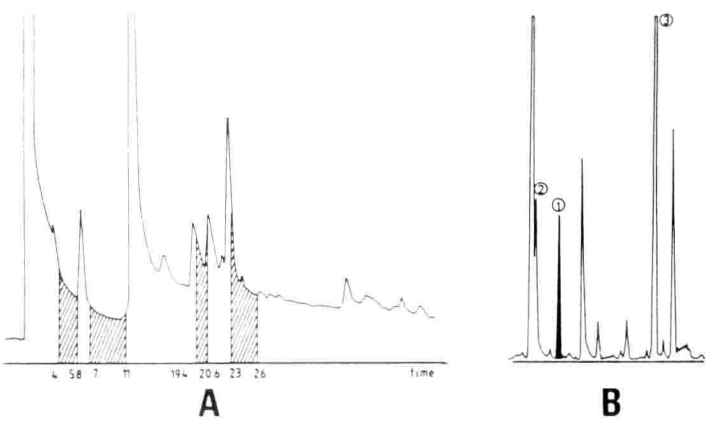

Figure 2.a. Chromatogram of cooked cauliflower extract obtained on packed pre-column; cutting areas are indicated [5].
b. Total ion chromatogram of definite cuts of cauliflower extracts; fraction 19.4-20.6 and 23-26 minutes [5].

Simultaneous sniffing during MS acquisition showed that the component marked (1) in Figure 2-b was the one with a cooked cauliflower odour. A clean mass spectrum was now obtained. In our institute we have chosen a cheaper solution, the two-dimensional switching system called Music (Multiple Switching Intelligent Controller) developed by Chrompack in the Netherlands (10).

The set-up of this system is depicted in Figure 1-b: the pre-column is a 10 m * 0.53 mm (i.d.) CP Sil5 fused silica column, analytical column a 25 m * 0.25mm (i.d.) CP Wax 52CB fused silica column.

We adapted the system by introducing a split, either between the pre-column and the detector or between the analytical column and the detector.

By this 1:10 split 10% of the effluent was led to the detector and 90% to a sniff port.

We used this system for the analysis of a commercial fruit flavour. Three fractions were first selected on the apolar column possessing a flavour characteristic of this particular fruit.

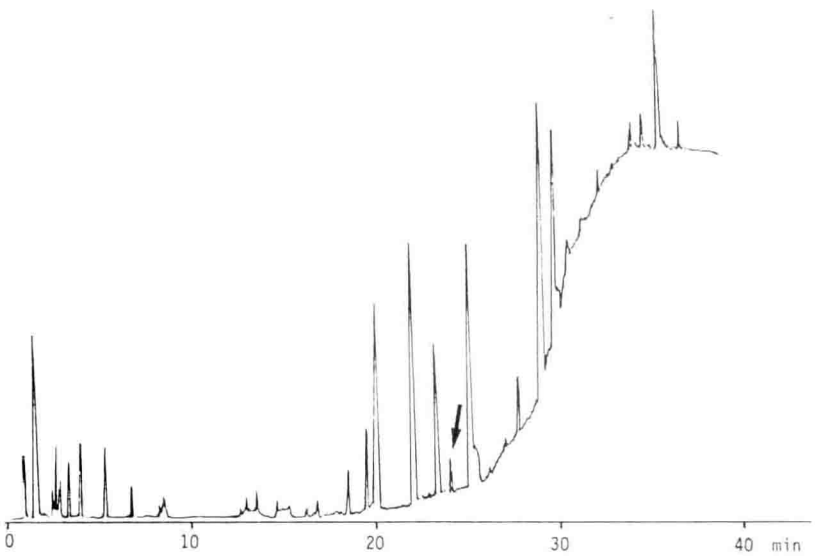

Figure 3. Chromatogram of a fraction with a characteristic flavour: the arrow indicates the place in the chromatogram where a catty odour was observed after further separation of a selected column fraction.

In a second run these three fractions were trapped on a piece of de-activated fused silica capillary. These fractions were further separated on the second, polar column. By sniffing, the peaks responsible for the characteristic flavour were selected. In a final run the fractions were trapped and re-injected into a GC-MS system and the selected peaks were identified. The device for intermediate trapping was also used for trapping the fractions for GC-MS analysis. In one of the fractions an important flavour was described as Buchu-like (Figure 3).

This small peak was identified as 8-mercapto-p-menthan-3-one; this compound has been identified in Buchu oil [11], it has a very low odour threshold value and its odour is described as catty or ribes-like. This illustrates that our system is a very powerful tool in identifying flavour compounds.

We also use the MUSIC system for the quantitative analysis of ethyl carbamate in alcoholic beverages [12] and of carbitol in flavour concentrates [13].

2.2 Determination of odour threshold values

Odour and flavour threshold values are important properties of odorous volatile compounds. Knowledge of these values is indespensible in order:

- to get an idea of the importance of compounds for the flavour of a product.
- to find out whether the instrumental detection limit is sufficiently low, preferably at least as low as the threshold value. This plays a part only for compounds contributing negatively to the flavour of a product.
- to estimate maximum allowable concentrations of a compounds causing off-odours and/or off-flavours in foods, raw materials and related products (e.g. packaging materials [14]).

The outcome of threshold value determinations is strongly dependent on the experimental conditions. Interlaboratory results can easily differ by a factor of 10 and even more. Sensory experiments with compounds having very low threshold certainly require careful consideration of all relevant aspects [14].

In our laboratory odour detection threshold values of several chlorophenols and chloroanisoles have been determined. The results of this study have been reported elsewhere [14]. Only the description of one of the techniques used in that study is relevant to the scope of this paper.

For the determination of the odour threshold values in air an olfactometer was used. This is an apparatus capable of producing airflows with a wide range of concentrations of volatile compounds. This airflow is presented, together with two odourless airflows, to a panel of 8 members. After smelling they are asked to indicate which of the three is the odorous one.

To check the purity of the compounds, standard solutions were first injected splitless on to a GC column. The end of the column was connected to a splitter which led part of the effluent to a FID detector and the other part directly out of the oven. During elution a 45-litre Teflon bag was connected to the splitter outlet. The concentration of the pure compound in the bag was calculated from the concentration of the standard solution, the injection volume and the split ratio at the end of the column. In this way, odour threshold values of chloroanisoles have been determined [14].

2.3 Selection of compounds contributing significantly to flavours

2.3.1 *Gas Chromatography*

All foods and beverages contain hundreds of volatile compounds and it is therefore essential to select those constituents that contribute significantly to the flavour of a product.

Roche and Thomas [15] suggested the use of 'aroma value', being the ratio of the concentration of a flavour compound in a product to its odour threshold value. Guadagni et al. [16] called the same factor 'odour unit' and Mulders [17] 'odour value'. In this paper the term 'odour unit' is used. Although this approach has its limitations and has been criticised [e.g. 18] its usefulness is beyond all doubt.

Odour units can be calculated only if the concentration and the threshold value of compounds are known. This means that major flavour compounds are selected after identification of a large number of constituents. This is very laborious and costly and does not guarantee that all important flavour compounds are taken into consideration.

As described in Section 2 the sniff technique is being used by many investigators to provide odour information on compounds separated by GC. Recording the intensity of the perceived odour gives additional information on the contribution of compounds to the flavour of a product [e.g. 19]. Recently two new methods for determining these volatiles in food that are significant of flavour have been presented [20 - 22].

Acree et al. applied their method to volatiles in apples [23]. Their procedure is also based on the 'odour unit' concept, but they determine relative odour detection thresholds of components in a flavour extract using the GC-sniff technique. They calculated 'Charm Values' on the basis of sensory responses maintained during GC effluent sniffing of dilutions of the original extract. Charm values are directly proportional to odour units.

Grosch et al. [21,22] used a similar but simpler method. An aroma extract is stepwise diluted with a solvent until no more odorous compounds are observed in the GC effluent. The highest dilution at which a substance is still smelled is its flavour dilution (FD) factor. By definition the FD factor of an undiluted sample is 1. An FD factor of 20 means that the concentration of the odorous compound in the aroma extract was 20 times its odour threshold value as perceived by the GC effluent sniffing. FD factors are proportional to odour units.

This aroma extract dilution analysis was applied by Schieberle and Grosch [22] to wheat and rye bread crusts. Part of the results are given in Figure 4 showing the FD factor versus the retention index in an 'aromagram'. This name is somewaht confusing: other authors understand aromagrams to mean chromatograms, indicating also the flavour descriptions of the compounds observed at a sniff port. We therefore suggest the name 'flavour dilution chromatogram'.

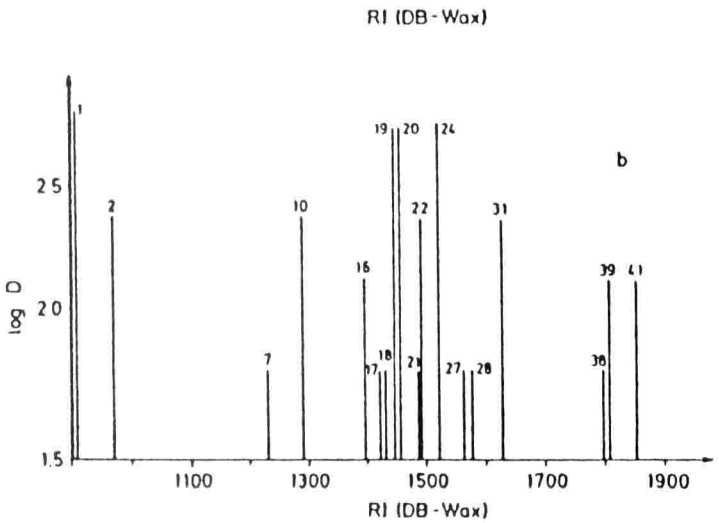

Figure 4. Flavour dilution chromatogram of the aroma extract of rye bread crust. Peaks numbered as follows:

1. 3-methylbutanal 2. diacetyl
7. 4-cis-heptenal 10. 1-octen-3-one
16.a.trimethylpyrazine 16.b.2-methyl-3-ethylpyrazine
17. 2-tr-octenal 18. 2,5-dimethyl-3-ethylpyrazine
19. unknown 20.a. furan-2-al
20.b. 2,6-dimethyl-3-ethylpyrazine 21 & 22. unknown
24. 2-tr-nonenal 27. 5-methyl-2-furaldehyde
28. 2-tr-6-cis-nonadienal 31. phenylacetaldehyde
28. 2-tr-4-tr-decadienal 39 & 41. unknown

The results clearly show that some compounds that contribute to the flavour of rye bread crust are still unknown.

2.3.2 High-pressure liquid chromatography (HPLC)

In the analysis of distilled alcoholic beverages HPLC is routinely used for the determination of acids, phenols, phenolic acids and aldehydes, and sugars. Also methods for the determination of aliphatic carbonyl compounds, as their dinitrophenylhydrazone derivitives, have been worked out [24].

Apart from these quantitative HPLC analyses, identification of unknown high-boiling or non-volatile flavour compounds is possible with HPLC-MS combinations [25] which are now commercially available.

In the literature no methods have been described that enable the selection of important flavour compounds in the HPLC eluent. The reasons are obvious:

- a "taste port" cannot be used because tasting takes more time than smelling.